REVIEW

Folia Microbiol. **49** (4), 339–352 (2004) **http://www.biomed.cas.cz/mbu/folia/**

Natural Microbial UV Radiation Filters – Mycosporine-like Amino Acids

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Received 11 December 2003
Revised version 11 March 2004

ABSTRACT. Ozone depletion by anthropogenic gases has increased the atmospheric transmission of solar ultraviolet-B radiation (UV-B, 280–315 nm). There is a logical link between the natural defenses of terrestrial and marine organisms against UV radiation and the prevention of UV-induced damage to human skin. UV light degrades organic molecules such as proteins and nucleic acids, giving rise to structural changes that directly affect their biological function. These compounds offer the potential for development of novel UV blockers for human use. The biological role of mycosporine-like amino acids (MAAs) and scytonemin as a defense against solar radiation in organisms, together with their structure, synthesis, distribution, regulation and effectiveness, are reviewed in this article. This review points to the role of MAAs as a natural defense against UV radiation.

Abbreviations

UV-A	ultraviolet-A radiation (315–400 nm)
UV-B	ultraviolet-B radiation (280–315 nm)
UV-C	ultraviolet-C radiation (100–280 nm)
MAA(s)	mycosporine-like amino acid
LC–ESI-MS	liquid chromatography coupled with electrospray ionization mass spectrometry

CONTENTS

1 INTRODUCTION

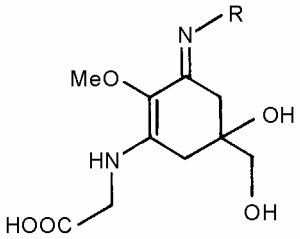
Solar radiation with short wavelength has been shown to reach ecologically significant depths in terrestrial, freshwater, and marine ecosystems. Drastic stratospheric ozone depletion over both the Antarctic and Arctic, as well as moderate decreases in total ozone column over high and mid-latitude waters have recently been reported (Kane 2002; Saraf and Beig 2003; Ha-Duong *et al.* 2003; Jiang *et al.* 2004). Anthropogenically released atmospheric pollutants such as halogenated carbons (usually chloro and/or fluoro derivatives) are responsible for the continued depletion of the stratospheric ozone layer, and consequently an increase in solar UV radiation (UV-B, 280–315 nm, UV-C, 100–280 nm) reaching the Earth's surface (McCulloch 2003; Platt and Honninger 2003). Continuing depletion of the stratospheric ozone layer by atmospheric pollutants, in particular chlorofluorocarbons, has resulted in an increasing incidence of solar UV-B at the Earth's surface (McCulloch 2003; Platt and Honninger 2003).

Although most aquatic as well as terrestrial organisms possess effective protective and repair mechanisms, excessive exposure to solar UV radiation may overload their capabilities. Significant effects of solar UV on aquatic ecosystems may result in decreased biomass productivity. The impact of this decrease would be reflected through all levels of the intricate food web, resulting in reduced food production for hu-

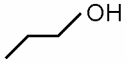
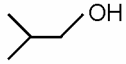
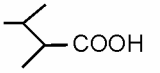
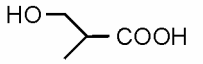
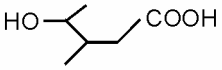
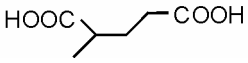
mans (Hader and Worrest 1997; Hader *et al.* 1998), reduced sink capacity for atmospheric carbon dioxide (Takahashi *et al.* 1997), as well as changes in species composition and ecosystem integrity. However, the potential impact of ozone depletion on atmospheric carbon dioxide, mediated through inhibition of marine primary production, is uncertain and a more rigorous and detailed analysis is urgently needed. Reviews on various aspects of UV effect on terrestrial and aquatic ecosystems have been published (Hader and Worrest 1997; Dunlap and Shick 1998).

Wittenburg (1960) was first to report a strong UV-B absorbing agent (λ_{max} 305 nm) in the gas gland of the epipelagic Portuguese man-of-war in 1960, but the isolated substance (λ_{max} 310 nm) was fully characterized only later (Price and Forrest 1969). Soon thereafter, UV-absorbing materials were found to be characteristic of the macrophytic red algae (Tsujino 1961). In 1969 Shibata (1969) discovered the presence of UV-absorbing substances in corals, observing that aqueous extracts of 5 *Acropora* species, 1 *Pocillopora* species, and a cyanobacterium from the Great Barrier Reef contained large quantities of a water-soluble material (named as S-320) having a broad absorbance maximum (λ_{max}) at ≈320 nm. Sivalingam *et al.* (1974) reported similar absorption peaks in 70 species of marine algae representing four phyla. Maragos (1972) demonstrated that the absorbance by S-320 in colonies of *Porities lobata* is inversely proportional to depth, presumably in compensation for the ambient levels of solar UV radiation prevailing in their environment.

MAAs have been identified in taxonomically diverse organisms, including a marine heterotrophic bacterium (Arai *et al.* 1992), cyanobacteria (Garcia-Pichel and Castenholtz 1993; Karsten and Garcia-Pichel 1996), microalgae (Okaichi and Tokumura 1980; Carreto *et al.* 1990; Vernet and Whitehead 1996; Shashar *et al.* 1997), and macroalgae (*for review see* Dunlap and Shick 1998). Within nonsymbiotic marine invertebrates, MAAs have been identified in echinoderms, a mussel, a sea hare, brine shrimp, and in an ascidian (Dunlap and Shick 1998). MAAs are also found in the eyes, skin, and reproductive tissues of tropical and temperate region fishes (Shick and Dunlap 2002). MAAs are common in microalgal–invertebrate symbioses on coral reefs and elsewhere, including: a sponge, scleractinian corals and their eggs and mucus, sea anemones, octocorals, a zoanthid, a scyphozoan jellyfish, a tridacnid clam, and an ascidian (Shick and Dunlap 2002). MAAs are one of nature's sunscreens, with 21 structurally distinct MAAs presently identified in marine and/or terrestrial organisms (*see structures below*).



