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FRAGMENTATION OF THE UNSUBSTITUTED CARBOHYDRATE UNITS OF CARDENOLIDE MONOSIDES

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UDC 543.51+547.926

In the mass spectra of unsubstituted monosides of cardenolide nature are observed the M^+ peaks, and also, in each case, three characteristic processes of the fragmentation of the carbohydrate unit. The formation of the ions $AglOCH{=}OH^+$ is the most universal property of these compounds. The stability of ions of the type under consideration depends on the nature and position of attachment of the sugar residue and on the number of polar groups in the aglycone. The laws of the fragmentation of the carbohydrate unit are extended to the spectra of glycosides of other classes.

Mass spectrometry is widely used to detect new carbohydrate-containing plant compounds. In this process, the wider use of "mild" methods of ionization, with the aid of which the peaks of the molecular ions of unsubstituted glycosides are obtained with incomparably greater intensity than on the use of electron impact (EI), is of no little importance. importance.

This was first demonstrated for the case of cardenolides by Brown et al. [1], who compared the field ionization (FI) and EI spectra of the aglycones digitoxigenin and strophanthidin and their mono-, bi-, and trioside and also individual monosaccharides. Furthermore, it has been found that in the FI spectra the fragments formed by the sequenation of the carbohydrate chain are more stable.

The fragmentation of glycosides under the action of EI takes place less selectively, but the spectra obtained by this method contain the peaks of the ions arising on the cleavage of the bonds of the carbohydrate chain. This feature of the spectra is not discussed by Brown et al. [1]. Nevertheless, it permits useful conclusion to be drawn in a comparison of the spectra of glycosides with different sugar residues or with different aglycones.

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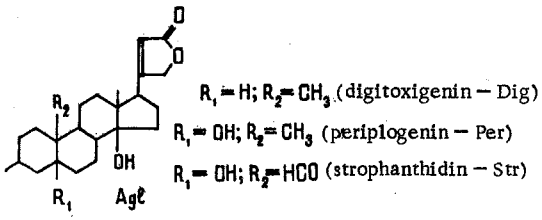
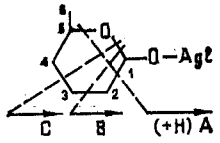
TABLE 1. Mass Numbers (m/z), Relative Intensities (I, %), the Main Fragments, and the Characteristics of the Fragments of the Carbohydrate Units in the Spectra of the Monosides (I-XII)





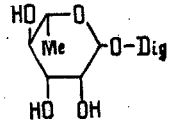
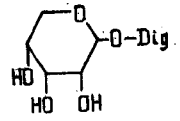
Monoside	Type of fragment	Accompanying process	m/z (I, %)	Other fragments in the spectrum
 (Rha) I	A	—	403 (21)	520, M^+ (2,8), 502 (0,3), 484 (0,3), 476 (0,1), 466 (0,1), 448 (0,05), 374 (6,5), 357 (100), 356 (80), 339 (67), 323 (2), 322 (1), 321 (1) 311 (1), 275 (6), 257 (6,5), 246 (54), 231 (10), 217 (2,5), 215 (2,5), 213 (3,5), 203 (86), 189 (7), 181 (18), 177 (16), 162 (15), 161 (9), 149 (10), 147 (16), 129 (16), 111 (15), 95 (29), 81 (20), 73 (17).
	A	$-H_2O$	385 (1,3)	
	B	—	416 (5,2)	
	C	$+H-H_2O$	429 (1,1)	
	2*—3,4—5 or 1 2, 3—4	$-H_2O$	442 (0,3)	
	1—0, 4—5	$-H_2O$	458 (0,3)	
 (Rib) II	A	—	403 (1,5)	506, M^+ (3,9), 488 (0,4), 470 (0,2), 452 (0,4), 375 (1,5), 374 (1,9), 357 (100), 356 (33), 339 (46), 323 (1,7) 322 (1 7) 321 (1), 275 (4,8), 261 (2), 255 (12), 246 (14), 231 (4,8), 213 (2,8), 203 (32), 201 (2,9), 189 (3,8), 18 (12), 135 (8,8), 121 (11), 111 (6), 109 (16), 95 (24), 81 (22), 73 (32)
	C	$+H-H_2O$	429 (0,5)	

