STEROLS OF THE BROWN ALGA *Desmarestia viridis*

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Continuing a study of the chemical composition of the brown alga *Desmarestia viridis* [1] collected in June in Troitsa Bay, Sea of Jap , from 1.1 kg of dry algae using the method described by Idler and Wiseman [2] we have obtained 3.72 g of unsaponifiable lipid fraction, which has been investigated with the aim of identifying the steroid components. Chromatography of the material obtained on a column of silica gel L (Czechoslovakia) in benzene–ethyl acetate systems with gradually increasing amounts of ethyl acetate from 0 to 10% gave two steroid fractions. Fraction A (1.54 g) was similar in chromatographic behavior [TLC; benzene–ethyl acetate (9:1)] to cholesterol, and fraction B (0.03 g) contained mainly more polar components.

The sterol mixtures of both fractions were analyzed by the GLC method in the form of the free alcohols and their acetates using a Pye Unicam 104 chromatograph with a flame-ionization detector fitted with a glass column (200 × 0.3 cm) containing 5% of SE-30 on Chromaton NAW-HMDS as the stationary phase. The temperature of analysis was 260°C, and the carrier gas helium (20 ml/min).

After acetylation, fraction A, consisting of two components, was separated on a column of silica gel impregnated with $AgNO_3$ (20%) in the hexane–ethyl acetate (9:1) system. The acetate of component (I) (mp 117.5–118°C) was identified by its spectral properties and retention time on GLC as fucosterol acetate, and the acetate of component (II) (mp 134–135°C) as 24-methylenecholesterol acetate. Fraction B contained cholesterol, 24-ketocholesterol, and saringosterol, which were identified by chromato-mass spectrometry (LKB 9000 S chromato-mass spectrometer, column 300 × 0.3 cm with 1.5% of SE 30 on chromaton N-AW-HMDS, 210°C, helium – 20 ml/min, ionization energy 70 eV).

On the whole, in its steroid composition (main components fucosterol and 24-methylenecholesterol) *D. viridis* is close to the majority of other species of brown algae studied [3, 4].

TABLE 1. Sterols of *Desmarestia viridis*

Name	Amount, %	mp (acetate), °C		Retention time		Mass spectra of the acetates, m/e
		found	lit. figures [3]	found	lit. figures [3]	
Fucosterol	94	117.5–118	118	1,60	1,60	394 (M–60), 379, 296, 291, 255, 253, 228
24-Methylene-cholesterol	4,09	134–135	135–136	1,27	1,27	380 (M–60), 365, 296, 272, 259, 255, 253, 228, 213
Saringosterol	tr.		176–178	2,44	2,43	410 (M–60–18), 392, 377, 367, 349, 296, 283, 253, 213
24-Ketocho-lesterol	tr.		127–128	2,15	2,17	382 (M–60), 367, 296, 281, 261, 255, 228, 213
Cholesterol	tr.		114–115	1	1	368 (M–60), 353, 260, 255, 253, 247, 213

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ISOLATION OF ASTEROSTEROL FROM THE SEA-CUCUMBER *Cucumaria fraudatrix*

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Sterols with 26 carbon atoms have recently been identified as minor components in marine organisms [1, 2]. The study of the steroid composition of the Far-Eastern sea-cucumber *Cucumaria fraudatrix* has shown an anomalously high content (10.1%) of a C_{26} component. For its identification, the total sterol fraction obtained by the usual method [3] was acetylated and the acetates were separated by column chromatography on KSK silica gel impregnated with 20% silver nitrate in the hexane–benzene system with a gradually increasing amount of benzene. The acetate of the C_{26} sterol with mp 134-136°C was isolated in the chromatographically individual state. GLC analysis was carried out on a Pye Unicam 104 chromatograph in 200 × 0.4 cm glass columns with 5% of SE-30 on Chromaton N-AW-HMDS at 280°C and a rate of flow of carrier gas (helium) of 20 ml/min.

The mass spectrum of this compound showed that it was a derivative of a C_{26}-diunsaturated steroid alcohol (M^+ 412) having double bonds in positions 22,23 (m/e 300) and 7,8 (m/e 273, 271, 255, 246, 229). The following signals appeared in the PMR spectrum, ppm: C_{18} – 0.54, s, 3 H; C_{19} – 0.81, s 3 H; C_{25}, C_{26} – 0.94, d 7 Hz, 6 H; C_{21} – 1.01, d, 6 Hz, 3 H; C_3 acetoxymethine proton – 4.45-4.85, m, 1 H; olefinic protons at C_7 – 5.15, m, 1 H; and C_{22}, C_{23} – 5.70, m, 2 H. A comparison of the spectral characteristics, constants, and retention times on GLC shows the identity of the sterol acetate isolated with the acetate 24-nor-5α-cholesta-7,trans-22-dien-3β-ol (asterosterol), obtained by the acetylation of the C_{26} sterol from the starfish *Asterias amurensis* [4].

Asterosterol has not previously been isolated from extracts of sea-cucumbers.

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