ALKALOIDS OF *Rauvolfia salicifolia* GRISEB SPECIES

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Received December 23rd, 1981

Dedicated to Professor Holger Erdtman on the occasion of his 80th birthday.

From the endemic Cuban species *Rauvolfia salicifolia* GRISEB nine alkaloids were isolated of which the following seven had been already described: (+)-ajmalidine (*I*), (−)-reserpiline (*II*), (−)-isoreserpiline (*III*), (−)-isocarapanaubine (*IV*), (−)-ajmalicine (*V*), (+)-vellosimine (*VI*), and (+)-yohimbine (*VII*). The structure of (−)-raucubaine (*VIII*) had been previously determined by X-ray diffraction and the structure of the alkaloid (−)-raucubainine (*IX*) was suggested on the basis of its conversion to (−)-raucubaine (*VIII*). The absolute configuration of (−)-raucubaine and (−)-raucubainine was elucidated by CD spectroscopy.

Rauvolfia salicifolia GRISEB represents one of the three endemic Cuban species of the *Rauvolfia* genus. This species was phytochemically studied in 1957 by Korzun and coworkers[1] who proved the presence of deserpidine, reserpiline, rescinamine and reserpine in the extract. The alkaloids were characterized only by paper chromatographic comparison with the authentic compounds.

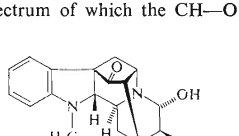
In this study we describe the isolation of nine alkaloids: From the root bark we isolated (+)-ajmalidine (*I*), (−)-reserpiline (*II*), (−)-isoreserpiline (*III*) and (−)-isocarapanaubine (*IV*). The principal alkaloid present in the plant is reserpiline. Isocarapanaubine was isolated from the *Rauvolfia* genus for the second time, the first isolation being from *Rauvolfia vomitoria*[2]. From the tree bark we obtained (−)-reserpiline (*II*), (−)-ajmalicine (*V*), (+)-vellosimine (*VI*) and (+)-yohimbine (*VII*). The leaves afforded (−)-reserpiline (*II*), (−)-ajmalicine (*V*) and the new alkaloids (−)-raucubaine (*VIII*) and (−)-raucubainine (*IX*).

The structure of raucubaine (*VIII*) was determined already by X-ray analysis[3,4]. Its ^{1}H-NMR spectrum displays signals of four aromatic protons whose mutual interactions indicate an *ortho*-disubstituted benzene nucleus, a singlet at δ 2·71 due

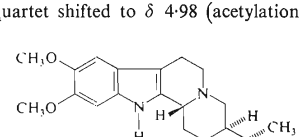
* Part XLVI in the series Plant Substances; Part XLV: This Journal *47*, 644 (1982).

** This work represents part of the Thesis of P. Sierra, Institute of Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague 1981.

to an N-methyl group and signals of a $-\overset{|}{C}-CH(OH)-CH_3$ grouping (a doublet at δ 1·28, J = 6·4 Hz, 3 H and a quartet at δ 3·64, J = 6·4 Hz, 1 H). The presence of a secondary hydroxyl was proved by transformation of *VIII* into the acetate *X* in the spectrum of which the CH—O quartet shifted to δ 4·98 (acetylation shift



I



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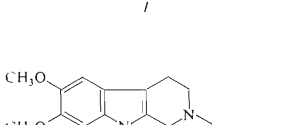
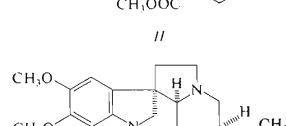
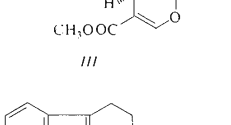


