Pak. J. Bot., 19(2): 253–257, 1987.

CHEMICAL CONSTITUENTS OF RED ALGAE *ACANTHOPHORA DENDROIDES* AND *HALYMENIA PORPHYROIDES*

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Abstract

The ethyl acetate fraction of methanolic extracts of *Acanthophora dendroides* Harvey and *Halymenia porphyroides* Børgesen yielded a mixture of fatty acids and cholesterol as a major compound, while 7-oxocholesterol was a minor constituent of *H. porphyroides,* which is being reported for the first time from any red alga. The fatty acid constituents of both seaweeds analysed by GC/MS, revealed the presence of 7 saturated and 8 unsaturated fatty acids. Hexadecanoic acid and its methyl ester were found as major fatty acids in both algae.

Introduction

Acanthophora dendroides Harvey of the order Ceramiales has a filiform, cartilaginous, irregularly branched and pyramidally ramified thallus (Børgesen, 1933) whereas *Halymenia porphyroides* Børgesen of the order Cryptonemiales is a tough, elastic, broadly cordate, leaf-like and rosy red alga (Anand, 1943). Both of these algae occur in the sublittoral region at the coast of Karachi, though *A. dendroides* grows on shallower rocks and is less frequent and less abundant than *H. porphyroides.* The morphology and anatomy of these algae have been studied (Anand, 1943). In the present paper the chemical constituents of *A. dendroides* and *H. porphyroides* is reported.

Materials and Methods

Fresh specimens of *A. dendroides* (1.5 kg) detached from lower littoral rocks and *H. porphyroides* (1 kg) as drift material were collected during July-September 1985 from Buleji near Karachi. Fresh algae were percolated in MeOH for 2 weeks and the methanolic extract evaporated in vacuum to dryness and partitioned between EtOAc and H_2O. The ethyl acetate fraction of *A. dendroides* and *H. porphyroides* yielded respectively 1.2 and 1 gm of crude extract which were subjected to column chromatography using hexane, hexane: ether, chloroform and methanol in increasing order of polarity. The fractions eluted with hexane: ether (80:20) yielded a mixture of fatty acids. Part of this mixture was purified on preparative chromatography developed in hexane: ether (1:1), which afforded two major compounds, hexadecanoic acid and its methyl ester.

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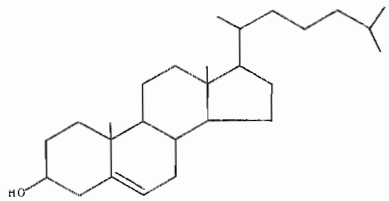
Results and Discussion

Cholesterol was found as major sterol in both the algae and 7-oxocholesterol was isolated as a minor constituent of *H. porphyroides* only. The fraction from both algal specimens eluted with hexane: ether (70:20) purified on preparative TLC developed in hexane: ether: acetic acid (1:1: 0.8%), gave a 10 mg pure compound, characterised with the help of Pmr and mass spectroscopic techniques as cholesterol [1]:



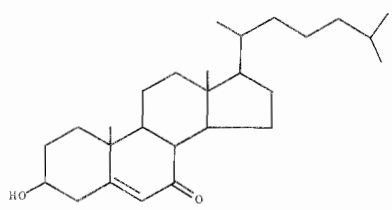
[1]

Pmr ($CDCl_3$): δ 0.67 (s, H-18), 0.86 (d, J = 6.5 Hz, H-26 & H-27), 0.91 (d, H-21), 1.0 (s, H-19), 3.6 (m H-3), 5.3 (t, H-5).

Mass: m/z 386 (M^+-$C_{27}H_{46}O$), 353 (M^+-H_2O-Me), 273 (M^+-side chain), 255, 213.

The UV spectrum showed the absorption at 236 nm, characteristic of an unstaurated ketone. The mass spectrum showed the molecular ion peak at m/z 400.33769 corresponding to the molecular formula $C_{27}H_{44}O_2$. The fragmentation pattern of this compound was similar to sterol and was further supported by Pmr spectrum, which showed the chemical shift of methyl signals similar to the cholesterol as reported by Rubinstein *et al.*, (1976). A downfield methyl at δ 1.2 appeared for H-19 and a sharp singlet at δ 5.76 assigned for H-4 characteristic of 5-en-7-one as mentioned by Bhacca & Williams (1966). The carbinylic proton appeared as multiplet at δ 3.65 assigned for H-3.

