A COMPARISON OF THE MASS SPECTRA OF ISOMERIC HYDROXY AND METHOXY ANALOGS OF DEOXYPEGANINE AND DEOXYVASICINONE

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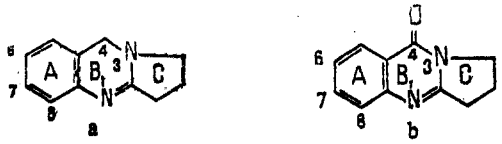
The mass spectra of 6-, 7-, and 8-hydroxy and -methoxy derivatives of deoxypeganine (Ia) and of deoxyvasicinone (Ib) have been studied. It has been shown that in the case of the derivatives of (Ia) the main fragmentation process is the formation of the stable $(M - H)^+$ ion. Qualitative and quantitative differences are observed in the mass spectra of the methoxy derivatives of (Ib).

Continuing a study of the fragmentation of natural and synthetic quinazoline derivatives, we have studied the mass spectra of a series of aromatic hydroxy and methoxy isomers of deoxypeganine (DOP, Ia) and deoxyvasicinone (DOV, Ib) with the aim of elucidating the influence of isomerism on the breakdown of the quinazoline (a) and quinazolane (b) structures under electron impact.



Ia	Deoxypeganine (DOP)	Ib	Deoxyvasicinone (DOV)
IIa	6-Hydroxy-DOP	IIb	6-Hydroxy-DOV
IIIa	7-Hydroxy-DOP	IIIb	7-Hydroxy-DOV
IVa	8-Hydroxy-DOP	IVb	8-Hydroxy-DOV
Va	6-Methoxy-DOP	Vb	6-Methoxy-DOV
VIa	7-Methoxy-DOP	VIb	7-Methoxy-DOV
VIIa	8-Methoxy-DOP	VIIb	8-Methoxy-DOV

In the literature, the fragmentation of the simplest isomeric hydroxy- and methoxyquinazolines containing no alicyclic ring has been considered [1]. The mass spectra of isomeric methoxy- and hydroxyquinolines, which have much in common with the mass spectra of the substances under consideration, have been described [2].

The presence of the five-membered alicyclic ring C and the absence of a $N_3 - C_4$ double bond has a substantial influence on the behavior of these compounds under electron impact. While quinazoline and its 6- and 7-hydroxy analogs are characterized by breakdown with the successive elimination of two molecules of HCN [1], DOP (Ia) and its hydroxy and methoxy derivatives eliminate H, forming the stable quinazoline ion $(M - H)^+$, the peak of which is the maximum peak in each of the spectra of (Ia-VIIa) (Table 1 and scheme 1). Peganidine [3] and peganine (vasicine) [4] behave similarly under electron impact. In the case of the methoxy derivatives (Va-VIIa) the fragmentation processes with the participation of the methoxy group acquire a more pronounced nature. Thus, for compounds (Va) and (VIIa) we observe the successive elimination of CH_3 and CO, which is characteristic for the corresponding methoxyquinazolines and methoxyquinolines [1, 2] (scheme 2). Fragmentation processes affecting ring C and the quinazoline system are hardly expressed.

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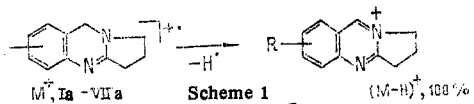
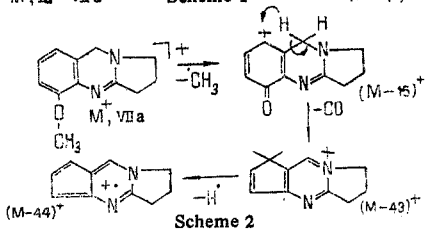
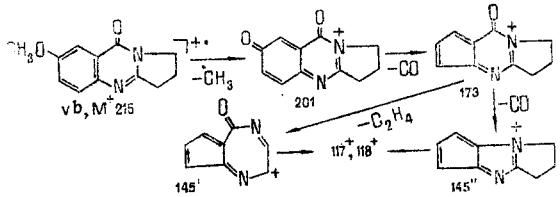


