Labidiasteroside A, a Novel Saponin from the Antarctic 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 (¹H-NMR, ¹³C-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 lamopas 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 1H-NMR data of their (+)-(R)- and (-)-(S)-α-methoxy-(α-trifluoromethyl)-phenylacetic acid esters with those of related steroids.

![Diagram of Labidiosteroid A and Ovarian asterosaponin 1]

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References and Notes