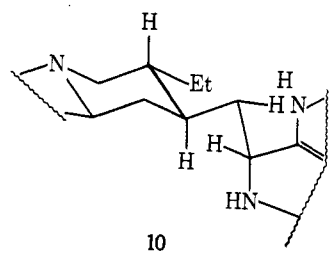
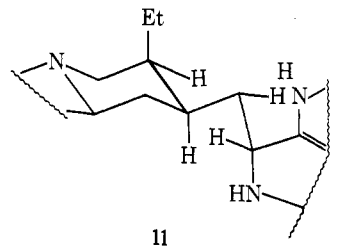
H(15) experiences nonbonded interaction from $N_{b'}$, whereas **2a** represented by rotamer **7b** and **2b** by **7a** lead to much more severe nonbonded interaction of H(15) with $N_{a'}$. The same consideration of nonbonded interactions supports the preference of ochrolifuanine A (**1a**) for rotamer **7a** instead of **7b** except that in the case of this alkaloid rotamer **7b** suffers from an additional, unfavorable interaction, i.e., repulsion of C(17) and C(19). Conformational structures **10**, **11**, and **12** portray the preferred orientations of rings D and C′ toward each other in ochrolifuanine A (**1a**) and isomers **2a** and **2b**, respectively.



10



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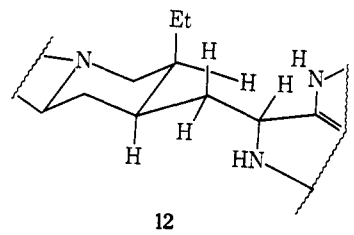
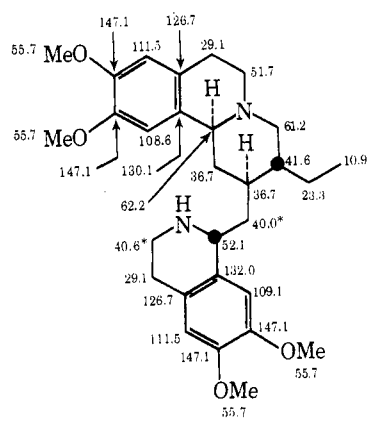


12

Ochrolifuanine A (**1a**) has a phenylalanine-derived alkaloid relative in emetine (**13**). The ^{13}C NMR data for the ochrolifuanines and their steroisomers (vide supra) as well as for the isoquinoline alkaloids laudanosine and tetrahydropalmatine[8] permit the assignment of the carbon shifts of emetine, as shown in formula **13**. It is noteworthy and of possible diagnostic value in the alkaloid field that benzylic methylenes within a tetrahydroisoquinoline nucleus are strongly deshielded on comparison with those in a tetrahydrocarboline unit.



13

Experimental Section

The carbon shifts in Table I were recorded on a Varian XL-100-15 spectrometer operating at 25.20 MHz equipped to operate in the pulsed Fourier transform mode with Transform Technology Inc. computer and pulse hardware. The shifts denoted on formula **13** were obtained from a chloroform solution [$\delta(Me_4Si) = \delta(CHCl_3) + 77.2$ ppm] with a Varian DP-60 spectrometer operating at 15.08 MHz in the Fourier transform mode. The asterisks on formula **13** indicate permissible signal reversal.

Registry No.—**1a**, 35527-46-9; **1b**, 35471-11-5; **2a**, 51820-26-9; **2b**, 51820-25-8; **3**, 17019-01-1; **4**, 239-15-6; **5a**, 7762-19-8; **5b**, 14509-88-7; **13**, 483-18-1.

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Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. XXXIV. Monomeric Quinolinic *Melodinus* Alkaloids[1]

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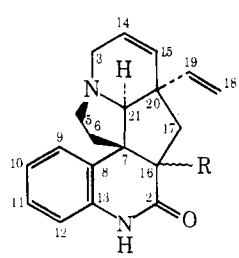
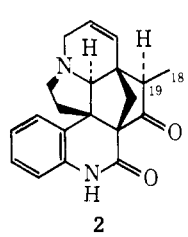
Received March 25, 1975

Investigations of the chemical constituents of the New Caledonian plant *Melodinus scandens* Forst. have shown this species to contain known *Aspidosperma* alkaloids as well as new bases structurally related to the former by oxidative rearrangement.[2-4] Structures **1a**, **1b**, **1c**, and **2** were



1a, R = β-H
b, R = α-H
c, R = α-CO_2Me
d, R = β-CO_2Me



2

assigned to meloscine,[2] epimeloscine,[2] scandine,[2] and meloscandonine,[4] respectively, primarily by spectroscopic means and the full structure of meloscine (**1a**) and absolute configuration were determined by X-ray analysis.[4] In view of the recent success in structure correlation of the *Aspidosperma* bases by ^{13}C NMR spectroscopy[5] the four quinolones were submitted to ^{13}C NMR analysis.

