

## Mycosporine-like amino acids (MAAs): Chemical structure, biosynthesis and significance as UV-absorbing/screening compounds

Shailendra P Singh, Sunita Kumari, Rajesh P Rastogi, Kanchan L Singh & Rajeshwar P Sinha\*

Centre of Advanced Study in Botany, Banaras Hindu University, Varanasi 221 005, India

Continuous depletion of the stratospheric ozone layer has resulted in an increase in ultraviolet-B (UV-B; 280-315 nm) radiation on the earth's surface which inhibits photochemical and photobiological processes. However, certain photosynthetic organisms have evolved mechanisms to counteract the toxicity of ultraviolet or high photosynthetically active radiation by synthesizing the UV-absorbing/screening compounds, such as mycosporine-like amino acids (MAAs) and scytonemin besides the repair of UV-induced damage of DNA and accumulation of carotenoids and detoxifying enzymes or radical quenchers and antioxidants. Chemical structure of various MAAs, their possible biochemical routes of synthesis and role as photoprotective compounds in various organisms are discussed.

**Keywords:** Cyanobacteria, Macroalgae, Mycosporine-like amino acids (MAAs), Phytoplankton, UV radiation

Absorption of solar energy to drive photosynthesis exposes photosynthetic organisms to potentially damaging ultraviolet (UV) radiation in their natural habitats. Continued depletion of stratospheric ozone layer due to atmospheric pollutants such as chlorofluorocarbons (CFCs), chlorocarbons (CCs) and organobromides (OBs) has resulted in an increase in ultraviolet-B (UV-B; 280-315 nm) radiation on earth's surface<sup>1-4</sup>. Ozone depletion has been reported both in Antarctic and Arctic regions, declining by more than 70% during late winter and early spring due to a phenomenon known as polar vortex<sup>5,6</sup>. Harmful doses of UV-B radiation penetrate deep into a water column influencing the photosynthetic denizens<sup>7</sup>. The optical properties of water determine the extent of penetration. Depth of 20 m in oceanic water and only a few centimeters in brown humic lakes and river affords 90% protection against UV-B irradiation<sup>8</sup>. UV-B is the most effective radiation causing cell damage by directly meddling with the DNA and proteins and indirectly *via* producing reactive oxygen species<sup>9-11</sup>. The survival, growth, pigmentation, photosynthetic oxygen production, motility, N<sub>2</sub> metabolism, phycobiliprotein composition and <sup>14</sup>CO<sub>2</sub> uptake are the main physiological and biochemical processes affected by UV-B radiation<sup>7,12-17</sup>.

A number of photosynthetic organisms which are simultaneously exposed to visible and UV radiation have evolved mechanisms to circumvent the damaging effects of UV radiation. These mechanisms include light driven repair of UV-induced damage of DNA<sup>18,19</sup>, spore germination and reproduction<sup>20</sup>, accumulation of carotenoids, detoxifying enzymes, radical quenchers and antioxidants<sup>21,22</sup>, and synthesis of UV-absorbing or screening compounds<sup>23,24</sup>. Among UV-absorbing/screening compounds mycosporine-like amino acids (MAAs) have received much attention for their putative role in UV photoprotection, which were originally identified in fungi as having role in UV-induced sporulation<sup>25</sup>. The following text reviews the available information on the structure, biosynthesis and evolution of MAAs and their photoprotective role in various organisms.

### Structure and biosynthesis of MAAs

The MAAs, found in various organisms from tropical to polar regions<sup>23,26,27</sup>, are small (<400 Da), colorless, water-soluble compounds composed of cyclohexenone or cyclohexenimine chromophore conjugated with the nitrogen substituent of an amino acids or its imino alcohol<sup>24</sup>.

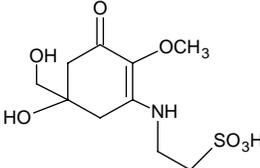
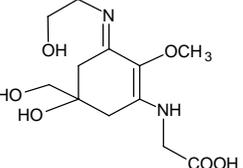
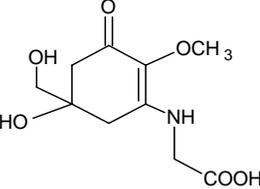
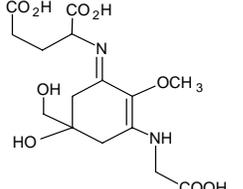
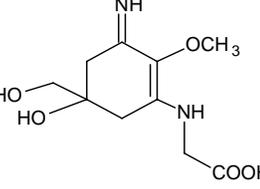
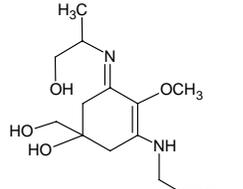
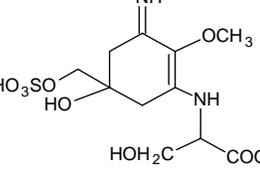
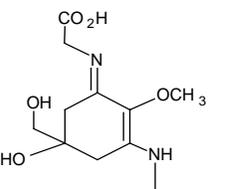
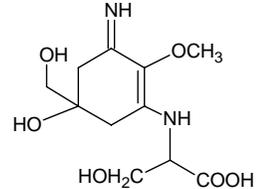
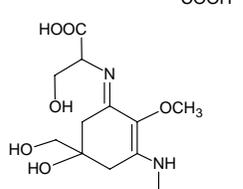
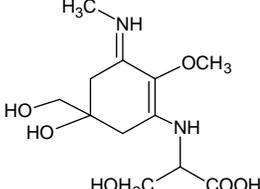
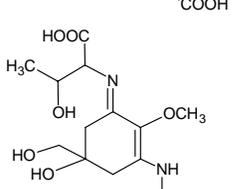
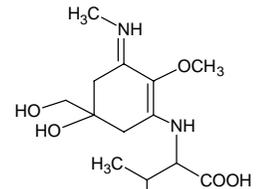
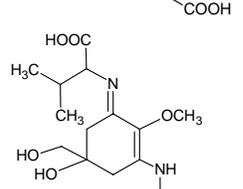
There are more than 20 different MAAs found in various organism some of which are shown in Table 1. Generally, the ring system contains a glycine subunit at third carbon atom. Some MAAs also contain sulfate esters or glycosidic linkages through the imine substituents<sup>28</sup>. Difference in the absorption

