

A STEROIDAL SAPONIN FROM A PAPUA NEW GUINEAN SPONGE

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Abstract

A steroidal saponin has been isolated from a sponge, collected at Salmaua in Papua New Guinea. The structure of the saponin has been assigned as 3 β -hydroxy-4,4-dimethylcholesta-8, 24-dien-23-one with five sugars on basis of the spectroscopic data.

Results and Discussion

Saponins are the predominant metabolites of starfishes and sea cucumbers. Although sponges are a rich source of many interesting compounds, only a few saponins have ever been isolated from sponges (D'AURIA, M. V. *et al.*, 1992). We wish to report on the isolation and partial structural characterization of a saponin isolated from a Papua New Guinean sponge.

Twenty kinds of sponges were collected at Salamua (Papua New Guinea) during December of 1991. The animals were frozen immediately after collection and kept frozen (-60 to -20°) until extraction. They were cut into small pieces and soaked in methanol. The combined methanol extracts were evaporated under reduced pressure. Samples of each extract were submitted for biological testing including antibacterial, antifungal, antiviral and cytotoxicity. While waiting for the biological testing results, chemical studies were begun on one of the sponges.

The methanol extract of the sponge (4.3kg) was partitioned between water and *n*-butanol. A portion (4.07 g) of the *n*-butanol extract (20.6 g) was chromatographed over a column of silica gel using dichloromethane with methanol and water and increasing proportions of methanol and water to elute the column. The fractions (1.68 g) eluted with dichloromethane-methanol-water (13 : 7 : 2) were further separated on a C₁₈ reversed-phase column and elution with water-methanol mixture and increasing proportions of methanol to give a glycosidic mixture (756 mg). The mixture was submitted to a column of LH-20 and elution with methanol followed by HPLC chromatography using a C₁₈ reversed-phase column with methanol and water (9 : 1) to afford compound (1) (57 mg) as an amorphous powder.

The IR spectrum of the compound (1) exhibited absorption bands due to a hydroxyl group at 3450 cm⁻¹ and a carbonyl group (an α , β -unsaturated carbonyl and/or an amide group) at 1680-1640 cm⁻¹. In the ¹H NMR spectrum singlet signals due to three methyl protons on a 4,4-dimethyl steroid were observed at δ 0.67, 1.06 and 1.38. A double doublet at δ 3.22 (1H, *J*=4.4 and 11.4 Hz) suggested the presence of a 3 β -hydroxy-4,4-dimethyl arrangement. Two singlets at δ 2.05 and 2.08 (3H each) were due to two acetyl groups. Three singlets at δ 1.78 (3H, *s*), 2.23 (3H, *s*) and 6.18 (1H, *br s*) were assigned to a (CH₃)₂C=CHCO moiety, which was consistent with the ¹³C NMR spectral data (δ 20.6, 27.3, 125.0, 154.0 and 200.7). Four doublets at δ 4.69 (1H, *d*, *J*=7.3 Hz), 5.26 (1H, *d*, *J*=7.7 Hz), 5.31 (1H, *d*, *J*=8.4 Hz), 5.47 (1H, *d*, *J*=7.3 Hz) and 5.62 (1H, *d*, *J*=8.1 Hz) were indicative of

five sugars. The presence of tetra-substituted double bond at C-8 was determined by comparing the ^{13}C NMR spectrum of 1 [δ 127.7 (C-8) and 136.3 (C-9)] with that of (5 α)-cholest-8-en-3 β -ol.

Therefore, the aglycone of 1 is tentatively assigned as 3 β -hydroxy-4,4-dimethylcholesta-8, 24-dien-23-one (SCHMITZ, F. J. *et al.*, 1988).

These are results that have been obtained to date. Work is now progressing on the task of identifying the sugar residues. It will be interesting to compare the structure of this saponin with the structure of other saponins isolated from quite different and unrelated marine organisms.

References

- D'AURIA, M.V., PALOMA, L.G., MINALE, L. and RICCIO, R. 1992. *Tetrahedron* 48 : 491-498 and references cited therein.
- SCHMITZ, F.J., KSEBATI, M.B., GUNASEKERA, S.P. and AGARWAL, S. 1988. *J. Org. Chem.* 53 : 5941-5947.