

TRITERPENOIDS FROM *BALANOPHORA ABBREVIATA* AND  
*BALANOPHORA INDICA*

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The genus *Balanophora* (Balanophoraceae) consists of several species of fleshy fungus-like herb parasites which are considered to be rare (1). They mostly grow on roots of large trees and shrubs belonging to *Macarandra*, *Hibiscus*, and *Coffea*. Chemical investigation of the parasitic plants will be of immense importance in understanding the host-parasite interactions, and hence a systematic examination of *Balanophora abbreviata* Bl. and *Balanophora indica* Wall was undertaken. Extraction of the rhizomes of *B. abbreviata* afforded the known triterpenes,  $\alpha$ -amyrin acetate,  $\beta$ -amyrin acetate, and lupeol acetate, while *B. indica* yielded  $\beta$ -amyrin palmitate, taraxasterol, and taraxastenone. The structures of these compounds were confirmed by their spectral data and by comparison with reference compounds.

EXPERIMENTAL<sup>1</sup>

PLANT MATERIAL.—*B. abbreviata* is rare and was collected from Ranganthittu (Karnataka), while *B. indica*, commonly found in coffee plantations, was collected from the Biligirirangan hills in the Mysore district (Karnataka).

EXTRACTION AND ISOLATION.—Air-dried and powdered rhizomes of *B. abbreviata* (100 g) were extracted successively with hexane and MeOH. The hexane extract was concentrated and the resulting gum (5 g) was chromatographed on silica gel (100 g) and eluted with hexane- $C_6H_6$  (9:1). The first fraction (3 g), obtained as an oil, consisted of mostly long-chain fatty alcohols. The second and third fractions gave positive tests for triterpenoids. These two fractions were combined and separated into three components by preparative tlc and were identified as  $\alpha$ -amyrin acetate,  $\beta$ -amyrin acetate, and lupeol acetate by mp, ir, ms, and <sup>1</sup>H-nmr, and finally by comparison with authentic samples.

Air-dried rhizomes of *B. indica* (100 g) were similarly extracted with hexane and MeOH, successively. Both the extracts showed the same compounds on tlc, and hence, were combined and chromatographed on silica gel (200 g). The fractions of hexane- $C_6H_6$  (9:1) afforded  $\beta$ -amyrin palmitate (500 mg); hexane- $C_6H_6$  (7:3) gave taraxastenone (700 mg); and hexane- $C_6H_6$  (1:1) afforded taraxasterol (1.5 g). These compounds were identified by mp, ir, ms, <sup>1</sup>H-nmr, and finally by comparison with authentic samples.

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<sup>1</sup>Full details of the isolation and identification are available on request to the senior author.

MARINE ORGANIC CHEMISTRY, III. ISOLATION OF 3 $\beta$ , 6 $\alpha$ -DIHYDROXY-5 $\alpha$ -  
CHOLEST-9(11)-EN-23-ONE FROM THE STARFISH *STICHAETER STRIATUS*

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The presence of toxic saponins in starfish has been reported several times (1,2). These saponins are hemolytic, cytotoxic and antiviral, and induce escape reactions in mollusks (3-5), etc.

Since then, several steroidal saponinogenins have been isolated by hydrolysis of the saponin mixture of starfish (6,7).

Continuing with our work on biologically active compounds of marine origin (8-11), we have been working on saponin constituents of the abundant Chilean starfish *Stichaster striatus* Mueller and Troschel and have isolated, by acid hydrolysis of the saponin mixture, a steroidal saponinogenin of the structure 3 $\beta$ , 6 $\alpha$ -dihydroxy-5 $\alpha$ -cholest-9(11)-en-23-one.

#### EXPERIMENTAL

**ANIMAL COLLECTION AND EXTRACTION.**—Starfish collected in February, 1981, in Cocholhue (36° 36' S; 72° 59' W) were chopped and extracted with 50% aqueous EtOH.

**ISOLATION OF THE SAPOGENIN.**—Hydrolysis of the crude extracts with 2.5 N HCl at 100° for 3 h furnished a mixture of water-insoluble aglycones, which were partially separated by silica gel column chromatography using petroleum ether-EtOAc mixtures as eluant. Tlc on silica gel PF 254 with solvent systems CHCl<sub>3</sub>-MeOH (9:1) and EtOAc-petroleum ether (7:3) still revealed a few spots, so further purification was necessary using medium pressure chromatography with silica gel.

**IDENTIFICATION OF THE SAPOGENIN.**—The major aglycone crystallized from MeOH (1.4 × 10<sup>-3</sup>% dry weight of starfish) mp 162-165°. M<sup>+</sup> 416, 323994 C<sub>27</sub>H<sub>44</sub>O<sub>3</sub>,  $\lambda$  max (MeOH) no distinctive uv absorption maximum,  $\nu$  max (KBr) 3330, 1710 cm<sup>-1</sup>. Its high resolution mass spectrum contained a peak of *m/z* 316 (M-100, 17.8%) indicative of a 23-oxo function and interpreted as cleavage of a 20-22 bond and 1H transfer from C-17, and also peaks at 416 (M<sup>+</sup>, 0.85%), 316 (17.81%), 301 (6.02%), 298 (7.4%), 285 (100%), 283 (10.9%), 267 (7.21%), 245 (0.84%).

Its <sup>1</sup>H-nmr spectrum (360 MHz) depicted  $\delta$  CDCl<sub>3</sub>, 0.63 (s, 13-Me), 0.915 and 0.90 (3 × 3H, each d, *J* 8 Hz, 20-Me and 25-Me<sub>2</sub>), 0.95 (s, 10-Me) a carbinol methine at 3.58 (m, 3 $\alpha$  and 6 $\beta$ -H), and an olefinic proton at 5.29 ppm (d, *J* 5 Hz, 11-H). These data indicate that the major aglycone is dihydromarthasterone [3 $\beta$ , 6 $\alpha$ -dihydroxy-5 $\alpha$ -cholest-9(11)-en-23-one], which was first reported in *Martbasterias glacialis* (12). Cholesterol and  $\Delta^7$ -cholestenol (lathosterol) were also isolated; their structure determination was based on their physical constants. Work on minor genins of *S. striatus* is currently in progress.

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