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Study on UV Absorption Materials Derived from Red Algae *Gloiopeltis fucatas* and *Mazzaella* sp. in Russia

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Abstract

We investigated ultraviolet (UV) absorption materials from Russian seaweeds. First, the UV absorptivities of five seaweeds *Gloiopeltis fucatas, Mazzaella sp., Mastocarpus pacificus, Laminaria cichorioides, Saccharina japonica* were evaluated by a UV spectrometer. Of these seaweeds, *Gloiopeltis fucatas* and *Mazzaella* sp. showed high levels of UV absorption. Column chromatography of active 50% aqueous ethanol extracts from *Gloiopeltis fucatas* and *Mazzaella* sp. resulted in the purification of two known compounds. Spectroscopic techniques identified their structures as shinorine and palythine. These materials exhibited UV absorptive capabilities at wavelengths of 333 and 320 nm, respectively. These results suggest that *Gloiopeltis fucatas* and *Mazzaella* sp. may be useful as natural cosmeceutical sources.

Key words: *Gloiopeltis fucatas*., *Mazzaella* sp., Russian seaweeds, Shinorine, Palythine

Introduction

Gloiopeltis fucatas red algae belonging to the family Endocladiaceae, have been traditionally consumed as medicines and food thickeners in China and Japan (Schachat and Glicksman, 1959). Various beneficial effects have been reported, such as anti-inflammatory and anti-tumor activities (Niu et al., 2003; Bae and Choi, 2007). *Mazzaella* sp. belong to the family Gigartinaceae and are distributed in the north and west Pacific, around Pacific South America, Gough Island and off South Africa (Hommersand et al., 1993). They are well known as sources of carrageenan which is used as a food additive.

Ultraviolet (UV) radiation is one of the most harmful exogenous agents and affects numerous biological functions in all sun-exposed living organisms. Organisms are exposed to solar radiation, including harmful UV-B (280-320 nm) and UV-A (315-400 nm) radiation, in their natural habitats. Repetitive exposure to sun causes premature skin aging (Marrot and Meunier, 2008) and skin cancer (Afaq et al., 2005; de Gruijl and Ananthaswamy, 2010). In response to intense solar radiation, organisms have evolved certain mechanisms, such as avoidance, repair, and protection by synthesizing or accumulating photoprotective compounds, such as mycosporine-like amino acids (MAAs).

In the present study, we investigated the UV absorption power of Russian seaweeds and isolated UV-absorbing constituents from them.

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Materials and Methods

Samples

Five species of seaweed were collected at Sacchalin, Russia, from February to July 2011 (Table 1) by the TINRO-center, and stored frozen at -20°C.

Extraction

The seaweeds samples were extracted in 10 volumes of 0%, 50%, and 100% aqueous ethanol a using sonicator. The extracts were evaporated using a rotary evaporator.

Isolates derived from *Gloiopeltis fucatas* and *Mazzaella* sp. in Russia

The 50% aqueous ethanol extracts from *Gloiopeltis fucatas* (0.5 g) and *Mazzaella* sp. (0.5 g) were subjected to column chromatography over silica gel (silica gel 60, 0.063-0.200 mm; Merck, Darmstadt, Gerrmany) and eluted with 80% aqueous acetonitrile, to yield four subfractions (G 1-4) and five subfractions (M 1-3) based on thin layer chromatography analysis, respectively. Then, separations of fractions G 3 (0.35 g) and M 4 (0.35 g) were carried out on a Dionxe P690 HPLC system equipped with a UV detector (Dionex UVD 170U; Thermo Scientific, San Jose, CA, USA). High-performance liquid chromatography conditions were as follows: guard column, C18 (i.d. 4.6 × 7.5 mm, 5 U; Alltech, Woodridge, IL, USA); column, Intersil ODS-3V (i.d. 4.6 × 150 mm, 5 µm; GL Science Inc., Tokyo, Japan); flow rate, 0.7 mL/min; detection wavelengths, 320 and 333 nm. An eluent solvent was followed by 50% acetonitrile (in 0.2% acetic acid) within 30 min. The structures were analyzed from spectral data using nuclear magnetic resonance and electrospray ionization mass spectrometry.

Measurements of UV absorption spectra

UV absorption spectra of seaweed extracts were evaluated using an Optizen 2120UV spectrophotometer (Mecasys, Daejeon, Korea) for wavelengths of 240 to 720 nm at a concentration of 1 mg/mL (Oyamada et al., 2008).

Table 1. The yield of five Russian seaweeds (%)

Phylum	Classification	Yield (%)*
Phodophyta	*Gloiopeltis fucatas*	10.32
	Mazzaella sp.	11.77
	Mastocarpus pacificus	8.23
Phaeophyta	*Laminaria cichorioides*	5.23
	Saccharina japonica	7.35

* The yield was expressed as percentage and calculated with the 50% aqueous ethanol extract weight per dry sample weight.

