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ALGAE ALONG QATAR COASTS UTILIZATION AND FUTURE PROSPECTS

By

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ABSTRACT :

Most of marine algae have no equivalent on earth and therefore could be considered as irreplaceable sources of primary and secondary metabolites. This is especially the case for hydrocolloids from red and brown algae that are cultured and used at an industrial scale for food-processing (carrageenans and agars from red algae and alginates from brown algae are widely used as gelling agents and thickeners) but also for pharmaceutical uses (agar gels for culture of microorganisms). Others main applications of primary metabolites from algae concern pahrmacological activities, agronomic uses and cosmetic industry. Secondary metabolites form marine algae are also widely used, especially as source of fine chemicals such as antibiotics, vitamins, antioxidants and binders for radioelements.

Most of algae from Arabian Gulf are known and recent publications are available. Many of them are presented according to the marine biodiversity of the whole region and according to the main orders with a usable point of view. Studies on primary and secondary metabolites of some algae from Qatar coasts are in progress. Potential applications of some compounds isolated from red and brown algae from Qatar are presented and discussed along with potential applications of other species available on Qatar coasts but not yet studied.

INTRODUCTION

Basically, plant kingdom is based on photosynthesis then, a plant can be defined as an energy converter which realizes conversion of light energy into chemical energy as polysaccharides. So formed, this chemical energy is stored as two completely different groups of polysaccharides : storage products which only act as food reserve and are reusable (e.g. starch) and cell-wall components which only have structural functions and are not reusable (e.g. cellulose). Then, in a first approximation and according to the nature of the three main biochemical criteria : photosynthetic pigments, chemical nature of storage products and chemical nature of cell-wall components, three «botanical worlds» can be distinguished for macroscopic marine algae, as resumed on Table 1.

Table 1. The 3 « botanical worlds » for macroscopic marine algae.

BIOCHEMICAL CRITERIA	GREEN WORLD Chlorophyceae	RED WORLD Rhodophyceae	BROWN WORLD Phaeophyceae
PHOTOSYNTHETIC PIGMENTS	Chlorophylls a and b Carotenoids	Chlorophyll a Phycobilins Carotenoids	Chlorophylls a and c Carotenoids
MAIN STORAGE PRODUCTS	Starch α-1,4-glucans	Floridean starch α-1,4-glucans	Laminaran α-1,3-glucans
MAIN CELL-WALL COMPONENTS	Cellulose β-1,4-glucans	Carrageenans heavily sulfated galactans	Alginic acids poly-D-mannuronic acid poly-L-guluronic acid
		Agars slightly sulfated galactans	Fucinic acids β-1,2-sulfated fucans

So, for cell-wall components Chlorophyceae are based on D-glucose, Rhodophyceae are based on D-galactose and Phaeophyceae are based on D-mannose and its 5-epimer L-gulose. Now. it is obvious that marine algae did not appear in the ocean at the same time and Figure 1 summarizes the accepted evolution Figure for algae and plant on earth (1). It is largely accepted that all living organisms originate from primitive ocean then, for some phyla have been adapted to freshwater and lastly, for a few number of phyla, come on earth. Concerning the plant Kingdom only the «green world» has succeeded to aerial life and all land plants derive from Chlorophyceae. Consequently, land plants still have the same main biochemical features such as chlorophylls a and b, starch and cellulose.

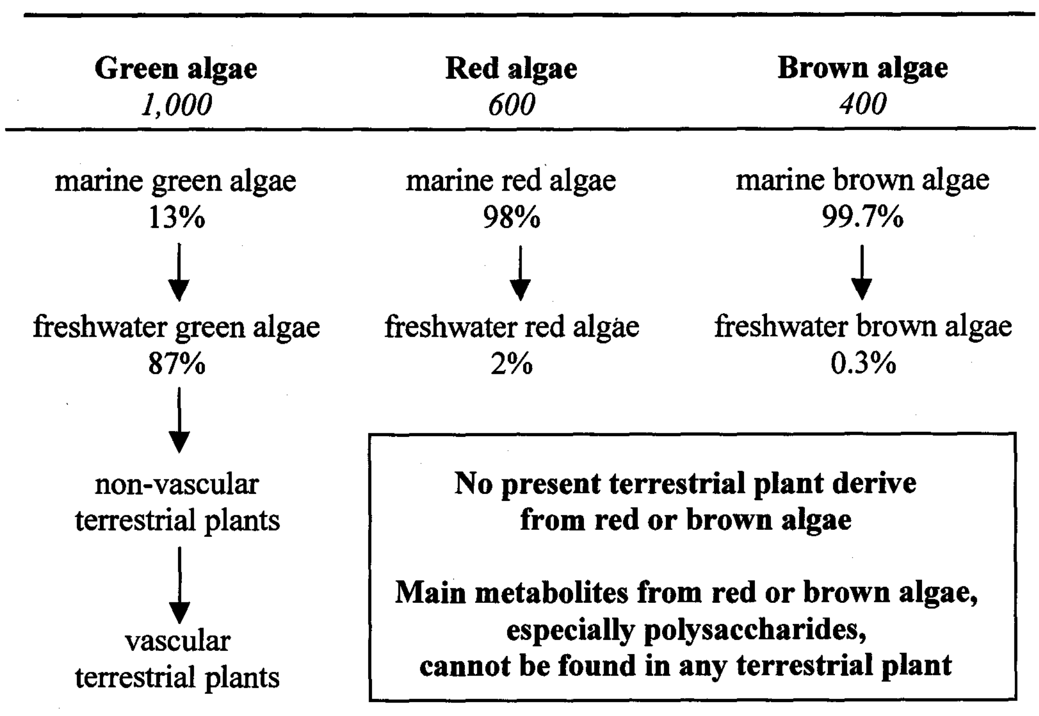


Figure 1. Evolution scheme for the 3 « botanical worlds ».

