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An Overview of Natural Sunscreens: Recent Research Updates

Tổng quan về kem chống nắng thiên nhiên: cập nhật một số nghiên cứu gần đây

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Abstract

Overexposure to UV rays is the main cause of several human skin conditions and diseases, such as sunburn, contact dermatitis, blistering, peeling, premature skin-aging, and even skin carcinogenesis. Therefore, dermatologists recommend daily use of sunscreen, particularly the broad-spectrum sunscreen which provides both UVA and UVB protection. However, some key ingredients in sunscreen can cause adverse skin effects or endocrine disruption. In particular, the release of active ingredients, such as oxybenzone in organic sunscreens, or nano-oxide in physical sunscreens into marine ecosystems causes significant adverse consequences, killing coral reefs, accumulating in aquatic species, and altering food sources. Therefore, recent studies focus on sunscreens derived from natural sources that are safe for human skin while simultaneously protecting coral reefs and aquatic life. This article presents some of the latest research on the application of naturally derived compounds that offer UV protection and are environmentally friendly for marine ecosystems.

Keywords: sunscreen, pollen, mycosporine-like amino acids (MAAs), Perilla frutescens, sun protection factor (SPF)

Tóm tắt

Tiếp xúc trực tiếp trong thời gian dài với tia UV là nguyên nhân hàng đầu gây ra một số bệnh về da ở người, như cháy nắng, viêm da tiếp xúc, mụn rộp, lột da, lão hoá sớm, thậm chí là ung thư da. Do đó, các chuyên gia da liễu đều khuyên dùng kem chống nắng hàng ngày, đặc biệt là các loại kem chống nắng phổ rộng có thể bảo vệ làn da khỏi tác động của cả tia UVA và UVB. Tuy vậy, một số thành phần chủ chốt trong kem chống nắng có thể gây ra các tác dụng phụ trên da hoặc gây rối loạn nội tiết. Đặc biệt, việc phát thải các thành phần như oxybenzone trong kem chống nắng hữu cơ hoặc nano oxide trong kem chống nắng vật lý đều gây ra các tác hại to lớn đến môi trường sinh thái biển, làm chết san hô, tích tụ trong các loài thuỷ sinh và biến đổi nguồn thức ăn trong hệ sinh thái biển. Do vậy, nhiều nghiên cứu hiện nay tập trung vào các kem chống nắng có nguồn gốc thiên nhiên, an toàn, lành tính với làn da đồng thời bảo vệ các rặng san hô và các loài thuỷ sinh. Bài này giới thiệu một số nghiên cứu mới nhất về ứng dụng của các hợp chất có nguồn gốc thiên nhiên có tác dụng chống tia UV và thân thiện với môi trường biển.

Từ khoá: kem chống nắng, phấn hoa, amino acid kiểu mycosporine (MAAs), hạt tía tô, chỉ số chống nắng (SPF)

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1. Introduction

Solar radiation is a continuous spectrum of electromagnetic radiation, categorized by wavelength into three main regions: ultraviolet (UV, 100–400 nm), visible light (400–780 nm), and infrared (> 780 nm). Depending on the wavelength, UV radiation can be classified into three main categories: UVC (100-280 nm), UVB (280-320 nm), and UVA (320-400 nm). The highly energetic UVC radiation and a major part of UVB (90-95%) do not reach the Earth's surface due to absorption by the ozone layer and atmospheric scattering. A minor part of solar UVB (about 10% of total irradiation), and UVA radiations, the one of lower energy but longer wavelengths, reach the ground.

