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MASS SPECTRA OF POLYHYDROSYSTEROIDS OF THE STARFISH *Patiria pectinifera*

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UDC 543.51:547.925

The electron-impact fragmentation of six polyhydroxysteroids from the starfish *Patiria pectinifera*, including three glycosides, has been studied. In addition to the directions of fragmentation that are characteristic for sterols from other sources and for steroid compounds of other classes, fragments have been found that result from the unusual arrangement of hydroxy groups in the molecules of the samples investigated. Two breakdown pathways of the furanose ring have been found in the spectra of the glycosides.

In recent years a number of communications have appeared on the isolation from various species of starfish of sterols containing from five to eight hydroxy groups [1-4], and also of corresponding glycosides [5-7]. The structures of these compounds have been established mainly with the aid of ^1H and ^{13}C NMR spectroscopy. The maximum usage of mass-spectrometric information has amounted to a list of the main ions in the spectra with an indication of the nature of the fragments formed by the splitting out of the substituent at C-17 [2].

Nevertheless, on the one hand, a more profound study of the mass spectra of the polyhydroxysteroids and the glycosides would lead to the establishment of the laws of the fragmentation of these compounds with mutual positions of the OH groups uncharacteristic for substances known previously and, on the other hand, this work may have analytical value for predicting the structures of new compounds.

With this aim, we have studied the electron-impact mass spectra of six sterols from the starfish *Patiria pectinifera* [3, 4, 7] – three polyols and three glycosides, including one sulfate, namely: 5α-cholestane-3β,6α,8β,16β,26-hexaol (I), 5α-cholestane-3β,6α,7α,8β,15α,16β,26-heptaol (II), 5α-cholestane-3β,4β,6α,7α,8β,15α,16β,26-octoal (III), which has also been isolated from another species of Pacific Ocean starfish [2], and 24ξ-(3'-O-methyl-α-L-arabinofuranosyloxy)-5α-cholestane-3β,6α,8β,15α-tetraol (IV) and its 5'-O-sulfate (V), and 29-(α-L-arabinofuranosyloxy)-5α-stigmastane-3β,6α,8β,15α,16β-pentaol (VI). The formulas of compounds (I)-(VI) with indications of the main fragmentation pathways of the skeleton, confirmed by the results of a determination of the elementary compositions of the ions and by the mass numbers and relative intensities of all the main ions are given in Table 1.

The spectra of the hexaol (I) and of the pentaol (II) contained peaks of the molecular ions with low intensities, and the spectra of the octaol (III) and the arabinoside (VI) showed peaks of the $(M - H_2O)^+$ ions. The fragment of the spectrum of the other glycoside (IV) with the highest mass number corresponds to the $(M - 2H_2O)^+$ ion. The sulfate (V) possessed a volatility no smaller than that of its desulfated derivative (IV) but, nevertheless, it underwent thermal degradation in the inlet system and gave the peak of the $(M - NaHSO_4 - 4H_2O)^+$ ion. We may mention immediately that the only direct proof of the presence

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek, SSR, Tashkent. Pacific Ocean Institute of Bioogranic Chemistry, Far Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 361-367, May-June, 1985. Original article submitted May 23, 1984.

0009-3130/85/2103-0337$09.50

TABLE 1. Mass Numbers, Relative Intensities (%), and Origins of the Main Ions in the Mass Spectra of Compounds (I-VI).

