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PHYTOCHEMICAL STUDIES ON THE MARINE ALGAE OF QATAR, ARABIAN GULF

By

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ABSTRACT

The most dominant twenty three algal species representing the main three groups of benthic macroalgae, chlorophyceae, Phaeophyceae and Rhodophyceae were collected from the coastal zones of the Qatar peninsula. These algae were screened for alkaloids, coumarins, flavonoids, saponins and tannins. The moisture, ash, protein, lipid, carbohydrate, minerals and trace elements content of the investigated algal species were determined.

INTRODUCTION

The algal flora of the Arabian Gulf has received but little attention. Only some scattered reports were recorded by Borgensen (1939), Newton (1955), Nizamuddin and Gessner (1970); Basson (1979) and Kamel (1981) who described and classified many algal species from different parts of the Arabian Gulf. However, the marine algae of the coasts of the Qatar peninsula have not been studied so far. The present work represents the preliminary study in an extensive investigation sponsored by the Scientific and Applied Research Centre of Qatar University to evaluate the chemical, nutritional, pharmaceutical and economical importance of the algal community present in the Qatari waters.

EXPERIMENTAL

A) Collection and treatment of samples

The algal species were collected from several localities in the coastal intertidal and subtidal zones of the Qatari peninsula during the spring of 1987. The samples were cleaned, air-dried and powdered.

B) Chemical analysis

1. Moisture content:

The moisture content was calculated after heating the air-dried samples for 5 hours at 105-110°C.

2. Ash content:

The powdered samples were ashed at 500°C for 6 hours and the ash was left to cool in a desiccator, than the weight of the ash was determined.

3. Total lipid:

The lipid fraction was extracted by soaking the dried material in methanol - chloroform (1:1) for 24 hours. The extract was reduced by evaporation at 40°C and the residue weighed.

4. Protein content:

The protein content was determined by multiplying the concentration of the organic nitrogen, measured by the Kjeldahl method (Augier and Santimone, 1978), by the factor 6.25.

5. Carbohydrate content:

The carbohydrate content was calculated, in the moisture-free material, from the equation.

$$\text{carbohydrate} = 100 - (\text{ash \%} + \text{protein \%} + \text{fat \%})$$

6. Mineral and trace elements:

The mineral and trace elements in the ash were determined by atomic absorption spectrophotometry.

7. Phytochemical screening:

The methods employed for the phytochemical screening were described in a previous publication (Rizk, 1982).

RESULTS AND DISCUSSION

The algae studied in the present investigation represent the most abundant species of the algal flora present in the Qatari coasts.

The results of the phytochemical screening and chemical composition of the marine algae of Qatar (Tables 1, 2, and 3) may indicate their possible use as pharmaceutical preparations, fertilizers, animal feeds or sources of some mineral salts. In this respect the studied algae could be considered as potential sources for Na, K, Ca and Mg which are present in relative abundance in nearly all the investigated algal species.

Table (1)