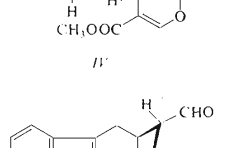
III



IV



V



VI

$\Delta\delta$ = 1·34). The spectrum exhibits also the AB system of an isolated CH_2 group which, according to the coupling constant and chemical shifts (J_{gem} = 16·0 Hz; δ 2·69 and 3·29), is attached to a nitrogen atom and belongs thus to a $-\overset{|}{C}-CH_2-N$ fragment. Further we detected a four-spin grouping $N-CH_2-CH_2-\overset{|}{C}-$ with signals at δ 3·37, 2·78, 1·93 and 1·46. The remaining protons in the molecule form a six-proton fragment $-\overset{|}{CH}-\overset{|}{CH}-CH_2-\overset{|}{CH}-\overset{|}{CH}-$, as follows from coupling constants. The ^{1}H-NMR data, summarized in Tables I and II, are thus consistent with the structure *VIII*. To achieve a better comparison with the compound *IX*, we measured the compound *VIII* also in hexadeuteriobenzene. The thus-obtained

parameters, together with the aromatic solvent induced shifts (ASIS) for the single protons, are also given in Tables I and II.

As expected, the ^{1}H-NMR data of the acetate *X* (Table I) are very similar to those of the parent hydroxy derivative *VIII*, marked differences existing only in cases of the $C_{(19)}$—H and the $C_{(15)}$—H signals. Acetylation shift of the former signal is $\Delta\delta = +1{\cdot}34$ ppm whereas the latter is shifted upfield ($-0{\cdot}43$ ppm), obviously as the result of different bulkiness of the near $C_{(19)}$—OH or $C_{(19)}$—$OCOCH_3$ groups. Reflux of the alkaloid *VIII* with sodium methoxide solution resulted in opening of the lactone ring. Howewer, as soon as the reaction mixture was extracted with chloroform at pH 7, the ring was again closed and the original alkaloid *VIII* was obtained. Also its attempted hydrolysis with hydrochloric acid was not successful, the starting alkaloid *VIII* being again recovered. Its reduction with lithium alu-

TABLE I

Chemical shifts (δ, ppm) in ^{1}H-NMR spectra of alkaloids *VIII*—*X*

Proton	*VIII*			*X*	*IX*			δ^a
	($CDCl_3$)	(C_6D_6)	(ASIS)	($CDCl_3$)	($CDCl_3$)	(C_6F_6)	(ASIS)	(C_6D_6)
H-2	2·55 s	1·96 s	−0·59	2·55 s	2·51 s	2·05 s	−0·46	2·70
H-3	3·98 bd	3·68 bd	−0·30	4·03 bd	4·12 bd	3·81 bd	−0·31	2·60
H-5	3·37 ddd	3·29 ddd	−0·08	3·39 ddd	3·83 ddd	3·91 ddd	+0·08	3·90
H-5′	2·78 dd	2·40 dd	−0·38	2·81 dd	2·52 dd	2·34 dd	−0·18	2·80
H-6	1·93 ddd	2·00 ddd	+0·07	1·95 ddd	2·65	2·78 ddd	+0·13	2·30
H-6′	1·46 dd	1·42 dd	−0·04	1·48 dd	1·63 dd	1·78 dd	+0·15	1·80
H-9	7·42 dd	7·78 dd	+0·36	7·47 dd	7·05 dd	7·39 dd	+0·34	6·6—7·2
H-10	6·83 dt	6·86 dt	+0·03	6·86 dt	6·72 dt	6·81 dt	+0·09	6·6—7·2
H-11	7·08 dt	7·06 dt	−0·02	7·16 dt	7·12 dt	7·09 dt	−0·03	6·6—7·2
H-12	6·65 bd	6·44 bd	−0·21	6·69 bd	6·63 bd	6·48 bd	−0·15	6·6—7·2
H-14	2·11 ddd	1·58 ddd	−0·53	2·17 ddd	2·70	2·47 ddd	−0·23	2·33
H-14′	1·72 ddd	0·99 ddd	−0·73	1·73 ddd	1·69 ddd	1·00 ddd	−0·69	1·00
H-15	3·10 ddd	2·75 ddd	−0·35	2·68 ddd	2·70	2·61 bq	−0·09	3·84
H-16	3·35 d	2·99 d	−0·36	3·37 d	2·97 d	2·71 d	−0·26	2·05
18-CH_3	1·28 d	0·89 d	−0·39	1·31 d	1·28 d	1·16 d	−0·12	1·17
H-19	3·64 q	3·16 q	−0·48	4·98 q	3·06 q	2·66 q	−0·40	2·64
H-21	3·29 d	2·94 d	−0·35	3·37 d	3·49 d	3·70 d	+0·21	3·60
H-21′	2·69 d	2·40 d	−0·39	2·78 d	2·28 d	2·22 d	−0·06	2·12
N—CH_3	2·71 s	2·28 s	−0·43	2·73 s	2·70 s	2·31 s	−0·39	2·34
$COOCH_3$	—	—	—	—	3·76 s	3·30 s	−0·46	3·30
$OCOCH_3$	—	—	—	—	—	—	—	—