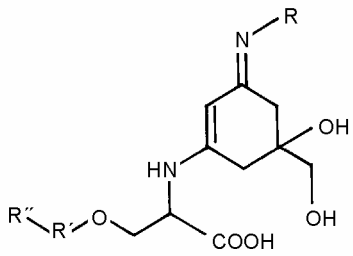
1a–j

	R	Name	λ_{max}, nm
1a	H	palythine	320
1b		usujirene	357
1c		palythene	360
1d		asterina	330
1e		palythiol	332
1f		mycosporine-2Gly	330
1g		mycosporine-Gly:Val	335
1h		shinorine	334
1i		porphyra	334
1j		mycosporine-Glu:Gly	330

2 SEPARATION OF MYCOSPORINE-LIKE AMINO ACIDS

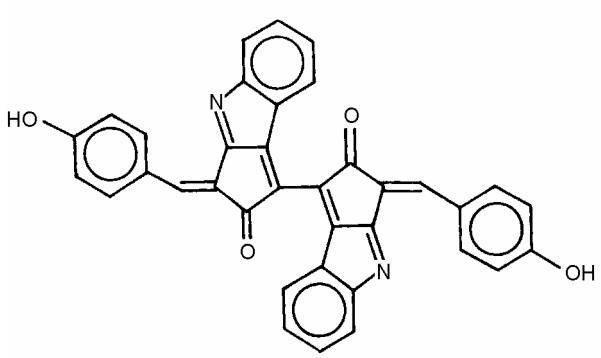
High-performance liquid chromatography (HPLC) is the common method which was used for MAA detection and separation, followed by detection at characteristic UV wavelengths (generally 310 and 340 nm) or obtaining entire UV scans *via* diode array detection (Dunlap *et al.* 1986; Whitehead and Hedges 2002).

A common difficulty has been the lack of commercially available MAA standards, the preparation of which is costly and time consuming. Therefore, much of the characterization of MAA has been accomplished using the distinctive nature of their absorption spectra. In addition, there are instances where closely related compounds share similar absorption maxima and an isocratic HPLC retention time, which further complicates the identification process. Lastly, characterization of unknown UV-absorbing compounds is initially limited to obtaining the retention time and wavelength maxima, without additional information relating to their structural features and classification. Therefore, to better assess the diversity and concentrations of MAA in aquatic environments, we present a mass spectral approach to MAA characterization utilizing liquid chromatography coupled with electrospray ionization mass spectrometry (LC–ESI-MS) (Montero and Lubian 2003). Utilizing this approach it is possible to distinguish essentially all known MAAs based on their individual retention times, wavelength maxima, and molar masses. With a mass spectral approach, the characteristic fragmentation patterns can eventually be utilized to examine MAA structural diversity, even in the absence of well-defined standards (Whitehead and Hedges 2002).



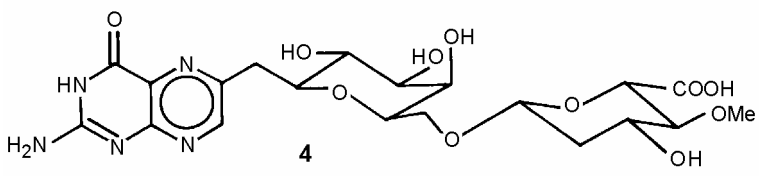
2a–b

	R	R′	R″	Name	λ_{max}, nm
2a	H	H	–	palythine-serine	320
2b	HOOC—CH(O—R′)—R″	Gal, Xyl, GlcU	Gal, Glc, GlcU	E 335	335



3

scytonemin λ_{max} = 386 nm



4

cyanopterin λ_{max} = 345 nm

3 CYANOBACTERIA AND LICHEN PHOTOBIONT SPECIES

Cyanobacteria are a group of prokaryotes that possess a higher plant-type oxygenic photosynthesis. In addition to being a key player in aquatic productivity, several of these organisms are capable of fixing atmospheric nitrogen either as free-living organisms or in symbiosis with many other species including protists, animals and plants (Sinha and Hader 1997). They use nitrogenase to reduce atmospheric nitrogen to ammonium ions, which they make available for aquatic eukaryotic phytoplankton as well as higher plants (Sinha and Hader 1996; Kumar *et al.* 1996). The agricultural potential of cyanobacteria has been recognized as a biological fertilizer for wet soils such as in rice paddies (Banerjee and Hader 1996). Cyanobacteria are cosmopolitan and must possess a high potential of adaptation to diverse environmental factors. UV-B is known to affect processes such as growth, survival, pigmentation, motility, as well as the enzymes of nitrogen metabolism and CO_2 fixation (Donkor and Hader 1996, 1997). Depending on the species, growth and survival decrease within a few hours of UV-B irradiation. Cyanobacteria also fix nitrogen in mid latitude agricultural systems, though not as massively as in paddy rice fields; therefore UV-B effects on these organisms could also be relevant on a global scale (Figs 1 and 2).

Cyanobacteria are conspicuous in many superficial habitats exposed to high solar irradiance, or even shaded habitats that are periodically desiccated. High exposure sites dominated by cyanobacteria include most terrestrial hot spring habitats, intertidal marine flats inundated so infrequently that most eucaryotic competitors and herbivores are absent, and the benthos of shallow hypersaline pools and lagoons. On rocky marine substrates, many cyanobacteria form crusts or small cushions in the high intertidal or supratidal zone. Some oligotrophic lakes with severe nitrogen limitation have benthic turfs dominated by cyanobacteria. Unexpected cyanobacterial dominance also occurs in benthic microbial mats in cold water springs, ponds, and lakes, especially in the Antarctic and Arctic (Nealeet *et al.* 1998). In exposed or shaded terrestrial habitats with periodic or long-term desiccation, cyanobacteria thrive by possessing high desiccation tolerance but presumably also because of a high tolerance to UV radiation imparted mainly by an extracellular sheath pigment, scytonemin, which functions during these periods of metabolic shutdown (*more later*). The terrestrial habitats with conspicuous cyanobacterial mats or crusts include many of the warm and cold deserts of the Earth where the cyanobacteria may form a soil cover. The harder terrestrial substrates, such as cliff faces, are often covered by periodically wetted, dark cyanobacterial crusts referred to as "tintenstriche" (ink streaks). Pure scytonemin (Prouteau *et al.* 1993) was extracted from natural samples of intertidal cyanobacterial mats, dominated by *Lyngbya aestuarii*. Table I summarizes the occurrence of photo-protective compounds in cyanobacteria, from diverse habitats and on various collection dates. In addition to the MAAs and scytonemin, some unknown compounds which absorb in the UV range have also been included in the list.