Class and Species	Location and date of collection	Frequency of occurrence	Alkaloids		Coumarins	Saponins	Flavonoides	Tannins	Used as/ treatment of
			MR	WR					
I. CHLOROPHYCEAE									
1) <i>Acetabularia calyculus</i> Quoy et Gaimard	Dukhan March, 1987	O	-	-	-	-	-	turbid	
2) <i>Cladophora sericoides</i> Borgesen	Al-Wakrah March, 1987	C	-	-	-	-	-	-	Some Cladophora sp. have antimicrobial activity (Demina et al., 1981)
3) <i>Dictyosphaeria cavernosa</i> (Forskal) Borgesen	Al-Areesh March, 1987	C	-	+	-	-	-	-	
II. PHAEOPHYCEAE									
4) <i>Colpomenia sinuosa</i> (Mertens ex Roth) Derbes et Solier	Al-Wakrah March, 1987	V.C	-	-	-	-	-	-	Antibacterial: (Maurer, 1965). Cytotoxic: (Biard and Verbist, 1981)
5) <i>Cystoseira trinodis</i> (Forskal) C. Agardh	Dukhan April, 1987	C	-	-	-	-	-	-	Antibiotic: (Glombitza et al., 1975). Antifungal: (Sayed et al., 1982)
6) <i>Dictyota cernicornis</i> Kutzing	Al-Wakrah March, 1987	C	+	++	-	+	-	-	<i>Dictyota</i> sp. possesses: Antibiotic activity (Finer et al., 1979).
7) <i>Hormophysa triquetra</i> (C. Agardh) Kutzing	Dukhan April, 1987	V.C	-	+	-	-	-	-	
8) <i>Padina gymnospora</i> (Kutzing) Vickers	Al-Wakrah March, 1987	C	-	-	-	-	-	-	
9) <i>Sargassum binderi</i> Sonder	Al-Areesh March, 1987	C	-	+	-	-	-	-	<i>Sargassum</i> sp. showed Antibacterial activity (Rao et al., 1986; Nakayama et al., 1980)

Table (1) Cont.

Class and Species	Location and date of collection	Frequency of occurrence	Alkaloids		Coumarins	Saponins	Flavonoides	Tannins	Used as/ treatment of
			MR	WR					
10) <i>Sargassum boveanum</i> J. Agardh	Doha February, 1987	V.C	-	-	-	-	-	-	Antitumer: (Fujihara et al., 1985; Ito and Sugura, 1976).
11) <i>Sargassum denticulatum</i> (Forskål) Borgesen	Al-Wakrah March, 1987	O	-	-	-	-	-	-	Antifungal: Nadal et al., 1964) Hypocholesterolemic: (Iizimo-Mizui et al., 1985
12) <i>Sargassum heteromorphum</i> J. Agardh		C	++	+++	-	-	Weak	-	
III. RHODOPHYCEAE									
13) <i>Amphiroa fragilissima</i> (L.) Lamour	Al-Wakrah March, 1987	C	-	+	+	-	-	-	
14) <i>Chondria collinsiana</i> Howe	Dukhan April, 1987	C	+	+++	-	-	-	-	<i>Chondria</i> sp. have: antibiotic activity: (Wratten & Kulkarni, 1976) Antifungal & antifoulant: (Nadal, 1964) antibacterial: (Rao & Parekh, 1981); (Hope, 1979); (Hornsey & Hide 1974); hypotensive: (Nagvi et al., 1980); Agglutinin (Shiomi 1983); antimitotic:

Table (1) Cont.

Class and Species	Location and date of collection	Frequency of occurrence	Alkaloids		Coumarins	Saponins	Flavonoides	Tannins	Used as/ treatment of
			MR	WR					
15) <i>Chondria dasypylla</i> (Woodward) C. Agardh	Dukhan March, 1987	C	-	-	-	-	-	-	Chenieux <i>et al.</i> , 1980); Inotropic (Baker, 1984); antifungal (Hoppe, 1979; Olesen <i>et al.</i> , 1964); Antitumor: (Nadal <i>et al.</i> , 1964); Verifuge: Michanek, 1979); Anthelminthic (Hoppe, 1979; Michanek, 1979); Hemolytic: (Hashimoto <i>et al.</i> , 1972).
16) <i>Digenia simplex</i> (Wulfen) C. Agardh	Al-Areesh March, 1987	C	-	+	-	-	-	-	Antibacterial (Hornsey and Hide, 1974). antimitotic (Chenieux <i>et al.</i> , 1980).
17) <i>Laurencia paniculata</i> (C. Agardh) J. Agardh	Al-Areesh March, 1987	C	+	++	-	-	-	-	Vermifuge: (Fenical, 1983); anthelminthic: Fenical, 1983).
18) <i>Laurencia papillosa</i> (Forskål) Greville	Al-Areesh March, 1987	C	-	+	-	-	-	-	<i>Laurencia</i> sp. showed: Cytotoxic properties: (Pettit <i>et al.</i> , 1977; Tanalki <i>et al.</i> , 1978); Antimicrobial: (Glombitzka, 1979).

