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FEATURES OF THE MASS SPECTRA OF HETISINE BASES WITH AN OH GROUP AT C-14

E. G. Mil'grom, Ya. V. Raskes, and I. A. Bessanova

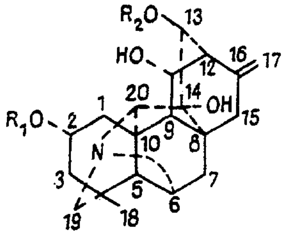
UDC 513.51+547.944/945

The EI mass spectra of five hetisine bases with an OH group at C-14 have been investigated. The main directions of fragmentation are initiated by the cleavage of the C-14—C-20 bond. With the aid of measurements of the elementary compositions of the molecular and fragmentary ions and of a comparison of the B/E linked-scanning and metastable defocusing spectra, the mechanism of the formation of the key fragments has been established and alternative methods for the production of certain ions have been revealed.

We have previously given a detailed discussion of the fragmentation of C_{20}-diterpene bases with the hetisine skeleton [1].

In recent years, a number of publications on the isolation of hetisine alkaloids with substituents in the C13—C14 chain have appeared [2, 3]. In [2], details of the overall mass spectra of 2-acetyl-14-hydroxyhetisine and of 2-isobutyryl-14-hydroxyhetisine and schemes of the fragmentation these bases are given. In the opinion of the authors concerned, the $(M - 28)^+$ ions, the peaks of which are some of the most intense in the spectra, are formed either by the ejection of CH_2N or by the splitting out of a molecule of ethylene from ring B. These processes are accompanied by the elimination of the CO molecule, giving $(M - 56)^+$ ions with the compositions $(M - C_2H_2NO)^+$ and $(M - C_3H_4O)^+$, respectively.

We had available a number of analogous bases with different substituents at C-2 and C-13, and it was therefore of interest to confirm the hypotheses put forward in [2] and also to study the influence of a hydroxy group at C-14 and the nature of the substituents at C-2 and C-13 on the nature of fragmentation under EI and to find alternative methods for the formation of ions with identical masses. For this purpose we used high-resolution mass spectrometry, metastable defocusing (MD) spectra, and B/E = const linked-scanning spectra.



I. $R_1=R_2=H$
II. $R_1=Ac$; $R_2=H$
III. $R_1=COCH_2CH_3$; $R_2=H$
IV. $R_1=COCH(CH_3)_2$; $R_2=H$
V. $R_1=COCH(CH_3)_2$; $R_2=Ac$

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TABLE 1. Mass Numbers (m/z), Relative Intensities (%), and Elementary Compositions of the Main Fragments in the Mass Spectrum of Compound (I-V)

I. 345 ($M^+, C_{20}H_{27}NO_4$;87), 330(70), 328(100), 317($C_{19}H_{27}NO_3$; 49) 316(40), 312($C_{19}H_{22}NO_3$;11), 310(7), 302($C_{18}H_{24}NO_3$;11, 300($C_{19}H_{26}NO_2$;71), 298($C_{19}H_{24}NO_2$;21) 289($C_{18}H_{27}NO_2$;41), 288(21), 282($C_{19}H_{24}NO$;8), 274(7) 272($C_{18}H_{22}NO_2$;6 272($C_{13}H_{26}NO$;12), 270(6)

II. 387($M^+, C_{22}H_{29}NO_5$;100), 372(30), 370(95), 359($C_{21}H_{29}NO_4$;56), 358(37), 354($C_{21}H_{24}NO_4$;6) 344(10), 342($C_{21}H_{28}NO_3$;70), 340($C_{21}H_{26}NO_3$;19), 331($C_{20}H_{29}NO_3$;44), 330(22), 328($C_{20}H_{26}NO_3$;52), 326(14), 314($C_{19}H_{24}NO_3$;5) 314($C_{20}H_{28}NO_2$,10) 312($C_{19}H_{22}NO_3$;25), 312($C_{20}H_{28}NO_2$;6), 310($C_{20}H_{24}NO_2$;13), 300($C_{19}H_{26}NO_2$;13), 298(7)

