2. The leaves of B. exilis have yielded a new triterpene, for which the structure of 3α,20(S),25-trihydroxydammar-23-ene is proposed, and a four-component mixture of epimers at C-3 and C-24 of the compound 3ξ,20(S),24ξ-trihydroxydammar-25-ene. The composition of the mixture and the ratio of the components were determiend n the basis of chemical and spectral characteristics.

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A NEW STEROID GLYCOSIDE FROM THE STARFISH Patiria pectinifera

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From the glycoside fraction of the starfish Patiria pectinifera, after its desulfation, an artefactural glycoside has been obtained: 29(α-L-arabinofuranosyloxy)-5α-stigmastane-3β,6α,8,15α,16β-pentaol (I). The structure of (I) was shown by ^{1}H and ^{13}C NMR spectra and mass spectra and by acetylation and high-temperature hydrogenation.

Continuing an investigation of the steroid glycosides of the Far Eastern starfish Patiria pectinifera, among the products of mild desulfation of these compounds we have detected and isolated a new steroid derivative: 29-(α-L-arabinofuranosyloxy)-5α-stigmastane-3β,6α,8,15α,16β-pentaol (I).

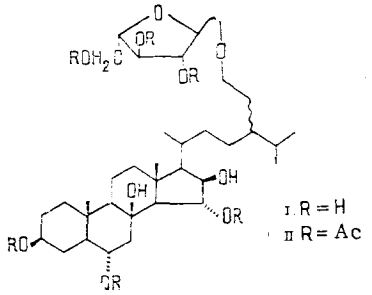

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TABLE 1. ^{13}C NMR Spectra of the Glycoside (I) and of Its Acetate (II)* (C_5D_5N, δ, TMS = 0)

Atom	I	II	Atom	I	II
C-1	39,3	38,3	C-18	17,2	17,0
C-2	32,0	27,2	C-19	14,5	14,0
C-3	71,4	73,8	C-20	29,7	29,6
C-4	33,2	28,5	C-21	18,5	18,3
C-5	53,8	49,9	C-22	34,0	34,0
C-6	66,6	71,0	C-23	28,2	28,5
C-7	50,9	45,8	C-24	41,6	41,5
C-8	75,5	74,5	C-25	30,4	30,3
C-9	56,9	56,2	C-26	18,7	18,8
C-10	37,3	37,5	C-27	19,9	19,9
C-11	19,1	18,8	C-28	31,1	31,0
C-12	42,8	42,3	C-29	67,5	67,3
C-13	44,8	44,7	C-1′	109,7	106,5
C-14	64,6	60,9	C-2′	83,6	82,2
C-15	80,8	84,5	-3′	78,8	78,2
C-16	82,6	79,3	C-4′	85,6	81,2
C-17	60,0	60,3	C-5′	62,9	64,0

*OAc: 20.6 (×2); 21.0 (×3); 21.2 (×1).

The acid hydrolysis of (I) gave a single monosaccharide, which was identified as L-arabinose (PC, GLC, $[\alpha]_D$). In the ^{13}C NMR spectra of (I), signals at 109.7, 83.6, 78.8, 85.6, and 62.9 ppm (Table 1) were close to the corresponding signals from the spectrum of methyl α-L-arabinofuranoside [1], and on this basis we established the α configuration of the glycosidic bond and the size of the ring in the monosaccharide.

The coincidence of the signals of the C-1–C-21 carbon atoms (Table 1) and of the characteristic signals of the H-3, H-4, H-6, H-7, H-14, H-15, and H-16 protons (Table 2) in the spectra of glycoside (I) and the corresponding spectra of 5α-cholestane-3β,6α,8,15α,16β,26-hexaol (III) from the same starfish [2] indicated that the aglycone in compound (I) had a saturated steroid nucleus with hydroxy groups in the 3β, 6α, 8, 15α, and 16β positions and the monosaccharide residue was attached to the side chain. This was confirmed by the coincidence of the mass numbers of the characteristic ions in the mass spectra of (I) and (III) in the 340-260 a.m.u. interval.

In addition to the signals in the ^{13}C NMR spectrum of (I) revealed for the C-20 and C-21 atoms (29.7 and 18.5 ppm), the signals at (ppm) 67.5 (t), 41.6 (d), 34.0 (t), 31.1 (t), 30.4 (d), 28.2 (t), 19.9 (q), and 18.7 (q) had to be assigned to the side chain. The splitting out from M^+ for (I) of the monosaccharide residue formed an ion with m/z 478, composition $C_{29}H_{50}O_5$, and the products of its subsequent dehydration with m/z 460, 442, and 424. In view of the presence of doublets at 0.821 and 0.789 ppm (J = 7.1 Hz) that are characteristic for its isopropyl group in the ^1H NMR spectrum of the glycoside, and its ^{13}C NMR spectrum and the mass spectrum, it was possible to conclude that the aglycone contained 29 carbon atoms and its side chain contained 10 atoms and included an isopropyl group.

