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## Bromine Content in Some Seaweeds of Goa (Central West Coast of India)

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### Abstract

Nineteen species of seaweeds from the coast of Goa were examined for their bromine content following the spectrophotometric method involving ashing with  $\text{Na}_2\text{CO}_3$ , oxidation of bromide to bromine with chloramine-T and measuring the absorbance in chloroform at 400 and 650 nm. The bromine content, on a dry weight basis, varied from 0.024 to 0.247% for the green algae, from 0.020 to 0.400% for the red algae, and from 0.015 to 0.054% for the brown algae. Only two species *Chondria armata* and *Codium elongatum* showed relatively high bromine contents 0.400% and 0.247% respectively. A large fraction of the bromine in these species appears to be organically bound.

### Introduction

Marine natural products differ from their terrestrial counterparts in several respects. The most obvious variation is the frequent occurrence of halogeno-compounds seldom found in terrestrial plants and animals. This is probably because at least two halogens namely chlorine and bromine occur in sea water in high concentrations.

Chemical studies on the Indian seaweeds were started in the early fifties. These studies largely dealt with the poly-saccharides (agar and alginic acid), proteins and mineral constituents (Umamaheswara Rao 1970). Among the halogens, only the iodine has been studied in some detail (Pillai 1956, Kappanna and Rao 1962, Dave *et al.* 1969, Solimabi and Das 1977). Practically no information is available on the bromine content of the Indian seaweeds so far. The bromo-compounds from marine algae have been reported to possess a number of interesting biological activities (Bhakuni and Silva 1974). This prompted us to survey the marine algae from the Goa region for their bromine content and identify the species which might contain such compounds. This study was undertaken as a part of the project on biodynamic compounds from marine flora and fauna.

### Material and Methods

Algal samples used for the analysis were collected from the intertidal zone during the premonsoon or post-monsoon periods depending upon their seasonal availability. These were washed with fresh water, briefly rinsed with distilled water and dried at room tempera-

ture. The material was ground to a fine powder and dried in an oven for three hours at 60 °C. Small quantities (3 to 5 g) were taken in silica crucibles with 10 ml of 10%  $\text{Na}_2\text{CO}_3$  solution. These crucibles were then kept in a muffle furnace at 450–500 °C for 12 hours for ashing. The ash was repeatedly extracted with water and the filtrate made up to 100 ml.

A few samples were also refluxed with alcoholic KOH for 24 hours followed by ashing of the dried mass at 450–500 °C. Identical results were obtained from both these methods indicating that 10 ml of  $\text{Na}_2\text{CO}_3$  solution is sufficient to react with bromine completely.

From the solutions prepared following the above procedure, bromine was estimated from the method given by Saenger (1972). 20 ml of the solution was taken in a separating funnel to which 5 ml of  $\text{H}_2\text{SO}_4$  (16 N), 5 ml of chloroform and 1.5 ml of chloramine-T solution (1.5%) were added. The mixture was shaken vigorously for 3 minutes and the chloroform-phase, upon separation, was used for the analysis. The analysis was done using a Beckman ACTA-C III double-beam spectrophotometer. Absorbances at 400 and 650 nm were read directly instead of adopting the scanning mode as suggested by Saenger (1972). Absorbance at 650 nm was subtracted from that at 400 nm to allow for the turbidity of the samples. New calibration curves were prepared using KBr solutions of different concentrations each time a fresh reagent was prepared.

The precision of the above method was determined by analysing 10 replicate samples of the seaweed *Chondria armata*. The coefficient of variation thus obtained was  $\pm 1.56\%$ .

## Results and Discussion

The bromine content of nineteen species of Chlorophyta, Phaeophyta and Rhodophyta is given in Table I. Lower values were obtained for the brown algae as compared to the green and red algae. Bromine content within the three phyla varied from 0.024 to 0.247% for green algae, from 0.020 to 0.400% for red algae, and from 0.015 to 0.054% for brown algae.

Bromine is a major constituent of sea water and occurs in concentrations of about 0.067 g/kg in sea water of 35‰ salinity, bearing a constant ratio with chlorinity (Culkin 1965, Naqvi and Reddy 1978). Owing to the relatively small changes in the concentration of this element in sea water, it is expected that no appreciable variation in the bromine content of the same species can occur with geographical locations. There could, however, be some seasonal variation associated with the different stages of developmental cycle. In contrast to this, the iodine content of marine algae varies greatly probably due to the greater variations in its concentration in sea water (Solimabi and Das 1977). This communication perhaps gives the first report on the distribution of bromine in marine algae from the Indian coast. Moreover, a number of species have been examined

here for the first time for their bromine content. Therefore, we could not find much data in the literature with which to compare our results.

Saenger (1972) reported high bromine content (1.45%) for the alg *Chondrococcus hornemanni* collected from the Riet river. Another species belonging to the same genus, examined by us, gave no more than 0.053% bromine. This clearly shows that even within the same genus, there could be large variations in the bromine content. The value obtained by us for *Gracilaria corticata* (0.078%), however, is close to 0.095% reported by Saenger (1972) for *Gracilaria beckeri*.

Several species of red algae, especially those belonging to the family Rhodomelaceae, are known to possess bromine in high concentrations (Vinogradov 1953, Augier 1953, Saenger 1972). This is probably due to the occurrence of bromo-compounds mostly consisting of brominated phenols (Bhakuni and Silva 1974). Of the seven species of red algae examined, two (*Acanthophora specifera* and *Chondria armata*) belong to the family Rhodomelaceae. Out of these only *Chondria armata* gave relatively high value (0.40%). It is interesting to note that this species also contains iodine in high concentration (0.74%, Das, pers. comm.) suggesting a similar mechanism for the accumulation of these two elements. High value (0.247%) was also obtained for the green alga *Codium elongatum*.

The two species, *Chondria armata* and *Codium elongatum* have been used for further studies in view of their high bromine content. 300 g of powdered dried alga, *Chondria armata*, were extracted thrice at room temperature with 95% methanol. The extract was concentrated to dryness at 50 °C under reduced pressure. The dried extract (ca. 10 g) was subjected to repeated extractions with ether and the residue was finally extracted with ethyl acetate. Both ether and ethyl acetate-soluble fractions were found to have bromine in high concentrations. The nature of these bromo-compounds and their biological activities are under investigation, the results of which will be communicated later.

Tab. I. Bromine content of marine algae from the coast of Goa

Species	Bromine % (On dry weight basis)
<b>CHLOROPHYTA</b>	
<i>Cladophora</i> sp.	0.024
<i>Chaetomorpha media</i>	0.105
<i>Enteromorpha</i> sp.	0.032
<i>Caulerpa racemosa</i>	0.130
<i>Caulerpa sertularioides</i>	0.027
<i>Codium elongatum</i>	0.247
<b>RHODOPHYTA</b>	
<i>Gracilaria corticata</i>	0.078
<i>Hypnea musciformis</i>	0.027
<i>Acanthophora specifera</i>	0.095
<i>Chondria armata</i>	0.400
<i>Chondrococcus</i> sp.	0.054
<i>Corallina</i> sp.	0.020
<i>Centroceras clavulatum</i>	0.063
<b>PHAEOPHYTA</b>	
<i>Sargassum tenerrimum</i>	0.040
<i>Dictyota dumosa</i>	0.022
<i>Padina tetrastratica</i>	0.022
<i>Spatoglossum asperum</i>	0.055
<i>Dictyota bartayresii</i>	0.015
<i>Dictyopteris australis</i>	0.039

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