\*Correspondent author

Phone: +91 542 2307147; Fax: + 91 542 2368174

E-mail: r.p.sinha@gmx.net

Table 1—MAAs with their corresponding absorption maxima and molecular structure

Mycosporine-like amino acids	$\lambda_{\max}$ (nm)	Molecular structure	Mycosporine-like amino acids	$\lambda_{\max}$ (nm)	Molecular structure
Mycosporine-aurine	309		Asterina-330	330	
Mycosporine-glycine	310		Mycosporine-glutamic acid-glycine	330	
Palythine	320		Palythanol	332	
Palythine-serine-sulfate	320		Mycosporine-2-glycine	334	
Palythine-serine	320		Shinorine	334	
Mycosporine-methylamine-serine	327		Porphyra-334	334	
Mycosporine-methylamine-threonine	327		Mycosporine-glycine-valine	335	

Contd.

Table 1—MAAs with their corresponding absorption maxima and molecular structure—*Contd*

Mycosporine-like amino acids	$\lambda_{\max}$ (nm)	Molecular structure
Palythenic acid	337	
Usujirene	357	
Palythene	360	
Euhalothece-362	362	

spectra of MAAs is due to the variations in the attached side groups and nitrogen substituents. The most common methods for MAA detection and quantification are high-performance liquid chromatography (HPLC) based on their retention times and absorption maxima and obtaining entire UV scans *via* diode array detection (DAD)<sup>24,29,30</sup>. The electrospray ionization mass spectrometry coupled with liquid chromatography (LC/MS) has also been used to analyze the MAAs in aquatic environment<sup>31,32</sup>. Recently Torres *et al.*<sup>33</sup> have reported the structure and molecular formula of Porphyra-334 by the application of MS in conjunction with <sup>1</sup>H and <sup>13</sup>C NMR data. A number of MAAs are still to be chemically characterized and an exhaustive survey of organisms may reveal enormous diversity of these compounds.

The biosynthesis of MAAs is presumed to be occurring *via* the first part of shikimate pathway (Fig. 1), but concluding evidences are lacking to a great extent. It has been found that 3-dehydroquinate,

which is formed during shikimate pathway, acts as a precursor for the synthesis of fungal mycosporines and MAAs *via* gadusols<sup>26,34</sup>. This view is supported by the inhibition of MAAs synthesis in *Stylophora pistillata* by the application of glyphosate which is a specific shikimate pathway inhibitor<sup>35</sup>. The primary MAA mycosporine-glycine thus synthesized by shikimate pathway is then transformed through chemical and/or biochemical conversions into secondary MAAs<sup>36-38</sup> (Fig. 1). The synthesis of MAAs occurs in bacteria, cyanobacteria, phytoplankton and macroalgae but not in animals, because they lack the shikimate pathway.

### Role of MAAs in photoprotection

The strong UV absorption maxima between 310-362 nm, high molar extinction coefficient ( $\epsilon = 28,100-50,000$ ) and photostability in distilled and sea water in presence of photosensitizers<sup>39</sup>, support the contention that MAAs have a photoprotective role<sup>40,41</sup>. These compounds are capable of effectively dissipating absorbed radiation without producing reactive oxygen species<sup>42</sup>. As these compounds provide photoprotection in organisms having shikimate pathway, certain marine animals such as arthropods, rotifers, molluscs, fish, cnidarians, tunicates, eubacteriobionts, poriferans, nemertineans, echinodermites, platyhelminthes, polychaetes, bryozoans and protozoans have also been reported to protect themselves from UV radiation by MAAs. However, studies have shown that in these shikimate pathway lacking animals these compounds are derived from their algal diet<sup>43,44</sup>. Thus, MAAs provide protection from UV radiation not only in their producers but also to primary and secondary consumers<sup>45</sup>. MAAs have also been shown to be highly resistant against abiotic stressors such as temperature, UV radiation, various solvents and pH<sup>46,47</sup>.

### MAAs in cyanobacteria

Cyanobacteria have a cosmopolitan distribution in both aquatic and terrestrial ecosystems ranging from hot springs to the Antarctic and Arctic regions. The prominent role of N<sub>2</sub>-fixing cyanobacteria in improving the soil fertility is well documented<sup>48</sup>. They are also significant constituents of marine ecosystems and account for a high percentage of oceanic primary productivity. Palaeobotanical studies reveal their appearance to the Precambrian era and the presence of



UV-absorbing compounds like MAAs presumably may have supported their existence at that time when there was no stratospheric ozone layer. The accumulation of large amount of MAAs in cyanobacteria was first reported in 1969 by Shibata<sup>49</sup>.

MAA-producing cyanobacteria are abundant in hyper saline environments. Garcia-Pichel *et al.*<sup>50</sup> examined the morphology, physiology and 16s rRNA gene sequence of 13 MAAs-containing strains of unicellular halophilic cyanobacteria. These strains shared a common complement of MAAs. From a community of unicellular cyanobacterium (*Euhalothece* sp.) inhabiting the upper layer of a gypsum crust developing on the bottom of a hyper saline saltern pond, two MAAs having absorption maximum at 331 and 362 nm, were isolated when grown at high light intensities. The compound absorbing at 331 nm was purified and identified as mycosporine-2-glycine. This was the first report of mycosporine-2-glycine in the cyanobacteria<sup>51</sup>. Recently Volkmann *et al.*<sup>52</sup> have identified and given the structure of another 362 nm absorbing compound (euhalothece-362). It seems that *Euhalothece* sp. produces two UV absorbing MAAs, mycosporine-2-glycine and euhalothece-362. Four different mycosporine-like amino acids have also been detected in members of the halophilic filamentous genus *Microcoleus*<sup>53</sup>. Zhang *et al.*<sup>54</sup> isolated and characterized three MAAs, M-tau (UV-B sunscreen), dehydroxylusujirene and M-343 in *Synechocystis* sp. PCC 6803 and observed that dehydroxylusujirene and M-343 induction was mainly UV-A dependent but M-tau could be induced by both UV-A and UV-B. The MAAs such as asterina-330, shinorine, palythanol and mycosporine-glycine have been found to play a photoprotective role in epilithic cyanobacteria from a fresh water lake<sup>55</sup>. *Microcystis aeruginosa*, a common bloom forming cyanobacterium was able to synthesize MAAs (shinorine and porphyra-334) which directly absorbed UVR. This enabled cyanobacterium to develop and maintain surface bloom even in the presence of high solar irradiance including ultraviolet radiation<sup>56</sup>.

