

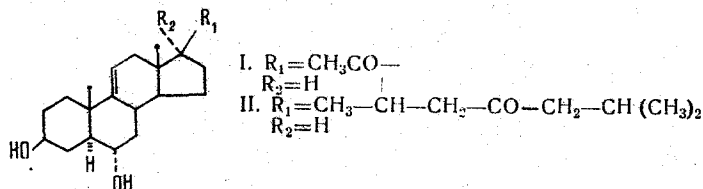
ASTEROSAPONIN FROM THE STARFISH *Linckia guildingi*

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We have studied the steroid glycosides of the Pacific Ocean starfish *Linckia guildingi*. The crude mixture of glycosides obtained by a known method [1] was chromatographed on a column of Polikhrom as we have described previously [2]. From the purified glycoside fraction by subsequent chromatography on a column of KSK silica gel (150 mesh) in chloroform-methanol-water systems with increasing concentrations of methanol and water from 15:15:2 to 15:30:3 we isolated a chromatographically individual glycoside which we have called asterosaponin L. It is a colorless amorphous substance with mp 222-225°C,  $[\alpha]_D^{20} -22.5^\circ$  (c 0.23; water). Asterosaponin L is similar in its chromatographic characteristics to asterosaponin B [3] [TLC, KSK silica gel, chloroform-methanol-water (60:30:4) and butan-1-ol-acetic acid-water (12:3:5) systems] and, like the latter, contains a carbonyl group (IR:  $\nu_{C=O} 1700 \text{ cm}^{-1}$ ).

The hydrolysis of asterosaponin L (2 N HCl, 90°C, 2 h) gave a mixture of two asterogenins. The main product was identified by gas-liquid chromatography (GLC) (3% of SE-30 on Chromaton, 270°C) and by a comparison of mass spectra (MS) with an authentic sample of 3 $\beta$ ,6 $\alpha$ -dihydroxy-5 $\alpha$ -pregn-9(11)-en-20-one (I):  $M^+$  332, m/e 314, 299, 296, 281, 229, 230, 211, 95, 43. The minor asterogenin was identified similarly as 24,25-dihydromarthasterone (II)  $M^+$  416, m/e 316, 301, 298, 265, 108, 95, 85, 57.



To determine the monosaccharide composition, the sugars formed in the hydrolysis of the asterosaponin were analyzed by the GLC-MS method (3% of QF-1 on Gas-Chrom, Q, 110-240°C) in the form of the corresponding aldonitriles by comparison with the corresponding standard derivatives. It was shown that the carbohydrate chain of asterosaponin L consists of fucose, quinovose, and xylose. Thus, asterosaponin L is a new steroid glycoside "of marine origin" giving on hydrolysis as the main asterogenin the same product as asterogenin B but differing from the latter by the absence of galactose in the carbohydrate chain.

Samples of asterosaponin B and of genins (I) and (II) were kindly supplied by Prof. A. Maki and Sh. Ikegami.

LITERATURE CITED

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