A new pteridine glycoside, called cyanopterin, was isolated from *Synechocystis* sp. PCC 6803 and its structure was elucidated as 6-[4-*O*-methyl-α-D-glucuronyl-(1→6)-β-D-galactosyloxy]methylpterin. The *in vivo* oxidation state of cyanopterin is primarily the fully reduced 5,6,7,8-tetrahydro form. The cellular function is unknown at present. The findings have established a model system, using *Synechocystis* sp. PCC 6803, for studies of the physiological functions of unconjugated pteridine glycosides found mostly in cyanobacteria (Lee *et al.* 1999).

Nostoc-containing lichens are the dominant primary producers in some landscapes (Galun 1988). The *Nostoc* cyanobiont exists in three genera of lichens: *Nephroma*, *Peltigera* and *Collema* (Rai 1993). Little information is available about the metabolites produced by *Nostoc* lichen – cyanobiont.

4 FUNGUS AND LICHEN MYCOBIONTS

Mycosporines were first discovered in terrestrial fungi (Favre-Bonvin *et al.* 1976) and these metabolites are believed to provide UV protection to fungal spores while exposed to solar radiation during atmospheric dispersal (Young and Patterson 1982). Fungal metabolites strongly absorbing UV-B (λ_{max} 310 nm), first described by Leach (1965) and notionally designated P-310, were present in the mycelia of several genera when sporulation had been induced with near-UV radiation, but were absent from nonsporulating colonies grown in darkness. The first P-310 substance was isolated from *Stereum hirsutum*, and its structure was elucidated (Favre-Bonvin *et al.* 1976) as 2-methoxy-3-bis(hydroxymethyl)methylamino-5-hydroxy-5-hydroxymethyl-2-cyclohexene-1-one (*i.e.*, mycosporine-serinol). An early review (Arpin *et al.* 1979) indicated that mycosporines are widespread among fungi, with the exception of *Agaricales*, but their presumed sporogenic activity was questioned on finding mycosporines only in conidiospores within the mycelium during sexual development. These UV-absorbing metabolites were later postulated to provide protection to fungal spores (*Glomerella cingulata*) exposed to solar radiation during atmospheric dispersal (Young and Patterson 1982).

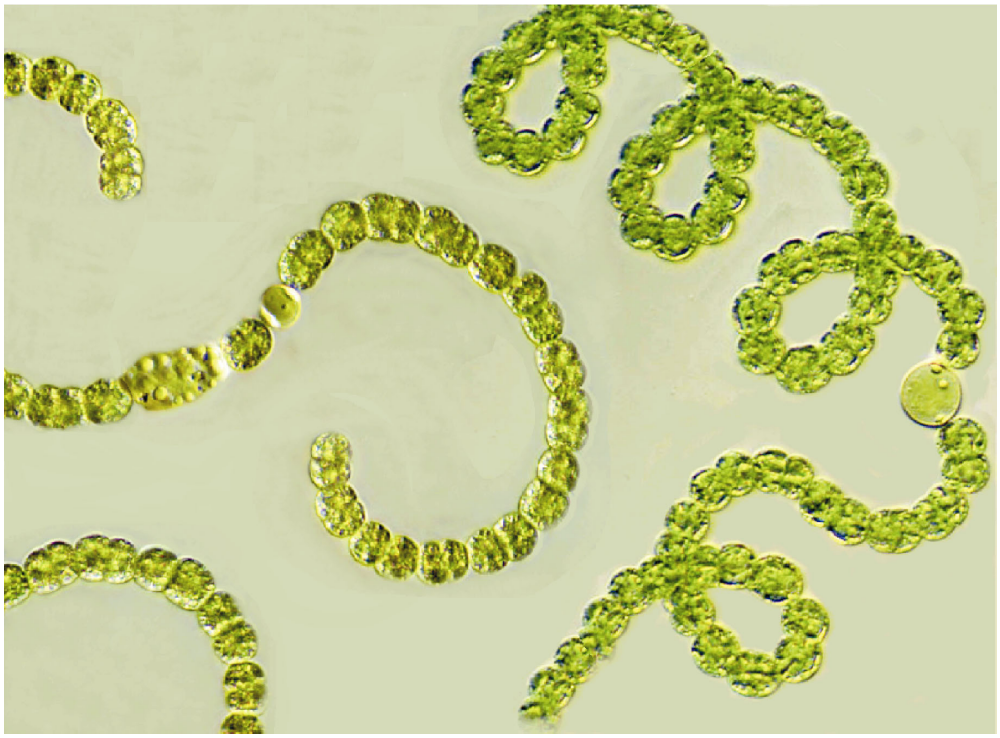


Fig. 1. Cyanobacterium *Anabaena flos-aqua* (*Nostocaceae*, *Anabaenoidea*) producing MAAs. *Anabaena* is one of 4 genera of cyanobacteria capable of producing neurotoxins along with *Oscillatoria*, *Lyngbya* and *Aphanizomenon*. *Anabaena flos-aqua* is a major producer of neurotoxins.

