New Natural Sunscreens based on Biologically Produced Mycosporine-like Amino Acids through their Efficient Charge Resonance Absorption

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The UV-protective ability of mycosporine-like amino acids (MAAs) has been well documented, but not much explored nor investigated. Indeed, this effect is believed to serve as a protecting capability of marine organisms from solar radiation. Nevertheless, the effective UV absorption by MAAs has not been easily correlated to neutral MAA structures. In this study, the origin of UV-protecting ability of MAAs was elucidated by experimental spectroscopy and theoretical investigations. The absorption maxima of mycosporine-related molecules in the UVA region were practically unaffected over a wide range of pH4-10 and only slightly blue-shifted at pH 1-2. It was revealed that the zwitterionic nature of the amino acid residue facilitates the protonation to the chromophoric 3-aminocyclohexenone and 1-amino-3-iminocyclohexene moieties and the operation of the charge resonance in the protonated species well accounts for their allowed low-energy transitions in the UVA region. The theoretical calculations for the protonated forms well reproduced the observed transition energies and oscillator strengths of MAAs with slight systematic overestimations. This study clearly demonstrated that the 3-aminocyclohexenone as well as 1-amino-3-iminocyclohexene moieties, which are readily protonated at a wide range of pH, are responsible for the UVprotective ability of aqueous solution of MAAs. Based on these considerations, together with the study on the stability and photoliability of the species, we further tried to develop the novel sunscreens that absorb in the different wavelength that covers whole the UVA regions.