Beyond its fundamental role in photosynthesis in plants, solar radiation directly influences and dictates the survival of animal species. In humans, moderate sunlight exposure provides energy, mediates vitamin D synthesis, supports metabolic and neurotransmission pathways, and enhances mental well-being. However, overexposure to high-intensity solar radiation, a prevalent condition in regions such as Central Vietnam, poses severe risks to human skin and eyes, mainly due to UV radiation [1]. UVB radiation, although constituting a smaller fraction (1.5%) compared to UVA (6.3% of total solar UV radiation), it is responsible for the burning impacts on the epidermis layer. It triggers immediate cutaneous responses, including erythema (redness), sunburn, blistering, and peeling. Furthermore, UVB directly stimulates melanocytes to hyperproduce melanin, culminating in stubborn hyperpigmentation, melasma, and freckles. Having lower energy and longer wavelength than UVB, UVA radiation silently penetrates clouds, glass, and thin clothing to reach the dermis layers of the skin. These radiations are responsible for the degradation of the structural integrity of collagen and elastin, two critical proteins that maintain skin firmness and elasticity, thereby inducing premature photoaging, manifested by deep wrinkles and sagging skin (Figure 1). In severe cases, both UVB- and UVA-induced reactive oxygen species (ROS) interact with epidermal cells, DNA, and lipids, leading to the oxidation and structural damage of skin layers. Consequently, this deep structural skin damage can ultimately culminate in photocarcinogenesis. Therefore, to achieve effective photoprotection, dermatologists recommend daily sunscreen use alongside physical shielding and avoiding outdoor activities during peak UV hours. Based on the chemical nature of the active ingredients, sunscreen can be classified into two groups, *i.e.*, inorganic, and organic sunscreen (Figure 2). The inorganic UV block molecules involve mainly nanoparticles of zinc oxide or titanium dioxide, while the organic UV filters are much more diverse in structure.

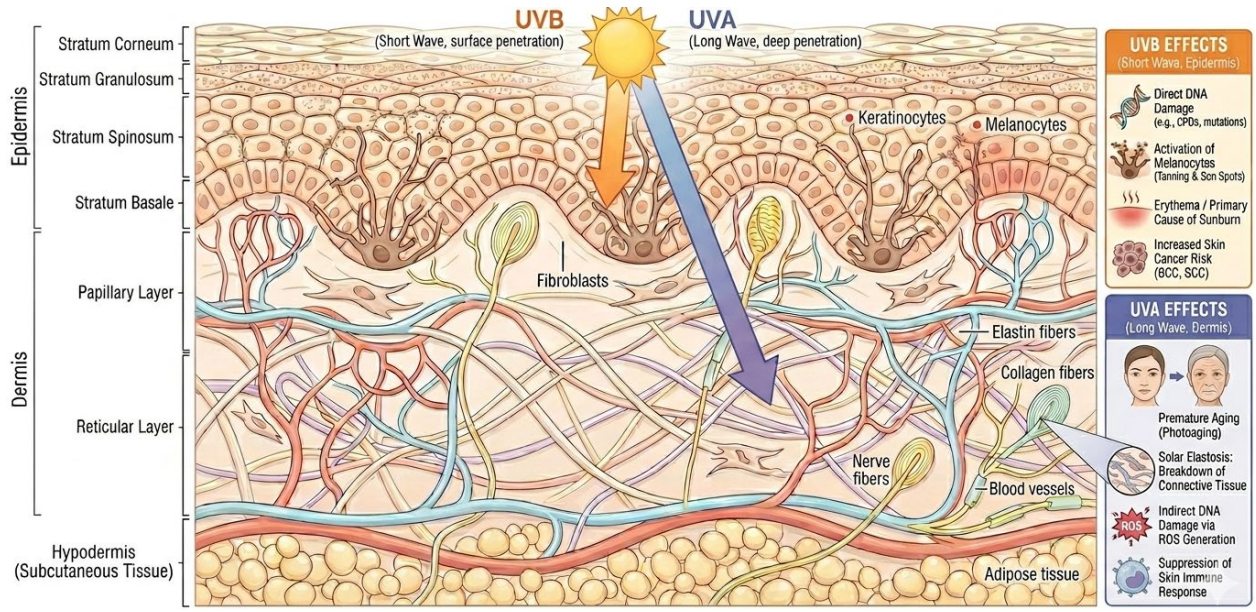


Figure 1. Harmful effects of UVR on human skin.

Currently, although the use of broad-spectrum sunscreens that protect against both UVA and UVB radiation is highly prevalent and generally considered safe, certain formulation ingredients may still cause adverse cutaneous reactions depending on individual skin type [2]. In particular, certain chemicals, such as oxybenzone, along with fragrances, are associated with contact dermatitis [3], erythema, or stinging sensations in individuals with sensitive skin or rosacea [4, 5]. Furthermore, several *in vitro* and *in vivo* studies indicate that the body can absorb small amounts of oxybenzone through the skin into the bloodstream. This has sparked controversies regarding its potential for endocrine disruption [6], although definitive large-scale clinical evidence has yet to establish a direct causal link. Crucially, the severe adverse impacts of sunscreens extend beyond human health to encompass marine ecosystems [7, 8]. Each year, an estimated 5,000 to 14,000 tons of sunscreen are washed off swimmers and into oceanic waters. This anthropogenic influx triggers silent ecological disasters. For instance, oxybenzone and octinoxate are the primary chemicals driving coral bleaching, a process that strips symbiotic algae of their hosts and deprives diverse marine organisms of critical habitats and food sources. Consequently, numerous regions worldwide, including Hawaii (USA), the US Virgin Islands, Palau, and national marine parks in Thailand, have enacted strict bans on sunscreens containing oxybenzone and octinoxate to safeguard coral reefs and marine biodiversity. Furthermore, inorganic sunblock nanoparticles, predominantly nano-zinc oxide and nano-titanium dioxide, used in physical sunscreens, easily penetrate the tissues of marine fauna due to their ultra-small dimensions. These particles bioaccumulate within tissues, inducing reproductive impairment and behavioral alterations across various species [9, 10].