Numbers in italics give the age of the oldest known fossil in millions of years so, Chlorophyceae the most primitive pluricellular organisms are about 1 billion years old ! Other numbers give the percentages of living species. Then, it clearly appears form Figure 1 that most of primitive marine green algae are now adapted to freshwater but the most striking point is that almost all red and brown algae are still living in seawater. This is very important from an ecological and industrial point of view because polysaccharides form both red and brown algae are widely used as food in Far East and Asia, and as food-additive, mainly thickeners and gelling-agents all over the world. It is impossible to get these kinds of polysaccharides form any land plant and so, it is extremely important for men to manage red and brown algae resources.

Marine macroalgae from the Gulf

From a general point of view the Gulf mainly contains green, red and brown algae well distributed among all orders but green algae are found in less extent than the two other classes. However, all genera and species that can can be found in the Gulf are not yet known and the following numbers will raise with the increase of taxonomic researches. These data are summarized in Tables 2,3 and 4 (2-6 and references therein).

Table 2, Orders and Genera identified in the Gulf

Orders	Identified Genera
Bryopsidales	*Avrainvillea, Bryopsis, Caulerpa, Codium, Trichosolen*
Chaetophorales	*Acrochaete (= Endoderma), Phaeophila*
Cladophorales	*Chaetomorpha, Cladophora, Rhizoclonium*
Dasycladales	*Acetabularia*
Siphonocladales	*Boodlea, Cladophoropsis, Dictyosphaeria, Siphonocladus, Valonia*
Ulvales	*Blidingia, Enteromorpha, Ulva*

Table 3. Rhodophyceae: the 54 genera identified in the Gulf.

Orders	Identified Genera
	BANGIOPHYCEAE
Bangiales	*Bangia, Erythrocladia*
Compsopogonales	*Erythrotrichia*
Goniotrichales	*Asterocystis*
Porphyridiales	*Chroodactylon*
	FLORIDEOPHYCEAE
Acrochaetiales	*Acrochaetium*
Ceramiales	*Acanthophora, Aglaothamnion, Anotrichium (=Griffithsia), Antithamnion, Centroceras, Ceramium, Chondria, Crouania, Dasya, Digenea, Eupogodon, Herposiphonia, Heterosiphonia, Hypoglossum, Laurencia, Leveillea, Lophocladia, Murrayella, Myriogramme, Polysiphonia, Spyridia, Tolypiocladia (= Roschera)*
Cryptonemiales	*Amphiroa, Fosliella, Grateloupia, Hydrolithon, Jania, Lithophyllum, Lithothamnion, Melobesia (= Pneophyllum), Sporolithon*
Gelidiales	*Gelidiella, Gelidium, Wurdemannia*
Gigartinales	*Ahnfeltia, Dudresnaya, Gracilaria, Hypnea, Peyssonnelia, Sarconema, Solieria*
Nemaliales	*Asparagopsis (= Falkenbergia), Galaxaura, Liagora*
Rhodymeniales	*Botryocladia, Champia, Fauchea, Lomentaria*

Table 4. Phaeophyceae: the 25 genera identified in the Gulf

Orders	Identified Genera
Chordariales	*Cladosiphon, Myriactula, Nemacystus, Stilophora*
Dictyotales	*Dictyopteris, Dictyota, Dilophus, Lobophora, Padina, Spatoglossum, Taonia, Zonaria*
Dictyosiphonales	*Colpomenia, Hydroclathrus, Iyengaria, Rosenvigea*
Ectocarpales	*Ectocarpus, Feldmannia, Giffordia, Hincksia*
Fucales	*Cystoseira, Hormophysa, Sargassum, Turbinaria*
Sphacelariales	*Sphacelaria*

Is there any relations between marine macrophytes from the Gulf and those from the Red Sea? The question could be asked due to huge and regular oceanic motions consecutive to winter and summer monsoons and so, it is important to compare algae distribution at both genera and species levels, between Gulf and Red Sea. Figure 2 resumes these two distributions according to the data available from literature (7).

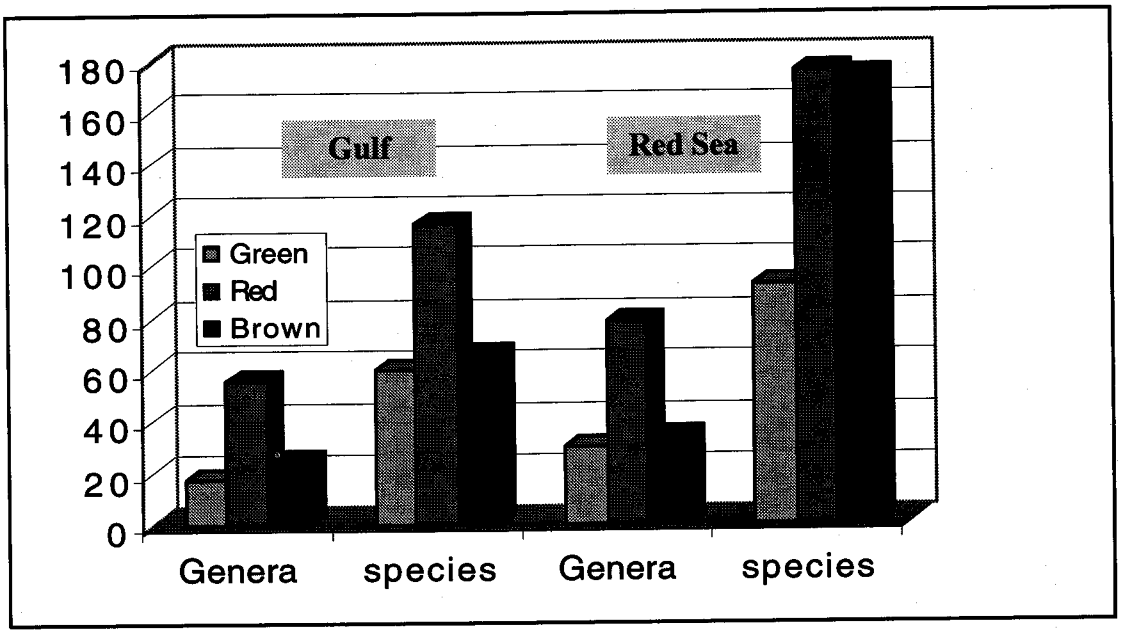


Figure 2. Distribution of the 3 classes of marine macrophytes between Gulf and Red Sea.

