Rendiconti
Accademia Nazionale delle Scienze detta dei XL
Memorie di Scienze Fisiche e Naturali
98° (1979-80), Vol. IV, fasc. 9, pagg. 137-152.

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Carbon-13 NMR spectroscopy in the structure elucidation of monomeric and dimeric Strychnos alkaloids (***)

SUMMARY. — ^{13}C NMR data of sixteen indole alkaloids belonging to seven different groups, isolated from *Strychnos* genus, are reported and discussed. Through the comparison of the assignments some useful indications can be drawn in order to elucidate the structures of new indole alkaloids. These structures can be also found in alkaloids isolated from Apocynaceae and Rubiaceae.

INTRODUCTION

^1H NMR spectroscopy and, more recently, ^{13}C NMR spectroscopy have been a very powerful tool for structural and stereochemical studies of natural products [1]. In particular, the chemical shifts and their assignments for all (or nearly all) carbon atoms of wider and wider number of natural compounds, have made ^{13}C NMR spectroscopy particularly profitable in homogeneous classes of substances (for instance isoquinoline, indole alkaloids) for the easy identification of the known ones (through computerized data too) as well as for the study of the new ones.

Some alkaloids of *Strychnos* genus (Loganiaceae) are here examined. These are indole derivatives, which originate from a tryptamine unit with a C-10 (or

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(***) Memoria presentata dall'Accademico dei XL, G.B. MARINI-BETTOLO il 27 Dicembre 1979.

ISSN 0370-2480

C-9) unit, generated by mevalonic acid pathway. These moieties give rise to various groups of monomeric alkaloids, according to their fundamental skeleton, i.e. strychnine, corynantheine, sarpagine, mavacurine, ajmalicine, oxindole, yohimbine and akagerine. Some of the aforementioned alkaloids were also found in plants of Apocynaceae and Rubiaceae families [2].

In some *Strychnos* species dimeric alkaloids occur. They result:

a) from the symmetrical union of two identical or very similar units having strychnine-like structure, i.e. C-curarine or C-alkaloid H;

b) from the asymmetrical union of two strychnine-like units, i.e. strychnobiline;

c) from the union of two different moieties, for example corynantheine and tryptamine, to give rise to nigritanins and other usambarane derivatives.

Some monomeric and dimeric alkaloids occur in plants as quaternary salts. Dimeric quaternary alkaloids display high curarizing activity and they are the main ingredients of the arrow curare poison.

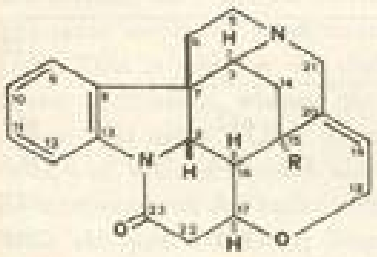
In the present paper we report, in comparative form, the ^{13}C NMR data of several new and less common *Strychnos* alkaloids recently isolated by us, in order to contribute with new data to the spectroscopical characterization and structure elucidation of *Strychnos* alkaloids. In effect although so far several papers have reported ^{13}C NMR spectra of indole alkaloids, only few have regarded the *Strychnos* ones [3].

