REVIEW

Photoprotective compounds from marine organisms

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Abstract The substantial loss in the stratospheric ozone layer and consequent increase in solar ultraviolet radiation on the earth's surface have augmented the interest in searching for natural photoprotective compounds in organisms of marine as well as freshwater ecosystems. A number of photoprotective compounds such as mycosporine-like amino acids (MAAs), scytonemin, carotenoids and several other UV-absorbing substances of unknown chemical structure have been identified from different organisms. MAAs form the most common class of UV-absorbing compounds known to occur widely in various marine organisms; however, several compounds having UV-screening properties still need to be identified. The synthesis of scytonemin, a predominant UV-A-photoprotective pigment, is exclusively reported in cyanobacteria. Carotenoids are important components of the photosynthetic apparatus that serve both light-harvesting and photoprotective functions, either by direct quenching of the singlet oxygen or other toxic reactive oxygen species or by dissipating the excess energy in the photosynthetic apparatus. The production of photoprotective compounds is affected by several environmental factors such as different wavelengths of UVR, desiccation, nutrients, salt concentration, light as well as dark period, and still there is controversy about the biosynthesis of various photoprotective compounds. Recent studies have focused on marine organisms as a source of natural bioactive molecules having a photoprotective role, their biosynthesis and commercial application. However, there is a need for extensive work to explore the photoprotective role of various UV-absorbing compounds from marine habitats so that a range of biotechnological and pharmaceutical applications can be found.

Keywords Cyanobacteria · Macroalgae · Phytoplankton · Mycosporine-like amino acids · Scytonemin

Introduction

There is growing interest in marine organisms to explore the bioactivity of various marine compounds associated with human life. A variety of marine natural products with their specific activities, such as antimalarial, antituberculosis, anticancer, antifoulants, anti-inflammatory, anti-HIV, etc., have been reported from diverse marine organisms such as cyanobacteria, macroalgae, phytoplankton and animals [22, 28]. In recent years, natural products from marine organisms have gained increasing research awareness, and a number of novel marine compounds of potential economic importance have been reported from different marine organisms [22, 60, 61, 111, 123, 216, 230, 231].

During the past 2 decades, a substantial loss in the stratospheric ozone layer has been noticed that has aroused concern about the effects of increased solar ultraviolet radiation (UVR), particularly UV-B radiation (280–315 nm), on the earth's surface. Solar UV-B radiation is detrimental for most sun-exposed organisms, including humans [84, 88, 187, 192, 193]. An increase in UV-B radiation has aroused interest in searching for the natural photoprotective compounds from various organisms such

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as microorganisms, plants and animals of marine as well as freshwater ecosystems.

A number of photoprotective compounds, such as melanins, mycosporines, mycosporine-like amino acids (MAAs), scytonemin, parietin, usnic acid, carotenoids, phycobiliproteins, phenylpropanoids and flavonoids and several other UV-absorbing substances of unknown chemical structure, have been identified from different organisms (Fig. 1) [21, 42, 75, 93, 94, 97, 102, 110–112, 124, 194]. There have been a number of reviews about diverse classes of compounds from natural sources including marine habitats, but the occurrence of photoprotectants from marine sources has only partially been elucidated. This review summarizes the occurrence and biosynthesis of important UV-absorbing/screening compounds from various marine sources and their extensive commercial application.

## Marine photoprotective compounds

UVR is one of the most harmful exogenous agents and may affect a number of biological functions in all sun-exposed living organisms. Solar radiation exposes the organisms to harmful doses of UV-B and UV-A (315–400 nm) radiation in their natural habitats. In response to intense solar radiation, organisms have evolved certain mechanisms such as avoidance, repair and protection by synthesizing or accumulating a series of photoprotective compounds, such as MAAs, scytonemin, carotenoids and certain other compounds to counteract the toxicity of UV (particularly UV-B) radiation [64, 111, 184, 188, 194, 198]. Furthermore, MAAs are the most common compounds with a potential role as UV sunscreens in marine organisms.

Mycosporine-like amino acids

Mycosporine-like amino acids have been reported in diverse organisms; they are a family of secondary metabolites that directly or indirectly absorb the energy of solar radiation and protect organisms exposed to enhanced solar UVR [84]. MAAs are intracellular, small (<400 Da), colorless and water-soluble compounds that consist of cyclohexenone or cyclohexenimine chromophores conjugated with the nitrogen substituent of amino acids or its imino alcohol [184]. In general, MAAs have a glycine subunit at the third carbon atom, although some MAAs contain sulfate esters or glycosidic linkages through the imine substituents [225]. MAAs are favored as photoprotective compounds because they have maximum UV absorption between 310 and 362 nm, high molar extinction coefficients ($\varepsilon = 28{,}100$–$50{,}000$ M^{-1} cm^{-1}), the capability to dissipate absorbed radiation efficiently as heat without producing reactive oxygen species (ROS), and photostability and resistance to several abiotic stressors [44, 81, 223].

It has been found that MAAs provide protection from UVR not only for their producers, but also to primary and secondary consumers through the food chain [90]. MAAs have been reported extensively from taxonomically diverse organisms, including many marine groups such as heterotrophic bacteria [4], cyanobacteria and micro/macroalgae. Many animals such as arthropods, rotifers, molluscs, fish, cnidarians, tunicates, eubacteriobionts, poriferans, nemertineans, echinodermates, platyhelminthes, polychaetes, bryozoans and protozoans have also been reported to protect themselves from UVR by MAAs [194]. Recently, an MAA, mycosporine-glycine (MG), has been isolated from the marine lichen *Lichina pygmaea* [41]. Presently, about 21 MAAs have been reported from terrestrial, freshwater and marine organisms.

Fig. 1 Occurrence of different photoprotective compounds in diverse organisms
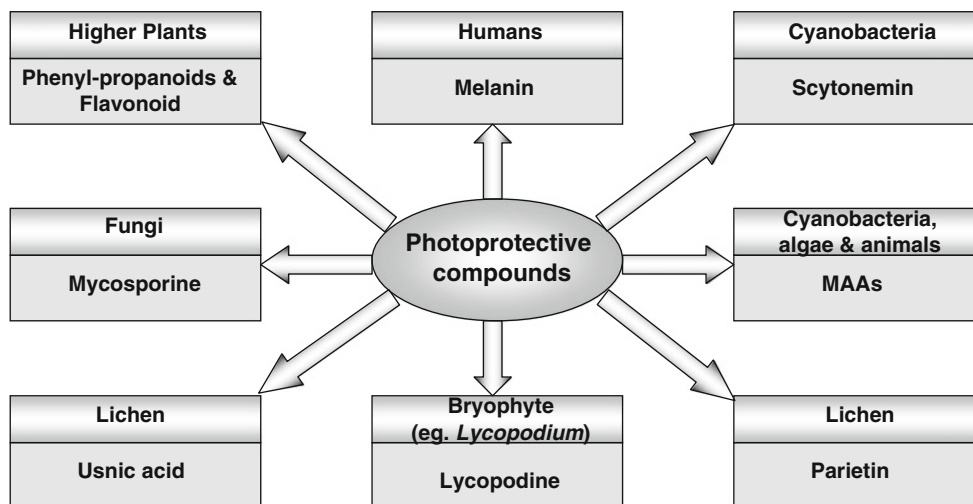
High performance liquid chromatography (HPLC) is the common method to detect the particular MAA using the distinctive nature of their retention times and absorption spectra (Fig. 2). However, certain closely related unknown compounds have similar absorption maxima and retention times, which still cause difficulties in the identification process. Liquid chromatography coupled with electrospray ionization mass spectrometry (LC-ESI-MS) can be utilized to examine MAAs' structural diversity [222].

MAAs in marine cyanobacteria

Cyanobacteria are prominent in many superficial habitats exposed to high solar irradiance, including intertidal marine flats swamped so infrequently that most eukaryotic competitors and herbivores are absent. On rocky marine substrates, many cyanobacteria form crusts or small cushions in the high intertidal or supratidal zone. They are significant constituents of marine ecosystems and account for a high percentage of oceanic primary productivity. The presence of UV-absorbing compounds like MAAs presumably may have supported the existence of cyanobacteria in the Precambrian era when there was no stratospheric ozone layer. The accumulation of large amounts of MAAs in cyanobacteria was first reported by

Shibata [174] from the Great Barrier Reef. Accumulation of MAAs in cells are regulated by an osmotic mechanism that may be evident by the accumulation of high concentrations of MAAs in the field populations of halotolerant cyanobacteria [151]. The probability that MAAs act as UV-B-absorbing compounds has been derived from the fact that the distribution of MAAs in marine organisms shows a significant correlation with depth, which in turn controls the exposure of UV or PAR (photosynthetically active radiation) [57]. Shinorine and porphyra-334 have been found to be the most dominant MAAs in several species of marine cyanobacteria [105, 186, 190] (Table 1). The cyanobacterium *Nodularia spumigena* is known worldwide for developing toxic blooms, e.g., in the Baltic Sea [116]. Sinha et al. [186] reported three species of this cyanobacterium, *Nodularia spumigena*, *Nodularia baltica* and *Nodularia harveyana*, from the Baltic Sea that produce the MAAs porphyra-334 and shinorine upon UV-B irradiation. MAA-producing cyanobacteria are abundant in hypersaline environments. On the basis of the 16s rRNA gene sequence of 13 MAAs-containing strains of unicellular halophilic cyanobacteria, Garcia-Pichel et al. [73] found a common complement of MAAs in all of them. The majority of halotolerant cyanobacterial populations accumulate high concentrations of MAAs as photoprotective compounds [151].
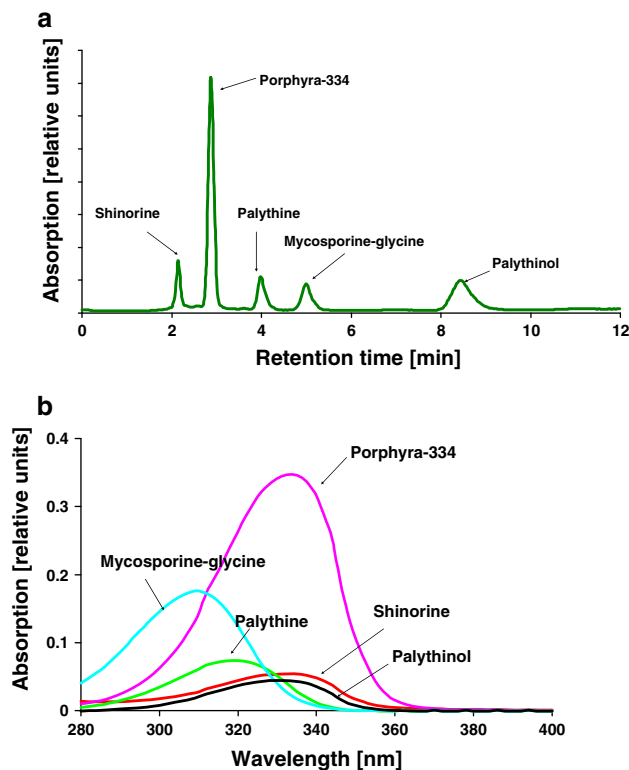
MAAs in marine macroalgae

Several species of macroalgae, belonging to Rhodophyceae (red), Phaeophyceae (brown) and Chlorophyceae (green algae), are used as foodstuffs in the diets of people from Pacific, Asian, Canadian and Icelandic cultures [229]. Besides their food value, many macroalgal species that are commonly exposed to elevated solar radiation synthesize and accumulate high concentrations of MAAs as UV-sunscreen compounds. The presence of UV-absorbing substances in a macroalgal species was first reported by Tsujino and Saito [215]. Later several scientists reported these compounds in all major taxonomic groups [194]. Several species of red algae, such as *Acanthophora*, *Bangia*, *Bostrychia*, *Caloglossa*, *Catenella*, *Devaleraea*, *Ceramium*, *Chondrus*, *Corallina*, *Devaleraea*, *Gelidiella*, *Gelidium*, *Gracilaria*, *Iridea*, *Palmaria*, *Phyllophora*, *Polysiphonia*, *Porphyra*, *Stictosiphonia*, etc., have been reported to produce high concentrations of different MAAs [194]. Recently, Karsten et al. [103] reported three main MAAs, palythine, shinorine and porphyra-334, from *Porphyra umbilicalis* isolated from the rocky upper littoral zone of the island Helgoland, Germany, in the North Sea. Six different MAAs, palythine, shinorine, asterina-330, porphyra-334, the medium polarity palythinol, and the low

Fig. 2 HPDLC chromatograms of some MAAs (**a**) and their absorption spectra (**b**)

Table 1 Occurrence of MAAs in some marine cyanobacteria, macroalgae and phytoplankton

Organisms	MG	PT	AS	PL	PR	SH	PE	MGV	PNA	MMS	M328/360	SME	MT	PS	M2G	M333	M320	US	M335/360	References
Lichen	+																			[41]
Cyanobacteria				+	+															[105, 186]
Macroalgae																				
Red algae	+	+	+	+	+	+	+									+	+	+	+	[20, 23, 36, 41, 107, 149]
Brown algae	+	+	+	+	+	+														[102, 106, 146]
Green algae	+	+	+	+	+	+														[102, 108, 146]
Microalgae/ phytoplankton	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	[35, 36, 89, 119, 141, 168]

MG mycosporine-glycine, *PT* palythine, *AS* asterina-330, *PL* palythinol, *PR* porphyra-334, *SH* shinorine, *PE* palythene, *MGV* mycosporine-glycine-valine, *PNA* palythenic acid, *MMS* mycosporine-methylamine-serine, *M* mycosporine-like amino acids, *SME* shinorine methyl ester, *MT* mycosporine-taurine, *PS* palythine-serine, *M2G* mycosporine-2-glycine, *US* usurijene

polarity usujirene, have been reported for the first time from the edible red alga, *Palmaria palmata* (dulse) harvested from the west and east coasts of Grand Manan Island, New Brunswick [230]. Coba et al. [41] recently reported the presence of the MAAs porphyra-334 and shinorine from the red alga *Porphyra rosengurttii*, asterina-330 and palythine from *Gelidium corneum*, as well as shinorine from *Ahnfeltiopsis devoniensis*. Prophyra-334 is an MAA widely distributed among marine algae. The imino-MAAs porphyra-334 and shinorine, isolated from the red alga *Gracilaria cornea*, have been found to be highly stable against UV and heat stress [189]. Zhaohui et al. [232] reported prophyra-334 from a marine alga that was quite stable in water at a temperature of 60°C. A high degree of MAA diversity has been found in the majority of Rhodophyceae; for instance, *Gracilaria changii* contains up to seven different UV-absorbing compounds [108].

In contrast to Rhodophyceae the occurrence of MAAs in Chlorophyceae and Phaeophyceae is limited. Within the Chlorophyceae, most species do not contain MAAs or only trace concentrations of these compounds [108]. In an investigation of the occurrence of MAAs in 13 macroalgal Chlorophyceae collected from the intertidal zone of the tropical island Hainan, Karsten et al. [108] found a significant concentration of photoprotective compounds, such as mycosporine-glycine and porphyra-334, only in two green algae, *Boodlea composita* and *Caulerpa racemosa*, respectively. Post and Larkum [161] reported certain UV-absorbing compounds of unknown chemical nature from green algae. Han and Han [86] reported the induction of UV-B-absorbing compounds with a prominent absorption maximum at 294 nm in the green alga *Ulva pertusa* by using different cutoff filters.

