Natural Microbial UV Radiation Filters – Mycosporine-like Amino Acids

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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 000
2 Separation of mycosporine-like amino acids 111
3 Cyanobacteria and lichen photobiont species 222
4 Fungus and lichen mycobionts 333
5 Microalgae 444
6 Conclusion 555
References 666

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 \textit{et al.} 2003; Jiang \textit{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 ($\lambda_{\text{max}}$ 305 nm) in the gas gland of the epipelagic Portuguese man-of-war in 1960, but the isolated substance ($\lambda_{\text{max}}$ 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 ($\lambda_{\text{max}}$) at $\approx$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 Porites 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).

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).