[a] Data for quaternoxine from ref.[6].

minium hydride in dioxane did not afford the diol but a compound whose mass spectrum corresponded to the lactol *XI*. Very similar properties were observed with catharantine lactone by Kutney and coworkers[5]. Mamatas-Kalamaras and coworkers[6] isolated from *Alstonia quaternata* the alkaloid quaternoline with very similar properties to raucubaine. Since quaternoline was obtained only as an unsufficiently described minor constituent, we compare the alkaloid *IX* with the corresponding alkaloid quaternoxine which was also isolated by Mamatas-Kalamaras and coworkers[6,7] and was better characterized.

The UV spectrum of the alkaloid *IX* exhibits bands at 252 and 296 nm, characteristic for a dihydroindole chromophore. Its IR spectrum indicates the presence of a $-COOCH_3$ group (band at 1 735 cm^{-1}) and the mass spectrum displays molecular peak of m/z 354·1943, in accord with the formula $C_{21}H_{26}N_2O_3$. No active hydrogen

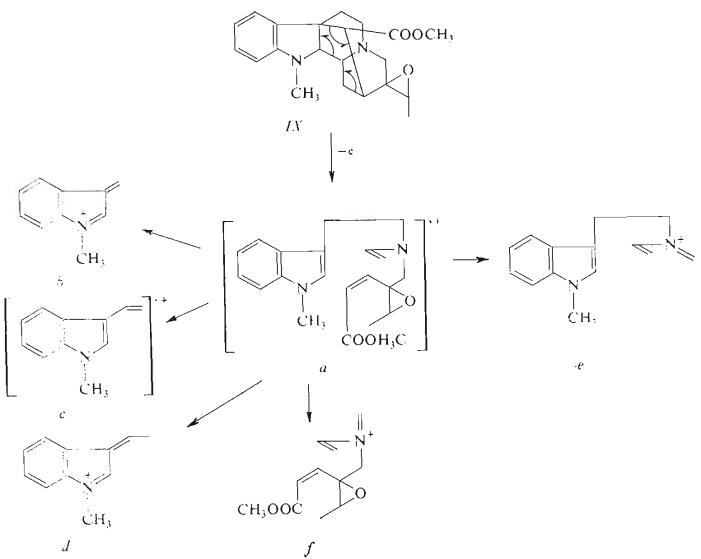
TABLE II

Coupling constants (J, Hz) in ^{1}H-NMR spectra of alkaloids *VIII* and *IX*

$J_{H,H}$	*VIII* ($CDCl_3$)	*VIII* (C_6D_6)	*IX* ($CDCl_3$)	*IX* (C_6D_6)
$J_{2,3}$	0	0	0	0
$J_{3,14}$	4·5	4·4	4·9	5·4
$J_{3,14'}$	1·5	1·5	1·5	1·5
$J_{5,5'}$	14·1	14·1	13·4	13·7
$J_{5,6}$	11·4	11·5	13·4	13·7
$J_{5,6'}$	7·2	7·2	4·6	4·5
$J_{5',6}$	7·9	7·9	6·5	6·5
$J_{5',6'}$	0	0	0	0
$J_{6,6'}$	15·3	15·2	14·5	15·1
$J_{9,10}$	7·2	7·2	7·4	7·3
$J_{9,11}$	1·4	1·4	1·1	1·3
$J_{9,12}$	0·6	0·5	0·5	0·5
$J_{10,11}$	7·6	7·7	7·6	7·6
$J_{10,11}$	0·9	1·0	0·8	1·0
$J_{11,12}$	7·8	7·6	7·8	7·8
$J_{14,14'}$	14·6	14·3	14·8	14·0
$J_{14,15}$	1·5	1·5	[a]	3·4
$J_{14',15}$	4·5	4·5	4·5	3·5
$J_{15,16}$	8·0	8·1	3·9	5·7
$J_{18,19}$	6·4	6·4	5·8	5·7
$J_{21,21'}$	16·0	16·1	15·7	15·6

[a] Not determined.

