Glycoside B, which we have called yuccaloeside B is (25R)-5α-spirostan-3β-ol 3-{[O-β-D-glucopyranosyl-(1→2)]-[O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→3)]-O-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside}, and glycoside C, which we have called yuccaloeside C is (25R)-5α-spirostan-3β-ol 3-{[O-β-D-glucopyranosyl(1→3)-O-β-D-glucopyranosyl-(1→2)]-[O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→3)]-O-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside}.

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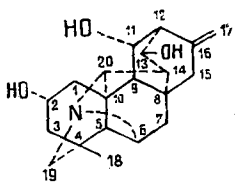
MASS SPECTRA OF DITERPENE ALKALOIDS WITH THE HETISINE SKELETON

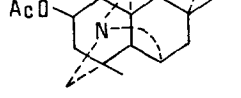
Yu. V. Rashkes, M. S. Yunusov, E. G. Sirotenko, and Z. M. Vaisov

UDC 543.51+547.944/945

An analysis of literature material has shown that the stability of the M^+ ions of bases with the hetisine skeleton decreases considerably when an OR group is present at C-1, C-6, or C-9. The directions of fragmentation are not monotypical and depend greatly on the positions of the oxygen substituents. A similar conclusion can be made from a study of the group and individual features of the breakdown of hetisine, nominine, talatisine, and their derivatives revealed with the aid of high-resolution mass spectrometry and MD spectra. An unusual property of these spectra is the formation of nitrogen-free fragments. The mass spectra of hetisine alkaloids of a new type — zeraconine and its N-oxide — have been characterized.

The interest in diterpene alkaloids that has been increasing in the last quinquennium has been accompanied by an increase in the number of publications on questions of isolating and demonstrating the structure of C_{20} bases with the hetisine skeleton (I) [1]. The volume of mass-spectrometric information contained in these publications is small, and there is practically no information on the laws of their fragmentation. Nor are there any special investigations in the literature of the mass spectra of alkaloids of this series, although the method has been used successfully in determining the structures of diterpene bases of other groups.

I  [1]

II  [6]

553(+), 474(100), 414

Institute of the Chemistry of Plant Substances of the Uzbek SSR Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 542-553, July-August, 1987. Original article submitted January 13, 1987.

0009-3130/87/2304-0452$12.50

We set ourselves the aim of elucidating the laws of the breakdown of the hetisine alkaloids by analyzing literature information on the mass numbers, relative intensities, and elementary compositions of the ions and comparing this information with the properties of diterpene bases of other groups, and also a detailed study of the hetisine alkaloids available to us.

The mass-spectrometric information given in a number of publications on hetisine bases cannot be used for any kind of generalizations, since the authors limit themselves to giving the mass numbers and elementary compositions of the M^+ ions [2-4] or give a list of fragmentary ions without information on their relative intensities [5]. Other papers [6-12] contain information on the mass numbers of the 100% peaks and give lists of the main ions with statements of their relative intensities and the compositions of the fragments split off. The most voluminous information is contained in a paper by Grina et al. [13] devoted to an investigation of the alkaloids geyeridine (XX), geyerine (XXI), and geyerinine (XXII). They give m/z and I, %, of all the main fragments and the elementary compositions of the molecular and some key ions, and for geyerinine (XXII), the EI spectrum of which lacks the M^+ ion, they obtained a chemical ionization spectrum revealing quasi-molecular ions with m/z 486 and 488.

On the following page we give the formulas of the hetisine bases (II-XXII) discussed in the literature [6-13] and also the mass-spectrometric information contained there, on the basis of which it is possible to draw valuable conclusions.

The peaks of the M^+ ions of bases (III-VII, X, XI, XVIII, and XIX) have 100% intensities, in spite of the presence in some of the compounds of ester groupings at C-2 (XVIII, XIX) and at C-11 (III, IV, VI, VII, and XIX). The presence of oxygen substituents at C-1, C-6, or C-9 leads to a fall in the stability of M^+, but the formation of the 100% peaks of the $(M - OR)^+$ ions is characteristic for compounds with OR groups at C-1 (II, XV, and XVI) and C-9 (XIII and XIV). When an OH group is present at C-6, however, the role of competing fragmentation processes – the splitting out of acyloxy radicals from C-13 (XX) or C-11 (XXI, XXII) – increases. The nature of the participation of the C–OH group in breakdown remains obscure: thus, in the spectrum of spiradine (XII), the maximum peak is that of the $(M - 28)^+$ ion.

The detachment of $\dot{O}H$ from C-9 has a greater effect on the stability of M^+ than the detachment of a similar radical from C-1 [compare (XIII), (XIV), and (XVI)], but the splitting out of $Ac\dot{O}$ from C-1 quantitatively exceeds the detachment of $\dot{O}H$ from C-9 when these two substituents are present simultaneously (XV). For the detachment of $\dot{O}H$ from C-9 in compounds (XIII) and (XIV), Sakai et al. [10] suggested as the first act of fragmentation the cleavage of the C-1–C-20 bridge bond which, as is considered [14], precedes the splitting out of radicals from C-1.