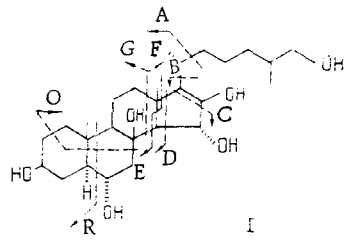
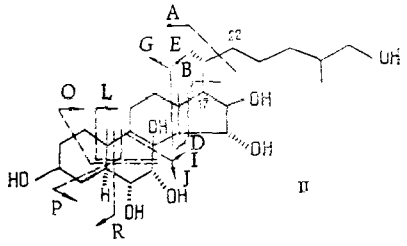
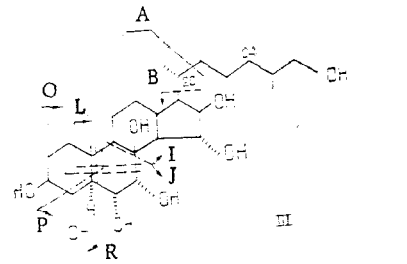
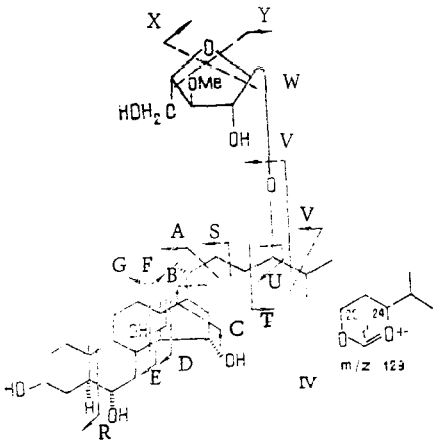
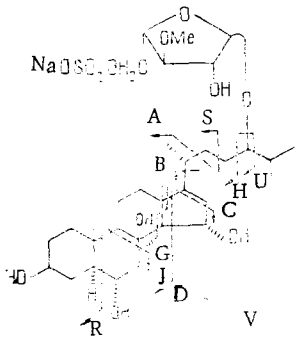
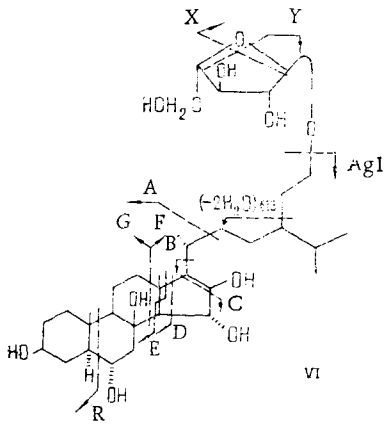
 I	468 (M^+; 0,4), 450 (14), 435 (4), 432 (12), 417 (10), 414 (12), 399 (8), 396 (5), 386 ($M-3H_2O-CO$, 3), 368 (386—H_2O, 3), 352 (П—H, 4), 331 (A—$2H_2O$, 13), 321 (B—H_2O, 16), 313 (A—$3H_2O$,6), 304 (B + H—$2H_2O$, 12), 303 (B—$2H_2O$, 27), 285 (B—$3H_2O$, 20), 279 (C+H—H_2O, 7), 278 (C—H_2O, 7), 267 (B—$4H_2O$, 12), 251 (E—2H, 14), 249 (D+H—H_2O, 12), 225 (F+H—H_2O, 45), 225 (G—H, 18), 207 (34), 95 (R+H—H_2O, 100)
 II	434 (M^+; 0,4), 466 (9), 448 (85), 433(12), 430 (55), 415 (22), 412 (41), 401 ($M-3H_2O-HCO$, 10), 397 (13), 384 ($M-4H_2O-CO$, 4), 366 (P—$2H_2O$+3H, 10), 365 (K_n—H_2O, 5), 363 (K_n—2H—H_2O, 18), 352 (O—H, 10), 347 (A—$2H_2O$, 14), 339 (L, 15), 338 (L—H, 18), 337 (L—2H, 8), 337 (B—H_2O, 8), 329 (A—$3H_2O$, 33), 321 (L—H_2O, 14), 320 (L—H—H_2O, 15), 320 (B+H—$2H_2O$, 15), 319 (L—2H—H_2O, 9), 319 (B—$2H_2O$, 18), 312 (I, 10), 312 (A—H—$4H_2O$, 9), 302 (B+H—$3H_2O$, 33), 301 (B—$3H_2O$, 46), 293 (I—H—H_2O, 98), 283 (B—$4H_2O$, 27), 275 (I—H—$2H_2O$, 35), 247 (D+H—$2H_2O$, 35), 225 (F+H—H_2O, 20), 223 (G—H—H_2O, 20), 207 (23), 154 (J—H_2O, 58), 136 (J—$2H_2O$, 73), 95 (R+H—H_2O, 100)
 III	Mol. wt. 500 482 (35), 467 (6), 465 (26), 464 (15), 447 (17), 446 (21), 431 (11), 428 (17), 417 ($M-3H_2O-HCO$, 5), 413 (10), 410 (10), 400 ($M-4H_2O-CO$, 7), 365 (K_n—H_2O, 3), 364 (P—$3H_2O$+3H, 6), 363 (K_n—2H—H_2O, 4), 363 (A—$2H_2O$, 4), 353 (O, 4), 352 (O—H, 8), 347 (A+2H—$3H_2O$, 7), 345 (A—$3H_2O$, 8), 345 (K_n—2H—$2H_2O$, 5), 339 (L, 4), 337 (L—2H, 3), 337 (B—2H—$2H_2O$, 3), 336 (B+H—$2H_2O$, 8), 335 (B—$2H_2O$, 10), 317 (B—$3H_2O$, 30), 315 (B—2H—$3H_2O$, 24), 299 (B—$4H_2O$, 28), 293 (I—H—H_2O, 26), 281 (B—$5H_2O$, 19), 263 (B—$6H_2O$, 34), 152 (J—$2H_2O$, 80), 129 (R+H, 100)
 IV	Mol. wt. 598 562 ($M-2H_2O$; 0.3), 544 (0.4), 537 (V—H_2O, 8), 531 (M—$2H_2O$—CH_3O; 0,9), 519 (V—$2H_2O$; 0,8), 519 (Y—H—H_2O; 0,4), 501 (V—$3H_2O$; 1,3), 479 (X—H; 3.5), 463 (X+H—H_2O, 31), 445 (463—H_2O, 29), 434 (Agl-OH—H_2O, 9), 427 (463—$2H_2O$, 50), 417 (Agl—H_2O, 67), 407 (W—H, 8), 399 (417—H_2O, 100), 391 (U—H, 77), 381 (417—$2H_2O$, 92), 373 (391—H_2O, 68), 363 (417—$3H_2O$, 19), 355 (391—$2H_2O$, 90), 347 (S—H_2O, 8), 337 (391—$3H_2O$, 34), 333 (A—H_2O, 8), 332 (A—H—H_2O, 7), 315 (K_n—AraOH—H_2O, 3), 315 (A—$2H_2O$, 7), 305 (333—CO, 6), 305 (B—H_2O, 17), 303 (B—2H—H_2O, 17), 287 (333—CO—H_2O, 7), 287 (B—$2H_2O$, 44), 285 (303—H_2O, 16), 277 (C—H—H_2O, 35), 269 (287—H_2O, 56), 251 (269—H_2O, 16), 251 (E—2H, 17), 249 (D+H—H_2O, 30), 225 (G—H, 60), 191 (F+H—H_2O—AraOH, 65), 183 (T—$2H_2O$, 42), 175 ($C_{13}H_{19}$+$C_{12}H_{15}O$, 64), 173 ($C_{13}H_{17}$+$C_{12}H_{13}O$,48), 159 (53), 147 (68), 129 (55), 109 (C_8H_{13}+C_7H_9O, 99), 97 (C_7H_{13}+C_6H_9O, 85), 95 (R+H—H_2O, 81)