TABLE 1 (continued)

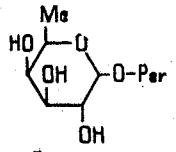
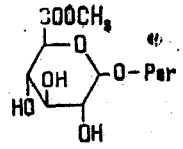
Monoside	Type of fragment	Accompanying process	m/z (I, %)	Other fragments in the spectrum
III Rha-O-Per	A	—	419 (0,6)	536, M^+ (0,5), 518 (0,4), 500 (0,6), 482 (0,3), 474 (0,2), 391 (21), 390 (3,7), 373 (50), 372 (10), 355 (100), 354 (21), 337 (21), 318 (50), 275 (9,2), 257 (3,8), 250 (5), 229 (5), 219 (7), 201 (32), 175 (29), 129 (64), 111 (38)
	A	$-H_2O$	401 (6,2)	
	B	—	432 (3,2)	
	B	$+H-H_2O$	415 (1,1)	
	B	$-H_2O$	414 (0,6)	
	B	$+H-2H_2O$	397 (1,5)	
	C	$+H-H_2O$	415 (0,6)	
	C	$-H-H_2O$	443 (0,2)	
 (Fuc) IV	A	—	419 (0,4)	536, M^+ (0,2), 518 (0,3), 500 (0,2), 482 (0,1), 474 (0,1), 391 (19), 390 (3,6), 373 (38), 355 (63), 354 (12), 337 (13), 318 (103), 275 (5,8), 257 (2,6), 219 (10), 201 (31), 175 (18), 124 (21), 111 (18), 81 (33)
	A	$-H_2O$	401 (0,9)	
	B	$+H-H_2O$	415 (0,2)	
	B	$+H-2H_2O$	397 (0,7)	
	C	$-H-H_2O$	443 (0,1)	
 (GlcUA) V	A	—	419 (0,4)	580, M^+ (0,2), 562 (0,2), 548 (0,1), 544 (0,6), 526 (0,3), 512 (0,3), 508 (0,3), 391 (1,6), 390 (1,4), 389 (0,8), 373 (18), 372 (17), 355 (56), 354 (89), 339 (15), 336 (58), 322 (6), 321 (19), 318 (100), 300 (15), 219 (17), 217 (14), 201 (56), 195 (11), 18 (10), 181 (15), 179 (17), 175 (18), 161 (14), 160 (14), 159 (22), 111 (30)
	A	$-H_2O$	401 (2,5)	
	B	—	432 (0,4)	
	B	$+H-H_2O$	415 (0,3)	
	B	$-H_2O$	414 (0,4)	
	B	$+H-2H_2O$	397 (0,7)	

TABLE 1 (continued)

