

This is the first time that either substance has been isolated from the *Eucalyptus* species mentioned.

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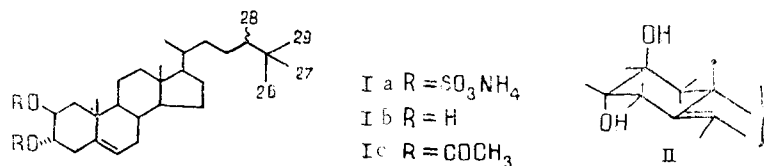
#### STEROID COMPOUNDS OF MARINE SPONGES.

#### V. 24 $\xi$ ,25-DIMETHYLCHOLEST-5-ENE-2 $\beta$ ,3 $\alpha$ -DIOL DI(AMMONIUM SULFATE) — A NEW POLYHYDROXYLATED STEROID FROM A SPONGE *Halichondria* sp.

T. N. Makar'eva, L. K. Shubina,  
A. I. Kalinovskii, and V. A. Stonik

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Continuing an investigation of the steroid composition of sponges of the family *Halichondriidae* [1-4], from an aqueous extract of a sponge *Halichondria* sp., collected in the north-western littoral of the island of Madagascar in December, 1981 (Scientific-Research Ship "Professor Bogorov"), by column chromatography on Polikhrom-1 (water  $\rightarrow$  50% ethanol) and silica gel ( $\text{CHCl}_3\text{-C}_2\text{H}_5\text{OH-H}_2\text{O}$  (20:20:1)) we have isolated a previously unknown sulfated steroid (Ia); yield 0.03%, mp 205-207°C,  $[\alpha]_D^{20} - 14.2^\circ$  (c 0.12; pyridine). IR spectrum:  $\nu_{\text{max}}^{\text{KBr}}$  1236  $\text{cm}^{-1}$  ( $\text{SO}_3$ ). Mass spectrum (m/z): 394 ( $\text{M}^+ - 2\text{NH}_4\text{HSO}_4$ ); 253, 211.



The acid hydrolysis (9% HCl, 90°C, 1.5 h) of (Ia) gave sulfuric acid and a diol (Ib) with mp 257-260°C,  $[\alpha]_D^{20} - 32^\circ$  (c 0.05; ethanol). Mass spectrum (m/z): 430 ( $\text{M}^+$ ), 415, 412 ( $\text{M}^+ - \text{H}_2\text{O}$ ), 397, 379, 253, 211.

The acetylation of (Ib) with a mixture of acetic anhydride and pyridine (1:1) led to a diacetate (Ic) with mp 189-191°C. Mass spectrum (m/z): 454 ( $\text{M}^+ - \text{CH}_3\text{COOH}$ ), 439, 412, 394 ( $\text{M}^+ - 2\text{CH}_3\text{COOH}$ ), 379, 253, 211.

The structure of the side chain of the compound obtained (Ia) followed from a comparison of the high-resolution  $^1\text{H}$  NMR spectra of (Ia-c) with the corresponding spectra of halistanol sulfate, halistanol, and halistanol triacetate. Almost complete coincidence of the signals was observed for the  $\text{CH}_3$ -28 and the  $\text{CH}_3$ -26, -27, and -29 groups, and a small difference for the  $\text{CH}_3$ -18, and  $\text{CH}_3$ -21 groups ( $-0.02$  to  $0.03$  ppm) [2, 5].

From this it was concluded that the structures of the side chains for (Ia-c) and halistanol sulfate were identical.

The presence of fragment (II) in the steroid nucleus of compounds (Ia-c) followed from double-resonance experiments with differential decoupling for (Ib). Starting from the  $\text{CH}_3$ -19

signal (1.62 ppm) in the spectrum of (Ib), by double resonance multiplets were detected for the protons H-1a [2.11 ppm, dd,  $J = 14.1$  Hz (1a,1e); 3.6 Hz (1a,2e); and 0.5 Hz (1a,19)] and H-1e [2.22 ppm, ddd,  $J = 14.1$  Hz (1e,1a); 3.1 Hz, (1e,2e); and 0.8 Hz (1e,3e)].

The simultaneous irradiation of both multiplets, H-2e and H-3e (4.45 and 4.51 ppm), converted the signals of the H-1a,e protons into an AB system with broadened H-1a signals and revealed the signals of the protons H-4a [3.43 ppm, dm,  $J = 14.2$  Hz (4a,4e)] and H-4e (2.42 ppm, ddd,  $J = 14.2$  Hz (4e,4a); 0.9 Hz (4e,2e); and 2.7 Hz (4e,3e)]. The H-4e signal was converted on double resonance into a doublet ( $J = 14.2$  Hz). In its turn, the decoupling of H-4e left the H-6 multiplet (5.69 ppm, dt,  $J = 5.2, 1.5$  and  $1.5$  Hz) unchanged, while H-4e decoupling converted it into dd ( $J = 5.2$  and  $1.5$  Hz). In the H-4a and H-4e multiplets the geminal constant had disappeared completely.

Below, we give the details of the  $^1\text{H}$  NMR spectra of compounds (Ia-c) (solvents: for (Ia and b) —  $\text{C}_5\text{H}_5\text{N}$ ; for (Ic) —  $\text{CDCl}_3$ ;  $\delta$ , TMS — 0; Bruker WM-250 spectrometer):

Compound	H-2	H-3	H-6	$\text{CH}_3$ -18	$\text{CH}_3$ -19	$\text{CH}_3$ -21	$\text{CH}_3$ -28	$\text{CH}_3$ -26, 27, 29
Ia	5.60	5.63m	5.38m	0.64s	1.32s	0.97d	0.86d	0.87s
Ib	4.45	4.51m	5.60m	0.71s	1.62s	1.00d	0.86d	0.88s
Ic	4.87	4.95m	5.34m	0.68s	1.11s	0.94d	0.81d	0.85s

Atomic absorption analysis showed the absence of sodium and potassium ions from (Ia). The counter-ion in the sulfate groups was determined as ammonium (positive Nessler test). Thus, the structure of (Ia) has been determined as 24 $\xi$ ,25-dimethylcholest-5-ene-2 $\beta$ ,3 $\alpha$ -diol di-(ammonium sulfate).

Compound (Ia) was possibly an artefactual product formed as the result of the degradation of halistanol sulfate during chromatography on silica gel.

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