A comparison of the stability of the M^+ ions of C-1–OH compounds with the songorine [14] and the hetisine [crassicauline B (XVI)] skeletons shows that it is considerably higher in the former than in the latter.

A decrease in the stability of the M^+ ion takes place in the 13-dehydro bases (VIII) and (IX). This fact is difficult to explain without knowing the distribution of the intensities of the other peaks in the spectra of these compounds.

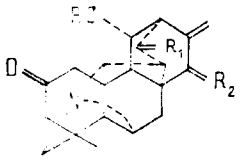
In not one of the publications cited [5-13] are the ions formed by the splitting out of parts of the diterpene skeleton considered, although the lists of fragments contain some of such ions.

Let us further consider in detail the general and individual properties of the mass spectra of a number of hetisine bases the molecules of which contain one [nominine (XI)] or three (hetisine (I), talatisine (XXII) [15]) hydroxy groups, and also compounds with a reduced $\Delta^{16(17)}$-bond – dihydrodeoxynominine (XXIV) [16] and hydrotalatisine (XXV) [17].

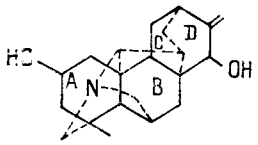
The molecular ions of all the compounds mentioned are characterized by a high stability (W_{M^+}), which is the greatest for the oxygen-free compound (XXIV):

Base	W_{M^+}	$S_{(M-OH)^+}$
I	48.1	18.5
XI	54.7	3.5
XXIII	31.5	4.5
XXIV	63.3	–
XXV	43.8	4.6

Compound	R	R_1, R_2	M^+, %
III	—Bz	R_1=R_2=βOH, αH	100
IV	—Bz	R_1=βOH, αH; R_2=βOAc, αH	100
V	—Bz	R_1=R_2=βOAc, αH	100
VI	—H	R_1=R_2=βOH, αH	100
VII	—Bz	R_1=βOH, αH; R_2=O	100
VIII	—Bz	R_1=O, R_2=βOH, αH	30
IX	—Bz	R_1=O, R_2=βOAc, αH	45

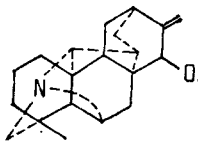


[7]

X 

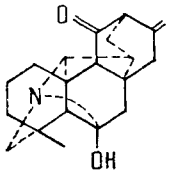
[8]

313 (M+, 100), 296 (M — OH, 50)

XI 

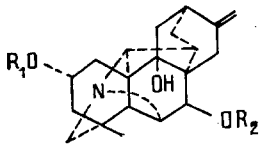
[9]

297 (M^+, 100), 282 (11), 146 (21)

XII 

[9]

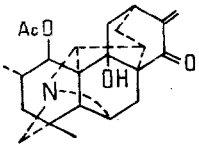
311 (M^+, 64), 283 (100)



[10]

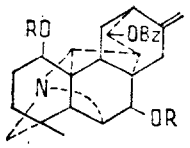
XIII. R_1 = Bz, R_2 = H ;
433(M^+, 20), 416 (M — OH, 100), 312 (M — OBz, 21)

XIV. R_1 = Bz, R_2 = Ac;
475(M^+, 26), 458 (M — OH, 100), 415 (M — AcOH, 38)

XV C_6H_5COO 

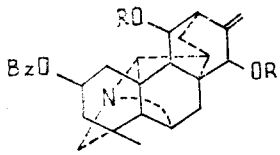
[11]

430 (M — CH_3CO_2, 100)



[12]

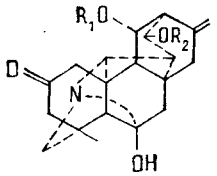
XVI. R=H; 433 (M^+, 65), 416 (100), 312 (M — BzO, 12)
XVII. R = Ac; 517 (22), 458 (43), 457 (100)



[12]

XVIII. R=H; 433 (M^+, 100), 312 (38)

XIX. R = Ac; 517 (M^+, 10), 474 (18), 306 (M — OBz, 60)



[13]

