

The Absolute Configuration of Julifloridine

Viqar Uddin Ahmad* and Sabiha Qazi
H. E. J. Research Institute of Chemistry
University of Karachi, Karachi-32/Pakistan

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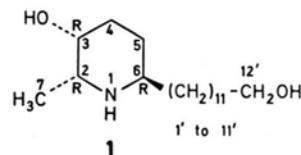
The absolute configuration of julifloridine is proposed to be 2 R, 3 R, 6 R through ^{13}C Spectra, ^1H NMR Spectra.

Some years ago, we reported [1] the isolation of alkaloid julifloridine from *Prosopis juliflora* and proposed the structure of 2-methyl-6-(12'-hydroxy-dodecyl)-piperidin-3-ol for it. However the absolute configuration at carbon atoms 2, 3 and 6 could not be investigated at that time due to the paucity of the material available to us.

With the publication of ^{13}C NMR data of 2-hydroxy 3-methyl-6-alkyl piperidine alkaloids like spectraline [2], juliprosopine [3], *iso*-6-cassine [2] it became apparent that the ^{13}C NMR chemical shifts of C-2, C-3 and C-6 of juliprosopine and spectraline, having S,S, and R configuration at these carbon atoms respectively, differ considerably from those of *iso*-6-cassine which has the R configuration at all of these three carbon atoms. The absolute configuration of the latter alkaloid has also been confirmed through X-ray diffraction studies [4]. Thus the ^{13}C NMR signals for C-2, C-3 and C-6 in spectraline and juliprosopine (values in parenthesis) appear at 57.0 (57.2), 67.6 (67.8), 55.7 (55.7 ppm) respectively. The values for these carbon atoms in *iso*-6-cassine are, on the other hand, 50.4, 68.9 and 49.5 ppm.

We recently repeated our isolation of julifloridine and measured the ^{13}C NMR spectrum in CDCl_3 . The spectrum showed peaks⁺ at 50.09 (d, C-2), 69.25 (d, C-3) and 49.70 ppm (d, C-6) which are close to

those of *iso*-6-cassine series rather than those of juliprosopine and spectraline. The chemical shift of the methyl carbon signal at 15.85 ppm (q) is also nearer to the corresponding value for *iso*-6-cassine (15.7 ppm) rather than spectraline (19.0 ppm) or julifloridine (18.9 ppm). We therefore suggest that julifloridine belongs to the 2R, 3R, 6R series (I). The ^{13}C NMR spectrum shows other peaks at 25.73 (C-10'), 26.61 (C-5), 27.73 (C-4), 29.55 (t, C-2' to C-9'), 32.80 (C-11'), 33.00 ppm (C-1'). The proposal for a primary alcoholic group in julifloridine was confirmed by the peak at 63.01 ppm (t, C-12') which is characteristic for a methylene carbon carrying a hydroxyl group.



The above proposal of stereochemistry of julifloridine finds a measure of support from the 100 MHz ^1H NMR spectrum of the alkaloid. In spectraline [2] the H-2 signal is a broad multiplet at δ 2.90 and the H-3 signal is a broad singlet ($W^{1/2} = 6$ Hz). In *iso*-6-cassine, on the other hand, the H-2 signal is an octet at δ 3.06 whereas the H-3 signal is a quintet at δ 3.66 ($J_{3,4} = 6.5$ Hz, $J_{3,4'} = 3.2$ Hz). This indicates the clear difference in the chemical shift and coupling constants of the H-2 and H-3 signals between the two series. In julifloridine the H-2 signal is an octet centred at δ 3.10 with $J_{2,7} = 6.5$ Hz and $J_{2,3} = 3$ Hz, which resembles that of *iso*-6-cassine rather than that of spectraline. The H-3 signal is masked by the H-12 tripled centred at δ 3.63.

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* Requests for reprints to Dr. V. U. Ahmad.

+ The ^{13}C NMR broad band spectrum was scanned in CDCl_3 for better comparison with literature values. For the off resonance spectrum, a few drops of ^{12}C - CD_3OD had to be added in order to make the compound more soluble.

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