

Revision of the Structure of Ajmalimine

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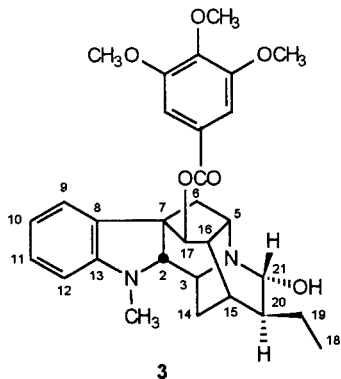
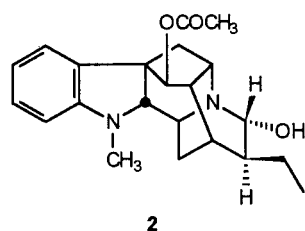
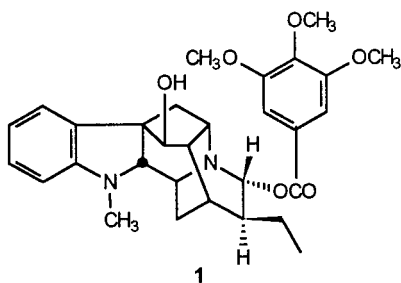
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Careful reexamination of the published ^1H and ^{13}C NMR spectral data of ajmalimine (**1**), an indole alkaloid from the roots of *Rauvolfia serpentina*, indicates that, in reality, the compound is (+)-17*R*-*O*-(3',4',5'-trimethoxybenzoyl)ajmaline (**3**).

Just over 10 years ago Siddiqui et al.¹ isolated from the roots of *Rauvolfia serpentina* Benth. (Apocynaceae) an indole alkaloid which they called ajmalimine. Mostly on the basis of spectroscopic data they proposed structure **1** for the isolated compound.

In our opinion² the reported ^1H and ^{13}C NMR spectral data do not fit well with the proposed structure **1**. In particular, the ^{13}C shift value δ 88.6 found for C-21 clearly indicates that the C-21 hydroxyl group cannot be benzyloated.



Mainly on the basis of the comparison of the spectral data of (+)-ajmalimine (**1**→**1'**) and 17-*O*-acetylajmaline (**2**)³ (Table 1), we now propose that ajmalimine isolated from *R. serpentina*¹ in reality is (+)-17*R*-*O*-(3',4',5'-trimethoxy-

Table 1. ^1H and ^{13}C NMR Data for Compounds **1**, **2**, and **1'** (Signals of **1'** Are for Compound **1** after Reassignment)^a

position	1		2 ^b		1'	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}
2	2.68	80.5	2.73	79.0	2.68	78.1 ^a
3	3.67	46.4	3.69	43.0	3.67	44.7
5	n.r. ^c	54.5	3.04	53.2	n.r.	54.5
6 α	n.r.	35.8	2.16	35.5	n.r.	35.8
6 β	n.r.		1.91		n.r.	
7		57.1		54.5		57.1
8		134.7		131.8		134.7
9	7.46	124.3	7.26	122.4	7.46	124.3
10	6.80	120.4	6.77	119.3	6.80	120.4
11	7.16	128.4	7.15	127.7	7.16	128.4
12	6.66	110.5	6.66	109.8	6.66	110.5
13		154.6		153.6		154.6
14 α	n.r.	31.9	1.9	31.1	n.r.	31.9
14 β	n.r.		1.63		n.r.	
15	2.41	29.8	2.46	28.0	2.41	29.8
16	2.02	50.4	2.09	43.3	2.02	46.4
17	4.50	78.1	5.26	79.9	5.43	80.5
18	1.02	12.6	0.96	12.0	1.02	12.6
19	1.40	26.3	1.4	25.7	1.40	26.3
19'	1.40		1.5		1.40	
20	n.r.	44.7	1.5	48.0	n.r.	50.4
21	5.43	88.6	4.31	88.6	4.50	88.6
N-CH ₃	2.75	34.9	2.80	34.2	2.75	34.9
O-COR		165.6		170.4		165.6

^a Signals reassigned by the authors of the present note are indicated by underlining. ^b Values taken from ref 3. ^c n.r. = not recorded.

benzoyl)ajmaline (**3**).⁴ The stereostructures proposed for C-17, C-20, and C-21 [analogous to those of 17-*O*-acetylajmaline (**2**)] are supported by the low coupling constants (broad singlets) reported for $J_{16,17}$ and $J_{20,21}$.¹ Agreement among the signals is improved when the ^1H NMR signals of **1** at δ 4.50 and 5.43 ppm are assigned not to C-17-H and C-21-H, respectively, but in the reverse order (Table 1; compound **1'**). Moreover, in the ^{13}C NMR spectrum of compound **1** the signals at δ 80.5, 46.4, 50.4, 78.1, and 44.7 ppm need to be reassigned (Table 1; compound **1'**). The occurrence of compound **3** in *Rauvolfia obscura* K. Schum. and *R. vomitoria* Afz. has been suggested by Timmins and Court,⁵ and Iwu,⁶ respectively.

References and Notes

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- (4) The "biogenetic numbering" of Le Men and Taylor is used throughout the present note. Le Men, J.; Taylor, W. I. *Experientia* **1965**, *21*, 508–510.
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