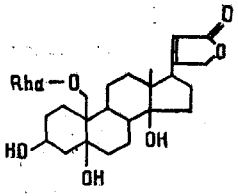
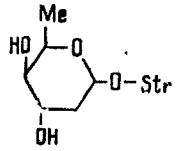
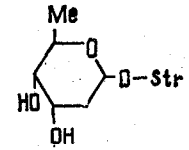
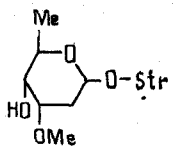
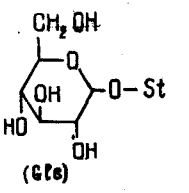
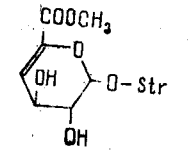
Monoside	Type of fragment	Accompanying process	m/z, (I, %)	Other fragments in the spectrum
 VI	A	—	435 (2,5)	552, M^+ (0,5), 516 (0,6), 498 (1,4), 480 (1), 389 (5),
	A	$-H_2O$	417 (7,1)	388 (9), 381 (9), 370 (43), 359 (29), 358 (57), 341 (71),
	A	$-2H_2O$	399 (5,1)	340 (100), 335 (36), 334 (46), 323 (27), 322 (50), 321 (61),
	A	$-3H_2O$	381 (9,0)	285 (11), 272 (19), 259 (13), 231 (49), 217 (35), 160 (50),
	B	$-H_2O$	430 (0,8)	147 (50), 129 (72), 110 (57), 91 (93)
	B	$-2H_2O$	412 (1,0)	
	C	$+H-2H_2O$	443 (0,7)	
VII	A	—	433 (0,7)	570, M^+ (0,6), 532 (0,1), 514 (0,07), 486 (0,8), 468 (0,6),
	A	$-H_2O$	415 (0,9)	405 (2,3), 404 (0,6), 388 (1,5), 387 (4,1), 384 (3,1), 369 (17),
Rha-O-Str	A	$-2H_2O$	397 (1,2)	368 (7), 359 (8,2), 358 (13), 340 (100), 323 (36), 322 (72),
	B	—	446 (0,3)	307 (9,1), 215 (9), 212 (13), 197 (16), 195 (10), 187 (16),
	C	$+H-H_2O$	459 (0,25)	161 (27), 160 (37), 147 (14), 145 (22), 111 (17), 91 (28), 85 (45)
 (Rsi) VIII	A	—	433 (0,02)	534, M^+ (0,02), 516 (0,03), 498 (0,04), 483 (0,1), 470 (0,1),
	A	$-H_2O$	415 (0,1)	452 (0,2), 405 (0,6), 404 (0,6), 388 (0,8), 387 (0,9), 386 (1,6),
	B	$+H$	431 (0,2)	376 (0,9), 369 (3,1), 368 (5,6), 358 (44), 340 (100), 322 (15),
	B	$+H-H_2O$	413 (0,1)	321 (11), 215 (30), 212 (11), 187 (72), 164 (50), 161 (63),
	B	$+H-2H_2O$	395 (0,2)	160 (98), 133 (72), 131 (94), 113 (95), 111 (53), 95 (72)
	C	$-H$	459 (0,05)	
	C	$+H-CO$	433 (0,02)	
	C	$+H-CO-H_2O$	415 (0,1)	

TABLE 1 (continued)

