Bioenergetics: Open Access
ISSN: 2167-7662

Rastogi et al., Bioenergetics 2016, 5:2
DOI: 10.4172/2167-7662.1000138

Short Communication Open Access

Cyanobacteria Synthesize their own UV-Sunscreens for Photoprotection

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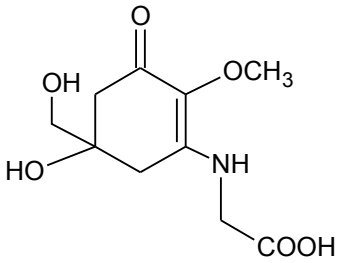
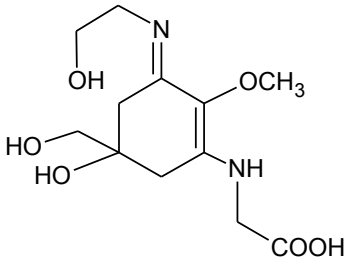
Rec date: July 11, 2016, **Acc date:** July 27, 2016, **Pub date:** July 29, 2016

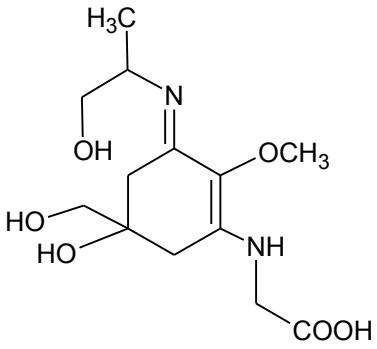
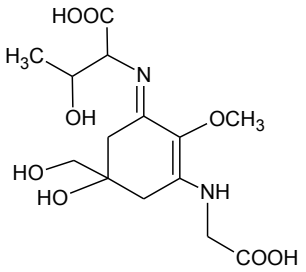
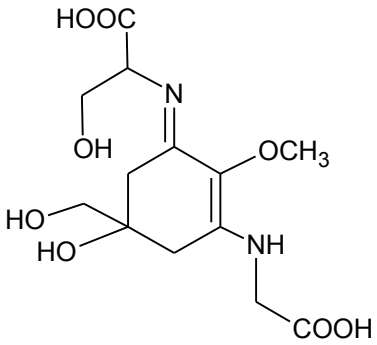
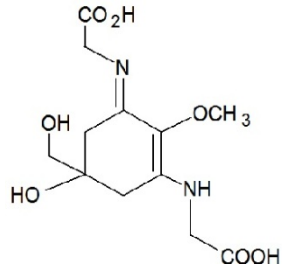
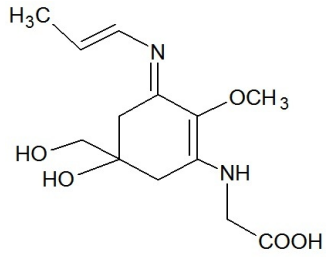
Introduction

Cyanobacteria are the most primitive group of photoautotrophic prokaryotic micro-flora, probably appeared on the Earth during Precambrian era while there was no ozone-shield [1] and intense solar light with high incidence of harmful ultraviolet (UV) radiation. Survival of life under extreme condition of UV radiation is highly menacing. The high-energetic UV (280–400 nm) radiation has great potential for cell damage either through direct effects on biologically relevant key machinery such as DNA, proteins and lipids, or indirect effects via the production of reactive oxygen species (ROS), leading to mutagenesis, and loss of fundamental cellular physiology and metabolic functions [2-5].

However, in the face of adverse effects of intense solar radiation, cyanobacteria developed some efficient repair mechanisms along with various enzymatic/non-enzymatic defense systems to counteract the harmful effects of UV radiation [6-9]. Moreover, owing to strong defense systems, cyanobacteria are so far surviving and thriving well as dominant primary producers over a wide range of aquatic and terrestrial ecosystems including the extreme habitats such as deserts, hot springs, acidic, saline, and extremely cold polar region [10].