The fraction from *H. porphyroides* eluted with hexane: ether (75:25) from the column of silica gel showed one major compound with some impurities, which when purified on preparative TLC developed in chloroform: methanol (9.75:0.25) yielded 5 mg of 7-oxocholesterol [2] in pure form. This was identified with Pmr, mass, I.R. and U.V. spectra:



[2]

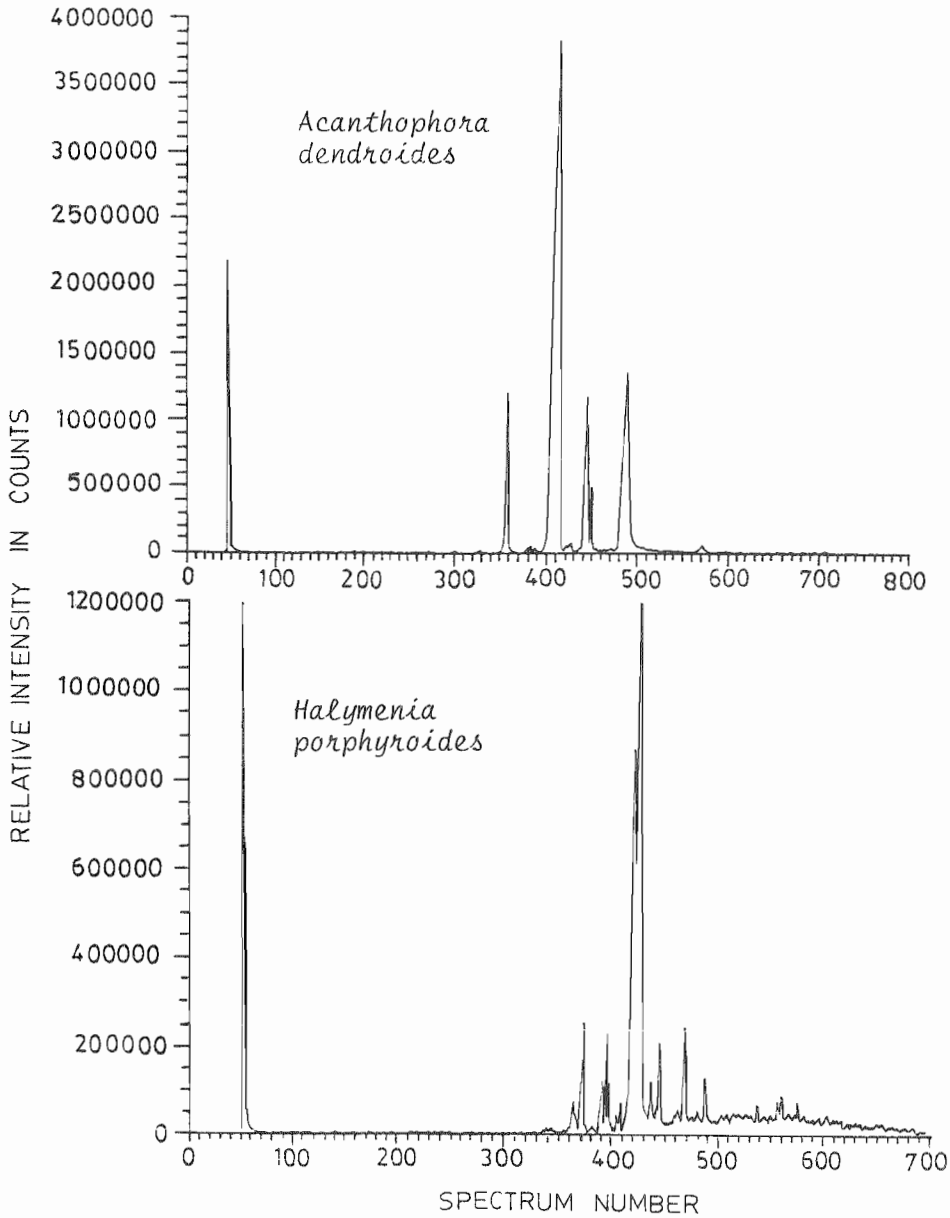


Fig. 1. Reproduction of GC/MS spectra of the fatty acids of *Acanthophora dendroides* and *Halymenia porphyroides*.