The *Leptolyngbya* mat in Antarctica showed significant photochemical inhibition under supplemental UV-B but was less prominent in a *Phormidium* mat because it was found to contain 25 times the concentration of UV protecting MAAs than to the *Leptolyngbya* mat<sup>57</sup>. A polychromatic action spectrum for the induction of MAAs in a rice-

field cyanobacterium *Anabaena* sp. showed a single prominent peak at 290 nm<sup>58</sup>. A prominent peak at 290 nm and a smaller peak at 312 nm in an action spectrum for MAAs induction have been shown for *Nostoc commune*<sup>59</sup>. Similarly Portwich and Garcia-Pichel<sup>60</sup> have shown a peak at 310 nm in an action spectrum of MAA synthesis in *Chlorogloeopsis* PCC 6912 and proposed a reduced pterin as a putative candidate for the induction of MAA shinorine. UV-B dependent induction of MAAs synthesis experiments in *Anabaena* sp., *Nostoc commune* and *Scytonema* sp. have revealed the presence of shinorine, which is a bi-substituted MAA, containing both a glycine and serine group with an absorption maximum at 334 nm<sup>29</sup>.

Sinha *et al.*<sup>61</sup> reported UV-B induced synthesis of two MAAs, shinorine and porphyra-334 (both having absorption maximum at 334 nm) in three species of *Nodularia* (*N. baltica*, *N. harveyana* and *N. spumigena*) by using the 395, 320 and 295 nm cut-off filters. In most of the cyanobacteria the exact location of MAAs is not known but in *Nostoc commune* it has been shown to be extracellular and linked to oligosaccharides in the sheath<sup>28</sup>. These glycosylated MAAs represent perhaps the only known example of MAAs that is actively excreted and accumulated extracellularly acting as true screening compounds<sup>62</sup>. The MAAs in single celled cyanobacterium *Gloeocapsa* sp. absorb only 10-30% of incident photons but its screening efficiency may be substantially increased in colony and mat forming cyanobacteria<sup>63,64</sup>. The MAAs are osmotically active compounds and their accumulation in the cell is regulated by osmotic mechanism. This is reflected by the fact that field populations of halotolerant cyanobacteria accumulate high concentration of MAAs<sup>65</sup>. Thus MAAs not only play a significant role as photoprotective compounds but also act as osmoregulators in certain cyanobacteria.

### MAAs in phytoplankton

Phytoplanktons are by far the major biomass producers in the oceans forming the base of the food web. Their productivity matches all terrestrial ecosystems taken together<sup>66</sup>. In addition, several genera of phytoplankton produce volatile substances, mainly dimethyl-sulfide (DMS). These volatile compounds act as precursors of cloud condensation nuclei and thus counteract the greenhouse effect. The cumulative effect of marine biota in the reduction of

CO<sub>2</sub> concentration and emission of DMS has been estimated to cool the atmosphere by up to 6°C<sup>67</sup>. Like cyanobacteria, phytoplanktons are also exposed to the harmful effects of UV radiation because these radiations can penetrate up to euphotic zone. Therefore, phytoplanktons have developed certain resistance mechanisms against UV radiation by inducing the MAAs synthesis<sup>68</sup>.

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 the depth, which in turn regulates the dosage of UV or PAR radiation<sup>40</sup>. So far MAAs have been reported to occur predominantly in members of the Dinophyceae, Bacillariophyceae and Haptophyceae. In larger cells, the MAAs are more effective because of large surface area, the smaller cells compensate it by forming dense populations<sup>69</sup>. In the dinoflagellate *Alexandrium excavatum*, isolated from the continental shelf near Buenos Aires, transfer from low to high PAR caused a change in MAAs composition and overall increase in UV absorption<sup>70</sup>. The *Prorocentrum micans* (dinoflagellate) showed high concentrations of MAAs when grown in presence of UV radiation<sup>71</sup>. Morrison and Nelson<sup>72</sup> presented time-series data collected at the Bermuda Atlantic Time-series study (BATS) site to document seasonal induction of enhanced UV absorption by MAAs in phytoplankton in the summer stratified surface water of the Sargasso Sea.

In the dinoflagellate *Gyrodinium dorsum*, the accumulation of MAAs was stimulated by PAR and UV radiation<sup>73</sup> while in *Phaeocystis antarctica* the induction of MAAs synthesis occur only by UV-A and UV-B radiation<sup>74</sup>. The protective function of MAAs is not necessarily restricted to the phytoplankton producing them because MAAs have been shown to be released from phytoplankton grown in cultures<sup>75</sup>. MAAs have been identified in colored or chromophoric dissolved organic matter (CDOM) of coastal water, where they might contribute up to 10% of the CDOM absorption at 330 nm<sup>76</sup>. Thus MAAs not only benefit their producers but also provide protection to other organisms against lethal UV-B in their habitats.