TABLE 1 (continued)

 V	Mol. wt. 700 508 (M—$NaHSO_4$—$4H_2O$, 1), 490 (508—H_2O, 1), 476 (508—CH_3OH, 7), 458 (476—H_2O, 11), 443 (5), 440 (5), 398 (AgI-OH—$3H_2O$, 7), 380 (398—H_2O, 16), 362 (51), 347 (40), 319 (U—H—$4H_2O$, 5), 308 (H+H—$4H_2O$, 5), 305 (H—2H—$4H_2O$, 3), 293 (S—$4H_2O$, 6), 279 (A—$4H_2O$, 17), 277 (A—2H—$4H_2O$, 25), 269 (B—$3H_2O$, 17), 251 (B—$4H_2O$, 74), 249 (B—2H—$4H_2O$, 24), 236 ($C_{16}H_{28}O$, 12), 236 (251—CH_3, 12), 225 (C+H—$4H_2O$, 11), 209 (D—3H—$3H_2O$, 27), 197 (E—2H—$3H_2O$, 25), 157 (J+H, 18), 129 ($C_7H_{13}O_2$,35), 111 (61), 109 (60) 97 (100), 95 (R+H—H_2O, 86), 64 (SO_2, 14)
 VI	Mol. wt. 628 610 (M—H_2O; 0,3), 592 (0,4), 574 (1), 556 (1), 549 (Y—H—H_2O; 1,4), 531 (549—H_2O; 0,8), 507 (X+H—H_2O, 5), 495 (AgIO; 1,6), 489 (507—H_2O, 11), 478 (AgI-OH—H_2O, 30), 471 (507—2H_2O, 22), 463 (478—CH_3, 9), 460 (478—H_2O, 32) 453 (507—$3H_2O$, 16), 445 (463—H_2O, 16), 443 (33), 442 (478—$2H_2O$, 34), 435 (507—$4H_2O$, 8), 427 (463—$2H_2O$,19), 424 (478—$3H_2O$, 26), 415 (7), 331 (A—$2H_2O$, 22), 321 (B—H_2O, 23) 313 (A—$3H_2O$, 13), 305 (B+2H—$2H_2O$, 24), 303 (B—$2H_2O$, 37), 287 (305—H_2O, 32), 285 (B—$3H_2O$, 40), 279 (C+H—H_2O, 14), 278 (C—H_2O 11), 269 (305—$2H_2O$, 39), 267 (B—$4H_2O$, 30), 253 (F+H—AraOH, 69), 253 (E, 7), 251 (E—2H, 26), 249 (D+H—H_2O, 10), 235 (253—H_2O, 47), 225 (G—H, 40), 123 ($C_8H_{11}O+C_9H_{15}$, 75), 121 (65), 109 (78), 107 (70), 97 (70), 95 (R+H—H_2O, 100)

