

MASS SPECTROMETRY OF SOME AMARYLLIDACEAE ALKALOIDS.

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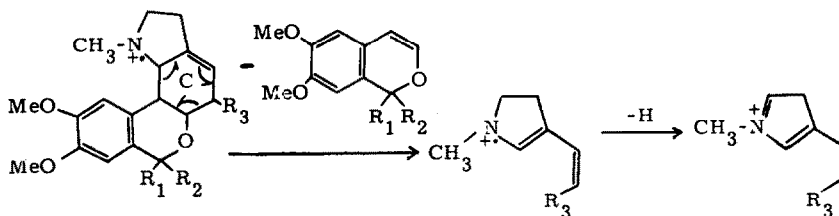
Recent report¹⁾ on the mass spectrometry of some Amaryllidaceae alkaloids prompted us to publish the results of our investigation* on lycorenine and lycorine type alkaloids of this family.

Lycorenine Type Alkaloids

The base peak ion in the mass spectra of lycorenine (I), homolycorine (II), and deoxylycorenine (III) occurs at m/e 109. A mechanism consistent with this evidence is depicted in Chart I in which ring C is fragmented by retro-Diels-Alder process²⁾ with formation of fragment A (m/e 109), and subsequent loss of a hydrogen from A would generate species B at m/e 108. The appearance of a metastable ion at m/e 107 substantiated at least a portion of the fragment ion B (m/e 108) originated from A (m/e 109).

* The mass spectra were measured on the Hitachi mass spectrometer model RMU-6D equipped with direct inlet system. High resolution mass spectra were measured by Dr. H. Sato, Hitachi Naka Works, to whom the authors are grateful.

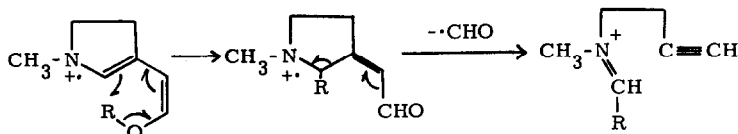
CHART I



- | | | |
|--------------------------|-----------------------------|-----------------------------|
| (I), $R_1=OH, R_2=R_3=H$ | <u>A</u> , $R_3=H, m/e 109$ | <u>B</u> , $R_3=H, m/e 108$ |
| (II), $R_1R_2=O, R_3=H$ | $R_3=OH, m/e 125$ | $R_3=OH, m/e 124$ |
| (III), $R_1=R_2=R_3=H$ | $R_3=OD, m/e 126$ | |
| (IV), $R_1R_2=O, R_3=OH$ | | |
| (V), $R_1R_2=O, R_3=OD$ | | |

The dominant and characteristic ion of hippastrine (IV) occurs at m/e 125, while a shift to m/e 126 is reflected in the mass spectrum of hippastrine-d (V), and their origins would best be depicted in Chart I (IV) \rightarrow A ($R_3=OH$), (V) \rightarrow A ($R_3=OD$). Expulsion of formyl radical from fragment A ($R_3=OH$) of hippastrine generates the reasonably strong peak at m/e 96, which shifted to m/e 97 in the spectrum of hippastrine-d (V) (Chart II).

CHART II

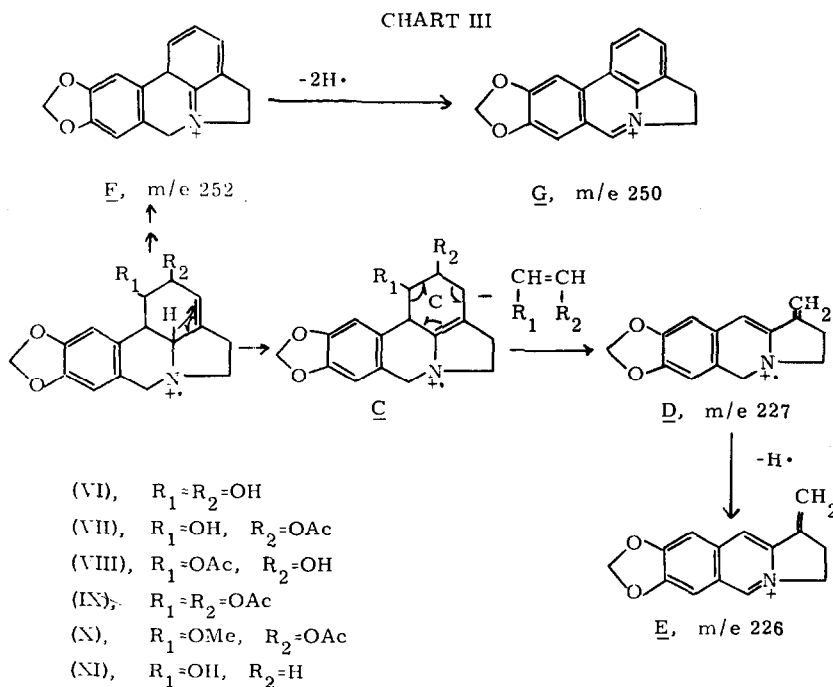


- | | |
|----------------|---------------|
| $R=H, m/e 125$ | $R=H, m/e 96$ |
| $R=D, m/e 126$ | $R=D, m/e 97$ |

Based on the above findings, it may be concluded that the strong, characteristic, and diagnostic peak of lycorenine type alkaloids is the fragment ion of type A.

Lycorine Type Alkaloids

The characteristic and diagnostic fragment ion peaks of lycorine type alkaloids lycorine (VI), O²-acetyllycorine (VII), O¹-acetyllycorine (VIII), diacetyllycorine (IX), O¹-methyl-O²-acetyllycorine (X), and caranine (XI) appear at m/e 227 and 226. High-resolution mass spectrometry established the composition of these peaks in the spectrum of diacetyllycorine (IX) as C₁₄H₁₃O₂N⁻ and C₁₄H₁₂O₂N⁺, respectively.



Such a fragmentation scheme is represented in Chart III ((VI)~(XI) \rightarrow C \rightarrow D (m/e 227) \rightarrow E (m/e 226) in which, following an initial hydrogen transfer, ring C is fragmented by retro-Diels-Alder process with the formation of fragment D and subsequent loss of a hydrogen generates the species E. These fragmentation steps C \rightarrow D and D \rightarrow E are supported, at least in part, by the presence of appropriate metastable ion peaks.

Another characteristic fragments (F³) and G) occurs at m/e 252 and 250 as reasonably strong peaks regardless of the substituents at C₁ and C₂ of the lycorine skeleton. Compounds (VI), (VII), (VIII), (IX), (X), and (XI) are fragmented by loss of HO[•], AcO[•], H[•], MeO[•], H₂O, AcOH, and MeOH etc., from respective molecular ions, forming ions m/e 252 and 250, though their fragmentation pathes may have minor difference.

References

- 1 A. M. Duffield, R. T. Aplin, H. Budzikiewicz, C. Djerassi, C. F. Murphy, and W. C. Wildman, J. Am. Chem. Soc., 1965, 87, 4902.
- 2 H. Budzikiewicz, J. H. Brauman and C. Djerassi, Tetrahedron, 1965, 21, 1855.
- 3 The structure of the ion F may be visualized in various ways.