is present in the molecule, since the molecular peak, labelled in the ion source by deuterated ethanol, remains intact. The indole m/z 144 (*b*), 157 (*c*) and 158 (*d*) fragment ions (Scheme 1) indicate that the indole nitrogen bears a methyl group and that no oxygen-containing substituents are attached to the aromatic nucleus. The M − 144 fragment (m/z 210; $C_{11}H_{16}NO_3$) can be formulated as *f* (Scheme 1). The m/z 213

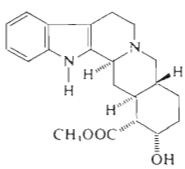


SCHEME 1

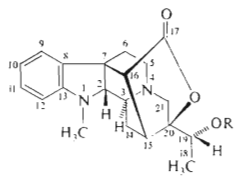
ion (*e*), characteristic for the picraline type of alkaloid, is in this case less abundant. On reaction with methanol in an acid medium, the alkaloid *IX* was transformed into the alkaloid *VIII* from which it differs by the presence of a methoxycarbonyl instead of lactone group and an epoxide instead of hydroxyl. Its ^{1}H-NMR spectrum (Tables I and II) displays signals due to all the structural elements, described for the alkaloid *VIII*, and moreover a methoxycarbonyl singlet at δ 3·76. Some small differences in chemical shifts and coupling constants of the corresponding protons in both the compounds can be fully explained by change of the mentioned functional groups without any significant change of the rigid skeleton. Since an overlap of several

signals around δ 2·70 did not allow a complete analysis of the spectrum in deuteriochloroform, the spectrum was taken also in hexadeuteriobenzene. The complete data, together with the ASIS values, are given in Tables I and II.

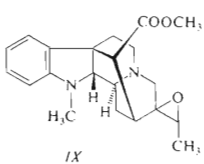
The alkaloid of the constitution *IX* was described by Mamatas-Kalamaras and coworkers[6,7]. For a solution in deuteriochloroform, these authors described only three methyl signals (δ 3·80, 2·70 and 1·17) of which the 18-methyl signal shows the largest difference from our values (δ 1·17 as compared with δ 1·28, found by us). Although for benzene solution the authors published chemical shifts of all the protons, they gave no data on the coupling constants. Comparison of the published δ values with those observed by us reveals marked differences for the 2-H, 3-H, 5-H, 6-H, 15-H and 16-H protons, although the spectrum as a whole shows values very similar