III. 401($M^+, C_{23}H_{31}NO_5$;83), 386(36), 384(100), 373($C_{22}H_{31}NO_4$;64), 372(42), 356($C_{22}H_{30}NO_3$;80) 356($C_{21}H_{26}NO_4$;16), 354($C_{22}H_{28}NO_3$);18), 354($C_{21}H_{24}NO_4$;3), 345($C_{21}H_{31}NO_3$;49), 344($C_{21}H_{30}NO_3$;24), 344($C_{20}H_{26}NO_4$;8), 340(9), 328($C_{20}H_{26}NO_3$;60), 328($C_{21}H_{30}NO_2$;15) 326($C_{20}H_{24}NO_3$;16), 326($C_{21}H_{28}NO_2$;4), 312($C_{19}H_{22}NO_3$;35), 312($C_{20}H_{28}NO_2$;5), 310($C_{20}H_{24}NO_2$;18), 310($C_{19}H_{20}NO_3$;6), 300($C_{19}H_{26}NO_2$;16), 298($C_{19}H_{24}NO_2$;12), 294(6), 290(5)

IV. 415(M^+, $C_{24}H_{33}NO_5$;100), 400(23). 398($C_{24}H_{32}NO_4$;84), 387($C_{23}H_{33}NO_4$;56) 386(37), 385(5), 384(4), 382(5), 372($C_{22}H_{30}NO_4$;4), 370($C_{23}H_{32}NO_3$;74), 368($C_{23}H_{30}NO_3$;19), 359($C_{22}H_{33}NO_3$;42), 358($C_{22}H_{32}NO_3$;21), 344($C_{21}H_{30}NO_3$;6) 344($C_{20}H_{26}NO_4$;4) 342($C_{22}H_{32}NO_2$;10), 342($C_{21}H_{28}NO_3$;5), 328($C_{20}H_{26}NO_3$;54). 326($C_{20}H_{24}NO_4$;16) 312($C_{19}H_{22}NO_3$;35), 310($C_{20}H_{24}NO_2$;19), 300(12), 298(7), 294(5)

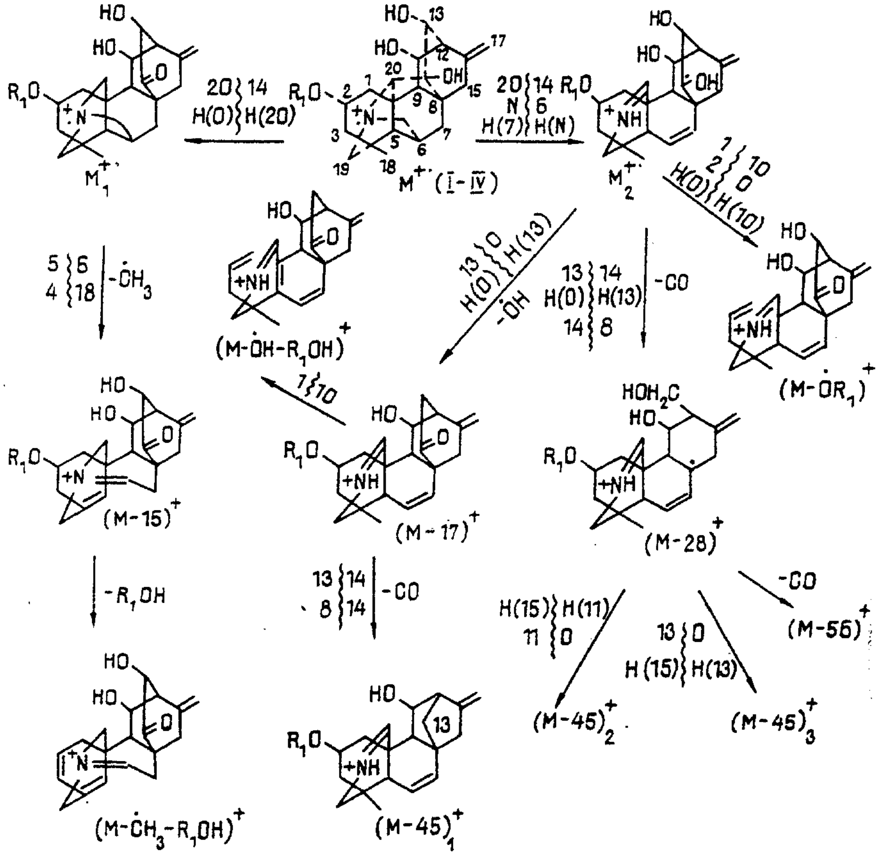
V. 457($M^+, C_{26}H_{35}NO_6$;46), 442(8), 440(6), 429($C_{25}H_{35}NO_5$;2), 428(2). 414($C_{24}H_{32}NO_5$;100) 412($C_{25}H_{34}NO_4$;2), 412($C_{24}H_{30}NO_5$;1), 398(46),386($C_{22}H_{28}NO_5$;2), 386($C_{23}H_{32}NO_4$;1), 384(1), 382(1), 370($C_{22}H_{28}NO_4$;4), 370($C_{23}H_{32}NO_3$;2), 368($C_{23}H_{30}NO_3$;5) 368($C_{22}H_{26}NO_4$;1), 354($C_{21}H_{24}NO_4$;10), 352($C_{23}H_{30}NO_2$;2), 352($C_{22}H_{26}NO_3$;1), 326($C_{20}H_{24}NO_3$;8), 310($C_{20}H_{24}NO_2$;6), 308(2), 298(2)

