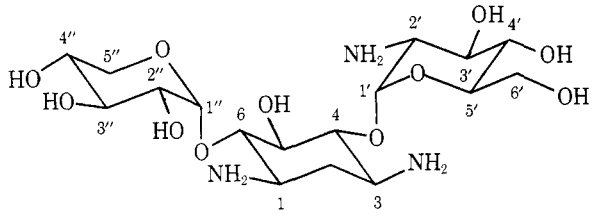
ppm and $\delta_{C\text{-}5}$ (A_2) − $\delta_{C\text{-}5}$ (Par) = −1.5 ppm in the bases and at pD 2, these are 9.3 and −1.2 ppm, respectively. These values are in excellent agreement with the values reported for structurally related compounds.[1a] Therefore, it can be concluded that in A_2 the α-xylopyranosyl unit is located at the 6-position of paromamine. The absolute configuration of xylose in A_2 has been shown by Nagabhushan and Daniels[10] to be D by a novel application of ^{13}C NMR spectroscopy. The structure of gentamicin A_2 is therefore as shown below.



gentamicin A_2

Registry No.—Gentamicin A_2, 55715-66-7.

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(11) The presence of xylose can best be demonstrated by hydrolyzing tri-*N*-acetylgentamicin A_2 with 1 *N* hydrochloric acid at 100° for 1.5 hr.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. XXXIII. The Ochrolifuanines and Emetine[1]

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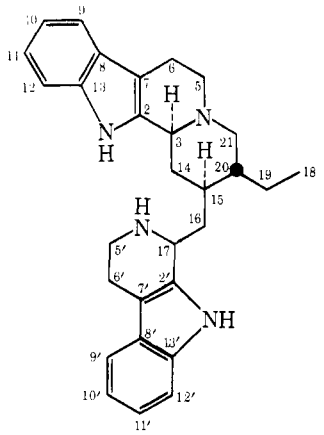
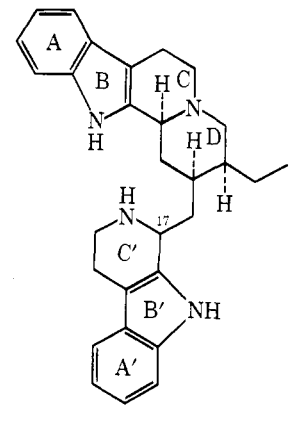
Recently two new alkaloids were isolated from *Ochrosia lifuana* Guillaumin and shown to possess structures **1a** and **1b**.[2,3] Their synthesis and that of two of their stereoisomers soon followed.[3] In view of the success in the use of ^{13}C NMR spectroscopy as an analytical tool for the differentiation of stereoisomers among yohimboid, ajmalicinoid, and corynanthoid alkaloids,[4,5] a ^{13}C NMR analysis of ochrolifuanine A (**1a**), ochrolifuanine B (**1b**), and the synthetic isomers **2a** and **2b** was undertaken. The ^{13}C NMR data[5] on models **3**, **4**, **5a**, and **5b** were used in this connection.



1a, 17β-H
b, 17α-H



2a, 17β-H
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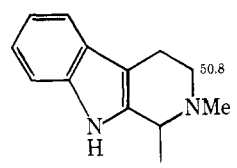

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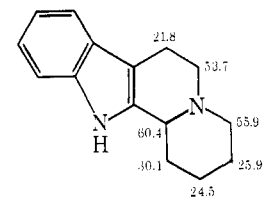

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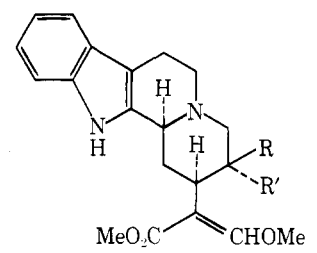


5a, R = H; R′ = Et
b, R = Et; R′ = H

The chemical shift information obtained from proton noise-decoupled and single-frequency off-resonance decoupled spectra of isomers **1a**, **1b**, **2a**, and **2b** as well as the data depicted on **3** and **4** and outlined in Table I for substances **5a** and **5b** permitted shift assignment for all carbons of the four substances under study except for two of their methylenes as well as two of their methines. Differentiation of the methylenes, C(14) and C(16), is based on the known C(14) shift of 37.2 ppm in yohimbane.[4] Ochrolifuanine A (**1a**) and ochrolifuanine B (**1b**) must have their C(14) more shielded owing to an added acyclic γ effect, while compounds **2a** and **2b** possess an even more shielded C(14) in view of the addition of another γ effect as a consequence of the axiality of their ethyl group. The distinction of the methines C(15) and C(20) of **1a** and **1b** is based on the idea of the shift similarity noted for the equivalent carbons in model **4** being retained in a case in which both carbons are equatorially ethylated and C(15) being shielded by the C(17) substituents. The same shift order can be expected for **2a** and **2b**. The total shift assignment portrayed in Table I was confirmed by a lanthanide shift study of **2b** with Yb(DPM)$_3$. The shift agent coordinates almost exclusively at the site of the secondary amine.

