MASS-SPECTROMETRIC ANALYSIS OF HOMOAPORPHINE BASES STRUCTURE OF SZOVITSININE

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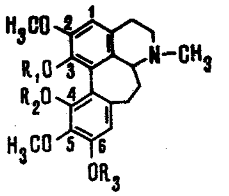
A series of homoaporphine bases isolated from colchicine-containing species of Liliaceae is known [1-6]. We have studied the mass spectra of merenderine (I), szovitsamine (II), O-methylkreysigine (III), O,O-diacetylmerenderine (IV), and szovitsine (V).



I. $R_1=R_3=H$; $R_2=CH_3$
II. $R_1=R_3=CH_3$; $R_2=H$
III. $R_1=R_2=R_3=CH_3$
IV. $R_1=R_3=COCH_3$; $R_2=CH_3$

Szovitsine (V) is a molecular compound with the composition $C_{42}H_{50}NO_{10}$ consisting of two isomeric bases: 2,4-dihydroxy-3,5,6-trimethoxyhomoaporphine and 3,6-dihydroxy-2,4,5-trimethoxyhomoaporphine (or 3,5-dihydroxy-2,4,6-trimethyoxyhomoaporphine).

The relative intensities of the main ions in the mass spectra studied are given below (%):

Ion, *m/e*	*I*	*II*	*III*	*IV*	*V*
M^+	55	33	23	11	50
$(M-1)^+$	21	5	4	2	9
$(M-15)^+$	35	15	17	3	20
$(M-17)^+$	100	6	—	3	100
$(M-19)^+$	4	—	—	—	5
$(M-29)^+$	17	7	10	—	12
$(M-31)^+$	25	100	100	—	60
$(M-33)^+$	15	4	—	—	11
$(M-43)^+$	5	3	2	20	5
$(M-45)^+$	4	3	4	—	4
$(M-47)^+$	10	4	4	—	9
m/e 204	12	2	6	—	12

Analysis of these figures shows that the homoaporphines differ in their manner of fragmentation from the aporphine bases [7, 8]. In the mass spectra of the homoaporphines the maximum peak is that of the ions formed by the elimination of the C_3 substituent. When a hydroxy group is present in this position (merenderine), the maximum peak is that of the ion $(M-17)^+$, and in the case of a methoxy group (szovitsamine, O-methylkreysigine) the peak of the ion $(M-31)^+$, and when it is an acetyl group (O,O-diacetylmerenderine) it is the peak of the ion $(M-59)^+$.

The formation of the fragment mentioned takes place in the following way. Localization of the positive charge on the nitrogen leads to the cleavage of of the C_9-C_{10a} bond and then, through free rotation around the $C_{3a}-C_{4a}$ bond and attack of the radical, elimination of the C_3 substituent with simultaneous ring closure takes place. The formation of the next most intense ion $(M-15)^+$ is probably connected with the localization of the positive charge in ring D, as is shown for merenderine in the Scheme. The same Scheme gives the routes of decomposition of the ions $(M-19)^+$, $(M-29)^+$, and $(M-43)^+$.

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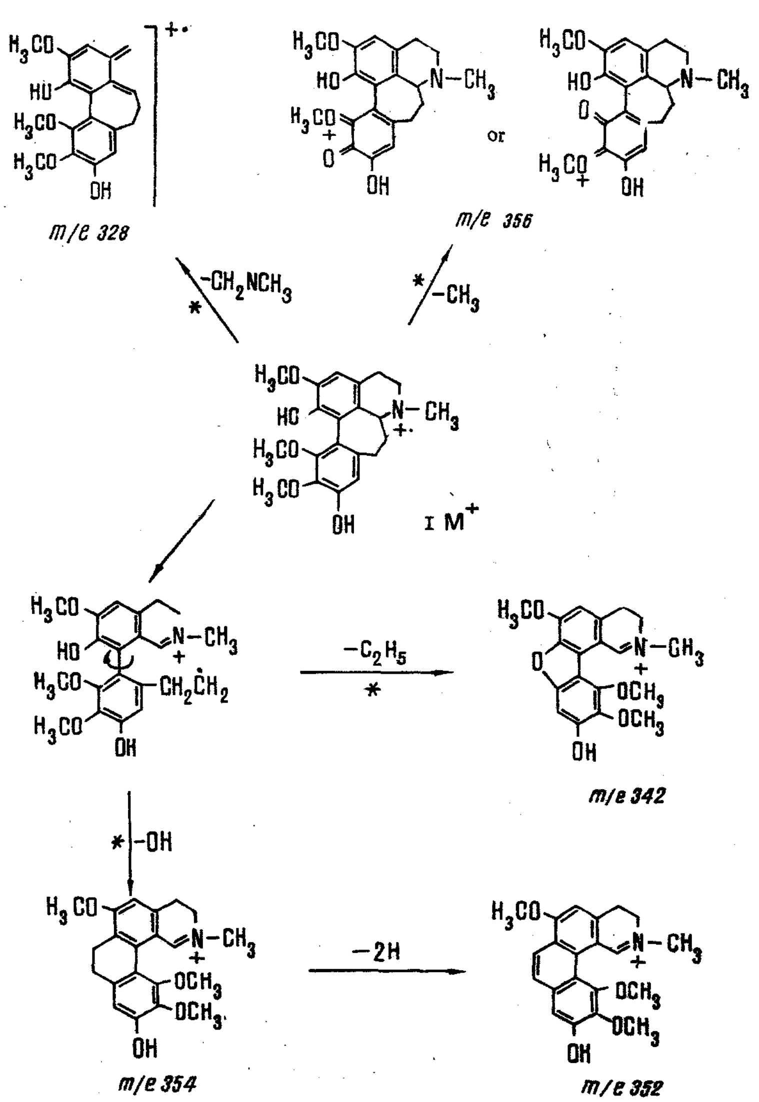