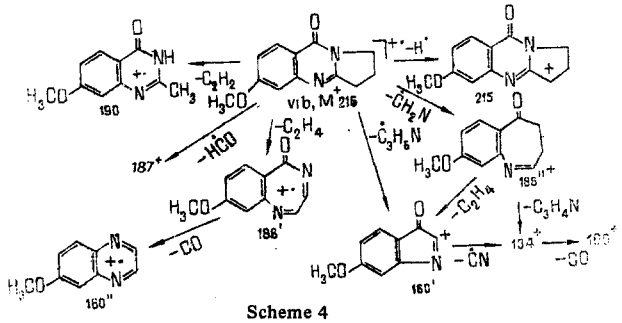
Scheme 1



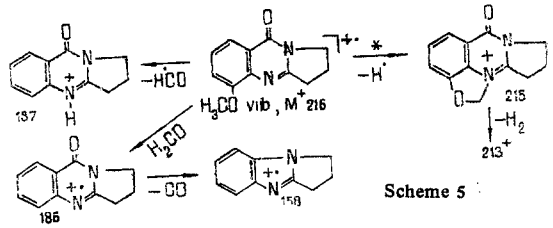
Scheme 2



Scheme 3



Scheme 4



Scheme 5

On considering the group of hydroxy isomers of DOV (IIb-IVb), it was established that their mass spectra not infrequently differ from one another and from the analogous mass spectrum of DOV (Ib) [5]. The main difference in these spectra consists in the relative intensitiesof the peaks of the M^+ and $(M - H)^+$ ions (see Table 1). Furthermore, in the spectrum of 8-hydroxy-DOV (IVb) the intensity of the peak of the ion with m/z 174 $(M - CO)^+$ is increased. A similar difference has been observed in a comparison of the spectra of 6- and 7-hydroxyquinolines with the spectrum of 8-hydroxyquinolines [2], but in the fragmentation of the latter the elimination of CO was accompanied by an intensive loss of HCN. In the case of 8-hydroxy-DOV, however, this process takes place after the loss by the ion with m/z 174 of a formyl radical with the participation of the C_4-O group. The mass spectra and elementary composition of the fragmentary ions of (IVb), which has recently been isolated from a filtrate of a culture of *Klebsiella* bacteria, have been published [6].

Competition between the processes of elimination of a methoxy group and of the elements of the acylic ring C affect the behavior of the isomeric methoxydeoxyvasicinones (Vb-VIIb). In the first acts of fragmentation, the 6- and 8-methoxy derivatives (Vb) and (VIIb) behave

TABLE 1. Relative Intensities (%) of the Peaks of the Ions in the Mass Spectra of Compounds (Ia-VIIa) and (IIb-IVb)

m/z	Ia	m/z	IIa	IIIa	IV	m/z	Va	VIa	VIIa	m/z	IIb	IIIb	IVb
M^+172	50	M^+188	60	46	60	M^+202	70	45	83	M^+202	100	94	100
171	100	187	100	100	100	201	100	100	100	201	67	100	32
169	4	185	3	5	4	187	18	6	30	187	1	3	1
143	2	159	5	8	4	173	2	3	5	185	2	7	1
129	5	158	4	7	3	159	9	5	13	176	5	6	4
116	6	135	3	9	3	158	30	12	46	174	2	2	11
63	35	132	4	11	10	146	2	3	3	173	4	6	5
										160	2	4	1
										146	7	6	8
										145	7	5	14
										119	5	2	4
										118	3	2	10
										117	2	2	6
										106	5	4	24
										63	7	5	28

TABLE 2. Results of Measurements of the Accurate Masses of the Fragmentary Ions of Compounds (Vb-VIIb)

Mass	C	H	N	O	Mass	C	H	N	O
Vb					VIb				
M^+ 216,092	12	12	2	2	M^+ 216,092	12	12	2	2
173,073	10	9	2	1	190,074	10	10	2	2
( )* 145,040′	8	5	2	1	(1) 188,059′	10	8	2	2
(4) 145,077″	9	9	2		(2) 188,071″	11	10	1	2
(2) 118,065′	8	8	1		187,085	11	11	2	1
(1) 118,053″	7	6	2		185,070	11	9	2	1
(4) 118,030‴	7	4	1	1	173,072	10	9	2	1
(2) 117,056′	8	7	1		172,065	10	8	2	1
(1) 117,047″	7	5	2		(3) 160,039′	9	6	1	2
(1) 117,022‴	7	3	1	1	(1) 160,065″	9	8	2	1
VIIb									
M^+ 216,092	12	12	2	2	(2) 145,076″	9	9	2	
187,086	11	11	2	1	(1) 145,042′	8	5	2	1
186,079	11	10	2	1	134,037	8	6		2
173,073	10	9	2	1	(20) 118,029‴	7	4	1	1
158,085	10	10	2		(1) 118,056″	7	6	2	
(1) 145,041′	8	5	2	1	(1) 117,058′	8	7	1	
(2) 145,076″	9	9	2		(1) 117,047″	7	5	2	
					(10) 117,023‴	7	3	1	1

