with height. As canm be seen from Table 1, appreciable differences are observed in the qualitative and quantitative composition of the triterpenoids in the leaves of B. pendula with height only on passing from one height zone of vegetation to another.

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STEROID COMPOUNDS OF MARINE SPONGES.

IX. STEROL COMPOSITION OF THREE SPECIES OF FAR EASTERN SPONGES

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Continuing a study of steroidal sponges [1], we have investigated the sterols of the sponges Halichondria panicea (1 and 2, different samples), Hymeniacidon assimiles and Suberites japonicus gathered in July-August, 1986, during the second voyage of the Scientific Research ship Akademic Operin. The H. panicea (1) was collected in the sea of Okhotsk on the Kashevarova bank from a depth of 147 m by beam trawl, H. panicea (2) in Cratee Bay, Island of Ushishir (Kurile Islands) from a depth of 10-15 m, and H. assimiles and S. japonicus were collected by sigsbee trawl on the oceanic side of the island of Urup (Kurile Islands), from depths of 125 and 64 m, respectively.

Fractions of free sterols were isolated as described in [2]. Then part of the free sterols was acetylated with acetic anhydride in pyridine (1:1). The resulting acetates of the sterols from H. panicea (1), H. assimiles, and S. japonicus were separated into fractions by preparative TLC (hexane–benzene (4:1)) on silica gel impregnated with silver nitrate.

The combined free sterols and the acetate fractions obtained from the three species of sponges were analyzed in a similar manner to that described previously [2].

The steroidal components were identified from their mass spectra with consideration of their chromatographic behavior in capillary GLC. In total, 19 components were identified in H. panicea (1), nine in H. panicea (2), 14 in H. assimiles, and 12 in S. japonicus. The results of the analyses are given in Table 1.

As can be seen from Table 1, 27 known steroids were identified in the sterol fractions of the sponges studied. The total sterol fractions consisted of C_{26}–C_{30} steroid alcohols and were characterized by high levels of the C_{27} compounds. Great interest is presented by the two isomeric C_{27}-stanols detected in fractions from the sponge S. japonicus. We identified one of them by the methods of GLC, GLC-MS, and ^1H NMR as 5α-cholestanol (5). Its isomer (6) has a large RRT and does not coincide in chromatographic mobility with the sterols known previously. It is possible that this compound possesses a less branched side chain and is 27-methyl-26-nor-5α-cholestanol. No such side chain has hiterto been detected in natural sterols, although an analogous C_{26}-sterol has been found among the minor steroids of the sponge Axiella cannabina [3].

We must also mention the presence in the fractions studied of new isomers of $C_{26}\Delta^{7,22}$ (4) and $C_{27}\Delta^{7}$ (7) sterols not coinciding in their RRTs with known natural steroids.

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TABLE 1. Composition of the Sterol Fractions from Sponges, %

Sterol	Structural features	M+	H. panicea (1)	H. panicea (2)	H. assimilis	S. japonicus	RRT (rel. cholesterol)
1. 24-Nor-5α-cholestan-3 β-ol	$C_{26}\Delta^{0}$	374	—	—	—	4,4	0,81
2. 24-Nor-5α-cholest-22-en-3 β-ol	$C_{26}\Delta^{22}$	372	0,4	0,6	3,5	—	0,71
3. 24-Nor-5α-cholesta-7, 22-dien-3β-ol	$C_{26}\Delta^{7,22}$	370	1,1	—	—	—	0,73
	$C_{26}\Delta^{7,22}$	370	1,64	Tr.	—	—	0,77
4. Sterol	$C_{27}\Delta^{0}$	388	1,9	91,2	59,6	49,5	1,02
5. 5 α-Cholestan-3 β-ol	$C_{27}\Delta^{0}$	388	—	—	—	13,8	1,03
6. Sterol	$C_{27}\Delta^{7}$	386	23,8	—	—	—	1,01
7. Sterol	$C_{27}\Delta^{7}$	386	38,5	—	—	—	1,09
8. 5 α-Cholest-7-en-3β-ol							
9. 24-Methyl-27-nor-5α-cholest-22-en-3 β-ol	$C_{27}\Delta^{22}$	386	0,4	—	4,0	—	0,91
10. 5 α-Cholest-22β -ol	$C_{27}\Delta^{22}$	386	—	1,8	6,6	—	0,94
11. 24-Methyl-27-nor-5α-cholesta-7, 22-dien-3β -ol	$C_{27}\Delta^{7,22}$	384	0,9	—	—	—	0,94
12. 5 α-Cholesta-7,22-dien-3β -ol	$C_{27}\Delta^{7,22}$	384	Tr.	—	—	—	1,01
13. Unidentified sterol		386	—	4,8	—	—	1,08
14. Unidentified sterol		384	9,7	—	—	—	1,16
15. 5 α-Cholest-5,7,9(11)-trien-3 β-ol	$C_{27}\Delta^{5,7,9}$	382	Tr.	—	—	—	1,19
16. 24-Methyl-5 α-cholest-7-en-3 β-ol	$C_{28}\Delta^{7}$	400	3,0	—	—	—	1,34
17. 24-Methyl-5 α-cholest-22-en-3 β-ol	$C_{28}\Delta^{22}$	400	Сл.	—	9,8	1,7	1,11
18. 24-Methyl-5 α-cholesta-7, 22-dien-3β -ol	$C_{28}\Delta^{7,22}$	398	9,8	—	—	—	1,20
19. 24-Methyl-5 α-cholestan-3 β-ol	$C_{28}\Delta^{0}$	402	1,6	0,3	1,5	14,7	1,24
20. 24-Methyl-5 α-cholest-24(28)-en-3β -ol	$C_{28}\Delta^{24\,(28)}$	400	1,0	0,2	Tr.	4,8	1,25
21. 24-Methyl-5 α-cholest-7,24(28)-dien-3 β-ol	$C_{28}\Delta^{7,24\,(28)}$	398	3,4	—	—	—	1,32
22. 24-Ethyl-5α -cholestan-3β -ol	$C_{29}\Delta^{0}$	416	0,7	0,1	4,3	1,8	1,48
23. 24-Ethyl-5α -cholest-5-en-3 β-ol	$C_{29}\Delta^{5}$	414	—	0,1	—	2,3	1,44
24. 24-Ethyl-5α -cholest-7-en-3 β-ol	$C_{29}\Delta^{7}$	414	1,9	—	—	—	1,59
25. 24-Ethyl-5α -cholest-24(28)-en-3 β-ol	$C_{29}\Delta^{24\,(28)}$	414	—	0,2	Tr.	1,5	1,50
26. 24-Ethyl-5α -cholest-22-en-3 β-ol	$C_{29}\Delta^{22}$	414	—	—	0,9	—	1,33
27. 24-Ethyl-5α -cholesta-22-dien-3 β-ol	$C_{29}\Delta^{7,22}$	412	Tr.	—	6,5	—	1,48
28. 24-Propyl-5 α-cholestan-3 β-ol	$C_{30}\Delta^{0}$	430	—	—	0,5	0,3	1,70
29. 24-Propyl-5 α-cholest-5-en-3 β-ol	$C_{30}\Delta^{5}$	428	—	—	—	1,8	1,66
30. 24-Propylidene-5 α-cholest-5-en-3 β-ol	$C_{30}\Delta^{5,24\,(28)}$	426	—	—	—	1,0	1,58
31. 24E-Propylidene-5 α-cholestan-3 β-ol	$C_{30}\Delta^{24\,(28)E}$	428	—	—	0,5	—	1,64
32. 24Z-Propylidene-5 α-cholestan-3 β-ol.	$C_{30}\Delta^{24\,(28)Z}$	428	—	—	2,2	—	1,72

