

## Mycosporine like amino acids in brown algae

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Seaweed, also known as macroalgae, represents organisms that shares similarities with plants, that can exist as single cell organisms or groups of cell forming a colony. They can usually be found attached to rocks or other hard enough substrata in seashore.

In the middle of the XIX century, the Irish botanist Willian Henry Harvey(1811-1866) divided macroalgae in 3 distinct groups. This division was based on the pigmantation:

- phylum Ochrophyta(green algae)
- phylum Rhodophyta(red algae)
- phylum Phaeophyceae(brown algae)

The members of this three groups are different in more then just pigmantation, like biochemical aspect regarding photosynthetic pigments, compound in the cells walls, chloroplasts structure, connections between cells in colony, storage compounds, presence of flagella or the absence of it.

Phaeophyceae represents a group of macroalgae that, besides chlorophyll a and chlorophyll c, contains the xanthophyll pigment fucoxanthin that cause the characteristic greenish-brown color. The color can range from dark brown to olive green, depending on the proportion in which the pigments are found.

Most brown algae adaptated to marine environment, very few species are found in freshwaters. The brown pigmantation apparently is an important adaptation to deep sea.

There are aproximatly 1500-2000 species of brown algae throughout the world, mostly been found in temperate zones in the Northern Hemisphere.

### Classification:

Domain Eukaryota  
Kingdom Protista  
Phylum Heterokontophyta  
Class Phaeophyceae

Phaeophyceae are a complex organism. The cell walls are composed of cellulose and alginic acid. Alginic acid is a long chain heteropolysaccharide. Food reserves are usually represented by complex polysaccharides, sugars and higher alcohols. Laminarian is the main carbohydrate reserve.

Brown algae (Fig.1) can be very varied regarding the size and form. It can vary from small filamentous epiphytes to the complex giant kelps (order Laminariales, can range between 1 metre and 100 metres).

Like other evolved algae species, they present both sexual or asexual reproduction.

Higher phaeophyta have a life cycle that presents generation alternation, meaning they have both diploid and haploid stages.

The haploid stage is represented by the thallus and the diploid stages can be either isomorphic or heteromorphic.

Sexual reproduction may be isogamous, oogamous, or anisogamous. There is evidence of the sex chromosome (Lewis R.J. 1998).

Phaeophyta used to be harvest to for the extraction of iodine and potash. In recent years it has been extensively used for extracting the alginic acid. Alginic acid can be derivated in alginate, which is used in industries. Alginate is a major colloidal gel that is used and as a stabilizer, emulsifier and binder.

Alginate is used in fabric printing, as a stabilizer in baking and ice cream industry, toothpaste, soap, meat preservation.

Phaeophyta is also used in agriculture for manufacturing agriculture sprays. Laminaria is also used in the food industry. Man-made algal ponds are used to cultivate and harvest the brown algae for production of food supplements and alginates. The harvested algae are processed in order to prepare seaweed meals. The high protein seaweed meals are then exported to various countries, especially to solve malnutrition.

Brown algae are also used in cosmetics, there is a wide variety of products based on algae extract.

Ultraviolet radiation represents a type of electromagnetic radiation that can cause much harm to living organisms, interfering with metabolic reactions, causing atomic bonds to split, etc. The genetic information codified in the molecular structure of nucleic acids can be altered by exposure to UV light.

UV light can lead to cancer and premature skin aging. UVA region, which has a lower energy but it can penetrate deeper the skin, is responsible for the premature skin aging effect of sun light.

Organisms exposed to solar radiation can experience harmful doses of UV in their natural habitats.

In order to protect themselves from the damaging effects of radiation different organisms have developed defence mechanisms.

One such mechanism is the biosynthesis of compounds called mycosporin-like amino acids, defence used by different types of microorganisms.

Biosynthesis of mycosporine and accumulation in cells serves as protection, by shielding the cells sensitive molecules. Mycosporine-like amino acids (MAAs) are derivated compounds of mycosporine that contains an amino-cyclohexenimine ring linked to an amino acid, amino alcohol or amino group. They present absorption maximum between 320 and 360 nm.

MAAs have been reported in different types of organism, such as cyanobacteria, algae and animals. MAA represents a family of secondary metabolites that, directly or indirectly, absorb the energy of harmful radiation, protecting the organisms from them. MAAs are small intracellular compounds, with a mass of approximately 400 Da, colorless and water-soluble.

In general, MAAs has a glycine subunit at the third carbon atom, although some MAAs contains sulphate esters or glycosidic linkages (1997).

MAAs are preferred as photoprotective compounds, not only because their absorption UV maximum, but also because they have a high molar extinction coefficient ( $\epsilon=28,100-50,000$  per M $\cdot$ cm), can dissipate absorbed radiation efficiently in form of heat without producing reactive oxygen species, are photostable and presents resistance to several (Whitehead and Hedges 2005).

Studies indicate that this compounds manifest their protecting properties not only in the organism that produces them but also in the primary and secondary consumers in the food web (Helbling, 2002).