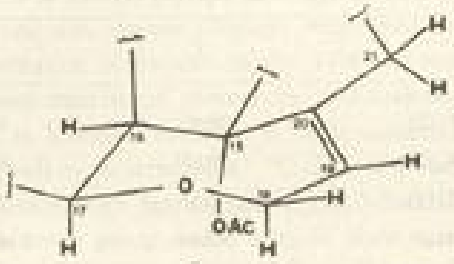
Strychnine group

"Normal" series

15-hydroxystrychnine *1* (fig. 1) is a new alkaloid recently isolated from seeds of *Strychnos nux vomica* L. [4]. As strychnine *2*, *1* belongs to the "normal" series and its structure was determined by analysis of ^1H NMR data of its 0-acetyl derivative *3*. By comparison of ^{13}C NMR spectrum of *3* (Table 1) with that of *2* [5], the effects due to the presence of the 15-acetoxy group in *3* are evident: the α effect (+ 46 ppm) on C(15), the β effects on C(14) (+ 3.8 ppm) and C(16) (+ 2.4 ppm) as well as the shielding effect on C(17) (− 3.3 ppm). The last effect is due to gauche-butane type interaction between C(17) and the acetoxy group in the rigidly held chair conformation of the tetrahydrooxepinic ring (a, fig. 1). The same shielding was observed between 15-hydroxyicajine *4* and icajine *5*, wherein C(17) resonates at 73.3 and 77.9 ppm, respectively [6]. It is interesting to report the multiplicity of C(14) signal in *3*, easily recognizable as it is the highest field methylene, in the ^{13}C off-resonance spectrum: C(14) appears as a double doublet instead of a triplet shape on account of the non equivalence of its two protons. This phenomenon, usually observed in ^1H NMR spectroscopy, it is possible in ^{13}C NMR spectra, as well [7].

11-methoxydiaboline *6* is another alkaloid of the "normal" series widely spread in South American *Strychnos* species and also present in African species.





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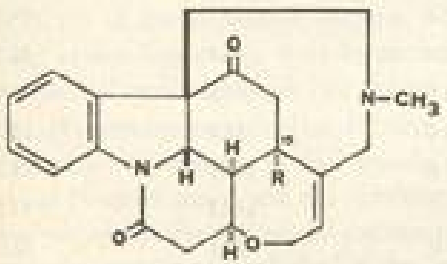
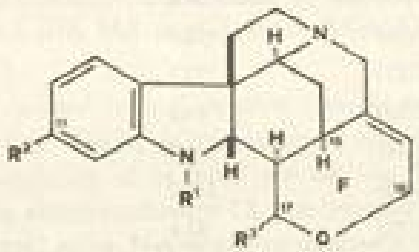
	R
1 15-hydroxystrychnine	OH
2 strychnine	H
3 15-acetoxystrychnine	OAc





	R
4 15-hydroxyicajine	OH
5 icajine	H

	R^1	R^2	R^3	
6 11-methoxydiaboline	Ac	OCH_3	OH	
7 diaboline	Ac	H	OH	
8 W.G. aldehyde	H	H	OH	
9 isocondensamine	Ac	OCH_3	OAc	α
10 henningsamine	Ac	H	OAc	β

Fig. 1

TABLE 1

	2[a]	3	9	12
C(2)	59.9[b]	61.3[b]	64.2	66.8
C(3)	59.8[b]	62.6[b]	58.5	91.8
C(5)	50.1	51.7	51.2	52.1[b]
C(6)	42.6	42.5	38.4	39.0
C(7)	51.7	51.5	57.6	58.7
C(8)	132.4	131.2	124.7	132.1
C(9)	121.9	122.2	121.4	126.7
C(10)	123.8	124.3	109.2	119.4
C(11)	128.1	128.7	139.3	127.5
C(12)	115.8	116.1	105.8	109.7
C(13)	141.8	142.2	139.7	149.4
C(14)	26.7	30.5	25.0	36.2
C(15)	31.4	77.4	29.5	34.9
C(16)	48.0	50.4	45.4	41.5
C(17)	77.3	74.0	93.6	70.7
C(18)	64.3	64.0	61.8	18.2
C(19)	126.8	131.6	122.7	75.8
C(20)	140.2	137.7	142.9	37.1
C(21)	52.4	54.0	53.1	53.6[b]
C(22)	42.2	42.5	23.1[c]	
C(23)	168.0	168.6	169.2[c]	
C=O		168.6	168.3	
CH_3		21.3	20.9	
OCH_3			55.3	

[a] Assignments reported by Wenkert et al. [5]

[b] Within a given column assignments may be interchanged.

[c] The signal belongs to N-acetyl group.

