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AN OVERVIEW OF THE RED ALGA *HALYMENIA*

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Abstract:Red algae are not only being used as nutritional supplements but also, they are being used in skincare ingredients. They have been used in traditional medicines for ages. Various biological activities have been reported in various red algae. *Halymenia*, a red alga, has also been reported to show many different biological activities such as anti-coagulant, antitumor, antibacterial, hypocholesterolemic, antiaging etc. various classes of chemical constituents have been reported from *Halymenia* which include, fatty acids, esters, triterpenes, sterols and sphingosines etc. Present article compiles the chemical constituents and biological activities reported from *Halymenia* extracts and compounds isolated from them.

***Keywords*- Red Alga, *Halymenia*, chemical constituents, biological activities**

INTRODUCTION

The algae form one of the largest groups of the innumerable organisms that make the ocean their habitat. The seaweeds (*Gelidium, Gracilaria, Chondrus*, etc.) belonging to rhodophyta are known for a long time as good sources for agar, algin, and iodine and profitably exploited on an industrial scale in many countries. Agar and carrageenin[10] are two red algal mucilages that are widely used for gelling and thickening purposes in the food and pharmaceutical industries. Some of the algae are known as food (*Porphyra*) and fodder. It may be noted that the secondary metabolites from this abundant marine resource do indeed demand careful chemical investigation in respect of the types of compounds for prospective pharmacological and related uses to be followed by exploitation with profit.

There are four major groups of macroscopic algae that make-up most of the benthic flora, namely Cyanophyta (blue-green algae), the Chlorophyta (green algae), the Phaeophyta (brown algae) and the Rhodophyta (red algae). However, their numbers and populations in a locality vary, depending on different climatic and environmental conditions that exist. Among these, algae of Rhodophyta are of considerable interest.

The red algae (Rhodophyta) are a large group of mostly multicellular, marine algae, including many types of seaweeds. Red algae such as 'dulce' and 'nori' are a traditional part of European and Asian cuisine and are used to make certain products like agar and food additives[2]. Red algae are pigmented with chlorophyll 'a' and various proteins called phycobilins, which gives them a distinctive red color. There are approximately 6000 species of red algae, most are marine, only a few occur in fresh water. They usually grow attached to rocks or other algae. The coralline red algae deposit calcium carbonate in their walls making them particularly tough and stony. They are often abundant, ecologically important, and widespread from the arctic regions to the tropics and play an important role in building tropical reef communities. Coralline red algae can form an algal ridge that absorbs wave energy and thereby protects the more delicate organisms that inhabit the sheltered lagoons and back-reef habitats.

The present review deals with chemical investigation of the red alga *Halymenia porphyroides*, which belongs to the family halymeniaceae. It can be classified as Phylum: Rhodophyta, Class: Rhodophyceae, Order: Cryptonemiales, Family: Halymeniaceae, Genus: *Halymenia. Halymenia* has a critical account of confused nomenclature. The accepted name for *H.porphyroides* is *H. porphyraeformis.* Other species of the genus *Halymenia* are: *H. acuminata, H. bermindensis, H. ceylanica, H. dichotoma, H. duchassaingii, H. durvillaei, H. floresia, H. floridana, H. formosa, H. furcellata, H. integra, H. latifolia, H. latissimum, H. ligulatum, H. microcarpa, H. monardiana, H. patens, H. platycarpa, H. rosaceae, H. spathulata, H. trigon.* These are cylindrical, compressed or foliose, lanceolate to orbiculate, entire, cleft, forked or proliferous, distinctly stipitate. These are attached to the substratum by a holdfast, which is basal disc, soft gelatinous to firm, monoecious where known.These are widely distributed in warm temperate to tropical seas of India, Kenya, Pakistan, and Sri Lanka.

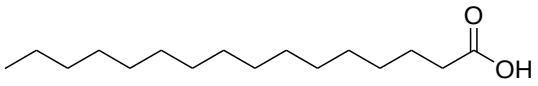
CHEMICAL CONSTITUENTS

Different classes of compounds have been reported from *Halymenia* such as fatty acids derivatives, steroids, triterpenes, ceramides, alkaloids etc. The methanol and hexane extracts of *Halymenia sp*. have shown[3] to contain 5 classes active compounds namely, alkaloids, flavonoids, tannins, triterpenonids and saponins.