Since the occurrence of MAAs is restricted in Chlorophyceae as well as in Phaeophyceae, certain other UV-absorbing compounds might be present in them to protect against UV radiation damage. Pavia et al. [154] reported the occurrence of a polyphenolic compound, phlorotannin, as an UV-absorbing compound (absorbing between 280 and 320 nm) from the brown alga *Ascophyllum nodosum*. A number of Phaeophyceae produce and accumulate phlorotannins in high concentrations (up to 20% of their dry weight); however, the potential sunscreen functions of phlorotannins need further comprehensive study. Some common macroalgae and their photoprotective products from marine or hypersaline habitats are listed in Table 1.

MAAs in marine phytoplankton/microalgae

Phytoplankton are undoubtedly the major biomass producers in marine ecosystems. In addition to playing a major role in the food web, many genera of phytoplankton produce certain volatile substances such as dimethyl-sulfide (DMS) that serve as an antecedent of cloud condensation nuclei (CCN) and neutralize the greenhouse effect [39]. The cumulative effect of marine biota in the reduction of CO_2 concentration and emission of DMS has been estimated to cool the atmosphere by up to 6°C [220]. Like in cyanobacteria and macroalgae, several MAAs (Table 1) have also been isolated and identified from a number of marine phytoplankton species [34, 87, 110, 120, 125, 226]. MAAs have been reported to occur predominantly in members of the Dinophyceae, Bacillariophyceae and Haptophyceae (or Prymnesiophyceae). Some species of dinoflagellates such as *Alexandrium excavatum* [34] and

the prymnesiophyte *Phaeocystis pouchetii* [133] are known to produce MAAs in high concentrations. It has been found that accumulation of MAAs may occur as a result of UV-induced alterations in the synthesis of amino acids [77]. Elevated levels of PAR (400–700 nm) [34], blue light (400–500 nm) [37], UV-A [37, 63] and UV-B wavelengths [125] have been implicated in the MAA induction response. However, Davidson et al. [49] reported the synthesis of MAAs insensitive to UV-B radiation in five common antarctic diatoms. The dinoflagellate *Alexandrium excavatum*, isolated from the continental shelf near Buenos Aires shows changes in the MAA composition and an overall increase in UV absorption under low to high PAR [37]. An increase in MAA concentration was shown in the dinoflagellate *Prorocentrum micans* in the presence of only UV radiation [125]. Photoinduction of MAA synthesis was also found in the dinoflagellate *Gyrodinium dorsum* in the presence of PAR [110] and only UV-A and UV-B radiation [168]. Time-series data collected at the Bermuda Atlantic time-series study (BATS) site represents the seasonal induction of enhanced UV absorption by MAAs in phytoplankton in the summer-stratified surface water of the Sargasso Sea [142]. In Antarctica, high in vivo absorption at wavelengths indicative of MAAs was characteristic of assemblages dominated by prymnesiophytes [218] and by the chain-forming diatom *Thalassiosira gravida* [63]. Seasonal variations also affect the MAA concentrations in phytoplankton. Recently, Riemer et al. [169] reported the variation in the concentration of the MAA, mycosporine-glycine and two other UVR-absorbing substances in phytoplankton during different months. UVR-mediated induction of UV-absorbing compounds, with maximal absorption at 334 nm, has recently been observed in *Skeletonema costatum*, which is a cosmopolitan marine diatom and known as a major component of most red tides in eutrophic regions [224]. It has been suggested that a significant fraction of the UVR reaching the marine diatoms could be absorbed by frustule-bound MAAs. Ingalls et al. [94] for the first time analyzed the diatom frustule-bound organic matter in opal-rich Southern Ocean plankton and sediments and revealed the presence of several MAAs such as palythine, porphyra-334, shinorine as well as traces of asterina-330, palythinol and palythinic acid. The occurrence of MAAs in close association with a mineral phase shows that the mineral matrix can stabilize these compounds and may increase photoprotection against the harmful effects of UVR [94].

MAAs in marine animals

Identification and characterization of different MAAs from various animals such as arthropods, rotifers, molluscs, fishes, cnidarians, tunicates, eubacteriobionts, poriferans, nemertineans, echinodermates, platythelminthes, polychaetes, bryozoans and protozoans has been reported [194]. In nonsymbiotic marine invertebrates, MAAs have been identified in echinoderms, a mussel, a sea hare, brine shrimp and an ascidian [57]. MAAs are common in micro-algal-invertebrate symbioses on coral reefs and other habitats [176]. Other than the algal-invertebrate symbioses, there is not much information regarding the occurrence of MAAs in marine alga-bearing protists [57, 176]. However, Sommaruga et al. [198] reported for the first time some photoprotective compounds (shinorine, palythenic acid, palythine, mycosporine-2-glycine and porphyra-334) in a marine algal-bearing ciliate *Maristentor dinoferus* isolated from coral reefs in Guam, Mariana Islands [130]. A number of MAAs were identified by McClintock and Karentz [136] in 34 species of benthic marine invertebrates. Likewise, in a survey of occurrence of MAAs in marine organisms (48 invertebrates and 1 fish), Karentz et al. [102] accounted for different types of MAAs as photoprotective compounds. The presence of four MAAs, palythine, porphyra-334, asterina-330 and shinorine, and their seasonal variations (summer vs. winter) was investigated in various species of soft corals isolated from the Eastern Red Sea Coast, and palythine was found as the dominant photoprotective compound in *Sinularia polydactyla* and *Sarcophyton trocheliophorum* [2]. Concentrations of MAAs vary seasonally and decrease with increasing depth. In most corals there is a positive correlation between MAA concentration and solar UVR [18, 213]. A change in the PAR and UVR components of the solar spectrum with increasing depth significantly affects the primary productivity and the biosynthesis of MAAs in the reef-building coral *Montastraea faveolata* [126]. Interestingly, MAA concentrations in corals decrease with low water flow and are directly related to rates of photosynthesis [100]. A considerable increase in MAA concentration (up to 67 and 56% for *Lobophytum compactum* and *Sinularia flexibilis*, respectively) was shown in female soft corals prior to spawning in comparison to male colonies, which indicates that the parent is providing photoprotectants to its offspring for better survival and furthermore supports the sex-specific variations in levels of photo-protecting mycosporine-like amino acids (MAAs) [137]. At least 14 different MAAs have been characterized in many coral species. Recently, a major novel MAA, palythine-threonine ($C_{12}H_{21}N_2O_6^+$) (Fig. 3), has been reported from the hermatypic coral *Pocillopora capitata* and also from *P. eydouxi* and *Stylophora pistillata* [33]. Occurrence of four major MAAs such as mycosporine-taurine, shinorine, porphyra-334, and mycosporine-2 glycine was found in the four sympatric species of sea anemones in the genus *Anthopleura* collected from intertidal habitats on the
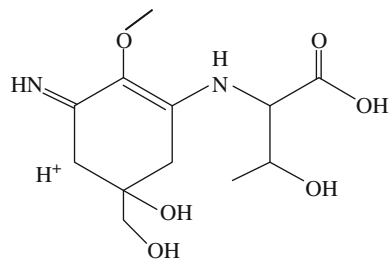
Fig. 3 Proposed structure of palythine-threonine isolated from the hermatypic coral *Pocillopora capitata*

Pacific Coast of temperate North America [177]. Moreover, diverse groups of marine animals have been reported to synthesize MAAs (Table 2), which may render organisms more tolerant to oxidative toxicity and increase their survival under the force of stresses such as UVR that mediate production of ROS. It seems that photoprotective compounds are generally produced by the lower photosynthetic organisms including microbes, and marine animals indirectly benefit from the accumulation of MAAs.

Biosynthesis of MAAs

There is still a great deal of controversy concerning the precise mechanisms of MAA biosynthesis. However, it is evident that 3-dehydroquinate formed during the early stages of the shikimate pathway (Fig. 4) serves as a precursor for the synthesis of fungal mycosporines and MAAs via gadusols [176, 184]. The inhibition of MAA synthesis

in a hermatypic coral, *Stylophora pistillata*, by the addition of *N*-phosphonomethlyglycine (= glyphosate; a specific shikimate pathway inhibitor) has provided the first direct evidence for MAA synthesis through the shikimate pathway in marine organisms [179]. Gadusol (3,5,6-trihydroxy-5-hydroxymethyl-2-methoxycyclohex-2-en-1-one) and deoxygadusol (3,5-dihydroxy-5-hydroxymethyl-2-methoxycyclohex-2-en-1-one) are structurally and biosynthetically related to the MAAs that have been found in roes of cod and other marine fish [40, 156] as well as in eggs, ovaries and larvae of various marine invertebrates [13, 80]. Recently, Singh et al. [183] revealed the probable role of certain genes involved in MAA biosynthesis in cyanobacteria and proposed that the YP_324358 and YP_324357 gene products are involved in the biosynthesis of the common core (deoxygadusol) of all MAAs. The YP_324879 gene product is exclusively involved in the shikimate pathway catalyzing the formation of dehydroquinate, while the YP_324358 gene product in conjunction with the YP_324357 gene product (*O*-methyltransferase) catalyzes the formation of deoxygadusol, which is the core of all MAAs (Fig. 5).

The synthesis of MAAs is restricted to bacteria, cyanobacteria, phytoplankton and macroalgae and does not occur in animals (metazoa), as they lack the shikimate pathway and take up MAAs via their food. However, recently Starcevic et al. [204] reported the genes encoding enzymes for the shikimate pathway in an animal, the starlet sea anemone *Nematostella vectensis*, and challenged the universality of this traditional view. Even so, certain

Table 2 Occurrence of MAAs in some marine animals

Organism	MG	PT	AS	PL	PR	SH	PE	MGV	PNA	MMS	MT	PSS	MMT	PS	M2G	MSE	PTT	References
Copepods	+	+			+	+	+											[102]
Krill	+	+	+	+	+	+	+	+	+									[102, 146]
Sea spiders	+	+			+	+	+	+										[102]
Isopods	+	+			+	+	+	+										[90, 102, 136]
Amphipods	+	+	+	+	+	+	+	+										[90, 102, 149]
Molluscs	+	+	+	+	+	+	+	+	+						+			[95, 102, 136, 163, 222]
Fish	+	+	+	+	+	+	+	+										[58, 102, 163]
Sea anemones	+	+	+		+	+	+	+			+				+			[10, 36, 96, 136, 177, 207]
Jelly fish	+				+	+												[207]
Corals	+	+	+	+	+	+	+			+	+	+	+	+	+	+	+	[33, 36, 178, 179, 212, 213]
Ascdians	+	+	+		+	+	+	+										[102, 136]
Sponge	+	+		+	+	+		+										[136]
Sea urchins	+	+	+		+	+		+										[1, 136]
Sea stars	+	+	+		+	+		+										[102, 136]
Sea cucumbers	+	+	+	+	+	+									+			[13, 136]
Sea hares	+	+	+		+	+									+			[32]

PSS palythine-serine sulfate, *MMT* mycosporine-methylamine-threonine, *MSE* mycosporine sulfate ester; palythine-threonine. Other abbreviations as in Table 1

Fig. 4 The supposed biosynthetic routes of MAAs through the shikimate pathway and their possible interconversion. *Broken line* represents the putative biosynthetic correlation among 3-dehydroquinate, gadusols and MAAs. The steps of the shikimate pathway are represented by *thick arrows*, and the number (1–7) represents the involvement of seven enzymes that catalyze the sequential steps of the pathway. *1*: 3-deoxy-D-arabinoheptulosinate-7-phosphate (DAHP) synthase; *2*: dehydroquinate (DHQ) synthase; *3*: DHQ dehydratase; *4*: shikimate dehydrogenase; *5*: shikimate kinase; *6*: 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase; *7*: chorismate synthase (for details of shikimate pathway, see [176])
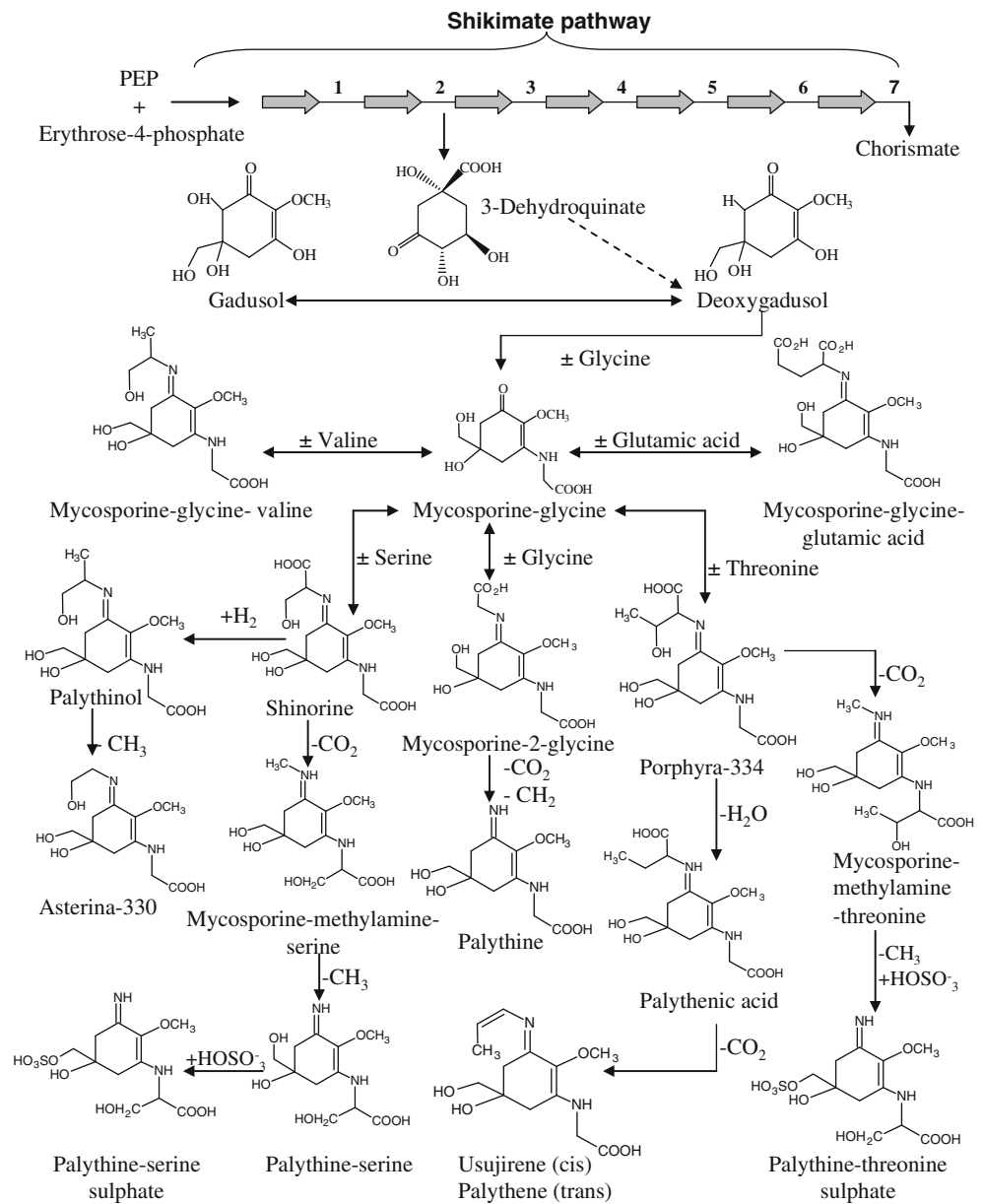
marine animals such as arthropods (copepods, krill, sea spiders, isopods, amphipods), molluscs, chordates (fish), cnidarians (sea anemones, jelly fish, corals), protochordates (ascdians), eubacteriobionts, poriferans (sponge), nemertineans (ribbon worm), echinodermates (sea urchins, sea stars, brittle stars, sea cucumbers, sea hares, star fish), crinoids, platyhelminthes (planarian), annelids (polychaetes), bryozoans and protozoans have also been reported to have MAAs [194] derived from their diet or from symbiotic partnerships [57, 140, 148, 169]. Thus, MAAs provide protection from UV radiation not only in their producers, but also to primary and secondary consumers. Richards et al. [166] identified genes involved in all of the steps of the shikimate pathway in both green and red algae (*Chlamydomonas reinhardtii* and *Cyanidoschyzon merolae*,

respectively) as well as in the diatom *Thalassiosira pseudonana*.