### MAAs in macroalgae

Macroalgae are the major biomass producers along the coastlines and on the continental shelves. They are exploited commercially on a large scale and provide

habitat for larval stages of economically important animals. Both short and long-term exposure to solar radiation inhibits growth in adult stages of several species of macroalgae due to the destruction in chloroplast, mitochondria, and occurrence of metabolites produced under UV stress<sup>77</sup>. The photoprotective role of UV-absorbing compounds in macroalgae was first reported in 1961<sup>78</sup>. Since then many qualitative and quantitative studies have been carried out to survey the distribution of MAAs among commercially important macroalgae. The MAAs content in macroalgae varies between classes and with increasing depth and latitudes. Deep water algal species do not contain MAAs<sup>79,80</sup>. MAA content is an important factor controlling the biogeographic distribution of macroalgae, since species from lower, high-solar latitudes always exhibit more MAAs than individuals from higher, low-solar latitudes<sup>81</sup>.

Many macroalgae produce one or several UV absorbing substances<sup>82</sup>. Most MAA-producing macroalgae belong to Rhodophyceae, followed by Phaeophyceae, and only a few green algae produce MAAs<sup>98</sup>. Three different types of protection by MAAs have been reported: (i) the sub littoral algae which are not likely to be exposed to higher doses of solar UV do not synthesize MAAs at all, (ii) majority of the supralittoral algae with maximum exposure to UV-B radiation produce high amount of MAAs. They cannot be further induced by exposure to any radiation<sup>83</sup>, and (iii) some supralittoral algae in which MAAs production can be induced by solar radiation. Hoyer *et al.*<sup>84</sup> studied the formation of MAAs as a photoprotective strategy against harmful UV radiation in 18 species of Antarctic red macroalgae by giving radiation treatment at 400-700, 320-700 and 295-700 nm and reported induction and accumulation of MAAs only in 8 species, while remaining ten, mainly deep water species, did not remain unaffected. Table 2 shows different algal groups divided into three physiological response type, based on MAA synthesis in response to radiation treatment<sup>85,86</sup>.

Recently Arróniz-Crespo *et al.*<sup>87</sup> have reported the occurrence of MAAs (porphyra-334 and mycosporine-glycine) in red alga *Lemanea fluviatilis*. They found that mycosporine-glycine was specifically induced by UV-B radiation. Korbee *et al.*<sup>88</sup> studied the effect of light quality on accumulation of UV-absorbing MAAs in red alga *Porphyra leucosticta* and found that blue light favored the accumulation of porphyra-334, palythine and asterina-330 whereas the

Table 2—Three physiological algal groups having different pattern of MAAs accumulation in response to UV radiation

Group	Response	Organism	Reference
I	High initial MAA content and no induction during light/radiation treatment	<i>Lemanea fluviatilis</i>	85
		<i>Porphyra endiviifolium</i>	82
		<i>Gymnogongrus turquetii</i>	82
		<i>Porphyra umbilicalis</i>	83
		<i>Mastocarpus stellatus</i>	84
		<i>Ceramium rubrum</i>	84
		<i>Gracilaria cornea</i>	47
II	Low MAA content with an induction during light/radiation treatment	<i>Kallymonia antarctica</i>	82
		<i>Gymnogongrus antarcticus</i>	80
		<i>Palmaria decipiens</i>	82
		<i>Porphyra plocamiestris</i>	82
		<i>Chondrus crispus</i>	23
III	No initial MAA and no induction during light/radiation treatment	<i>Neuroglossum ligulatum</i>	82
		<i>Plocamium cartilagineum</i>	82
		<i>Polyides rotundus</i>	84

white, yellow, green and red lights favored the accumulation of shinorine. Induction of mycosporine-glycine has also been found in *Laminaria saccharina*<sup>89</sup>. Volkmann *et al*<sup>90</sup> reported the synthesis of mycosporine-glutaminol-glucoside in presence of photosynthetically active radiation and UV radiation, suggesting a photoprotective function<sup>91</sup>. In the chlorophyte *Dasycladus vermicularis*, UV-absorbing compounds have been detected<sup>92</sup>. A polychromatic action spectrum was determined for the induction of MAAs in the chlorophyte *Prasiola stipitata* showing a clear maxima at 300 nm<sup>93</sup>.

The sub-aerial green macroalga *Prasiola crispa* sub sp. *antarctica* contained high concentration of a unique UV-absorbing compound with an absorption maxima at 324 nm. It was characterized as a putative MAA due to chromatographic properties<sup>94</sup>. This MAA has been recently identified in other green algae closely related to *Prasiola* sp. except in *Myrmecia incisa* which had 322 nm-MAA<sup>95</sup>. Han and Han<sup>96</sup> reported UV-B absorbing compounds with a prominent absorption maximum at 294 nm in green alga *Ulva pertusa* by using different cut-off filters. These compounds were synthesized only in response to UV-B treatment but their chemical structure is yet to be determined.

#### Evolution of MAAs as UV-absorbing compounds

The level of UV-C and UV-B radiation flux was higher on earth's surface prior to the formation of ozone layer that occurred when oxygen concentration increased during the early Proterozoic by

cyanobacterial photosynthesis. It was therefore necessary for these aquatic photosynthetic organisms to protect themselves against UV-induced destruction of complex organic molecules<sup>97</sup>, through the synthesis of organic molecules like MAAs<sup>98</sup>. The chemistry of the first specific UV-screening molecules on Archean Earth is not well known but it is hypothesized that aromatic-containing reaction centers were some of the earliest UV-screens that later on started to perform a light harvesting role in photosynthesis<sup>99</sup>.

The evolutionary origin of UV-screening compounds is still unknown. It is presumed that many of them evolved for other physiological roles but later adapted to UV-screening function under selection pressure. MAAs function as osmotic regulators in some cyanobacteria<sup>65</sup> and such alternative roles may have given rise to the first UV-screening MAAs<sup>100</sup>. Many of the simpler MAAs such as mycosporine-glycine might be predominantly absorbing in UV-B region but later as the oxygen level increased the absorption of UV-A became necessary since it resulted in the formation of oxygen free radicals<sup>101</sup>. This was done by replacing the ketone function by nitrogen atom in UV-B absorbing compounds. This had a greater mesomeric effect on the benzene ring shifting the absorbance to UV-A zone. In addition, mutation in UV-B screening compound might have also caused a shift in UV-A absorption. In eukaryotic algae, the MAAs have been thought to be passed by cyanobacteria in the plastidic line<sup>41</sup> and if green algae were the true origin of land plants, it may be

speculated that early land plants might have initially been depended on MAAs instead of flavanoids which protect them from UV radiation in present time.