The ^1H NMR spectrum of the glycoside lacked the multiplet signal of H-24 in the weak field that is characteristic for the 24-O-glycosylated polyols of starfish [3]. In place of this there were two one-proton multiplets at 3.58 and 4.07 ppm. Since these multiplets partially overlapped with the signals of the protons of the steroid skeleton, we acetylated (I) and obtained the hexaacetate (II). In its ^1H NMR spectrum, the corresponding signals were located at 3.59 and 3.95 ppm. Selective decoupling from protons with successive irradiation of the multiplets at 3.59 and 3.95 ppm gave in the ^{13}C NMR spectra of (II) in both cases a diffuse doublet instead of a triplet at 67.3 ppm. Recording the Overhauser effect with irradiation of the anomeric proton of the arabinofuranosyl residue (H-1′) at 5.55 ppm in the ^1H NMR spectrum of (I) showed an intensification of the multiplet at 3.58 ppm and a somewhat smaller intensification of the multiplet at 4.07 ppm. In its turn, the successive irradiation of the multiplets at 3.59 and 3.95 ppm in the ^1H NMR spectra of (II) gave an intensification of the H-1′ signal (5.39 ppm) and of the multiplets at 3.95 and 3.59 ppm, respectively. Differential decoupling on irradiation of the multiplet at 3.59 or 3.95 ppm in the ^1H NMR spectrum of (II) showed signals in the position of the other multiplet (3.95

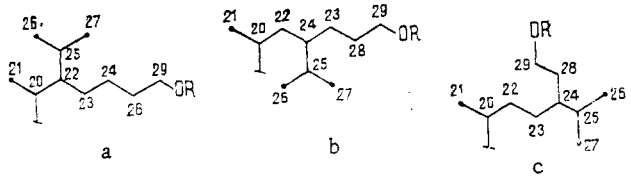
TABLE 2. ^{1}H NMR Spectra of Glycoside (I) and of Its Acetate (II)* (C_5D_5N, δ, TMS = 0)

Proton	I	II	Proton	I	II
	δ, ppm; J, Hz	δ, ppm		δ, ppm; J, Hz	δ, ppm, J, Hz
H-3	4,02 m	4,97m	CH_3-18	1,763 s	1,700 s
H-6	4,39 td (6,7a) = 10,3	5,57 td	CH_3-19	1,476 s	1,359 s
H-15	4,98 dd (15,16) = 2,3	5,64 dd	CH_3-21	1,128 d (20,21)=6,6	1,101d
H-16	4,75 dd (16,17) = 7,3	4,37 dd	CH_3-26	0,821d (25,26)=7,1	0,861d
H-29	3,58 td	3,59 td	CH_3-27	0,789 d	0,845d
H-29′	4 07 td	3 95 ddd	H-1′	5,55 d (1,2) =2,3	5,39 s
H-4e	3,15 dm	2,26 m	H-2′	5,00 A dd (2,3)=4.7	5,57d (3,2)=1,7
H-4a	1,86 m	1,70m	H-3′	4,85 B dd (3.4)=7,0	5,43dd (3.4)=4,6
H-5	1,56 m	1,53 m	H-4′	4,75 m	4,64 dd
H-7e	3,51 dd(7e ,6)=4,2	2,59 dd	H-5′	4,27 B dd(5′,4)=4,6	4,56 dd (5′, 4)=5,6
H-7a	2,24dd (7e, 7a)=13,6	1,77 dd	H-5″	4,40 A dd (5″,4)=3,2	4,80 dd (5″, 4)=3,0
H-14	1,89 d (14, 15) =10,7	1,68 d		(5′, 5″)=12,0	(5′,5″)=11,3
H-17	1,56 dd (17,20)=11,2	1,45 dd			
H-20	2,36 m	2,26 m			

*OAc 2.07 (×1); 2.06 (×1); 2.05 (×1); 2.02 (×2); 2.01 (×1).

or 3.59 ppm) and the same two multiplets in the strong field at 1.53 and 1.70 ppm. It followed from these facts that the signals of the protons at 3.58 and 4.07 ppm and of the carbon atom at 67.5 ppm in the ^{1}H and ^{13}C NMR spectra of (I) belonged to atoms present at the point of attachment of the arabinofuranosyl residue to the side chain, and the composition of this part of the molecule included the following fragment: $-CH_2-CH_2-O-\alpha$-L-arabinofuranose.