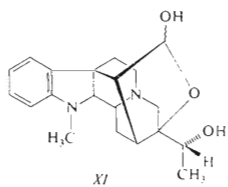
VII



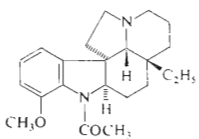
VIII, R = H
X, R = $COCH_3$



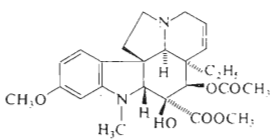
IX



XI



XII



XIII

to ours. It seems likely that the authors[6,7] assigned differently the signals to some of the hydrogens. Unfortunately, without direct comparison of spectra of both compounds the reasons of the mentioned differences cannot unequivocally be determined. If the compounds are not identical (as suggested by different melting points, optical rotations and CD band intensities), it is most likely that the compounds differ in configuration at $C_{(19)}$ or $C_{(20)}$. We have no direct information about the configuration at these carbon atoms in the compound *IX*. Inspection of models and evaluation of steric interactions of the epoxide ring with the $C_{(6)}$ methylene and of the 18-methyl group with the methoxycarbonyl group in the possible $C_{(19)}$ and $C_{(20)}$ epimers shows that the 19*S*,20*R* epimer should be energetically the most advantageous. On the other hand, the French authors[6,7] suggest the 19*R*,20*S* configuration.

The absolute configuration of our alkaloids was assigned by the CD spectra. First of all, we compared the CD spectra of the alkaloids *VIII* and *IX* (Fig. 1), exhibiting marked positive dichroic band at about 250 nm, with those of (−)-aspidospermine (*XII*) and (+)-vindoline (*XIII*) (Fig. 2) which have different configuration at $C_{(7)}$. The chiral center at this atom is closest to the aromatic chromophore and is decisive for the determination of the sign of dichroic transitions in the aromatic nucleus, and thus also of the intense band at 250 nm, obviously due to the B_{2u} transition of the benzene nucleus (see ref.[8−14]). The absolute configuration of (−)-aspidospermine has already been[15,16] determined. The CD curves of the alkaloids *VIII* and *IX* are mirror images of that of (−)-aspidospermine and we can therefore justifiably assume that they have an opposite absolute configuration at $C_{(7)}$ (*i.e.* the same as in (+)-vindoline[17,18]). Similarly as in the case of (−)-aspidospermine, the combination of CD and X-ray data determines the absolute configuration at all the chirality centres in our alkaloids *VIII* and *IX*, including also that at the $C_{(2)}$ atom.

According to arrangement of their skeleton, the alkaloids *VIII* and *IX* belong to the picraline type. Unfortunately, no chiroptical data on other compounds of this type are available Nevertheless, the same sign of specific rotation, $[\alpha]_D$, of all known alkaloids of this type with a tetragonal arrangement at $C_{(2)}$ leads to the same conclusion about the absolute configuration of *VIII* and *IX* as the above-mentioned comparison of CD curves. Also biosynthetic considerations[19] agree with this results. Alkaloids of the picraline type are derived from the corynanthine alkaloids of configuration 15*R*. The relation between configuration at $C_{(15)}$ and $C_{(16)}$ in picraline and akuammiline alkaloids is also described[20]; this determines also the configuration at $C_{(7)}$ and $C_{(3)}$. We can therefore describe the absolute configuration at these chiral centres in *VIII* and *IX* as 2*R*, 3*S*, 7*R*, 15*R* and 16*R*.

The structural similarity of both alkaloids pairs, quaternoxine and quaternoline on the one hand and raucubaine and raucubainine on the other hand, seems to be unquestionable. We may assume that both pairs differ probably in the relative configuration at some of the chiral centers. The difference in configuration at $C_{(7)}$

does not seem likely since the CD spectra of both pairs are of the same type. As the most probable we consider the configurational difference at $C_{(19)}$ and $C_{(20)}$.

EXPERIMENTAL

The melting points were determined on a Leitz–Wetler instrument and are uncorrected. The optical rotations were measured on a Polartronic I polarimeter. The UV spectra were taken in methanol on a Unicam SP-1800 spectrophotometer, IR spectra in KBr pellets on a UR-20 (Karl Zeiss) instrument. ^{1}H-NMR spectra were measured in the FT mode on a Varian XL-200 (200 MHz) spectrometer in deuteriochloroform or hexadeuteriobenzene with tetramethylsilane as internal standard. The signals were assigned using the double resonance technique and arguments following from the chemical shifts. The chemical shifts and coupling constants were obtained from the spectra by first order analysis. Mass spectra were measured on RMU-60, Atlas CN-4B and AEI-MS-902 spectrometers, CD spectra on a Roussel-Jouan II dichrograph in methanol and ethanol. Thin-layer chromatography was carried out on a Merck silica gel type 60, column chromatography on alumina (Merck, Brockmann activity II; eightyfold excess).