The elimination of $CH_2=N-CH_3$ is not characteristic for the homoaporphines, and the peaks of this ion have a low intensity in their mass spectra.

The compositions of the main merenderine ions have been confirmed by high-resolution mass spectra and in addition, it has been established that the $(M-33)^+$ ion is formed as the result of the elimination of a methoxy group and two hydrogen atoms:

m/e found	m/e calculated	Composition of the ion
371.1743	371.1726	$C_{21}H_{25}NO_5$
356.1489	356.1492	$C_{20}H_{22}NO_5$
354.1718	356.1699	$C_{21}H_{24}NO_4$
342.1349	342.1336	$C_{19}H_{20}NO_5$
340.1543	340.1543	$C_{20}H_{22}NO_4$
338.1402	338.1387	$C_{20}H_{20}NO_4$
328.1290	328.1305	$C_{19}H_{20}O_5$

The $(M-43)^+$ ion in the spectrum of O-methylkreysiginine is a doublet. The first member of the doublet is formed by the elimination of $CH_3=NCH_3$ through a retrodiene decomposition (found: 356.1611; calculated 356.1617), and the second by the elimination of a C_3H_7 radical (found: 356.1490; calculated 356.1492).

Under mass-spectrometric conditions, szovitsine (V) decomposes with the formation of two isomeric substances having the composition $C_{12}H_{25}NO_3$ (mass spectrometrically). The presence in its mass spectrum of the peaks of the $(M-17)^+$ and $(M-31)^+$ ions as the most intense shows the substitution of the C_3 position in the decomposition products by different groups: in one of them a hydroxy and in the other a methoxy group. At the same time, in the spectrum of metastable transitions obtained by the DADI [direct analysis of daughter ions] method the two peaks corresponding to the elimination of OH and OCH_3 groups are the maximum.

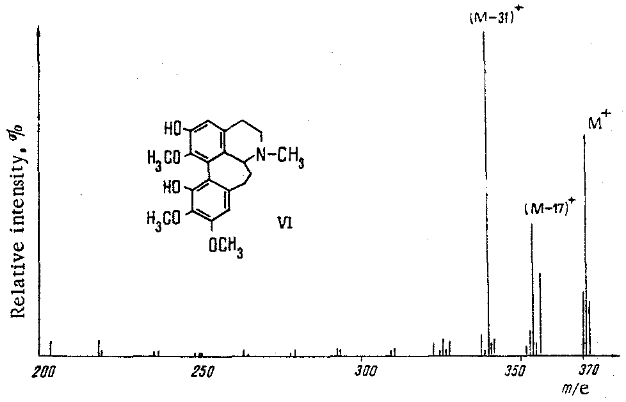

Fig. 1. Mass spectrum of szovitsinine.

We have also studied the mass spectrum of szovitsinine (VI) – an alkaloid of hitherto unknown structure.

Szovitsinine, a base isolated from Colchicum szovitsii Fisch. et Mey, has the composition $C_{21}H_{25}NO_5$ (mass spectrometrically). Its mass spectrum is shown in Fig. 1. Analysis of the spectrum enables szovitsinine to be assigned to the group of aporphine compounds. Its spectrum includes the peaks of an ion with m/e 328 $(M-43)^+$, which shows the presence of a N-methyl group. The maximum peak is that of an ion with m/e 340 $(M-31)^+$, which shows the substitution of position C_3 by a methoxy group. The composition of szovitsinine permits the conclusion that its molecule contains two hydroxy groups. Since the natural homoaporphines contain not more than one hydroxy group in each of the benzene rings, it is easy to represent the position of one of them in the C_2 position of ring A.