### Conclusion

UV-absorbing MAAs are prevalent throughout the microbial world especially in cyanobacteria, phytoplankton and macroalgae. These compounds not only protect the producers but the consumers also, against the harmful effects of UV radiation. A number of photoprotective compounds from diverse organisms are yet to be chemically characterized. Although, shikimate pathway has been suggested for the synthesis of MAAs, it is still to be well documented. The loci for synthesis and storage of MAAs in a cell have to be ascertained. Presently, only in *Porphyra yezoensis*, the MAAs are known to be located in chloroplasts<sup>102</sup>. Distribution of MAAs in phylogenetically related algae can perhaps prove to be of chemotaxonomic value.

Although, presence of higher concentration of MAAs in organisms exposed to intense solar radiation has been described as a contraption against UV damage<sup>24,63</sup>, there is no specific proof suggesting the exclusive role of MAAs as sunscreen. It is presumed that they play more than one role in the cellular metabolism<sup>10,64,65</sup>. The UV-A absorption properties of the crude methanolic extract of *Porphyra-334* have been determined against two commercial sun care products in terms of mean critical wavelength, mean UV-A/UV-B ratios and UV-A protection category<sup>33</sup>. The data suggest that it can serve as a UV-A protecting sunscreen by providing wide protection against UV radiation. It has also been reported that MAAs may also act as antioxidants to prevent cellular damage resulting from UV-induced production of active oxygen species<sup>103</sup>. Further work is needed to test the potentialities of MAAs as antioxidants and thereby opening the way for industrial or pharmacological development of the biological sunscreens and antioxidants.

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### References

- Crutzen P J, Ultraviolet on the increase, *Nature*, 356 (1992) 104.
- Kerr J B & McElory C T, Evidence for large upward trend of ultraviolet-B radiation linked to ozone depletion, *Science*, 262 (1993) 1032.
- Lubin D & Jensen E H, Effects of clouds and stratospheric ozone depletion on ultraviolet radiation trends, *Nature*, 377 (1995) 710.
- Weatherhead E C & Andersen S B, The search for signs of recovery of the ozone layer, *Nature*, 441 (2006) 39.
- Smith R C, Prezelin B B, Baker K S, Bidigare R R, Boucher N P, Coley T, Karentz D, McIntyre S, Matlick H A, Menzies D, Ondrusek M, Wan Z & Waters K J, Ozone depletion: ultraviolet radiation and phytoplankton biology in Antarctic waters, *Science*, 255 (1992) 952.
- von der Gathen P, Rex M, Harris N R P, Lucic D, Knudsen B M, Braathen G O, De Backer H, Fabian R, Fast H, Gil M, Kyrö E, Mikkelsen I S, Rummukainen M, Stähelin J & Varotsos C, Observational evidence for chemical ozone depletion over the Arctic in winter 1991-1992, *Nature*, 375 (1995) 131.
- Häder D-P, Kumar H D, Smith R C & Worrest R C, Effects of solar UV radiation on aquatic ecosystems and interactions with climate change, *Photochem Photobiol Sci*, 6 (2007) 267.
- Kirk J T O, Optics of UV-B radiation in natural waters, *Arch Hydrobiol*, 43 (1994) 1.
- Karentz D, Cleaver J E & Mitchell D L, DNA damage in the Antarctic, *Nature*, 350 (1991) 28.
- Vincent W F & Roy S, Solar ultraviolet-B radiation and aquatic primary production: damage, protection and recovery, *Environ Rev*, 1 (1993) 1.
- Bothwell M L, Sherbot D M J & Pollock C M, Ecosystem response to solar ultraviolet-B radiation: influence of trophic level interactions, *Science*, 265 (1994) 97.
- Sinha R P, Lebert M, Kumar A, Kumar H D & Häder D-P, Spectroscopic and biochemical analyses of UV effects on phycobiliproteins of *Anabaena* sp. and *Nostoc commune*, *Bot Acta*, 180 (1995) 87.
- Sinha R P, Lebert M, Kumar A, Kumar H D & Häder D-P, Disintegration of phycobilisomes in a rice field cyanobacterium *Nostoc* sp. following UV irradiation, *Biochem Mol Biol Int*, 37 (1995) 697.
- Sinha R P, Singh N, Kumar A, Kumar H D, Häder M & Häder D-P, Effects of UV irradiation on certain physiological and biochemical process in cyanobacteria, *J Photochem Photobiol B: Biol*, 32 (1996) 107.
- Sinha R P, Singh N, Kumar A, Kumar H D & Häder D-P, Impacts of ultraviolet-B irradiation on nitrogen-fixing cyanobacteria of rice paddy fields, *J Plant Physiol*, 150 (1997) 188.
- Xue L, Zhang Y, Zhang T, An L & Wang X, Effects of enhanced ultraviolet-B radiation on algae and cyanobacteria, *Crit Rev Microbiol*, 31 (2005) 79.
- Helbling E W, Fariás M E, Zenoff M V F & Villafañe V E, In situ responses of phytoplankton from the subtropical Lake La Angostura (Tucumán, Argentina) in relation to solar ultraviolet radiation exposure and mixing conditions, *Hydrobiol*, 559 (2006) 123.
- Sinha R P & Häder D-P, UV-induced DNA damage and repair: a review, *Photochem Photobiol Sci*, 1 (2002) 225.
- Häder D-P & Sinha R P, Solar ultraviolet radiation-induced DNA damage in aquatic organisms: potential environmental impact, *Mut Res*, 571 (2005) 221.
- Han T, Kong J-A, Han Y-S, Kong S-H & Häder D-P, UV-A/blue light-induced reactivation of spore germination in