From Figure 2 it clearly appears that the distribution of algae between Gulf and Red Sea is identical at the genera level but not at the species level. In the Gulf Rhodophycea clearly dominate contrary to Red Sea for which Red and brown algae cooccur with the same importance. Now, it is interesting to compare, for each of the 3 classes, algae species that have been identified both in the Gulf and in the Red Sea and algae species that have been identified only in the Gulf but not yet in the Red Sea (Figure3).

Thus, it clearly appears form Figure 3 that about 1/2 of the green algae, 1/2 of the red algae and 1/3 of the brown algae identified in the Gulf can be considered as endemic.

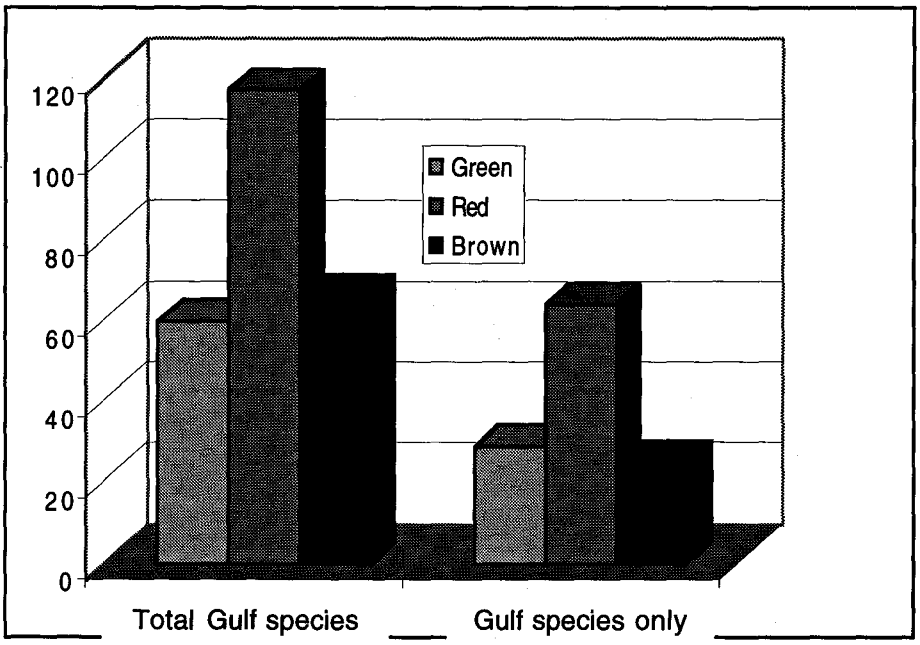


Figure 3. Part of endemic Gulf species *versus* total Gulf species.

The research program on marine algae at the University of Qatar.

A research program on algae from Qatar coasts began in 1995 and associates the University of Qatar and the University of Nantes, France. A first task of this program was to identify all, or almost all marine algae available on Qatar coasts. Although this kind of work is never finished the *Algarium of Qatar* is available for researchers at the Department of Marine Science, Faculty of Science, University of Qatar (8). A second aim of this program was to collect and study the main algae for their primary metabolites (mainly polysaccharides) and secondary metabolites (total lipid fraction, i.e. fatty acids, steroids and terpenes) to find potential biological activities. In this context algae species were collected all around Qatar coasts but especially in the following areas : Umm Bab, Dukhan, Az Zubarah, Al Khuwayr, Al Khawr, Doha and Al Safiliyah Island, Al Wakrah, Umm Said, Khwar Al Udaid and Halul Island off the Qatar coasts.

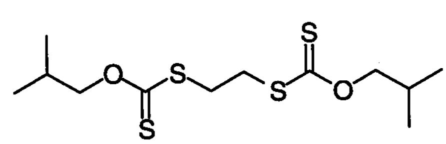
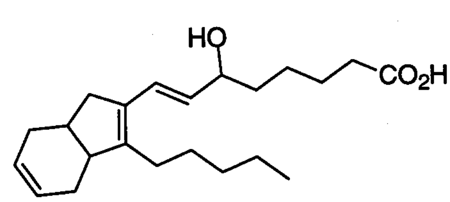
Many of algae are endemic and new from a biochemical point of view. Thus, the purpose of this lecture is to give a global overview on possibilities offered by seaweeds of the Gulf and especially those available along Qatar coasts. These potentialities will be examined for primary metabolites, mainly polysaccharides, and secondary metabolites as well.

Chlorophyceae - utilization and future prospects

From a general point of view there are very few utilizations of polysaccharides from green algae. However, polysaccharides from green algae contain *α-L-rhamnose,* a rare sugar that is used in cosmetics industry to fix fragrances. *α-L-rhamnose* occur in cell-wall constituents of species belonging to Dasycladales, especially *Acetabularia* and Ulvales, especially *Enteromorpha* and *Ulva*. *α-L-rhamnose* is one of the most expensive commecially available sugar; its current price is about 20US$ for 5 grams.

For a more academic point of view and maybe for biological applications it could be interesting to study secondary metabolites form *Dictyosphaeria cavernosa,* a small Siphonocladale but easy to recognize and to collect. Form Marin lit database (9) only three species of *Dictyosphaeria* genus are known but only two have been chemically studied for their secondary metabolites. Table 5 summarizes all available data concerning this genus.