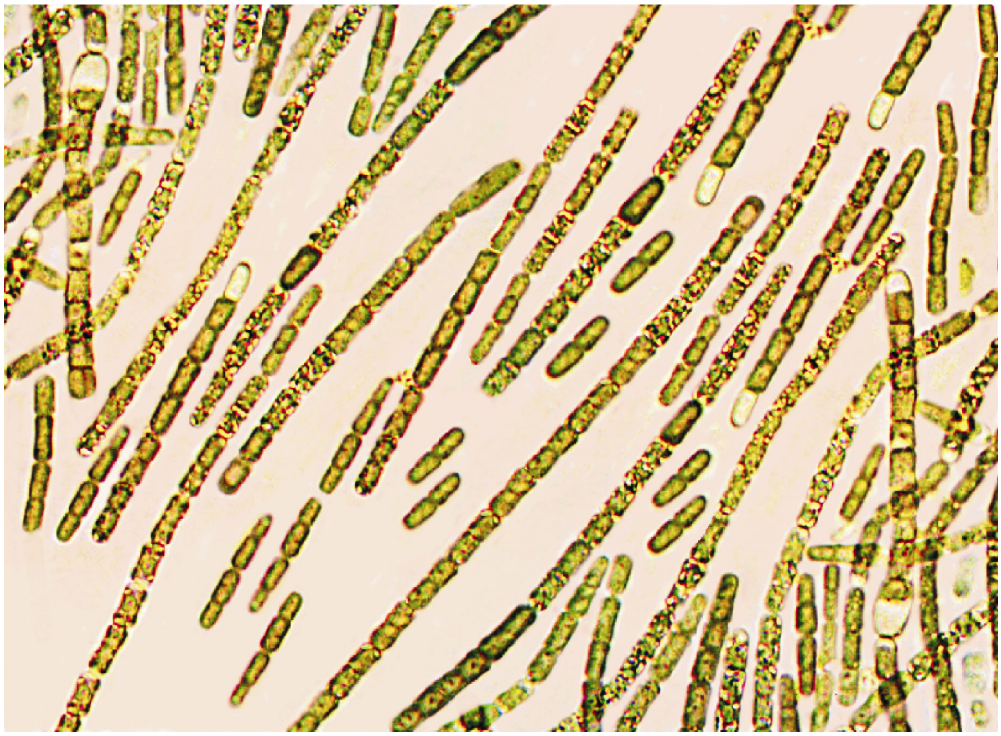


Fig. 2. Cyanobacterium *Calothrix* sp. (*Nostocales*, *Rivulariaceae*) producing MAAs. Dark green cyanobacterium consists of trichomes to 7 μm in diameter and 2.5 μm long, little constricted at cross walls. The trichomes are attenuated at apices, sometimes forming long hyaline hairs. Cells ⅓–½ as long as broad; heterocysts length is variable and up to 12.5 μm. A thick sheath is readily apparent and the trichome gradually tapers to a colorless, pointed apex.

Table I. Distribution of MAA and other photoprotective compounds in cyanobacterial species[a]

Species	Collection site, habitat[b]	Year	ST	MG	PT	AS	PL	PR	SH	PE	UC	Reference
Anabaena sp.	Varanasi (India), rice paddy fields	1993							+			Sinha *et al.* 1999
Aphanocapsa sp.	Schaffhausen (Switzerland), rock desert	1990	+									Garcia-Pichel and Castenholz 1991
Aphanothece halophytica	Eilat, Israel	1994							+	+		Oren 1997
Calothrix sp.	Yellowstone Nat. Park (USA), TE	1988	+	+			+					Gröniger *et al.* 2000
	Antarctica		+									Vincent *et al.* 1993
C. crustacea	Baja California (Mexico), sand flats	1988	+									Garcia-Pichel and Castenholz 1991
C. parietina	Oregon (USA), concrete	1989	+	+			+		+		+	Garcia-Pichel and Castenholz 1993
	Oregon (USA), rock, desert	1989	+									Garcia-Pichel and Castenholz 1991
Chlorogloeopsis sp.	Oregon (USA), concrete	1989	+				+				+	Garcia-Pichel *et al.* 1992
Chlorogloeopsis sp. PCC 6912	Arizona (USA), University	2002		+					+			Portwich and Garcia-Pichel 2000
Chlorogloeopsis sp.	Schaffhausen (Switzerland), rock, desert	1990	+									Garcia-Pichel and Castenholz 1991
Chroococcus sp.	Catalonia (Spain), lime stone	1990	+									*ditto*
Chroococcidiopsis sp.	Baja California (USA), rock, desert	1988	+									*ditto*
Chrysocapsa sp.	concrete										+	Turian 1985
Diplocolon sp.	Baja California (Mexico), granite	1988	+	+								Garcia-Pichel and Castenholz 1991
Entophysalis granulosa	Baja California (Mexico), rock, desert	1988	+									*ditto*
Euhalothleve sp.	Dead Sea, Gypssum Crust	2000		+								Kedar *et al.* 2002
Gloeocapsa sp.	Antarctica, freshwater habitat		+									Garcia-Pichel and Castenholz 1991
	Bermuda (USA), rock, desert	1982	+								+	Garcia-Pichel and Castenholz 1993
	Central Alps, Austria, freshwater habitat	1996	+	+	+	+			+		+	Sommaruga and Garcia-Pichel 1999
	Catalonia (Spain), lime stone	1990	+	+								Garcia-Pichel *et al.* 1993
	Hawaii (USA), tree bark					+					+	Garcia-Pichel and Castenholz 1993
Haplosiphon sp.	Hawaii (USA), tree bark	1990	+									*ditto*
Lyngbya sp.	Varanasi (India), tree bark	1997	+									Sinha *et al.* 1999
	Huahine (France)	1992	+									Proteau *et al.* 1993
	Bermuda (USA), rock	1982	+									Garcia-Pichel and Castenholz 1991
L. aestuarii	Massachusetts (USA), sand flats	1983, 1987	+			+						Sinha *et al.* 1999
	Baja California (Mexico), sand flats	1988	+									Proteau *et al.* 1993
	Shark Bay (Australia)	1996	+									Garcia-Pichel and Castenholz 1991
	Sydney (Australia), sand flats	1995–1996	+									*ditto*
Microcoleus chthonoplastes	Sydney (Australia), sand flats	1995–1996							+		+	Karsten and Garcia-Pichel 1996
	Dichato Marine Station (Chile), HPM	1994							+		+	*ditto*
	Guerrero Negro (Mexico), HPM	1993							+		+	*ditto*
	Rachel Carson Estuarine, Reserve USA, HPM	1993							+		+	*ditto*
	Sippewisset Salt Marsh (USA), HPM	1993							+		+	*ditto*
	Sinai Peninsula (Egypt), HPM	1993							+		+	*ditto*
	North Sea (Germany), HPM	1993							+		+	*ditto*