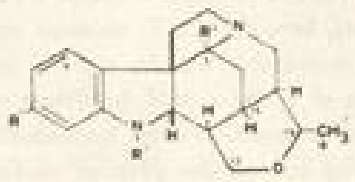
This alkaloid, as well as diaboline *7* and Wieland Gumlich aldehyde (N-desacetyldiaboline) *8* (often found in the same plant), have the C(17) anomeric center and the emiacetalic equilibrium in solution is responsible for the scarcely intelligible ^1H and ^{13}C NMR spectra. The acetylation of *6* under mild conditions yields, as sole product, the 0-acetyl-α isomer, identical to natural product isocondensamine *9*. The seven membered tetrahydrooxepinic ring can assume different conformations [5]. Thus in diaboline the chair conformation is present in the 17-α-hydroxy isomer (OH axial), whereas the boat conformation is present in 17-β-hydroxy isomer (OH axial). Chair conformation is however common to both anomeric isomers of Wieland Gumlich aldehyde as well as to strychnine. ^{13}C data of *9* can be interpreted on the basis of the comparison with henningsamine (N, 0-diacetyl W.G. aldehyde) *10*, having β-equatorial acetoxy group and F ring in chair conformation: the differences for C(17) ($\Delta\delta = -8.5$ ppm), C(18) ($\Delta\delta = -2.5$ ppm) and C(15) ($\Delta\delta = -3.7$ ppm) would suggest for *9* a boat conformation instead of a chair conformation for the oxepinic ring, which lays the acetoxy group in the preferred equatorial position.

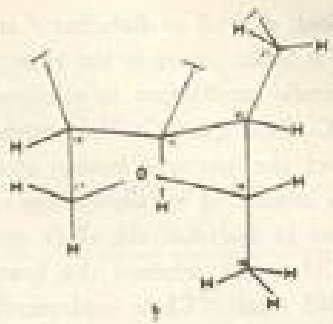
"Pseudo" series

The "pseudo" series is characterized by the presence of an hydroxy group on C(3) of the strychnine skeleton. The resulting carbinolamine structure can react as seco keto-aminic form by methylation with MeI to give rise to "N-methyl-*seco*-pseudo" series alkaloids (see below) [8].

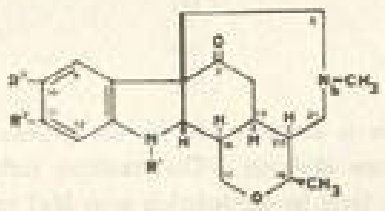
N-acetylstrychnosplendine *11* (fig. 2), isolated from *S. fendleri* Sprague and Sandwith [8], belongs to the "pseudo" series. Owing to the restricted rotation of its N-acetyl group and the resulting complexity of its NMR spectra, the ^{13}C analysis was performed on the corresponding strychnosplendine *12*. In comparison with the corresponding alkaloid of the "normal" series, N-desacetylspermostrychnine *13* [5], the presence in *12* of 3-hydroxy group shifts C(3) *downfield* ($\Delta\delta = +30.3$ ppm), whereas C(9) undergoes the deshielding effect ($\Delta\delta = +4.8$ ppm) (already observed for H-9 in ^1H NMR [8]), due to electric dipolar moment and to anisotropy of magnetic susceptibility of the same hydroxy group.

The stereochemistry of the methyl group of the tetrahydropiranic ring can be assigned unambiguously on the basis of several ^{13}C chemical shift data. In effect, whereas in ^1H NMR spectroscopy only the value of the methyl group is diagnostic for its stereochemistry (β-equatorial methyl groups resonate at higher fields than the α-axial ones [8, 9]), in the ^{13}C NMR C(15), C(17), C(18) and C(19) are consistent with the different stereochemistry. Their chemical shifts in *12* (β-equatorial methyl group) are higher than in analogous compounds having α-axial methyl group [5] on account of absence of 1,3 diaxial interaction (b, fig. 2).

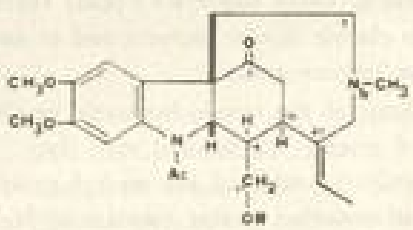




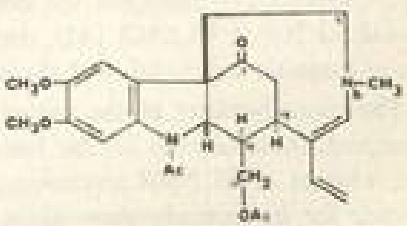
	R^1	R^2	R^3	
11 N-acetylstrychnosplendline	Ac	OH	H	CH_3
12 strychnosplendline	H	OH	H	CH_3
13 N-desacetylspermostrychnine	H	H	H	CH_3
21 strychnospermine	Ac	H	OCH_3	CH_3