XX. R_1 = H, R_2=Ac; 385 (M^+, 35), 367 (7), 326 (M — OAc, 100), 325 (22)

XXI. R_1 = COC_4H_9, R_2 = H

427 (16) — $C_{25}H_{33}NO_5$

410 (5) — $C_{25}H_{32}NO_4$

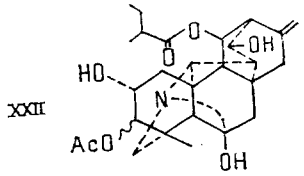
342 (10) — $C_{20}H_{24}NO_4$

$(M - C_4H_9CO)^+$

326 (100) — $C_{20}H_{24}NO_3$

$(M - C_4H_9COO)^+$

325 (20) — $C_{20}H_{23}NO_3$

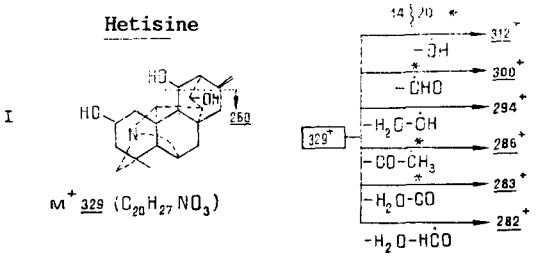


XXII [13]

MS CI NH_3	MS EI
488 (M+H, 48)	428 (9)
486 (16)	427 (8)
470 (12)	386 (2)
428 (5)	385 (1)
426 (33)	57 (100)
386 (M — C_4H_9COO, 84)	
326 (100)	

The smallest value of W_{M^+} is characteristic for talatisine (XXIII), the breakdown of which is less selective (scheme 3). This can be seen particularly from the stability S of the $(M - OH)^+$ ions of the isomers (XI) and (XXIII) (18.5 and 4.5%, respectively).

A comparison of the two structures permits the assumption that in the formation of the $(M - OH)^+$ ion for hetisine (I) it is mainly ȮH from C-13 that splits off after the cleavage of the C-20—C-14 bond. Below we shall show that the latter act is extremely characteristic for bases of the hetisine series.

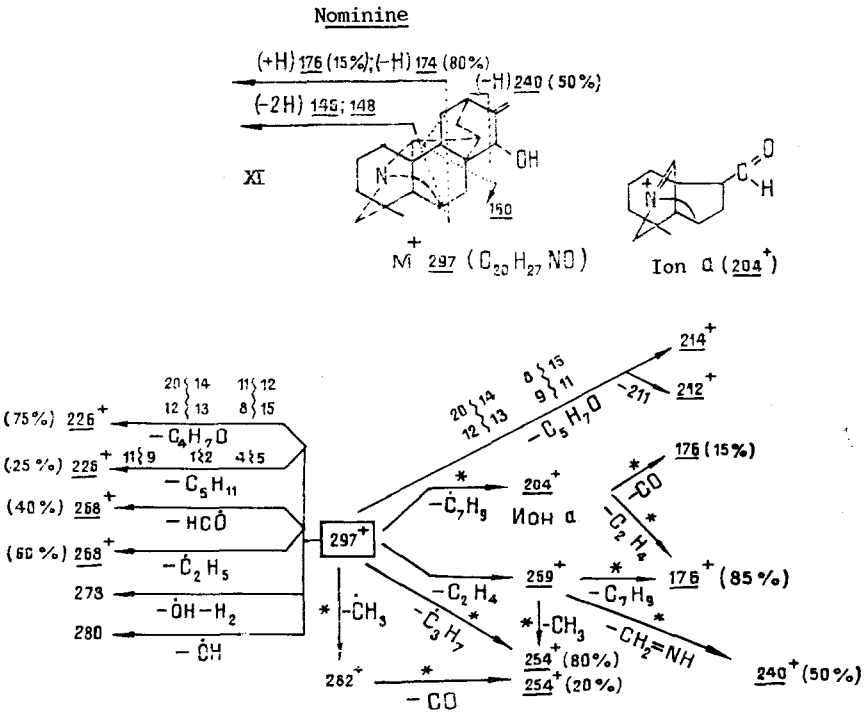


Scheme 1

m/z	I, %	m/z	I, %
329	100	256	2.6
312	39	247	3.0
300	7.7	246	2.4
298	2.4	242	2.1
294	4.3	217	3,0
286	3.8	2.5	3,2
283	12	176	3.8
282	12	162	3.6
260	3.8		

The formation of the stable fragment $(M - OH)^+$ from hetisine (I) suppresses other breakdown processes. They are represented in the spectrum by peaks of ions with medium and low intensities (scheme 1; here and below the mass numbers of the ions for which the elementary compositions have been measured are underlined; for doublets and triplets the contributions of the corresponding components, %, are given in parentheses; asterisks denote metastable transitions recorded by the metastable defocussing (MD) method; and the mass numbers of the ions with a statement of their relative intensities, %, are also given.

The greatest importance in structural studies of natural compounds is possessed by the key fragments formed in the breakdown of the skeletal bonds. In the spectrum of hetisine, the contribution of these ions is minimal. Only an ion with m/z 260 ($C_{16}H_{22}NO_2$) can be fairly definitely represented as a product of breakdown at the bonds of rings C and D.