Monoside	Type of fragment	Accompanying process	m/z (I, %)	Other fragments in the spectrum
 (Dgx) IX	A	—	433 (0,05)	534, M^+ (0,1), 516 (0,06), 498 (0,04), 488 (0,07), 470 (0,1), 452 (0,1), 405 (1,1), 404 (0,9), 388 (1), 387 (1,7), 386 (1,7), 376 (0,9), 372 (1,2), 369 (3,7), 368 (4,4), 358 (46), 340 (100), 322 (11), 321 (7,3), 215 (18), 187 (44), 161 (34), 160 (74), 133 (31), 131 (48), 111 (20), 95 (23), 91 (22)
	B	+H	431 (1,0)	
	B	$+H-H_2O$	413 (0,4)	
	B	$+H-2H_2O$	395 (0,5)	
	C	—H	459 (0,05)	
	C	+H—CO	433 (0,05)	
 (Cym) X	A	—	433 (0,3)	548, M^+ (0,04), 530 (0,1), 502 (0,3), 484 (0,3), 470 (0,3), 452 (0,2), 404 (2,2), 401 (1,8), 388 (4), 387 (3), 386 (3), 385 (4), 376 (8), 370 (5,5), 369 (17), 368 (7), 359 (8,2), 358 (13), 351 (10), 340 (100), 323 (36), 322 (72), 321 (15), 307 (9), 215 (9), 212 (13), 197 (15), 195 (10), 187 (15), 161 (12), 160 (7), 145 (71), 113 (65), 111 (7), 95 (10), 87 (25)
	A	$-H_2O$	415 (4,0)	
	A	$-2H_2O$	397 (0,8)	
	A	$-CH_3OH$	401 (3,0)	
	B	+H	431 (3,0)	
	B	$+H-H_2O$	413 (1,3)	
	B	$+H-2H_2O$	395 (1,2)	
	B	—	447 (0,25)	
		$CH_3\overset{+}{O}=CHO-Agl$		
 (Glc) XI	A	—	433 (0,6)	566, M^+ (0,1), 548 (0,2), 530 (0,2), 502 (0,6), 501 (0,3), 484 (0,2), 405 (1,5), 404 (2,2), 387 (5), 386 (5,5), 369 (10), 368 (10), 358 (19), 340 (100), 339 (35), 323 (35), 322 (60), 321 (30), 215 (35), 202 (30), 187 (50), 161 (40), 160 (60), 146 (50), 145 (50), 133 (50), 131 (50), 111 (40), 91 (60)
	A	$-H_2O$	415 (0,3)	
	A	$-2H_2O$	397 (0,3)	
	C	$-H_2O$	458 (0,25)	
 XII	A	$-H_2O$	415 (0,3)	576, M^+ (0,05) 558 (0,05), 540 (0,1), 522 (0,1), 512 (0,7) 504 (0,1), 494 (0,6), 476 (0,7), 384 (3), 372 (3), 368 (8), 358 (11), 354 (14), 340 (87), 322 (100), 307 (12), 281 (8), 268 (7) 233 (8), 231 (10), 215 (15), 212 (22), 203 (10), 201 (8), 195 (24), 193 (20), 187 (33), 185 (33), 170 (48), 161 (30), 160 (52), 154 (57), 146 (35), 145 (39), 122 (93), 111 (40), 95 (98)
	A	$-2H_2O$	397 (0,6)	
	B	—	446 (0,2)	
	B	$-H_2O$	428 (0,2)	
	B	— CO	418 (0,3)	
	B	— HCO	417 (0,4)	
	B	$-H_2O-CO$	400 (1,0)	
	B	$-H_2O-HCO$	399 (1,1)	

*Cleavage of a bond between atoms of the pyranose ring.

We had available a set of natural and semisynthetic [2] cardiac monoglycosides the study of the mass spectra of which has enabled us: to determine general rules of the fragmentation of the sugar moiety of the molecule; to establish the influence of the structure of a pyranose ring and the position of its attachment on the nature of fragmentation; to evaluate the real dependence of these processes on the structure of the aglycone; and to elucidate in some measure the applicability of the laws found to the spectra of glycosides with aglycones of other classes. On the practical level, the aim has been followed of determining identifying features of the mass spectra characteristic of unetherified glycosides.

Table 1 gives the formulas of the majority of monosides studied (I-XII) and characteristics of the fragmentation of their carbohydrate units, and also a list of the most important fragments.

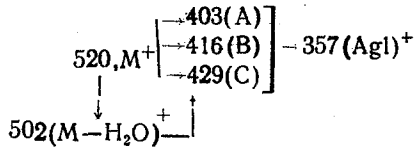
The spectrum of each one of the compounds included in Table 1 has the peak of the molecular ion (from 0.02 to 3.9% rel.), and it is possible to trace a tendency to a fall in its intensity as the degree of oxidation of the aglycones increases. It was found that the presence of M^+ serves as a necessary, but not always sufficient, condition for the appearance of the fragmentary ions considered in the present paper produced by the cleavage of bonds in the pyranose rings. For example, there are no ions of this type in the spectrum of strophanthidin 5β-rhamnoside (XIII), although the M^+ ion is present here. The spectra of the riboside (XIV) and of the methyl esters of the 3β-glucosiduronic acid (XV) and the galactosiduronic acid (XVI) of strophanthidin show the absence of both these and other ions.

Three main methods for the fragmentation of the carbohydrate unit (A, B, and C) are shown schematically in Table 1.