Each MAA generally contains a glycine moiety on the C3 of the cyclohexenimine ring and a second amino acid (ex: porphyra-334, shinorine, mycosporine-2-glycine, mycosporine-glycine-glutamic acid). Instead of secondary amino acid it can contain an amino alcohol (ex: palythanol; asterina-330) or an enaminone system (palythene, usujirene) linked to the C1. It has been discovered that in some corals the glycine radical has been replaced by methyl amine (mycosporine-methyl-aminoserine, mycosporine-methylamine-threonine) (Teai T, Raharivelomanana P, Bianchini JP, Faura R, Martín PMV, Cambon).

Another exception is the apparently unique MAA that is commonly found in several sea anemones, mycosporine-aurine.

In the past decades there have been an interest in the shielding properties of MAA.

Many scientist have been performing experiments with extracts that contains MAA obtained from different species.

In order to obtain an MAA extract from algae, the most used method is the one used by Carreto, Carignan, and Montoya (2005).

Acording to them, the algae samples where soaked overnight before in water. Then methanol was added over and the solution sonicated on ice-bath. After sonication , the samples where centrifuged. The supernatant was colected, and the remaining algae samples were procesed twice more with methanol and sonication.

The resulting supernatant was the concentrated using rotary evaporation.

Another method that can be used to obtain an MAA extract is by soaking the samples overnight in water, and then adding a 20% methanol solution and leaving the samples 2 hours at 45 degress. The solution is colected and the algae samples are extracted twice more. The colected solution is then concentrated using rotary evaporation.

Afterwords, the MAA can be separated and analysed based on their absorbtion and molecular mass, using HPLC analysis and MS analysis.

With the recent climate changes, the distruction of ozone layer, there is an increase in the need to develop new methods of protection agains harmful agents like solar radiation.

MAAs proprieties makes then a perfect candidate for countermeasures agains UV radiation.

The fact that this compounds offers protection not only in the organisms that synthesis them but can also exert their protective properties in organisms that dont. They can prove to be quit usefull in preventing UV exposure caused diseases, mutations, photoaging indused by reactive oxygen species, and improve our life and protect it.

## References

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Fig.1 Brown algae

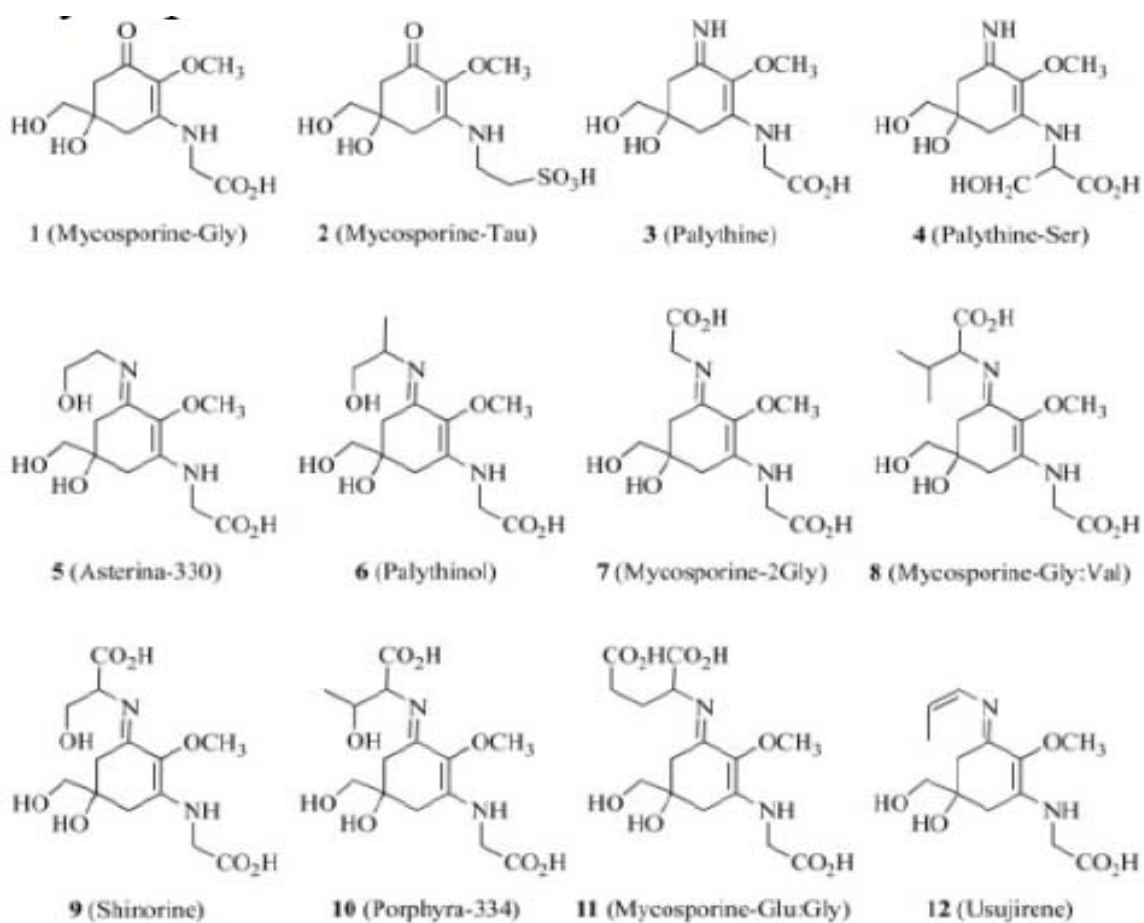


Fig.2 Mycosporine-like amino acids