The presence of the signals with the chemical shifts of the methyl radicals of an isopropyl group in the strong field (Table 1) showed that there was an alkyl substituent in the β position to C-26 and C-27. It followed from this that three variants of the structure of the side chain in (I) were possible: *a*, b, and c (where R represents an α-L-arabinofuranose residue).



Structures *a* and b are biogenetically improbable. It is known that asterosaponins are the products of sterol metabolism in starfish [4]. Sterols with side chains of types *a* and b have not been found hitherto in starfish, while sterols of type c with a side chain acylated at C-24 are common in starfish [5].

Structure *a* can be excluded, since the ^{13}C NMR spectrum of (I) showed no upfield shift of the C-17 and C-21 signals in comparison with the spectrum of the hexaol (III) [2] under the influence of the isopropyl substituent at C-22 such as takes place in C-22 hydroxy derivatives [6].

In the case of structure b, the C-20 signals in the ^{13}C spectrum of (I) should also be present in a stronger field than that of C-20 in the hexaol (III) [2], while in actual fact these values were identical.

In order to make a stricter choice between the structural variants b and c, we calculated the chemical shifts of the C-21–C-29 carbon atoms by Lindeman and Adams' scheme for hydrocarbons [7]. The calculation was made first for variants b' and c', in which the monosaccharide residue had been replaced by a methyl group, and then for b and c, taking into account the effects of the replacement of the methyl group by a hydroxy group [8] and the effects of the glycosylation of the hydroxy group [3, 9, 10]. The calculated values of the chemical shfits of the carbon atoms for variants b', c', b, and c are given in Table 3. Kelecom [11] made similar calculations for the side chains of cholesterol, 24-methylcholesterol, 24-ethylcholesterol, and 24,27-dimethylcholesterol and compared them with the experimental values. We drew the following conclusions: In the first place, the maximum discrepancy between the calculated and the experimental values does not exceed 2.7 ppm (such a considerable discrepancy was observed in only one case, for the C-23 atom of 24,27-dimethylcholesterol); and, in the second place, experimental values 1 ppm higher than the calculated values for C-21

TABLE 3. Values of the Chemical Shifts of the Carbon Atoms of the Side Chains of Structural Variants b', c', b, and c of Glycoside (I) and of 24-Ethylcholesterol

Compound	Method of determination	C-21	C-22	C-23	C-24	C-25	C-26	C-27	C-28	C-29
Structural variant b'	Calculation	18,6	36,5	31,1	41,5	30,4	19,6	19,6	30,0	22,8
Structural variant c'	Calculation	18,1	32,7	28,4	43,6	30,4	19,6	19,6	33,8	20,6
Structural variant b*	Calculation	18,6	36,5	29,4	41,5	30,4	19,6	19,6	28,3	67,2
Structural variant c*	Calculation	18,1	32,7	28,4	41,9	30,4	19,6	19,6	32,1	65,4
Glycoside (I)	Experimental	18,3	34,0	28,2	41,6	30,4	18,7	19,9	31,1	67,5
26-Ethylcholesterol (epimeric pair)	Experimental	18,7 18,7	33,8 33,6	26,0 26,3	45,6 45,8	29,0 28,8	19,7 19,5	19,0 18,9	23,0 22,9	11,9 12,2

*The α and β effects of glycosylation (~+5.0 ppm and ~−2.2 ppm, respectively) were obtained from the literature [3, 9, 10].

and C-22 have a systematic nature and are apparently due to a particular stereochemistry of ring D, the carbon atoms of which were considered in the calculation.

It can be seen from Table 3 that the calculated value for C-22 in case b is 36.5 ppm, and in case c it is 32.7 ppm. Taking into account the correction of +1 ppm for the calculated chemical shifts and comparing the values obtained with the experimental results for C-22 of glycoside (I) (34.0 ppm), it can be seen that for variant b the difference (3.5 ppm) exceeds the maximum possible discrepancy (2.7 ppm), while for variant c the difference is small (0.3 ppm). The greatest discrepancy for variant c of 2.1 ppm was observed for the chemical shift of the C-29 atom (see below). Thus, taking into account the slight influence of substituents in ring D on the chemical shifts of the C-21 and C-22 atoms (−0.1 and −0.3 ppm, respectively) following from a comparison of the hexaol (III) and cholesterol [2, 9], it may be concluded that the values for structure c agree best with the experimental results for glycoside (I). Furthermore, the presence in (I) of a side chain of type c was confirmed by comparing the ^{13}C NMR spectrum of glycoside (I) with the corresponding spectrum for 24-ethylcholesterol (III) [9]. The C-23 and C-25 signals for (I) were shifted downfield, and that of C-24 upfield as compared with the corresponding signals of 24-ethylcholesterol, which is explained by the presence of the substituent at C-29. the magnitude of the α effect of glycosylation at a primary alcohol group is 5-7.8 ppm [10, 12, 13] and depends on the configuration of the glycosidic bond [13]. Apparently, the most acceptable magnitude for our case if the α effect of glycosylation by an α-L-arabinofuranoside residue of +5.0 ppm [10]. In view of the fact that the C-29 chemical shift in the ^{13}C NMR spectrum of 3β,29-dihydrosystigmast-5-ene is 62.1 ppm [14], for C-29 in the spectrum of (I) one may expect 67.1 ppm, which is close to the observed value of 67.5 ppm (Table 1).