	Sydney (Australia), HPM	1993				+	+	*ditto*
	Baltic Sea (Germany), HPM	1994				+	+	*ditto*
M. paludosus	*University of Cambridge* (UK), soil material	1950				+		Karsten and Garcia-Pichel 1996
Nostoc sp.	Java (Indonesia), soil material	1992					+	de Chazal and Smith 1994
N. commune	Antarctica, freshwater habitat	1990	+					Garcia-Pichel and Castenholz 1991
	Hunan (China), soil material	1990	+					Ehling-Schulz *et al.* 1997
	Ningshia, Wuhan (China), soil material		+			+		Scherer *et al.* 1988
	South Germany, soil material	1992	+			+		Bohm *et al.* 1995
	Antarctica, freshwater habitat		+					Vincent *et al.* 1993
N. microscopicum	Antarctica, freshwater habitat	1990	+					Garcia-Pichel and Castenholz 1991
	Yellowstone National Park (USA), TE	1989	+					*ditto*
N. parmelioides	Oregon (USA), rock	1988	+					*ditto*
N. pruniforme	Oregon (USA), cold spring	1988	+					*ditto*
N. spongiaeforme	Varanasi (India), rice paddy fields						+	Kumar *et al.* 1996
Nodularia baltica					+	+		Sinha *et al.* 2003
N. harveyana					+	+		*ditto*
N. spumigena					+	+		*ditto*
Oscillatoria priestleyi	Antarctica, freshwater habitat						+	Vincent *et al.* 1993
Pleurocapsa sp.	Antarctica, freshwater habitat		+					Garcia-Pichel and Castenholz 1991
	Oregon (USA), concrete	1989	+					*ditto*
Rivularia sp.	Oregon (USA), rock	1989	+					*ditto*
	Yellowstone Nat. Park (USA), TE	1989	+					*ditto*
	Yorkshire (UK), soil material	1950	+					*ditto*
R. atra	Oregon (USA), rock	1989	+					Pentecost 1993
Schizothrix sp.	Oregon (USA), HPM	1989	+					Garcia-Pichel and Castenholz 1991
Scytonema sp.	Texas (USA) and collection		+	+			+	Garcia-Pichel and Castenholz 1991
	Arctic (Canada), collection		+					Garcia-Pichel and Castenholz 1993
	Majuro Atoll, Marshall Islands, soil material		+					Quesada *et al.* 1999
	Curacao (Netherlands)	1991	+					Proteau *et al.* 1993
	Hawaii (USA), rock	1989	+					Garcia-Pichel and Castenholz 1991
	Varanasi (India), rice paddy fields	1993	+			+		Gröniger *et al.* 2000
S. hofmanii	Varanasi (India), rice paddy fields	1993	+	+				Kumar *et al.* 1996
S. javanicum	Bermuda (USA), wall	1989	+					Garcia-Pichel and Castenholz 1991
S. myochrous	Yorkshire (UK), soil material		+					Pentecost *et al.* 1993
Stigonema sp.	Oregon (USA), decaying plant matter	1989	+					Garcia-Pichel and Castenholz 1991
	Oregon (USA), herbarium	1978	+					*ditto*
Synechococcus sp.	Oregon (USA), concrete		+	+				Garcia-Pichel and Castenholz 1993
Tolypothrix sp.	Yellowstone Nat. Park (USA), TE	1989	+					Garcia-Pichel and Castenholz 1991
T. byssoidea	Konark (India), rock		+					Adhikary *et al.* 1998

continued

T. distorta	Konark (India), collection		+			Garcia-Pichel and Castenholz 1991
T. rupestris	Konark (India), collection	1978	+			*ditto*

[a]AS – asterina-330 MG – mycosporine-glycine PE – palythene PL – palythinol PR – porphyra-334 PT – palythine
SH – shinorine ST – scytonemin UC – unknown compounds
[b]HPM – hypersaline pond/marine TE – thermal environment

Although this contention is arguable (Bandaranayake 1998), an evolutionary divide appears between the parent class of mycosporines expressed by fungi exclusively as oxo-carbonyl chromophores (absorbing UV-B) and MAAs in aquatic organisms and terrestrial cyanobacteria containing mainly imino-carbonyl constituents (absorbing UV-B and principally the short wavelengths of UV-A).

The occurrence of UV-absorbing substances like scytonemin and mycosporine-glycine have been reported by Büdel *et al.* (1997) for cyanobacterial lichens of the genera *Collema*, *Gonohymenia* and *Peltula*, all coming from high-light intensity habitats. Except for *Collema* with the filamentous *Nostoc*, all other cyanobionts belong to the unicellular genera *Chroococcidiopsis*, *Cyanosarcina*, *Gloeocapsa* or *Myxosarcina*. The pigmentation (scytonemin) is located extracellularly in the sheath of the outer thallus parts. Fluorescence microscopy and microprobe measurements clearly show UV radiation into the lichen thallus and hence the relevance of UV sunscreens for the protection of the organism (Büdel *et al.* 1997).

Recently, it was found that rock-inhabiting fungi also produce considerable amounts of mycosporine-glutaminol-glucoside absorbing in the UV range with wavelength maxima centered around 310 nm (Gorbushina *et al.* 2003). Mycosporines were initially described as differentiation or reproduction markers in fungal spores (Gorbushina *et al.* 2003) and mycelia of *Morchella esculenta* (Buscot and Bernillon 1991) but presently multiple cellular functions, such as osmoprotective (Oren 1997) and antioxidant (Dunlap and Yamamoto 1995) roles, are ascribed to these substances (Bandaranayake 1998). As mycosporines are biotechnologically promising both as UV-screening compounds and antioxidants, it was decided to isolate and characterize the mycosporines from rock-inhabiting fungi.