In the mass spectrum of szovitsinine, the peak of the ion $(M-17)^+$, due to the elimination of hydroxyl, is also strong. Because of a tendency to the elimination of a hydroxyl at C_4 that is greater than for other positions, it may be assumed that one of the hydroxy groups is located in this position.

The results of the mass-spectral analysis of szovitsinine agree with the NMR spectrum, in which there a are the signals of a N-methyl group (2.38 ppm) and of three methoxy groups (3.50, 3.80, and 3.82 ppm). The resonance of two aromatic protons gives singlet signals in the weak field (6.52 and 6.60 ppm). According to the mass spectrum, the C_3 position of ring A is occupied by a methoxy group, and therefore the three-proton singlet at 3.50 may [1] be assigned to this group, and there is a hydroxy group in the C_4 position.

On the basis of the facts given, the structure 2,4-dihydroxy-3,5,6-trimethoxyhomoaporphine (VI) is proposed as the most probable for szovitsinine.

Szovitsinine was shown chromatographically to be identical with one of the substances obtained from the decomposition of szovitsine, for which the structure of 2,4-dihydroxy-3,5,6-trimethoxyhomoaporphine has been established.

SUMMARY

The mass spectra of homoaporphine bases have been studied. The main decomposition of these bases is connected with the elimination of the substituent in position C_3.

The mass spectrum of the new base szovitsinine has been studied and the structure of 2,4-dihydroxy-3,5,6-trimethoxyhomoaporphine has been proposed as the most probable form of it.

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THE STRUCTURE OF MAGNOLAMINE

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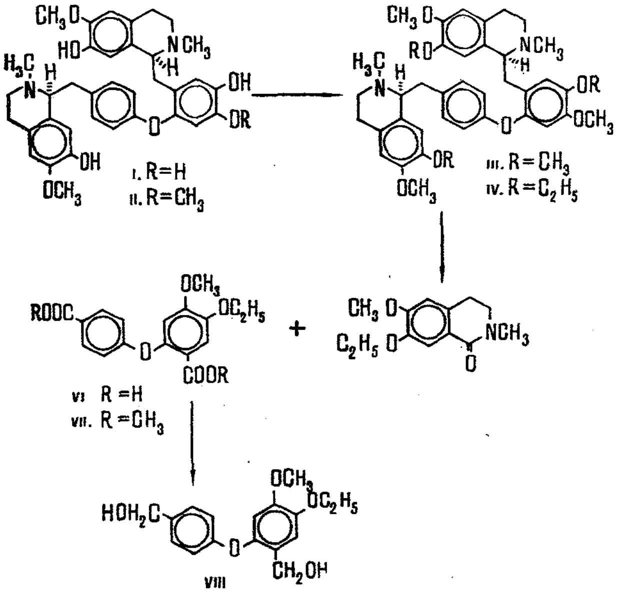
The bisbenzylisoquinoline alkaloid magnolamine was first isolated from the leaves of Michelia fuscata Blume (synonym Magnolia fuscata Andr.) in 1938, and the structure (I) was proposed for it [1-4].

Continuing the study of magnolamine, we have found that its spectral characteristics contradict formula(I).

The NMR spectrum of magnolamine (Fig. 1) contains, in addition to the protons of the bisbenzylisoquinoline skeleton, two singlets of N-methyl groups at 2.34 and 2.43 ppm and the sharp singlets of three aryl methoxy groups at 3.74, 3.76, and 3.78 ppm. At the same time, according to (I) there should be the signals of only two methoxy groups. A quantitative determination of methoxyls by the method of Vieböck and Brecher confirmed the presence of three methoxy groups in the magnolamine molecule. It must also be noted that magnolamine does not show the color reaction with ferric chloride that is characteristic for an orthodiphenyl group.



The methylation of magnolamine with diazomethane led to a hexamethoxy derivative (III), identical with that described previously [2]. The NMR spectrum of this compound has the singlets of six methoxy groups at 3.57 (3H), 3.60 (3H), 3.74 (6H), and 3.80 (6H) ppm.

The ethylation of magnolamine with diazomethane gave a substance (IV) with mp 101-102°C (from ethanol) which, according to its NMR spectrum, had three methoxy groups [3.83 (3H), 3.88 (6H), ppm] and three ethoxy groups [1.46 (9H), 3.70-4.18 (6H) ppm].

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