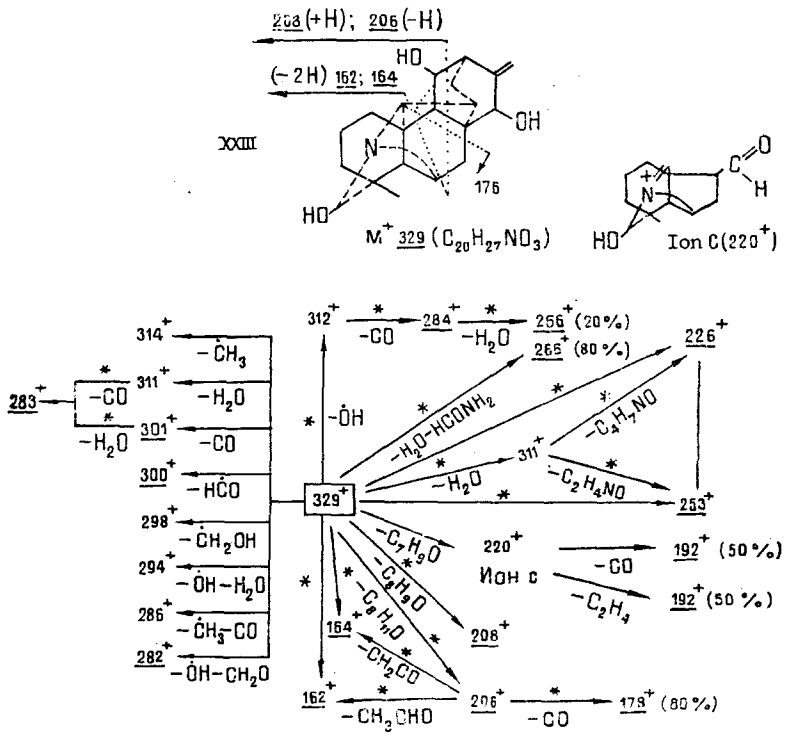


Scheme 2

m/z	I, %	m/z	I, %	m/z	I, %
297	100	240	1,9	176	3,2
282	8,3	226	1,5	174	2,9
280	6,4	214	1,7	160	6,4
278	2,8	212	1,5	148	5,8
269	7,5	206	2,8	146	22
268	3,0	204	0,8		
254	2,6	177	3,6		

In the spectra of nominine (XI) and talatisine (XXIII) (schemes 2 and 3), several common directions of the cleavage of the bonds of the skeleton, beginning with the cleavage of the C-20–C-14 bridge bond, can be seen. The subsequent breakdown of ring B gives ions with m/z 146, 148, and 160 (XI), and 162, 164, and 176 (XXIII). The breakdown of rings B and C leads to the formation of ions with m/z 174 and 176 (XI), and 206 and 208 (XXIII). Analysis of the MD spectra of the ions with m/z 146 (XI) and 162 (XXIII) shows that, in addition to M^+, precursors of these ions are ions with m/z 174 and 206, respectively, i.e., the first of the two types of fragments mentioned can arise from the second by the elimination of the C-9, C-11 chain. There is some difference in the contributions of the different ions in the two compounds: while for talatisine the ions with m/z 208 and 206 consist wholly of the particles $C_{12}H_{18}NO_2$ and $C_{12}H_{16}NO_2$, for nominine the $C_{12}H_{18}N$ ions form only 1/6 of the height of the peak with m/z 176, while the $C_{12}H_{16}N$ ions make up 4/5 of the total height of the peaks of the ions with m/z 174. The remaining parts of these ions have the compositions $C_{11}H_{14}NO$ and $C_{11}H_{12}NO$. The elimination from the M^+ ion of nominine of a chain of nine carbon atoms with the retention of the C_{15}–OH group in one stage is improbable. The MD spectrum of the ions with m/z 176 gives ions with m/z 204 and 269 as precursors. Summarizing these facts, the formation of the $C_{11}H_{14}NO$ ion can be represented as a process of the alternative

Talatisine



Scheme 3

m/z	I, %	m/z	I, %	m/z	I, %	m/z	I, %
329	100	286	2,7	227	5,5	190	6,0
314	11	284	4,4	226	6,0	179	6,5
312	14	283	4,4	220	1,1	178	12
311	16	282	5,5	209	6,6	176	5,0
301	9,3	266	5,5	208	7,7	164	22
300	6,6	254	3,0	206	6,6	162	17
298	8,2	253	3,3	193	3,8	133	11
294	2,4	228	2,7	192	3,8		

sequential elimination of C_2H_4 from the elements of ring A and C_7H_9 at the expense of the elements of ring B-D (scheme 2). The composition of the ion with m/z 177 is $C_{11}H_{15}NO$, and it obviously includes the same structural elements.