Mycosporine-glycine is considered as a prime MAA synthesized in the shikimate pathway that further goes through chemical and/or biochemical conversions to produce secondary MAAs (Fig. 4) [29, 36, 45]. Portwich and Garcia-Pichel [160] have observed the specific incorporation of ^{14}C-glycine and ^{14}C-serine into the consequent side chains of mycosporine glycine and shinorine using radiolabelled amino acids, indicating that these free amino acids are their direct precursors. Moreover, it has been assumed that the high diversity of MAAs present in marine organisms is derived from the transformation of mycosporine-glycine, porphyra-334, shinorine and other MAA bisubstituted by amino acids [35, 36, 175]. After irradiation

Fig. 5 Probable roles of YP 324357 (Ava 3857) and YP 324358 (Ava 3858) genes in the biosynthesis of MAA, shinorine in a cyanobacterium *Anabaena variabilis* PCC 7937 (modified from [183])
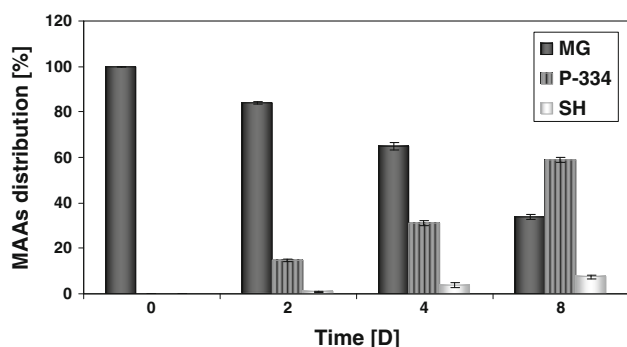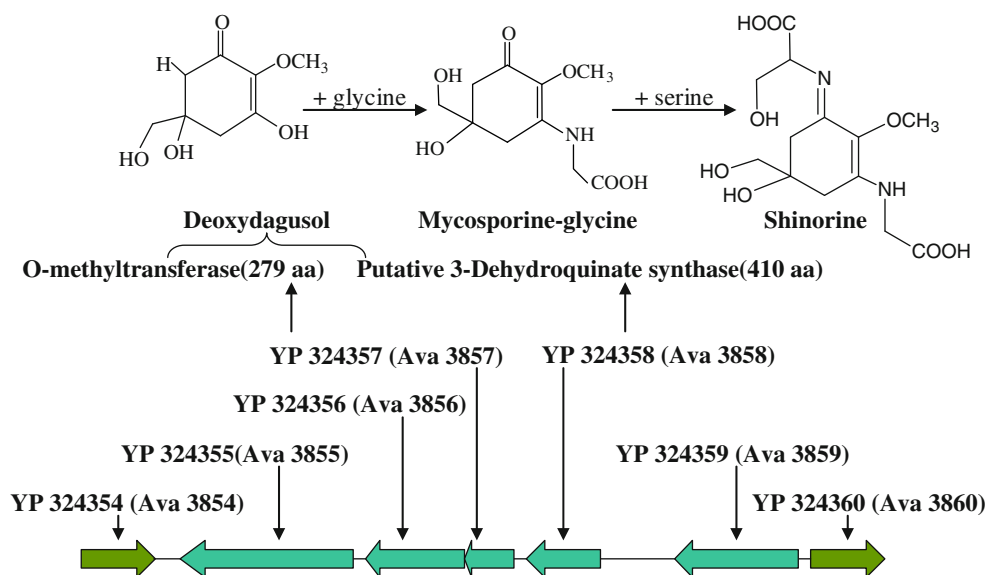

Fig. 6 Biotransformation of MAAs influenced by PAR and UVR (UV-A, UV-B) radiation in *A. doliolum* (modified from [185])

Fig. 7 Structure of scytonemin (**a**) and its absorption spectrum showing a maximum at 386 nm (**b**)

of the toxic dinoflagellate *Alexandrium tamarense* at photoinhibitory irradiation levels, the concentrations of palythenic acid, usujirene and palythene were found to increase with a simultaneous decrease of the porphyra-334 level [35]. It shows that changes in the level of UVR also play an important role in the interconversions of different MAAs [37]. Recently, Singh et al. [185] also observed the conversion of mycosporine-glycine into two MAAs, porphyra-334 and shinorine, under the influence by PAR and UVR in the cyanobacterium *Anabaena doliolum* (Fig. 6). Overall, some aspects of the biosynthesis and in particular biotransformations of different MAAs in marine algae and phototropic symbiotic organisms are still unsolved and need more investigation.

Scytonemin

The photoprotective compound scytonemin is a yellow–brown, lipid-soluble pigment deposited in the exopoly-
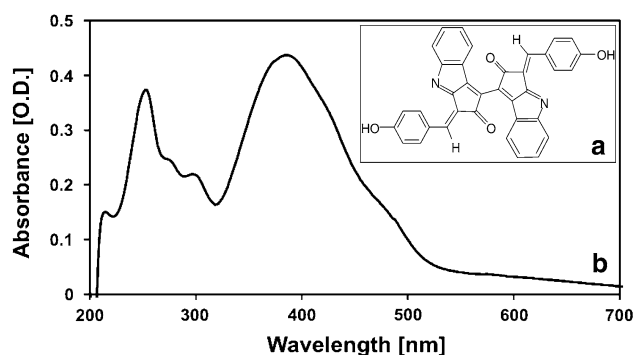
saccharide sheaths of some strains of cyanobacteria inhabiting soil and rock surfaces, barks of trees and marine intertidal mats [71, 72, 162, 170, 191]. This photoprotective pigment was first reported in some terrestrial cyanobacteria [145]. Recently, Richter et al. [167] extracted scytonemin from *Lyngbya* sp. inhabiting rocks at the shore near Sao Fransisco do Sul, Brasil. It is a dimeric compound composed of indolic and phenolic subunits having a molecular mass of 544 Da (Fig. 7a) and acts as a passive sunscreen in the protection of cyanobacteria against ultraviolet radiation in marine and freshwater environments [162]. The linkage between the two subunits in scytonemin is an olefinic carbon atom that is exclusive among natural products. This complexity of the ring structures of scytonemin generates a specific pattern of UV absorbance [162]. Scytonemin is mainly found in the green oxidized form; however, two other forms of scytonemin such as the oxidized (yellow; e.g., fuscochlorin) and the reduced (red; e.g., fuscorhodin) have been reported to be produced depending on the redox and acid-base conditions during the extraction process [72].

Fig. 8 Structures of dimethoxyscytonemin (**a**), tetramethoxyscytonemin (**b**) and scytonin (**c**)
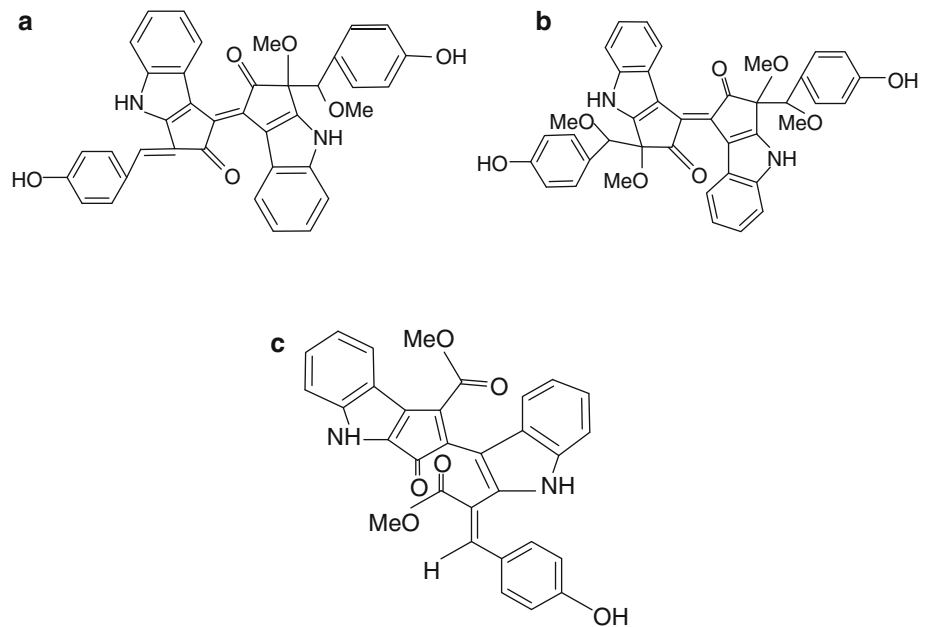
Three new pigments, dimethoxyscytonemin, tetramethoxyscytonemin and scytonin (Fig. 8), were recently isolated from the organic extracts of *Scytonema* sp. They are derived from the scytoneman skeleton of scytonemin. Their structures were allocated principally on the basis of ^{1}H and ^{13}C NMR and MS experiments [27]. Scytonemin has an in vivo absorption maximum at 370 nm, while purified scytonemin has a highest absorption at 386 nm, although it also absorbs significantly at 252, 278 and 300 nm (Fig. 7b), and so it probably helps cyanobacteria to survive lethal UV (UV-A and UV-B) radiation. Scytonemin is the predominant UV-A-photoprotective pigment in the cyanobacterial sheath that reduces the penetration of UV-A radiation into the cell by 90% [72, 74]. It has also been demonstrated that scytonemin alone is sufficient for substantial protection against UV-C damage [53]. It performs its screening activity without any further metabolic investment even after prolonged physiological inactivity; hence, it can be a suitable candidate for use as a natural UV screening compound for humans.

Biosynthesis of scytonemin

The biosynthesis of scytonemin probably involves tryptophan and tyrosine derivatives that absorb ambient UVR [208]. The biochemical and photoprotective role of scytonemin is well known, and very recently a number of papers about the biosynthesis and molecular genetics of this compound in cyanobacteria have been published [8, 101, 181, 199–202]. A scytonemin-deficient *Nostoc punctiforme* ATCC 29133 mutant was created using random transposon mutagenesis [202]. The authors found the specific region in the genome of *N. punctiforme* ATCC 29133 and revealed a cluster of 18 genes, *NpR1259–NpR1276*, associated with scytonemin biosynthesis (Fig. 9). All 18 genes are co-transcribed as a single transcriptional unit that is upregulated by UV radiation [200]. Based on genetic, biochemical and sequence similarity evidence, Soule et al. [201] illustrated that six putative genes in the scytonemin gene cluster (*NpR1276* to *NpR1271*) with no previously known protein functions are likely involved in the assembly of scytonemin from central metabolites. The assessment of these gene clusters disclosed the occurrence of redundant copies of genes responsible for aromatic amino acid biosynthesis. The evolutionary phylogenetic analysis revealed that the scytonemin gene cluster is distributed across several cyanobacterial lineages, which led to the proposal that the distribution of this gene cluster is best explained by assuming an ancient evolutionary origin [199]. Balskus and Walsh [8] presented the probable biosynthetic route for scytonemin biosynthesis and identified the acyloin reaction as a key step in constructing the carbon framework of this ecologically and evolutionary important pigment. They functionally characterized two enzymes determined by ORFs NpR1275 and NpR1276 from the gene cluster identified by Soule et al. [202], which are involved in the initial step of scytonemin biosynthesis [181] (Fig. 9). NpR1275, which resembles a leucine dehydrogenase, was shown to catalyze the oxidative deamination of tryptophan to form indole-3-pyruvic acid (IPA). IPA, along with the tyrosine precursor *p*-hydroxyphenylpyruvic acid, acts as the substrate for an acyloin reaction catalyzed by NpR1276 [a homolog to thiamine
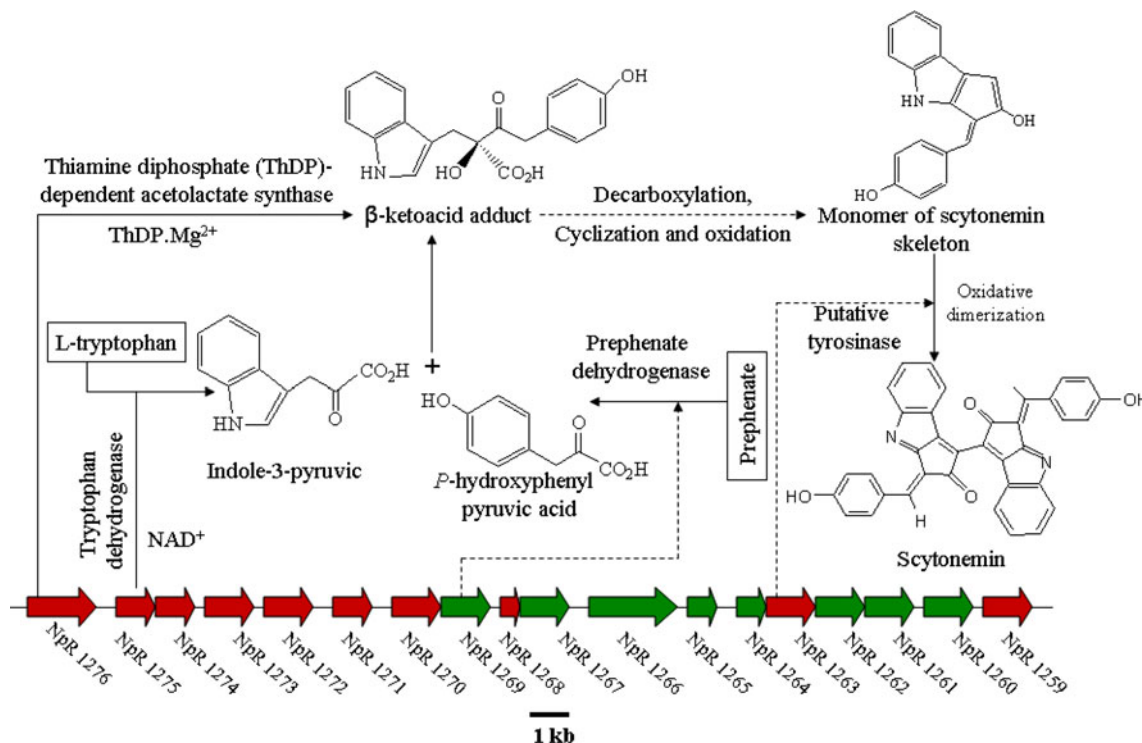
Fig. 9 Proposed biosynthetic pathway for the photoprotective compound scytonemin and associated gene (NpR1259–NpR1276) products. *Continuous arrows* signify gene products that are functionally characterized, whereas *broken arrows* indicate the gene products that are still to be functionally characterized for their involvement in subsequent steps. Most of the ORFs in the gene cluster represented by bold arrows from NpR1260–NpR1262, NpR1264–NpR1267 and NpR1269 are predicted to be involved in the biosynthesis of aromatic amino acids while the rests represent ORFs of unknown function (for details, see [200–202])

diphosphate (ThDP)-dependent acetolactate synthase] (Fig. 9). The acyloin product arises from a single β-keto acid regioisomer and exhibits a highly selective reaction by the ThDP-dependent NpR1276 [8]. The products of NpR1263 and NpR1269 ORFs are still to be functionally characterized. From a comparative study of four other cyanobacterial strains, Soule et al. [201] suggested that two supplementary conserved clusters (NpF5232 to NpF5236) and a putative two-component regulatory system (NpF1277 and NpF1278) are possibly involved in scytonemin biosynthesis and regulation, respectively, on the basis of conservation and location.

