(22), 175 (12), 161 (100), 147 (17), 133 (35), 122 (40), 119 (17), 107 (35), 105 (31). On treatment with sulfuric acid in ether, this hydrocarbon was converted into α-neoclovene. On the basis of these facts, we identified the compound obtained as β-panasinsene [1].

Thus, the biomimetic cyclization of caryophyllene into β-panasinsine takes place under the action of mercury(II) acetate.

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NEW ARTEFACTUAL GENINS FROM THE COMBINED HOLOTHURINS OF THE PACIFIC OCEAN HOLOTHURIAN *Holothuria squamifera*

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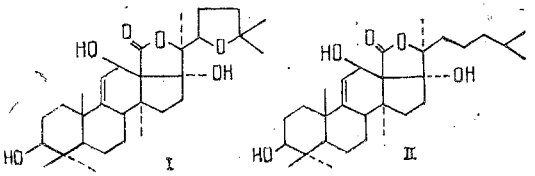
UDC 547.996+593.96

Continuing a study of the triterpene glycosides of holothurians of the family Holothuriidae, we have obtained the combined glycosides from the Pacific Ocean holothurian *Holothuria squamifera*. The native aglycones of the glycosides of the holothurians of the family Holothuriidae are unstable under the conditions for the hydrolysis of glycosidic bonds and are converted into artefactual products [1-3]. In actual fact, the acid hydrolysis (12% HCl, 90°C, 3 h) of the combined glycosides (50 mg) gave the sum of the artefactual genins.

Column chromatography on silica gel in the hexane—ethyl acetate (5:1) system led to the isolation of 10 mg of the completely transformed genin holothurin A, which was found to be identical with the known 22,25-epoxyholosta-7,9(11)-diene-3β,17α-diol [4]. Hexane—ethyl acetate (4:1 and 3:1) systems yielded the minor genins (I) and (II), which, according to ^{13}C and ^{1}H NMR spectroscopy, contained a 12β-hydroxy-9(11)-ene fragment. ^{13}C NMR ($CDCl_3$, ppm): 153.9 (C-9), 117.7 (C-11), 65.9 (C-12). PMR ($CDCl_3$, ppm): 5.16 (C-11, m, 1H), 4.53 (C-12. d, 1H), 3.25 (C-3, m, 1H).

Genins (I) and (II) have not been obtained previously.



22,25-Epoxyholost-9(11)-ene-3β,12α,17α-triol (I), $C_{30}H_{46}O_6$, mp 303-305°C, $[\alpha]_D^{20}$ −24° (c 0.5; $CHCl_3$). Mass spectrum: M^+ 502 m/z. Diacetate of the genin (I): mp 265-276°C, $[\alpha]_D^{20}$ −50° (c 0.42; $CHCl_3$). Mass spectrum, m/z 526 ($M^+ - CH_3COOH$), 466 ($M^+ - 2\ CH_3COOH$), 367.99 (100%); PMR ($CDCl_3$, δ, ppm): 5.73 (C-11, m, 1H, $J_{11,12}$ = 1.7 Hz), 5.06 (C-12, d, 1H), 4.50 (C-3, q, 1H), 4.06 (C-22, t, 1H), 2.08, 2.05 (C-3, C-12 $OCOCH_3$, 2s, 3H, 3H), 1.33 (C-21, s, 3H), 1.25 (C-32, s, 3H), 1.18 (C-19, s, 3H), 1.23, 1.22 (C-26, C-27, s, 3H, 3H), 0.91, 0.89 (C-30, C-31, s, 3H, 3H).