Table I
Chemical Shifts[a]

	1c	1a	1b	2
C (2)	170.2	171.9	173.0	169.0
C (3)	47.6	45.6	45.7	47.2
C (5)	53.2	52.4	51.7	54.8
C (6)	39.8	43.2	35.4	38.1
C (7)	57.7	56.8	55.3	54.8
C (8)	128.5	126.5	135.8[d]	130.5
C (9)	126.7[b]	127.2	122.3[c]	123.5[e]
C (10)	123.4	123.6	123.2[c]	123.4[e]
C (11)	127.2[b]	127.2	126.7	127.6
C (12)	115.5	115.4	116.2	116.3
C (13)	134.1	134.8	136.5[d]	136.5
C (14)	122.7	126.4	120.8	124.0
C (15)	131.2	134.2	130.9	127.4
C (16)	63.6	50.0	47.9	67.7
C (17)	44.0	40.8	34.0	36.0
C (18)	114.4	112.2	112.1	11.0
C (19)	142.0	142.4	144.3	50.7
C (20)	46.5	47.3	44.9	44.3
C (21)	83.5	81.1	71.5	69.9
C=O	169.3			210.0
OMe	52.4			

[a] In parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b-e] The signals bearing the same superscript may be reversed.

The assignment of the carbon shifts of the alkaloids has been carried out in the following manner. The aromatic carbon shifts can be designated by the use of acetanilide[6] and 3,3-dialkyloxindoles[7] as models. Residual coupling characteristics detected in the single-frequency off-resonance decoupled (sford) spectra differentiate the nuclear double bond carbons from the aromatic methines. Thus C(14) and C(15) show appreciably lower J_R values in sford spectra in which the decoupler frequency is at the upfield end of the ^1H NMR spectrum.[8] As in the *Aspidosperma* alkaloid series,[5] C(14) is distinguished from C(15) by taking into consideration their dissimilarity with respect to the C(20) substituents. Readily recognized by chemical shift and multiplicity, the carbons of the vinyl group of three of the alkaloids exhibit strong two-bond coupling with their hydrogens. The phenomenon of long-range coupling of allylic carbons attached to vinyl groups is useful in the differentiation of the quaternary sites C(7) and C(20) of compounds 1 after the initial recognition of all nonprotonated carbons by the low-power, proton noise-modulated decoupling technique.[8,9] Thus, the C(20) signal appears much more broadened than the signals of other nonprotonated centers in sford spectra in which the decoupler frequency is placed at the high-field extremum of the ^1H NMR spectrum. The same signal is sharpened selectively upon irradiation in the olefinic ^1H NMR region. The C(7) shift of the four alkaloids is nearly the same as that of the *Aspidosperma* bases in view of their similar C(7) environment. Carbon 16 of **1c** and **2** exhibits the lowest field signal among the quaternary carbons.

The sole aminomethine, C(21), is the methine of lowest field. Since H(21) is the lowest field, saturated methine hydrogen, the residual J_{C-H} values, from sford spectra with the decoupler at a high ^1H NMR field position, are larger for C(21) than the other methine. Similarly, both chemical shift and residual splitting distinguish the aminomethylenes from the other methylenes and C(3) from C(5). The differentiation of the methylenes C(6) and C(17) depends on more subtle arguments (vide infra). The chemical shifts of all alkaloids are listed in Table I.

The stereochemistry of epimeloscine (**1b**) restricts the ring system to a rigid framework in which H(9) is in close proximity to H(21) and the C(9)–H and C(21)–H bonds are nearly coplanar. This requirement for a strong, reciprocal γ effect is missing in meloscine (**1a**), whose stereochemistry permits far more flexibility of the ring system. Both the ^1H NMR[2] and ^{13}C NMR data reveal the steric relationship between C(9)–H and C(21)–H. In epimeloscine (**1b**) H-21 is deshielded by 0.4 ppm from its field position in meloscine (**1a**) because of the anisotropy of the aromatic ring and C(9) and C(21) are shielded by ca. 5 and 10 ppm, respectively. Meloscandonine (**2**) expectedly shows the same ^{13}C NMR behavior at C(9) and C(21) as epimeloscine (**1b**). The lack of like ^{13}C NMR characteristics of scandine (**1c**) militates against its accepted structure and suggests it to be isomeric at C(16), in conformity with the similarity of its C(9) and C(21) shifts with those of meloscine (**1a**).

The same conclusion is reached by consideration of the C(6) and C(17) methylene resonances. Feeling a reciprocal γ effect, the two methylenes of epimeloscine (**1b**) are shielded strongly in comparison with the equivalent centers of meloscine (**1a**). The introduction of a 16-carbomethoxy group can be expected to deshield C(17) of either **1a** or **1b**, while shielding C(6) of **1a** or leaving C(6) of **1b** unaffected. Comparison of the methylene shift differences of scandine and meloscine (**1a**) as well as epimeloscine (**1b**) without regard to which signal belongs to C(6) or C(17) leads to only one set of rational values. They force the allocation of the methylene shifts of the three alkaloids to be as depicted in Table I and limit scandine to structure **1d**.[10] The previous assessment of the C(16) stereochemistry of scandine was based on the interpretation of upfield H(21) and methoxy shifts being due to shielding by the carbomethoxy group and the benzene ring, respectively.[2] In structure **1d** H(21) is in a lower aromatic deshielding zone than in epimeloscine (**1b**) and, to a smaller extent, in meloscine (**1a**) and the methoxy group is within the shielding influence of the lactam carbonyl function and/or the benzene ring.

Experimental Section

The spectra were recorded on a Varian XL-100-15 spectrometer operating at 25.204 MHz equipped to operate in the pulsed Fourier transform mode with Transform Technology Inc. computer and pulse hardware.

Registry No.—**1a**, 24314-51-0; **1b**, 24314-58-7; **1c**, 24314-59-8; **2**, 28645-27-4.

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