Only a few sponges have Δ^7-sterols as their main component. At the same time, we detected such compounds in the deep-sea sample of H. panicea while stanols predominated in the other sample of the same species. Hitherto, Δ^5-sterols and, more rarely, Δ^0-sterols have been detected exclusively in sponges of the family Halichondriidae.

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CHEMICAL INVESTIGATION OF BIOMASS OF A CULTURE OF GINSENG CELLS.

II. 6-O-ACYL DERIVATIVES OF β-SITOSTEROL β-GLUCOSIDE

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The isolation of β-sitosterol, β-sitosterol β-D-glucoside, and a glycoside of oleanolic acid from the crude glycosidic fraction (CGF) of a methanolic extract of a culture of gingseng cells has been reported previously [1].

In the present paper we give the results of further investigations of a CGF of gingseng cells (strain BIO-2, Omutninsk Chemical Factory). The CGF was obtained by chromatographing a methanolic extract of the gingseng biomass on Polychrome-1 (water → 50% ethanol) [2] in order to free it from organic salts, free sugars, and amino acids [3]. The feebly polar part of the CGF was found to contain a feebly polar fraction, FPF, which, in TLC (SiO_2 L 5/40, Czechoslovakia) in system 1 (benzene—chloroform—methanol (15:15:3)) appeared in the form of a single spot with a R_f value of 0.5 and had the coloration characteristic for compounds of triterpene and steroid nature. The spot was revealed with 10% H_2SO_4 in ethanol followed by heating at 120-200°C. The FPF was isolated by preparative thin-layer chromatography in solvent system 1 and was recrystallized from acetone (7 mg was obtained — 0.017% calculated on the dry weight of the sample).

The IR spectrum of the FPF showed an absorption band at 1727 cm^{-7} characteristic of the stretching vibrations of an ester group.

The FPF was treated with a 5% solution of KOH in ethanol for 18-20 h at room temperature. Then the reaction mixture was diluted with water, neutralized with KU-2-8 ion-exchange resin (H^+ form), and extracted successively with pentane and chloroform. The chloroform extract contained a single compound, which was identified as β-sitosterol β-D-glucoside. The extractive substances that had passed into the pentane were treated with a saturated solution of diazomethane in ether for an hour, and the products were analyzed by GLC under the conditions given in [1]. This showed the presence of two compounds the RRTs of which were identical with the RRTs of authentic samples of methyl palmitate and linoleate in a ratio of 1:2:3 [sic], respectively. Consequently, the FPF is a mixture of β-sitosterol palmitoyl- and linoleoyl-β-D-glucosides.

A comparison of the chemical shifts in the ^1H NMR spectra of β-sitosterol β-D-glucoside and its acyl derivatives showed that in each case the acyl substitutent substituted the primary hydroxy group of the glucose residue [4].

The structures of the acyl derivatives of β-sitosterol β-D-glucose were confirmed by the performance of independent synthesis through the transesterification of methyl palmitate and linoleate with β-sitosterol β-D-glucoside in N,N-dimethylformamide in the presence of potassium carbonate [5].

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