Table 1. Fatty acid constitutents of *Acanthophora dendroides* and *Halymenia porphyroides*.

S. No.	Fatty acid	M^+	Mol. Formula	*Acanthophora dendroides*	*Halymenia porphyroides*
	I. SATURATED FATTY ACIDS:				
1.	Dodecanoic acid Me-ester	214	$C_{13}H_{26}O_2$	+	+
2.	Tridecanoic acid Me-ester	228	$C_{14}H_{28}O_2$	+	+
3.	Tetradecanoic acid Me-ester	242	$C_{15}H_{30}O_2$	+	+
4.	Hexadecanoic acid	256	$C_{16}H_{32}O_2$	+	+
5.	Hexadecanoic acid Me-ester	270	$C_{17}H_{34}O_2$	+	+
6	Heptadecanoic acid Me-ester	284	$C_{18}H_{36}O_2$	–	+
7.	Octadecanoic acid Me-ester	298	$C_{19}H_{38}O_2$	+	+
	II. UNSATURATED FATTY ACIDS:				
1.	Tridecenoic acid Me-ester	240	$C_{15}H_{28}O_2$	–	+
2.	Hexadecenoic acid	254	$C_{16}H_{30}O_2$	+	+
3.	Heptadecatrienoic acid	278	$C_{18}H_{30}O_2$	–	+
4.	Heptadecadienoic acid Me-ester	280	$C_{18}H_{32}O_2$	–	+
5.	Heptadecenoic acid Me-ester	282	$C_{18}H_{34}O_2$	–	+
6.	Octadecadienoic acid Me-ester	294	$C_{19}H_{34}O_2$	+	+
7.	Octadecenoic acid Me-ester	296	$C_{19}H_{36}O_2$	+	+
8.	Nonadecenoic acid Me-ester	310	$C_{20}H_{38}O_2$	–	+

Pmr ($CDCl_3$): δ 0.68 (s, 3H, H-18), 0.86 (d, 6H, J = 6 Hz, H-26 & H-27), 0.92 (d, J = 6.5 Hz, H-21), 3.65 (m, H-3), 5.76 (s, H-6).

Mass: m/z 400.33769 (M^+, $C_{27}H_{44}O$), 368.30515 ($C_{26}H_{40}O_2$), 315.2047 ($C_{21}H_{31}O_2$), 287.20171 ($C_{19}H_{27}O_2$).

I.R. ($CDCl_3$): 3370 (OH), 1675 cm^{-1} (C = O).

VU (MeOH): λ_{max} = 236 nm.

The 7-oxocholesterol has been reported in a number of marine animals. Delseth *et al.* (1978) identified it in a sponge, *Damiriana hawaiiana* formed due to auto-oxidation of cholesterol. The 7-oxocholesterol has not been identified so far in any red alga,

but a compound, cholesta-3,5-dien-7-one has been identified in red algae, which is unusual and suggests the presence of cholesta-5-en-7-one-3-ol. The 7-oxocholesterol in *H. porphyroides* has been identified on the basis of spectroscopic data.

Extract from *A. dendroides* and *H. porphyroides* yielded a mixture of fatty acids (Fig. 1). The Pmr of mixture of hydrocarbons of both seaweeds showed the typical pattern of methyl ester of long chain fatty acids, a singlet at δ 3.6 appeared due to OMe group and olifinic proton appeared at δ 5.3 showing also the pesence of unsaturated fatty acid ester. Individual fatty acid esters were identified through fragmentation pattern in GC/MS (Table 1). Hexadecanoic acid and its methyl ester were found as major fatty acids in both algae. These were also isolated in pure form through preparative TLC and characterised after comparison of their mass and nmr data with previous data as reported by Bano *et al.* (1986, 1987). Seven saturated and 8 unsaturated fatty acids were found in *H. porphyroides.* In *A. dendroides* one saturated and 5 unsaturated fatty acids were found lacking. Whether this difference is due to the unlike taxonomic positions of the algae or due to variations in their thallus structure needs investigations.

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(Received for publication 26 March 1987)