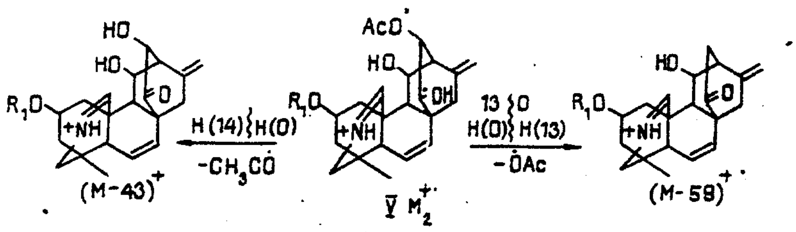
The introduction of a OH group into the C-14 position sharply diminishes the stability of the molecular ion: For hetisine (VI) it amounts to 48.1% [1], while for bases (I-V) W_{M^+} ranged from 9.6 to 15.5%. This hydroxyl activates the α-cleavage of C-20–C-14 bond, after which the molecular ion $M_1^{+\cdot}$ isomerizes into $M_2^{+\cdot}$, these two molecular ions being the sources of the main fragments in the spectra of compounds (I-V) (see scheme at top of following page).

Each of the mass spectra of bases (I-IV) (Table 1) is characterized by an intense peak of the $(M - 15)^+$ ion, which is almost completely absent in the case of hetisine. The $(M - 15)^+$ ions are formed after a series of cleavages with the elimination of the $18\text{-}CH_3$ group (see scheme). The subsequent breakdown of these ions takes place predominantly with the ejection of a R_1OH molecule (see scheme). The peaks of the corresponding ions – for (I), $(M - 33)^+$; for (II), $(M - 75)^+$; for (III), $(M - 89)^+$; and for (IV) and (V), $(M - 103)^+$ – are fairly intense (see Table 1). What has been stated above is confirmed by the elementary compositions of these ions, the presence of the maximum metastable peaks (MPs) of the $(M - 15)^+ \to (M - 15 - R_1OH)^+$ transition in the B/E spectra of the $(M - 15)^+$ ions, and the MD spectra of the $(M - 15 - R_1OH)^+$ ions (Tables 2 and 3; Fig. 1). The values of A_{MD}, i.e., the ratio of the intensities of the peaks of the metastable and parental ions in percentages [4] of the $(M - 15)^+ \to (M - 15 - R_1OH)^+$ transition are, respectively, 17, 21, 22, and 13 for compounds (II-V); for 14-hydroxyhetisine (I) this magnitude is far lower (4.1), which is probably due to alternative sources of the elimination of an H_2O molecule (see Table 2).

Another direction of the fragmentation of bases with a C-13–C-14 diol chain, leading to the main (100%) peaks (I, III) or to the second most intense peaks (II and IV) is the splitting out of a hydroxyl, the main source of which is apparently the C_{13}–OH group (see scheme).