of the sulfo group in compound (V), as, incidently, in the spectra of the other sulfates, is the presence of an ion with m/z 64 (SO_2).

The products of the successive degradation of M^+, as far as the formation of hydrocarbon fragments, can be traced in all the spectra. The presence of α-diol and triol groupings is probably responsible for the fact that some of the oxygen substituents are eliminated in the form of the particles CO and HCO· together with the carbon atoms of the skeleton belonging to them. But these processes are characteristic of the unsturated fragments formed after the elimination of several molecules of water. The presence of vicinal hydroxyls is also responsible for a number of directions of the fragmentations of the steroid skeleton that are less pronounced in the case of sterols with a small number of OH groups.

But before we swell on these features of the spectra of (I-VI), we may note those properties which link them to the spectra of other sterols and also those of steroid compounds of other groups with substituents containing from eight to 10 carbon atoms at C-17.

The most universsal property of the spectra of these compounds is the above-mentioned cleavage of the C-17—C-20 bond (ions B), which is observed in the steroid hydrocarbons and the alcohols of the cholestene series [8, 9], and also in the phytoecdysteroids. Distinguishing features of the occurrence of this process in compounds (I-VI) consist of the fact that together with the simple cleavage of the C-17—C-20 bond there is a rearrangement of the hydrogen atoms, and in the polyols (I-III) and the glycoside (VI) migration is directed to the charged fragment, and the contribution of the corresponding ions rises with an increase in the number of OH groups in the initial molecule. For the arabinoside (IV), conversely, the migration of hydrogen takes place in the direction of the neutral fragment. Since, as a rule, the transfer of hydrogen atoms takes places to the more unsaturated part of the ion, it follows from this that in compounds (I-III and VI) the predominant dehydration of the steroid nucleus takes place first, and in the glycoside (VI) that of the carbohydrate unit.

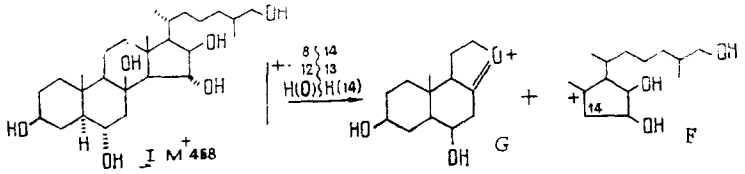
Because of the thermolability of the sulfate (V), the process under consideration takes place after the dehydration of the steroid nucleus, and the type B ion with the greatest intensity is a hydrocarbon ion with the composition $C_{19}H_{23}$.

Another important property of compounds with a cholestane or stigmastane skeleton is the cleavage of the C-20—C-22 bond (A ions). This process is intensified when a double bond is present in the side chain (stigmasterol [9], desmosterol [11]), and the constant presence of an OH group at C-22 in the phytoecdysteroids makes this type of breakdown one of the main one [10, 12]. In the spectrum of the hexaol (I), the heptaol (II), and the glycoside (VI), the peaks of the A ions had intensities only slightly less than those of the B ions. In the other spectra, the contribution of this process was less pronounced, although in the case of the sulfate (V) the peak of the A in with m/z 277 ($C_{21}H_{25}$) formed with the additional loss of a molecule of hydrogen, was the second in intensity in the central part of the spectrum.

