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AJMALINIMINE IS AN ARTIFACT NOT AN ALKALOID

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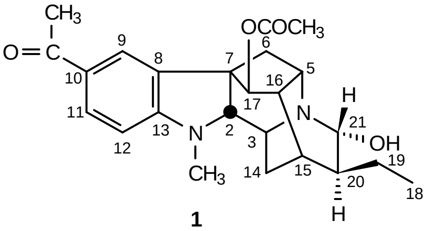
Abstract - It is suggested that ajmalinimine (**1**), isolated from *Rauwolfia serpentina* Benth, is an artifact formed from 17-*O*-acetylajmaline (**2**) during the isolation and/or purification procedure.

In 1987 Siddiqui *et al.*[1] reported the isolation from *Rauwolfia serpentina* Benth of a compound they called ajmalinimine and which they claimed to be a new alkaloid of ajmaline type. On the basis of spectroscopic data they proposed structure **1** for the new compound.[2]



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Comparison of the spectral data of ajmalinimine (**1**), particularly the ^{13}C NMR data, with that of 17-*O*-acetylajmaline (**2**)[3,4] confirms in our view the structure they proposed (Figure 1). Nevertheless, it seems to us that the shift value 78.0 ppm given for C-21 of ajmalinimine (**1**)[1] may be a printing error, and the real value should be 88.0 ppm. Moreover, the originally given[1] signals at δ 26.1 ppm, δ 35.5 ppm, δ 46.6 ppm, and δ 48.0 ppm needed[4] to be reassigned.

However, the presence of an acetyl group at C-10, which has never been detected in the alkaloids of the present series, urges caution. Repeated use of acetic acid and ethyl acetate in the isolation and purification procedures[1] strongly suggests that the acylation at C-10 is artificial. Although no Lewis acid was present, an acylation may well have taken place. Mechanistically it can be considered to start as a nitrogen assisted nucleophilic attack of 17-*O*-acetylajmaline (**2**) to the carbonyl group (Scheme 1). The fairly low yield in the isolation of ajmalinimine (**1**) (6.6x10^{-4}%),[1] is notable.

Dedicated to Professor Yoshito Kishi on the occasion of his 70th birthday.

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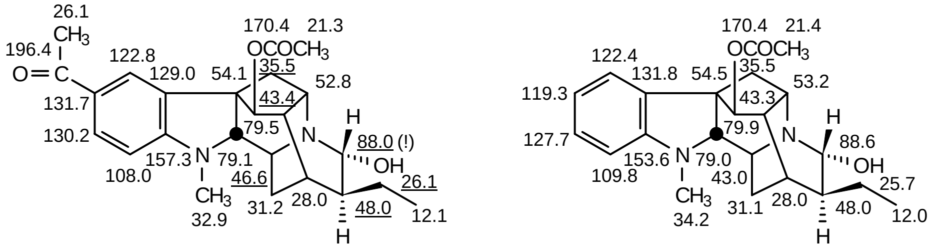
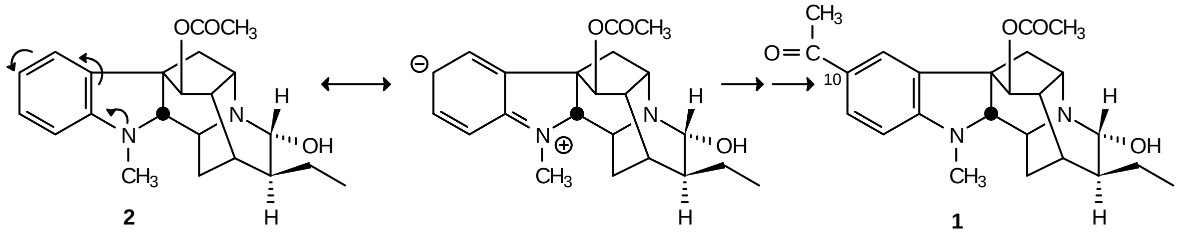


1 **2**

Figure 1. ^{13}C NMR Data of compounds (**1**) and (**2**). Signals reassigned by the authors of the present note are indicated by underlining. Values for compound (**2**) are taken from ref. 3.



Scheme 1. Nitrogen facilitated formation of ajmalinimine (**1**) from 17-*O*-acetylajmaline (**2**)

It is difficult to say what is the exact origin of the acetyl group but at least ajmalinimine (**1**) is not formed by a biogenetic process.[5,6] In our opinion, ajmalinimine (**1**) is not an alkaloid but an artifact formed during isolation and/or purification procedure from 17-*O*-acetylajmaline (**2**) (or from ajmaline itself, previously transformed to 17-*O*-acetylajmaline) (*vide supra*).

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