	R^1	R^2	
14 N-desacetylstrychnofendlerine	H	H	
15 strychnofendlerine	Ac	H	
16 strychnobrasiline	Ac	H	Δ^{20}
20 10, 11-dimethoxystrychnobrasiline	Ac	OCH_3	Δ^{20}



	R
17 tabascanine	H
18 O-acetyltabascanine	Ac



19 strychnosiline

Fig. 2

"N-methyl-sec-pseudo" series

Table 2 shows the ^{13}C chemical shift assignments of N-desacetylstrychnofendlerine *14*, obtained by desacetylation of strychnofendlerine *15*, isolated from *S. fendleri* Sprague and Sandwith [8], of strychnobrasiline *16*, of tabascanine *17*, of 0-acetyltabascanine *18* and of strychnosiline *19*, isolated from *S. alvimiana* Krukoff and Barneby. They belong to "N-methyl-*sec*-pseudo" series, wherein a carbonyl group in C(3) and a methyl group at N_b are present. In this series, in comparison with the "pseudo" series, the loss of the C(3)/N_b bond generates a highly flexible azacyclononane ring, responsable for the partial mobility of the N_b lone pair towards C(3) carbonyl group according to the following transannular interaction

As a result of this effect in *14*, *17* and *18*, C(21) is shifted inductively to lower fields in comparison with the "normal" and "pseudo" series, whereas this effect for C(5) is partially compensated by the shielding of C(3) carbonyl group cone. Furthermore, C(9) is deshielded by carbonyl group in C(3) through a mechanism similar to that already observed in the "pseudo" series.

Furthermore, as a result of the same transannular amidic interaction, the positive charge is partially delocalized from the carbonyl carbon towards nitrogen atom and consequently its resonance moves upfield respect to typical frequency of keto groups. In *16* the C(3) chemical shift is found at lower fields than in *14* ($\Delta\delta = +4.8$ ppm) because N_b lone pair is furtherly engaged in the mesomeric form $-\overset{+}{N}=CH-\overset{-}{C}-$ for the presence of 20, 21 double bond.

16 is a N-acetyl-indoline alkaloid, wherein, however, the large predominance of a conformer allows the spectroscopical analysis to perform on the original product. In the compounds of this series the *trans* conformation of the N-acetyl group is strictly assigned on the basis of H-12 NMR value (*ca.* 6.7 ppm). In 10, 11-dimethoxystrychnobrasiline *20*, having *cis* conformation for the N-acetyl group, H-12 resonates at 7.6 ppm [9]. However the different conformation of the N-acetyl group does not affect the chemical shift value of C(12) as also observed in the two rotamers of strychnospermine *21* at low temperature (− 26 °C) [5].

In comparison with *14*, the opening of the tetrahydropyranic ring in *17*, *18* and *19* does not affect the conformation of the azacyclononane ring, as proved by C(3) and C(5) chemical shift values. As a result of the opening of the tetrahydropyranic ring, *17* in comparison with *16* shows deshielding effect for C(16) and C(17) and a remarkable shielding effect for C(15) and C(20) due to the different simmetry. In *18* and *19* carbonyl signals due to O—Ac and N_a—Ac can be distinguished on the basis of the different relaxation time.