Within this context, research focusing on natural, biocompatible sunscreen ingredients that are safe for both human health and marine ecosystems, commonly referred to as reef-safe sunscreens, is of great interest. This review highlights some recent breakthroughs and state-of-the-art developments in identifying, discovering, and integrating natural compounds into topical formulations. The objective is to develop sunscreens that offer potent photoprotection while remaining gentle on human skin and ecologically sustainable.

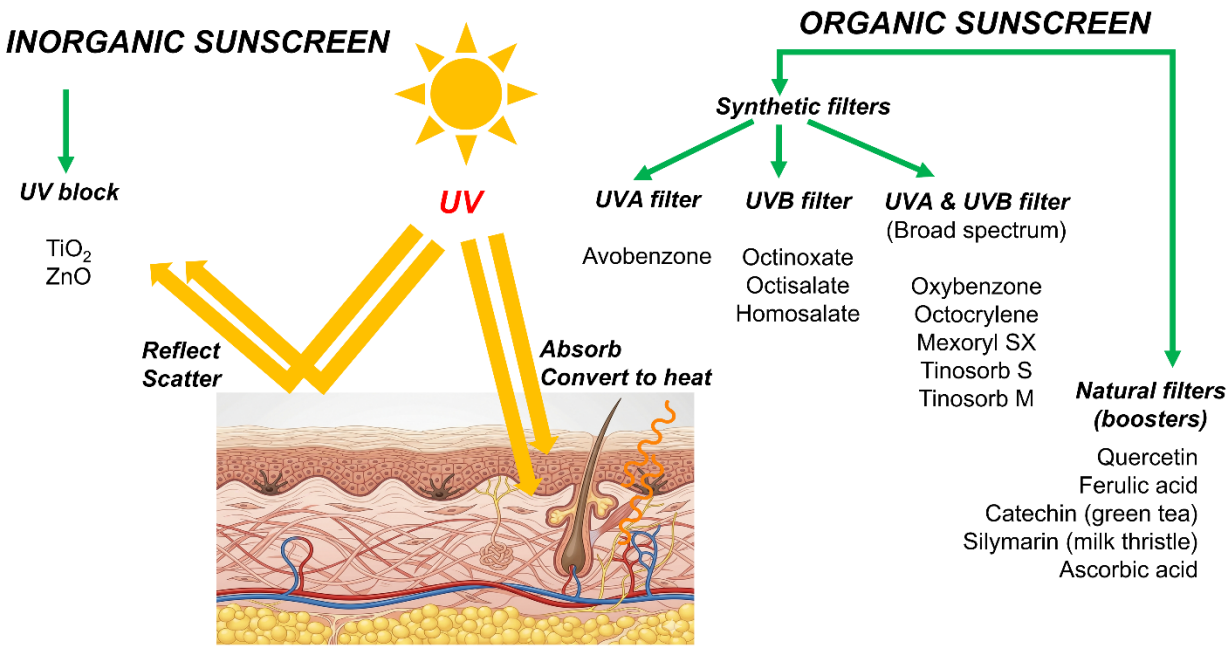


Figure 2. Active ingredients of inorganic and organic sunscreens.

2. Photoprotection activity of natural UV filters

One of the distinguishing properties of natural UV filters in comparison with the synthetic ones is their dual-action mechanism. In addition to their photoprotection function via direct absorption, reflection/scattering of UV radiation, and dissipation of excess energy as heat before it induces DNA damage, they simultaneously function as antioxidants and anti-inflammatory agents. Consequently, they maintain cellular resistance and neutralize reactive oxygen species (ROS) generated during UV exposure, thereby providing a secondary level of skin protection (Figure 3).

