

## CHAPTER VIII



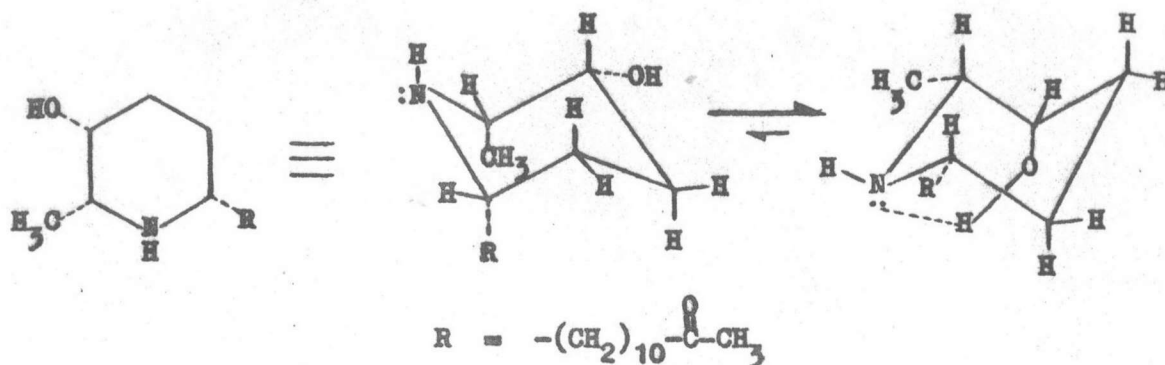
### DISCUSSION 2

Sp I hydrochloride melts at  $164^{\circ} - 165^{\circ}\text{C}$ . ( $\pm$ ) Cassine hydrochloride from Cassia excelsa Shrad. melts at  $164^{\circ} - 165^{\circ}\text{C}$  (269).

Sp I corresponds to cassine has the same  $hR_f$  value on Silica gel G/Chloroform, ethyl alcohol, 25% ammonium hydroxide solution, 9+1+0.2 and on Aluminium oxide G/Acetone, chloroform, 4+5.

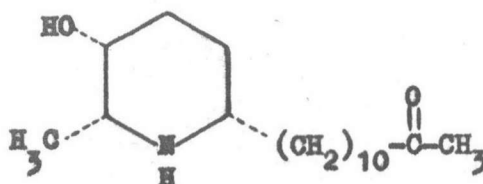
Sp I has an identical mass spectrum to cassine  $m/e(\%) = 297(M^+, 4.0)$ ;  $282(M^+ - CH_3, 7.5)$ ;  $240(M^+ - CH_3 - CO - CH_2-, 31.5)$ ; and  $114(100)$ .

The infrared absorption spectrum of Sp I in carbon tetrachloride solution clearly shows carbonyl peak at  $1720\text{ cm}^{-1}$  and also a large bonded hydroxyl at  $3520\text{ cm}^{-1}$ , and very small free hydroxyl band at  $3630\text{ cm}^{-1}$  as does the spectrum of cassine (7,269). This is characteristic of the all cis systems in which the most favourable conformation possesses the hydroxyl group in the axial configuration favourable to intramolecular hydrogen bonding with the N atom of the piperidine nucleus as shown below.



The signal of the carbinol hydrogen in the NMR spectrum at  $\delta = 3.55$  gave further confirmation: the width at half height ( $\omega_{1/2} = 6$  Hz) is known to be characteristic of an equatorial hydrogen in the 3-piperidinol derivatives<sup>(269,270,271)</sup>. (An axial carbinol hydrogen as in iso-3-cassine<sup>(269)</sup> would have appeared as a very broad singlet  $\omega_{1/2} \approx 22$  Hz). The hydroxyl signal at  $\delta = 2.00$  ppm and disappeared on  $D_2O$  exchange.

Sp I has been identified by UV, IR, NMR, Mass spectra, melting point and  $R_f$  values on TLC along with authentic sample kindly supplied by Dr. R. J. Highet at the National Heart Institute, National Institutes of Health, Bethesda 14, Maryland. It is therefore concluded that Sp I is cassine.

