GLYCOSIDES OF MARINE INVERTEBRATES.

CUCUMARIOSIDE G_1 FROM THE HOLOTHURIAN *Cucumaria fraudatrix*

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We have previously established that the glycosidic fraction from the holothurian *Cucumaria fraudatrix* contains cucumarioside G_1 and have determined the structure of the native aglycone of this glycoside as 16β-acetoxyholosta-7,24-dien-3β-ol [1].

Cucumarioside G_1 (I), mp 216-218°C (from MeOH), $[\alpha]_D^{20}$ −38.8° (c 0.5; C_2H_5OH—H_2O, (1:1)) was isolated from a methanolic extract of the holothurian by successive chromatography on silica gel in the $CHCl_3$—MeOH—H_2O (75:25:1) system and on silanized silica gel in the C_2H_5OH—H_2O (1:5) system.

The sum of the monosaccharides obtained after the acid hydrolysis of cucumarioside G_1 was analyzed by GLC-MS in the form of the corresponding aldononitrile acetates: xylose, quinovose, glucose, and 3-O-methylxylose (1:1:1:1) were found in it, and a measurement of the specific rotation of the mixture of sugars showed that they were all present in the D forms.

The solvolysis of cucumarioside G_1 gave the desulfated derivative (II), mp 185-187°C (C_2H_5OH—H_2O (1:1)), $[\alpha]_D^{20}$ −12.5° (c 1; MeOH). The Hakomori methylation [2] of (II) with subsequent methanolysis and acetylation led to the formation of methyl 2-O-acetyl-3,4-di-O-methyl-α-xylopyranoside, methyl 4-O-acetyl-2,3-di-O-methyl-α- and -β-quinovopyranosides, methyl 3-O-acetyl-2,4,6-tri-O-methyl-α- and -β-glucopyranosides, and methyl 2,3,4-tri-O-methyl-α- and -β-xylopyranosides.

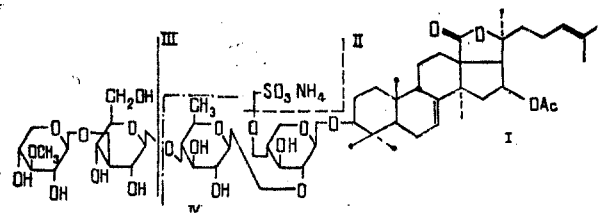
The results obtained showed that the carbohydrate chain is unbranched and has a terminal 3-O-methyl xylose or xylose residue.

To determine the sequence of the monosaccharides in the carbohydrate chain, we performed the enzymatic cleavage of cucumarioside C_1 with cellulase. This gave progenin (III), mp 186-188°C (from ethanol), $[\alpha]_D^{20}$ −22.5° (c 0.4; MeOH), yielding xylose and quinovose after acid hydrolysis.

The methylation, methanolysis, and acetylation of the solvolysis product of progenin (IV), mp 222-224°C (from ethanol), $[\alpha]_D^{20}$ − 20°C (c 0.9; MeOH), led to the formation of methyl 2-acetyl-3,4-di-O-methyl-α-pyranoside and of methyl 2,3,4-tri-O-methyl-α- and -β-quinovopyranosides.

The chemical shifts of the anomeric carbons amounted to 104.6, 104.0(2), and 103.3 ppm in the ^{13}C NMR spectrum of (I) (solvent DMSO-d_6) and 106.1, 105.5(2) and 104.8 ppm in the spectrum of (II) (with pyridine-d_5 as solvent). These values indicate the β configurations of all the glycosidic bonds.

On the basis of these facts and also the results of the periodate oxidation of (I) and (II), cucumarioside G_1 was determined as 16β-acetoxyholosta-7,24-dien-3β-ol 3-O-[O-(3-O-methyl-β-D-xylopyranosyl)-(1→3)-O-β-D-glucopyranosyl-(1→4)-O-β-D-quinovopyranosyl-(1→2)-(4-O-sulfato-β-D-xylopyranoside)]:



The feature of the carbohydrate chain of this glycoside is the presence of a 3-O-methyl-xylose residue; this is the first time that it has been detected in hydrolysates of holothurian glycosides.

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ALLANTOIN FROM THE HERBAGE OF SOME SPECIES OF *Phaseolus*

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We have previously reported the isolation from *Phaseolus vulgaris* L. (kidney bean) of derivatives of coumarin and cinnamic acid [1]. Continuing an investigation of the chemical composition of the epigeal parts of plants of the genus *Phaseolus* – kidney bean, scarlet runner bean (*Ph. coccineus* L.), and mung bean (*Ph. aureus* (Roxb.) Piper), we have obtained a nitrogen-containing substance. For its isolation, the comminuted herbage was extracted exhaustively with 80% ethanol. The extract was concentrated to an aqueous residue and this was treated successively with organic solvents [1], and the aqueous residue was left at 10-12°C. Colorless crystals deposited. After recrystallization from water, a compound was obtained with mol. wt. 158 (mass spectrometry) having the composition $C_4H_6N_4O_3$, mp 234-236°C (decomp.).

When it was chromatographed on Filtrak FN-1 paper in the following systems: butanol–acetic acid–water (4:1:2) and (4:2:2) (R_f 0.35 and 0.39); water-saturated butanol (R_f 0.30); and butanol–pyridine–water (6:4:3) (R_f 0.41), followed by treatment with a 1% solution of p-dimethylaminobenzaldehyde in ethanol containing 5% of hydrochloric acid with heating to 50-60°C, the substance was revealed in the form of a yellow spot, which is characteristic for urea derivatives [2].

IR spectrum (KBr tablet), had absorption bands characteristic for the following functional groups: NH_2 (3442, 3346, 1606 cm^{-1}), NH (3230, 3070, 1538 cm^{-1}), and C=O (772, 1665 cm^{-1}).

The PMR spectrum (DMSO) had signals at 5.24 ppm (doublet, J = 8 Hz), 5.78 ppm (singlet), 6.83 (doublet, J = 8 Hz), 8.04 ppm (singlet), and 10.08 ppm (singlet), which characterize the protons at C-5, N-8, N-6, N-1, and N-3.

From its elementary composition and mass, IR, and PMR spectra and a comparison with an authentic sample, the substance isolated was identified as allantoin (5-ureidohydantoin).

Allantoin has been detected previously in the roots of scarlet runner bean [3]. The presence of allantoin in plants of the genus *Phaseolus* may, in all probability, serve as a chemotaxonomic index.

This is the first time that allantoin has been isolated from the epigeal parts of the *Phaseolus* species studied.

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