It is interesting that both humans and plants possess the self-photoprotection mechanism. In humans, endogenous photoprotection is mediated by melanin, a natural pigment synthesized via melanogenesis. Melanin, specifically its primary forms, eumelanin and pheomelanin, acts as a physical sunscreen [11]. By functioning as a physical filter that blocks both visible light and UV radiation, higher concentrations of melanin (manifested as darker skin pigmentation) afford superior photoprotection [1]. In plants, upon excessive UV exposure, the phenylpropanoid pathway is upregulated to produce higher yields of these secondary metabolites, specifically flavonoids and hydroxycinnamic acids [12]. These molecules accumulate in the vacuoles of the epidermal cell layer, and act as an optical filter, which absorbs UV radiation while allowing the visible light needed for photosynthesis to pass right through to the deeper layers of the leaf. For that reason, most of the natural antioxidants such as flavonoids and polyphenols found in plants are highly efficient secondary UV filters that can provide strong photoprotection effects [13-15]. For example, quercetin and (-)-epigallocatechin-3-gallate (EGCG), a prominent flavonoid found in green tea, are well-documented for their ability to enhance the photostability of co-formulated UV filters while providing substantial ancillary antioxidant benefits [16]. By exploiting the endogenous photoprotective mechanisms of plants, sinapoyl malate, extracted from *Arabidopsis thaliana* (thale cress), has been identified as a specialized molecule capable of absorbing UVB radiation and dissipating heat via a *trans-to-cis*

isomerization mechanism [1, 17]. Under UV radiation, sinapoyl malate accumulates in the upper epidermal vacuolar layers, thereby shielding the highly sensitive underlying leaf cellular structures from UV-induced photodamage. Another example involves silymarin, the extract from the seed of the milk thistle plant (*Sylibum marianum*), which contains mostly flavonolignans, silybin (A and B), isosilybin, silychristin and silydianin [18]. This extract is highlighted as a promising sunscreen agent that protects against UV-induced damage by preventing DNA mutations and reducing oxidative processes [19, 20].

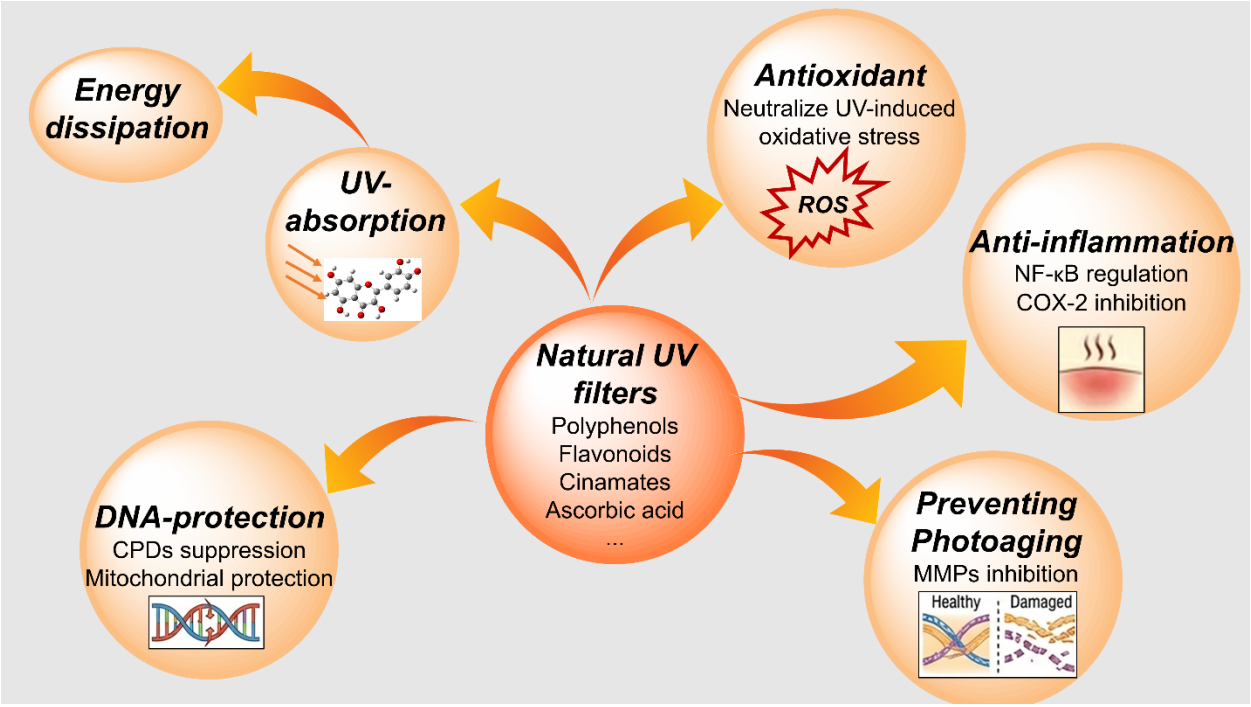


Figure 3. Photoprotection mechanism of natural UV filters.