The $(M - 17)^+$ ions are some of the precursors of the intense $(M - 45)^+$ fragments the mechanism of the formation of which we shall discuss somewhat later. Another direction of the breakdown of the $(M - 17)^+$ ions, judging from their B/E spectra, is the elimination of a R_1OH molecule (see scheme). The peaks of the corresponding ions in the overall spectra have a medium intensity. The values of A for the $(M - 17)^+ \to (M - 17 - R_1OH)^+$ transition (MD spectra) are of the same order: for (II), 2.0; for (III), 2.7; and for (IV), 2.1 (Table 2). For base (I) there is no point in calculating the value of A because of the probable occurrence of two transitions $(M - 17)^+ \to (M - 35)^+$ and $(M - 18)^+ \to (M - 35)^+$. The sequence of elimination of fragments that has been considered is not the only possibility for the formation of the $(M - 35)^+$, $(M - 77)^+$, $(M - 21)^+$, and $(M - 105)^+$ ions for compounds (I), (II), (III) and (IV and V), respectively. As can be seen from a comparison of the MD and B/E spectra, an alternative process may take place: the successive ejection of the substitu-





ent at C-2 and of a H_2O molecule. In addition to this, the measurement of the elementary compositions of the above-mentioned ions showed, in two cases, the presence of second components: In the case of (III), $C_{19}H_{20}NO_3$ (1/4), and in the case of (V), $C_{23}H_{30}NO_2$ (2/3); the predominance of this component in the case of base (V) and the change in the source of splitting out of the OH sharply alters the form of the MD spectrum of the $(M - 105)^+$ ion (see Fig. 1).

In addition to the ions already mentioned, the spectra of bases (I-IV) contain intense peaks of $(M - 28)^+$ ions. Measurements of the elementary compositions of these ions show that in this case only CO had been split out and not CH_2N and C_2H_4, as suggested in [1]. The ions under consideration are produced by the elimination of the CO molecule after the isomerization of the $M_1^{+\cdot}$ ion into $M_2^{+\cdot}$ and the cleavage of the C-13—C-14 and C-14—C-8 bonds with the migration of hydrogen from the hydroxy group at C-14 to C-8 (see scheme).

In the B/E linked-scanning spectrum of the M^+ ion of each of bases (I-IV), the peak of the metastable transition $M^+ \rightarrow (M - 28)^+$ is the maximum peak. Judging from the B/E spectra, the subsequent breakdown of the $(M - 28)^+$ ions takes place with the predominant ejection of OH or CO, giving the $(M - 45)^+$ and $(M - 56)^+$ ions, respectively.

The peaks of the $(M - 45)^+$ ions occupy one of the leading positions in the spectra of bases (I-IV). The composition of the ejected fragment, CHO_2, which corresponds to the elimination of CO and OH, and the presence in the MD spectra of the $(M - 45)^+$ ions of metastable peaks of three transitions — $M^+ \rightarrow (M - 45)^+$, $(M - 17)^+ \rightarrow (M - 45)^+$, and $(M - 28)^+ \rightarrow (M -$

TABLE 2. Values of A in the MD Spectra of Compounds (I-V)

Compound	Daughter ion						
	$(M-45)^+$			$(M-30)^+$		$(M-15-R_1OH)^+$	$(M-17-R_1OH)^+$
	parental ions						
		$(M-17)^+$	$(M-28)^+$	M^+	$(M-28)^+$	$(M-15)^+$	$(M-17)^+$
I	2,1	0,5	22	9,0	10	4.1	
II	1,9	0,9	12	6,9	5,8	17	2,0
III	1,4	0,7	23	7,3	8,1	21	2,7
IV	1,8	0,8	19	6,0	6.2	22	2,1
V	0,4	—	5,5	—	—	13	—

TABLE 3. Mass Numbers and Relative Intensities* of the Metastable Daughter Ions in the B/E Spectra of the Molecular and Fragmentary Ions of Compounds (I-V)