*The ratios of the intensities in the multiplet ions are given in parentheses.

similarly to the corresponding methoxyquinolines [2]: The molecular ion of (Vb) successively eliminates $\dot{C}H_3$ and CO, and the methoxy group of compound (VIIb) decomposes by the splitting out of $\dot{C}HO$ or CH_2O (Fig. 1). Furthermore, an extremely characteristic analogy exists in the appearance of the peak of the ion $(M - Z)^+$ in the spectrum of this compound [1, 2]. The breakdown of rings B and C in compound (Vb) takes place by the alternative elimination of CO or C_2H_4 from an ion with m/z 173 and the subsequent splitting out from the components of the doublet with m/z 145 of the particles C_2H_3, HCN, H_2CN, CO, and C_2H_4, which gives triplets of ions with m/z 118 and 117 (Table 2 and Scheme 3). In 8-methoxydeoxyvasicinone (VIIb), ring B breaks down mainly as the result of the loss of HCO or CO from the ions with m/z 187 and 186 (scheme 5).

The spectrum of 7-methoxy-DOV (VIb) greatly resembles that of the unsubstituted compound (Ib) (DOV) [5], particularly in the intensity of the $(M - H)^+$ peak. Here the processes involving the decomposition of the methoxy group are largely suppressed. Measurement of the elementary compositions of the ions confirmed that the fragments with m/z 190, 160, 134, and 106, which are uncharacteristic for the isomeric compounds (Vb) and (VIIb), are formed by the breakdown of rings C and B. In view of the fact that the scheme of formation of these fragments, especially the ions with m/z 160, was not completely obvious, we studied the metastable transitions of compound (VIb) with the aid of the method of metastable defocusing (MD). As was found, the precursor of the ions with m/z 160 and 134 is an ion with m/z 188,

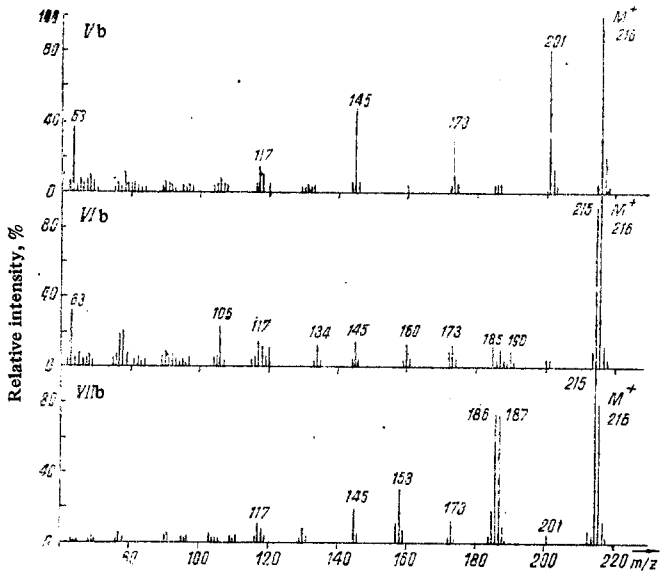


Fig. 1. Mass spectra of the isomeric methoxydeoxyvasicinones (Vb)-(VIIb).

the peak of which has a low intensity in the spectrum of (VIb). Judging from its composition (see Table 2), this ion is formed from M^+ by the alternative loss of the particles C_2H_4 and CH_2N. Both these are key fragments and explain the appearance of a whole series of other fragments (scheme 4).

It is interesting to note the fact that on the performance of the MD of the daughter ion with m/z 173, a metastable transition $188^+ \rightarrow 173^+$ was recorded, although the composition of the fragment given in Table 2 cannot be obtained by the splitting out of CH_3 from the two components of the ion with m/z 188. As a result of a careful search for minor components of the ion with m/z 173, weak peaks ($\simeq$ 0.04 of the main peak) were detected, the composition of which corresponded to the loss of CH_3 by both variants of the ion with m/z 188. In addition, the recording of this fragmentation pathway by the MD method is partially explained by a transition between the mono-^{13}C isotopic ions of another process, $183^+ \rightarrow 172^+$, which we also detected with the aid of the same method.

