Labidiasteroside A, a Novel Saponin from the Antartic Starfish *Labidiaster Annulatus*

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Abstract: Purification of the ethanolic extract of the starfish L. annulatus led to the isolation of two sulfated glycosides and a pentahydroxylated steroid. One of the saponins contains a novel pentasaccharide chain attached to C-6 of the steroidal aglycone.

Introduction

Starfish are characterized by the content of saponins, toxic compounds acting as defense agents against predators [1]. These compounds present a sulfate group at C-3 and a oligosaccharide moiety at C-6 of the steroidal aglycone. In continuation of our studies on antarctic echinoderms [2] and with the aim of evaluating the antiviral activity of the secondary metabolites isolated from these organisms, we have investigated the ethanolic extract of the starfish *L. annulatus*.

Experimental

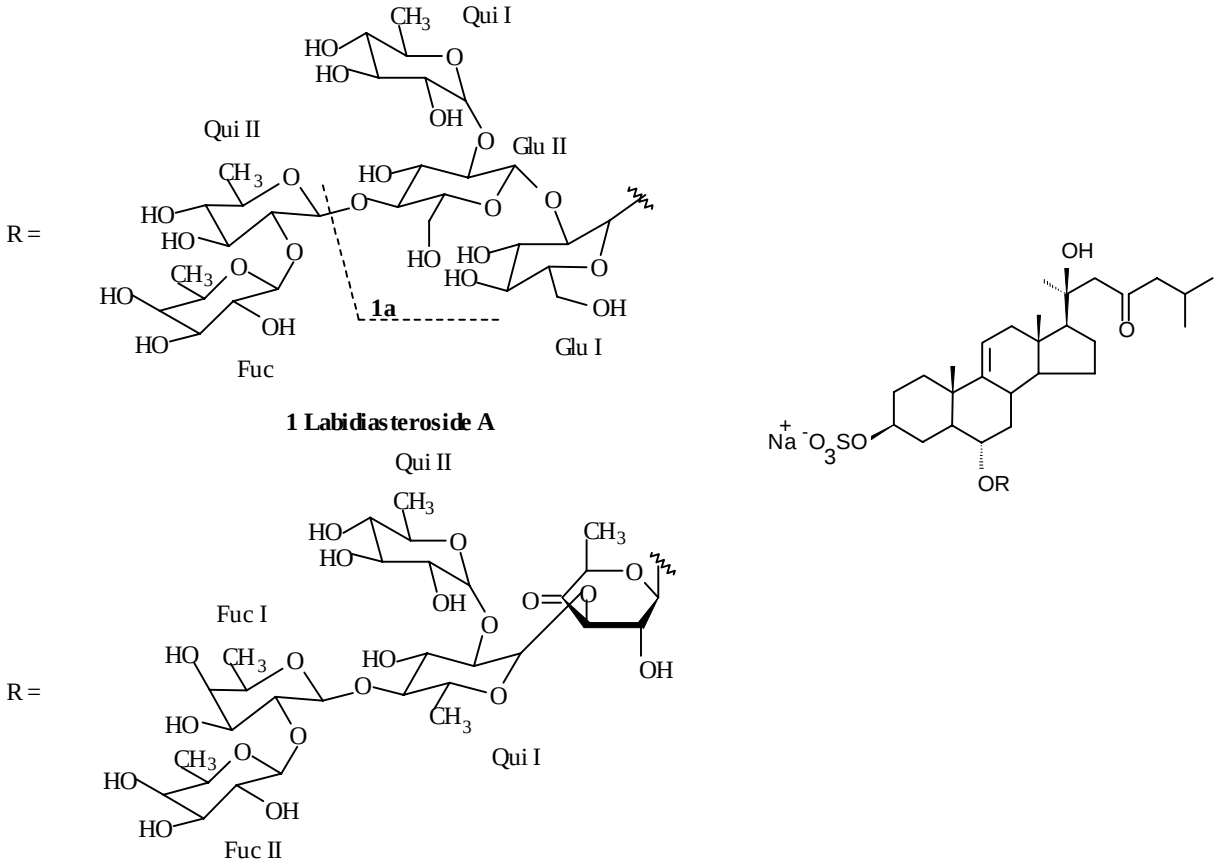
The organisms were extracted with ethanol and the aqueous extract was partitioned between water and cyclohexane. The aqueous phase was eluted through a column of Amberlite XAD-2, washed with water and eluted with methanol. The methanolic extract was purified by chromatography on Sephadex LH 60 and vacuum-dry column chromatography on silica gel C-18, using mixtures of methanol:water and methanol. Fractions containing the polar compounds were purified by HPLC.

Results and Discussion

Purification of the ethanolic extract from *L. annulatus* led to the isolation of two sulfated pentaglycosides (**1**, **2**). Both compounds show the same steroidal aglycone and differ in the oligosaccharide chain. Saponin **1** contains a novel oligosaccharide chain not previously reported for this type of compounds. In order to determine its structure, we performed spectroscopic studies (^{1}H-NMR, ^{13}C-NMR,

FABMS) as well as acid hydrolysis to obtain the monosaccharides, which were analyzed by glc as the peracetilated alditols. Enzymatic hydrolysis of saponin **1** with a glycosidase mixture of *Charonia lampas* rendered triglycoside **1a**.

On the other hand, purification of the less polar fractions led to the isolation of (25S)-5α-cholestane-3β,6β,15α,16β,26-pentaol. The configuration of C-25 was determined as *S* by correlating ^{1}H-NMR data of their (+)-(*R*)- and (-)-(*S*)-α-methoxy-(α-trifluoromethyl)-phenylacetic acid esters with those of related steroids.



1 Labidiasteroside A

2 Ovarian asterosaponin 1

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References and Notes

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