Exposures to various abiotic stresses have imposed cyanobacteria towards gradual evolution to maintain the cell viability. Particularly, an obligate requirement of solar-light energy in connection with photosynthesis-the most important life supporting biological phenomena of the Earth have exposed cyanobacteria to the wide range of solar radiations including harmful doses of UV-B (280-315 nm) and UV-A (315–400 nm) radiations in their natural habitats; which in turn, positively compelled them to synthesize a number of photon absorbing molecules [11-18] (Table 1).

MAAs	*Chemical structure*	*Mol. formula*	*MH +*	*UV λmax [nm]*	*Reference*
Mycosporine-glycine		C10H15NO6	244	310	[12,14]
Asterina-330		C12H20N2O6	289	330	[15,23]

Palythinol		C13H22N2O6	303	332	[12,15]
Porphyra-334		C14H22N2O8	347	334	[12,17]
Shinorine		C13H20N2O8	333	333	[12,25]
Mycosporine-2-glycine		C12H18N2O7	303	334	[16,29]
Palythene		C13H20N2O5	285	359	[35]

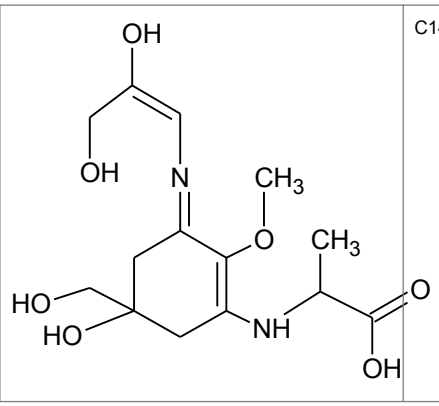
Euhalothece-362		C14H23N2O7	331	362	[16,18]

Table 1: Some common MAAs found in cyanobacteria.

Biosynthesis of a number of UV-absorbing compounds in diverse organisms has received much attention for their supposed role in photoprotection. Cyanobacteria synthesize their own sun-screening molecules such as mycosporine-like amino acids (MAAs) [19,20] and scytonemin (Scy) [21] to block the UV rays (Figure 1).

MAAs are small, colorless, hydrophilic molecules composed of a cyclohexenone or cyclohexenimine chromophores conjugated with the nitrogen substituent of an amino acid or its imino alcohol. Strong UV absorption (307–362 nm), high molar extinction coefficients and resistance to several abiotic stressors support their role as an effective natural photoprotectants.

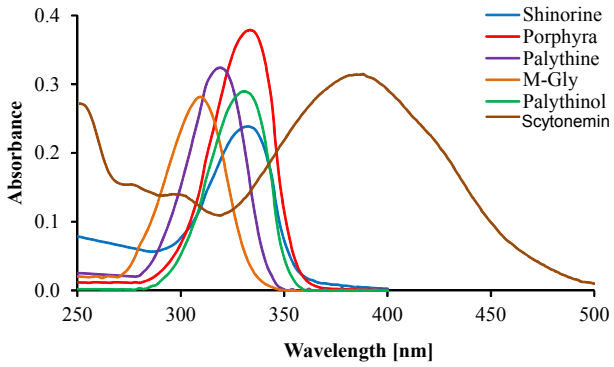


Figure 1: Absorption maxima of some common MAAs, and scytonemin found in cyanobacteria.

The cyanobacterial photoprotectant scytonemin is a yellow-brown lipid-soluble dimeric pigment molecule located in the extracellular polysaccharide sheath of several cyanobacterial species and provides photoprotection against a wide range of UV radiation due to their great capacity to absorb significantly at 384 nm, 300 nm, 278 nm and 252 nm [22] (Figure 1). Scytonemin has been reported to exist both in oxidized (Mw 544 Da) and reduced (Mw 546 Da) forms [11,23](Figure 2).

Both MAAs and Scy display a significant antioxidant activity and protect the cells by minimizing the formation of the most cytotoxic and mutagenic DNA lesions purine or pyrimidine dimers [21,24,25].