We may note that this ion is a precursor of an ion with m/z 160, differing from the latter in composition by OH. Consequently, the ions with m/z 160 (XI) and 176 (XXIII) can be formed by a route differing from that which is illustrated in the drawings of the molecules.

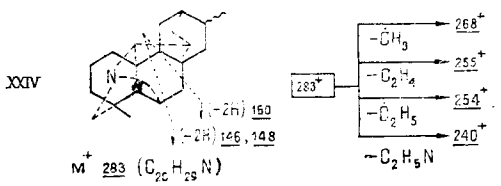
To the ions with m/z 174, 176, and 177 of nominine arising with retention of the C-15 atom may correspond weak peaks of ions with m/z 190, 192, and 193 from talatisine. The elementary compositions of the ions with m/z 192 correspond to this hypothesis.

Let us now turn to the individual characteristic features of the two spectra. Of the ions with m/z 240 from nominine, 50% correspond to the $(M - C_3H_5O)^+$ ions, i.e., they are formed by the elimination of the elements of ring D. The ejection of ethylene, $\dot{C}_2H_5$, and $\dot{C}_3H_7$ from M^+ obviously characterizes the fragmentation of ring A as similar to that for alkaloids with the songorine and denudatine skeleton [14, 18].

One more, unusual in nature, process for the fragmentation of ring A has been recorded in the spectrum of (XI): 25% of the ions with m/z 226 have the composition $C_{15}H_{16}NO$, which corresponds to the elimination of the C-1—C-4, C-18 chain from M^+ after the cleavage of the C-4—C-19 bond. The bulk of the ions with this mass have the composition $C_{16}H_{20}N$, which can be explained by the cleavage of the C-20—C-14, C-12—C-13, C-11—C-12, and C-8—C-15 bonds with the migration of 2 H to the neutral fragment.

The ions with m/z 212 ($C_{15}H_{18}N$) and 214 ($C_{15}H_{20}N$) in the nominine spectrum arise by a similar mechanism: in this case, in place of the cleavage of the C-11—C-12 bond, cleavage of C-9—C-11 bond takes place. The fragmentation of talatisine possesses the feature that, thanks to the presence of a substituent at C-11, its spectrum contains the peaks of ions with m/z 178 ($C_{11}H_{16}NO$, 80%), and 179 ($C_{11}H_{17}NO$, 50%), formed by the ejection of CO and $\dot{H}CO$ from the ions with m/z 206 and 208, respectively.

Dihydrodeoxynominine



m/z	I, %	m/z	I, %
283	100	214	0.8
268	8.0	212	0.8
255	3.6	192	1.8
254	2.4	174	2.0
240	3.9	160	7.6
228	1.3	148	3.2
226	0.8	146	22

Scheme 4

Without having information at our disposal on the elementary compositions of the ions in the region of medium mass numbers in the spectrum of geyeridine (XX) we can only assume that the fragments formed from it with m/z 223 (10), 192 (9), 176 (16), and 175 (25) [13] arise through the cleavage of the same bonds of the skeleton as the ions with m/z 208, 176, 164, and 162 in the talatisine spectrum.

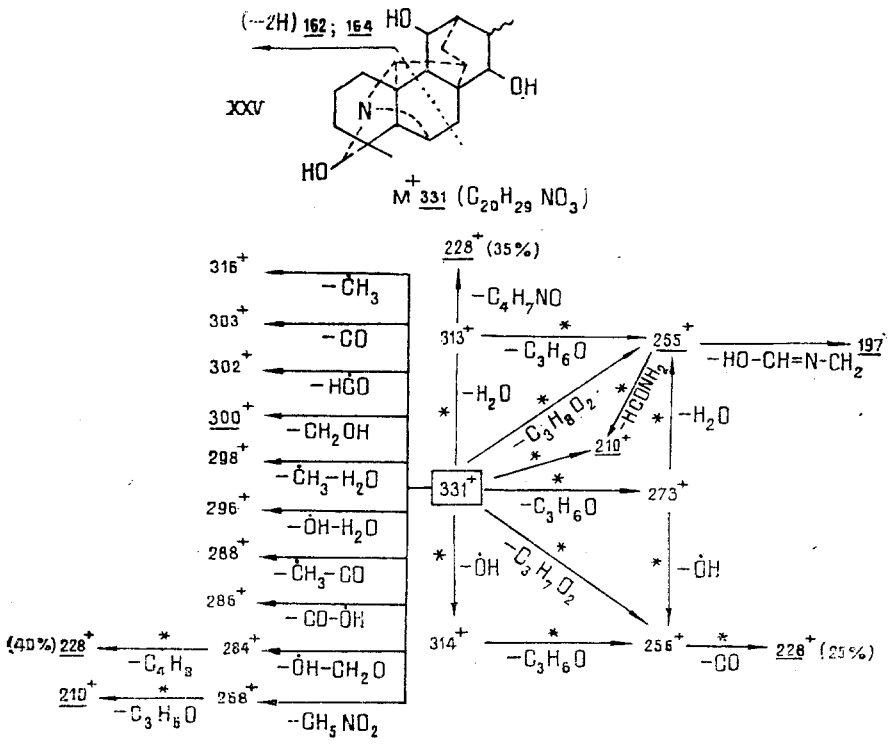
The most interesting and unusual property of the mass spectra of the hetisine alkaloids is the formation of nitrogen-free fragments in the region of medium masses. In the case of nominine, we recorded only one ion of this series — $(M - C_3H_7N)^+$ with m/z 240. Judging from its MD spectrum, it was formed as the result of the elimination of two particles: C_2H_4 (ring A) and CH_2—NH.