TABLE 2

	14	*16*	*17*	*18*	*19*
C(2)	63.4	62.8	66.4	64.4	61.9
C(3)	187.4	192.2	187.1	188.5	187.4
C(5)	55.4	53.2	53.0	53.0	52.3
C(6)	43.8	42.5*	41.7*	41.5	41.4
C(7)	57.5	57.0	55.6	55.4	55.6
C(8)	130.6	130.0	126.6	126.1	125.6
C(9)	125.3	124.0	107.7	107.9	108.0
C(10)	119.1	124.6	145.9	145.7	145.4
C(11)	128.0	127.4	147.6	147.9	147.6
C(12)	109.6	118.2	101.8	102.4	101.6
C(13)	148.6	136.2	134.5	133.2	134.3
C(14)	41.9	40.5*	42.9*	41.5	41.4
C(15)	37.8*	41.0*	35.2	31.9	30.4
C(16)	38.8*	41.2*	43.7	42.0	40.1
C(17)	70.7	67.2	69.5	69.2	63.5
C(18)	18.6	17.0	12.3	12.2	113.5
C(19)	77.3	76.6	122.3	124.2	142.2
C(20)	40.3	141.1	136.9	138.6	132.7
C(21)	60.0	129.7	62.8	64.4	136.9
C(22)		168.7	168.8	169.1	169.0
C(23)		23.3	22.3	22.2	22.1
C=O				168.8	168.8
CH_3				20.0	20.1
OCH_3			55.5	55.6	55.5
OCH_3			55.3	55.4	55.2
NCH_3	42.4	42.1	39.9	39.6	41.1

* Within a given column these assignments may be reversed.

Corynanthеine group

Yohimbine and ajmalicine alkaloids have been the object of studies concerning the determination of their stereochemistry using ^{13}C NMR spectroscopy [10].

Carbon atoms of C and D rings are highly affected by the configuration of C(3) chiral center; i.e. "normal" yohimbine (H-3 α) shows C(6) (22.5 ppm), C(5) (53.7 ppm), C(21) (61.9 ppm) and C(3) (60.2 ppm) at lower fields than "pseudo" yohimbine (H-3 β), wherein C(6), C(5), C(21) and C(3) are at 17.1, 51.4, 52.4 and 54.4 ppm, respectively [11]. In the latter stereoisomer the C/D ring cis-quinolizidine junction generates a considerable interaction between the aforementioned carbon atoms.

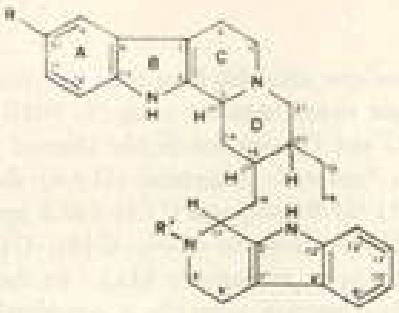
The information obtained from yohimbine and ajmalicine compounds can be used in the analysis of ^{13}C NMR data of nigritanins *22-25* (fig. 3). Nigritanins are bisindole alkaloids, found in African *Strychnos* [12, 13] whose structures can be derived from the junction of a corynane and a tryptamine moiety [14]. This biogenetic hypothesis was confirmed by the occurrence in the same plants of akagerine *26* and kribine *27* [15] and of 10-hydroxyakagerine *28* in *S. spinosa* Lam [16], ideal precursores of the corynane moiety through tautomeric form *29*. Nigritanin *22*, 18-dehydronigritanin *23*, 10-hydroxynigritanin *24* and 18-dehydro-10-hydroxynigritanin *25*, isolated from the leaves of *S. nigritana* Bak are here considered.

10-hydroxynigritanins *24* and *25* show not intelligible ^1H as well as ^{13}C NMR spectra in $CDCl_3$, owing to keto-enolic tautomerism present in A ring (1). For this reason the 0-acetyl derivative of *24*, *30*, and the 0-methyl derivative of *25*, *31*, were examined. Their ^{13}C NMR spectra, as well as those of *22* and *23* are reported in table 3.

The practical identity of C(3), C(5), C(6) and C(21) chemical shifts in *22*, *23*, *30* and *31* with the corresponding ones in "normal" yohimbine assigns the trans-quinolizidine junction for C/D rings unambiguously. The availability of ^{13}C data of two C(17) epimers, ochrolifuanine A *32* (H-17 β) and ochrolifuanine B *33* (H-17 α) [17] was specifically useful for the comparison with the corresponding data of nigritanins. By adding to C(5') and C(17) chemical shifts of *32* and *33* the contributions due to N-methylation, calculated by comparison of 2-methyl-N-methylpiperidine and 2-methylpiperidine ^{13}C data [11], the following values were deduced: for N-methylochrolifuanine A, 51.8 for C(5'), 55.3 for C(17) and for N-methylochrolifuanine B, 51.6 for C(5') and 58.4 for C(17). Owing to the practical identity of the latter datum set with the corresponding ones of nigritanins, the same H-α configuration for C(17) was assigned in the hypothesis of same C(16)/C(17) bond conformation.