Compound	Parental ion	Daughter ions
I	345 (M^+)	330 (38), 328 (42), 317 (100), 316 (37), 310 (2), 300 (8), 289 (35), 274 (1), 272 (1)
	330	312 (100), 300 (12)
	328	312 (30), 310 (100), 300 (30)
	317	300 (100), 289 (33), 274 (3), 272 (2)
	300	282 (100), 272 (20)
	289	274 (22), 272 (100)
II	387 (M^+)	372 (3), 370 (3), 359 (100), 344 (3), 342 (6), 340 (2), 331 (25), 328 (28), 326 (9), 300 (5)
	372	354 (42), 342 (25), 312 (100), 310 (42)
	370	354 (75), 342 (60), 312 (75), 310 (100)
	359	344 (16), 342 (54), 331 (100), 330 (16), 314 (10), 312 (10), 310 (7), 300 (25), 298 (27)
	342	312 (37), 298 (40), 282 (100)
	331	314 (86), 272 (100)
	328	310 (100), 298 (60)
III	401 (M^+)	386 (31), 384 (28), 373 (100), 353 (8), 345 (25), 328 (20)
	386	356 (71), 312 (100)
	384	356 (77), 340 (16), 326 (16), 312 (100), 310 (50)
	373	356 (100), 345 (30), 300 (4)
	356	338 (100), 298 (50)
	345	328 (100), 316 (9)
	328	310 (100)
IV	415 (M^+)	400 (33), 398 (42), 387 (100), 372 (4), 370 (8), 359 (34), 344 (4), 342 (2), 328 (11), 326 (4)
	400	370 (10), 328 (4), 312 (100)
	398	382 (70), 370 (38), 312 (100), 310 (43)
	387	370 (43), 368 (30), 359 (100), 344 (7), 342 (10), 300 (7), 298 (13)
	359	344 (47), 342 (100), 330 (33)
	328	310 (100), 298 (42)
V	457 (M^+)	442 (8), 440 (4), 429 (12), 414 (96), 398 (100), 386 (5), 370 (5), 368 (6)
	442	414 (8), 398 (3), 354 (100)
	440	398 (12), 352 (100)
	429	414 (54), 412 (100)
	414	3 6 (9), 386 (14), 368 (10), 326 (100)
	398	368 (38), 322 (32), 326 (29), 310 (100)
	370	352 (18), 326 (22), 310 (100)

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*The maximum in the given MD spectrum was taken as 100%.

$45)^+$ – indicates the possibility of the splitting out of CO and OH not only successively but also synchronously (see Fig. 1).

The mechanism of the formation of different variants of the $(M - 45)^+$ ions is shown in the scheme. In spite of the existence of at least three probable routes for the production of these ions, in the MD spectra of the $(M - 45)^+$ ions of bases I-IV all three factors coincide: the ratio of the heights of the MPs, the positions of the maxima of all the peaks, and the values of A for the three transitions – $A_{M^+\rightarrow(M-45)^+} = 1.4\text{-}2.1$, $A_{(M-17)^+\rightarrow(M-45)^+} = 0.5\text{-}0.9$, $A_{(M-28)\rightarrow(M-45)^+} = 12\text{-}23$ (Table 2). This shows not only the common nature of the mechanisms of the formation of the $(M - 45)^+$ ions but also equal ratios between the contributions of analogous methods of obtaining these ions.

