

OCCURRENCE OF 23,24 $\epsilon$ -dimethylcholesta-5,22-dien-3 $\beta$ -ol IN THE BRAZILIAN GORGONIAN  
*Phyllogorgia dilatata* (Octocorallia, Gorgonacea) AND IN ITS ASSOCIATED ZOOXANTHELLA

A. KELECOM, A.M. SOLE CAVA & G.J. KANNENGIESSER

SARSA - Unidade de Pesquisas  
 Rua do Rocha, 155 CEP 20960 Rio de Janeiro BRAZIL

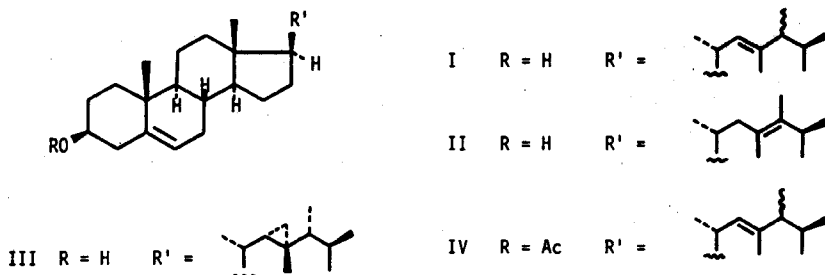
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23,24 $\epsilon$ -dimethylcholesta-5,22-dien-3 $\beta$ -ol(I)<sup>1</sup> and its  $\Delta^{23}$  homologue II<sup>2</sup> have been isolated from various soft corals<sup>3</sup> and may be considered as the two first representatives of a new sterol side chain alkylation series. Before its obtention from *Sarcophyton elegans*<sup>1</sup>, the existence of I had been postulated<sup>4</sup> as an intermediate in the biosynthesis of gorgosterol (III) to which it is clearly related<sup>5</sup>. With the exception of an unidentified species of zoanthid (Hexacorallia)<sup>3</sup>, sterol I seems to be restricted to alcyonarians (Octocorallia, Alcyonacea). To our knowledge, it had never been obtained from the closely related gorgonians (Octocorallia, Gorgonacea)<sup>6</sup>.

We have investigated the Brazilian endemic gorgonian *Phyllogorgia dilatata* (Esper, 1806) widely distributed along the coast from Rio de Janeiro to Pernambuco.

From the methylene chloride crude extract of the freeze-dried animal we obtained, by silica gel column chromatography, the crude free mono-hydroxy sterol fraction (yield = 0.2% of dry weight). Acetylation by usual methods and subsequent chromatography on argentic silica gel (15% AgNO<sub>3</sub>) afforded acetyl-I (IV) over 92% pure (by g.l.c.)<sup>7a</sup>. Identification of IV is based on high and low resolution mass spectrometry<sup>7b</sup> and on the <sup>1</sup>H-NMR spectrum<sup>7c</sup> identical by comparison with published data<sup>1,3</sup>. Double irradiation experiments agree with the identification. IV was obtained in high yield (12%) from the steryl acetate mixture and in 0.02% yield from the dry animal.

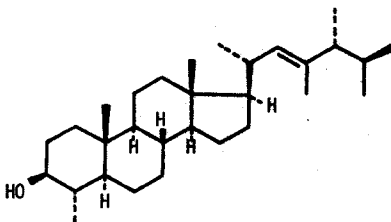
In alcyonarians, I is obtained together with gorgosterol (III)<sup>3</sup> in apparently reversed relative proportions<sup>3</sup>, whereas no C-30 sterols have been found in the crude sterol mixture of *P. dilatata*. Investigating geographic and/or seasonal variations responsible for the absence of III, we collected eight gorgonian samples from a) the Abrolhos archipelago (Bahia), b) Guarapari (Espírito Santo) and c) Cabo Frio (Rio de Janeiro), from the latter place at different periods of the year. I was always present and only slight variations in the sterol composition of the eight samples were observed. Gorgosterol (III), however, was found in none of them which may indicate a lack of the enzymatic system transforming I into III.



The occurrence of gorgosterol in coelenterates has been associated with the presence of symbiotic dinoflagellate algae, *i.e.* zooxanthellae<sup>8</sup>. One may thus speculate about the dinoflagellate origin of sterol I. Furthermore, dinosterol (V), a 4 $\alpha$ -methyl-5 $\alpha$ -stanol with the *same side chain alkylation* as I, has been isolated from free living dinoflagellates<sup>9-11</sup>, gorgonians<sup>12</sup> and also from the cultured zooxanthella isolated from the zoanthid *Zoanthus sociatus* but neither III nor I were found in this zooxanthella<sup>13</sup>.

Thus we isolated the zooxanthella of *P. dilatata* by known experimental procedures<sup>8</sup>. The crude free mono-hydroxy sterol fraction (yield = 1.7% from the dry alga) was acetylated and chromatographed on a column of silicic acid-15% AgNO<sub>3</sub>. GC examination<sup>7a</sup> of the eluted fractions showed the presence of acetyl-I (IV) unambiguously identified by co-injection with an authentic sample. Labeling experiments on cultured zooxanthella from *P. dilatata* could answer the problem of the dinoflagellate *versus* coelenterate origin of I.

V



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7. a) GC analysis were performed on a VARIAN 2440 apparatus equipped with a FID system on a 3% OV-17 on VARAPORT 30 column, operating in isotherm mode at 2909. In these conditions, IV (acetyl-I) has a retention time of 1.32 relative to cholesteryl-acetate.  
b) Mass spectra were determined on a VARIAN CH5-DF instrument.  
c) NMR spectra were recorded in CDCl<sub>3</sub> solutions on a VARIAN EM 390 apparatus equipped with the VARIAN-3930 spin decoupler; Me<sub>4</sub>Si was used as internal reference.
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