The assignment of C(20) stereochemistry for *22* and *30* can be further made by comparison with the spectral data of ochrolifuanines *33* and *34* which

(1) This phenomenon is common to all 10-hydroxyindole alkaloids and is confirmed by the high reactivity of H-4 (exchange with deuterium oxide) in 5-hydroxyindoles. (J.W. Daly and B. Witkop, « J. Am. Chem. Soc. », *89*, 1032 (1967)).



	R^1	R^2	H-17	H-20
22 nigritanin	H	CH_3	α	β
23 18-dehydronigritanin	H	CH_3	α	β Δ^{18}
24 10-hydroxynigritanin	OH	CH_3	α	β
25 18-dehydro-10-hydroxynigritanin	OH	CH_3	α	β Δ^{18}
30 10-acetoxynigritanin	OAc	CH_3	α	β
31 18-dehydro-10-methoxynigritanin	OCH_3	CH_3	α	β Δ^{18}
32 ochrolifuanine A	H	H	β	β
33 ochrolifuanine B	H	H	α	β
34	H	H	α	α

	R
26 akagerine	H
28 10-hydroxyakagerine	OH
35 anhydroakagerine	H Δ^{18}

	R^1	R^2
27 kribine	H	OH
	OH	H

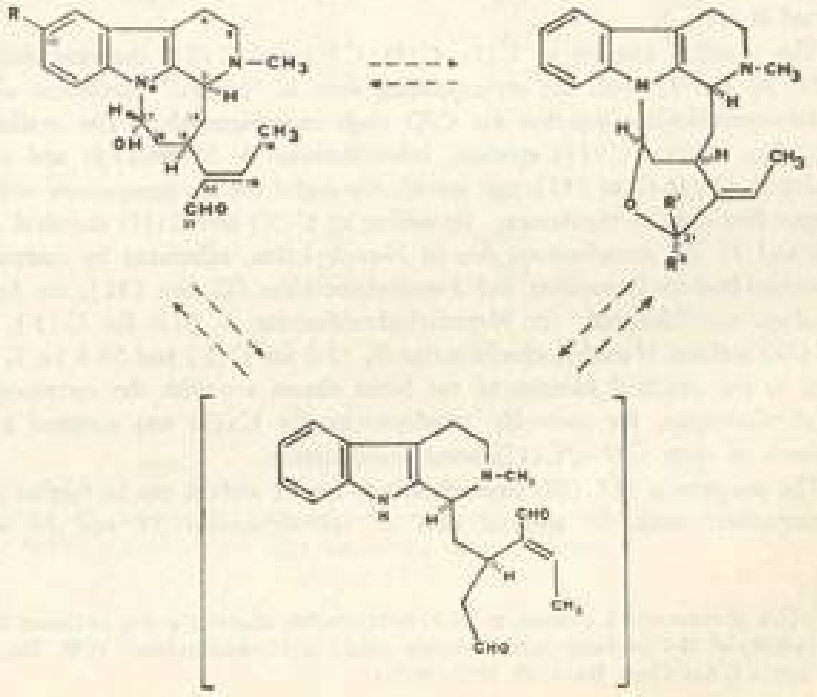


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Fig. 3

TABLE 3

	22	23	30	31
C(2), C(2')	134.7, 135.5	134.6, 135.6	136.1, 135.8	135.1, 135.5
C(3)	59.1	59.1	59.3	59.0
C(5)	53.0	52.8	53.0	52.6
C(5')	51.3	51.8	51.2	51.3
C(6)	21.5	21.6	21.6	21.6
C(6')	20.7	20.8	20.6	20.7
C(7), C(7')	107.1, 108.8	107.3, 109.2	107.6, 108.8	107.0, 108.9
C(8), C(8')	126.7, 127.0	126.9, 126.9	126.9, 127.4	126.7, 127.3
C(9)	117.5[a]	117.7[a]	111.3	100.2
C(9')	117.7[a]	118.0[a]	117.8	117.8
C(10)	120.4[b]	123.0[b]	143.9	155.5
C(10')	121.4[b]	121.7[b]	119.4	119.3
C(11)	118.8[c]	120.9[c]	114.5	110.4
C(11')	119.3[c]	119.0[c]	121.5	121.4
C(12), C(12')	110.8, 110.9	110.9, 111.0	110.0, 111.2	111.0, 111.4
C(13)	135.6[d]	135.7[d]	133.7	130.8
C(13')	137.7[d]	135.8[d]	136.7	135.7
C(14)	34.9	34.5	34.9	34.3
C(15)	35.8	35.8	36.0	35.7
C(16)	35.0	35.2	35.2	35.2
C(17)	58.6	58.8	58.6	58.6
C(18)	11.2	116.9	11.3	116.7
C(19)	23.7	140.0	23.7	140.0
C(20)	41.9	47.6	42.1	47.4
C(21)	60.2	61.0	60.4	60.9
NCH_3	42.7	42.6	42.7	42.6
C=O			170.6	
CH_3			21.1	
OCH_3				56.1

[a,b,c,d] In a column assignments having same letter may be reversed.

present opposite configuration at C-20 chiral center (series "normal" and "allo", respectively). The H-β configuration for C (20) in *22* and *30* could be inferred by the chemical shift similarity of C (19) and C (14) with the corresponding data of ochrolifuanine B *33* (23.8 and 36.4, respectively). The same carbon atoms are more shielded in its C (20) epimer *34* (17.5 and 32.4, respectively) on account of acyclic γ effect on the terminus of a gauche-butane structure due to the axiality of its ethyl group.

