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MASS SPECTRA OF PRONUCIFERINE AND STEPHARINE.

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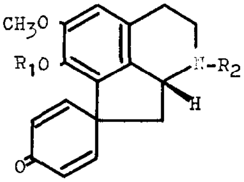
ALKALOIDS, such as pronuciferine 1) (I) and stepharine 2) (II) with a para-cyclohexadienone moiety, were proposed by Barton and Cohen 3) to be the precursor of aporphine alkaloids, and thereafter various alkaloids of this type have been isolated from natural sources.

Recently, Rapoport et al.[4)] found that glaziovine (III) showed mass spectral peaks at M^+(m/e 297), M-17, M-29, M-43, M-58 and m/e 165. However, no report concerning with the fragmentation mechanism of this type alkaloids, has been found in the literatures.



I. $R_1, R_2 = CH_3$

II. $R_1 = CH_3$, $R_2 = H$

III. $R_1 = H$, $R_2 = CH_3$

The aim of the present paper is to give the mass-spectral fragmentation mechanism of pronuciferine (I) and stepharine (II), on the basis of the existence of metastable peaks and the mass spectrometric shift technique.

In the spectra of pronuciferine (I)* (Fig. 1-a) and stepharine (II)* (Fig. 1-b), the characteristic feature is the appearance of strong molecular ion, M-1, M-29, and m/e 268 peaks. The peaks at m/e 310 (M-1) and m/e 282 (M-29) in the spectrum of pronuciferine (I), are displaced by 14 mass units in that of stepharine (II) owing to the absence of N-methyl function. The M-1 peaks should be due to the loss of a hydrogen atom with formation of species a , in which the positive charge is stabilized by conjugation with aromatic ring. This is verified by the appearance of metastable peak. (Table 1). The further loss of carbon monoxide from the dienone type fragment a , furnishes the ion b (M-29).

Additional peaks at m/e 268, 253, 237 and m/e 225 are observed in the spectra of both pronuciferine (I) and stepharine (II). The fragmentation process of these peaks is schematically illustrated in Chart 1 (ii). The molecular ion is decomposed to the ion c by a retro-Diels-Alder reaction of the tetrahydroisoquinoline ring, and this process is similar to the characteristic fragmentation of aporphine alkaloids [5]. The existence of a metastable peak seems to substantiate this fragmentation. The peak at m/e 268

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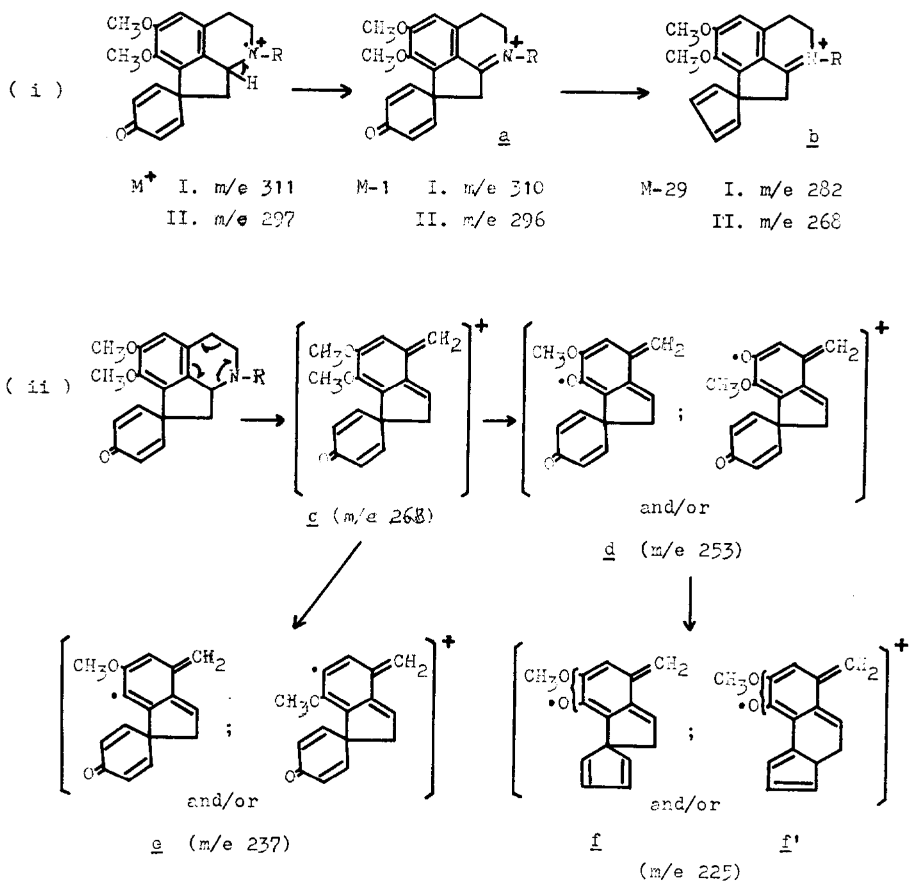
* Pronuciferine and stepharine used in this paper were isolated from lotus embryo (*Nelumbo nucifera* Gaertn.) and *Stephania rotunda* Loureiro, respectively. (Unpublished work)

Chart 1 .

