As can be seen from the table, the sterol fraction of the pyrosoma studied consisted of C_{26}–C_{30} steroid alcohols and was characterized by a high level not only of C_{27} but also of C_{28} compounds. The sterols isolated were stanols and Δ^{5}-, Δ^{22}-, $\Delta^{5,22}$-, and $\Delta^{5,24(28)}$-derivatives.

The steroid composition of P. giganteum has not been studied previously. However, the sterol fraction of a related species – Pyrosoma sp., living in the Atlantic Ocean – has been investigated [3]. The total sterols of O. giganteum and P. sp. proved to be similar. The composition of the total sterols of these free-floating colonial animals probably depends on their systematic position.

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A NEW ACETYLATED GLYCOSIDE FROM THE HOLOTHURIAN Cucumaria japonica

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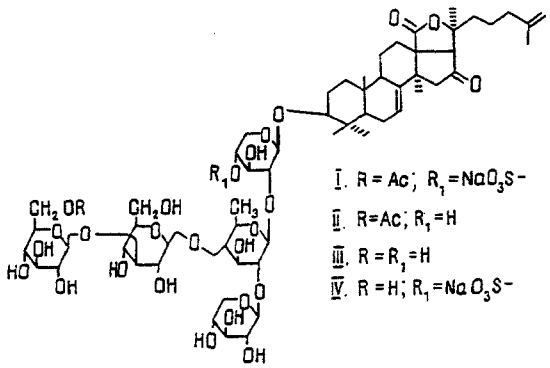
Continuing an investigation of the triterpene glycosides from the holothurian Cucumaria japonica [1], we have established the chemical structure of a new glycoside – cucumarioside A_1-2 (I). Compound (I) is a new holostane glycoside containing an acetylated monosaccharide residue in the carbohydrate chain.



The fraction of weakly polar glycosides containing (I) was obtained by chromatographing the total glycosides on silica gel [1]. It was not susceptible to further separation by the usual methods, but the desulfation of this fraction, followed by separation on silica gel [$CHCl_3$:CH_3OH (5:1)] and HPLC (Silasorb C-18, 60% C_2H_5OH), led to the isolation of the individual derivative (II), mp 201-203°C, $[\alpha]_{578}$ −96° (c 10; pyridine).

A comparison of the ^{13}C NMR spectra of (II) and of the desulfated derivative of cucumarioside A_1-2 (III) [1] permitted the conclusion that in (II), as compared with (III), an acetate group (170.4 and 20.6 ppm) was attached to the C-6 atom of the terminal glucose residue. In actual fact, in (II) the C-6 signal was shifted from 62.5 to 64.5 ppm and the C-5 signal from 78.1 to 75.1 ppm, which is explained by the acetylation effect [2]. Moreover, the assignment of these signals to the terminal glucose was confirmed by taking a series of

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partially relaxed spectra, in which a slower relaxation was observed for them than for the other monosaccharide residues [3].

The structure of (I) was also confirmed by the fact that when it was treated with a deacetylating agent (0.1% solution of NH_3 in 50% C_2H_5OH, 20 h), it gave (III) in quantitative yield, while the analogous treatment of the initial total glycosides did not change the impurity glycosides present in the initial fraction but converted (I) into the considerably more polar cucumarioside A_4-2 (IV) [1].

Thus, the structure of the aglycon, the sequence of linkage of the monosaccharide residues in the carbohydrate chain, and the position of the acetate group were established by a comparative study of (II) and (III), while the position of the sulfate group became clear after the formation of (IV), as described above. It follows unambiguously from this that cucumarioside A_1-2 (I) is 3β-O-{O-(6-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-β-D-glucopyranosyl-(1→4)-[O-β-D-xylopyranosyl-(1→2)]-O-β-D-quinovopyranosyl-(1→2)-(4-O-(sodium sulfato)-β-D-xylopyranosyl)}holosta-7,25-dien-16-one.

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A GLYCOSIDE OF SYRINGARESINOL FROM A TISSUE CULTURE OF *Scorsonera hispanica*

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Continuing a study of the chemical composition of a callous tumor tissue culture from *Scorsonera hispanica* [1], we have isolated syringaresinol O-β-D-glucopyranoside (I). The filtered cell mass was exhaustively extracted with 50% aqueous ethanol. The evaporated extract was fractionated in a continuous liquid–liquid extractor in the following systems: a) hexane–methanol (7:4) and b) chloroform–methanol–water (5:6:4). Glucoside (I) was isolated by droplet countercurrent chromatography in system (b) from the fraction of polar glycosides.

In nature, syringaresinol and its derivatives exist in the form of various stereoisomers or mixture of them [2]. The cells of *S. hispanica* produce a single stereoisomer, as follows from a consideration of chromatograms of an aqueous ethanolic extract of the tissue culture obtained by high-performance liquid chromatography. The structure of the syringaresinol glycoside was deduced from an analysis of the NMR spectra of its aglycon (II). These spectra showed that the molecule was completely symmetrical and agreed with literature information for a stereoisomer with the cis-linkage of the tetrahydrofuran rings and the pseudoequatorial arrangement of the aromatic substituents [3-6].

The aglycon (II) was obtained by the hydrolysis of (I) in boiling 5% caustic soda solution in an inert medium.

Contradictory information is given in the literature about the physicochemical constants of glycoside (I), and we therefore give our results in the scheme on the following page.

Syringaresinol O-β-D-glucopyranoside (I), $C_{28}H_{36}O_{13}$, white crystals, mp 177-179°C (ethanol), $[\alpha]_{546}^{25}$ −7° (c 0.72, ethanol). IR spectrum; ν_{max}^{KBR}, CM^{-1}: 3250-3500 (OH), 2830

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