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MASS SPECTROMETRIC STUDY OF THE STRUCTURE OF INDICAINE AND PLANTAGONINE

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The mass spectrum of indicaine [1] has strong peaks of ions with m/e 161 (88%), 160 (23%), 146 (100%), 133 (10%), 132 (34%), 118 (40%), 117 (65%), 91 (35%), and 77 (8%).

The presence of these peaks shows that the fragmentation of indicaine takes place mainly in two directions:

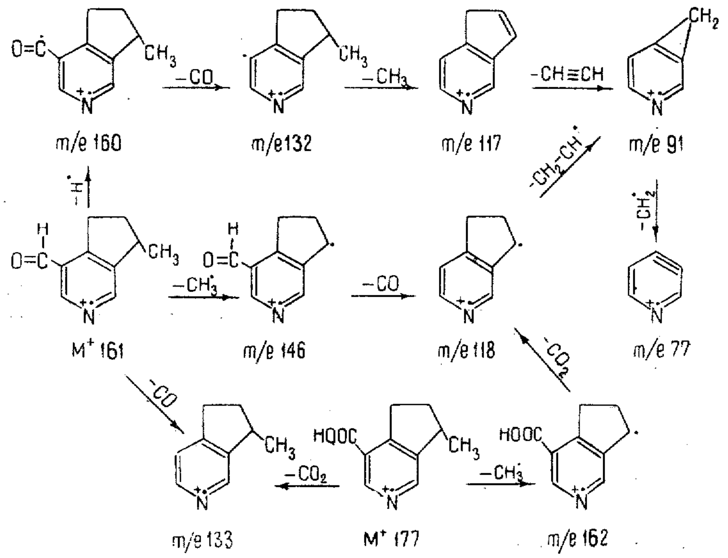
1) The methyl group is eliminated from the molecular ion with m/e 161 and the maximum peak with m/e 146 which loses a CO group appears and forms an ion with m/e 118. The presence of a metastable peak with m/e 95.5 (calculated, 95.4) confirms the transition m/e 146-118.

The ion with m/e 118 eliminates a CH_2-CH group, being converted into a fragment with m/e 91. The latter, by losing a $-CH_2$ group, gives an ion with m/e 77.

2) The fragmentation begins from the ion $(M-1)^+$ with m/e 160. The expulsion of the CO group from the ion with m/e 160 leads to the formation of an ion with m/e 132. By splitting out a methyl radical, this ion is converted into an ion with m/e 117. Then the ion with m/e 117 loses a $CH{\equiv}CH$ group, being converted into a fragment with m/e 91.

The mass spectrum of plantagonine has strong peaks of ions with m/e 117 (30%), 162 (50%), 133 (15%), 118 (100%), 91 (27%), 77 (9%).

The molecular ion of plantagonine, with m/e 177, loses a methyl group to form an ion with m/e 162, which loses a CO_2 group and is converted into an ion with m/e 118. Subsequent fragmentation takes place in the same way as for indicaine.



Thus, the spectra of these compounds reflect the great stability of the aromatic ring. This phenomenon is specific for the majority of pyridine alkaloids [2, 3].

The mass spectra were taken on an MKh-1303 instrument at 225° C with an energy of the ionizing electrons of 34-36 eV.

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STRUCTURE OF THALSIMIDINE

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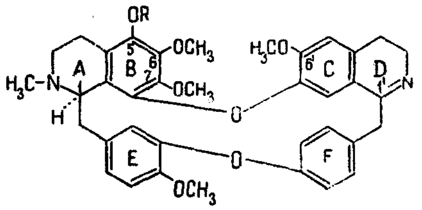
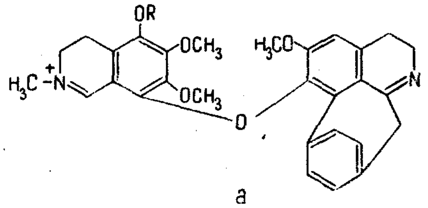
We have isolated thalsimidine $C_{37}H_{38}N_2O_7$ (I) from the epigeal part of Thalictrum simplex L. [1]. The products of the Hofmann degradation of N,O-dimethyldihydro-(I) were shown by TLC to be identical with the corresponding hernandezine derivatives. The methylation of thalsimidine with diazomethane gave thalsimine (II). Consequently, thalsimidine (I) is demethylthalsimine.

Sub-stance	m/e (relative intensity,%)								
	M^+	M^{++}	$(M-1)^+$	$(M-15)^+$	$(M-31)^+$	a	b	c	d
(I)	622 (100)	311 (28)	621 (60)	607 (56)	591 (20)	485 (10)	221 (8)	190 (10)	175 (6)
(II)	636 (100)	318 (24)	635 (64)	621 (51)	605 (17)	499 (11)	235 (12)	190 (11)	175 (5)

The presence in the mass spectrum of (I) of an ion with m/e 485 (fragment a, R = H) shows that the hydroxy group in the substance is present in the isoquinoline part of the molecule. The mass spectra of (I) and (II) can be judged from the figures in the table (the spectra were taken on a Hitachi RMU-6DC instrument).



I R = H
II R = CH_3



a

Fragment b is formed from $(M)^+$ by the loss of the successive rings C, D, E, and F. The splitting off of OCH_3 from the ion b leads to the production of fragment c. The ion with m/e 175 (fragment d) is formed by the loss by the molecular ion of the rings A, B, E, and F with closure of the ether bridge in position 1' [2]. By decomposing substance (I) with sodium in liquid ammonia, we obtained monomolecular compounds. If, in the bisbenzylisoquinoline bases the hydroxy group is in the ortho position to the ether bridge, the rupture of this bridge does not take place [3]. Therefore, there is no hydroxy group in positions 6' and 7 of c (I). On the basis of a positive Millon reaction [4], positions 6 and 6' are also excluded. Thus, position 5 remains the most probable one for the hydroxy group and the most probable structure for thalsimidine is (I) with the L-configuration at C-1.

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