It is noteworthy that the C(5), C(6), C(5′), and C(6′) shifts are constant in the four substances **1a**, **1b**, **2a**, and **2b** and that there is a distinct difference between the C(5) and C(5′) shifts and the C(6) and C(6′) resonances. The constancy of the C(3) shift reflects the identity of the *trans*-quinolizidine conformation in the four compounds.[5] The dissimilarity of the C(17) shifts is a result of differences of rotamer populations of the equatorial C(15) side chain

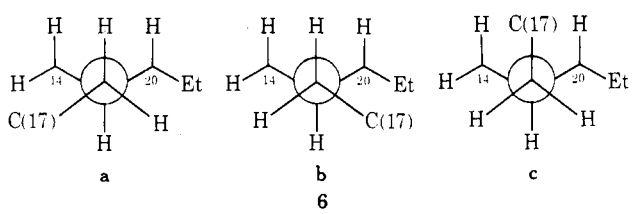
Table I
^{13}C Chemical Shifts[a]

	1a[b]	1b[b]	5a	2a[b]	2b[b]	5b
C(2), C(2′)	134.7, 135.5	134.6, 135.5		135.2, 135.4	135.1, 135.4	
C(3)	59.3	59.5	60.2	59.4	60.3	61.2
C(5)	52.6	52.9	53.1	53.1	53.1	53.4
C(6)	21.5	21.6	21.9	21.5	21.6	21.9
C(7), C(7′)	107.3, 108.1	107.3, 108.6		107.9, 108.7	107.3, 108.4	
C(8), C(8′)	127.0, 127.2	127.0, 127.2		127.3, 127.4	127.1, 127.2	
C(9), C(9′)	117.7, 117.9	117.7, 117.9		117.9, 118.0	117.7, 117.7	
C(10), C(10′)	121.0, 121.3	120.9, 121.6		120.9, 121.4	120.6, 121.2	
C(11), C(11′)	118.9, 119.0	118.9, 119.3		119.1, 119.2	118.8, 119.0	
C(12), C(12′)	110.6, 110.9	110.8, 110.8		110.6, 110.6	110.6, 110.6	
C(13), C(13′)	135.9, 136.1	135.8, 135.9		135.7, 136.0	135.8, 135.8	
C(14)	34.3	36.4	33.8	31.1	32.4	29.8
C(15)	35.8	37.8	38.7	35.1	36.1	40.8
C(16)	38.1	38.4		38.4	37.8	
C(17)	48.8	51.9		49.8	50.0	
C(18)	11.0	11.2	11.3	12.5	12.4	12.8
C(19)	23.2	23.8	24.4	18.6	17.5	19.1
C(20)	42.2	42.5	39.3	41.3	38.3	40.0
C(21)	59.9	60.1	61.3	57.3	57.5	57.9
C(5′)	42.2	42.0		42.3	42.2	
C(6′)	22.4	22.4		22.5	22.3	

[a] In parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b] The shifts of like carbons of the two indole units are undifferentiated.

(vide infra). The methyl group of axial ethyl functions is deshielded by ca. 1.5 ppm. In view of the 1,3-diaxial interaction C(14) and C(19) are shielded in the compounds possessing axial ethyl groups, i.e., **2a, 2b,** and **5b.** Carbon 21 is shielded in these substances also.

The C(14), C(15), C(17), and C(20) shifts are indicative of the conformational disposition of the two ring systems attached to C(16) with respect to each other. Carbon 16 serves the same structural function to the compounds **1a, 1b, 2a,** and **2b** as the oxygen bridge between two pyranosyl units and/or pyranosyl–inosityl units in disaccharides and related systems. Acyclic conformational analysis of such natural products has been aided immensely by ^{13}C NMR spectroscopy.[6] The rotamers **6a, 6b,** and **6c** represent the substituent arrangement around the C(15)–C(16) bond of ochrolifuanine A (**1a**) and B (**1b**) and rotamers **7a, 7b,** and **7c** the C(15)–C(16) environment of isomers **2a** and **2b.** Since, however, rotamers **6c** and **7c** incorporate an extra gauche-butane interaction, they can be discounted as important contributors to the structures in solution. The combination of identity of C(20) shifts and dissimilarity of C(14) shifts of **1a** and **1b** confirms this assignment for the alkaloids on the basis of the transmission of the γ effect via a carbon–hydrogen bond on the terminus of a gauche-butane structure.[7] The shielding of C(14) in **2a** with reference to **2b** and the concomitant deshielding of C(20) indicates that the predominant rotamer of **2a** is **7a** and that of **2b** is **7b.** The same C(14) shift argument leads to the assignment of rotamer **6a** for **1a** and **6b** for **1b.**