Carotenoids

Carotenoids (yellow, orange or red substances) are important components of the photosynthetic apparatus that serve both light-harvesting and photoprotective functions, either as direct quenchers of singlet oxygen and other toxic reactive oxygen species (ROS) or playing a role in the thermal dissipation of excess energy in the photosynthetic apparatus [59, 66, 139, 228]. These are derived from five-carbon isoprene units that are polymerized enzymatically to form regular highly conjugated 40-carbon structures with up to 15 conjugated double bonds. One or both ends of the carbon skeleton may go through cyclization to form ring β-ionone ring end groups, which additionally may be substituted by oxo, hydroxy or epoxy groups at dissimilar positions to form the different xanthophylls [197]. About 600 different carotenoids have been identified from different organisms such as cyanobacteria, bacteria, fungi, phytoplankton, macroalgae, plants and animals [43, 82, 158]. Animals lack the ability to synthesize carotenoids endogenously and thus have to take up these compounds by means of their diet [140]. The pigment astaxanthin, responsible for the pink/red coloration of crustaceans, shellfish and fish such as salmon, is one of the dominant carotenoids found in marine animals by modification of plant carotenoids obtained in the diet.

The role of carotenoids as photoprotective compounds is still controversial to some extent [42]; however, a significant increase ($\approx 50\%$) in the outer-membrane carotenoids echinenone and myxoxanthophyll was found in the cyanobacterium *Nostoc commune* after few hours of UV-B irradiation [62]. The photosynthetic activity of the cyanobacterium *Synechococcus* sp. was found to be more tolerant against UV-B radiation when having increased amounts of endogenous carotenoids caused by genetic manipulation [79]. A small increase in carotenoid content was found in a

marine cyanobacterium, *Oscillatoria* sp. strain BG 091600, after irradiation with UV-A at an irradiance of 10 W/m^2 [219]. Carotenoids such as diadinoxanthin, diatoxanthin and β-carotene were found to be induced in phytoplankton under high PAR and UVR [196], and they may play a role in reducing photoinhibition of photosynthesis [25]. Recently, Boulay et al. [24] reported the occurrence and role of the orange carotenoid protein (OCP) in photoprotective mechanisms in various cyanobacteria. Lamare and Hoffman [118] examined the variability in carotenoid concentration in the gonads and eggs of four sea urchin species (*Strongylocentrotus purpuratus*, *S. franciscanus*, *S. pallidus* and *S. droebachiensis*) to explore the possible role of carotenoids as photoprotective compounds and suggest that carotenoids may serve as photoprotectants against the damaging effects of UV radiation in echinoid eggs.

Photoprotection by the xanthophyll cycle is achieved as a result of dissipation of excess excitation energy as heat [11]. In dinoflagellates, this is mediated by the conversion of diadinoxanthin to diatoxanthin to deactivate excited chlorophyll [3]. Recently, Laurion and Roy [120] have examined the photoprotective role of carotenoids in species of dinoflagellates and diatoms with enhanced ultraviolet-B (UV-B) radiation exposure; they concluded that the xanthophyll cycle is even more important than the protection by MAAs, and the same was observed by Zudaire and Roy [233] for the marine diatom *Thalassiosira weissflogii* where photoprotective carotenoids (PPCs) dissipate excess energy via the xanthophyll cycle as a long-term UV acclimation response. A significant accumulation of carotenoids was found in the subtidal alga *Ptercladiella capillacea* after failure of MAA accumulation in response to 1.5–3.0 W m^{-2} UV-B radiation, which shows that carotenoids are involved in UV-B radiation defense in *P. capillacea* [124]. The presence or absence of certain carotenoids and their relative concentrations also provide information about the possible acclimation or photoprotection responses of the organisms. The presence of carotenoids implicated in the xanthophyll cycle (XC; conversion of violaxanthin into zeaxanthin via antheraxanthin) indicates the possibility that the organisms might utilize this photoprotection response [173]. In some groups of the Chromophyta, the XC consists of the interconversion of diadinoxanthin into diatoxanthin and thus both cycles are involved in the thermal dissipation of excess light that provides effective photoprotection to the photosynthetic apparatus [121]. Dimier et al. [55] recently described the photoprotective role of XC in marine diatoms. Regarding the biosynthetic pathway of carotenoids in diverse organisms, several studies have recently been published [30, 43, 46, 67]. Figure 10 represents the hypothesized biosynthetic pathway of some carotenoids and showing the XC. In a series of studies Hairston [85] concluded that carotenoids

generally function as photoprotectants in high light environments, since carotenoids are antioxidants neutralizing photoproduced radicals [78].

Other marine photoprotective compounds

Besides the occurrence of well-known photoprotective compounds in the marine organisms mentioned above, some other UVR absorbing/screening compounds have been identified in marine organisms including 3-hydroxy-kynurenine, sporopollenin, melanin and fluorescent pigments. A number of reviews on photoprotective compounds and their protective mechanisms are available that can be referred to for further information in other marine organisms as well as freshwater taxa [9, 42]. Some UV-absorbing compounds such as P380 have been found in the water column near phytoplankton blooms having broad absorbance bands from 300 to 470 nm [128]. Melanin, a complex polymeric structure containing aromatics and indole derivatives, provides UV-A and UV-B screening in humans and many vertebrates [113]. A number of bacteria are reported to produce melanin from phenolic degradation products, such as 3,4-dihydroxyphenylacetate, that accumulate during the catabolism of tyrosine. Tyrosine degradation generally requires multiple catalytic steps to convert tyrosine to melanin precursors [16, 144]. Synthesis of melanin has also been reported from a marine bacterium *Shewanella colwelliana* [69, 70]. The facultatively anaerobic marine bacterium *Shewanella algae* produces pyomelanin, but the availability of such soluble compounds in mineralized marine deposits is limited; hence, production of melanin is an important evolutionary adaptation and furthermore, like other organisms, *S. algae* produces melanin also for the protection from ultraviolet irradiation [157]. Two melanin-generating enzymes, tyrosinase and laccase, with a wide spectrum of activity, have been reported from another marine bacterium *Marinomonas mediterranea* [131, 172]. Besides the MAAs, large quantities of maristentorin (Fig. 11), a photoreceptor pigment structurally similar to stentorin and hypericin, have recently been reported in a marine ciliate *Maristentor dinoferus* that may have a protective role against UV irradiation; however, this conclusion needs further evidence [129, 143]. It has been found that the fluorescent pigment granules (FPGs) of corals may supplement the role of MAAs by blocking some of the UV-A [171]. A UV-A-absorbing pigment, biopterin glucoside (BG; a compound chemically related to the pteridine pigments found in butterfly wings) (Fig. 12), with absorption maxima at 256 and 362 nm, has been purified from a marine planktonic cyanobacterium *Oscillatoria* sp. collected from the coastal areas of Japan [134]. Also *Anacystis nidulans, Anabaena*
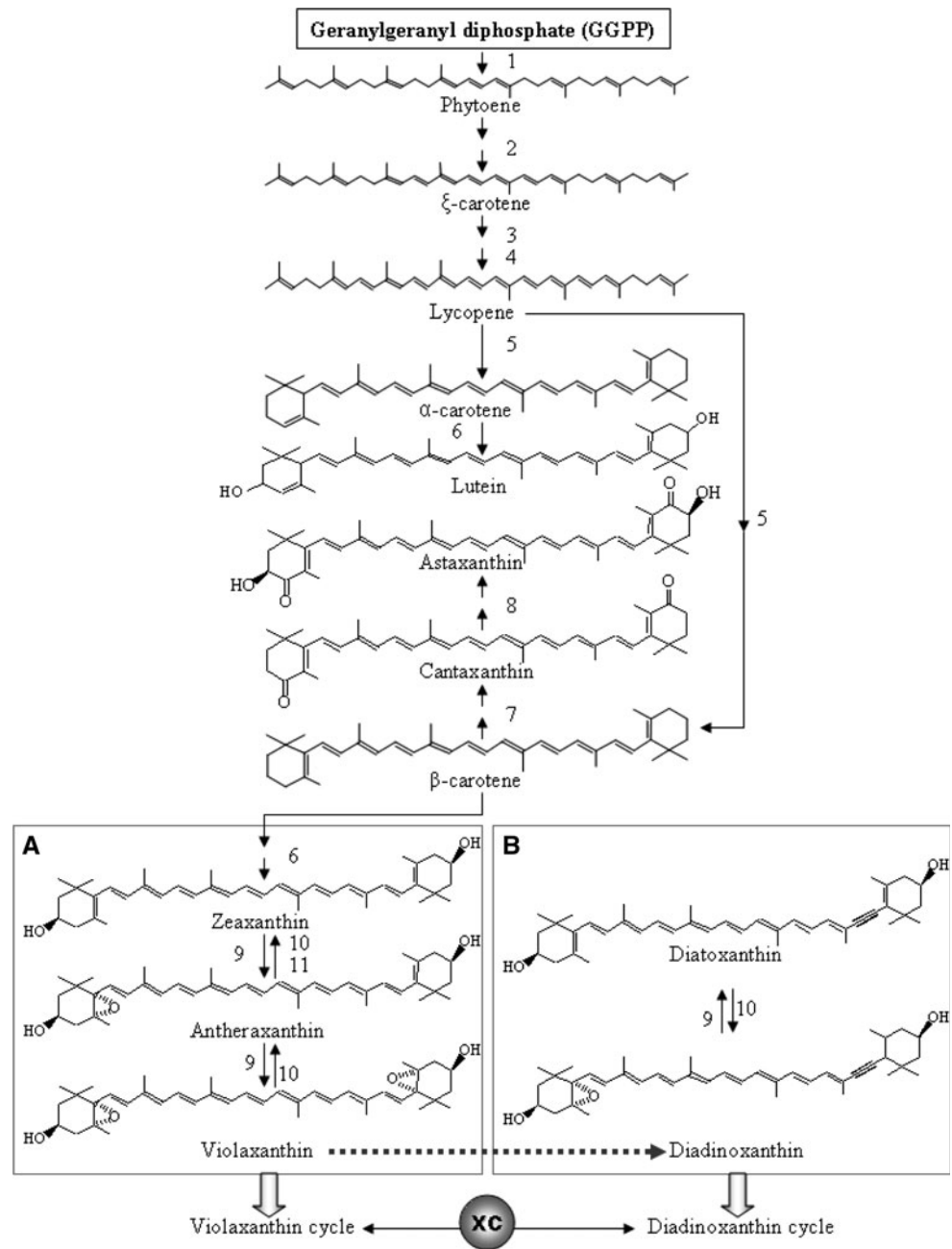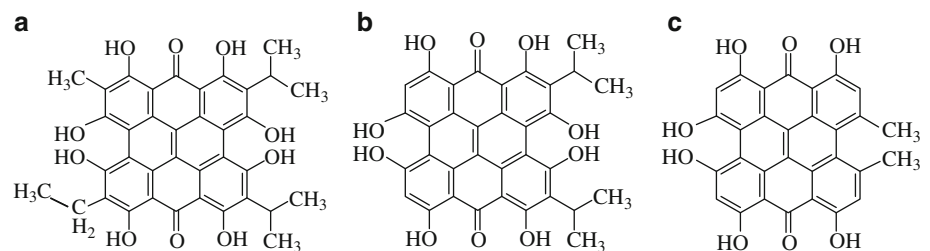
Fig. 11 Possible structures of a pigment maristentorin (**a**) isolated from marine ciliate *Maristentor dinoferus* and the structurally related compound stentorin (**b**) and hypericin (**c**)

variabilis, *Nostoc muscorum* and *Nostoc maseaum* were found to produce pteridines in relatively large concentrations. Recently, a compound thalassiolin B (Fig. 13) has

been extracted from the marine plant *Thalassia testudinum* that shows superb antioxidant activity and can efficiently repair UV-B-damaged skin upon its topical application
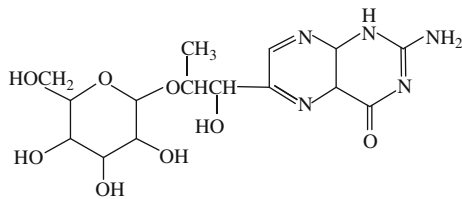
Fig. 12 Structure of the UV-absorbing compound, biopterin glucoside, isolated from the marine planktonic cyanobacterium *Oscillatoria* sp
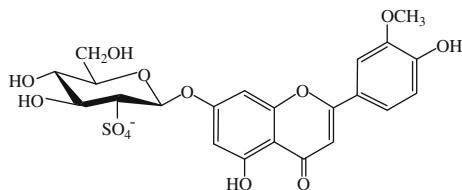

Fig. 13 Structure of thalassiolin B isolated from the marine plant *Thalassia testudinum*

[165]. It has been demonstrated that some seaweed extracts can help to protect skin from UVR [26, 68]. Overall, it seems that our knowledge regarding the assortment and characteristics of UV-absorbing/screening compounds is still in its formative years and much work is still required to elucidate the structure and function of several photoprotective compounds existing in nature.

Effect of environmental factors on the synthesis of photoprotective compounds

Several environmental factors such as different wavelength bands of UVR, desiccation, nutrients, salt concentration, light as well as dark periods have been found to affect the production of photoprotective compounds in various organisms. UVR-induced synthesis of some photoprotective compounds such as MAAs has been reported from diverse cyanobacteria, eukaryotic phytoplankton and macroalgae. In *Gyrodinium dorsum*, a nontoxic dinoflagellate, MAA was found to increase when induced by 310 nm radiation and also by UV-A radiation [110]. Similarly, a monochromatic action spectrum for photoinduction of the MAA shinorine was found in the red alga *Chondrus crispus* under UV-A radiation [117]. Photoinduction of MAAs by UVR has been reported in the marine dinoflagellate *Scrippsiella sweeneyae* and in diatoms [168, 210]. The photoprotective compounds (mainly MAAs and scytonemin) in cyanobacteria are highly responsive to UV-B radiation [190, 195].

It has been found that light is essential for MAA synthesis in cyanobacteria and algae. In an experiment, the circadian induction in MAAs (i.e., increasing during the light period and decreasing during the dark period) was found under alternating light (PAR or PAR + UVR) and dark conditions (Fig. 14) [190]. Furthermore, under natural solar radiation, increasing concentrations of the photoprotective compound shinorine, a bisubstituted MAA, were found only during the light periods, whereas more or less constant values of shinorine concentrations were found during and at the end of the dark period (Fig. 15) [190]. This suggests that synthesis of MAAs is an energy-dependent process and depends on solar energy for its maintenance in natural habitats. However, the role of PAR and photosynthesis in MAAs production is still in dispute, since biosynthesis of MAAs has been reported in the absence of PAR in the cyanobacterium *Chlorogloeopsis* PCC 6912 [159] as well as in nonphotosynthetic microorganisms such as fungi [122] and the marine bacterium *Micrococcus* sp. AK-334 [4]. Furthermore, PAR was shown to induce the UV-absorbing compounds in a marine macroalga *Chondrus crispus* [104] as well as the dinoflagellate *Alexandrium excavatum* when grown at 200 μmol photons m^{-2} s^{-1} as compared to 20 μmol photons m^{-2} s^{-1} [37]. Moreover, species of *Bangia* and *Porphyra* were found to accumulate UV-absorbing compounds not only in their natural environments, but also under long-term low-light laboratory conditions [92, 109]. The effect of different light qualities (white, blue, green, yellow and red light) on the accumulation of particular MAAs has also been observed. Korbee et al. [114] reported the favorable role of blue light in the accumulation of the MAAs porphyra-334, palythine and asterina-330, while shinorine was found to accumulate under white, green, yellow and red light in *Porphyra leucosticta* isolated from the intertidal zone of Lagos, Málaga, Southern Spain.