An additional confirmation of the structure of the side chain in (I) was obtained by the high-temperature hydrogenation of glycoside (I) and of stigmasterol in a current of hydrogen over $Pd/CaCO_3$ at 330°C. The same reaction products were formed in the two cases, among which stigmastane was identified by GLC and GLC–MS methods.

On the basis of what has been said above, the structure of the glycoside was established as (I). Astereosaponins studied previously have belonged to the cholestane series [15], and this is the first time that a glycoside with the stigmastane skeleton has been detected in starfish.

EXPERIMENTAL

All the spectral characteristics and physical constants were determined under the conditions given in [2].

Mass spectra with direct introduction of the sample were taken on MKh 1310 mass spectrometer at temperatures of the evaporator bulb and of the ionization chamber of 100-150°C

with a collector current of 60 μA and an ionizing energy of 50 eV. The masses of the ions were measured with an accuracy of $5 \cdot 10^{-6}$, the reference substance being perfluorokerosine.

The starfish Patiria pectinifera was collected in Posyet Bay, Sea of Japan, in August, 1981, at a depth of 1-3 m.

Solvolysis of the Glycosidic Fraction. The glycosidic fraction was isolated by a method described previously [3]. A solution of 88 mg of glycosidic fraction (a single spot on TLC) in a mixture of 18 ml of dry puridine and 4.5 ml of dry dioxane was heated without the access of moisture at 85-95°C for 2.5 h. The solvent was distilled off in vacuum and the dry residue was chromatographed twice on Florisil in the chloroform–ethanol–water (30:100:water to saturation) system. This gave 20 mg of the glycoside (I).

29-(α-L-Arabinofuranosyloxy(-5α-stigmastane-3β,6α,8,15α,16β-pentaol (I), $C_{34}H_{60}O_{10}$, mp 248-249°C, $[\alpha]_D$ +3.8 (c 0.29; methanol); mass spectrum, m/z (%): 610 (0.3); 592 (0.4); 574 (1); 556 (1); 549 (1.4); 531 (0.8); 507 (0.5); 495 (1.6); 489 (11); 478 (30); 471 (22); 463 (9); 460 (32); 453 (16); 445 (16); 443 (33); 442 (34); 435 (8); 427 (19); 424 (26); 415 (7); 331 (22); 321 (23); 313 (13); 305 (24); 303 (37); 287 (32); 285 (40); 279 (14); 278 (11); 269 (39); 267 (30); 253 (69); 251 (26); 249 (10); 235 (47); 225 (40); 123 (75); 121 (65); 109 (78); 107 (70); 97 (70); 95 (100).

The acid hydrolysis of 10 mg of glycoside I was performed with 2 N HCl at 85-95°C for 2 h. The aglycones were extracted with chloroform. The monoscaccharide was analyzed on Filtrak FN-15 paper in the butanol–pyridine–water (10:3:3) system and by GLC–MS in the form of aldononitrile peracetates. L-Arabinose was identified: $[\alpha]_D$ +101.5° (c 0.12; water). According to the literature [16]: $[\alpha]_D$ +105.5° (water).

29-(α-L-Arabinofuranosyloxy)-5α-stigmastane-3β,6α,8,15α,16β-pentaol 2',3,3',5',6,15-hexaacetate (II), amorphous after purification on Florisil, $[\alpha]_D$ +33.2° (c 0.38; chloroform); obtained on acetylation by the usual method.

High-Temperature Hydrogenation. After 3 mg of the glycoside (I) had been carefully mixed with 300 mg of 5% $Pd/CaCo_3$ catalyst, hydrogenation was performed in a current of hydrogen at 330°C as described by Harrison et al. [17]. Stigmasterol was hydrogenated in a similar manner. Stigamastane was identified in the reaction products by the GLC and GLC–MS methods.

SUMMARY

An artefactual glycoside has been isolated from a glycosidic fraction from the starfish Patiria pectinifera after its desulfation, and its structure has been established as 29-(α-L-arabinofuranosyloxy)-5α-stigmastane-3β,6α,8,15α,16β-pentaol. This is the first time that a glycoside of the stigmastane series has been detected in starfish.

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MASS SPECTRA OF POLYHYDROSYSTEROIDS OF THE STARFISH *Patiria pectinifera*

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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

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