Fragmentation Mechanism of Pronuciferine and Stepharine.

pronuciferine (I) : R = CH_3
stepharine (II) : R = H



in the spectrum of stepharine (II) seems to consist of the fragments b and c . Since ion c is an odd-electron, it is stabilized by the elimination of a methyl or a methoxyl radical from the isoquinoline moiety to produce the even-electron ions d (m/e 253) and e (m/e 237). The operation of these processes is suported by the existence of metastable peaks. Further loss of carbon monoxide from ion d , gives rise to an ion of m/e 225, which may be represented by f and/or f' .

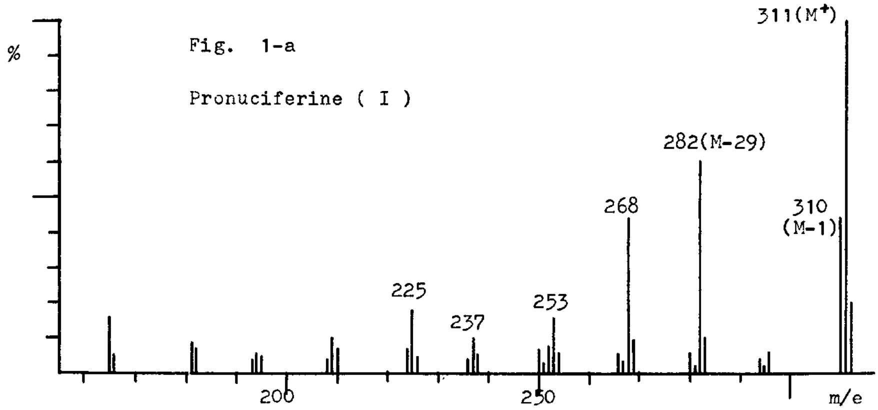


Fig. 1-a

Pronuciferine (I)

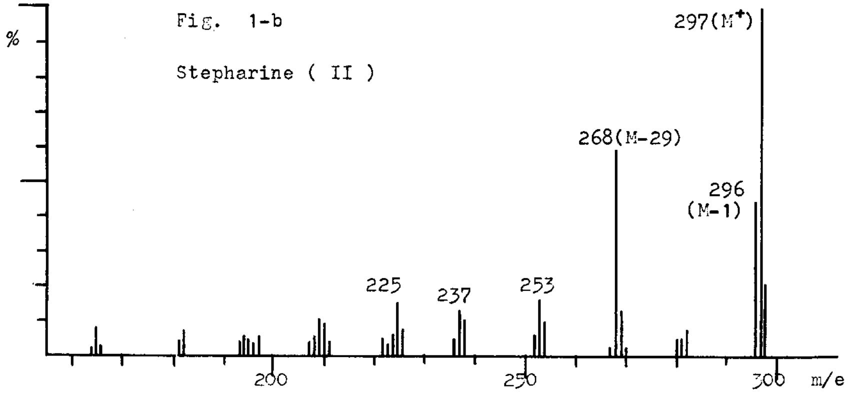


Fig. 1-b

Stepharine (II)

TABLE 1 .

	Pronuciferine (I)		Stepharine (II)	
	Calcd.	Obs.	Calcd.	Obs.
$M^{+} \longrightarrow \underline{a}$	$310^2/311 = 309.0$	309.0	$296^2/297 = 295.0$	295.0
$\underline{a} \longrightarrow \underline{b}$	$282^2/310 = 256.5$	256.0	$268^2/296 = 241.8$	242.0
$M \longrightarrow \underline{c}$	$268^2/311 = 230.9$	231.0		
$\underline{c} \longrightarrow \underline{d}$	$253^2/268 = 238.8$	239.0	$253^2/268 = 238.8$	239.0
$\underline{c} \longrightarrow \underline{e}$	$237^2/268 = 209.6$	210.0	$237^2/268 = 209.6$	209.5

Conclusion : In the mass spectra of pronuciferine (I) and stepharine (II) containing a para-cyclohexadienone moiety, it is concluded that the base peak is the molecular ion and the main fragmentation occurs by a type of retro-Diels-Alder decomposition.

The mass spectra were measured with a Hitachi Mass Spectrometer Model RMU 6D equipped with a all glass inlet system : Ion accel. voltage 1800 V ; Chamber voltage 70 eV ; Total emission 80 µA ; Target current 40 µA ; Evap. temp. 190° .

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