The spectrum richest in nitrogen-free fragments is that of talatisine. This is apparently due to the specific properties of the α-carbinolamine grouping and to the presence of two OH groups in rings C and D which, in combination with the C_{16}—C_{17} bond, promote the aromatization of these rings by the corresponding decomposition pathways. The nitrogen atom of talatisine is eliminated together with bridge carbon atoms: C-19 or C-19, C-20; 80% of the ions with a mass of 266 have the composition $C_{19}H_{22}O$, which corresponds to the elimination of $(H_2O + HCONH_2)$ from M^+ (scheme 3). The loss of C_2H_4NO from the $(M - H_2O)^+$ ion forms an ion with m/z 253. By losing a vinyl radical, the latter is converted into an ion with m/z 226 ($C_{16}H_{18}O$). The MD spectrum of this ion shows among its parental ions $(M - H_2O)^+$, i.e., a nitrogen-containing neutral fragment can be split out together with the elements of

ring A. Ions with m/z 228 andd 227 are also nitrogen-free, and the latter, by losing a molecule of water is converted into an ion with m/z 209 ($C_{16}H_{17}$).

Let us pass to the analysis of the spectra of compounds hydrogenated at the $C_{16}=C_{17}$ bond: dihydrodeoxynominine (XXIV) and hydrotalatisine (XXV).

Hydrotalatisine



Scheme 5

m/z	I, %	m/z	I, %	m/z	I, %	m/z	I, %
331	100	298	2.2	268	2.0	210	12
316	7.7	296	2.0	260	1.7	208	1.4
314	10	288	1.9	256	4.6	206	1.1
313	5.5	286	1.8	255	5.4	197	12
303	2.5	284	3.8	229	2.8	176	3.4
302	4.2	273	2.1	228	3.0	164	15
300	5.5	272	2.7	227	3.3	162	9.0

The spectrum of dihydrodeoxynominine (scheme 4) exhibits many features in common with the spectrum of nominine (XI), thanks primarily to the presence of the peak of an ion with m/z 146 ($C_{10}H_{12}N$), second with respect to intensity, and an ion with m/z 160 ($C_{11}H_{14}N$). Other parallels are shown by the appearance of weak peaks of ions with m/z 226, 214, 212, and 174. Ring A of compound (XXIV) decomposes by the elimination of C_2H_4 and $\dot{C}_2H_5$, but the $(M - 43)^+$ ions, in contrast to the spectra of other compounds, correspond to the splitting out not of C_3H_7 but of C_2H_5N (m/z 240), this process taking place in one stage.

Of the fundamentally important directions of breakdown uniting talatisine with hydrotalatisine (XXV), the spectrum of the latter retains the ions with m/z 162 and 164 arising through the cleavage of bonds of ring B. Here, ions with m/z 208, 206, and 176 have third-degree importance, but in return, the peaks with ions with m/z 210 ($C_{16}H_{18}$) and 197 ($C_{15}H_{17}$) stand out by their intensities. The MD spectra are the key factors for an understanding of the processes involved in the formations of these ions, showing that one of the precursors is an ion with m/z 255 (scheme 5). In its turn, this ion arises as the result of a synchronous or successive elimination from M^+ of a water molecule and a propionaldehyde molecule at the expense of the C-15–C-17 bonds. A similar process of the splitting out of the elements of ring D is characteristic of compounds with the denudatine skeleton [18, 19].

The subsequent breakdown of the fragments with m/z 225 with the elimination of a formaldehyde molecule or a $\dot{C}H_2$–N=CH–OH radical leads to stable fragments with m/z 210 and 197. The pathway for the formation of the ion with m/z 210 also has an alternative nature: the

splitting out of (H_2O + $HCONH_2$) from M^+ gives a fragment with the composition $C_{19}H_{24}O$, m/z 268, which then loses a propionaldehyde molecule.