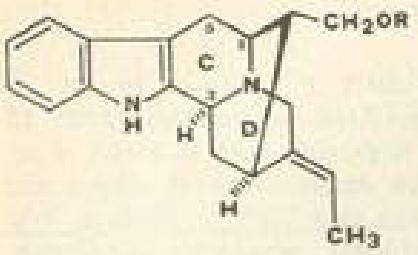
Akagerine group

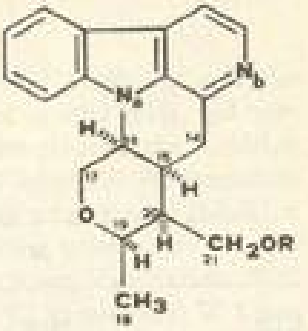
Akagerine *26*, isolated from some African *Strychnos* (*S. nigritana* Bak [15], *S. barteri* Solered [13], *S. dale* and *S. oleocarpa* [18], and *S. usambarensis* [19]), and from South American *Strychnos* [20] (*S. gardneri* A. DC., *S. jobertiana* Krukoff and Barneby and *S. parvifolia* D.C.) presents a tetracyclic skeleton. The terpenoid moiety is linked to N_a of N_b-methyltetrahydro-β-carboline system in such a way to form an azacycloeptane ring. The former moiety shows ^{13}C NMR data practically identical with the corresponding ones of nigritanins. The chemical shift of C (17) (75.4 ppm) is in agreement with the carbinolamine structure. It moves downfield in the spectrum of anhydroakagerine *35*, obtained by easy dehydration of *26*; on account of the double bond α to N_a, *35* shows, in comparison with akagerine *26*, the deshielding of all the carbon atoms of the indole moiety, as well as of C (3), C (5) and C (6). The difference in the olefinic C (19) and C (20) chemical shifts between *26* and *35* can be explained by the different orientation of the side chain, which is equatorial in respect to the azacycloeptane ring in *26*, whereas in *35* the plane of C (14), C (15), C (16), C (17) and N_a bisectes the C (15) $\langle^{C=}_{H}$ angle.(2)

Sarpagine group

As representative of this group, the ^{13}C NMR data of 0-acetylnormacusine B *36* is reported in table 4. *36* was obtained by acetylation of normacusine B *37*, isolated from *S. rubiginosa* D.C. [21] and *S. medeola* Sagot ex Progel [22]. In *36* the particular five cycle system rigidly holds the C/D junction in cis-quinolizidine form, having C ring in hemi-chair and D and E rings in boat conformations. In this structure C (3) (49.9 ppm) suffers, in comparison with the corresponding

(2) The chemical shifts of CHO and CH_3-18 account for their trans relationship (E-isomer) in agreement with the corresponding values of tiglic aldehyde (V. Vogel, W. von Philipsborn, « Org. Magn. Resonance », *7*, 617 (1975).