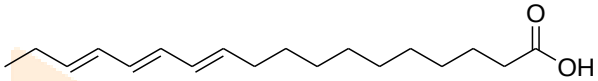
Fatty acids and terpenoids

A large number of long chain saturated and unsaturated fatty acids have been isolated and identified from rhodophytes *Halymenia porphyroides*[4]. Two fatty acids viz. palmitic acid and α-linoleic acid were reported from the ethyl acetate extract of red alga *H. durvillei*. Bicyclo [2.2.1] heptane, Dodecanoic acid, Tridecanoic acid, Hexadecanal, Clofibric acid, Pentadecanoic acid , 2-Undecanone, 2,2,2-Trifluoroethyl 3-cyclohexylpropionate , Palmitoleic acid , (Z)-7-Hexadecene , n-Hexadecanoic acid, Bicyclo[2.2.2]oct-2-ene, 2-Thiophenemethanol, methylester, Z-11-Pentadecenol , Shikimic acid , 1-Naphthalenamine, 1-Nonadecene, (Z, Z)-9,12-Octadecadienoic acid, 2-Butyl-5-hexyloctahydro-1H-indene and Octadecanoic acid were reported[5] from ethyacetate fraction of *H. durvillei.*

Diethyl Phthalate, 1-Hexadecanol 9-Hexadecenoic acid & its methyl ester, Hexadecanoic acid & its methyl ester, n-Hexadecanoic acid, Oleic Acid, 8,11-Octadecadienoic acid & its methyl ester, 9-Octadecenoic acid and its (Z)-methyl ester, Z)-9-Hexadecenoic acid (Z)-9-octadecenyl ester, 11,13-Dimethyl-12-tetradecen-1-ol acetate were identified from methanolic extract of *H.dilatata* by GC-MS analysis[6]. Phytol, Hexadecanoic acid, methyl ester, Ether, (2-ethyl-1-cyclodecen-1-yl), methyl methyl, 5-Isopropyl-6-methylhepta-3,5-dien-2-ol, Citronellol epoxide (R or S) and 3-Tetradecene, (E)- were isolated from *H. palmatata* and identified by GC-MS[7].



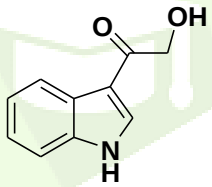
Palmitic Acid



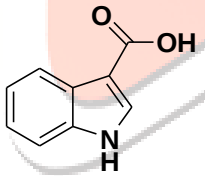
α-linoleic acid

Alkaloids / heterocycles/Amines

5-(1-tert-Butyl-1H-pyrrol-2-ylmethylene)- 1- (4-ethoxyphenyl) pyrimidine-2, 4, 6- trione, benzidine, Indole, 3-(hydroxyacetyl) indole and indole-3-carboxylic acid were isolated[5] from the ethyl acetate extract of red alga *H. durvillei*. 2-propamine which may be responsible for mosquito-toxicity in a fraction of phytochemical extracts of *Halymenia palmata*. The larvicidal activity of methanolic crude extract of seaweed, *H. palmata* (HPMe) and its fractions (Hpf-1 and Hpf-2) fractioned by chromatographic technique were assessed against the mosquito larvae of *Aedes aegypti*.



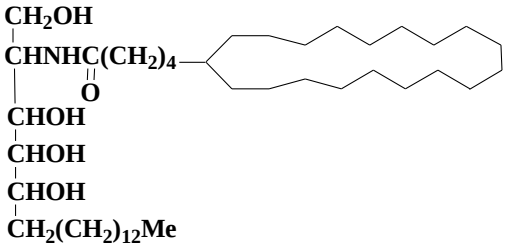
3-(hydroxyacetyl) indole



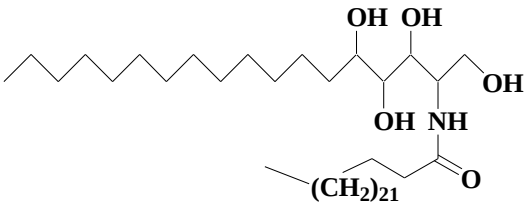
indole-3-carboxylic acid

Sphingosine Derivatives

A new N-acylsphingosine, named halyminine was isolated[8] from *H.porphyroides*. A sphingosine derivative has been isolated[9] from *H.durvillei*



Halyminin



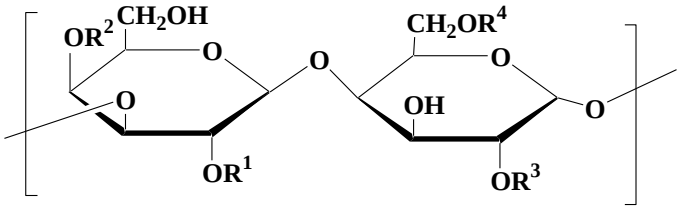
sphingosine derivative

Sterols:

Cholesterol was found a s a major constituent and 7-oxo-sterol as minor constituent in *H.porphyroides*[10]. Lathosterol was isolated from *Halymenia dilatata*.