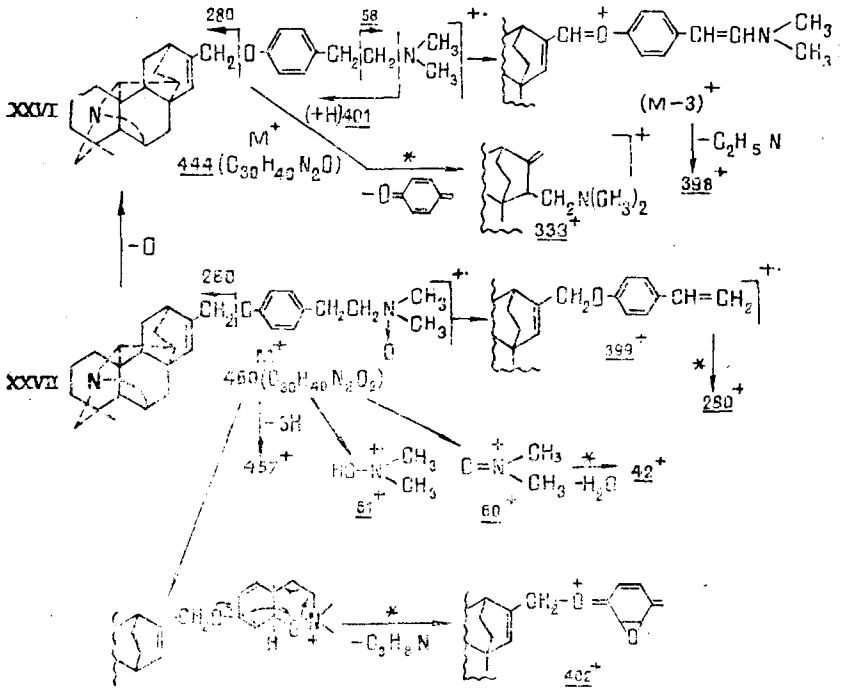
In spite of formal considerations, the ion with m/z 228 of hydrotalatisine is not nitrogen-free by analogy with the m/z 226 ions of talatisine. In addition to the $C_{16}H_{20}O$ component there are $C_{16}H_{22}N$ and $C_{15}H_{18}NO$ ions. Their formation is reflected in scheme 5 and agrees with the MD spectrum of the m/z 228 ion. Recently, two new alkaloids have been isolated from the epigeal part of Aconitum zeravschanicum: zeraconine (XXVI) and its N-oxide (XXVII) [16].

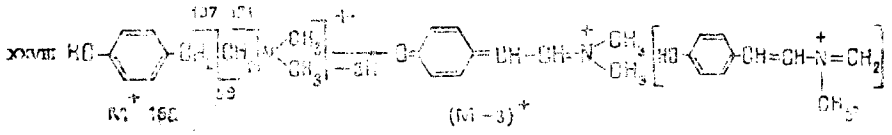
Each of the mass spectra of these compounds contains three clearly separated regions: a region of the M^+ ions and of ions formed by the splitting out of small particles; a region of the fragments of the hetisine nucleus; and a region of fragments of the phenethylamine moiety. In the center part of the spectrum, ions with m/z 146, 160, and 174, which are characteristic for hetisine bases, are weakly expressed. This is obviously due to the fact that the main fragment of the hetisine series with m/z 280 ($C_{20}H_{26}N$) was formed by the localization of the charge at the point of cleavage of the CH_2—O bond stabilized by the C_{15}=C_{16} bond.

The breakdown of the ions with m/z 280 gives a number of uncharacteristic fragments through the elimination of radicals and molecules of hydrocarbon composition (m/z 264, 252-250, 238-236, 224, 210, etc.).

The molecular ion of zeraconine is fairly stable, but for (XXVII) it is very weak, which is typical for N-oxides [20]. Characteristic for both substances is the process of forming the $(M - 3)^+$ ions. In the spectrum of the N-oxide, the peak of this ion is several times stronger than that of the molecular ion. As has been found, a similar process takes place in the breakdown of hordenine (XXVIII), in the spectrum of which the peaks of the $(M - 1)^+$ and $(M - 3)^+$ ions are fairly strong. However, the structures of the $(M - 3)^+$ ions of (XXVI), (XXVII), and (XXVIII) must be represented differently (scheme 6). The ion with m/z 398 from zeraconine must also be formed by an alternative pathway — by the elimination of 3 H from the ions with m/z 401. The breakdown of the phenethylamine substituent in zeraconine and its N-oxide has individual features. In the case of (XXVI), elimination of a H_2C=N—CH_3 molecule takes place either from M^+ or from the $(M - 3)^+$ ion with the formation of ions having m/z 401 and 398. The molecular ion of the N-oxide (XXVII) undergoes a Cope degradation in which a pair of ions with m/z 399 and 61 arise. Judging from the MD spectrum, the first of these two ions is the main precursor of the ion with m/z 280.

