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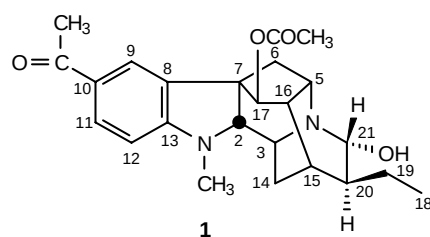
AJMALINIMINE IS AN ARTIFACT NOT AN ALKALOID

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Abstract - It is suggested that ajmalininimine (**1**), isolated from *Rauwolfia serpentina* Benth, is an artifact formed from 17-*O*-acetyljmaline (**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 ajmalininimine 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



Comparison of the spectral data of ajmalininimine (**1**), particularly the ¹³C NMR data, with that of 17-*O*-acetyljmaline (**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 ajmalininimine (**1**)¹ may be a printing error, and the real value should be 88.0 ppm. Moreover, the originally given¹ signals at δ 26.1 ppm, δ 35.5 ppm, δ 46.6 ppm, and δ 48.0 ppm needed⁴ 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 procedures¹ 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*-acetyljmaline (**2**) to the carbonyl group (Scheme 1). The fairly low yield in the isolation of ajmalininimine (**1**) ($6.6 \times 10^{-4}\%$),¹ is notable.

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

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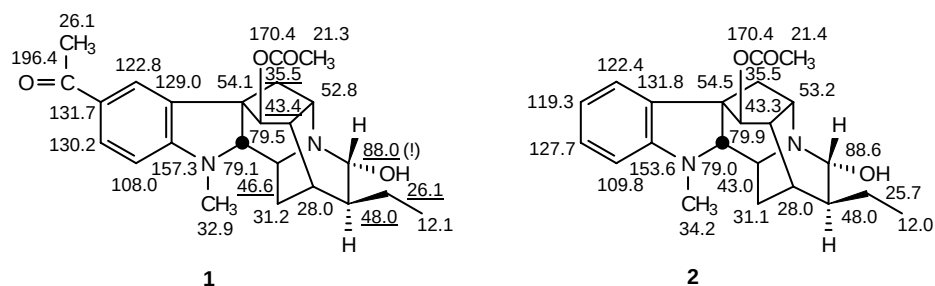
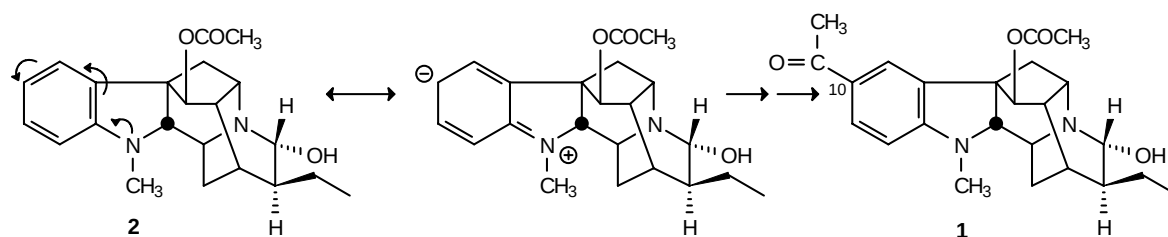


Figure 1. ^{13}C NMR Data of compounds (1) and (2). Signals reassigned by the authors of the present note are indicated by underlining. Values for compound (2) are taken from ref. 3.



Scheme 1. Nitrogen facilitated formation of ajmalinin (1) from 17-O-acetyljmaline (2)

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

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