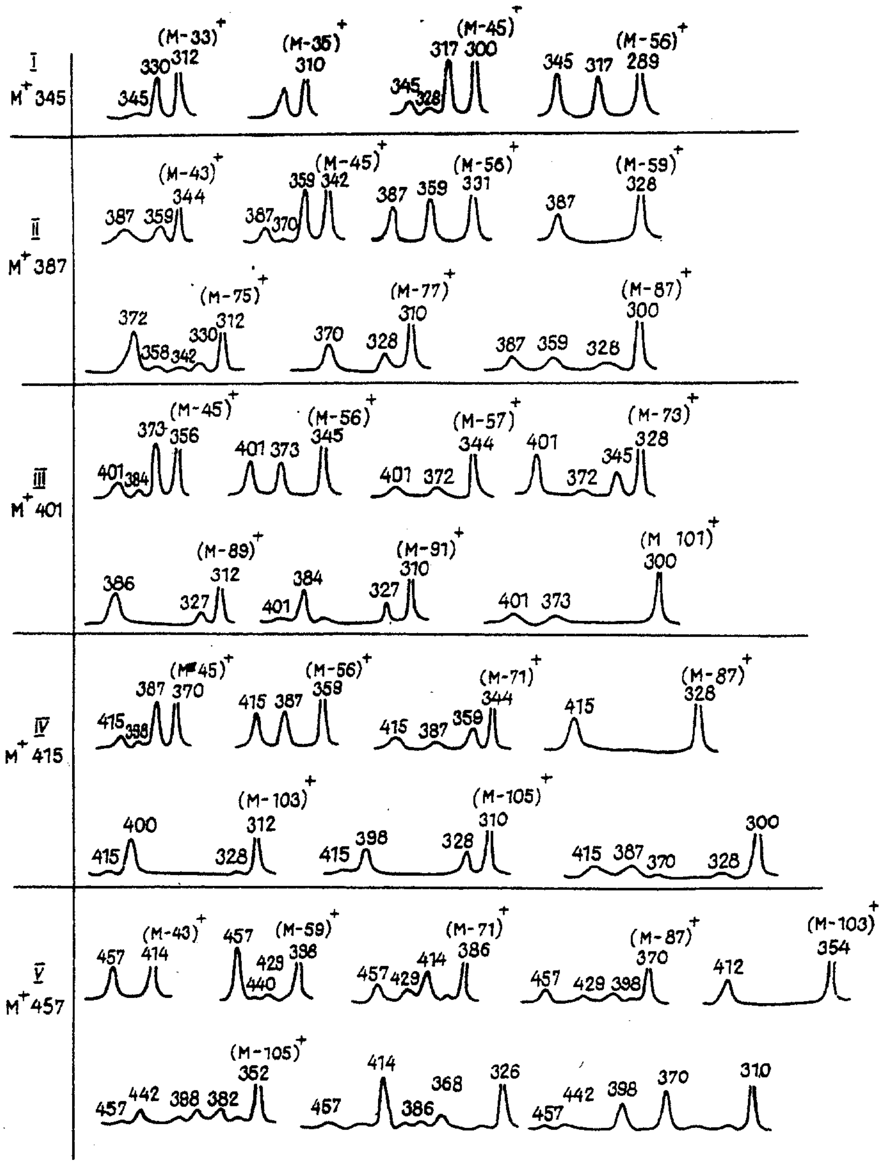

Fig. 1. MD spectra of fragmentary ions of bases (I-V).

In the B/E spectra of the $(M - 15)^+$ ions of bases (I)-(IV) there is, in each case, a metastable peak corresponding to the $(M - 15)^+ \rightarrow (M - 45)^+$ transition (Table 3), i.e., the splitting out of 45 m.u. takes place in the form of $CH_3 + CH_2O$; however, the contribution of this process is so slight that on measuring the elementary compositions of the $(M - 45)^+$ ions for bases (I), (II), and (IV) this component was not detected, and only for acoridine (III) did it amount to 1/5 (see Table 1).

The ejection of two CO molecules (see Table I and scheme) may take place either successively or synchronously. This is shown by the MPs of two transitions in the MD spectra – $M^+ \rightarrow (M - 56)^+$ and $(M - 28)^+ \rightarrow (M - 56)^+$ – and also by the presence of the MP of the $M^+ \rightarrow (M - 56)^+$ transition in the B/E spectra of the M^+ ions (see Fig. 1 and Table 3). The mechanism of the elimination of the two CO molecules is apparently the same for bases (I)-(IV), since the parameters of the MD spectra of their $(M - 56)^+$ ions, containing two MPs of equal height, coincide and the values of A of the corresponding transitions range within a narrow interval – $A_{M^+ \rightarrow (M-56)^+} = 6.9\text{-}9.0$, $A_{(M-28)^+ \rightarrow (M-56)^+} = 5.8\text{-}10$ (see Fig. 1 and Table 2). The common nature of the mechanisms for the formation of these ions is also shown by the closeness of the relative intensities of the MPs of the $M^+ \rightarrow (M - 56)^+$ transitions in the B/E spectra of the M^+ ions (see Table 3). The source of the splitting out of a C_2O_2 fragment is probably the C-13–C-14 diol chain. This is also confirmed by the complete absence of the peaks of the $(M - 56)^+$ ions in the spectrum of a base acetylated at the C-13 hydroxyl (V) (see Table 1).

