



Fig. 1. Diagrams of the gel filtration of soda lignin: 1) initial; 2) reduced photoelectrochemically.

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ALKYL SULFATES FROM THE ASCIDIAN *Holocynthia roretzii*

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Continuing investigation in the field of sulfated derivatives from marine organisms [1], we have studied ethanolic extracts of the ascidian *Holocynthia roretzii*.

The animals were collected in May in Peter the Great Bay at a depth of 3-5 m, and were comminuted and extracted with ethanol. The extract from 70 specimens of ascidians was evaporated to dryness and treated with 1000 ml of water. The aqueous solution was separated and passed through a column filled with Teflon powder, which was washed first with water and then with ethanol. The ethanol-containing fractions were evaporated to dryness and, after chromatography on columns of silica gel [$\text{CHCl}_3\text{-EtOH}$ (7:1 and 2:1)] and Sephadex LH-20 [$\text{CHCl}_3\text{-EtOH}$ (2:1)], 1 g of a mixture of ammonium salts of alkyl sulfates was isolated in the form of an amorphous white powder with R_f 0.42 [TLC on silica gel: $\text{CHCl}_3\text{-EtOH-H}_2\text{O}$ (90:30:1)]; $[\alpha]_D^{25} 0^\circ$ (H_2O).

The results of elementary analysis for C, H, N, and S corresponded to those calculated for ammonium salts of alkyl sulfates with 9 and 10 carbon atoms in the chain in a ratio of 1:1. The IR spectrum showed absorption bands at 1200 and 1415 cm^{-1} , which are characteristic for organic sulfates, and a strong broad band with a maximum at 3200 cm^{-1} , characteristic for NH_4^+ [2].

Solvolysis of the mixture of alkyl sulfates in dioxane at 100°C for 4 h [3] led to the formation of a mixture of alcohols consisting, according to GLC (Chromaton N-AW-HWDS, 5% of SE-30) of 13 components, the two main ones making up 39% and 25% of the total amount. The

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two main alcohols were isolated in the individual state with the aid of preparative GLC (Chromaton N-AW-HMDS, 3% of SE-30).

On the basis of the results of IR, mass, and ^1H and ^{13}C NMR spectroscopy their structures were established as 2,6-dimethylheptanol (I) and dec-3-enol (II). The acetate of (I) was obtained. The catalytic hydrogenation of (II) led to decanol.

2,6-Dimethylheptanol (I), n_D^{20} 1.4322. Mass spectrum: 126 ($\text{M}^+ - \text{H}_2\text{O}$). IR spectrum (cm^{-1}): 3472 (bound OH group); 3627 (free OH group); 1384 and 1364 (gem-dimethyl doublet). PMR (CDCl_3 , δ ppm): 0.87 (C-7 and C-9, 6 H, d, $J = 6.6$ Hz); 0.91 (C-8, 3 H, d, $J = 6.6$ Hz); 1.54 (C-6, 1 H, $J = 6.6$ Hz); 1.62 (C-2, 1 H, m); 3.44, AB part of the spectrum of an ABX system (C-1, 2 H, octet, $J_{\text{AX}} = J_{\text{BX}} = 6$ Hz, $J_{\text{AB}} = -10$ Hz).

^{13}C NMR (CDCl_3 , δ ppm): 16.7 (C-8, q); 22.6 (C-9, q); 22.7 (C-7, q); 24.8 (C-4 t); 28.0 (C-6, d); 35.5 (C-3, t); 35.9 (C-2, d); 39.4 (C-5, t); 68.3 (C-1, t).

Dec-3-enol (II). Mass spectrum: 156 (M^+ , weak); 138 ($\text{M}^+ - \text{H}_2\text{O}$). IR spectrum (cm^{-1}): 3454 (bound OH group); 3624 (free OH group). PMR (CDCl_3 , δ ppm): 0.90 (C-10, 3 H, t); 2.34 (C-2, 2 H, q, $J = 7.5$ Hz); 3.65 (C-1, 2 H, t, $J = 7.5$ Hz); 5.38 (C-3, 1 H, m); 5.58 (C-4, 1 H, m). ^{13}C NMR (δ , CDCl_3 , ppm): 14.1 (C-10, q); 22.7 (C-9, t); 27.5 (C-6, t); 29.1 (C-5, t); 29.8 (C-7, t); 30.9 (C-2, t); 31.8 (C-8, t); 62.4 (C-1, t); 125.1 (C-4, d); 133.4 (C-3, d).

Thus, the main components of the fraction that we isolated are ammonium 2,6-dimethylheptyl sulfate and ammonium dec-3-enyl sulfate.

Alkyl sulfates have not been detected previously in marine organisms.

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SYNTHESIS OF DERIVATIVES OF DIBENZO-18-CROWN-6 WITH A CHLOROMETHYL GROUP IN THE SIDE CHAIN

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Many benzocrowns possess ionophoric activity on i.e., the capacity for forming complexes with metal ions and transporting them through biological and artificial membranes.

Benzocrowns substituted in the benzene rings can be obtained either by condensing the corresponding pyrocatechol derivatives [1] or with the aid of electrophilic substitution reaction: nitration, acylation with carboxylic acids, alkylation with alcohols, and formylation with hexamethylenediamine [1-3]. The subsequent modification of the products of these reactions provides the possibility of obtaining benzocrowns containing various substituents in the side chain [4-6].

The ionic selectivity and the coefficient of the effective concentration capable of modifying biological and artificial membranes largely depend on the nature of the substituents of the benzocrowns [7].

We give the results of the chloromethylation of dibenzo-18-crown-6 (I) and some of its monosubstituted derivatives: 4'-tert-butyl-, 4'-acetyl-, and 4'-propionyl dibenzo-18-crown-6 (II), (III), and (IV), respectively.

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