EXPERIMENTAL

The low-resolution mass spectra were taken on an MKh-1303 instrument using a system of direct introduction with a temperature of the inlet system of 100-120°C, an ionizing voltage of 40 V, and an emission current of 50 μA. The measurement of the accurate masses of the ions and the recording of the transitions by the MD method were performed on a MKh-1310 instrument using a SVP-5 system for the direct introduction of the sample. The collector current was 40 μA, the temperature of the ionization chamber 100°C, the ionizing voltage 50 V, and the resolutions, 10,000 and 2000 (MD). The syntheses of the compounds have been published previously [7].

SUMMARY

It has been established that the dihydroquinazoline system eliminates hydrogen from C_4 regardless of the position of a substituent. Hydroxy substitution in the aromatic ring of the quinazoline skeleton has only a weak effect on the course of fragmentation. The isomeric 6- and 8-methoxydeoxyvasicinones break down in a similar manner to the corresponding methoxyquinolines and methoxyquinazolines, and the 7-methoxy isomer shows a fragmentation that is typical for deoxyvasicinone.

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STRUCTURE OF KORSEVERILINONE

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From the combined ether-extracted material of the epigeal part of *Korolkowia sewerzowii* a new base has been isolated — korseverilinone with mp 222-223°C $[\alpha]_D$ −18.8°, $C_{27}H_{43}NO_3$. On the basis of the results of a study of the IR, PMR, and mass spectra of korseverilinone and also its conversion into the known alkaloid korseveriline it has been established that korseverilinone has the structure of 3α, 14α-dihydroxycevanin-6-one.

Continuing a study of the epigeal part of *Korolkowoa sewerzowii* Rgl., gathered in the Fergana Province [1, 2], from the combined ether-extracted material we have isolated by column chromatography a new alkaloid — korseverilinone with mp 222-223°C $[\alpha]_D$ −18.8°, $C_{27}H_{43}NO_3$ (I).

Korseverilinone is a saturated tertiary base the IR spectrum of which exhibits absorption bands at (cm^{-1}) 3450 (OH), 2955-2860 and 1465 (CH_3-; $-CH_2-$), 2775 (trans-quinolizine), and 1710 (C=O). The mass spectrum of (I) has the peaks of ions with m/z 98, 111 (100%), 112, 124, 125, 149, 164, 166, 373, 396, 400, $(M-18)^+$, $(M-17)^+$, $(M-15)^+$, 429 M^+, which are characteristic for the C-nor-D-homosteroid alkaloids of the cevine group [3-5]. The PMR spectrum of (I) shows: a three-proton singlet at 0.66 ppm (19-CH_3), unresolved signals from the protons of secondary C-methyl groups in the form of singlets at 0.83 ppm (21-CH_3 and 27-CH_3), and a multiplet at 4.08 ppm (HC−OH).

The acetylation of (I) gave monoacetylkorseverilinone (II) in the IR spectrum of which absorption bands appear at (cm^{-1}) 3450, 1025 (OH), 2770 (trans-quinolizine), 1740, 1250 (ester C=O), and 1715 (C=O).

The PMR spectrum of (II) contained signals from the protons of C-methyl groups at 0.67 ppm (19-CH_3), and 0.83 ppm (21-CH_3 and 27-CH_3), a three-proton singlet from an acetoxy group at 1.96 ppm ($-OCOCH_3$), and a multiplet at 5.05 ppm (H, HC−OCOCH$_3$).

The reduction of (I) with sodium tetrahydroborate formed dihydrokorseverilinone (III), identical with korseveriline (mixed melting point, IR spectrum, R_f) [3]. The oxidation of (I) with chromium trioxide in acetic acid gave a diketone identical with korseverilinedione [3]. The identity of dihydrokorseverilinone with korseveriline and of the diketone with korseverilinedione shows that korseverilinone is a monoketone of korseveriline [3].

It remained to determine the position of the carbonyl group in the korseverilinone molecule. In the PMR spectrum of diacetylkorseveriline the multiplet at 4.86 ppm from the protons germinal to the acetoxy groups relates to $C_6\alpha$-H and that at 5.03 ppm to $C_3\beta$-H [3].

In acetylkorseverilinone, the proton geminal to the acetoxy group gives a signal at 5.05 ppm. Consequently, in the korseverilinone molecule the hydroxy group is present at C_3 and the carbonyl group at C_6. This is confirmed by the 23-Hz difference in the chemical shifts of the 19-CH_3 group between diacetylkorseverilinone and acetylkorseverilinone [3, 6]. According to these results, korseverilinone has the structure and configuration of 3α, 14α-dihydroxycevanin-6-one (I).

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