	R
36 O-acetylnormacusine B	Ac
37 normacusine B	H

	R
38 strychohirsutine *	H
39 tetradehydrostrychnohirsutine	H
40 O-acetyltetradehydrostrychnohirsutine	Ac

* In the above formula positions 3, 4, 5, 6 are hydrogenated, and the configuration of 3 is S.

Fig. 4

carbon of the "normal" cis-quinolizidine structure (54.4 ppm) [11], a further shielding effect; conversely C (5) and C (6) bear, respectively, the α and β effects, due to the substitution.

Ajmalicine group

Strychnohirsutine *38* and tetradehydrostrychnohirsutine *39* are new β-carboline alkaloids isolated from root bark of *S. hirsuta* Sprace ex Bentham [23]. These alkaloids, as well as alstonidine [24], may be correlated to ajmalicine by fission of its C (21)/N_b bond [23]. In *38* and *39* the pentacyclic system is there originated by bonding of C (16) with N_a. In table 4, ^{13}C NMR chemical shifts of 0-acetyltetradehydrostrychnohirsutine *40* are reported. By comparison with the spectra of carbazole, naphtalene and isoquinoline [25], the aromatic signals of *40* have been assigned. Carbon atoms adjacent to N_b are easily distinguishable on account of their low field positions. The D/E ring cis junction and the β-axial configuration of CH_3-18 group, strictly assigned on the basis of ^1H NMR spectroscopy [26], could not be confirmed by ^{13}C NMR spectroscopy, on account of the absence of proper models.

TABLE 4

	26	33	36	40
C(2)	135.8	137.4	134.0	140.4*
C(3)	60.5	62.6	49.9	140.6*
C(5)	50.0	53.9	54.5	136.0
C(6)	19.8	21.8	26.9	129.2
C(7)	108.3	110.6	103.9	126.2
C(8)	126.5	127.9	127.4	121.3
C(9)	118.1	119.1	117.9	113.7
C(10)	121.1	122.6	121.1	123.0
C(11)	119.1	120.9	119.1	120.6
C(12)	108.3	109.9	110.8	109.0
C(13)	136.1	136.7	136.3	140.4*
C(14)	35.9	35.2	33.2	28.6
C(15)	29.0	35.9	27.6	32.9
C(16)	37.5	112.3	40.8	47.1
C(17)	75.4	122.8	66.1	70.4
C(18)	15.1	15.8	12.7	18.3
C(19)	150.2	154.2	116.9	75.7
C(20)	147.7	146.2	138.1	42.5
C(21)	194.6	194.3	55.9	61.8
C=O			170.8	172.8
CH_3			20.9	21.0
NCH_3	42.1	43.4		

* Assignments may be reversed.

Experimental

Natural abundance ^{13}C NMR spectra were recorded employing a Varian XL 100 Fourier transform NMR spectrometer, operating at 25.2 MHz, and were run in 0.2-0.4 M deuterochloroform solutions, which also provided the deuterium lock signal. Deuterochloroform was used as internal reference; ^{13}C resonances were converted to Me_4Si scale involving the following correction: $\delta\,(Me_4Si) = \delta\,(CDCl_3) + 77.0$ ppm. Usual measurement conditions: pulse width: 15 μsec (approx. 20°); pulse delay: none; acquisition time: 0.8 sec; data points: 8192 (8 K); spectral width: 6000 Hz; probe temperature: 32 °C; sample tube: ∅ 5 mm. Alkaloids investigated were all isolated from natural sources and their derivatives obtained as described in the literature cited. For compounds *1*, *37* and *39* the analysis was performed on the corresponding o-acetyl derivatives instead of the original products, owing to the low solubility of the former in deuterochloroform; the use of other deuterated solvents was avoided in consideration of the differences often induced in chemical shift values by the solvents.

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Direttore resp.: Prof. P. De Mattei - Autorizz. Trib. di Roma n. 7269 del 28-11-1959 - Tip. della Pace, Roma