- UV-B irradiated *Ulva pertusa* (Chlorophyta), *J Phycol*, 40 (2004) 315.
- 21 Mittler R & Tel-Or E, Oxidative stress responses in the unicellular cyanobacterium *Synechococcus* PCC 7942, *Free Radical Res Commun*, 12 (1991) 845.
  - 22 Middleton E M & Teramura A H, The role of flavanol glycosides and carotenoids in protecting Soybean from ultraviolet-B damage, *Plant Physiol*, 103 (1993) 741.
  - 23 Karsten U, Sawall T & Wiencke C, A survey of the distribution of UV-absorbing substances in the tropical macroalgae, *Phycol Res*, 46 (1998) 271.
  - 24 Sinha R P, Klisch M, Gröniger A & Häder D-P, Ultraviolet-absorbing/screening substances in cyanobacteria, phytoplankton and macroalgae, *J Photochem Photobiol B: Biol*, 47 (1998) 83.
  - 25 Leach C M, Ultraviolet-absorbing substances associated with light-induced sporulation in fungi, *Can J Bot*, 43 (1965) 185.
  - 26 Shick J M & Dunlap W C, Mycosporine-like amino acids and related gadusols: biosynthesis, accumulation, and UV-protective function in aquatic organisms, *Annu Rev Physiol*, 64 (2002) 223.
  - 27 Huovinen P, Gómez I, Figueroa F L, Ulloa N, Morales V & Lovengreen C, Ultraviolet-absorbing mycosporine-like amino acids in red macroalgae from Chile, *Bot Mar*, 47 (2004) 21.
  - 28 Böhm G A, Pfleiderer W, Böger P & Scherer S, Structure of a novel oligosaccharide-mycosporine-amino acids ultraviolet A/B sunscreen pigment from the terrestrial cyanobacteria *Nostoc commune*, *J Biol Chem*, 270 (1995) 8536.
  - 29 Sinha R P, Klisch M, Helbling E W & Häder D-P, Induction of mycosporine-like amino acids (MAAs) in cyanobacteria by solar ultraviolet-B radiation, *J Photochem Photobiol B: Biol*, 60 (2001) 129.
  - 30 Dunlap W C, Chalker B E & Oliver J K, Bathymetric adaptations of reef-building corals at Davies Reef, Great Barrier Reef, Australia: III. UV-B absorbing compounds, *J Exp Mar Biol Ecol*, 104 (1986) 239.
  - 31 Cardozo K H M, Carvalho V M, Pinto E & Colepicolo P, Fragmentation of mycosporine-like amino acids by hydrogen/deuterium exchange and electrospray ionization tandem mass spectrometry, *Rapid Commun Mass Spectrom*, 20 (2006) 253.
  - 32 Sommaruga R, Whitehead K, Shick J M & Lobban C S, Mycosporine-like amino acids in the zooxanthella-ciliate symbiosis *Maristentor dinofereus*, *Protist*, 157 (2006) 185.
  - 33 Torres A, Enk C D, Hochberg M & Srebnik M, Porphyra-334, a potential natural source for UVA protective sunscreens, *Photochem Photobiol Sci*, 5 (2006) 432.
  - 34 Bandaranayake W M, Mycosporines: are they nature's sunscreen? *Nat Prod Rep*, 15 (1998) 159.
  - 35 Shick J M, Romaine-Lioud S, Ferrier-Pagès C & Gattuso J P, 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 (1999) 1667.
  - 36 Callone A I, Carignan M, Montoya N G & Carreto J I, Biotransformation of mycosporine like amino acids (MAAs) in the toxic dinoflagellate *Alexandrium tamarense*, *J Photochem Photobiol B: Biol*, 84 (2006) 204.
  - 37 Carreto J I, Carignan M O & Montoya N G, A high-resolution reverse-phase liquid chromatography method for the analysis of mycosporine-like amino acids (MAAs) in marine organisms, *Mar Biol*, 146 (2005) 237.
  - 38 Conde F R, Churio M S & Previtali C M, Experimental study of the excited-state properties and photostability of the mycosporine-like amino acid palythine in aqueous solution, *Photochem Photobiol Sci*, 6 (2007) 669.
  - 39 Whitehead K & Hedges J I, Photodegradation and photosensitization of mycosporine-like amino acids. *J Photochem Photobiol B: Biol*, 80 (2005) 115.
  - 40 Dunlap W C & Shick J M, Ultraviolet radiation-absorbing mycosporine-like amino acids in Coral reef organisms: a biochemical and environmental perspective, *J Phycol*, 34 (1998) 418.
  - 41 Cockell C S & Knowland J, Ultraviolet radiation screening compounds, *Biol Rev*, 74 (1999) 311.
  - 42 Conde F R, Churio M S & Previtali C M, The photoreceptor mechanism of mycosporine-like amino acids. Excited-state properties and photostability of porphyra-334 in aqueous solution, *Photochem Photobiol*, 56 (2000) 139.
  - 43 Helbling E W, Menchi C F & Villafañe V, Bioaccumulation and role of UV-absorbing compounds in two marine crustacean species from Patagonia, Argentina, *Photochem Photobiol Sci*, 1 (2002) 820.
  - 44 Newman S J, Dunlap W C, Nicol S & Ritz D, Antarctic Krill (*Euphausia superba*) acquires UV-absorbing mycosporine-like amino acids from dietary algae, *J Exp Mar Biol*, 255 (2000) 93.
  - 45 Whitehead K, Karentz D & Hedges J I, Mycosporine-like amino acids (MAAs) in phytoplankton, a herbivorous pteropod (*Limacina helicina*), and its pteropod predator (*Clione antarctica*) in McMurdo Bay, Antarctica, *Mar Biol*, 139 (2001) 1013.
  - 46 Gröniger A & Häder D-P, Stability of mycosporine-like amino acids, *Recent Res Devel Photochem Photobiol*, 4 (2000) 247.
  - 47 Sinha R P, Klisch M, Gröniger A & Häder D-P, Mycosporine-like amino acids in the marine red alga *Gracilaria cornea* - effects of UV and heat, *Env Exp Bot*, 43 (2000) 33.
  - 48 Vaishampayan A, Sinha R P, Häder D-P, Dey T, Gupta A K, Bhan U & Rao A L, Cyanobacterial biofertilizers in rice agriculture, *Bot Rev*, 67 (2001) 453.
  - 49 Shibata K, Pigments and a UV-absorbing substance in corals and a blue-green alga living on the Great Barrier Reef, *Plant Cell Physiol*, 10 (1969) 325.
  - 50 Garcia-Pichel F, Nübel U & Muyzer G, The phylogeny of unicellular, extremely halotolerant cyanobacteria, *Arch Microbiol*, 169 (1998) 469.
  - 51 Kedar L, Kashman Y & Oren A, Mycosporine-2-glycine is the major mycosporine-like amino acids in a unicellular cyanobacterium (*Euhalothece* sp.) isolated from a gypsum crust in hypersaline Satter pond, *FEMS Microbiol Lett*, 208 (2002) 233.
  - 52 Volkmann M, Gorbushina A A, Kedar L & Oren A, Structure of euhalothece-362, a novel red shifted mycosporine-like amino acid, from a halophilic cyanobacterium (*Euhalothece* sp.), *FEMS Microbiol Lett*, 258 (2006) 50.

