STUDIES ON THE STEROLS OF A BROWN SEAWEED
*HYENGARIA STELLATA* FROM PAKISTAN

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Abstract

The marine benthic brown algae *Hyengaria stellata* (Borg.) Borgesen, collected from the coast of Karachi was studied for its sterol composition. Analysis of ethyl acetate fraction of the methanolic extract of the seaweed by gas-liquid chromatography—mass spectrometry revealed the presence of cholesterol, 24-methyl cholesterol and ergosterol. The last two sterols are being reported for the first time from a brown seaweed.

Introduction

*Iyengaria stellata* (Scytosiphonales, Phaeophyta) was initially reported from the coast of Karachi as *Colpomenia sinuosa* f. *tuberculata* by Anand (1940) and later by Nizamuddin & Gessner (1970) as *I. stellata*. The morphology, anatomy and ecology of *I. stellata* has also been described (Nizamuddin & Begum, 1978). The chemical constituents of closely related seaweeds like *Colpomenia sinuosa* (Hussain, 1975, Hussain et al., 1983 Parekh et al., 1984), and *Endarachne binghamiae* (Bano et al., 1987) have been studied. *I. stellata* contains 1.27% crude oil, 15.15% of its total fat are sterols (Qasim, 1986). The sterol composition of *I. stellata* is presented here.

Materials and Methods

*I. stellata* collected from Buleji near Karachi was air dried, (970 g), ground and extracted with ethyl alcohol (EtOH) at room temperature. The extract (9.3 g) in methanol (MeOH) was refluxed with 100 ml I N KOH in water for 3 h and the reaction mixture evaporated to remove MeOH, diluted with water and then extracted with diethyl ether (Et2O). The unsaponifiable lipid (0.5 g) was chromatographed on silica gel in ethyl acetate (EtOAc): n-hexane (C6H14) yielding a fraction of sterols (0.5 mg). The GLC-mass spectrometry of sterol fraction was performed with FINNING-MAT 112 S mass spectrometer coupled with a Varian gas chromatograph equipped with a Sulpeco Sp-2100 glass capillary column (30 m x 0.25 mm i.d.) with carrier gas (N2) flow of 2 ml/min., at 260°C.

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Fig. 1: Gas chromatograms and mass spectra of the sterol fraction of *Iyengaria stellata*.
Results and Discussion

In *I. stellata* the GLC analysis, mass and fragmentation pattern of the sterol fraction indicated the presence of 3 constituents: predominantly a C<sub>27</sub> sterol (identified as cholesterol), together with minute quantity of C<sub>28</sub> sterol (identified as 24-methylcholesterol) and a small amount of a C<sub>28</sub> sterol (identified as ergosterol, Fig. 1). The relative retention time is given in Table 1. The respective identification of sterols through MS is given below:

**Cholesterol:** MS at m/z (assignments, abundance) 386.45 M<sup>+</sup> (C<sub>27</sub>H<sub>46</sub>O<sub>2</sub>, 622), 371 (M<sup>+</sup>-CH<sub>3</sub>, 332), 368 (M<sup>+</sup>-H<sub>2</sub>O, 362), 353 (M<sup>+</sup>-CH<sub>3</sub>-H<sub>2</sub>O, 373), 273 (M<sup>+</sup>-side chain, 168), 255 (M<sup>+</sup>-side chain-C<sub>16</sub>-C<sub>17</sub>, 77), 229 (M<sup>+</sup>-side chain-C<sub>16</sub>-C<sub>17</sub>-OH, 87), 231 (M<sup>+</sup>-side chain-ring D cleavage, 184), 213 (M<sup>+</sup>-side chain-H<sub>2</sub>O-ring D cleavage), 121 (156), 107 (251).

**24-methylcholesterol:** MS at m/z (assignments, abundance) 400.40 M<sup>+</sup> (C<sub>28</sub>H<sub>48</sub>O<sub>2</sub>, 60), 385 (M<sup>+</sup>-CH<sub>3</sub>, 4), 382 (M<sup>+</sup>-H<sub>2</sub>O, 19), 367 (M<sup>+</sup>-CH<sub>2</sub>-H<sub>2</sub>O, 2), 315 (86), 300 (86), 273 (M<sup>+</sup>-side chain, 7), 271 (134), 255 (48), 231 (43), 207 (156), 107 (110).

**Ergosterol:** MS at m/z (assignments, abundance) 396.25 (C<sub>28</sub>H<sub>44</sub>O<sub>2</sub>, 91), 381 (M<sup>+</sup>-CH<sub>3</sub>, 46), 325 (M<sup>+</sup>-C<sub>5</sub>H<sub>11</sub>, 61), 314 (M<sup>+</sup>-C<sub>6</sub>H<sub>10</sub>, 583), 300 (M<sup>+</sup>-C<sub>7</sub>H<sub>12</sub>, 83) 271 (M<sup>+</sup>-side chain, 112), 253 (M<sup>+</sup>-side chain-H<sub>2</sub>O, 84), 213 (109), 207 (154), 107 (128).

Cholesterol, a major component of Rhodophyta often been reported from brown seaweeds (Goad, 1978), was found as a major component in *I. stellata*. Although, 24-methylene cholesterol has been detected in the thalli of *Laminaria digitata* (Patterson, 1971) and *Endarachne binghamiae* (Bano *et al.*, 1987), but 24-methyl cholesterol has not been reported from any brown alga. In *Pelvetia canaliculata* 24-oxocholesterol has been reported as an artefact (Motzfeldt, 1970), hence methylation at 24th carbon is highly probable.

Table 1. Gas-liquid chromatographic retention time of the sterols of *Iyengaria stellata*.

<table>
<thead>
<tr>
<th>Trivial Name</th>
<th>Systematic Name</th>
<th>Mol. Formula</th>
<th>Mol. Wt.</th>
<th>Retention Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cholesterol</td>
<td>Cholest-5-en-3β-ol</td>
<td>C&lt;sub&gt;27&lt;/sub&gt;H&lt;sub&gt;46&lt;/sub&gt;O</td>
<td>386</td>
<td>20.89</td>
</tr>
<tr>
<td>24-Methyl Cholesterol</td>
<td>24-R-Methyl-cholester-5-en-3β-ol</td>
<td>C&lt;sub&gt;28&lt;/sub&gt;H&lt;sub&gt;48&lt;/sub&gt;O</td>
<td>400</td>
<td>21.43</td>
</tr>
<tr>
<td>Ergosterol</td>
<td>24-R-Methyl-cholesta-5, 7-22-trien-3β-ol</td>
<td>C&lt;sub&gt;28&lt;/sub&gt;H&lt;sub&gt;44&lt;/sub&gt;O</td>
<td>396</td>
<td>32.01</td>
</tr>
</tbody>
</table>
Ergosterol is the major component of fungi and higher plants. Although found in certain green and red seaweeds (Goodwin, 1974), it has not so far been reported from any brown alga. I. stellata appears peculiar in this regard as it contains small quantity of ergosterol. This would also indicate that I. stellata is a distinct taxon from Colpomenia sinuosa, with which it has been confused by certain taxonomists.

References


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