Table (1) Cont.

Class and Species	Location and date of collection	Frequency of occurrence	Alkaloids		Coumarins	Saponins	Flavonoides	Tannins	Used as/ treatment of
			MR	WR					
19) <i>Polysiphonia broadiae</i> (Dillwyn) Greville	Dukhan March, 1987	C	-	+	-	-	-	-	<i>Polysiphonia</i> sp. showed: Antibacteria (Rao and Parekh, 1981 <i>Biard et al.</i> , 1981;
20) <i>Polysiphonia crassicollis</i> Borgesen	Dukhan March, 1987	V.C	-	-	-	-	-	turbid	<i>Reichelt et al.</i> , 1984 Glombitza, 1979;
21) <i>Polysiphonia ferulacea</i> Suhr	Dukhan March, 1987	O	-	-	-	-	-	-	Antifungal: (<i>Biard et al.</i> 1980); Antimitotic Chenieux <i>et al.</i> 1980 Antibacterial : (Horns and Hide, 1974; Roos, 1957
22) <i>Polysiphonia kampsaxii</i> Borgesen	Al-Areesh March 1987	C	-	-	-	-	-	-	Agglutinin: (Shiomi, 1983).
23) <i>Spyridia filamentosa</i> (Wulven) Harvey	Al-Wakrah	C	+	++	-	-	-	-	

Mr: Mayer's Reagent (Rizk, 1982).

WR: Wagner's Reagent (Rizk, 1982).

C: Common

V.C: Very Common

O: Occasional

Table 2
Chemical Composition of Some Marine Algae From Qatar

Classes and Species	Moisture	Total Ash	Percentage of major components in the moisture free-material		
			Total Protein	Total Lipid	Total Carbohydrate
<i>Chlorophyceae</i>					
<i>Acetabularia calyculus</i>	5.00	57.30	4.50	4.21	33.39
<i>Cladophora serocoids</i>	4.00	46.31	8.31	7.29	38.09
<i>Dictyosphaeria cavernosa</i> (mean) ±SE	3.00	42.53	7.79	10.31	39.31
<i>Phaeopyceae</i>					
<i>Colpomenia sinuosa</i>	4.00	43.88	5.36	3.12	47.64
<i>Cytoseira trinodis</i>	8.00	30.43	6.69	4.35	58.53
<i>Dictyota cervicornis</i>	3.00	12.42	6.23	11.34	70.01
<i>Hormophysia triquetra</i>	4.00	25.04	8.93	7.29	58.74
<i>Padina gymnospora</i>	4.00	62.17	3.48	8.33	26.22
<i>Sargassum binderi</i>	8.00	38.54	6.61	4.35	50.05
<i>Sargassum boveanum</i>	10.00	34.62	4.73	3.33	48.32
<i>Sargassum denticulatum</i>	10.00	30.26	5.63	2.22	61.89
<i>Sargassum heteromorphum</i> (mean SE)	13.00	35.53	8.14	1.15	55.18
<i>Rhodophyceae</i>					
<i>Amphiroa fragilissima</i>	2.00	49.35	16.19	5.10	29.36
<i>Digenia simplex</i>	4.00	37.27	9.93	7.29	45.51
<i>Spyridia filamentosa</i>	6.00	47.54	4.73	3.19	44.54
<i>Chondria ciliinsiana</i>	7.00	29.43	12.36	5.37	52.84
<i>Chondria dasypylla</i>	8.00	43.77	11.95	2.17	42.11
<i>Laurencia paniculata</i>	5.00	33.71	9.21	8.42	48.66
<i>Laurencia papillosa</i>	4.00	23.06	5.41	5.21	66.32
<i>Polysiphonia broadiae</i>	3.00	42.59	5.03	12.37	40.01
<i>Polysiphonia crassicollis</i>	6.00	50.85	7.77	9.57	31.81
<i>Polysiphonia ferulacea</i>	6.00	50.00	5.52	3.19	41.29
<i>Polysiphonia kempsonii</i> (mean ±)	4.00	53.80	3.57	3.12	39.51
	(5.00) ±	(41.94) ±	(8.33) ±	(5.91) ±	(43.81) ±
	0.54	2.98	1.20	0.96	3.03