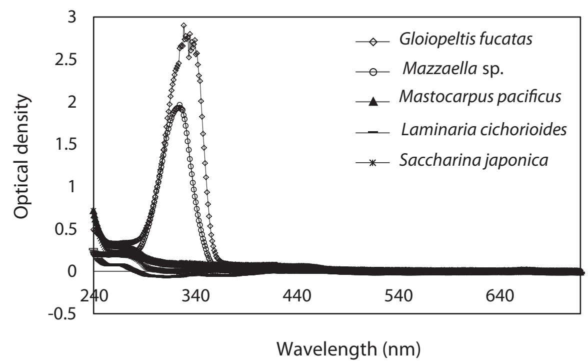

Fig. 1. Ultraviolet spectrum on 50% aqueous ethanol extracts of the five seaweeds from Russia.

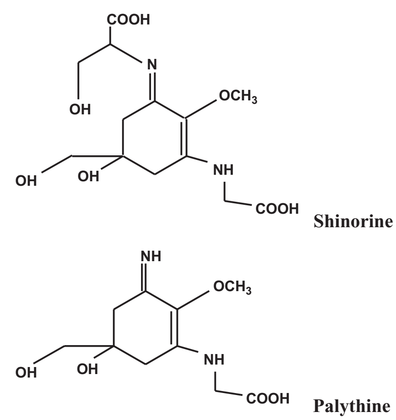

Fig. 2. Structures of compounds 1 and 2 isolated from *Gloiopeltis fucatas* and *Mazzaella* sp., respectively.

Results and Discussion

UV radiation is either reflected or absorbed by sunscreens. Different structural molecules have unique absorption wavelengths. An absorption spectrum will show a number of absorption bands that correspond to structural groups within the molecules.

In the present study, we examined the UV absorption properties of five Russian seaweeds within the range of 240 to 720 nm. Among the seaweeds, *Gloiopeltis fucatas* and *Mazzaella* sp. had the highest absorption peaks between 280 and 360 nm, while the other species did not show any absorption peaks (Fig. 1). We also measured the UV absorption activities of 0%, 50% and 100% aqueous ethanol extracts of *Gloiopeltis fucatas* and *Mazzaella* sp. to identify active UV-aborbing materials. Among these, 50% aqueous ethanol extracts from *Gloiopeltis fucatas* and *Mazzaella* sp. had high absorption peaks between 280 and 360 nm. These extracts were purified via column chromatography and two compounds were isolated. Their structures were identified as shinorine and palythine through comparisons with spectral data and the literature

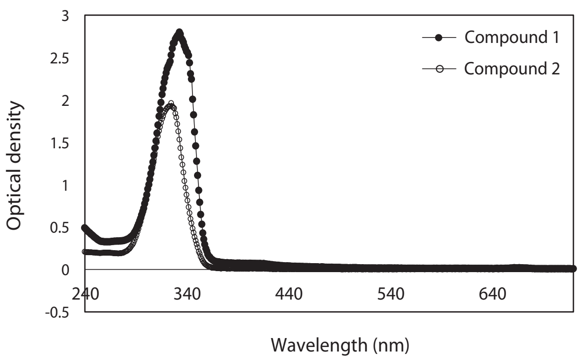

Fig. 3. Ultraviolet spectrum of the compound 1 and 2 isolated from *Gloiopeltis fucatas* and *Mazzaella* sp.

(Fig. 2) (Bandaranayake, 1998; Shick and Dunlap, 2002; Oyamada et al., 2008). This is the first time that these compounds have been isolated from *Gloiopeltis fucatas* and *Mazzaella* sp. Compound 1 and 2 showed maximum UV absorption peaks at 333 and 320 nm, respectively (Fig. 3).

Shinorine and palythine are MAAs. MAAs are colorless water-soluble secondary metabolites that have a cyclohexenone chromophore conjugated to a nitrogen substituent of either an amino acid or imino alcohol; they have been identified in fungal metabolites, cyanobacteria, red algae, and corals (Takano et al., 1978; Dunlap and Yamamoto, 1995; Bandaranayake, 1998; Shick and Dunlap, 2002). MAAs have high levels of absorption for UV-A and UV-B (280-400 nm) (Bandaranayake, 1998; Shick and Dunlap, 2002).

In conclusion, extracts from *Gloiopeltis fucatas* and *Mazzaella* sp. and MAAs derived from the extracts had strong UV absorption effects. Further study is needed to isolate and purify additional UV absorption materials from *Gloiopeltis fucatas* and *Mazzaella* sp. extracts.

Acknowledgments

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