- 53 Karsten U & Garcia-Pichel F, Carotenoids and mycosporine-like amino acid compound in the members of the genus *Microcoleus* (cyanobacteria): a chemosystematic study, *Syst Appl Microbiol*, 19 (1996) 285.
- 54 Zhang L, Li L & Wu Q, Protective effects of mycosporine-like amino acids of *Synechocystis* sp. PCC 6803 and their partial characterization, *J Photochem Photobiol B: Biol*, 86 (2007) 240.
- 55 Sommaruga R & Garcia-Pichel F, UV-absorbing mycosporine-like compounds in planktonic and benthic organisms from a high-mountain lake, *Hydrobiol*, 144 (1999) 255.
- 56 Zhengwen L, Häder D-P & Sommaruga R, Occurrence of mycosporine-like amino acids (MAAs) in the bloom forming cyanobacterium *Microcystis aeruginosa*, *J Plank Res*, 26 (2004) 963.
- 57 George A L, Murray A W & Montiel P O, Tolerance of Antarctic cyanobacterial mats to enhanced UV radiation, *FEMS Microbiol Ecol*, 37 (2001) 91.
- 58 Sinha R P, Sinha J P, Gröniger A & Häder D-P, 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 (2002) 47.
- 59 Sinha R P, Ambasht N K, Sinha J P & Häder D-P, Wavelength-dependent induction of a mycosporine-like amino acids in a rice-field cyanobacterium, *Nostoc commune*: role of inhibitors and salt stress, *Photochem Photobiol Sci*, 2 (2003) 171.
- 60 Portwich A & Garcia-Pichel F, A novel prokaryotic UV-B photoreceptor in the cyanobacterium *Chlorogloeopsis* PCC 61912, *Photochem Photobiol*, 71 (2000) 493.
- 61 Sinha R P, Ambasht N K, Sinha J P, Klisch M & Häder D-P, UV-B-induced synthesis of mycosporine-like amino acids in three strains of *Nodularia* (cyanobacteria), *J Photochem Photobiol B: Biol*, 71 (2003) 51.
- 62 Ehling-Schulz M, Bilger W & Scherer S, UV-B-induced synthesis of photoprotective pigments and extracellularly polysaccharides in the terrestrial cyanobacterium *Nostoc commune*, *J Bacteriol*, 179 (1997) 1940.
- 63 Garcia-Pichel F, Wingard C E & Castenholz R W, Evidence regarding the UV sunscreen role of a mycosporine-like compound in the cyanobacterium *Gloeocapsa* sp., *Appl Environ Microbiol*, 59 (1993) 170.
- 64 Castenholz R W, Multiple strategies for UV tolerance in cyanobacteria, *The Spectrum*, 10 (1997) 10.
- 65 Oren A, Mycosporine-like amino acids as osmotic solutes in a community of halophilic cyanobacteria, *Geomicrobiol J*, 14 (1997) 231.
- 66 Falkowski P, The Ocean's invisible forest, *Sci Am*, 287 (2002) 54.
- 67 Watson A J & Liss P S, Marine biological control on climate via the carbon and sulphur geochemical cycles, *Philos Trans R Soc Lond*, 353 (1998) 41.
- 68 Xiong F, Komenda J, Kopecky J & Nedball L, Strategies of ultraviolet-B protection in microscopic algae, *Physiol Plant*, 100 (1997) 378.
- 69 Garcia-Pichel F, The absorption of ultraviolet radiation by microalgae: simple optics and photobiological implications, *Sci Mar*, 60 (1996) 73.
- 70 Carreto J I, Lutz V A, De Marco S G & Carignan M O, Fluence and wavelength dependence of mycosporine-like amino acid synthesis in the dinoflagellate *Alexandrium excavatum*, in *Toxic Marine phytoplankton*, edited by E Graneli, L Edler, B Sundström & D M Anderson, (Elesvier, New York), 1990, 275.
- 71 Lesser M P, 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 (1996) 287.
- 72 Morrison J R & Nelson N B, Seasonal cycle of phytoplankton UV-absorption at the Bermuda Atlantic Time-series Study (BATS) site, *Limnol Oceanogr*, 49 (2004) 215.
- 73 Klisch M & Häder D-P, Wavelength dependence of mycosporine-like amino acids synthesis in *Gyrodinium dorsum*, *J Photochem Photobiol B: Biol*, 66 (2002) 60.
- 74 Riegger L & Robinson D, Photoinduction of UV-absorbing compounds in Antarctic diatoms and *Phaeocystis antarctica*, *Mar Ecol Prog Ser*, 160 (1997) 13.
- 75 Vernet M & Whitehead K, Release of ultraviolet-absorbing compounds by the red tide dinoflagellate *Lingulodinium polyedrum*, *Mar Biol*, 127 (1996) 35.
- 76 Whitehead K & Vernet M, Influence of mycosporine-like amino acids (MAAs) on UV-absorption by particulate and dissolved organic matter in La Jolla Bay, *Limnol Oceanogr*, 45 (2000) 1788.
- 77 Holzinger A & Lütz C, Algae and UV irradiation: Effect on ultrastructure and metabolic function, *Micron*, 37 (2006) 190.
- 78 Tsujino I & Satio T, Studies in the compounds specific for each group in marine algae. I. Presence of characteristic ultraviolet absorbing material in Rhodophyceae, *Bull Fac Fish*, 12 (1961) 49.
- 79 Maegawa M, Kunieda M & Kida W, Difference of the amount of UV-absorbing substance between shallow deep water red algae, *Jpn J Phycol*, 41 (1993) 351.
- 80 Karsten U, Sawall T, Hanelt D, Bischof K, Figueroa F L, Flores-Moya A & Wiencke C, An inventory of UV-absorbing mycosporine-like amino acids in macroalgae from polar to warm-temperate regions, *Bot Mar*, 41 (1998) 443.
- 81 Karsten U & West J A, 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 (2000) 221.
- 82 Karsten U & Wiencke C, Factors controlling the formation of UV-absorbing mycosporine-like amino acids in the marine red alga *Palmaria palmate* from Spitsbergen (Norway), *J Plant Physiol*, 155 (1999) 407.
- 83 Gröniger A, Sinha R P, Klisch M & Häder D-P, Photoprotective compounds in cyanobacteria, phytoplankton and macroalgae-a database, *J Photochem Photobiol B: Biol*, 58 (2000) 115.
- 84 Hoyer K, Karsten U & Wiencke C, Induction of sunscreen compound in Antarctic macroalgae by different radiation condition, *Mar Biol*, 141 (2002) 619.
- 85 Gröniger A, Hallier C & Häder D-P, Influence of UV-radiation and visible light on *Porphyra umbilicalis*: photoinhibition and MAA concentration, *J Appl Phycol*, 11 (1999) 437.
- 86 Sinha R P, Klisch M, Gröniger A & Häder D-P, Response of aquatic algae and cyanobacteria to solar UV-B, *Plant Ecol*, 154 (2001) 221.