Nutrient conditions also affect the biosynthesis of MAAs to a great extent. A remarkable decrease in MAA content was found in the marine dinoflagellates *Akashiwo sanguinea* (syn. *Gymnodinium sanguineum*) and *Gymnodinium* cf. *instriatum* under reduced nitrogen concentration [127]. Enriched ammonium concentrations have been shown to raise the contents of UV-absorbing compounds in the red macroalga *Porphyra* sp. [115, 155]. Recently, Singh et al. [182] also reported the induction of MAA synthesis by salt and ammonium in a concentration-dependent manner without UV stress in the cyanobacterium *Anabaena variabilis* PCC 7937.

Certain other factors such as osmotic stress, salt stress as well as temperature have also been found to affect the biosynthesis of MAAs in some cyanobacteria [159, 182, 189]. Portwich and Garcia-Pichel [159] have reported the induction of MAA synthesis by salt stress without PAR or UV radiation in the cyanobacterium *Chlorogloeopsis* sp. PCC 6912, which can live on up to 70% sea water salinity. Little is known concerning the effect of desiccation on the

Fig. 14 UV-B radiation-induced circadian induction of MAAs in cyanobacteria showing the distinct induction in the light phase (*L*) and no induction in dark phase (*D*). UV-A and PAR show only low level MAA induction relative to UV-B (adapted from [190])
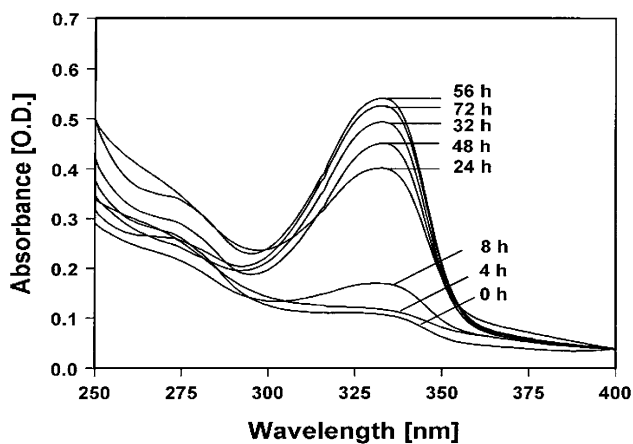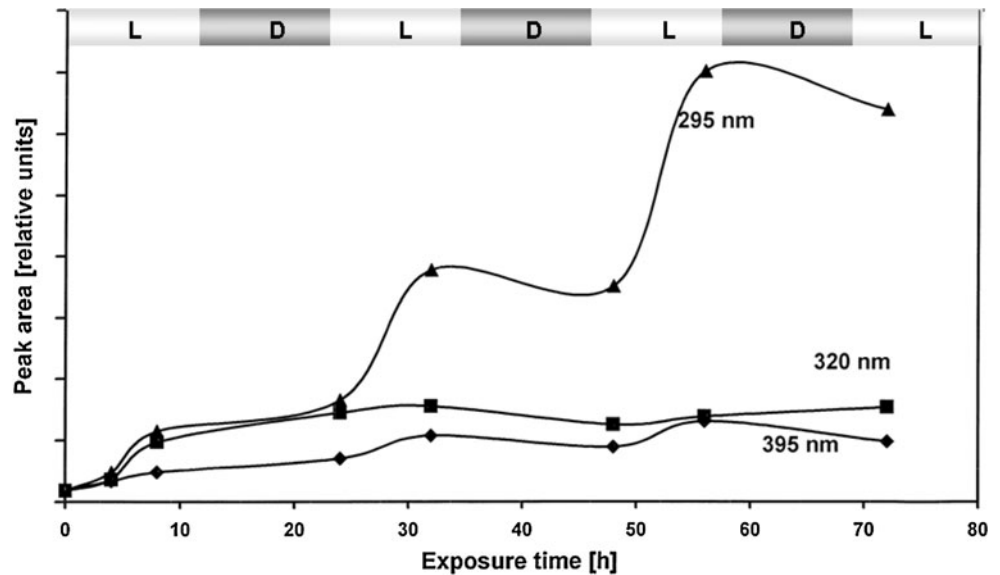

Fig. 15 Absorption spectra of the cells showing the induction of MAAs by UV-B (295 cut-off filter) radiation in a cyanobacterium *Nostoc commune* after different durations of irradiation. Cells were exposed under natural solar radiation, and aliquots were withdrawn at alternating light (4, 8, 24, 32 and 56 h) and dark (48 and 72 h) periods. The results show that MAAs were induced only during light periods, and during dark incubation the concentration of MAAs either remained as such or declined slightly (adapted from [190])

concentration of UV-absorbing/screening compounds of intertidal species that are often exposed and desiccated during low tides, though it has been investigated in other studies carried out with bryophytes, grass and lichens [132, 150] as well as cyanobacteria [64]. However, recently, Jiang et al. [99] reported the role of desiccation in maintaining a high concentration of UV-absorbing compounds in an intertidal red alga *Porphyra haitanensis*. The local climatic conditions also affect the concentrations of MAAs in a particular organism. Karsten et al. [104] demonstrated that the concentrations of MAAs in Rhodophyceae from polar (Spitsbergen) and cold-temperate (Helgoland, North

Sea) regions are usually only half of those in species from warm-temperate (Spain) localities. In marine organisms MAA levels also depend on depth, since most species of Rhodophyceae growing in deeper waters lack these compounds. In *Polysiphonia arctica* growing in the subtidal zone of Spitsbergen, a strong decrease in MAA concentration with increasing depth (1–7 m) has been found [104]. Thus, it may be concluded that lower MAA contents in species from higher latitudes or from deeper waters correlate with lower natural solar UV irradiances in the respective habitat.

The biosynthesis of scytonemin is strongly induced by UV-A and PAR at high photon fluence rates [72]. The effect of light quality has also been examined, and it has been found that UV-A treatment is very efficient in inducing scytonemin synthesis, whereas blue, green or red light at the same fluence rates does not cause any significant increase in scytonemin [72]. Dillon et al. [54] investigated the effect of other correlated stress factors including heat, osmotic and oxidative stress on the synthesis of scytonemin in the cyanobacterium *Chroococcidiopsis* sp. and showed that both increases in temperature and oxidative stress in combination with UV-A have a synergistic effect on high production of scytonemin. Recently, Fleming and Castenholz [65] have shown the effects of nitrogen sources on scytonemin synthesis in the cyanobacterium *Nostoc punctiforme* PCC 73102. Thus, scytonemin induction may be regulated as a part of a complex stress response pathway in which multiple environmental signals affect its synthesis.

In a study of the seasonal pigment pattern of surface phytoplankton, Barlow et al. [14] found that under low temperature and irradiance conditions, the photosynthetic carotenoids were prominent; however, as temperatures and

irradiance increased and nutrients declined, there was a significant increase in the proportion of photoprotective carotenoids. High levels ($\approx 80\%$ of total carotenoids) of photosynthetic carotenoids (PSCs) have been reported in high-productivity ecosystems dominated by large phytoplankton in contrast to low-chlorophyll surface waters with prominent small cells, where photoprotective carotenoids (PPCs) were dominant with >70% of the total carotenoid pool [15, 76]. These differences might be due to physiological responses to the variability in the environmental conditions [15, 76, 217]. Overall, it seems that MAAs have different signal transduction pathways (e.g., biochemical as well as photosensory and genetical) for the synthesis of MAAs; however, not much is known regarding the biosynthesis of MAAs, and further work is required to establish this assumption.

Photoprotective compounds: commercial applications

UVR is one of the major exogenous harmful factors to human health [52]. Photoprotective compounds such as MAAs, scytonemin, carotenoids and some other substances, identified in a wide variety of marine organisms, have anti-inflammatory and antioxidant properties with possible applications in the cosmetic and pharmaceutical industries [164]. MAAs with high absorption in the UV region can potentially be used in cosmetics and toiletries as UV protectors and activators of cell proliferation [44, 176, 214, 223]. The MAAs such as shinorine (SH), porphyra-334 (P-334) and mycosporine-glycine have potentials to protect the fibroblast cells from UVR-induced cell death [153]. The combined action of P-334 and shinorine, extracted from the red alga *Porphyra umbilicalis*, has been reported to suppress UV-induced aging in human skin [48]. MAAs exhibit a high antioxidant activity scavenging superoxide anions and inhibiting lipid peroxidation [50, 51] resulting from UV-induced production of ROS [152, 209]. Recently, Coba et al. [41] also reported the antioxidant activity of P-334 and shinorine from *Porphyra* and other red algae, maintaining the antioxidant defense system of the skin as well as Hsp70 expression. The antioxidant activities of the MAAs glycine and usujilene have been reported to inhibit lipid peroxidation in aqueous extracts of marine organisms and to scavenge $^1O_2$ generated from certain endogenous photosensitizers [147, 209]. Yoshiki et al. [227] reported a new antioxidant compound from the MAA porphyra-334 by heat treatment. MAAs can block the production of both 6–4 photoproduct and cyclobutane pyrimidine dimer (CPD) formation [138]. Certain synthetic analogues of MAAs, such as tetrahydropyridine derivatives, have been developed for commercial application as suncare products [19, 38, 56]. Moreover, a product called Helioguard® 365 that

contains mycosporine-like amino acids from the red alga *Porphyra umbilicalis* has been commercialized [31]. Besides the production of sun care products, MAAs have been commercially explored in the manufacture of several non-biological materials such as photostabilizing additives in plastics, paints and varnishes [12].

Scytonemin has dual kinase inhibitory activity that may be therapeutically important in acute and possibly chronic disorders of inflammation and proliferation. In human T-cell leukemia Jurkat cells, scytonemin repressed cell proliferation (IC50 = 7.8 μM) and induced apoptosis in 24% of the cells (at 3 μM). Scytonemin showed a concentration-dependent inhibition of phosphorylation of cdc25C mediated by a polo-like kinase 1 (PLK1) and plays a significant role in regulating the G2/M transition in the cell cycle [205]. The cyclic peptide scytonemin A from *Scytonema* sp. has been shown to be a calcium agonist [91]. Overall, scytonemin has immense pharmacological potential with antiinflammatory and antiproliferative activities [206] that could be used to build up several novel classes of therapeutically valuable drugs.

Carotenoids may also directly provide photoprotection against UVR-induced photooxidation in the skin and also provide protection against inflammation, ulcers due to *Helicobacter pylori* infection and age-related diseases [7, 17, 31, 83, 180]. It has been shown that β-carotene can modulate UV-A-induced gene expression in human keratinocytes [221]. Carotenoids have also been assessed in relation with their antioxidant properties [47] that can play a key role in reducing the incidence of several UVR-mediated diseases [6]. Several commercial values of carotenoids such as natural food coloring agents, food additives, drugs, enhancers of the color of egg yolks, improving the health and fertility of cattle, and use in the cosmetic industries have been reported [98, 203]. Arbeloa et al. [5] reported the occurrence of natural antioxidant gadusol (3,5,6-trihydroxy-5-hydroxymethyl-2-methoxycyclohex-2-en-1-one) in fish roes from the Argentine Sea and found that Brazilian sandperch (*Pinguipes brasilianus*) and Argentinian sandperch (*Pseudopercis semifasciata*) are useful sources of antioxidants for human consumption. Some carotenoids offer provitamin A activity [135], and high consumption of carotenoids may diminish threats of certain pathologies [211]. Overall, it seems that these photoprotective compounds may be of immense value in future biotechnological research for the production of a number of commercial products directly related to human health.

Conclusions

Synthesis and/or accumulation of a number of photoprotective compounds has been recognized from diverse

groups of marine organisms that may counteract several structural as well as physiological damages caused by UVR. MAAs are the imperative and ubiquitous group of sunscreen compounds in a large number of marine organisms that can potentially reduce the detrimental effects of UVR. Besides MAAs, scytonemin, carotenoids and several other compounds have also been found to play a significant role in mitigating the toxic effects of UVR in a number of marine organisms. The concentrations of photoprotective compounds in organisms are often positively correlated with the exposure to UV-R and other exogenous factors. Moreover, these photoprotective compounds have several other potential functions with therapeutic properties that may be exploited in a large amount of commercial applications, and further development of marine biotechnology for human photoprotection and research must be specially focused on the analysis, biosynthesis and mode of action of several unknown photoprotective compounds against several abnormalities induced by UVR.

References

1. Adams NL, Shick JM (2001) Mycosporine-like amino acids prevent UVB-induced abnormalities during early development of the green sea urchin *Strongylocentrotus droebachiensis*. Mar Biol 138:267–280

2. Al-Otaibi AA, Al-Sofyani A, Niaz GR, Al-Lihaibi SS (2006) Temporal and depth variation of photoprotective mycosporine-like amino acids in soft coral species from the eastern red sea coast. Mar Sci 17:169–180

3. Ambarsari I, Brown BE, Barlow RG, Britton G, Cummings D (1997) Fluctuations in algal chlorophyll and carotenoid pigments during solar bleaching in the coral *Goniastrea aspera* at Phuket, Thailand. Mar Ecol Prog Ser 159:303–307

4. Arai T, Nishijima M, Adachi K, Sano H (1992) Isolation and structure of a UV absorbing substance from the marine bacterium *Micrococcus* sp. AK-334. Marine Biotechnology Institute, Tokyo, pp 88–94

5. Arbeloa EM, Uez MJ, Bertolotti SG, Churio MS (2010) Antioxidant activity of gadusol and occurrence in fish roes from Argentine Sea. Food Chem 119:586–591

6. Astley SB, Hughes DA, Wright AJA, Elliott RM, Southon S (2004) DNA damage and susceptibility to oxidative damage in lymphocytes: effects of carotenoids in vitro and in vivo. Br J Nutr 91:53–61

7. Aust O, Stahl W, Sies H, Tronnier H, Heinrich U (2005) Supplementation with tomato-based products increases lycopene, phytofluene, and phytoene levels in human serum and protects against UV-light-induced erythema. Int J Vitam Nutr Res 75:54–60

8. Balskus EP, Walsh CT (2008) Investigating the initial steps in the biosynthesis of cyanobacterial sunscreen scytonemin. J Am Chem Soc 130:15260–115261

9. Banaszak AT, Lesser MP (2009) Effects of solar ultraviolet radiation on coral reef organisms. Photochem Photobiol Sci 8:1276–1294

10. Banaszak AT, Trench RK (1995) Effects of ultraviolet (UV) radiation on marine microalgal-invertebrate symbioses. II. The synthesis of mycosporine-like amino acids in response to exposure to UV in *Anthopleura elegantissima* and *Cassiopeia xamachana*. J Exp Mar Biol Ecol 194:233–250

11. Banaszak AT, Trench RK (2001) Ultraviolet sunscreens in Dinoflagellates. Protist 152:93–101

12. Bandaranayake WM (1998) Mycosporines: are they nature's sunscreens? Nat Prod Rep 15:159–172

13. Bandaranayake WM, Rocher AD (1999) Role of secondary metabolites and pigments in the epidermal tissues, ripe ovaries, viscera, gut contents and diet of the sea cucumber *Holothuria atra*. Mar Biol 133:163–169

14. Barlow R, Stuart V, Lutz V, Sessions H, Sathyendranath S, Platt T, Kyewalyanga M, Clementson L, Fukasawa M, Watanabe S, Devred E (2007) Seasonal pigment patterns of surface phytoplankton in the subtropical southern hemisphere. Deep Sea Res I 54:1687–1703

15. Barlow RG, Aiken J, Moore GF, Holligan PM, Lavender S (2004) Pigment adaptations in surface phytoplankton along the eastern boundary of the Atlantic Ocean. Mar Ecol Prog Ser 281:13–26

16. Barnett TA, Hageman JH (1983) Characterization of a brown pigment from *Bacillus subtilis* cultures. Can J Microbiol 29:309–315