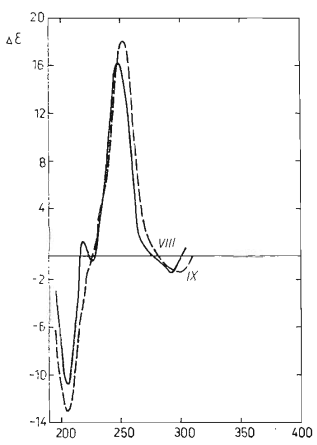


FIG. 1

CD Spectra of (−)-raucubaine (*VIII*) and (−)-raucubainine (*IX*) in methanol

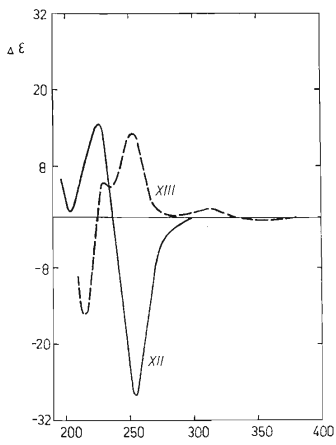


FIG. 2

CD Spectra of (+)-vindoline (*XIII*) and (−)-aspidospermine (*XII*) in methanol. For *XII* $[\alpha]_D$ −95.5° (methanol), for *XIII* $[\alpha]_D$ +42° (chloroform)

Extraction and Isolation of Alkaloids

The plant material was collected by Dr Herrera in Rio Maraví, province Guantánamo, Cuba. A sample of this material was deposited as No 29175 in the herbarium of the Botanical Institute, Cuban Academy of Sciences. The leaves, root bark and tree bark were dried at 40—50°C in a drier with air recirculation, extracted separately and separated according to basicity (fraction A, pH 2; fraction B, pH 7; fraction C, pH 10), the procedure being the same for all the three plant parts. The extraction was performed with benzene + 2% sulfamic acid in a Lörincz extractor.

a) *Root bark alkaloids*: Fraction A (13·75 g) of the root bark extract was chromatographed on a column of alumina (1 100 g). Elution with benzene–ether (1 : 3) afforded 2·50 g of ajmalidine (*I*), m.p. 24°C, $[\alpha]_D^{20}$ +4° (methanol), elution with benzene–ether (3 : 1) gave 2·93 g of reserpiline (*II*), m.p. 217°C (hydrochloride), $[\alpha]_D^{20}$ −38° (ethanol), elution with benzene–ether (9 : 1) yielded 2·53 g of isoreserpiline (*III*), m.p. 212°C, $[\alpha]_D^{20}$ −84° (ethanol). Chromatography (alumina; benzene–ether 1 : 3) of the fraction B (16·44 g) from the root bark extract afforded material which on thin-layer chromatography in ether–methanol (9 : 1) gave 0·40 g of amorphous isocarapanaubine (*IV*), $[\alpha]_D^{20}$ −64° (chloroform).

b) *Tree bark alkaloids*: Fraction A (4·9 g) from the tree bark extract was chromatographed on an alumina column (392 g). Elution with benzene–ether (9 : 1) afforded 0·25 g of ajmalicine (*V*), m.p. 254°C, $[\alpha]_D^{20}$ −62° (chloroform), elution with benzene–ether (3 : 1) gave 0·35 g of reserpiline (*II*). Fraction B (2·9 g) from the tree bark extract was chromatographed on a column of alumina (232 g). Elution with benzene–ether (1 : 3) yielded a fraction from which vellosimine (*VI*), m.p. 301°C $[\alpha]_D^{20}$ +43° (methanol), was obtained by thin-layer chromatography in ether–methanol (9 : 2), elution with benzene–ether (1 : 3) gave 0·20 g of yohimbine (*VII*), m.p. 242°C, $[\alpha]_D^{20}$ +44° (ethanol).