Microcolonial ascomycetes are known to inhabit bare rock surfaces in cold and hot deserts and thus are habitually exposed to high levels of solar radiation. Several of these stress-tolerant fungal isolates, cultivated in the laboratory under daylight illumination, were studied for the presence of effective UV radiation protection substances. Liquid chromatography–mass spectrometry and liquid chromatography–tandem mass spectrometry analyses allowed for efficient separation and structure clarification of two mycosporines. It was demonstrated that both mycosporine-glutamicol-glucoside and mycosporine-glutaminol-glucoside are natural and constitutive secondary metabolites of microcolonial fungi (Volkmann *et al.* 2003).

A novel photo-protective, mycosporine, named collemin A, was isolated from the lichenized ascomycete *Collema cristatum*. The mycobiont was cultivated and biological activity was measured in terms of protection against UV-B induced membrane destruction and pyrimidine dimer formation in cultured human keratinocytes, and prevention of UV-B-induced erythema. The pure isolated compound was found to prevent UV-B-induced cell destruction in a dose-dependent manner, it partially prevented pyrimidine dimer formation, and completely prevented UV-B-induced erythema when applied to the skin prior to irradiation (Enk *et al.* 2002; Torres *et al.* 2004).

5 MICROALGAE

Considerable recent work, covering a wide range of aquatic ecosystems, has contributed to an increased consensus that environmental UV-B, independent of ozone-related increases, is an important ecological stress that influences the growth, survival and distributions of phytoplankton. On a global scale, phytoplankton is the most important biomass producer in aquatic ecosystems (Rozema *et al.* 2002). The organisms populate the top layers of the oceans and freshwater habitats where they receive sufficient solar radiation for photosynthetic processes. This zone, phytoplankton, is simultaneously exposed to solar UV radiation, in addition to longer-wavelength radiation (Figs 3 and 4).

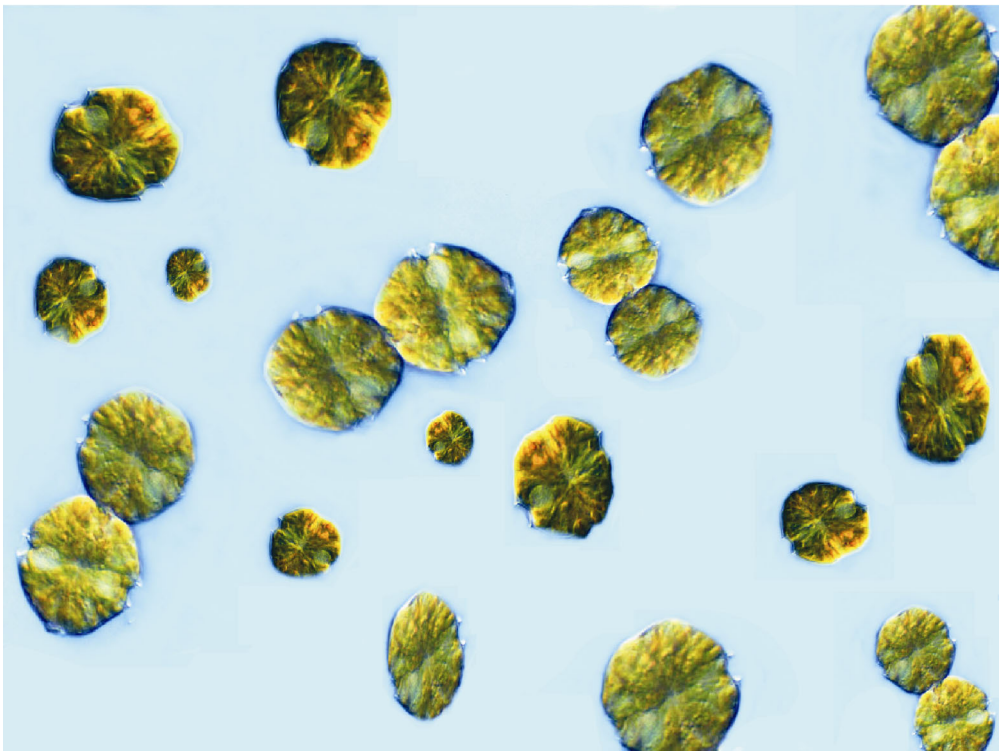


Fig. 3. Marine microalga *Alexandrium* sp. producing toxins and different MAAs. These organisms are called "armored" dinoflagellates because the cell is covered by 'thecal' plates. These plates are used to distinguish one *Alexandrium* species from another.