17. Bennedsen M, Wang X, Willen R, Wadstroem T, Andersen LP (1999) Treatment of *H. pylori* infected mice with antioxidant astaxanthin reduces gastric inflammation, bacterial load and modulates cytokine release by splenocytes. Immunol Lett 70:185–189

18. Ben-Yosef DZ, Kashman Y, Benayahu Y (2006) Response of the soft coral *Heteroxenia fuscescens* to ultraviolet radiation regimes as reflected by mycosporine-like amino acid biosynthesis. Mar Ecol 27:219–228

19. Bird G, Fitzmaurice N, Dunlap WC, Chalker BE, Bandaranayake WM (1987) Sunscreen compositions and compounds for use therein. International patent application PCT/AU87/00330, publication no. WO 88/02251. Australian patent 595075. ICI Australia Operations Pty Ltd and Australian Institute of Marine Science, Townsville

20. Bischof K, Kräbs G, Hanelt D, Wiencke C (2000) Photosynthetic characteristics and mycosporine-like amino acids under UV radiation: a competitive advantage of *Mastocarpus stellatus* over *Chondrus crispus* at the Helgoland shoreline? Helgol Mar Res 54:47–52

21. Bjerke JW, Lerfall K, Elvebakk A (2002) Effects of ultraviolet radiation and PAR on the content of usnic and divaricatic acids in two arctic-alpine lichens. Photochem Photobiol Sci 1:678–685

22. Blunt JW, Copp BR, Hu W-P, Munro MHG, Northcote PT, Prinsep MR (2007) Marine natural products. Nat Prod Rep 24:31–86

23. Boedeker C, Karsten U (2005) The occurrence of mycosporine-like amino acids in the gametophytic and sporophytic stages of *Bangia* (Bangiales, Rhodophyta). Phycologia 44:403–408

24. Boulay C, Abasova L, Six C, Vass I, Kirilovsky D (2008) Occurrence and function of the orange carotenoid protein in photoprotective mechanisms in various cyanobacteria. Biochim et Biophy Acta 1777:1344–1354

25. Brown BE, Ambarsari I, Warner ME, Fitt WK, Dunne RP, Gibb SW, Cummings DG (1999) Diurnal changes in photochemical efficiency and xanthophyll concentrations in shallow water reef corals: evidence for photoinhibition and photoprotection. Coral Reefs 18:99–105

26. Bulteau AL, Moreau M, Saunois A, Nizard C, Friguet B (2006) Algae extract mediated stimulation and protection of proteasome activity within human keratinocytes exposed to UVA and UVB irradiation. Antioxid Redox Signal 8:136–143

27. Bultel-Poncé V, Felix-Theodore F, Sarthon C, Ponge J-F, Bodo B (2004) New pigments from the terrestrial cyanobacterium *Scytonema* sp. collected on the Mitaraka Inselberg, French Guyana. J Nat Prod 67:678–681

28. Burja AM, Banaigs B, Abou-Mansour E, Burgess JG, Wright PC (2001) Marine cyanobacteria—a prolific source of natural products. Tetrahedron 57:9347–9377

29. Callone AI, Carignan M, Montoya NG, Carreto JI (2006) Biotransformation of mycosporine like amino acids (MAAs) in the toxic dinoflagellate *Alexandrium tamarense*. J Photochem Photobiol B Biol 84:204–212

30. Cardozo KHM, Guaratini T, Barros MP, Falcão VR, Tonon AP, Lopes NP, Campos S, Torres MA, Souza AO, Colepicolo P, Pinto E (2007) Metabolites from algae with economical impact. Comp Biochem Physiol 146:60–78

31. Cardozo KHM, Guaratini T, Barros MP, Falcão VR, Tonon AP, Lopes NP, Campos S, Torres MA, Souza AO, Colepicolo P, Pinto E (2007) Metabolites from algae with economical impact. Comp Biochem Physiol C 146:60–78

32. Carefoot TH, Harris M, Taylor BE, Donovan D, Karentz D (1998) Mycosporine-like amino acids: possible UV protection in eggs of the sea hare *Aplysia dactylomela*. Mar Biol 130:389–396

33. Carignan MO, Cardozo KHM, Oliveira-Silva D, Colepicolo P, Carreto JI (2009) Palythine–threonine, a major novel mycosporine-like amino acid (MAA) isolated from the hermatypic coral *Pocillopora capitata*. J Photochem Photobiol B Biol 94:191–200

34. Carreto JI, Carigan MO, Daleo G, DeMarco SG (1990) Occurrence of mycosporine-like amino acids in the red tide dinoflagellate *Alexandrium excavatum*: UV-protective compounds? J Plankton Res 12:909–921

35. Carreto JI, Carignan MO, Montoya NG (2001) Comparative studies on mycosporine-like amino acids, paralytic shellfish toxins and pigment profiles of the toxic dinoflagellates *Alexandrium tamarense*, *A. catenella* and *A. minutum*. Mar Ecol Progr Ser 223:49–60

36. Carreto JI, Carignan MO, Montoya NG (2005) A highresolution reverse-phase liquid chromatography method for the analysis of mycosporine-like amino acids (MAAs) in marine organisms. Mar Biol 146:237

37. Carreto JI, Lutz VA, Dc Marco SG, Carignan MO (1990) Fluence and wavelength dependence of mycosporine-like amino acid synthesis in the dinoflagellate *Alexandrium excavatum*. In: Graneli E, Edler L, Sundström B, Anderson DM (eds) Toxic marine phytoplankton. Elsevier, New York, pp 275–279

38. Chalmers PJ, Fitzmaurice N, Rigg DJ, Thang SH, Bird G (1990) UVabsorbing compounds and compositions. International Patent Application PCT/AU90/00078, publication no. WO 90/09995. Australian patent 653495. ICI Australia Operations Pty Ltd and Australian Institute of Marine Science, Townsville

39. Charlson RJ, Lovelock JE, Andreae MO, Warren SG (1987) Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature 326:655–661

40. Chioccara F, Della Gala A, De Rosa M, Novellino E, Prota G (1980) Mycosporine aminoacids and related compounds from the eggs of fishes. Bulletin de la Societé Chimique de Belgique 89:1101–1106

41. Coba FDL, Aguilera J, Figueroa FL, de Gálvez MV, Herrera E (2009) Antioxidant activity of mycosporine-like amino acids isolated from three red macroalgae and one marine lichen. J Appl Phycol 21:161–169

42. Cockell CS, Knowland J (1999) Ultraviolet radiation screening compounds. Biol Rev 74:311–345

43. Coesel S, Oborník M, Varela J, Falciatore A, Bowler C (2008) Evolutionary origins and functions of the carotenoid biosynthetic pathway in marine diatoms. PLoS ONE 3:e2896

44. Conde FR, Churio MS, Previtali CM (2000) The photoprotector mechanism of mycosporine-like amino acids. excited-state properties and photostability of porphyra-334 in aqueous solution. J Photochem Photobiol B Biol 56:139–144

45. Conde FR, Churio MS, Previtali CM (2007) Experimental study of the excited-state properties and photostability of the mycosporine-like amino acid palythine in aqueous solution. Photochem Photobiol Sci 6:669–674

46. Cunningham FX, Lee H, Gantt E (2007) Carotenoid biosynthesis in the primitive red alga *Cyanidioschyzon merolae*. Eukaryot Cell 6:533–545

47. Czeczuga B, Bartel R, Czeczuga-Semeniuk E (2002) Carotenoid content in eggs of Atlantic salmon (*Salmo salar* L.) and brown trout (*Salmo trutta* L.) entering Polish rivers for spawning or reared in fresh water. Acta Ichthyologica et Piscatoria 32:3–21

48. Daniel S, Cornelia S, Fred Z (2004) UV-A sunscreen from red algae for protection against premature skin aging. Cosmet Toilet Manuf Worldw 139–143

49. Davidson AT, Brarnich D, Marchant HJ, McMinn A (1994) Effects of UV-B irradiation on growth and survival of Antarctic marine diatoms. Mar Biol 119:507–515

50. De la Coba F, Aguilera J, Figueroa FL (2007) Use of mycosporine-type amino acid shinorine as an antioxidant. Intl Patent WO2007/026038A2

51. De la Coba F, Aguilera J, Figueroa FL (2007) Use of mycosporine-type amino acid Porphyra-334 as an antioxidant. Intl Patent WO2007/026035 A2

52. Diffey BL (1998) Ultraviolet radiation and human health. Clin Dermatol 16:83–89

53. Dillon JG, Castenholz RW (1999) Scytonemin, a cyanobacterial sheath pigment, protects against UVC radiation: implications for early photosynthetic life. J Phycol 35:673–681

54. Dillon JG, Tatsumi CM, Tandingan PG, Castenholz RW (2002) Effect of environmental factors on the synthesis of scytonemin, a UV-screening pigment, in a cyanobacterium (*Chroococcidiopsis* sp.). Arch Microbiol 177:322–331

55. Dimier C, Corato F, Tramontano F, Brunet C (2007) Photoprotection and xanthophyll-cycle activity in three marine diatoms. J Phycol 43:937–947

56. Dunlap WC, Chalker BE, Bandaranayake WM, Wu Won JJ (1998) Nature's sunscreen from the Great Barrier Reef, Australia. J Cosmet Sci 20:41–51

57. Dunlap WC, Shick JM (1998) Ultraviolet radiation-absorbing mycosporine-like amino acids in coral reef organisms: a biochemical and environmental perspective. J Phycol 34:418–430

58. Dunlap WC, Williams DM, Chalker BE, Banaszak AT (1989) Biochemical photoadaptations in vision: UV-absorbing pigments in fish eye tissues. Comp Biochem Physiol B 93:601–607

59. Edge R, McGarvey DJ, Truscott TG (1997) The carotenoids as anti-oxidants—a review. J Photochem Photobiol B Biol 41:189–200

60. Fenical W, Jensen PR (2006) Developing a new resource for drug discovery: marine actinomycete bacteria. Nat Chem Biol 2:666–673

61. Fenical W, Sethna KM, Lloyd GK (2002) Marine microorganisms as a developing resource for drug discovery. Pharm News 9:489–494

62. Ehling-Schulz M, Bilger W, Scherer S (1997) UV-B induced synthesis of photoprotective pigments and extracellular polysaccharides in the terrestrial cyanobacterium *Nostoc commune*. J Bacteriol 179:1940–1945

63. Ferreyra GA, Schloss I, Demers S, Neale PJ (1994) Phytoplankton responses to natural ultraviolet irradiance during early spring in the Weddell-Scotia Confluence: an experimental approach. Antarct J US 29:268–270

64. Fleming ED, Castenholz RW (2007) Effects of periodic desiccation on the synthesis of the UV-screening compound, scytonemin, in cyanobacteria. Environ Microbiol 9:1448–1455

65. Fleming ED, Castenholz RW (2008) Effects of nitrogen source on the synthesis of the UV screening compound, scytonemin, in the cyanobacterium *Nostoc punctiforme* PCC 73102. FEMS Microbiol Ecol 63:301–308

66. Foote CS, Chang YC, Denny RW (1970) Chemistry of singlet oxygen. X. Carotenoid quenching parallels biological protection. J Am Chem Soc 92:5216–5218

67. Frommolt R, Werner S, Paulsen H, Goss R, Wilhelm C, Zauner S, Maier UG, Grossman AR, Bhattacharya D, Lohr M (2008) Ancient recruitment by chromists of green algal genes encoding enzymes for carotenoid biosynthesis. Mol Biol Evol 25:2653–2667

68. Fujimura T, Tsukahara K, Moriwaki S, Kitahara T, Sano T, Takema Y (2002) Treatment of human skin with an extract of *Fucus vesiculosus* changes its thickness and mechanical properties. J Cosmet Sci 53:1–9

69. Fuqua WC, Coyne VE, Stein DC, Lin C-M, Weiner RM (1991) Characterization of *mel.4*: a gene encoding melanin biosynthesis from the marine bacterium *Shewanella colwelliana*. Gene 109:131–136

70. Fuqua WC, Weiner RM (1993) The *melA* gene is essential for melanin biosynthesis in the marine bacterium *Shewanella colwelliana*. J General Microbiol 139:1105–1114

71. Garcia-Pichel F, Belnap J (1996) Microenvironments and microscale productivity of cyanobacterial desert crusts. J Phycol 32:774–782

72. Garcia-Pichel F, Castenholz RW (1991) Characterization and biological implications of scytonemin, a cyanobacterial sheath pigment. J Phycol 27:395–409

73. Garcia-Pichel F, Nübel U, Muyzer G (1998) The phylogeny of unicellular, extremely halotolerant cyanobacteria. Arch Microbiol 169:469–482

74. Garcia-Pichel F, Sherry ND, Castenholz RW (1992) Evidence for an ultraviolet sunscreen role of the extracellular pigment scytonemin in the terrestrial cyanobacterium *Chlorogloeopsis* sp. Photochem Photobiol 56:17–23

75. Gauslaa Y, McEvoy M (2005) Seasonal changes in solar radiation drive acclimation of the sun-screening compound parietin in the lichen *Xanthoria parietina*. Basic Appl Ecol 6:75–82

76. Gibb SW, Barlow RG, Cummings DG, Rees NW, Trees CC, Holligan P, Suggett D (2000) Surface phytoplankton pigment distributions in the Atlantic ocean: an assessment of basin scale variability between 50°N and 50°S. Prog Oceano 45:339–368

77. Goes JI, Handa N, Taguchi S, Harna T, Saito H (1995) Impact of UV radiation on the production patterns and composition of dissolved free and combined amino acids in marine phytoplankton. J Plankton Res 17:1337–1362

78. Goodwin TW (1986) Metabolism, nutrition, and function of carotenoids. Ann Rev Nutr 6:273–297

79. Götz T, Windhovel U, Böger P, Sandmann G (1999) Protection of photosynthesis against UV-B radiation by carotenoids in transformants of the cyanobacterium *Synechococcus* PCC 7942. Plant Physiol 120:599–604

80. Grant PT, Plack PA, Thomson RH (1980) Gadusol, a metabolite from fish eggs. Tetrahedron Lett 21:4043–4044

81. Gröniger A, Häder D-P (2000) Stability of mycosporine-like amino acids. Recent Res Devel Photochem Photobiol 4:247–252

82. Grynbaum MD, Hentschel P, Putzbach K, Rehbein J, Krucker M, Nicholson G, Albert K (2005) Unambiguous detection of astaxanthin and astaxanthin fatty acid esters in krill (*Euphausia superba* Dana). J Sep Sci 28:1685–1693

83. Guerrin M, Huntley ME, Olaizola M (2003) Haematococcus astaxanthin: applications for human health and nutrition. Trends Biotechnol 21:210–216

84. Häder D-P, Kumar HD, Smith RC, Worrest RC (2007) Effects of solar UV radiation on aquatic ecosystems and interactions with climate change. Photochem Photobiol Sci 6:267–285

85. Hairston NG (1979) Adaptive significance of color polymorphism in 2 species of diaptomus (Copepoda). Limnol Oceanogr 24:15–37

86. Han Y-S, Han T (2005) UV-B induction of UV-B protection in *Ulva pertusa* (chlorophyta). J Phycol 41:523–530

87. Hannach G, Sigleo AC (1998) Photoinduction of UV-absorbing compounds in six species of marine phytoplankton. Mar Ecol Prog Ser 174:207–222

88. Hansson L-A, Hylander S (2009) Effects of ultraviolet radiation on pigmentation, photoenzymatic repair, behavior, and community ecology of zooplankton. Photochem Photobiol Sci 8:1266–1275

89. Helbling EW, Chalker BE, Dunlap WC, Holm-Hansen O, Villafañe VE (1996) Photoacclimation of Antarctic marine diatoms to solar ultraviolet radiation. J Exp Mar Biol Ecol 204:85–101