Biosynthesis of MAAs [26,27] and Scy is still under development. Moreover, a cluster of four genes (Ava_3858 to Ava_3855) was found to be responsible for MAA biosynthesis from sedoheptulose-7-phosphate in the cyanobacterium Anabaena variabilis [27]. The dehydroquinate synthase homologue Ava_3858 and the O-methyltransferase Ava_3857 synthesize 4-deoxygadusol (4-DG).

The ATP-grasp homologue Ava_3856 catalyzes the addition of glycine to 4-DG to produce mycosporine-glycine (M-Gly). Subsequently, Ava_3855 encoding a nonribosomal peptide synthetase, catalyzes the edition of serine to M-Gly to form shinorine [27]. The genetic and molecular basis of MAA biosynthetic pathway has recently been elucidated in some other cyanobacteria [28,29]. There are self-contradictory reports regarding the biosynthesis of sunscreening pigment scytonemin [20,30-32].

In the past few years, both MAAs and Scy isolated from different cyanobacteria have become one of the most promising natural substances in the field of biotechnology and biomedical research due to their non-toxic nature, strong UV absorption, ROS scavenging, potential antioxidant, and antiproliferative properties [21,24,33-35].

The role of MAAs in UV protective was demonstrated in vivo in mice [36] and in human fibroblast cells [37]. The effect of MAAs shinorine and porphyra-334 on central signaling cascades, such as transcription factor nuclear factor kappa b (NF-kB) activation, as well as tryptophan metabolism, was investigated in human myelomonocytic THP-1 and THP-1-Blue cells. Both MAAs were able to induce NF-kB activity in dose-dependent manner in unstimulated THP-1-Blue cells [38]. Inhibition of collagenase by MAAs was observed against Chlostridium histolyticum collagenase [39].

The MAAs like shinorine and porphyra-334 are already used in commercial sunscreen products such as Helioguard 365, M-Rose and Helionori to protect against UV-A radiation [3]. Cyanobacterial pigment Scy also has strong anti-proliferative and anti-inflammatory activities [13,33].

Overall, the commercial application of microbial sunscreen seems to have a huge potential and affirmative future. However, a more detailed risk-benefit assessment is suggested to explore these ecologically important biomolecules for development of daily care cosmeceuticals and other therapeutic products.

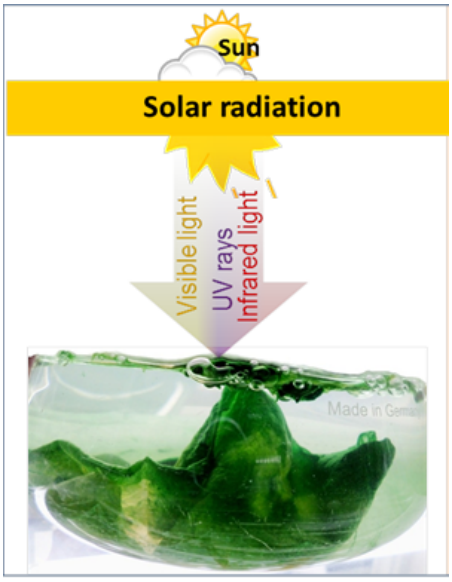


Figure 2: Damage caused to key cellular machinery by solar UV radiations.

Solar UV radiations may cause serious damage to key cellular machinery that can interrupt normal physiology, biochemistry or metabolic development of the cell. So in what way do cyanobacteria protect themselves from intense light facilitated fiery to a crisp? The study has unveiled that cyanobacteria produce their own sunscreens. These sunscreens are not like the artificial colorful paste or lotions that we use to protect from short wavelength solar UV drops. These are some unusual biomolecules, so-called, MAAs and Scytonemin that cyanobacteria produce and make natural barriers against harmful consequences of high UV photon flux.

Acknowledgement

Rajesh P. Rastogi is thankful to the University Grant Commission (UGC), New Delhi, India for Dr. D. S. Kothari Postdoctoral Research Grant (Grant No. F.4-2/2006(BSR)/13-966/2013(BSR)).

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