In the overall spectra of the bases under consideration, in addition to the peaks of the $(M - 28)^+$ and $(M - 56)^+$ ions there are the peaks of ions differing from those mentioned above by one mass unit – $(M - 29)^+$ and $(M - 57)^+$ – the intensities of which are 1.5-2 times smaller. In the majority of cases these ions contain one hydrogen atom less than the $(M - 28)^+$ and $(M - 56)^+$ ions, i.e., the residue eliminated is CHO $(M - 29)^+$ or C_2HO_2 (CO + CHO) $(M - 57)^+$; however, in the case of acoridine (III) there is also another possibility for the formation of the $(M - 57)^+$ ions – $(M - C_3H_5O)^+$ (1/4), which is apparently due to the splitting out of the propionyl substituent R_1 (see Table 1).

The elimination of the radical R_1 also takes place in the fragmentation of bases (II), (IV), and (V). However, in the case of acoridine (II) the C_2H_3O fragment can be split off not only in the form of the acetyl substituent but also by the direct ejection of CO + CH_3. This can be well seen from the MD spectra of the $(M - 43)^+$ ions which contain two MPs of the transitions $M^+ \rightarrow (M - 43)^+$ and $(M - 28)^+ \rightarrow (M - 43)^+$ (see Fig. 1). In the case of bases (IV) and (V), the $(M - 71)^+$ ions consist of two components – $(M - C_4H_7O)^+$ and $(M - C_3H_3O_2)^+$ – the ratio between which is 2:3 in the spectrum of (IV) and 2:1 for (V) (see Table 1). The first component corresponds to the elimination of an isobutyryl radical the routes to the formation of which are different, as follows from the B/E and MD spectra: For 2-isobutyryl-14-hydroxyhetisine (IV) the route is the successive ejection of two CO molecules accompanied by the elimination of $\dot{C}H_3$ and for base F (V) the splitting out an acetyl radical and a CO in one sequence or the other (see Fig. 1 and Table 3).

The peaks of ions corresponding in mass to the elimination of the substituent $\dot{O}R_1$ in the spectra of compounds (I-IV) are some of the most intense, but only for (II) and (IV) can one speak of the ejection of $\dot{O}R_1$ as the only method for the formation of the $(M - 59)^+$ and $(M - 87)^+$ ions, respectively. This is confirmed by the results of high-resolution mass spectrometry and by the B/E and MD spectra. The loss of 59 a.m.u. (II) corresponds to the elimination of $C_2H_3O_2$, and the loss of 87 a.m.u. (IV) to a loss of $C_4H_7O_2$, in one stage, since the MD spectrum of each of these ions contains only one MP, of the $M^+ \rightarrow (M - OR_1)^+$ transition (see Table 1 and Fig. 1).

Not only the substituent at C-2 but also other hydroxy groups participate in the formation of the $(M - 17)^+$ ions from 14-hydroxyhetisine (I).

The $(M - 73)^+$ ions of acoridine (III) contain two components – $(M - C_3H_5O_2)^+$ (4/5) and $(M - C_2HO_3)^+$ (1/5) (see Table 1) – the greater of which coincides with the ejection of the $O\dot{R}_1$ radical, while the $(M - C_2HO_3)^+$ ions represent the successive ejection of two CO molecules and the hydroxyl. These processes find their reflection in the MD spectra of the $(M - 73)^+$ ions which contain the MPs of the transitions $M^+ \rightarrow (M - 73)^+$, $(M - 28)^+ \rightarrow (M - 73)^+$, and $(M - 56)^+ \rightarrow (M - 73)^+$ and in the B/E spectra of the $(M - 56)^+$ ions – the MPs of the $(M - 56)^+ \rightarrow (M - 73)^+$ transition (see Fig. 1 and Table 3).