90. Helbling EW, Menchi CF, Villafañe VE (2002) Bioaccumulation and role of UV-absorbing compounds in two marine crustacean species from Patagonia, Argentina. Photochem Photobiol Sci 1:820–825

91. Helms GL, Moore RE, Niemczura WP, Patterson GML, Tomer KB, Gross ML (1988) Scytonemin A, a novel calcium antagonist from a blue-green alga. J Org Chem 53:1298–1307

92. Hoyer K, Karsten U, Wiencke C (2002) Induction of sunscreen compounds in Antarctic macroalgae by different radiation conditions. Mar Biol 141:619–627

93. Hylander S, Boeing WJ, Granéli W, Karlsson J, von Einem J, Gutseit K, Hansson L-S (2009) Complementary UV protective compounds in zooplankton. Limnol Oceanogr 54:1883–1893

94. Ingalls AE, Whitehead K, Bridoux MC (2010) Tinted windows: the presence of the UV absorbing compounds called mycosporine-like amino acids embedded in the frustules of marine diatoms. Geochim Cosmochim Acta 74:104–115

95. Ishikura M, Kato C, Maruyama T (1997) UV-absorbing substances in zooxanthellate and azooxanthellate clams. Mar Biol 128:649–655

96. Ito S, Hirata Y (1977) Isolation and structure of a mycosporine from the zoanthid *Palythoa tuberculosa*. Tetrahedron Lett 28:2429–2430

97. Jeffrey SW, Mactavish HS, Dunlap WC, Vesk M, Groenewoud K (1999) Occurrence of UVA- and UVB absorbing compounds in 152 species (206 strains) of marine microalgae. Mar Ecol Prog Ser 189:35–51

98. Jha RK, Zi-rong X (2004) Biomedical compounds from marine organisms. Mar Drugs 2:123–146

99. Jiang H, Gao K, Helbling EW (2008) UV-absorbing compounds in *Porphyra haitanensis* (Rhodophyta) with special reference to effects of desiccation. J Appl Phycol 20:387–395

100. Jokiel PL, Lesser MP, Ondrusek ME (1997) UV absorbing compounds in the coral *Pocillopora damicornis*: effects of light, water flow, and UV radiation. Limnol Oceanogr 42:1468–1473

101. Jones AC, Gu L, Sorrels CM, Sherman DH, Gerwick WH (2009) New tricks from ancient algae: natural products biosynthesis in marine cyanobacteria. Curr Opin Chem Biol 13:216–223

102. Karentz D, McEuen ES, Land MC, Dunlap WC (1991) Survey of mycosporine-like amino acid compounds in Antarctic marine organisms: potential protection from ultraviolet exposure. Mar Biol 108:157–166

103. Karsten U, Escoubeyrou K, Charles F (2009) The effect of re-dissolution solvents and HPLC columns on the analysis of mycosporine-like amino acids in the eulittoral macroalgae *Prasiola crispa* and *Porphyra umbilicalis*. Helgol Mar Res 63:231–238

104. Karsten U, Franklin LA, Lüning K, Wiencke C (1998) Natural ultraviolet radiation and photosynthetically active radiation induce formation of mycosporine-like amino acids in the marine macroalga *Chondrus crispus* (Rhodophyta). Planta 205:257–262

105. Karsten U, Garcia-Pichel F (1996) Carotenoids and mycosporine-like amino acid compounds in members of the genus *Microcoleus* (cyanobacteria): a chemosystematic study. Syst Appl Microbiol 19:285–294

106. Karsten U, Sawall T, Hanelt D, Bischof K, Figueroa FL, Flores-Moya A, Wiencke C (1998) An inventory of UV-absorbing mycosporine-like amino acids in macroalgae from polar to warm-temperate regions. Bot Mar 41:443–453

107. Karsten U, Sawall T, West J, Wiencke C (2000) Ultraviolet sunscreen compounds in epiphytic red algae from mangroves. Hydrobiology 432:159–171

108. Karsten U, Sawall T, Wiencke C (1998) A survey of the distribution of UV-absorbing substances in tropical macroalgae. Phycol Res 46:271–279

109. Karsten U, West JA (2000) Living in the intertidal zone–seasonal effects on heterosides and sun-screen compounds in the red alga *Bangia atropurpurea* (Bangiales). J Exp Mar Biol Ecol 254:221–234

110. Klisch M, Häder D-P (2002) Wavelength dependence of mycosporine-like amino acid synthesis in *Gyrodinium dorsum*. J Photochem Photobiol B Biol 66:60–66

111. Klisch M, Häder D-P (2008) Mycosporine-like amino acids and marine toxins—the common and the different. Mar Drugs 6:147–163

112. Klisch M, Sinha RP, Häder D-P (2002) UV-absorbing compounds in algae. Curr Top Plant Biol 3:113–120

113. Kollias N, Sayre RM, Zeise L, Chedekel MR (1991) Photoprotection by melanin. J Photochem Photobiol 9:135–160

114. Korbee N, Figueroa FL, Aguilera FJ (2005) Effect of light quality on the accumulation of photosynthetic pigments, proteins and mycosporine-like amino acids in the red alga *Porphyra leucosticta* (Bangiales, Rhodophyta). J Photochem Photobiol B Biol 80:71–78

115. Korbee N, Huovinen P, Figueroa FL, Aguilera J, Karsten U (2005) Availability of ammonium influences photosynthesis and the accumulation of mycosporine-like amino acids in two *Porphyra* species (Bangiales, Rhodophyta). Mar Biol 146:645–654

116. Koskenniemi K, Lyra C, Rajaniemi-Wacklin P, Jokela J, Sivonen K (2007) Quantitative real-time PCR detection of toxic *Nodularia* cyanobacteria in the Baltic Sea. Appl Environ Microbiol 73:2173–2179

117. Kräbs G, Watanabe M, Wiencke C (2004) A monochromatic action spectrum for the photoinduction of the UV-absorbing mycosporine-like amino acid shinorine in the red alga *Chondrus crispus*. Photochem Photobiol 79:515–519

118. Lamare MD, Hoffman J (2004) Natural variation of carotenoids in the eggs and gonads of the echinoid genus, *Strongylocentrotus*: implications for their role in ultraviolet radiation photoprotection. J Exp Mar Biol Ecol 312:215–233

119. Laurion I, Lami A, Sommaruga R (2002) Distribution of mycosporinelike amino acids and photoprotective carotenoids among freshwater phytoplankton assemblages. Aquatic Microbial Ecol 26:283–294

120. Laurion I, Roy S (2009) Growth and photoprotection in three dinoflagellates (including two strains of *Alexandrium tamarense*) and one diatom exposed to four weeks of natural and enhanced ultraviolet-B radiation. J Phycol 45:16–33

121. Lavaud J, Rotem A, Etienne A-L (2004) General features of photoprotection by energy dissipation in planktonic diatoms (Bacillariophyceae). J Phycol 40:130–137

122. Leach CM (1965) Substances associated with light-induced sporulation in fungi. Canad J Bot 43:185–200

123. Lebar MD, Heimbegner JL, Baker BJ (2007) Cold-water marine natural products. Nat Prod Rep 24:774–797

124. Lee T-M, Shiu C-T (2009) Implications of mycosporine-like amino acid and antioxidant defenses in UV-B radiation tolerance for the algae species *Ptercladiella capillacea* and *Gelidium amansii*. Mar Environ Res 67:8–16

125. Lesser MP (1996) Acclimation of phytoplankton to UV-B radiation: oxidative stress and photoinhibition of photosynthesis are not prevented by UV-absorbing compounds in the dinoflagellate *Prorocentrum micans*. Mar Ecol Prog Ser 132:287–297

126. Lesser MP (2000) Depth-dependent photoacclimatization to solar ultraviolet radiation in the Caribbean coral *Montastraea faveolata*. Mar Ecol Prog Ser 192:137–151

127. Litchman E, Neale PJ, Banaszak AT (2002) Increased sensitivity to ultraviolet radiation in nitrogen-limited dinoflagellates: photoprotection and repair. Limnol Oceanogr 47:86–94

128. Llewellyn CA, Mantoura RFC (1997) A UV absorbing compound in HPLC pigment chromatograms obtained from Icelandic basin phytoplankton. Mar Ecol Prog Ser 158:283–287

129. Lobban CS, Hallam SJ, Mukherjee P, Petrich JW (2007) Photophysics and multifunctionality of hypericin-like pigments in heterotrich ciliates: a phylogenetic perspective. Photochem Photobiol 83:1074–1094

130. Lobban CS, Schefter M, Simpson AGB, Pochon X, Pawlowski J, Foissner W (2002) *Maristentor dinoferus* n. gen., n. sp., a giant heterotrich ciliate (Spirotrichea: Heterotrichida) with zooxanthellae, from coral reefs on Guam, Mariana Island. Mar Biol 140:411–423

131. Lopez-Serrano D, Sanchez-Amat A, Solano F (2002) Cloning and molecular characterization of a SDS activated tyrosinase from *Marinomonas mediterranea*. Pigment Cell Res 15:104–111

132. Lud D, Huiskes AHL, Moerdijk TCW, Rozema J (2001) The effects of altered levels of UV-B radiation on an antarctic grass and lichen. Plant Ecol 154:87–99

133. Marchant HJ, Davidson AT, Kelly GJ (1991) UV-B protecting compounds in the marine alga *Phaeocystis pouchetji* from Antarctica. Mar Biol 109:391–395

134. Matsunaga T, Burgess JG, Yamada N, Komatsu K, Yoshida S, Wachi Y (1993) An ultraviolet (UV-A) absorbing biopterin glucoside from the marine planktonic cyanobacterium *Oscillatoria* sp. Appl Microbiol Biotechnol 39:250–253

135. Mayne ST (1996) β-Carotene, carotenoids and disease prevention in humans. FASEB J 10:690–701

136. McClintock JB, Karentz D (1997) Mycosporine-like amino acids in 38 species of subtidal marine organisms from McMurdo Sound, Antarctica. Antarctic Sci 9:392–398

137. Michalek-Wagner K (2001) Seasonal and sex-specific variations in levels of photo-protecting mycosporine-like amino acids (MAAs) in soft corals. Mar Biol 139:651–660

138. Misonou T, Saitoh J, Oshiba S, Tokitomo Y, Maegawa M, Inoue Y, Hori H, Sakurai T (2003) UV-absorbing substance in the red alga *Porphyra yezoensis* (Bangiales, Rhodophyta) block thymine dimer production. Mar Biotechnol 5:194–200

139. Mittler R, Tel-Or E (1991) Oxidative stress responses in the unicellular cyanobacterium *Synechococcus* PCC 7942. Free Rad Res Commun 12:845–850

140. Moeller RE, Gilroy S, Williamson CE, Grad G (2005) Dietary acquisition of photoprotective compounds (mycosporine-like amino acids, carotenoids) and acclimation to ultraviolet radiation in a freshwater copepod. Limnol Oceanogr 50:427–439

141. Montero O, Lubián LM (2003) Mycosporine-like amino acid (MAAs) production by *Heterocapasa* sp. (Dinophyceae) in indoor cultures. Biomol Engin 20:183–189

142. Morrison JR, Nelson NB (2004) Seasonal cycle of phytoplankton UV-absorption at the bermuda atlantic timeseries study (BATS) site. Limnol Oceanogr 49:215–224

143. Mukherjee P, Fulton DB, Halder M, Han X, Armstrong DW, Petrich JW, Lobban CS (2006) Maristentorin, a novel pigment from the positively phototactic marine ciliate *Maristentor dinoferus*, is structurally related to hypericin and stentorin. J Phys Chem B 110:6359–6364

144. Muller HE (1985) Production of brownish pigment by bacteria of the *Morganella-Proteus-Providencia* group. Zentralblat für Bakteriologie et Hygiene (Abt I Orig A) 260:428–435

145. Nägeli C (1849) Gattungen einzelliger Algen, physiologisch und systematisch bearbeitet, Neue Denkschrift Allg. Schweiz. Natur Ges 10:1–138

146. Nakamura H, Kobayashi J, Hirata Y (1982) Separation of mycosporinelike amino acids in marine organisms using reverse-phase high performance liquid chromatography. J Chromatogr 250:113–118

147. Nakayama R, Tamura Y, Kikuzaki H, Nakatani N (1999) Antioxidant effect of the constituents of susabinori (*Porphyra yezoensis*). JAOCS 76:649–653

148. Newman SJ, Dunlap WC, Nicol S, Ritz D (2000) Antarctic Krill (*Euphausia superba*) acquire UV-absorbing mycosporine-like amino acids from dietary algae. J Exp Mar Biol Ecol 255:93–110

149. Obermüller B, Karsten U, Abele D (2005) Response of oxidative stress parameters and sunscreening compounds in Arctic amphipods during experimental exposure to maximal natural UVB radiation. J Exp Mar Biol Ecol 323:100–117

150. Oliver MJ, Velten J, Wood AJ (2000) Bryophytes as experimental models for the study of environmental stress tolerance: *Tortula ruralis* and desiccation-tolerance in mosses. Plant Ecol 151:73–84

151. Oren A (1997) Mycosporine-like amino acids as osmotic solutes in a community of halophilic cyanobacteria. Geomicrobiol J 14:231–240

152. Oren A, Gunde-Cimerman N (2007) Mycosporines and mycosporine-like amino acids: UV protectants or multipurpose secondary metabolites? FEMS Microbiol Lett 269:1–10

153. Oyamada C, Kaneniwa M, Ebitani K, Murata M, Ishihara K (2008) Mycosporine-like amino acids extracted from Scallop (*Patinopecten yessoensis*) ovaries: UV protection and growth stimulation activities on human cells. Mar Biotech 10:141–150

154. Pavia H, Cervin G, Lindgren A, Åberg P (1997) Effects of UV-B radiation and simulated herbivory on phlorotannins in the brown alga *Ascophyllum nodosum*. Mar Ecol Prog Ser 157:139–146

155. Peinado NK, Díaz RTA, Figueroa FL, Helbling EW (2004) Ammonium and UV radiation stimulate the accumulation of mycosporine-like amino acids in *Porphyra columbina* (Rhodophyta) from Patagonia, Argentina. J Phycol 40:248–259

156. Plack PA, Fraser NW, Grant PT, Middleton C, Mitchell AI, Thomson RH (1981) Gadusol, an enolic derivative of cyclohexane-1, 3-dione present in the roes of cod and other marine fish. Biochemical J 199:741–747

157. Plonka PM, Grabacka M (2006) Melanin synthesis in microorganisms—biotechnological and medical aspects. Acta Biochim Pol 53:429–443

158. Polivka T, Sundström V (2004) Ultrafast dynamics of carotenoid excited states—from solution to natural and artificial systems. Chem Rev 104:2021–2071

159. Portwich A, Garcia-Pichel F (2000) A novel prokaryotic UVB photoreceptor in the cyanobacterium *Chlorogloeopsis* PCC 6912. Photochem Photobiol 71:493–498

160. Portwich A, Garcia-Pichel F (2003) Biosynthetic pathway of mycosporines (mycosporine-like amino acids) in the cyanobacterium *Chlorogloeopsis* sp. strain PCC 6912. Phycologia 42:384–392

161. Post A, Larkum AWD (1993) UV-absorbing pigments, photosynthesis and UV-exposure in Antarctica: comparison of terrestrial and marine algae. Aquat Bot 45:231–243

162. Proteau PJ, Gerwick WH, Garcia-Pichel F, Castenholz R (1993) The structure of scytonemin, an ultraviolet sunscreen pigment from the sheaths of cyanobacteria. Experientia 49:825–829

163. Przeslawski R, Benkendorff K, Davis AR (2005) A quantitative survey of mycosporine-like amino acids (MAAs) in intertidal egg masses from temperate rocky shores. J Chem Ecol 31:2417–2438