Table 5. Recent researches on *Dictyosphaeria* sp.

Dictyosphaeria cavernosa	Qatar	Sterols [10], Fatty acids [11]
Dictyosphaeria favulosa	India	ethylene-bis-isobutylxanthate [12, 13] 
Dictyosphaeria sericea	Australia	dictyosphaerin [14] 

From Table 5 it is very likely that *Dictyosphaeria cavernosa* that can be easily found along Qatar coasts, especially near Al Wakrah area, contains at least one original secondary metabolite.

Rhodophyceae-utilization and future prospects

Primary metabolites of red algae are well-known to contain specific food additives polysaccharides widely used as thickeners or gelling agents (cf. Dr. Olivier Barbaroux's lecture). The two main types of phycolloids: agars, mainly from Gelidiales species and carrageenans, mainly from Gigartinales species can be found on the Gulf coast. The south coast of the Gulf, from Koweit to Emirates is largely flat and sandy, two good conditions to develop algae farming. The best species that could be produced by culture could be *Gelidium* and *Gracilaria* for agar and *Hypnea* for κ-carrageenan. Other Gigartinales that could be studied for the carrageenan content could be *Solieria* for ι-carrageenan (Figure 4).

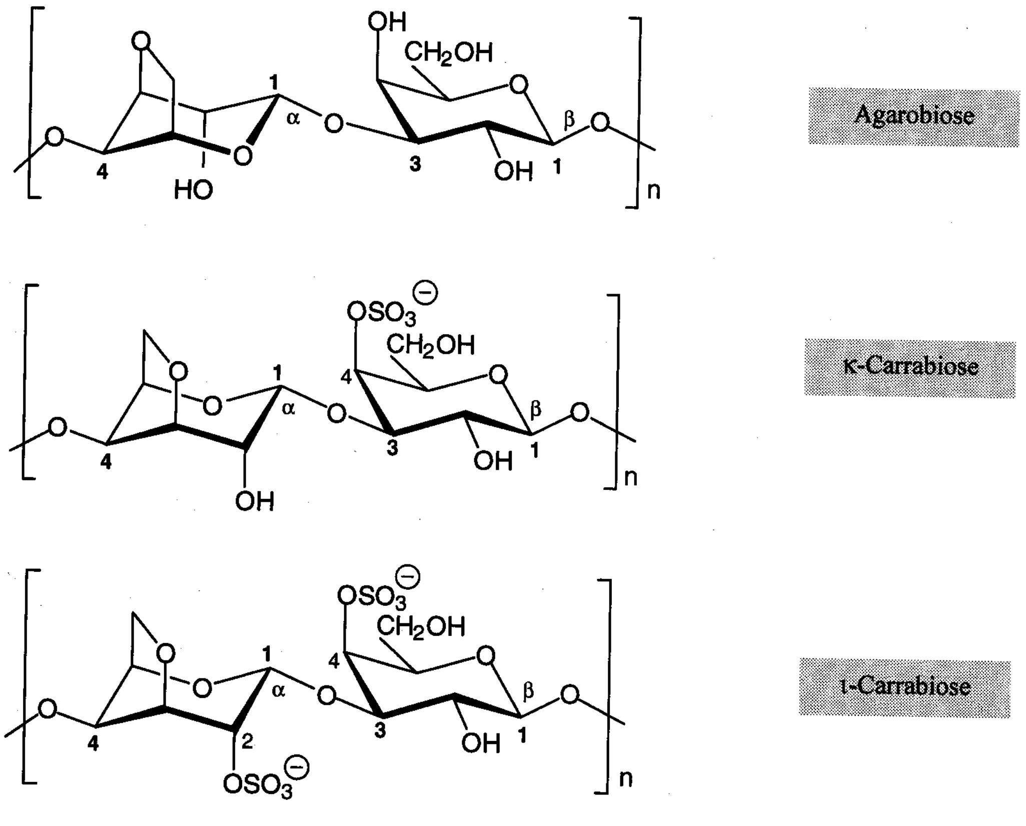
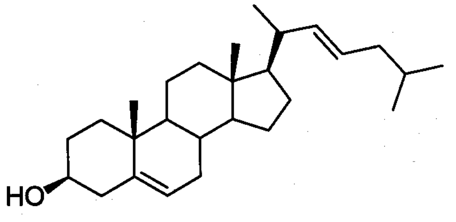


Figure 4. Basic structures for agar, κ- and ι-carrageenans.

Considering the secondary metabolites, *Hypnea* species were shown to contain some unusual compounds as 22-dehydrocholesterol in *Hypnea* sp. (15) and 5-iodo5'-deoxy-tubercidine in *Hypnea valentiae* (16) (Figure 5). This very unusual iodinated nucleoside analogue displayed antiviral activity, At least five species of *Hypnea : H. cervicornis, H. carnuta, H. musciformis, H. pannosa and H. valentiae* were shown to occur along Gulf coasts and three of them already identified along Qatar coasts. Then, it could be important to compare them for their sterol content and their biological activities, and their carrageenan content as well.



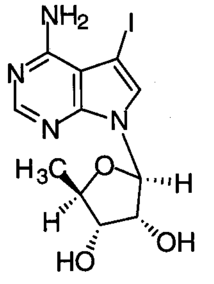


Figure 5. Structure of 22-dehydrocholesterol and 5-iodo-5'-deoxytubercidine

Natural products that display biological activity often contain nitrogen atoms. Then, it is important to know how nitrogen is frequently encountered in marine natural products from algae. Figure 6 displays the relative percentages of nitrogenous and non-nitrogenous compounds ever isolated form algae, all classes considered.

