

Some Chemical Constituents from Marine Algae of Karachi Coast (Arabian Sea).

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Some commonly available marine algae have been collected from the Karachi coast of Arabian Sea for the search of new chemical constituents having biological importance. The structures of purified samples have been elucidated with the aid of modern spectroscopic techniques. Among the known constituents a new metabolite (**1**) has been isolated from the brown alga *Iyengaria stellata*.

Key words: Stellatol; *Iyengaria stellata*; Marine brown alga; Arabian Sea.

Introduction

In recent years research on the chemistry of seaweeds (or more generally marine organisms) has experienced a tremendous increase due to the need for compounds possessing bioactivities of possible pharmaceutical applications or other potential economic properties. To this end, a variety of species have been assayed for their activity and a number of biodynamic molecules, often with toxic properties and unique structural features, have been isolated. Since marine organisms live in a significantly different environment from those of terrestrial organisms, it is reasonable to suppose that their secondary metabolites will differ considerably. After more than 25 years of fruitful research, marine natural product chemistry must now be considered to be approaching maturity. If the novelty and complexity of compounds discovered from marine sources were the only criteria, then the success of research in this area would be assured, for there are many marine natural products that have no counterparts in the terrestrial world.

We have already examined various algae collected from Karachi coast of Arabian Sea.¹⁻³ Some known and unknown constituents have been isolated and characterized with the aid of modern spectroscopic techniques including 2D-NMR.

Experimental

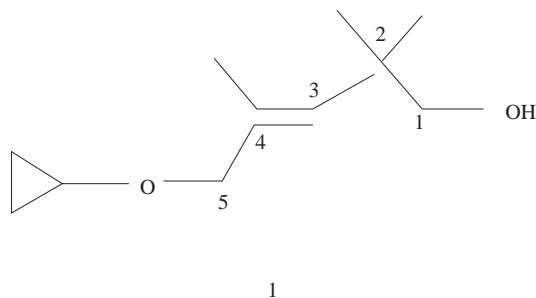
The alga *Iyengaria stellata* (wet wt. 2 kg) was collected from Karachi coast of Arabian Sea. This was identified by Prof. Mustafa Shammell, Department of Botany, University of Karachi. The fresh alga was

washed with water and dried under shade. It was soaked in ethanol (4.5 L) for a period of one month. The methanol was evaporated under reduced pressure. The gummy mass thus obtained, was partitioned between water and chloroform. The chloroform soluble part was condensed and loaded on silica gel column. The elution was carried out using hexane, chloroform, chloroform, chloroform:methanol and finally, pure methanol as mobile phase. Compound **1** was eluted with 50% chloroform in hexane (10.5 mg) as a mobile oil.

EIMS: m/z 184(M^+), 166 ($M^+ - H_2O$), 153 ($M^+ - CH_2OH$); **FDMS:** m/z 184; **HRMS:** m/z 184.2768 ($C_{11}H_{20}O_2, M^+$), 166.2619 ($C_{11}H_{18}O, M^+ - H_2O$); **1H -NMR** ($CDCl_3$, 300 MHz): δ 1.23 (2H, s), 1.25 (3H, s, Me), 1.50 (2H, m), 1.45 (3H, s, Me), 1.76 (3H, s, Me), 1.95 (2H, m), 1.76 (1H, m), 2.45 (1H, m), 4.31 (1H, m) and 5.60 (1H, s); **^{13}C -NMR** ($CDCl_3$, 75 MHz): δ **CH_3 :** 30.67, 27.05, 26.56 **CH_2 :** 47.39, 45.72, 29.70, 86.72 **CH:** 112.91, 66.77 **C:** 171.86, 182.49.

Results and Discussion

Further investigations on other algal genera are in progress. From the green alga *Codium elongatum*, stigmasterol⁴, hexadecanoic acid⁵ and decortinone⁶ were detected. The β -sitosterol⁷ was obtained from another green alga *Enteromorpha intestinalis*. From the red alga *Botrocladia leptopoda* various saturated and unsaturated fatty acids have been isolated. The brown alga *Iyengaria stellata* was also investigated and in addition to the cholesterol⁸ another new metabolite **1** was detected.



The **1** was isolated from the chloroform extract as a mobile oil. The EIMS of **1** showed the molecular ion peak at m/z 183. The loss of 18 a.m.u from the molecular ion peak confirms that the molecule may contain a hydroxyl group which was further confirmed by IR spectrum (3600 cm^{-1}). The molecular mass was confirmed by FDMS and the formula was established with the aid of HRMS which showed the peak at m/z 184.2768 calculated for $C_{11}H_{20}O_2$.

The proton NMR spectrum displayed three quaternary methyl singlets at δ 1.25, 1.45 and 1.76. The most downfield singlet at δ 1.76 was due to the methyl situated at double bond (C-4). Another downfield singlet at δ 5.6 in the proton spectrum was due to H-3 (double bond). The carbon spectrum of **1** showed altogether eleven carbon signals. The DEPT experiment resolved them into three methyls, four methylenes, two methines and remaining two quaternary carbon atoms. The signals at δ 112.91 and 182.49 were due to the double bond. The three methyl signals appeared at δ 26.56, 27.05 and 30.67 in the ^{13}C NMR spectrum. The signal at δ 27.05 was due to the methyl at double bond.

The remaining carbons, protons and their chemical shifts have been mentioned in the experimental section. The various proton and carbon atoms in the molecule were correlated with the help of hetero-Cosy experiment.

On the basis of above spectral informations the structure of **1** assigned as 5-O-cyclopropyl-2,2,4-trimethyl-3-en-1-pentanol and named as stellatol. Among the known constituents isolated from the mentioned sources only the stellatol was found new.

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