c) *Alkaloids from leaves*: Fraction A (8·3 g) from leaf extract on crystallization from methanol afforded 0·30 g of raucubaine (*VIII*) which exhibited pink coloration with $(NH_4)_2Ce(NO_3)_6$; m.p. 226°C, $[\alpha]_D^{20}$ −18° (chloroform). UV spectrum (methanol): 249 (4·47) and 290 (4·38) nm. IR spectrum (KBr): 3 450, 1 768 and 2 975 cm^{-1}. For ^{1}H-NMR spectrum see Table I. Mass spectrum: M_*^+ 340 (50), 213 (100), 196 (56), 158 (82), 157 (96), 144 (82), 70 (44). CD spectrum ($\Delta\varepsilon$): −11·56 (204 nm), +16·30 (246 nm), −1·59 (292 nm).

The mother liquor from crystallization of the abovementioned fraction A from leaf extract was chromatographed on a column of alumina (664 g). Elution with benzene–ether (9 : 1) afforded 0·24 g of ajmalicine (*V*), elution with benzene–ether (3 : 1) gave 0·18 g of reserpiline (*II*), and elution with benzene–ether (1 : 1) yielded 0·18 g of raucubainine (*IX*); pink coloration with $(NH_4)_2Ce(NO_3)_6$. M.p. 160°C (methanol), $[\alpha]_D^{20}$ −7° (chloroform). UV spectrum (methanol): 252 (4·49) and 296 nm (4·38). IR spectrum (KBr): 1 735 cm^{-1}; ^{1}H-NMR spectrum: see Tables I, II. Mass spectrum: M_*^+ 354 (79), 339 (9), 323 (7), 295 (8), 210 (72), 158 (100), 157 (95), 144 (80). CD spectrum ($\Delta\varepsilon$): −13·29 (205 nm), +17·92 (251 nm), −1·44 (295 nm).

Conversion of Raucubainine (*IX*) into Raucubaine (*VIII*)

A mixture of raucubainine (*IX*) (3·98 mg), methanol (10 ml) and concentrated hydrochloric acid (1 ml) was refluxed for 1 h. After this time the reaction was complete (thin-layer chromatography). The mixture was made alkaline with ammonia, the product taken up in chloroform, the extract dried over sodium sulfate, filtered and taken down *in vacuo*. The isolated product was in all respects (CD and mass spectrum, m.p. and mixture m.p.) identical with raucubaine (*VIII*).

Raucubaine Acetate (*X*)

A solution of raucubaine (*VIII*; 7·6 mg) in acetic anhydride (1 ml) and pyridine (1 ml) was set aside at room temperature overnight. After dilution with water and basification with ammonia the mixture was extracted with ether. The ethereal solution was washed several times with water, dried over sodium sulfate, filtered and taken down *in vacuo*. The residue was chromatographed on a thin layer of silica gel in chloroform–methanol (24 : 1) affording 6·05 mg of product, m.p. 72°C. ^{1}H-NMR spectrum: see Table I. Mass spectrum: M^+ 382 (44), 323 (10), 238 (30). 213 (100), 196 (16), 182 (13), 158 (48), 157 (58), 144 (56).

Reduction of Raucubaine with $LiAlH_4$

A solution of raucubaine (*VIII*; 10 mg) in dioxane (2 ml) was added dropwise to a suspension of lithium aluminium hydride in dioxane (8 ml; 5·23 mg/ml) and the mixture was refluxed for 24 h. After decomposition the ethereal portion was dried over sodium sulfate, filtered and taken down *in vacuo*. Chromatography of the residue on thin layer of silica gel in chloroform–methanol (9 : 1) afforded 8·1 mg of the non-crystalline product *XI*. Mass spectrum: M^+ 342 (62), 297 (8), 286 (9), 278 (22), 243 (12), 213 (100), 198 (25), 182 (22), 170 (15), 158 (52), 157 (33), 144 (35).

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Translated by M. Tichý.