The most universal type of ions are those formed by route A [AglOCH=O$^+$H], which appear in all the spectra included in Table 1. In all cases, this includes ions that have not additionally lost water molecules. Fragments of this type with migration of hydrogen in the opposite direction have been detected in the spectra of permethylates of disaccharides [3] and, among natural glycosides, in permethylates of spirostanol tetraosides [4], but as secondary fragmentation pathways. The formation of ions B is characteristic of the peracetates of oligosides of certain classes. Thus, the breakage of the C_1-O and C_2-C_3 bonds of the terminal carbohydrate units with the additional loss of a molecule of ketene from C_2-OAc is observed in the spectra of the peracetates of dioscin and spirostanol triosides related to it [5]. (By checking unsubstituted dioscin, we established that it forms an ion $(M-104)^+$ of type B, like the rhamnosides (I), (III), and (VII).) Fragments similar in relation to the positions of cleavage of the bonds of the pyranose ring have been detected in the spectra of the permethylates of oleanolic acid biosides [6] and of the permethylates of spirostanol tetraosides [4], but there are no similar ions in the spectra of permethylates of disaccharides.

Of the three types of ions, the C ions are the least characteristic and are detected in the spectra of the compounds most stable to EI. Such fragmentation processes have not been revealed in the group of carbohydrate-containing substances given above.

Using evomonoside (I) as an example, by the method of metastable defocusing (MD) we have determined the basic methods for the appearance and disappearance of the ions A, B, and C:



The spectra of the rhamnosides (I), (III), (VI), and (VII) each contains fragments of all three types, and, as a rule, their contribution exceeds the analogous magnitudes for other glycosides of the given aglycone (apart from cymarin (X)). A comparison of the stereomeric monosides (III) and (IV), the molecules of which contain a 6-deoxysugar residue also point in favor of the rhamnoside (III), the superiority in the intensities of the peaks being distributed over all three types of ions.

Among the monosides, the most stable are the ribosides and the methyl esters of the glycosiduronic acids. Thus, in the spectra of the corresponding glycosides of strophanthidin there are no ions with masses higher than Agl−H. The spectrum of digitoxigenin riboside (II) does not contain ions of the B types, and the intensities of the A and C ions are far less than for evomonoside (I). Ions of type C are absent from the spectra of methyl derivatives of periplogenin glucosiduronic acid (V).

A number of distinguishing features is characteristic of the spectra of the strophanthidin 2,6-dideoxyhexosides (VIII-X). Here, as a rule, the precursors of the B series of ions are the fragments B + H. In con-

trast to the majority of glycosides with a OH group in position 2 of the pyranose ring, the C ions in the spectrum of corchoroside (VII) and erysimin (IX) are formed with the migration of hydrogen into the neutral fragment. In these spectra, the ions with m/z 433 are doublets (1:1). The composition of one component corresponds to the A ions and that of the other to the C + H ions that have lost the CO molecule, probably at the expense of the aldehyde group at C_{10} of the aglycone.

A distinguishing feature of the spectrum of cymarin is the presence of the peak of an ion with m/z 477 having the formula $Agl-O-(C_2H_4O)$. It is most likely that this fragment is formed by the cleavage of the C_1-O bond, the migration of OCH_3 to C_1 from C_3 and the subsequent cleavage of the C_1-C_2 bond, which is characteristic for the permethylates of oligosaccharides [7].

Possible analogs of this ion (m/z 417) are present in the spectra of somalin (digitoxigenin + cymarose [8, 9]) and neriifolin (digitoxigenin + thevetose [1]).

In contrast to the methyl derivatives of the glycosiduronic acids (XIV) and (XV), the spectrum of compound (XII) with a modified sugar residue, contains the peaks of M^+ and of the ions $(A-H_2O)^+$ and $(A-2H_2O)^+$. The presence of a $\Delta^{4'}$-bond probably favors the occurrence of the breakdown of the pyranose ring by a retrodiene mechanism, which leads to a considerable increase in the contribution of the ions of series B (see Table 1).