Zeraconine and its N-oxide





Scheme 6

XXVI

m/z	I, %	m/z	I, %
444	15	250	0,2
441	0,07	238	0,3
429	0,4	237	0,2
401	0,4	236	0,3
398	0,2	224	0,4
338	0,5	210	0,5
280	16	174	1,4
264	0,4	160	1,0
252	0,3	146	1,1
251	0,3	58	100

XXVII

m/z	I, %	m/z	I, %	m/z	I, %
460	0,005	338	0,1	236	0,3
459	0,02	296	0,1	224	0,3
458	0,04	280	100	210	0,4
457	0,02	264	0,4	174	0,6
444	1,8	252	0,3	160	0,6
429	0,1	251	0,3	146	0,9
402	0,7	250	0,2	61	75
399	11	239	0,3	60	57
387	0,1	238	0,3	58	1,0
339	0,1	237	0,2	42	50

XXVIII

m/z	I, %	m/z	I, %
165	1,9	107	2,2
164	0,6	91	1,4
162	0,6	77	2,6
121	2,4	58	100
120	1,4	46	2,6
		42	2,9

The ion with m/z 402 has the composition $(M - C_3H_8N)^+$, i.e., it retains both oxygen atoms of the (XXVII) molecule. It has the M^+ ion as its only precursor. We represent the mechanism of this process within the framework of an oxygen rearrangement taking place through a 6-membered transition state by analogy with the rearrangement investigated by Chizhov's group [21].

The simple cleavage of the CH_2—N bond in the M^+ ion of the N-oxide leads to a dimethylnitroso ion with m/z 60. Together with an ion having m/z 61, this ion is the main qualitative characteristic of the spectrum of (XXVII).

The molecular ion of zeraconine and the corresponding ion with m/z 444 in the spectrum of the N-oxide are the parents of one more interesting rearrangement process accompanied by the ejection of a molecule of methylenecyclohexadienone and the migration of $CH_2N(CH_3)_2$ to the C-15 atom (scheme 6, the m/z 338 ion).

Experimental Conditions. MKh 1310 mass spectrometer with double focussing, SVP5 system for direct introduction of the sample, temperature of the ionization chamber 110-150°C, temperature of the heater bulb, 80-100°C, ionization voltage 50 V, collector current 40 μA. Defocussing: E, H = const., automatic scanning of the accelerating voltage from 2.0 to 4.5 kV at the rate of 0.1 kV/sec; chart speeds 5 and 10 mm/sec.

CONCLUSION

Analysis of literature material has shown that the stability of the M^+ ions of bases with the hetisine skeleton decreases considerably when an OR group is present at C-1, C-6, or C-9. The directions of fragmentation are not monotypical and depend greatly on the positions of the oxygen substituents.

A similar conclusion can be drawn from a study of the group and individual features of the breakdown of hetisine, nominine, and talatisine and their derivatives revealed with the aid of high-resolution mass spectrometry and MD spectra. An unusual property of these spectra is the formation of nitrogen-free fragments.

The mass spectra of hetisine alkaloids of a new type — zeraconine and its N-oxide — have been characterized.

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STRUCTURE OF AERUGINE FROM Pseudomonas aeruginosa

A. Zunnundzhanov, I. A. Bessonova,
N. D. Abdullaev, and D. K. Ogai

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A new optically active phenolic alkaloid with the composition $C_{10}H_{11}NO_2S$, mp 85-88°C, $[\alpha]_D$ +28° (c 1.0; chloroform) (I) has been isolated from the microorganism Pseudomonas aeruginosa (strain 590) and has been called aerugine. The action of diazomethane gave an O-methyl derivative (II). On the basis of the formation of ortho-cresol by the hydrogenolytic desulfuration reaction, a study of the IR, mass, and PMR spectra and (I) and its acetyl derivative (III), and also the ^{13}C NMR spectrum of (I), the structure of 4-hydroxymethyl-2-(o-hydroxyphenyl)-2-thiazoline has been established for aerugine. The spectral characteristics of the compounds mentioned are given.

The chromatography on a column of silica gel of the alkaloids from the culture liquid from Pseudomonas aeruginosa has given a new optically active base (I) with the composition $C_{10}H_{11}NO_2S$ (mass spectrometrically, M^+ 209), mp 85-88°C, $[\alpha]_D$ +28° (c 1.0; chloroform), which has been called aerugine. The alkaloid is readily soluble in organic solvents and in dilute aqueous solutions of acid and alkalies. It forms a crystalline hydrochloride. It crystallizes from hexane.

The alkali solubility, the green coloration with a solution of ferric chloride, and a formation of an O-methyl derivative showed that aerugine contained a phenolic hydroxy group. The IR spectrum of (I) contained absorption bands at (cm^{-1}) 3300 (OH) and 1620, 1600, 1580, and 750 (o-substituted benzene ring).

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