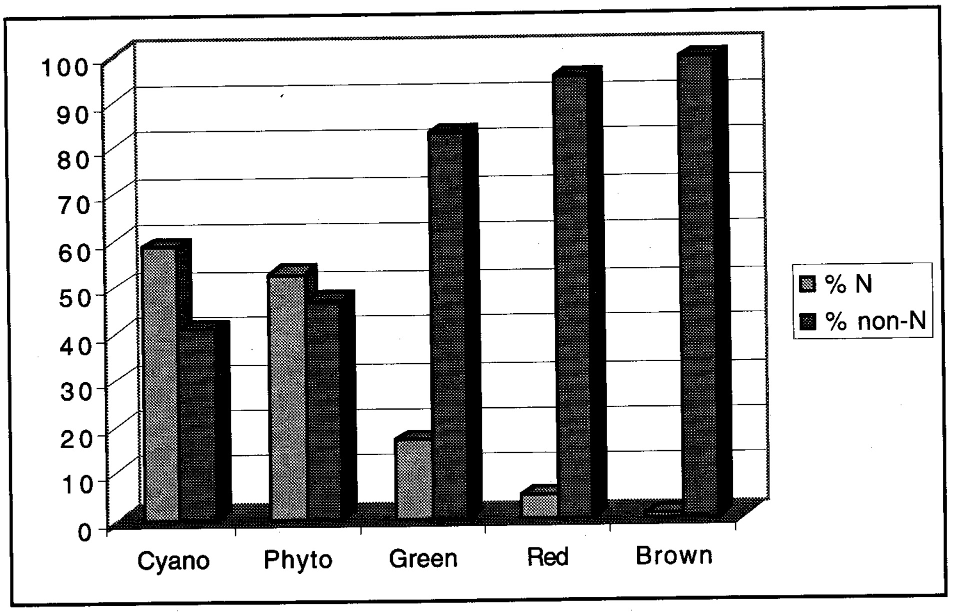


Figure 6. Distribution of nitrogenous and non-nitrogenous compounds within algae.

It appears form Figure 6 that the distribution of nitrogenous compounds among marine algae seems to be correlated with their evolution stage. Primitive prokaryotic cyanophceae are the richest in nitrogenous compounds, then come the unicellular but eukariotic microalgae known as phytoplankton and then, the pluricellular green red and brown algae, the most recent ones, that are the poorest in nitrogenous compounds. Considering the non-nitrogenous secondary metabolites, red algae is the richest class with a lot of halogenated compounds rarely encountered in green or in brown algae, Within the Rhodophyceae class, the genus *Laurencia* is the richest and the more extensively studied of all algae genera. Table 6 summarizes why *Laurencia* species are so intensively studied all over the world.

Table 6, Interest of *Laurencia* genus for marine chemists.

* 118 identified species all over the world [17].
* 59 chemically studied species (50% of the identified species [90]).
* 452 papers published on secondary metabolites from *Laurencia* [9].
* 580 elucidated structures, most of them unknown from earth organisms. The most frequent compounds are halogenated terpenes and linear C15 acetogenins, often halogenated and containing oxygenated heterocycles [9].

Any new *Laurencia* species very likely contains at least on new compound and this was the case for *Laurencia paniculata* from Qatar Coast (AL-Zubarah). This species was shown to contain a new and unusual brominated tricyclic diterpene, we called it painculatol (18). This diterpene appears to be related to *ent*-isoconcinndiol as manoyloxide is related to sclareol. Then, it is likely that a postulated *epi-* paniculatol related to the known isoconcinndiol will be find later either in *Laurencia paniculata,* or in another *Laurencia* species (Figure 7).

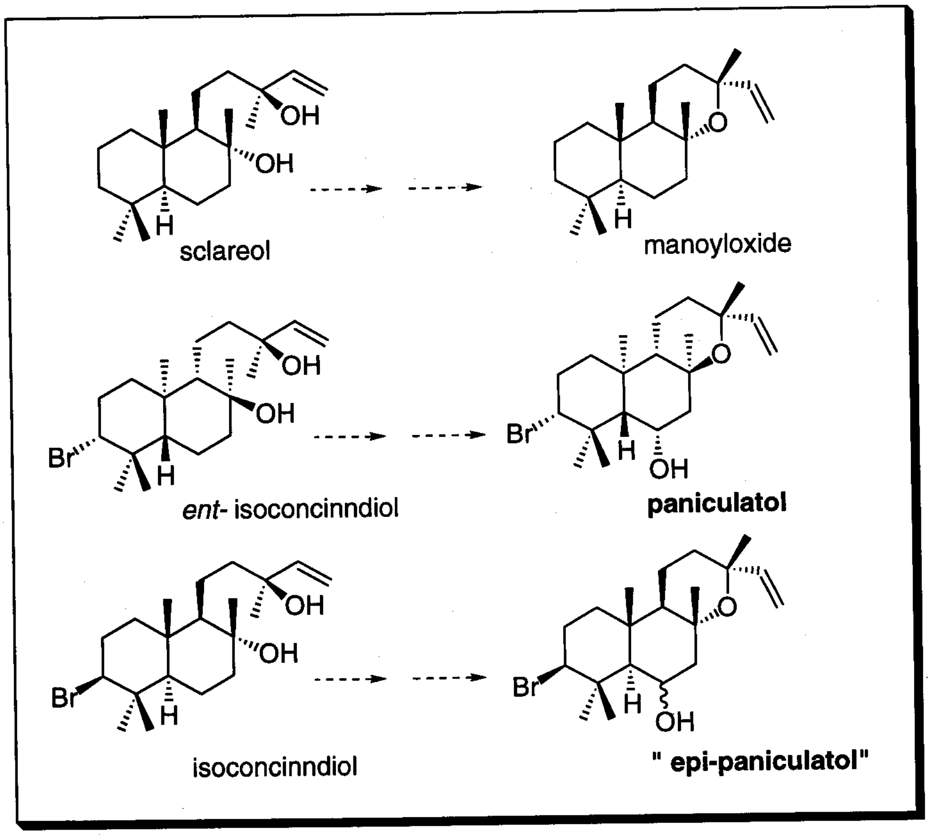


Figure 7. Position of paniculatol among known earth and marine diterpenes.