In the cosmetics industry, although the natural organic UV filters are increasingly recognized as vital synergistic components in natural sunscreen formulations, they are rarely used as the sole sunscreen agent. First, most of these filters cannot provide a complete and efficient UV protection, often required with an SPF value in the range of 30-50. Second, increasing the concentration of these UV filters often degrades the formulation's quality. Most importantly, natural UV filters are generally less thermostable than the synthetic compounds, requiring the chilled storage conditions and reapplication more frequently than the synthetic ones for maximum sun protection. Therefore, to date, these molecules are mainly considered booster agents (0.5-2% of the formulation), providing a synergistic effect with inorganic nanoparticles or synthetic filters, and particularly offering additional bioeffects for healthy skin [13, 20].

3. Some updated research on natural sunscreens

3.1. UV filter from pollen

Nature uses pollen to safeguard plant genetic material from harsh solar radiation. This protection is primarily provided by the outer layer, the sporopollenin exine, which contains antioxidative and UV-absorbing phenolic compounds like p-coumaric acid and ferulic acid. Taking benefit from this, Yang *et al.* developed a specific process to convert hard Camellia or sunflower pollen into a topical microgel [21]. First, natural pollen is treated

with water, acetone, and diethyl ether to remove fatty contents and potential allergens. Then the resulting sporopollenin exine capsules (SEC) undergo a mild alkaline treatment (KOH) to create a suspension of pliable particulates (microgel) suitable for uniform coating on the skin. Interestingly, the phenolic compounds such as p-coumaric and ferulic acids are preserved throughout the chemical transformation from natural pollen to microgel, allowing the material to maintain its inherent UV-shielding capabilities. *In vitro* testing of camellia pollen microgels yielded an SPF of 27.31, comparable to some commercial sunscreens (SPF ~30) at the same concentration, with no cytotoxicity. Tests on human keratinocytes, i.e., HaCaT cells, showed that pollen microgels significantly suppressed the production of reactive oxygen species (ROS) induced by UVA and UVB exposure. In the presence of camellia microgel, cell viability remained above 98%, even 48 hours after intense UVB irradiation, whereas unprotected cells showed a drop to roughly 10%.

Using an ICR mouse model of UV-induced skin damage, the authors found that topical application of pollen microgel provided comprehensive protection. It successfully prevented epidermal thinning and collagen fiber denaturation in the dermis. The microgel suppressed the upregulation of pro-fibrotic and pro-inflammatory genes, such as IL-1b and IL-6, and prevented the depletion of mast cells, which are vital for skin healing. Moreover, microgel-coated skin surfaces remained approximately 5 °C cooler than bare skin under direct sunlight. This cooling effect is attributed to the microgel's ability to selectively filter visible and near-infrared thermal radiation, thereby limiting photothermal conversion.

Regarding the environmental effects, while commercial sunscreens often cause rapid coral bleaching, camellia and sunflower microgels keep *Acropora sp.* corals cultured in simulated seawater healthy and retain their color for up to 60 days. This result suggests that pollen microgel UV filters are environmentally friendly for the marine ecosystems.