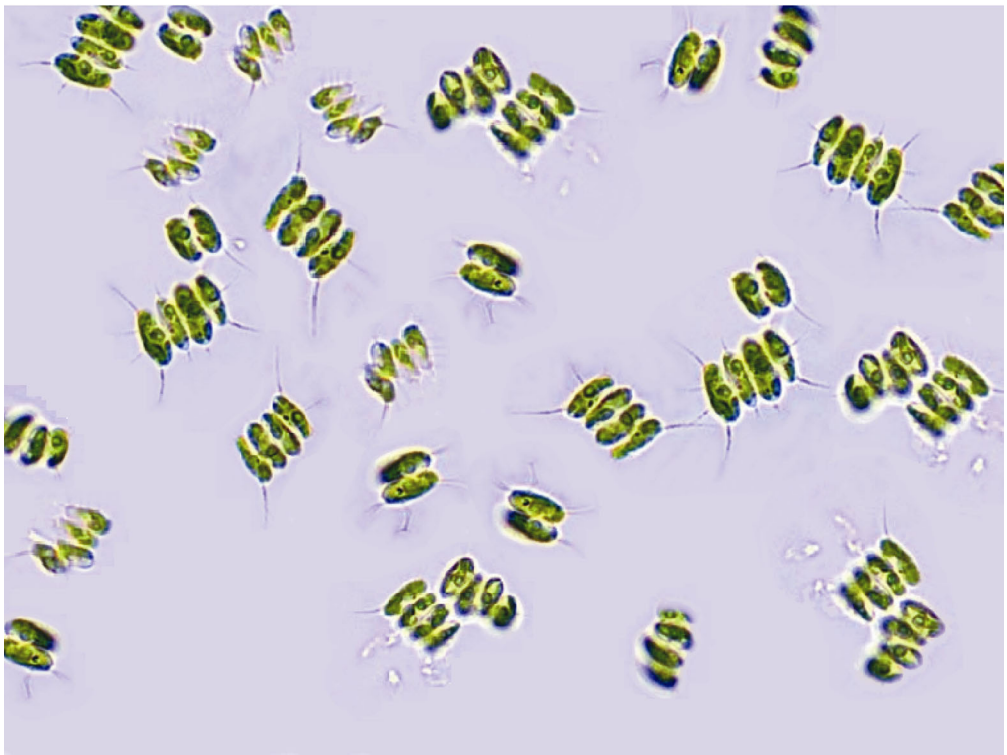


Fig. 4. Freshwater green microalga *Scenedesmus* sp. (*Chlorococcales*, *Scenedesmaceae*) producing MAAs. Colonies of cells were attached side by side, arranged linearly or zig-zag; cell body is elliptical or spindle or crescent in shape; terminal cells have spiny projections in many species; cell wall is usually smooth, but in some species granulated or dented or ridged. *Scenedesmus* sp. is a non-motile colonial alga consisting of 2, 4 or 8 elongated cells, often with long spines on the terminal cells as in the specimens shown. They are very common in ponds and as planktonic forms in rivers and lakes.

Table II. Distribution of MAA and other photoprotective compounds in freshwater and marine microalgae[a]

Species	Collection site	Habitat[b]	MG	PT	AS	PL	PR	SH	PE	UC	Reference
Alexandrium excavatum	Buenos Aires (Brasilia), culture collection	M	+	+		+	+	+	+	+	Carreto *et al.* 1990
Amphidinium carterae	Brixham Harbour (UK), culture collection	M	+								Hannach and Sigleo 1998
Ankistrodesmus spiralis	Copenhagen (Denmark), culture collection	F			+			+			Xiong *et al.* 1999
Chaetoceros sp.	Weddell Sea (Antarctica), culture collection	M			+			+			Riegger and Robinson 1997
Chlorella minutissima	New Zealand, culture collection (Třeboň, Czechia)	F			+			+			Xiong *et al.* 1997, 1999
C. sorokiniana	Piešťany (Slovakia), thermal spring, culture collection	F		+			+	+		+	*ditto*
Corethron criophilum	Antarctica	M					+	+	+	+	Helbling *et al.* 1996
Cosinodiscus centralis	Weddell Sea (Antarctica), culture collection	M					+	+			Riegger and Robinson 1997
Dunaliella tertiolecta	Puget Sound, Washington (USA), culture collection	M					+	+			Hannach and Sigleo 1998
Fragilariopsis cylindrus	Antarctica	M					+	+		+	Hannach and Sigleo 1998
	Weddell Sea (Antarctica), culture collection	M					+	+			Helbling *et al.* 1996
Gyrodinium dorsum	Germany, culture collection	M		+	+		+	+		+	Gröniger *et al.* 2000
Heterocapsa triquetra	*Lund University* (Sweden), culture collection	M								+	Wangberg *et al.* 1997
Isochrysis sp.	*University of Washington*, Seattle (USA), culture collection	M	+								Hannach and Sigleo 1998
Lingulodinium polyedra	culture collection	M		+		+	+		+	+	Vernet and Whitehead 1996
Pavlova gyrans	*University of Washington*, Seattle (USA), culture collection	M	+							+	Hannach and Sigleo 1998
Phaeocystis pouchetii	Prydz Bay (Antarctica), culture collection	M								+	Marchant 1991
P. antarctica	Weddell Sea (Antarctica), culture collection	M								+	Riegger and Robinson 1997
Porosira glacialis	Weddell Sea (Antarctica), culture collection	M					+	+			*ditto*
P. pseudodenticulata	Weddell Sea (Antarctica), culture collection	M					+	+			*ditto*
Probiscia inemis	Weddell Sea, Antarctica, culture collection	M					+	+			*ditto*
Prorocentrum micans	*Provasoli-Guillard National Center for Culture of Marine Phytoplankton* (USA)		+		+		+	+			Lesser 1996
P. minimum	Lisboa (Portugal), culture collection	M		+				+			Sinha *et al.* 1998
Pseudonitschia sp.	Antarctica	M					+				Helbling *et al.* 1996
Pyramimonas parkeae	Santa Catalina Island, California (USA), culture collection	M	+								Hannach and Sigleo 1998
Scenedesmus sp.	*Institute of Botany*, Třeboň (Czechia), culture collection	F		+	+		+	+		+	Xiong *et al.* 1997, 1999
Stellarima microtrias	Weddell Sea (Antarctica), culture collection	M					+	+			Riegger and Robinson 1997
Thalassiosira antarctica	Weddell Sea (Antarctica), culture collection	M					+	+			*ditto*
Thalassiosira sp.	Antarctica	M					+	+			Helbling *et al.* 1996
T. tumida	Weddell Sea (Antarctica), culture collection	M					+	+			Riegger and Robinson 1997
T. weissflogii	Long Island, New York (USA), culture collection	M	+				+	+			Hannach and Sigleo 1998