164. Rastogi RP, Sinha RP (2009) Biotechnological and industrial significance of cyanobacterial secondary metabolites. Biotechnol Adv 27:521–539

165. Regalado EL, Rodríguez M, Menéndez R, Concepción AA, Nogueiras C, Laguna A, Rodríguez AA, Williams DE, Lorenzo-Luaces P, Valdés O, Hernandez Y (2009) Repair of UVB-damaged skin by the antioxidant sulphated flavone glycoside thalassiolin B isolated from the marine plant *Thalassia testudinum* Banks ex König. Mar Biotechnol 11:74–80

166. Richards TA, Dacks JB, Campbell SA, Blanchard JL, Foster PG, McLeod R, Roberts CW (2006) Evolutionary origins of the eukaryotic shikimate pathway: gene fusions, horizontal gene transfer, and endosymbiotic replacements. Eukaryot Cell 5:1517–1531

167. Richter PR, Sinha RP, Häder D-P (2006) Scytonemin-rich epilithic cyanobacteria survive acetone treatment. Curr Trends Microbiol 2:13–19

168. Riegger L, Robinson D (1997) Photoinduction of UV-absorbing compounds in Antarctic diatoms and *Phaeocystis Antarctica*. Mar Ecol Prog Ser 160:13–25

169. Riemer U, Lamare MD, Peake BM (2007) Temporal concentrations of sunscreen compounds (Mycosporine-like Amino Acids) in phytoplankton and in the New Zealand krill, *Nyctiphanes australis* G.O. Sars. J Plankton Res 29:1077–1086

170. Rothrock M, Garcia-Pichel F (2005) Microbial diversity of benthic mats along a tidal desiccation gradient. Environ Microbiol 7:593–601

171. Salih A, Hoegh-Guldberg O, Cox G (1998) Photoprotection of symbiotic dinoflagellates by fluorescent pigments in reef corals. In: Greenwood JG, Hall NJ (eds) ACRS proceedings—75th anniversary conference, Heron Island, October 1997. School of Marine Science. The University of Queensland, Brisbane, pp 217–230

172. Sanchez-Amat A, Lucas-Elio P, Fernandez E, Garcia-Borron J, Solano F (2001) Molecular cloning and characterization of a unique multipotent polyphenol oxidase from *Marinomonas mediterranea*. Biochim Biophys Acta 1547:104–116

173. Schubert N, García-Mendoza E, Pacheco-Ruiz I (2006) Carotenoid composition of marine red algae. J Phycol 42:1208–1216

174. Shibata K (1969) Pigments and a UV-absorbing substance in coral and a blue-green alga living on the Great barrier reef. Plant Cell Physiol 10:325–335

175. Shick JM (2004) The continuity and intensity of ultraviolet irradiation affect the kinetics of biosynthesis, accumulation, and conversion of mycosporine-like amino acids (MAAs) in the coral *Stylophora pistillata*. Limnol Oceanogr 49:442–458

176. Shick JM, Dunlap WC (2002) Mycosporine-like amino acids and related gadusols: biosynthesis, accumulation, and UV protective function in aquatic organisms. Annu Rev Physiol 64:223–262

177. Shick JM, Dunlap WC, Pearse JS, Pearse VB (2002) Mycosporinelike amino acid content in four species of sea anemones in the genus *Anthopleura* reflects phylogenetic but not environmental or symbiotic relationships. Biol Bull 203:315–330

178. Shick JM, Lesser MP, Dunlap WC, Stochaj WR, Chalker BE, Wu Won J (1995) Depth-dependent responses to solar

ultraviolet radiation and oxidative stress in the zooxanthellate coral *Acropora microphthalma*. Mar Biol 122:41–51

179. Shick JM, Romaine-Lioud S, Ferrier-Pagès C, Gattuso JP (1999) Ultraviolet-B radiation stimulated shikimate pathway dependent accumulation of mycosporine-like amino acids in the coral *Stylophora pistillata* despite decrease in its population of symbiotic dinoflagellates. Limnol Oceanogr 44:1667–1682

180. Sies H, Stahl W (2004) Nutritional protection against skin damage from sunlight. Annu Rev Nutr 24:173–200

181. Singh SP, Häder D-P, Sinha RP (2010) Cyanobacteria and ultraviolet radiation (UVR) stress: mitigation strategies. Ageing Res Rev 9:79–90

182. Singh SP, Klisch M, Sinha RP, Häder D-P (2008) Effects of abiotic stressors on synthesis of the mycosporine-like amino acid shinorine in the cyanobacterium *Anabaena variabilis* PCC 7937. Photochem Photobiol 84:1500–1505

183. Singh SP, Klisch M, Sinha RP, Häder D-P (2010) Genome mining of mycosporine-like amino acid (MAA) synthesizing and non-synthesizing cyanobacteria: a bioinformatics study. Genomics 95:120–128

184. Singh SP, Kumari S, Rastogi RP, Singh KL, Sinha RP (2008) Mycosporine-like amino acids (MAAs): chemical structure, biosynthesis and significance as UV-absorbing/screening compounds. Ind J Exp Biol 46:7–17

185. Singh SP, Sinha RP, Klisch M, Häder D-P (2008) Mycosporine-like amino acids (MAAs) profile of a rice-field cyanobacterium *Anabaena doliolum* as influenced by PAR and UVR. Planta 229:225–233

186. Sinha RP, Ambasht NK, Sinha JP, Klisch M, Häder D-P (2003) UVB-induced synthesis of mycosporine-like amino acids in three strains of *Nodularia* (cyanobacteria). J Photochem Photobiol B Biol 71:51–58

187. Sinha RP, Häder D-P (2002) UV-induced DNA damage and repair: a review. Photochem Photobiol Sci 1:225–236

188. Sinha RP, Häder D-P (2008) UV-protectants in cyanobacteria. Plant Sci 174:278–289

189. Sinha RP, Klisch M, Gröniger A, Häder D-P (2000) Mycosporine-like amino acids in the marine red alga *Gracilaria cornea*—effects of UV and heat. Environ Exp Bot 43:33–43

190. Sinha RP, Klisch M, Helbling EW, Häder D-P (2001) Induction of mycosporine-like amino acids (MAAs) in cyanobacteria by solar ultraviolet-B radiation. J Photochem Photobiol B Biol 60:129–135

191. Sinha RP, Klisch M, Vaishampayan A, Häder D-P (1999) Biochemical and spectroscopic characterization of the cyanobacterium *Lyngbya* sp. inhabiting mango (*Mangifera indica*) trees: presence of an ultraviolet absorbing pigment, scytonemin. Acta Protozool 38:291–298

192. Sinha RP, Kumari S, Rastogi RP (2008) Impacts of ultraviolet-B radiation on cyanobacteria: photoprotection and repair. J Sci Res 52:125–142

193. Sinha RP, Rastogi RP, Ambasht NK, Häder D-P (2008) Life of wetland cyanobacteria under enhancing solar UV-B radiation. Proc Natl Acad Sci India B 78:53–65

194. Sinha RP, Singh SP, Häder D-P (2007) Database on mycosporines and mycosporine-like amino acids (MAAs) in fungi, cyanobacteria, macroalgae, phytoplankton and animals. J Photochem Photobiol B Biol 89:29–35

195. Sinha RP, Sinha JP, Gröniger A, Häder D-P (2002) Polychromatic action spectrum for the induction of a mycosporine-like amino acid in a rice-field cyanobacterium, *Anabaena* sp. J Photochem Photobiol B Biol 66:47–53

196. Smith RC, Prézelin BB, Baker KS, Bidigare RR, Boucher NP, Coley T (1992) Ozone depletion: ultraviolet radiation and phytoplankton biology in Antarctic waters. Science 255:952–959

197. Solomons NW, Bulux J (1994) Plant sources of pro-vitamin A and human nutriture. Nutr Rev 51:199–204

198. Sommaruga R, Whitehead K, Shick JM, Lobban CS (2006) Mycosporine-like amino acids in the zooxanthella-ciliate symbiosis *Maristentor dinoferus*. Protist 157:185–191

199. Sorrels CM, Proteau PJ, Gerwick WH (2009) Organization, evolution, and expression analysis of the biosynthetic gene cluster for scytonemin, a cyanobacterial UV-absorbing pigment. Appl Environ Microbiol 75:4861–4869

200. Soule T, Garcia-Pichel F, Stout V (2009) Gene expression patterns associated with the biosynthesis of the sunscreen scytonemin in *Nostoc punctiforme* ATCC 29133 in response to UVA radiation. J Bacteriol 191:4639–4646

201. Soule T, Palmer K, Gao Q, Potrafka RM, Stout V, Garcia-Pichel F (2009) A comparative genomics approach to understanding the biosynthesis of the sunscreen scytonemin in cyanobacteria. BMC Genomics 10:336–345

202. Soule T, Stout V, Swingley WD, Meeks JC, Garcia-Pichel F (2007) Molecular genetics and genomic analysis of scytonemin biosynthesis in *Nostoc punctiforme* ATCC 29133. J Bacteriol 189:4465–4472

203. Stahl W, Sies H (2007) Carotenoids and flavonoids contribute to nutritional protection against skin damage from sunlight. Mol Biotechnol 37:26–30

204. Starcevic A, Akthar S, Dunlap WC, Shick JM, Hranueli D, Cullum J, Long PF (2008) Enzymes of the shikimic acid pathway encoded in the genome of a basal metazoan, *Nematostella vectensis*, have microbial origins. PNAS 105:2533–2537

205. Stevenson CS, Capper EA, Roshak AK, Marquez B, Eichman C, Jackson JR, Mattern M, Gerwick WH, Jacobs RS, Marshall LA (2002) The identification and characterization of the marine natural product scytonemin as a novel antiproliferative pharmacophore. JPET 303:858–866

206. Stevenson CS, Capper EA, Roshak AK, Marquez B, Grace K, Gerwick WG, Jacobs RS, Marshall LA (2002) Scytonemin, a marine natural product inhibitor of kinases key in hyperproliferative inflammatory diseases. Inflamm Res 51:112–114

207. Stochaj WR, Dunlap WC, Shick JM (1994) Two new UV-absorbing mycosporine-like amino acids from the sea anemone *Anthopleura elegantissima* and the effects of zooxanthellae and spectral irradiance on chemical composition and content. Mar Biol 118:149–156

208. Strickland EH, Horwitz J, Billups C (1970) Near-ultraviolet absorption bands of tryptophan, studies using indole and 3-methylindole as models. Biochemistry 9:4914–4921

209. Suh H-J, Lee H-W, Jung J (2003) Mycosporine glycine protects biological systems against photodynamic damage by quenching singlet oxygen with a high efficiency. Photochem Photobiol 78:109–113

210. Taira H, Aoki S, Yamanoha B, Taguchi S (2004) Daily variation in cellular content of UV-absorbing compounds mycosporine-like amino acids in the marine dinoflagellate *Scrippsiella sweeneyae*. J Photochem Photobiol B Biol 75:145–155

211. Tapiero H, Townsend DM, Tew KD (2004) The role of carotenoids in the prevention of human pathologies. Biomed Pharmacother 58:100–110

212. Teai T, Drollet JH, Bianchini J-P, Cambon A, Martin PMV (1997) Widespread occurrence of mycosporine-like amino acid compounds in scleractinians from French Polynesia. Coral Reefs 16:169–176

213. Torregiani JH, Lesser MP (2007) The effects of short-term exposures to ultraviolet radiation in the Hawaiian Coral *Montipora verrucosa*. J Exp Mar Biol Ecol 340:194–203

214. Torres A, Enk CD, Hochberg M, Srebnik M (2006) Porphyra-334, a potential natural source for UVA protective sunscreens. Photochem Photobiol Sci 5:432–435

215. Tsujino I, Saito T (1961) Studies on the compounds specific for each group of marine algae. Presence of characteristic ultraviolet absorbing material in Rhodophyceae. Bull Fac Fish Hokkaido Univ 12:49–58

216. Usami Y (2009) Recent synthetic studies leading to structural revisions of marine natural products. Mar Drugs 7:314–330

217. Veldhuis MJW, Kraay GW (2004) Phytoplankton in the subtropical Atlantic Ocean: towards a better assessment of biomass and composition. Deep Sea Res I 51:507–530

218. Vernet M, Brody EA, Holm-Hansen O, Mitchell BG (1994) The response of antarctic phytoplankton to ultraviolet radiation: absorption, photosynthesis, and taxonomic composition. In: Weiler CS, Penhale PA (eds) Ultraviolet radiation in Antarctica: measurements and biological effects. Antarct Res Ser, vol 62, p 143

219. Wachi Y, Burgess JG, Iwamoto K, Yamada N, Nakamura N, Matsunaga T (1995) Effect of ultraviolet-A (UV-A) light on growth, photosynthetic activity and production of biopterin glucoside by the marine UV-A resistant cyanobacterium *Oscillatoria* sp. Biochimica et Biophysics Acta 1244:165–168

220. Watson AJ, Liss PS (1998) Marine biological control on climate via the carbon and sulphur geochemical cycles. Philos Trans R Soc Lond 353:41–51

221. Wertz K, Hunziker-Buchwald P, Seifert N, Riss G, Neeb M, Steiner G, Goralczyk R (2005) Beta-carotene interferes with ultraviolet light A-induced gene expression by multiple pathways. J Invest Dermatol 124:428–434

222. Whitehead K, Hedges JI (2002) Analysis of mycosporine-like amino acids in plankton by liquid chromatography electrospray ionization maas spectrometry. Mar Chem 80:27–39

223. Whitehead K, Hedges JI (2005) Photodegradation and photosensitization of mycosporine-like amino acids. J Photochem Photobiol 80:115–121

224. Wu H, Gao K, Wu H (2009) Responses of a marine red tide alga *Skeletonema costatum* (Bacillariophyceae) to long-term UV radiation exposures. J Photochem Photobiol B Biol 94:82–86

225. Wu Won JJ, Chalker BE, Rideout JA (1997) Two new UV-absorbing compounds from *Stylophora pistillata*: sulfate esters of mycosporine-like amino acids. Tetrahedron Lett 38:2525–2526

226. Xiong F, Komenda J, Kopecky J, Nedball L (1997) Strategies of ultraviolet-B protection in microscopic algae. Physiol Plant 100:378–388

227. Yoshiki M, Tsuge K, Tsuruta Y, Yoshimura T, Koganemaru K, Sumi T, Matsui T, Matsumoto K (2009) Production of new antioxidant compound from mycosporine-like amino acid, porphyra-334 by heat treatment. Food Chem 113:1127–1132

228. Young AJ (1991) The photoprotective role of carotenoids in higher plants. Physiol Plantarum 83:702–708

229. Yuan YV (2008) Marine algal constituents. In: Barrow C, Shahidi F (eds) Marine nutraceuticals and functional foods. Taylor and Francis, Boca Raton, pp 259–296

230. Yuan YV, Westcott ND, Hu C, Kitts DD (2009) Mycosporine-like amino acid composition of the edible red alga, *Palmaria palmata* (dulse) harvested from the west and east coasts of Grand Manan Island, New Brunswick. Food Chem 112:321–328

231. Zhang Y, Mu J, Gu X, Zhao C, Wang X, Xie Z (2009) A marine sulfate-reducing bacterium producing multiple antibiotics: biological and chemical investigation. Mar Drugs 7:341–354

232. Zhaohui Z, Xin G, Tashiro Y, Matsukawa S, Ogawa H (2005) The isolation of prophyra-334 from marine algae and its UV-absorption behavior. Chin J Oceanol Limnol 23:400–405

233. Zudaire L, Roy S (2001) Photoprotection and long-term acclimation to UV radiation in the marine diatom *Thalassiosira weissflogii*. J Photochem Photobiol B Biol 62:26–34