The most typical method of fragmentation of the steroid skeleton that is characteristic not only for cholestanes but also for the majority of types of steroid compounds, is the cleavage of the C-13—C-17 and C-14—C-15 bonds of ring D [8]. In all the spectra under consideration apart from that of the octaol (III) this process was represented by peaks of medium intensity (D ions). In the polyols (I) and (II) and the glycosides (IV) and (VI) it was accompanied by the transfer of hydrogen atoms to the charged fragment (m/z 249 (I, IV, and VI) and 247 (II)), and for the sulfate (V) the stabilization of the fragment of this series began only with the elimination of three water molecules and, in addition, the aromatization of rings A-C (m/z 209).

Compounds containing no hydroxy groups at C-4 and C-7 showed appreciable peaks of the ions of the C_{15} (E) series (m/z 251 (I, IV, and VI) and 197 (V)), formed by a complex mechanism through the cleavage of the bonds of rings C and D and characteristic of all cardenolides [8] and of some ecdysteroids [12]. The same group of compounds gave ions of the C_{17} (C) series, formed by the cleavage of the C-15—C-16 and C-13—C-17 bonds. These ions are characteristic for cholestanes [8] but are absent from the spectra of the ecdysteroids.

Very important from the analytical point of view is the cleavage of the bonds of ring C: C-8—C-14 and C-12—C-13, giving the peaks of the G and F ions with medium and high intensities. The main reason for the stability of these mutually supplementing fragments is obviously the presence of a hydroxy group at C-8, the hydrogen of which participates in the rearrangement:



The role of this process was retained in the spectra of the glycosides (IV) and (VI) but decreased for different reasons in the spectra of the sulfate (V) and that of the octaol (III). So far as concerns the latter compound, this can be explained by an increase in the proportion of cleavages in rings A and B because of the presence of additional OH groups. This feature of the spectra of the heptaol (II) and the octaol (III) can be seen clearly in the table given.

A common property of compounds (I-VI) is the breakdown of ring B at the C-5—C-6 and C-9—C-10 bonds with the stabilization of the charge on the elements of rings A (R ions). In these circumstances, the octaol (II) formed an ion with m/z 129, and all the other compounds, containing no OH at C-4, gave fragments of very high intensity with m/z 95.

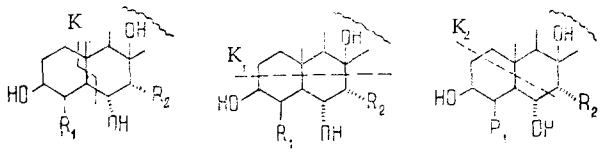
Other types of breakdown of rings A and B were uncharacteristic for glycosides (IV-VI) but presented an extremely uniform pattern in the spectra of the polyols (I-III). They consisted in the splitting out of a chain of 5-9 carbon atoms, and in determining the nature of these ions the accurate measurement of their masses and a careful comparison of the results obtained for the three compounds was of decisive importance.

The spectra of compounds (I-III) each contained the peak of an ion with m/z 352, composition $C_{21}H_{36}O_4$, with a low intensity. The only possible method for the splitting out of a chain of six carbon atoms leading to fragments with the same mass number is a cleavage of type O.

Other types of breakdown of rings A and B were due mainly to the appearance of a hydroxyl at C-7 and therefore more characteristic for the heptaol (II) and the octaol (III). Analytically the most important in these spectra is the pair of ions I and J formed by the cleavage of C-7–C-8 and C-9–C-10 bonds. The identification of the J ions is favored not only by the high intensity of their peaks but also by their even mass numbers. The lower tendency of substances without OH at C-7 (I) to undergo this type of fragmentation was confirmed by the fact that the heights of the peaks with m/z 293 and 138 corresponding to the I and J series of ions amounts to only 2 and 6% rel. in this spectrum.

With an increase in the number of OH groups in the series of compounds (I)-(III), the contribution of the $(M - nH_2O)^+$ ions increased and simultaneously the selectivity of fragmentation fell. Thus, the peaks of the L ions of the C_{20} series for the heptaol (II) had medium intensities, and in the spectrum of the octaol (III) their heights were considerably smaller.

