Studies on the Structure of Juliflorine

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Summary: A partial structure for juliflorine, an alkaloid from Prosopis juliflora, DC has been proposed.

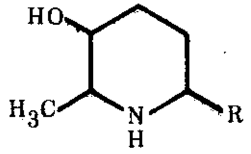
Some time ago we reported[1] the isolation of three new alkaloids juliflorine, julifloricine and julifloridine from *Prosopis juliflora* DC. A structure for the minor alkaloid julifloridine was also suggested. In the present communication we wish to report the preliminary studies carried out so far on the structure of juliflorine. It is worth mentioning here that juliflorine has also been found to occur in *Prosopis glandulosa*.

Juliflorine, when crystallised from acetone, melted at 58-60°C. However, in subsequent workings we have been able to obtain another polymorph of the alkaloid, m.p. 146°. The two samples, though differing greatly in melting point, were identical chromatographically as well as spectroscopically. It analyses for $C_{40}H_{75}N_3O_2$ with 4 active hydrogen atoms determined according to Zerewitinoff's method.

In the ultra-violet spectrum juliflorine does not show any absorption above 220 nm, indicating the absence of conjugated double bonds in it.

The IR spectrum of the base shows peaks at 3366 cm^{-1} a broad band at 3600-3100 cm^{-1} (NH/OH) and absorption due to CH_2 peaks at 2925 and 2830 cm^{-1}. There was no peak which could be ascribed to a carbonyl group. A peak at 1630 cm^{-1} is assigned to C=C stretching vibration.

The mass spectrum of juliflorine shows molecular peak at m/e 629.5857 ($C_{40}H_{75}N_3O_2$ requires 629.5858). In addition, there were peaks at m/e 628 $(M-H)^+$, 612 $(M-OH)^+$, 611 $(M-H_2O)^+$, 610 $(M-H_2O-H)^+$, 596 $(M-CH_3-H_2O)^+$, 593 $(M-2H_2O)^+$. The base peak at m/e 389 corresponds to the formula $C_{25}H_{45}N_2O$ according to the high resolution mass spectrum indicating the cleavage of $C_{15}H_{30}NO$ unit from the molecule. The peak due to this latter unit is also visible at m/e 240, although of a much less intensity. Strong peaks at m/e 114 ($C_6H_{12}NO$), 96, 84, 70 all indicate the presence of the moiety A in the molecule[2,3].



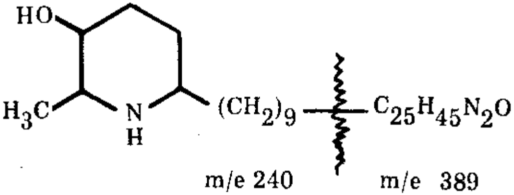
In addition, there are other peaks which correspond to the cleavage of one or more piperidine rings according to the known fragmentation pattern.

The nmr spectrum of julflorine in $CDCl_3$ shows a doublet at δ 1.13 (J=6.5 Hz) (9H) due to the methyl groups attached to the piperidine ring, a broad singlet at δ 1.26 (~38H) due to CH_2 groups in the side chain, a signal at δ 1.45 (~4H) arising probably from theCH_2 group of the piperidine ring, a broad multiplet between δ 1.5 and 2.1 (~10H), signals between δ 2.45 and 2.90 (4H) due to protons at position 2 and 6 in the ring. In addition there are signals at δ 3.05-3.25 (2H), 3.35 (broad hump, about 5H). The latter signals are reduced in intensity on shaking with D_2O and is partly due to mobile protons (OH,NH). Another hump at δ 3.55 is due to protons attached to carbon bearing the hydroxyl group. There is a another broad hump at δ 3.35 due to an olefinic proton.

In the ^{13}C-n.m.r. of juliflorine, the presence of an olefinic double bond is clearly established by the presence of peaks at 136.05 and 123.87 ppm. The latter peak splits into a doublet in the off resonance spectrum whereas the former does not, indicating that one of the olefinic carbon atoms contains a hydrogen atom and the other has no hydrogen atoms attached to it.

The peak at 29.43 ppm is the strongest and splits into a triplet in the off resonance spectrum. It is apparently due to several CH_2 groups in the middle of the chain. Other peaks are at 67.78, 65.45, 57.08, 55.66, 55.20, 54.41, 42.52. 36.83., 35.01, 33.07, 31.99, 29.94, 26.66, 27.84, 26.47, 25.96, 25.68, 21.30, 18.51 ppm. The last peak is due to a methyl group as it splits into a quartet in off resonance spectrum. On the other hand, peaks at ppm 67.78, 65.45, 57.08 55.66 all split into doublets.

It is concluded that juliflorine contains the partial



It is likely that the compound contains two or even three piperidine rings. However, the elucidation of the structure of the unit $C_{25}H_{45}N_2O$, which also contains the double bond, would have to await further work, particularly on the degradation of the alkaloid.

References:

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