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 ($M^+ - H_2O$). 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, $J_{AX} = J_{BX} = 6$ Hz, $J_{AB} = -10$ 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 ($M^+ - H_2O$). 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'-propionyldibenzo-18-crown-6 (II), (III), and (IV), respectively.

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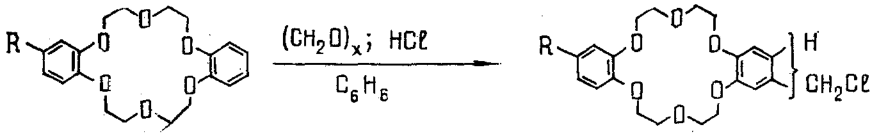

I–IV V–VIII

I,V. $R=H$ II,VI. $R-C(CH_3)_3$ III,VII. $R=COCH_3$ IV,VIII. $R=COC_2H_5$

The starting materials (I-IV) were obtained by analogy with published methods [2, 3]. The structures of the compounds obtained were confirmed by their IR, PMR, and mass spectra.

Chloromethylation was carried out by a modified procedure [8] with paraformaldehyde in solution in benzene or another organic solvent saturated with gaseous HCl at an elevated temperature with vigorous stirring. The course of the reaction was monitored by TLC. The chloromethylation of (I) gave a 70% yield of a mixture containing, according to its mass spectra, 80% of mono- and 20% dichloromethylated derivatives, mp 124-130°C. Mol. wt. found 408; calculated for $C_{21}H_{25}O_6Cl$, mol. wt. 408.87; mol. wt. found 4.57; calculated for $C_{22}H_{26}\cdot O_6Cl_2$ mol. wt. 457.35. Compound (VI) was obtained with an 80% yield, mp 110-117°C. mol. wt. found 464; calculated for $C_{25}H_{33}O_6Cl$, mol wt. 464.98. The chloromethylation of (III) was accompanied by a self-condensation reaction at the acetyl group, which imparted a coloration to the reaction mixture and lowered the yield of end-product (30%), mp 127-135°C. mol. wt. found 450; calculated for $C_{23}H_{27}O_7Cl$, mol. wt. 450.91.

The self-condensation product — a dark brown powder with mp > 280° (decomp.) — was not specially investigated; it is apparently an analog of dypnone. Compound (VIII) was obtained with a yield of 50%, mp 135-150°C. mol. wt. found 464, calculated for $C_{24}H_{29}O_7Cl$, mol. wt. 464.94. The PMR spectra showed a singlet in the 4.4-4.5 ppm region corresponding to the protons of a CH_2Cl group. The IR spectra also corresponded in the proposed formulas. The possibility has been shown of replacing the halogen of compound (V) by hydroxy, ethoxy, and acetyl groups.

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