- 87 Arróniz-Crespo M, Sinha R P, Martínez-Abaigar J, Núñez-olivera E & Häder D-P, Ultraviolet radiation induced changes in mycosporine-like amino acids and physiological variables in the red alga *Lemanea fluviatilis*, *J Freshwater Ecol*, 20 (2005) 677.
- 88 Korbee N, Figueroa F L & Aguilera J, 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 (2005) 71.
- 89 Apprill A M & Lesser M P, Effects of ultraviolet radiation on *Laminaria saccharina* in relation to depth and tidal height in the Gulf of Maine, *Mar Ecol Prog Ser*, 256 (2003) 75.
- 90 Volkmann M, Whitehead K, Rütters H, Rullkötter J & Gorbushina A A, Mycosporine-glutamicol-glucoside: a natural UV-absorbing secondary metabolite of rock inhabiting microcolonial fungi, *Rapid Commun Mass Spectrom*, 17 (2003) 879.
- 91 Libkind D, Perez P, Sommaruga R, D'ieguez M D C, Ferraro M, Brizzio S, Zagarese H & Brook M V, Constitutive and UV-inducible synthesis of photoprotective compounds (carotenoids and mycosporines) by freshwater yeasts, *Photochem Photobiol Sci*, 3 (2004) 281.
- 92 Pérez-Rodríguez E, Gómez I, Karsten U & Figueroa F L, Effect of UV radiation on photosynthesis and excretion of UV-absorbing compounds of *Dasycladus vermicularis* (Dasycladales, chlorophyta) from Southern Spain, *Phycologia*, 37 (1998) 379.
- 93 Gröniger A & Häder D-P, Induction of the synthesis of an UV-absorbing substance in the green alga *Prasiola stipitata*, *J Photochem Photobiol B: Biol*, 66 (2002) 54.
- 94 Hoyer K, Karsten U & Wiencke C, Photoprotective substances in Antarctic macroalgae and their variation with respect to depth distribution, different tissues and developmental stages, *Mar Ecol Prog Ser*, 211 (2001) 117.
- 95 Karsten U, Friedl T, Schumann R, Hoyer K & Lembcke S, Mycosporine-like amino acids and phylogenies in green algae: *Prasiola* and its relatives from the Trebouxioophyceae (Chlorophyta), *J Phycol*, 41 (2005) 557.
- 96 Han Y-S & Han T, UV-B induction of UV-B protection in *Ulva pertusa* (chlorophyta), *J Phycol*, 41 (2005) 523.
- 97 Cleaves H J & Miller S L, Oceanic protection of prebiotic organic compound from UV radiation, *Proc Natl Acad Sci USA*, 95 (1998) 7260.
- 98 Sagan C, Ultraviolet radiation selection pressure on the earliest organisms, *J Theoret Biol*, 39 (1973) 195.
- 99 Mulkidjanian A Y & Junge W, On the origin of photosynthesis as inferred from sequence analysis, *Photosyn Res*, 51 (1997) 27.
- 100 Cockell C S, The biological effects of UV radiation on early earth- a theoretical evolution, *J Theoret Biol*, 193 (1998) 719.
- 101 Garcia-Pichel F, Solar ultraviolet and evolutionary history of cyanobacteria, *Orig Life Evolut Biosph*, 28 (1998) 321.
- 102 Yoshida T & Sivalingam P M, Isolation and characterization of the 337 m $\mu$  UV-absorbing substances in red alga *Porphyra yezoensis* UEDA, *Plant Cell Physiol*, 11 (1970) 427.
- 103 Dunlap W C & Yamamoto Y, Small-molecule antioxidants in marine organisms: antioxidant activity of mycosporine-glycine, *Comp Biochem Physiol*, 112 (1995) 105.