Table 3
 Percentage of mineral elements and trace elements
 (based on dry weight substance)

Class and Species	Na	K	Ca	Mg	Fe	Zn	Co	Cu	Mn	Pb	Al
<i>Chlorophyceae</i>											
<i>Acetabularia calyculus</i>	6.1396	7.9707	14.3257	1.077	0.0538	0.0047	0.0032	0.0001	0.0002	0.0019	0.0005
<i>Cladophora sericooides</i>	4.0979	6.7357	11.416	1.756	0.0876	0.0039	0.0025	0.0004	0.0001	0.0017	0.0001
<i>Dictyosphaeria cavernosa</i>	4.2449	5.3566	6.9736	1.4349	0.0485	0.0028	0.0016	0.0009	0.0003	0.001	0.0004
Mean ± SE	4.8275	6.6664	10.9051	1.4226	0.0633	0.0038	0.0024	0.0005	0.0002	0.0015	0.0003
	±0.6582	±0.7371	±2.1376	±0.1961	±0.0122	±0.0005	±0.0005	±0.0002	±0.0006	±0.0003	±0.0001
<i>Phaeophyceae</i>											
<i>Colpomenia sinuosa</i>	5.4336	3.588	12.2613	2.2545	0.0964	0.0049	0.0025	0.0018	0.0013	0.0014	0.0001
<i>Cytosira trinodis</i>	4.6719	4.1327	4.4920	1.2576	0.0610	0.0037	0.0027	0.0001	0.0007	0.0012	0.0002
<i>Dictyota cervicornis</i>	4.0737	6.4762	5.5362	0.6058	0.0355	0.0027	0.0004	0.0001	0.0002	0.0005	0.0001
<i>Hormophysa triquetra</i>	4.3023	5.1627	3.461	1.434	0.042	0.0026	0.0017	0.0002	0.0002	0.001	0.0001
<i>Padina gymnospora</i>	7.4672	6.8697	13.1626	2.8872	0.0955	0.0079	0.0027	0.0014	0.0033	0.0015	0.0003
<i>Sargassum binderi</i>	6.4812	3.6759	1.7412	1.5477	0.0503	0.0019	0.0034	0.0009	0.0005	0.0009	0.0001
<i>Sargassum boveanum</i>	5.1168	4.1114	2.7408	3.3256	0.0767	0.0025	0.0023	0.0015	0.0012	0.0016	0.0003
<i>Sargassum denticulatum</i>	5.3581	4.8882	4.2300	1.5039	0.0376	0.0039	0.0022	0.0008	0.0009	0.0016	0.0006
<i>Sargassum heteromorphum</i>	4.9987	6.1523	5.210	1.4801	0.0788	0.0021	0.0013	0.0006	0.0006	0.0012	0.0001
Mean ± SE	5.3249	5.0063	4.5372	1.8107	0.0637	0.0036	0.0021	0.0008	0.001	0.0012	0.0002
	±0.3567	±0.4133	±1.0853	±0.2844	±0.008	±0.0006	±0.0003	±0.0002	±0.0003	±0.0001	±0.0001
<i>Rhodophyceae</i>											
<i>Amphiroa fragilissima</i>	6.1702	7.9695	21.2096	3.036	0.1542	0.0177	0.0029	0.0002	0.0014	0.0025	0.0001
<i>Chondria collinsiana</i>	5.4266	5.0390	3.0233	1.4729	0.0639	0.0060	0.0018	0.0003	0.0005	0.0007	0.0001
<i>Chondria dasypylla</i>	4.380	3.2328	4.8177	1.5017	0.0646	0.0112	0.0029	0.0004	0.0009	0.0012	0.0002
<i>Digenia simplex</i>	3.333	6.4581	4.7914	0.9582	0.0729	0.0035	0.0001	0.0003	0.0062	0.0010	0.0001
<i>Laurencia paniculata</i>	8.844	4.6024	4.350	1.245	0.0523	0.0047	0.0012	0.0001	0.0004	0.0012	0.0001
<i>Lairemcoa -a-o.,psa</i>	4.3846	6.3532	2.6844	0.8767	0.0447	0.0050	0.0007	0.0006	0.0004	0.0009	0.0002
<i>Polysiphonia broadiae</i>	4.3088	5.7698	5.8365	1.1946	0.0587	0.0050	0.0024	0.0001	0.0008	0.0014	0.0001
<i>Polysiphonia crassicollis</i>	6.9252	6.7356	8.7467	1.5748	0.0899	0.0034	0.0031	0.0015	0.0010	0.0016	0.0001
<i>Polysiphonia ferulacea</i>	5.3845	5.762	8.1325	1.6435	0.0812	0.0013	0.0038	0.0013	0.0010	0.0009	0.0001
<i>Polysiphonia kemp saxii</i>	8.0253	5.7782	14.0134	1.9041	0.1305	0.0004	0.0039	0.0015	0.0017	0.0015	0.0002
<i>Spyridia filamentosa</i>	3.8036	4.1578	11.2346	4.0715	0.1327	0.0030	0.0032	0.0035	0.0009	0.0018	0.0002
Mean ± SE	5.544	5.6235	8.0764	1.7708	0.086	0.0056	0.0024	0.0009	0.0014	0.0013	0.0001
	±0.5135	±0.3949	±1.6853	±0.2894	±0.0121	±1.4772	±0.0004	±0.0003	±0.0005	±0.0001	±0.0001