Sulfated Polysaccharides:

Carrageenan, a sulfated polysaccharide, was isolated from *Halymenia porphyroides*[11, 1], *H. venusta*[12] and other red algae. From *H. porphyroides*[11], it was obtained in 36.18% yield. Carrageenin, a product of commercial importance, is a complex mixture of polysaccharides obtained from red seaweeds composed of galactans, the proportion of which varies with species, season and environment. The biochemical composition and carrageenan content of three species of *Halymenia* (*Halymenia durvillaea*, *Halymenia maculata* and *Halymenia dilatata*) that occurred along the coast of Iligan Bay was determined[13].



$R_1=R_3=R_4=SO_3^-$, R=H

Sulfated Polysaccharide

Inorganic biochemical constituents.

The relationship between the nutritive components and the variation of the biochemical composition like organic and inorganic constituents were mainly analyzed in a study where sodium and potassium contents were observed in higher amount in marine red alga *Halymenia porphyroides*. Calcium, Magnesium, Iron, Sodium, Potassium, Phosphorus, Zinc and Copper were the main inorganic constituents[13].

BIOLOGICAL ACTIVITIES REPORTED

The lambda-like carrageenan[11] obtained from *Halymenia durvillaei* Bory De Sainte Vincent, a red alga common in Philippine coastal waters was found out to exhibit hypocholesterolemic property[5]. Aside from having hypocholesterolemic property, this lambda-like carrageenan effected significant higher anti-blood coagulant activity[14] (*in vitro*) than kappa and iota type of carrageenan. Insecticidal properties of red alga, *Halymenia palmata* was reported[15] for the first time by Deepak et al. The larvicidal activity of methanolic crude extract of seaweed, *H. palmata* (HPMe) and its fractions (Hpf-1 and Hpf-2) fractioned by chromatographic technique were assessed against the mosquito larvae of *Aedes aegypti*. The anticoagulant activity of sulfated polysaccharides fractions obtained from an aqueous extracted from the red alga *Halymenia floresia* were determined[16]. Methanol extracts of seaweed *Halymenia* sp. had strong antibacterial activity[3] against the test bacteria namely, *S. typhi*, *A. hydrophila* and *V. harveyi*, but was not active against the bacteria *E.coli*. 3-(hydroxyacetyl)indole and indole-3-carboxylic acid both were found to inhibit moderately A549 lung cancer cells and exhibited an increased proportion of in vivo anti-aging activity in *C. elegans*. A sulfated galactan[17] isolated from the marine red algae *H. floresia* had promising effects on GI motor functions, which included myocontractile effect on rat duodenum. Many compounds were reported to possess antimicrobial, antioxidant, anti-inflammatory, antitumor and antifouling properties reported[6] from *Halymenia dilatata*. Antioxidant activity and in vivo Anti-aging assay of crude extracts and the *in vitro* antioxidant capacities of crude extracts were evaluated[3]. A computational study showed potential bioactive compounds[18] as SARS-CoV-2 inhibitors from extracts of the marine red alga *Halymenia durvillei*. The potentials of compounds 1–2 tetradecandiol and E, E, Z-1,3,12 -nonadecatriene-5,14-diol were identified for therapeutic purposes based on pharmacophore study, while cholest-5-En-3-Ol (3-Beta)- had been found to have a high fitness score in molecular docking studies both in monomer and dimer state compared to the N3 inhibitor and remdesivir affinity scores.

CONCLUSION

Due the multiple faceted utilities of the red alga *Halymenia* which include its uses as food supplement, skin care ingredients, cosmetics and food additives it has remained a seaweed of interest from centuries. Different biological activities have been reported in the extracts and also it has shown potential bioactive compounds as SARS-CoV-2 inhibitors requiring further assessment and validation. Presence of diverse secondary metabolites in *Halymenia* extracts and versatile biological activities thereof invites attention for further investigation to isolate bioactive compounds and their structural elucidation in the quest of new chemical entities in drug discovery process.

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