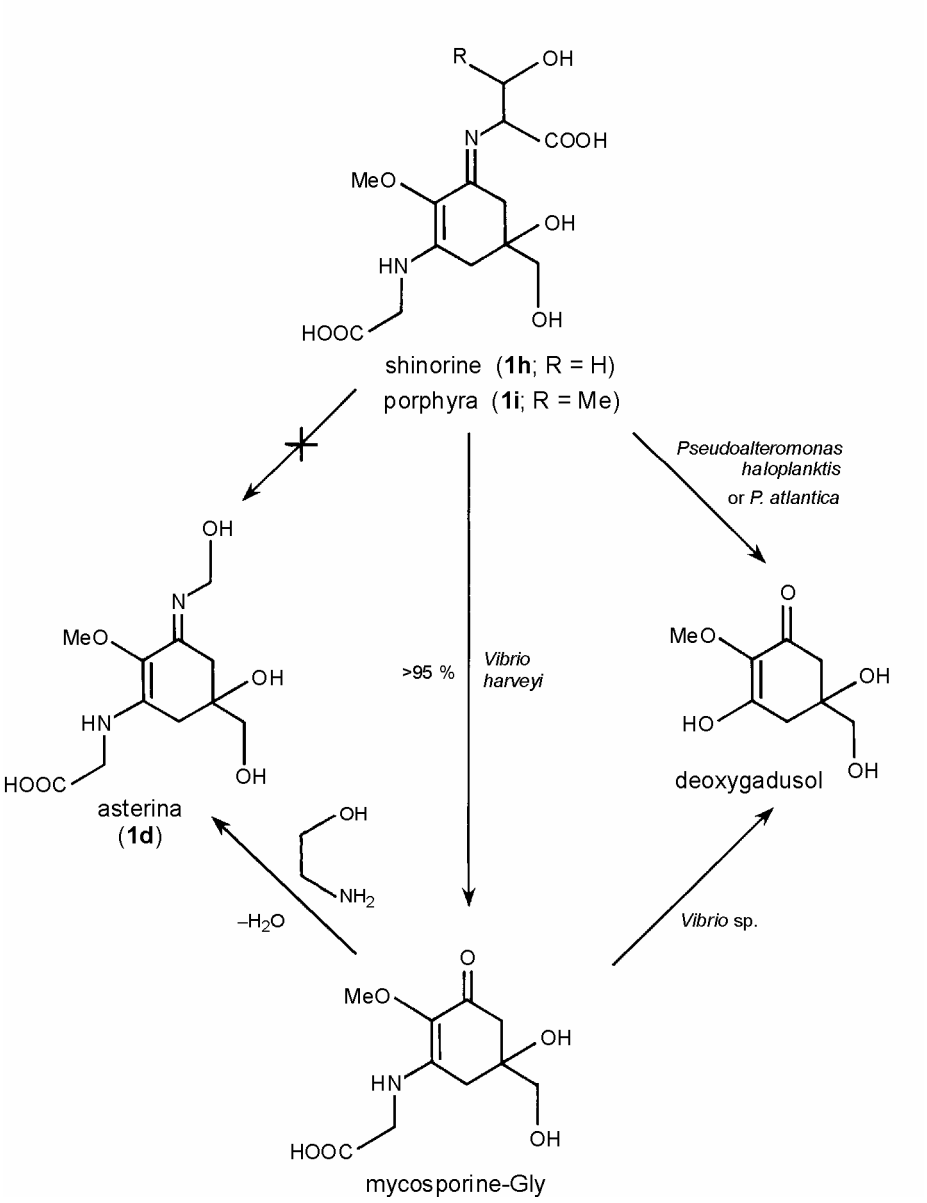
[a]AS – asterina-330 MG – mycosporine-glycine PE – palythene PL – palythinol PR – porphyra-334 PT – palythine
SH – shinorine UC – unknown compounds
[b]M – marine F – freshwater

Information required to quantitatively estimate ozone-related UV-B damage to phytoplankton include:

– the spectral characteristics of solar radiation penetrating to depth and its space-time variability;
– a biological weighting function of the biological effect;
– an exposure–response curve;
– a quantitative model of phytoplankton inhibition by UV-B;
– an assessment of how vertical mixing influences variable irradiance exposures of phytoplankton and its physiological response (Vernet and Smith 1997).

Table II summarizes the occurrence of MAAs and/or photoprotective compounds in microalgae, from diverse habitats and on various collection sites.

Although sometimes listed as sources of MAAs (Karentz 2001; Roy 2000), marine bacteria have not been systematically examined for their ability to synthesize these compounds. Only one bacterium, *Micrococcus* sp., is reported to contain an MAA, shinorine (Arai *et al.* 1992), although several species in the genera *Pseudoalteromonas* and *Vibrio* can convert the algal MAAs shinorine and porphyra in the medium to mycosporine-glycine or to the related 4-deoxygadusol (Dunlap *et al.* 1998; Scheme 1).



Scheme 1. Conversion of shinorine (**1h**) and porphyra (**1i**) to asterina (**1d**) in tropical holothuroids, and biosynthetic conversion to the strong antioxidant, 4-deoxygadusol (proposed).

6 CONCLUSION

Many marine species are rich in imino-MAAs. A prior study (Masaki *et al.*, in press) has shown that the marine bacterium *Vibrio harveyi* efficiently converts algal MAAs, shinorine and porphyra, to mycosporine-glycine in the enteric process of MAA absorption in deposit-feeding holothurians leading to the trophic accumulation of asterina (Shick *et al.* 1992). The occurrence and physiological importance of MAAs are becoming standard parts of studies of the effects of UV radiation on aquatic as well as terrestrial organisms. Most involve environmental correlations between levels of UV radiation and MAA, particularly in the light of stratospheric ozone depletion, and more intensive and extensive sampling may discern a match between the UV absorption maxima of diverse MAA and the UV spectral irradiance in the habitats where they occur. Molecular studies of UV signal-transduction eliciting biosynthesis of MAAs can be expected, particularly as researchers studying cyanobacteria, micro-algae, and invertebrates extend their collaborations to include workers on higher plants, where UV-signaling is of intense interest. The possibility that MAAs themselves serve as chemical messengers or otherwise regulate physiological function will be examined further. Structures, UV-absorbing, and redox properties of unidentified MAAs will be elucidated, particularly in cyanobacteria, perhaps in the context of their protecting biological nitrogen fixation from UV radiation. The study of symbiotic associations will continue to broaden the professional horizons of algal, bacterial, and fungal physiologists alike.

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