Fe, Zn, Co, Cu, Mn, Pb and Al are present in smaller amounts in decreasing order of abundance. The only statistically significant elemental difference observed was in the calcium content, which was found to be higher in both Chlorophyceae and Rhodophyceae than in Phaeophyceae ($P < 0.025$ and 0.05 respectively). This was found to be accompanied by similar differences in the total ash content which was significantly higher in Chlorophyceae and Rhodophyceae than in Phaeophyceae ($P < 0.01$ and 0.025 respectively). This type of relationship was also observed by Khalil and El Tawil, 1982) in the Red Sea algae who considered high ash content as an indication of the calcareous nature of the algae. The presently studied calcareous algae *Acetabularia calyculus*, *Padina gymnospora* and *Amphiroa fragilissima* (Dawson, 1966) all showed high ash and calcium contents.

It seems that there is an inverse relationship between the moisture and ash contents. Phaeophyceae, that showed the lowest ash content, showed the highest (air-dried) moisture content ($P < 0.25$ and < 0.05) compared with Chlorophyceae and Rhodophyceae. A similar observation was made in the Red Sea algae (Khalil and El Tawil, 1982), while the Rhodophyceae species of the Mediterranean sea showed the highest moisture content (El-Tawil and Khalil, 1983). In the Phaeophyceae, *Sargassum* species had a mean value of moisture of 10.25 ± 1.03 , compared to a value of 4.6 ± 0.87 for the other Phaeophyceae species, and this difference was shown to be statistically significant ($P < 0.05$). The highest value in Rhodophyceae is that of *Chondria* species, 7.5 ± 0.5 , followed by *Polysiphonia* 4.75 ± 0.71 ($P < 0.25$), *Laurencia* species, 4.5 ± 0.5 ($P < 0.05$), then by *Amphiroa fragilissima*, *Degenia simplex* and *Spyridia filamentosa*, 4.0 ± 1.15 (< 0.05). A similar trend has been observed in the Red Sea algae (Khalil and El-Tawil, 1982) and the Mediterranean Sea algae (El-Tawil and Khalil, 1983).