In the fragmentation of compound (V) the peaks of the $(M - 87)^+$ ions are formed to the extent of 2/3 by the splitting out of the isobutyryloxy substituent and 1/3 by the ejection of OAc and CO; however, as follows from the MD spectrum of the $(M - 87)^+$ ions the combination of two fragments leading to ions with the same composition also takes place (see Fig. 1).

The ejection of the substituent OR_1 in the case of the bases (I-IV) may be preceded or accompanied by the splitting out of a CO molecule, giving peaks of ions of medium intensity (see Tables 1 and 3; Fig. 1).

In contrast to the fragmentation of compounds (I-IV) described above, characterized by several competing directions of breakdown leading to the formation of peaks of ions close in intensity, base F (V) exhibits well-defined selective fragmentation.

In the spectrum of this compound, in addition to the peak of the stable M^+ ion, it is possible to single out the ions $(M - 43)^+$ and $(M - 59)^+$ (see Table 1). The ion forming the maximum peak $(M - 43)^+$ is due to the splitting out of a C_2H_3O fragment. The MD spectrum of the $(M - 43)^+$ ion contains one MD transition, $M^+ \rightarrow (M - 43)^+$, i.e., the ions under discussion are formed mainly through the ejection of an acetyl radical from the C-13-OAc group of $M_2^{+\cdot}$ and the migration of hydrogen from C-14 to the oxygen atom at C-13 (see scheme). However, analysis of the B/E spectra of the $(M - 15)^+$ and $(M - 28)^+$ ions revealed another method for the formation of the $(M - 43)^+$ ions – the ejection of a CH_3 radical and a CO molecule in different sequences (see Table 3).

The main source of formation of the peak of the $(M - 59)^+$ ion (the second most intense), is also the acetoxy group at C-13 (see scheme). Nevertheless, $(M - 59)^+$ ions with different compositions can be obtained by the elimination of the fragments $CH\dot{O} + CH_2O$ and $\dot{O}H + CH_2CO$ (see Fig. 1 and Table 3).

The $(M - 43)^+$ and $(M - 59)^+$ fragments of compound (V) partially decompose, splitting out the constituent OR_1 in the form of a molecule of the acid which leads to the appearance of ions with m/z 326 and 310, respectively (see Fig. 1; Tables and 3).

Thus, the main directions of the fragmentation of bases (I-V) are determined by the presence of the OH group at C-14 and, in contrast to the hetisine alkaloids of other groups [1], the elimination of the elements of ring A, B, and C with the formation of nitrogen-free fragments is uncharacteristic. Base (V) is characterized by a high selectivity of its breakdown due to the acetoxy group at C-13.

EXPERIMENTAL

MKh 1310 mass spectrometer with double focusing, SVP 5 system for the direct introduction of the sample, temperature of the ionization chamber 140-170°C, temperature of the heating ampul 100-160°C, ionizing voltage 70 V, collector current 16 μA. For the conditions for obtaining the MD spectra, see [4], and for the B/E = const spectra, see [5].

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A NEW SYNTHESIS OF BRASSICASTEROL

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and E. V. Zhernosek

UDC 547.92

A new method has been developed for obtaining brassicasterol – the initial compound for the synthesis of the natural brassinosteroid epibrassinolide.

In 1988, Ikekawa et al. [1] isolated from broad beans Vicia faba L. the new phytohormone 24-epibrassinolide (EB) (I) belonging to the class of brassinosteroids [2]. Its synthesis as one of the closest structural analogues of brassinolide [2] has been performed previously by American authors [3] and it was later shown that with respect to its level of plant growth stimulating activity it was comparable with brassinolide. This fact, and also the relatively wide distribution in nature of Δ^{22}-sterols with a carbon skeleton corresponding to the structure of (I) [ergosterol (III), brassicasterol (IV)], which permits them to be considered as convenient starting compounds for synthesis, attracted the intense attention of researchers to EB. A subsequent comparative study of various brassinosteroids under field conditions from the point of view of their influence on crop yield showed the advantageous nature of EB and good prospects of its practical use in agriculture [5, 6].

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