Holost-9(11)-ene-3β,12β,17α-triol (II), $C_{30}H_{48}O_5$, mp 262-264°C, $[\alpha]_D^{20}$ −31° (c 0.2; $CHCl_3$). Mass spectrum, m/z: 488 (M^+). The diacetate of the genin (II) had mp 256-258°C. Mass spectrum, m/z: 512 ($M^+ - CH_3COOH$, 100%), 452 ($M^+ - 2\ CH_3COOH$), 293 ($M^+ - 2\ CH_3COOH - CH_3 - CO_2$). PMR ($CDCl_3$, δ, ppm): 5.75 C-11, m, 1H, $J_{11,12}$ = 1.75 Hz), 5.05 (C-12, d, 1H), 4.50 (C-3, q, 1H), 2.7 (C-8, m, 1H), 2.05, 2.03 (C-3, C-12 $OCOCH_3$, s, 3H, 3H), 1.30 (C-21, s, 3H), 1.23 (C-32, s, 3H), 1.15 (C-19, s, 3H), 0.89 (C-26, C-27, d, 6H), 3H, 3H).

Genin(I) was the product of the partial transformation of the native aglycone holothurin A [5].

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PREPARATIVE SYNTHESIS OF β-SITOSTEROL TETRAACETYL-β-D-GLUCOPYRANOSIDE

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UDC 547.918+547.926

β-Sitosterol β-D-glucoside (I) is widely distributed in the vegetable kindgom [1, 2]. It exhibits a hypocholesteremic action [3] and inhibits prostaglandin synthetase [4]. It must be mentioned that (I) is a component of the glycoside preparation synthesized from the total sterols of tall oil, which possesses an antipyretic and antiinflammatory action [5]. The broad action spectrum and relative accessibility of the initial sterol [6] is stimulating the development of convenient methods of synthesis [1]. Several syntheses of β-sitosterol tetraacetyl-β-D-glucoside (II) carried out on decigram amounts of β-sitosterol have been described. Salway obtained (II) with a yield of 20% when the glycosylation reaction was performed under the Koenigs-Knorr conditions [7]. Pegel and Walker synthesized (II) by adding a twofold excess of α-acetobromoglucose (α-ABG) in toluene to a boiling mixture of β-sitosterol and silver carbonate in toluene with the simultaneous removal of the water formed by azeotropic distillation with the toluene [4]. The yield of (II) after crystallization from ethanol was 30%.

We have synthesized (II) under the conditions proposed for obtaining steroidal aryl glucuronides [8], with a change in the order of adding the components to the reaction mixture.

A solution of 7.0 g (17 mmole) of β-sitosterol and 8.7 g (21.2 mmole) of α-ABG in 80 ml of toluene was added dropwise over half an hour to a boiling suspension of 3.6 g (21.3 mmole) of cadmium carbonate (ch. ["pure"] grade) in 250 ml of toluene (kh.ch. ["chemically pure"] grade) with the simultaneous distillation of an azeotropic mixture of water and solvent. Boiling was continued for 2 h with the volume being kept constant. After the end of the reaction (TLC: absence of α-ABG), the catalyst was filtered off and was washed with a small amount of chloroform, and the solution was evaporated to a syrupy consistency. The residue was treated with 50 ml of methanol. The precipitate that deposited was separated from the mother liquor and crystallized from 400 ml of hexane. This gave chromatographically homogeneous crystalline (II) with a yield of 5.8 g (46%), mp 165-167°C, showing no depression of the melting point in a mixture with an authentic sample. The mother liquor contained mainly by-products of the glycosylation reaction: an acetate and di-β-sitosteryl ether, with trace amounts of (II) and its α anomer. The addition of the reagents in the order given by Conrow and Bernstein [8] led to a fall in the yield of (II) to 36%.

A solution of 3.3 g of (II) in 30 ml of absolute ethanol was treated with 5 ml of 0.1 N sodium methanolate in methanol. The mixture was stirred at room temperature for a day. The precipitate that had deposited was filtered off and washed with a small amount of methanol to give 2.3 g (yield 90%) of chromatographically homogeneous (I), identical with an authentic sample.

The high stereospecificity of glycosylation, the good yield, the ready availability of the reagents, and the ease of isolation of the product make the proposed modification convenient for use in the preparative synthesis of (II).

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