No statistically significant differences were found in the protein content of the studied algae except within the Rhodophyceae where *Chondria* species showed a mean value of 12.15 ± 0.02 which is significantly higher than the mean value of other Rhodophyceae which was found to be 17.48 ± 1.3 ($P < 0.005$). However, *Amphiroa fragilissima* showed the highest protein content (16 - 19%).

Regional comparison showed that the protein content in the algae of Qatar, Arabian Gulf, was markedly lower than those of the Red and Mediterranean Seas (Table 4). Increase of nitrogen content has been reported to be due to either low temperature (Simpson and Schacklock, 1979) or low salinity (Laycock et al. 1981). The higher temperature and salinity in the Arabian Gulf may explain the variation of the algal protein in the three regions.

Polysiphonia broadiae, *Dictyota carviformis* and *Dictyosphaeria cavernosa* showed the highest lipid contents (12.37 %, 11.34 %, and 10.31 %)

respectively, while the lowest lipid content was found among the Phaeophyceae *Sargassum* species with a mean value of 2.76 ± 0.69 which is statistically significantly lower than the mean values of other Phaeophyceae species (6.89 ± 1.46 , $P < 0.025$).

Phaeophyceae showed statistically significantly higher total carbohydrate content than chlorophyceae ($P < 0.05$). The level in Rhodophyceae was significantly higher than that in Chlorophyceae ($P < 0.05$). Within the Rhodophyceae, *Laurencia* and *Polydiphonis* species showed a mean value of 57.49 ± 8.33 and 38.15 ± 2.15 respectively, and the difference was found to be statistically significant ($P < 0.05$).

Referring the carbohydrate content of the studied species to organic ash-free material, instead of total dry material, the values will be 88%, 85% and 85% corresponding to Phaeophyceae, Rhodophyceae and Chlorophyceae respectively.

These values are slightly higher than those reported for the Red and Mediterranean Seas (Table 4). This result agrees with the finding that carbohydrate is a function of the intensity of light (Dalev *et al.*, 1957; Morgan and Simpson, 1981).

Table 4
Regional variation in the mean chemical composition
of the different algal groups

	Chlorophyceae			Phaeophyceae			Rhodophyceae		
	A.G	R.S	M.S	A.G	R.S	M.S	A.G	R.S	.S.
Moisture	4.0	6.04	9.85	7.11	13.34	11.93	5.0	7.59	16.99
Ash	48.71	32.75	21.27	34.76	22.08	25.80	41.94	44.99	18.16
Total Protein	6.87	17.0	49.6	6.20	9.25	15.33	8.33	14.40	30.04
Total lipid	7.27	2.0	6.08	5.05	6.32	5.20	5.91	3.57	7.60
Carbohydrate	37.13*	81.0**	44.32**	52.95*	84.42**	79.47**	43.81*	82.01**	62.36**

* Based on dry weight material

** Based on organic ash free material

A.G Arabian Gulf

R.S Red Sea (Khalil and El-Tawil, 1982)

M.S Mediterranean Sea (El-Tawil and Khalil, 1983)

Phytochemical screening of the studied species revealed the presence of alkaloids in twelve species, seven of them belong to Rhodophyceae. Coumarins, flavonoids and saponins existed only in one species, whereas the tannins were found to be weakly recognized in two species (Table 1).

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دراسة المكونات الكيميائية لبعض الطحالب البحرية التي تنمو على سواحل قطر

**حلمي إسماعيل هيبة و محمد موسى درغام و سهير علي النجدي
وعبد الفتاح محمد رزق**

يشمل البحث المسح الكيميائي لثلاثة وعشرين طحلاً تمثل أكثر الأنواع انتشاراً على سواحل دولة قطر وذلك لتحديد نسبة ما تحتويه من بروتين - كربوهيدرات - معادن وكذلك الكشف عن وجود القلويادات - الكومارينات - الفلافونيدات - السابونينات والثانينات .