Researches with *Laurencia paniculata* from Qatar are under investigations, according to the general extraction procedure displayed on Figure 8.

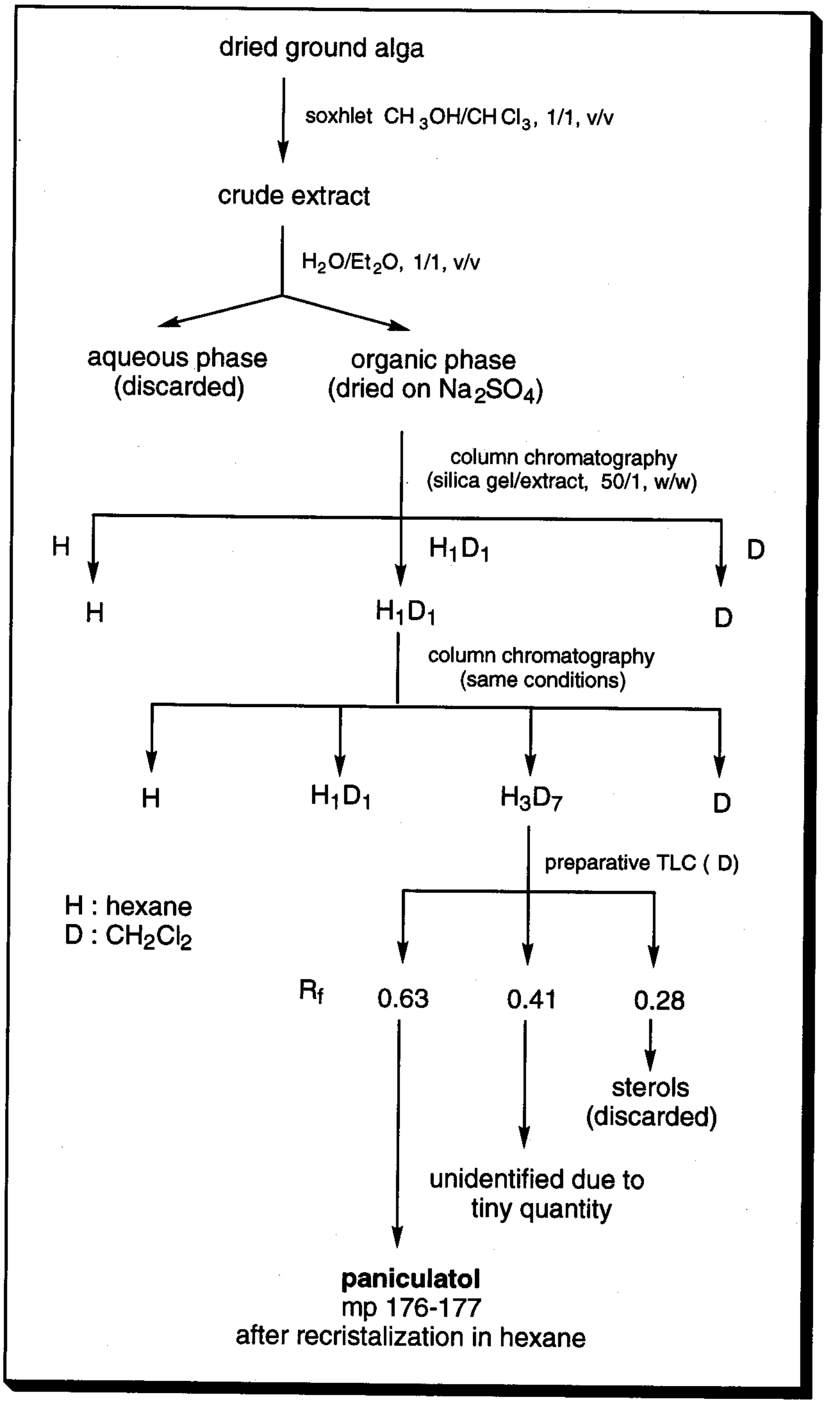


Figure 8. General extraction procedure for *Laurencia paniculata.*

Two other *Laurencia* species have been shown to occur on Qatar coasts, namely *L. papillosa* and *L. perforata.* Both of them have already been studied but in another parts of the world and it is likely that these species form the Gulf could contain new other secondary metabolites. *Laurencia papillosa* is considered as especially important because the Australian species was shown to display antimalarial activity due to *para-* methoxybenzaldhyde (19). *Laurencia perforata* from Spin contained at least 20 sesqui - and diterpenes, most of them being halogenated (6,9). It is very likely that new halogenated terpenes could be found in the Gulf variety of *L. perforata.*

Phaeophyceae - utilization and future prospects

As Rhodphyceae, Phaeophyceae are insteresting form their both primary and secondary metabolites. Concerning polysaccharides brown algae are characterized by the presence of alginates that are complex polyholosides built from β-D-mannuroinc and α-L-guluronic acid. in first approximation alginates could be considered as a succesion of «blocks» each of them being regularly constituted by association of mannuronic acid (MM blocks). guluronic acid (GG blocks) and mixed mannuronic and guluronic acids (MG blocks). Due to conformations of individual uronic acids the shape and size of blocks are different (Figure 9).