A comparison of the spectra of the monosides with identical sugar residues attached to one and the same atom of the steroid skeleton – for example, the rhamnosides (I), (III), and (VII) – shows that a rise in the number of oxygen functions in the aglycone leads to a decrease in the total intensity of the peaks of fragments A, B, and C. This observation is in harmony with the relative stabilities of the molecular and fragmentary ions in the spectra of the corresponding aglycones: digitoxigenin, periplogenin, and strophanthidin [11].

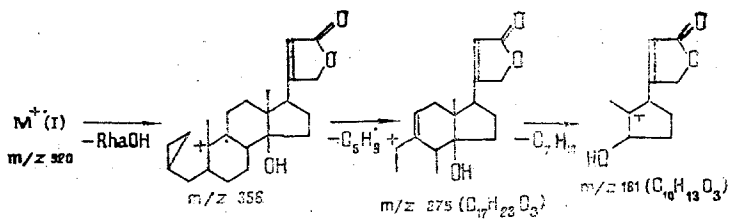
The greater stability to EI of the rhamnosides of digitoxigenin (I) and periplogenin (III) is shown in the appearance in their spectra of two additional processes for the fragmentation of the carbohydrate unit. The ions with m/z 458 and 442 from (I) have the compositions $(M-C_2H_6O_2)^+$ and $(M-C_2H_6O_3)^+$. The probable ways in which they arise are given in Table 1. In the spectrum of periplogenin rhamnoside (III) the corresponding peaks of ions with m/z 474 and 458 are present but they are weaker.

A substantial influence on the contribution of the A, B, and C ions is exerted by the nature of the OH group of the aglycone through which the carbohydrate unit is attached. In the case where the glycosidic bond is formed with the participation of a primary hydroxyl (strophanthidol 19-rhamnoside (VI)), the peaks of these ions are considerably stronger than for the 3β-rhamnoside (VII) and even (III). In its turn, strophanthidin 3β-rhamnoside (VII) is more stable than the 5β-rhamnoside of the same aglycone.

The carbohydrate unit of a monoside also affects the fragmentation of the aglycone moiety. This influence is not limited to increasing the contribution of the even-electron fragments $AglOH_2^+$ and Agl^+ that are usual for the compounds of this type and the products of their subsequent breakdown with the loss of the neutral fragments H_2O, CO, and CH_2O.

In the spectrum of each of the digitoxin and periplogenin glycosides (I-V) there is the peak of an ion of medium intensity with m/z 275 having the composition $C_{17}H_{23}O_3$. The MD spectrum of this ion in the case of compounds (I) and (II) shows as precursor an ion with m/z 356 $(Agl-H)^+$. The composition of the eliminated fragment of 81 a.m.u. is C_6H_9. The coincidence of the mass numbers of the daughter ions in the glycosides of digitoxigenin and of periplogenin indicate the detachment of the C_1-C_6 chain from the $(Agl-H)^+$ ion. Thus, the ions with m/z 275 are related by their origin to the ions with m/z 272 of the 8,19-epoxycardenolides [12].

It was found by the MD method that the ion with m/z 275 is, in its turn, the precursor of an ion with m/z 181 formed by the cleavage of the C_8-C_{14} and $C_{12}-C_{13}$ bonds. The whole process can be illustrated schematically as:



Even greater similarity to the epoxycardenolides in fragmentation was detected in the spectrum of stro-

TABLE 2. Ions of Types A, B, and C in the Mass Spectra of Monosides of Various Classes