The greatest difficulties are presented by the interpretation of the processes involved in the splitting out of a chain of five carbon atoms. Analysis of the spectra of (II) and (III) showed that there were at least two processes leading to C_{22} ions. One of them was represented by fragments with m/z 366 (II) and 364 (III). The distinguishing element – the C-4 atom – must be retained in the structures of these ions. If the less probable cleavage of part of ring C is excluded, only one variant of the formation of these fragments remains – of the O type, although for this there must be a migration of 3 H to the charged fragment. In addition to the ions mentioned, both spectra showed C_{22} ions with identical masses – (365 and 363). Below, we give three variants of the elimination of the five-carbon chain satisfying this conditions and the m/z values of the ions that should be formed



I. $R_1=R_2=H$	383	365	347	367	349	331	367	349	331
II. $R_1=H$; $R_2=OH$	399	381	363	367	349	331	383	365	347
III. $R_1=R_2=OH$	399	381	363	367	349	331	383	365	347

For comparison we also included the results of measurements of the elementary compositions of a number of peaks in the same region of the spectrum of the hexaol (I). It was possible to detect C_{22} fragments only in the case of the ions with m/z 365 and 345 of the spectrum of (I). This fact does not permit preference to be given to any one of the variants K-K_2 put forward and requires involvement of additional compounds.

Let us now pass to the features of the mass spectra of the glycosides (IV-VI) due to the presence of a furanose ring. We may note that here it is impossible to discuss the usual comparison of the spectra of the aglycone and the glycoside, since the spectra of the aglycones of compounds (IV-VI) are lacking. Consequently, some of the fragments under consideration could also arise in the corresponding aglycone as the result of the appearance of OH groups at C-24 and C-29. These ions include the V ions in the spectrum of the methylarabinoside (IV) (C-24–C-25 cleavage), the H ions in the spectrum of the sulfate (V) (C-23–C-24 cleavage), and ions with m/z 415 (VI) (C-24–C-28 cleavage).

Other features of the spectra of (IV-VI) are due both to the breakdown of the carbohydrate unit and also its complete splitting off, accompanied by the elimination of part of the side chain at C-17.

The nonsulfated furanose ring of glycosides (IV) and (VI) broke down in two directions (X and Y ions). Ions of the X type have been detected previously in the spectra of unesterified pyranosides with aglycones with different natures [13], and also in permethylates of spirostanol oligosides [14]. In the case of the metylarabinofuranoside (IV) the ions of this series were formed with the migration of hydrogen both to the charged and to the neutral fragment (m/z 463 and 479) were fairly stable. In the spectrum of glycoside (VI) the $(X - H)^+$ ions were barely detectable.

A type Y cleavage is uncharacteristic for pyranosides. In the case of the glycoside (IV) the mass number of the ions of the V and Y series coincided, but they had different elementary compositions, so that they could be distinguished.

In all three spectra, the Agl-OH (where Agl represents the aglycone residue) ions were unstable; the stability of these fragments rose after they had lost water molecules, and in the case of the sulfate (V) the ion $(Agl\text{-}OH - 3H_2O)^+$ was relatively stable. The splitting out of the furanose ring also took place in other directions, as a result of which the fragments Agl^+ or $AglO^+$ arose. The former possibly acted as precursors of the S ions (C-22–C-23 cleavage) and of the U ions (C-24–C-25 cleavage), and the latter generted ions of the W type (IV). So far as concerns the C-23–C-24 cleavage, it is less characteristic – in the case of the arabinoside (IV) we observed the T ion and in the case of the sulfate (V) the H ion.

Attention is attracted by the presence in the spectra of the 24-O-arabinosides (IV) and (V) of the strong peak of a fragment with m/z 129, composition $C_7H_{13}O_2$. We assume that it arose from the type X ions on the subsequent cleavage of the C-20–C-22 bond and the formation of a 1,3-dioxane ring by the fragment produced (see Table 1). There was no such fragment in the pectrum of the stigmastane (VI).

In the 129-95 a.m.u. region of the spectra of glycoside (IV-VI), a whole series of other high-intensity peaks appeared (Table 1) which were most probably formed by the elements of the side chain at C-17 after the elimination of the sugar residue from it.

Experimental Procedure. MKh 1310 mass spectrometer, SVP 5 system for the direct introduction of the sample, temperatures of the evaporator bulb and ionization chamber 100-150°C; collector current 60 μA; ionizing voltage 50 V. The masses of the ions were measured with an accuracy of $5 \cdot 10^{-6}$, the reference substance being perfluorokerosine.

SUMMARY

The electron-impact fragmentation of six polyhydroxysteroids from the starfish Patiria pectinifera, including three glycosides, has been studied. In addition to the directions of fragmentation that are characteristic for sterols from other sources and for steroid compounds of other classes, fragments were found that results from the unusual arrangement of the hydroxy groups in the molecules of the sterols investigated. Two fragmentation pathways of the furanose ring have been found in the spectra of the glycosides.

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