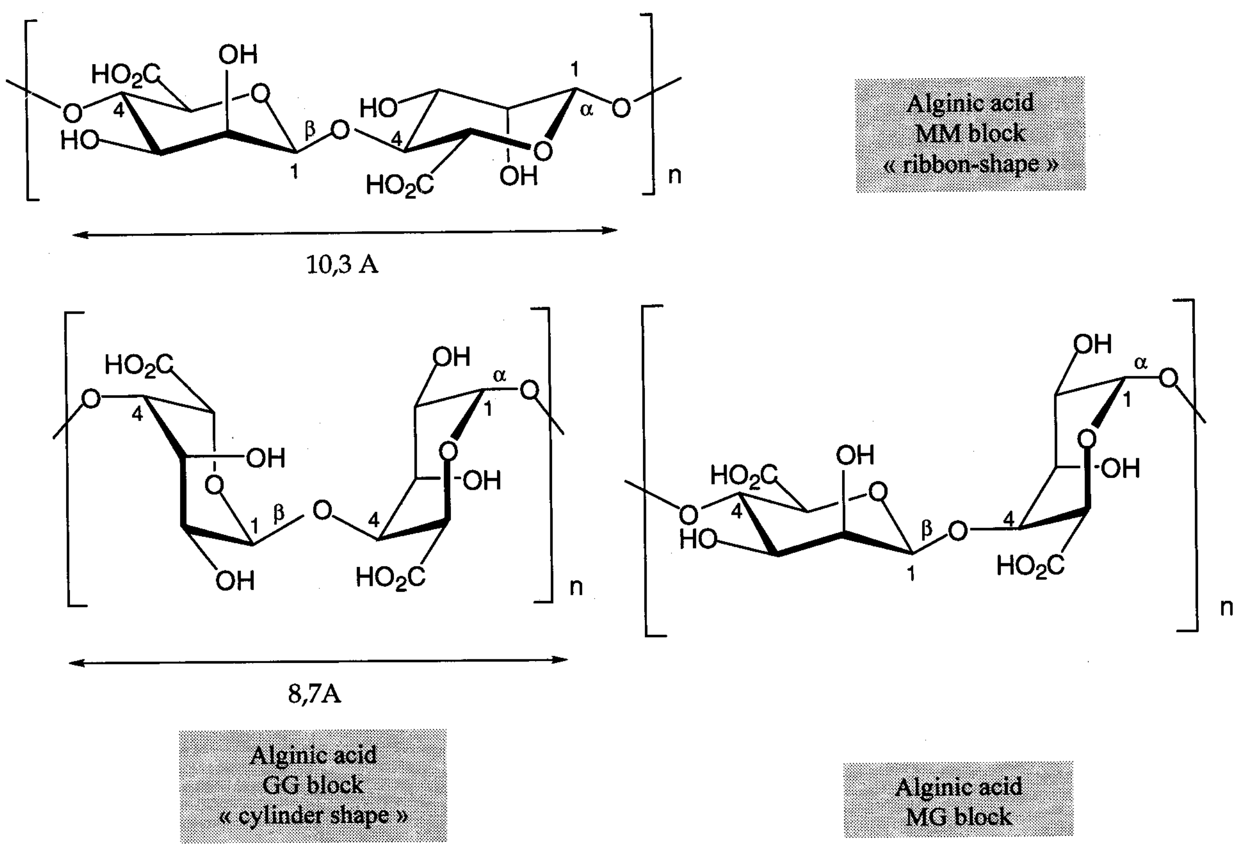


Figure 9. Structural units for « alginic acid ».

These complex structures for alginates have consequences for their physiochemical properties, especially concerning rheology. Most of these relationships between structure and activity can be deduced from the M/G ratio. Thus, in a general way M/G ratio is correlated with temperature and for brown algae growing in cold seas M/G ratio is high (from 1.5 to 3.0) and the alginate will be a good thickener. For brown algae growing in warm seas, M/G ratio is low (from 0.2 to 1.4) and the alginate will be a good gelling-agent. Another important property of alginate is their ability to complex with cations from heavy metals. In a general way, the lower M/G ratio, the higher affinity for heavy metal cations. Thus, for competitions between calcium and strontium it would be better to use an alginate with a low M/G ratio value. This is very important for detoxification with radioactive 90 strontium. Tests have been made with success after Chernobyl disaster.

Of course, Gulf can be considered as a warm sea and thus, alginates from brown algae such as *Cystoseira, Hormophysa. Sargassum* or *Turbinaria,* to mention the most abundant genera, should be studied for their M/G ratio values all over their life cycle. Furthermore, at a regional point of view these alginates could be used as food additives for brown algae that contain a good yield of alginate. The determination of alginate content and M/G ratio are not difficult but need time and thorough work. The general procedures are summarized on Figures 11 and 11 (20,21).

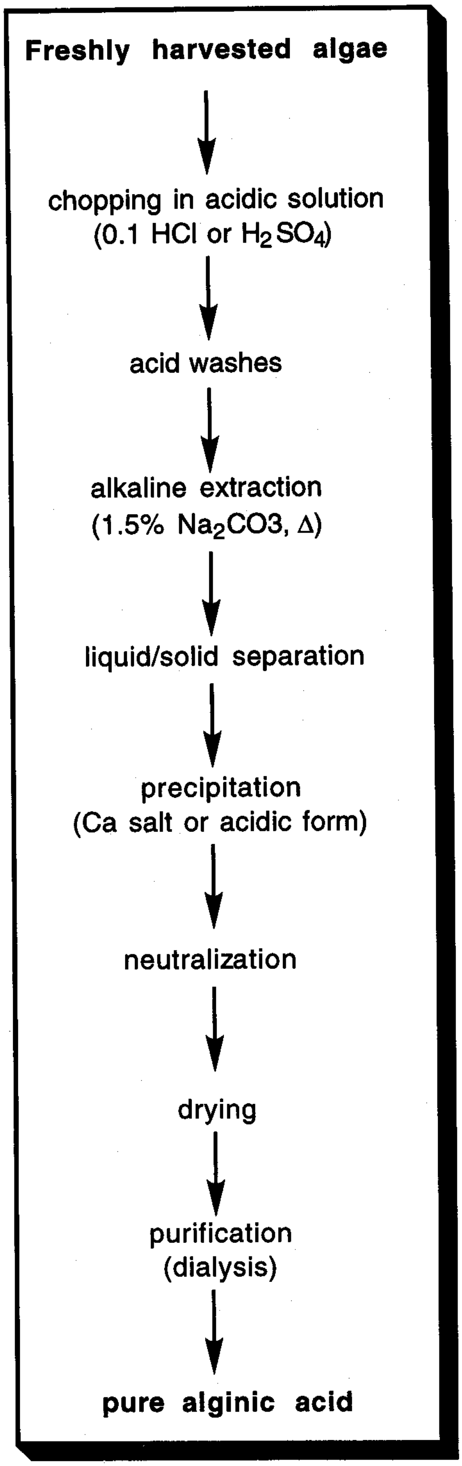


Figure 10. Extraction of alginic acid.