Name of the compound (class of aglycone)	Chemical name	Literature	M+ (I, %)	m/z of the 100% peak	A		B		C	
					m/z (I, %)	APs*	m/z (I, %)	APs*	m/z (I, %)	APs*
XVII. Skimmin (coumarin)	Umbelliferone 7-O-β-D-glucopyranoside	13	324 (0,2)	162	191 (1)	—	204 (0,8) (205 (1,8)	— +H	217 (0,?)	+H—H_2O
XVIII. Scopolin (coumarin)	Scopoletin 7-O-β-D-glucopyranoside	14	354 (0,05)	192	221 (0,2)	—	234 (0,5) 235 (0,4)	— +H	264 (0,2)	—
XIX. (Coumarin)	Fraxetin 7-O-β-D-glucopyranoside	15	370 (0,05)	208	237 (0,3) 222 (0,4) 219 (0,5)	— $-CH_3$ $-H_2O$	250 (0,3) 251 (0,3)	— +H	280 (0,1) 262 (0,4)	— $-H_2O$
XX. Petisinine (steroid alkaloid)	Petisine 3-β-D-glucopyranoside	16	589 (7,2)	410	456 (4,7)	—	469 (0,2)	—		
XXI. Edpetiline (steroid alkaloid	Imperialine 3-β-D-glucopyranoside	17	591 (7)	112	458 (0,7)	—	471 (0,4) 453 (0,8)	— $-H_2O$		
XXII. (Cycloartane)	Cyclosiversigenin 6-O-β-D-glucopyranoside	18	652 (0,03)	143	501 (0,2)	$-H_2O$	532 (0,03) 514 (0,06)	— $-H_2O$		
XXIII. (Cycloartane)	Cycloasgenin C 3-O-β-D-xylopyranoside	19	624 (0)	474	503 (3,4)	$-H_2O$	534 (0,4) 516 (0,4)	— $-H_2O$		
XXIV. (Cycloartane)	Cyclosiversigenin 3-O-β-D-xylopyranoside	18	622 (1)	472	501 (2)	$-H_2O$				
XXV. Glycoperine (quinoline alkaloid	Haplopine 7-O-L-rhamnopyranoside	20	391 (1,4)	245	274 (0,6)	—	287 (0,9) 288 (1)	— +H	300 (0,2)	+H−H_2O

*APs – accompanying processes.

phanthidol 19-rhamnoside, where the peaks of ions of medium intensity with m/z 259, 272, and 285 are observed. This fact indicates the possible splitting out under EI of a RhaOH molecule with the formation of an 8,19-epoxy group.

In order to check the applicability of the laws of the fragmentation of a carbohydrate unit that have been found to compounds of other classes, we have included the spectra of the glycosides (XVII-XXV) having as aglycones coumarins, steroid and quinoline alkaloids, and cycloartanes (Table 2). Each of the spectra, apart from that of cycloasgenin C xylopyranoside (XXIII), contains the peak of the molecular ion. The formation of ions of type A was always recorded, but only for the cycloartanes (XXII-XXIV) were these fragments stabilized after additional loss of a molecule of water. Ions B are also characteristic of all the compounds apart from (XXIV). A feature of the fragmentation of glycosides with aromatic aglycones (XVII-XIX, XXV) is that the B + H peaks compete with the peaks of ions B in intensity. The same compounds form ions of type C.

The increased tendency of rhamnosides to undergo fragmentation of the pyranose ring is also followed in a comparison of the compounds included in Table 2 – only in the spectrum of glycoperine (XXV) are there, in addition to the ions of types A, B, and C, the ions $(M-78)^*$ and $(M-62)^*$ analogous in their origin to ions with m/z 442 and 458 in the spectrum of evomonoside (I).

Thus, it is possible to draw a practical conclusion concerning the possibility of detecting a glycosidic bond in an unknown substance when the ions $(AglOH + 29)^+$ (A) and $(AglOH + 42)^+$ (B) are present in its mass spectrum.

Experimental conditions: MKh 1310 mass spectrometer, direct introduction of the sample, temperature of the evaporator-ampul and of the ionization chamber 170-250°C, ionizing voltage 50 V, collector current 60 μA. Accuracy of the determination of mass $5 \cdot 10^{-6}$. The MD spectra were obtained as described previously [12].

SUMMARY

Three main types of fragmentation of the carbohydrate unit are observed in the mass spectrum of unsubstituted monosides of cardenolide nature. The formation of the AglOCH=OH ions is the most universal property of these compounds. The stability of the ions of the types under consideration depends on the nature and position of attachment of the sugar residue, and also on the nature of the aglycone. The laws of fragmentation of the carbohydrate unit can be extended to the spectra of glycosides of other classes.

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