

### New Alkaloids from *Prosopis juliflora* DC

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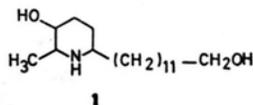
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*Prosopis juliflora*, Piperidine Alkaloids

The isolation of three new alkaloids from *Prosopis juliflora* is reported. A structure for the minor alkaloid julifloridine is suggested.

*Prosopis juliflora* DC. (mesquite) grows abundantly as a weed in Sind and Punjab Provinces of Pakistan. In view of the antibiotic properties attributed [1] to the extracts of this plant, a chemical examination of the leaves was undertaken. As a result of this study three new alkaloids, named as juliflorine (m. p. 58-60 °C), julifloricine (obtained as a gum) and julifloridine (m. p. 82-83 °C) in order of increasing polarity on T. L. C. plate, were isolated in pure state. In the present paper the structure of julifloridine is discussed. Julifloridine analyses for  $C_{18}H_{37}NO_2$  with 3 active hydrogen atoms. On the basis of spectral data the structure 1 is suggested for the alkaloid.



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In the IR spectrum (KBr), julifloridine shows bands at 3347, 3232, 3077  $cm^{-1}$  (OH/NH) but no carbonyl absorption. The NMR spectrum ( $CDCl_3$ ) of the base shows a doublet (3H) at  $\delta$  1.12 due to the methyl group attached to piperidine ring. No other methyl peaks are visible. The signal due to methylene protons occurs as a singlet at  $\delta$  1.30. There is another broad singlet at  $\delta$  2.33 (2H) which disappears on shaking with  $CD_3OD$  and therefore appears to be due to the two OH groups. A distorted triplet (2H) at  $\delta$  3.65 arises from  $-CH_2-OH$  protons in the side chain. In addition, there are other signals due to protons on the piperidine ring.

The protons at C-4 and C-5 absorb as multiplet in the region  $\delta$  1.5-1.8. On the other hand, the protons at C-2 and C-6 at  $\alpha$  position to piperidine nitrogen atom as well as at C-3 appear as a broad signal at  $\delta$  2.56-3.15.

The fragmentation pattern in the mass spectrum (Chart I) resembles that of cassine [2], carnauvaline [2] and spicigerine [3, 4]. The 2-methyl-3-hydroxypiperidine ring system is clearly indicated by the presence of peaks at 114, 96 and 70 m. u. The molecular peak at 299.2814 ( $C_{18}H_{37}NO_2$ ) requires 299.2814) confirms the molecular formula. In addition there were important peaks at 298 (M-H)<sup>+</sup>, 284 (M-CH<sub>3</sub>)<sup>+</sup> and 282 (M-OH)<sup>+</sup>. The peaks at 268, 254, 240, 226, 198, 184, 170, 156, 142 and 128, i.e. at intervals of 14 m. u. arise from the progressive splitting of methylene groups from the side chain. The peak at 240 m. u. is however stronger and appears to arise also from the cleavage of the piperidine ring as mentioned in the case of cassine [2] and spicigerine [3]. The formulae of all of the above peaks have been confirmed by high resolution mass spectroscopy.

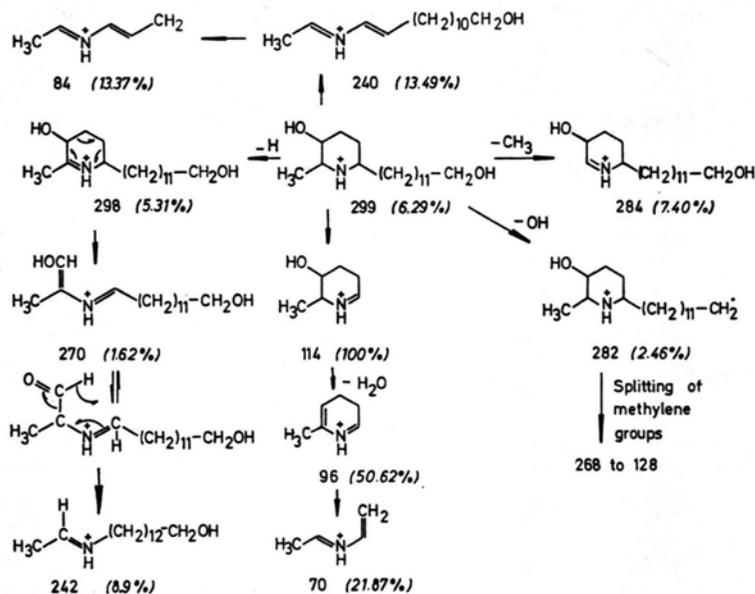


Chart. I. Fragmentation pattern of julifloridine (intensities of peaks in parentheses).

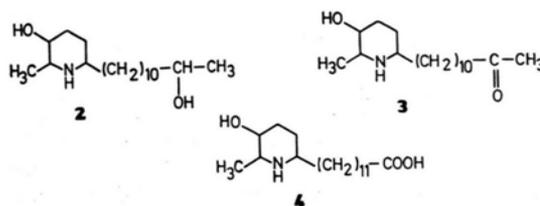
In addition, there is a peak at 242 (M-57) which, according to high resolution spectrum, corresponds to the molecular formula  $C_{15}H_{32}NO$ . A corresponding M-57 peak is apparently also present in the mass spectrum of spicigerine [3] although its origin has not been discussed by the authors. It is hereby proposed that it arises from the retro-Diels-Alder reaction of the M-H peak and subsequent loss of carbon monoxide through a cyclic transition state.

The absolute and relative configuration of juliflorine has still to be determined. However, it is probable that it also has the all *cis* configuration like cassine, carnavaline, spicigerine *etc.* On acetylation with acetic anhydride and pyridine, julifloridine yields a triacetyl derivative which was obtained as a gum. Its mass spectrum showed peaks at 425

(M<sup>+</sup>), 410 (M-CH<sub>3</sub>), 366 (M-CH<sub>3</sub>-C(=O)-), 365

(M-CH<sub>3</sub>-C(=O)-OH)<sup>+</sup>. The strong peaks at 198, 156, 138 and 96 have the same structure as described in case of methyl-diacetyl-spicigerine [3].

Julifloridine (1) is, therefore, an isomer of carnavaline (2), differing from the latter only in the position of hydroxyl group in the side chain. Thus it is also related to cassine (3) which possesses a ketonic group instead of the secondary alcoholic group of carnavaline. The biogenetic relationship between julifloridine and spicigerine (4) is apparent as the two alkaloids differ only in the oxidation levels of the terminal functional group, spicigerine having a carboxylic group in lieu of a -CH<sub>2</sub>OH group of julifloridine at the end of the side chain.



The alkaloids juliflorine and julifloricine also possess the 2-methyl-3-hydroxy piperidine ring system but have more complicated structures. Work on the elucidation of their constitutions is in progress.

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