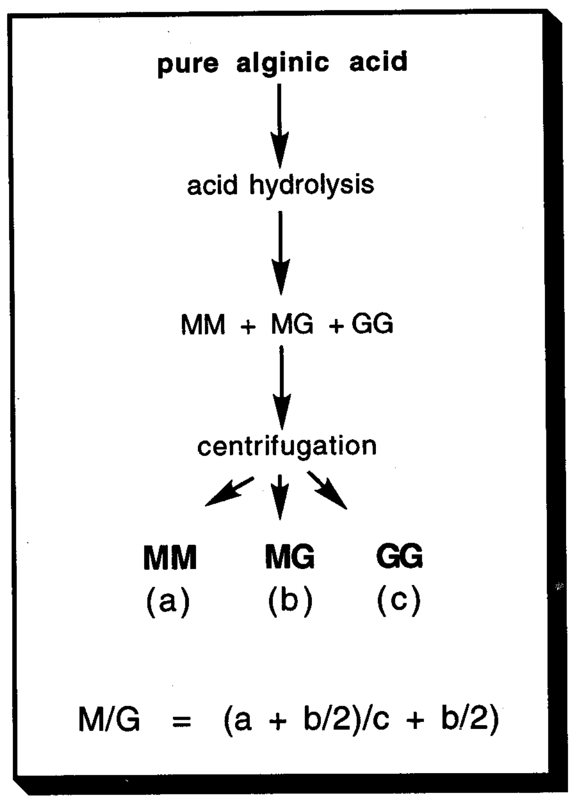


Figure 11. Determination of M/G ratio.

Preliminary results performed on brown algae from Qatar coasts gave the following results (Table 7).

Table 7. Alginate content and M/G ratio for 3 brown algae from Qatar [21].

	Hormophysa triquetra	*Cystoseira trinodis*	*Sargassum binderi*
Alginate (%/dry weight)	14	18.5	14
M/G ratio	0.46	0.55	0.80

Thus, it appears that the study of alginates of brown algae form the Gulf is especially interesting due to their low M/G ratio. These algae could have important applications as binders for heavy metal cations and, last but not the least they could also be used as gelling agents.

The chemistry of secondary metabolites from brown algae is very rich, especially for Dictyotales and Fucales orders and it appears that both orders are well represented in the Gulf with 8 genera for Dictyotales and only 4 genera for Fucales. For this latter order 2 genera, *Hormophysa* and *Turbinaria* are quite unknown from a chemical point of view.

Dictyotales are well-known to contain a lot of cyclic diterpenes usually devoid of halogen atoms, especially the ubiquist genus *Dictyota* from which 235 compounds, most of them terpenes, were published (9). It is very likely that *Dictyota species* growing in Gulf contain new diterpenes. Also of interest for their terpene content are the genera *Dictyopteris, Doplophus, Lobophora, Spatoglossum, Taonia* and *Zonaria* (6,9). Fucales also contain a lot of secondary metabolites but completely different from those of Dictyotales. In Fucales genera, most of diterpenes are linear instead of cyclic and most of them are meroditerpenes with hydroquinone or quinone moieties or complex phenolic compounds (phlorotannins). The chemistry of Fucales from the Gulf could be very interesting due the fact many species are still unknown *(Hormophysa triquetra)* or belong to genus for which much is known in other seas but not in the Gulf area *(Cystoseira, Sargassum, Turbinaria).* Thus, in 1997 near Halul Island we found (Scuba diving) a lot of Turbinaria sp. that could be *T. conoides.* Very few is known about this genus however, *T. conoides* from Taiwan and *T. ornata* from Japan have been shown to contain a highly cytotoxic hydroperoxysterol (22) and turbinaric acid respectively (Figure 12). The latter compound is a very unusual squalene derivative that displayed in *vitro* cytotoxicity against human colon carcinoma (23).

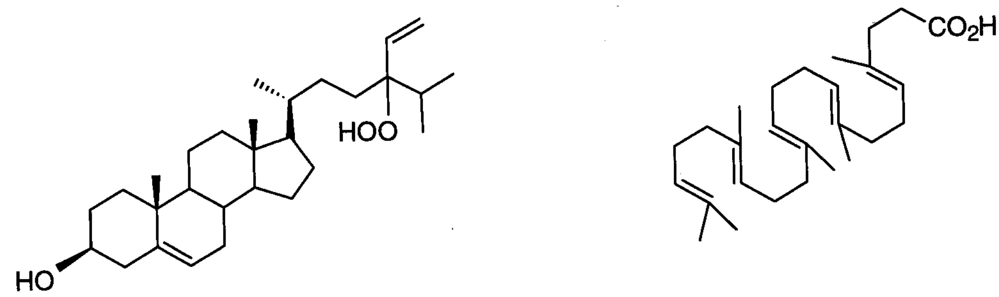


Figure 12. Strucutres of 24-hydroperoxy-24-vinylcholesterol and turbinaric acid

Of course, it could be of great interest to study *Turbinaria* sp. from Qatar for biological activity.

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