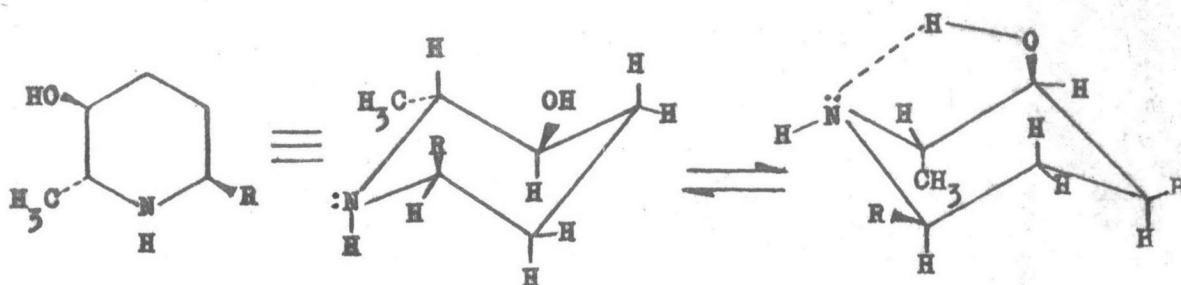


Cassine

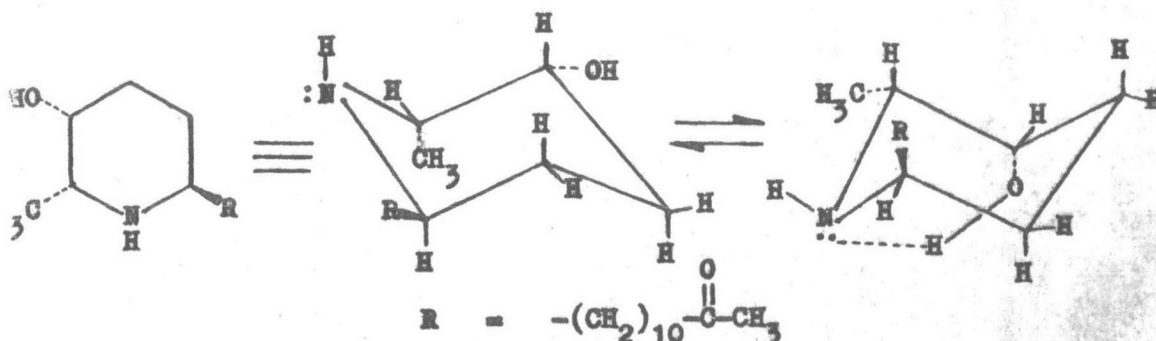
Sp II has a very similar mass spectrum to cassine  $m/e$  (%) = 297 ( $M^+$ , 2.2); 282 ( $M^+ - CH_3$ , 4.2); 240 ( $M^+ - CH_3 - CO - CH_2 -$ , 14.0); 114 (100).

The infrared absorption spectrum of Sp II in carbon tetrachloride solution shows carbonyl peak at  $1720\text{ cm}^{-1}$  and both free ( $3620\text{ cm}^{-1}$ ) and bonded ( $3510\text{ cm}^{-1}$ ) hydroxyls of approximately equal height. This observation means that either the side chain, or the methyl group is trans to the other two substituents<sup>(272)</sup>. In both cases, two conformations with and without intramolecular hydrogen bond possibility are favourable

as shown below.

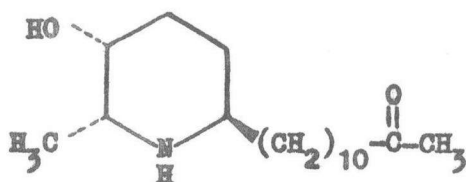


a) Methyl group is trans to the other two substituents



b) The side chain (R) is trans to the other two substituents

The C-3 hydrogen signal in NMR spectrum is at 3.75 with a width at half height ( $\omega_{1/2} = 14$  Hz) wider than for cassine. The weighted average coupling constants deduced from the NMR spectrum showed that the hydrogen at C-2 ( $\delta = 3.22$ ,  $J_{H^2H^3} = 4$  Hz) is cis with regard to the hydrogen at C-3<sup>(15,271)</sup>. Because these spectra values are not identical with these reported in the literature and the authentic compound is not available for comparison, then it is difficult to conclude that Sp II is definitely iso-6-cassine. In any case, the details in the spectra suggest that Sp II could probably be iso-6-cassine.



Iso-6-cassine

There are two major alkaloids, cassine and probably iso-6-cassine in the leaves of Cassia spectabilis DC. that growing in Thailand. This differs from that reported by Christofidis et al. <sup>(15)</sup>, who found spectaline (opposite stereoisomeric configuration,  $(\text{CH}_2)_{12}$  side chain) and iso-6-cassine were major alkaloids in the leaves of Cassia spectabilis DC. from Zaire. They have also reported that there are spectaline, iso-6-cassine, spectalinine, and iso-6-carnavaline in the seeds of this plant <sup>(137)</sup>. Mulchandani et al. <sup>(16)</sup> obtained the leaves and stem of Cassia spectabilis DC. from Bombay but its original habitat is Argentina. The major alkaloid found is cassine; the second major one reported as cassinicine <sup>(16)</sup> (no definite stereoisomeric configuration,  $(\text{CH}_2)_{12}$  side chain). This might be identical with spectaline or casselsine.

It was reported that at least 17 species of Cassia contain alkaloids. Most of which are unknown alkaloids. Four species of them; Cassia carnaval Speg., C. excelsa Shrad., C. jahnii Britton et Rose, and C. spectabilis DC. contain piperidine alkaloids.

There are about 500-600 species of Cassia <sup>(273)</sup>. There are many problems in identification. The study of the chemical constituents in the plants of this genus might be helpful as an aid for identification and also in chemical taxonomy of these plants.