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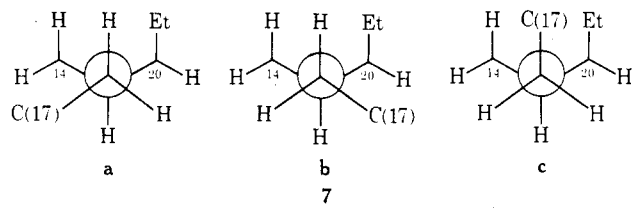

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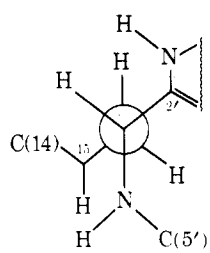
The shielding of C(15) with respect to C(20) in all four substances implies a nonbonded interaction of H(15) with $N_{b'}$ and/or C(2′). Furthermore, the shielding of C(14) in **1a** vs. **1b** and in **2a** vs. **2b** is explicable only in terms of a nonbonded interaction of H(17) with C(14) in **1a** and **2a.** Similarly, the shielding of C(20) in **2b** vs. **2a** must reflect a nonbonded interaction of H(17) with C(20) in **2b.** As a consequence, the rotamer **8** is preferred for compounds **1a** and **2a** and the rotamer **9** for **2b,** in accord with their C(17) configurations. Unfortunately, the rotamer preference of **1b** is difficult to assess. The 2 ppm or more deshielding of both C(15) and C(17) in **1b** as contrasted to its three isomers shows the lowering of reciprocal γ effects and hence increased H(15)–H(17) nonbonded interaction. The serious nonbonded interaction between C(17) and C(19) may be responsible for the lessening of the energy difference between various C(16)–C(17) bond rotamers.



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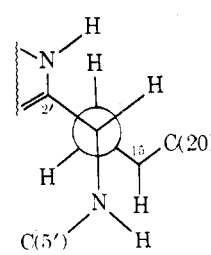

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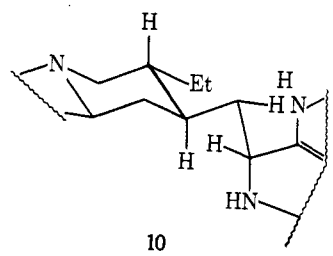
Since an axial 20-ethyl group can be expected to exert little effect on the energy content of the C(15)–C(16) bond rotamers **7a** and **7b** and since compound **2a** shows a preference for **7a,** while **2b** prefers **7b** instead, this unusual behavior must be the result of the difference of the C(17) chirality in the two compounds. An inspection of models indicates that in the overall structures **2a–7a–8** and **2b–7b–9**

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.



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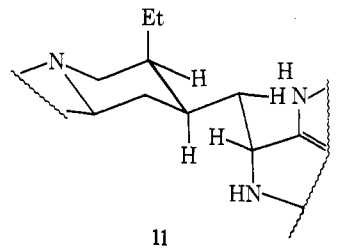

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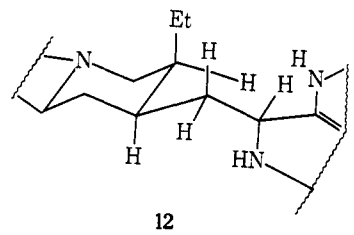
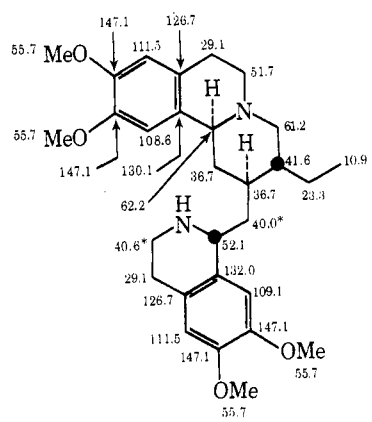


12

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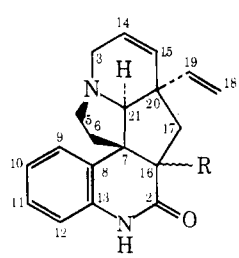
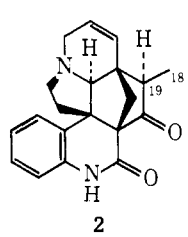
Investigations of the chemical constituents of the New Caledonian plant *Melodinus scandens* Forst. have shown this species to contain known *Aspidosperma* alkaloids as well as new bases structurally related to the former by oxidative rearrangement.[2-4] Structures **1a**, **1b**, **1c**, and **2** were



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.