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SYNTHESIS OF 5α-CHOLEST-7-ENE-3β,5,6β-TRIOL AND ITS 6α-ISOMER

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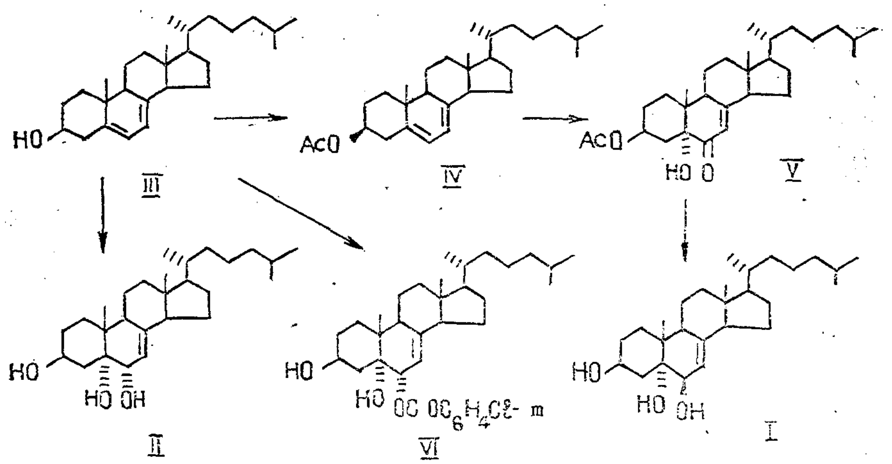
UDC 547.92

One of the hydroxysteroids of the bryozoan Myriapora truncata [1] and of a number of marine sponges [2, 3] is 5α-cholest-7-ene-3β,5,6β-triol (I). In natural materials one must also expect the presence of the compound isomeric with it at C_6 — 5α-cholest-7-ene-3β,5,6α-triol (II), which has recently been synthesized [4]. In continuation of an investigation on the synthesis of trihydroxysteroids of marine invertebrates [5, 6], we have developed convenient methods for obtaining compounds (I) and (II) from 7-dehydrocholesterol (III).



The Jones oxidation ($H_2Cr_2O_7$, acetone, 0°C, 0.5 h) of the acetate (IV) obtained in the usual way from 7-dehydrocholesterol led to 3β-acetoxy-5-hydroxy-5α-cholest-7-en-6-one (V). Yield 48%, mp 232-237°C (hexane—ether). Reduction of the 3β-acetoxy-6-ketone (V) with lithium tetrahydroaluminate (ether, 20°C, 40 min) gave the required triol (I). Yield 89%, mp 207-210°C (hexane), lit. [2]: mp 227-229°C. In an attempt to synthesize the 3β,5,6α-triol by the method of Miglinolo et al. [4], using the m-chloroperbenzoic acid oxidation of 7-dehydrocholesterol (III), we obtained the 6-m-chlorobenzoate (VI). Yield 9%, mp 88-93°C. The extremely low yield of compound (VI) forced us to develop an alternative method of obtaining the triol (II). The Criegee cis-hydroxylation of 7-dehydrocholesterol (OsO_4, pyridine, 20°C, 19.5 h) led to the desired compound (II) in a single stage. Yield 34%, mp 238-242°C (hexane—chloroform), lit. [4]: mp 231-232°C.

The structures of all the compounds synthesized were shown unambiguously with the aid of IR, PMR, and mass spectra. The spectroscopic characteristics for the steroids (I) and (II) that we had obtained agreed well with those known from the literature [2, 4].

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CUCUMARIOSIDE G_3 – A MINOR TRITERPENE GLYCOSIDE FROM THE HOLOTHURIAN Eupentacta fraudatrix

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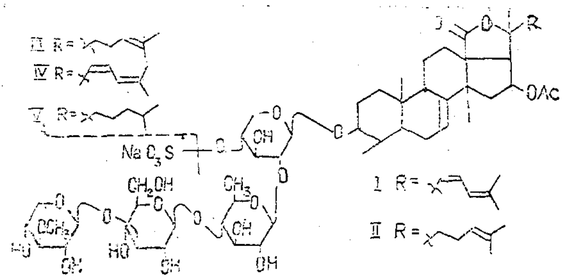
From the total triterpene glycosides of the holothurian, Eupentacta fraudatrix, by chromatography on silica gel (chloroform—methanol—water (65:25:4)) and with the aid of HPLC (Zorbax-ODS, 4.8 × 250 mm, 1 ml/min, water —methanol (65:35)), we have isolated a minor glycosidic component – cucumarioside G_3 (I), mp 208-211°C, $[\alpha]_D^{20}$ –85° (c 0.1, pyridine).



It followed from a comparison of the ^{13}C NMR spectra of cucumariosides G_1 (II) [1] and G_3 (I) and of their desulfated derivatives (III) and (IV), respectively, that these substances had identical carbohydrate chains and differed only by the structures of the aglycons. On the other hand, the signals in the ^{13}C and ^{1}H NMR spectra of the aglycon moiety of cucumarioside G_3 coincided completely with the corresponding signals in the spectra of cucumarioside C_1 [2] isolated from the same total glycosides earlier and having 16β-acetoxyholosta-7,22Z,24-trien-3β-ol as its aglycon. On the basis of these facts it was concluded that the structure of cucumarioside G_3 corresponded to formula (I).

To confirm this conclusion, desulfated cucumarioside G_3 (IV), mp 250°C (decomp.), $[\alpha]_D^{20}$ –13° (c 0.1, pyridine) was subjected to catalytic hydrogenation, giving the tetrahydro derivative (V), identical in its physicochemical and spectral characteristics, and also in the results of monosaccharide analysis (GLC—MS in the form of aldononitrile peracetates), with the hydrogenated desulfated derivative of cucumariosdie C_1 [2].

Cucumarioside G_3 is the first glycoside containing both a dienic system in the side-chain of the aglycon and also an even number of monosaccharide units [2, 3].

Thus, cucumarioside G_3 is 16β-acetoxy-3β-[O-(3-O-methyl-β-D-xylopyranosyl-(1→3)-O-β-D-glucopyranosyl-(1→4)-O-β-D-quinovopyranosyl (1→2)-(4-O-(sodium sulfator)-β-D-xylopyranosyloxy]holosta-7-22Z,24-triene.

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