3.2. UV filter from Perilla seed extract

A recent study by Chalermthiralert *et al.* described a sunscreen formulated with Perilla seed extract (*Perilla frutescens*) as a broad-spectrum, reef-friendly photoprotective agent that combines traditional UV filtration with bioactive skin benefits such as antioxidant and anti-aging properties [22]. The perilla seed extract is rich in phenolic compounds, triterpenoids, and polyunsaturated fatty acids, particularly linolenic acid (omega-3), with predominant concentration (about 45%). The authors indicated that maceration in 95% ethanol for one week is the most effective method, yielding an extract with an intrinsic SPF of approximately 22.61. A sunscreen emulsion containing 1% of perilla seed extract demonstrated high-performance protection with an SPF of 29.5 and a UVA protection rating PA++++. The critical wavelength of this emulsion was found to be 382 nm, exceeding the 370 nm required for broad-spectrum designation. Moreover, perilla seed extract serves as a natural SPF booster, providing effective protection while potentially reducing the concentration of synthetic chemical filters. Regarding dermatological safety, the extract is practically non-toxic to HaCaT keratinocyte cells with an IC50 value of about 12.9 mg/mL. Transepidermal water loss (TEWL) test in clinical trials shows that the formulation does not disrupt the skin barrier or cause erythema. In human volunteers, the perilla-enhanced sunscreen significantly reduced UV-induced melatonin levels and maintained skin brightness. It reduced the melanin index by 1.32%, whereas

the base formulation increased a melanin by 0.64%. Moreover, the perilla formulation also mitigates photoaging by downregulating matrix metalloproteinases (MMPs), which are responsible for collagen degradation and wrinkle formation. Overall, the perilla sunscreen exhibits an Environmental Safety Score (S score) of 80.31, meeting the criteria for a "reef-friendly" product.

Although the perilla extract offers dual benefits, human skin photoprotection and environmental safety, there remain several limitations regarding the stability of the formulation. The high content of unsaturated fatty acids in the perilla seed extract makes the formulation susceptible to oxidation and yellowing when exposed to heat and light over time. The storage at room temperature and in chilled conditions is stable but high temperature (> 45 ºC) and extended periods can lead to phase separation and a decrease in the viscosity of the formulation.

3.3. UV filter from microorganisms - Mycosporine-like amino acids (MAAs)

Mycosporine-like amino acids (MAAs) are the most common class of natural UV-absorbing compounds found in marine organisms, such as cyanobacteria, microalgae, and macroalgae (Figure 4). These small, water-soluble molecules act as high-performance nature's sunscreens by absorbing solar radiation and protecting organisms from the harmful effects of UV exposure. MAAs have maximum UV absorption peaks between 310 and 365 nm, which cover much of the UVA and UVB spectrum. They possess high molar extinction coefficients (ε = 28,100 - 50,000 $M^{-1}cm^{-1}$) and the unique ability to dissipate absorbed radiation as heat through rapid structural transformations without generating harmful reactive oxygen species (ROS). These compounds are notably photostable and resistant to various abiotic stressors, including heat (up to 60 ºC) and pH changes, making them ideal for long-term solar protection [23].

Similar to other natural UV filters, MAAs also offer several bioactive skin benefits beyond their direct UV-filtering action. MAAs exhibit high antioxidant activity, scavenging superoxide anions and inhibiting lipid peroxidation caused by UV-induced ROS [24]. For example, mycosporine-glycine exhibits an eight-fold higher antioxidant activity when compared with ascorbic acid [24, 25]. Porphyra-334 also acts as an antioxidant in human skin fibroblasts, showing a dose-dependent reduction in intracellular UVA-induced ROS generation [26]. Mycosporine-glycine and shinorine have been shown to inhibit the expression of the COX-2 gene, which is a key marker of tissue inflammation [27]. Furthermore, mycosporine-glutaminol glucoside (MGG) can protect human fibroblast cells from UV-induced death and block the formation of DNA lesions such as cyclobutane pyrimidine dimers (CPDs) [28].

While isolated MAAs typically provide minimal sun protection with SPF values between 4 and 6, they are powerful SPF boosters when combined with other ingredients [29]. For example, blending synthetic MAAs derivatives at 10% concentration has been shown to enhance the efficacy of synthetic filters like avobenzone and octinoxate by two to three times. Due to their safety and efficacy, MAAs are used in luxury skincare products and toiletries. Commercial examples include Helioguard 365 and Helionori, amongst others. Helioguard 365, which contains porphyra-334 and shinorine extracted from the red alga *Porphyra umbilicalis*, has been shown to boost SPF from 7.2 to 8.2 and significantly reduce wrinkles and lines after four weeks of use. Helionori, another commercial product containing palythine, porphyra-334, and shinorine, provides

maximum protection for DNA and lipid membranes by increasing cell viability up to 57 and 135% in cultures of keratinocytes and fibroblast cell lines.

Finally, MAAs gain considerable attention for being eco-friendly to the marine ecosystem. They are natural, biodegradable, and conjugable to biopolymers or nanoparticles, e.g., chitosan, to improve their stability, water resistance, and delivery for wider use in luxury cosmetics and toiletries.

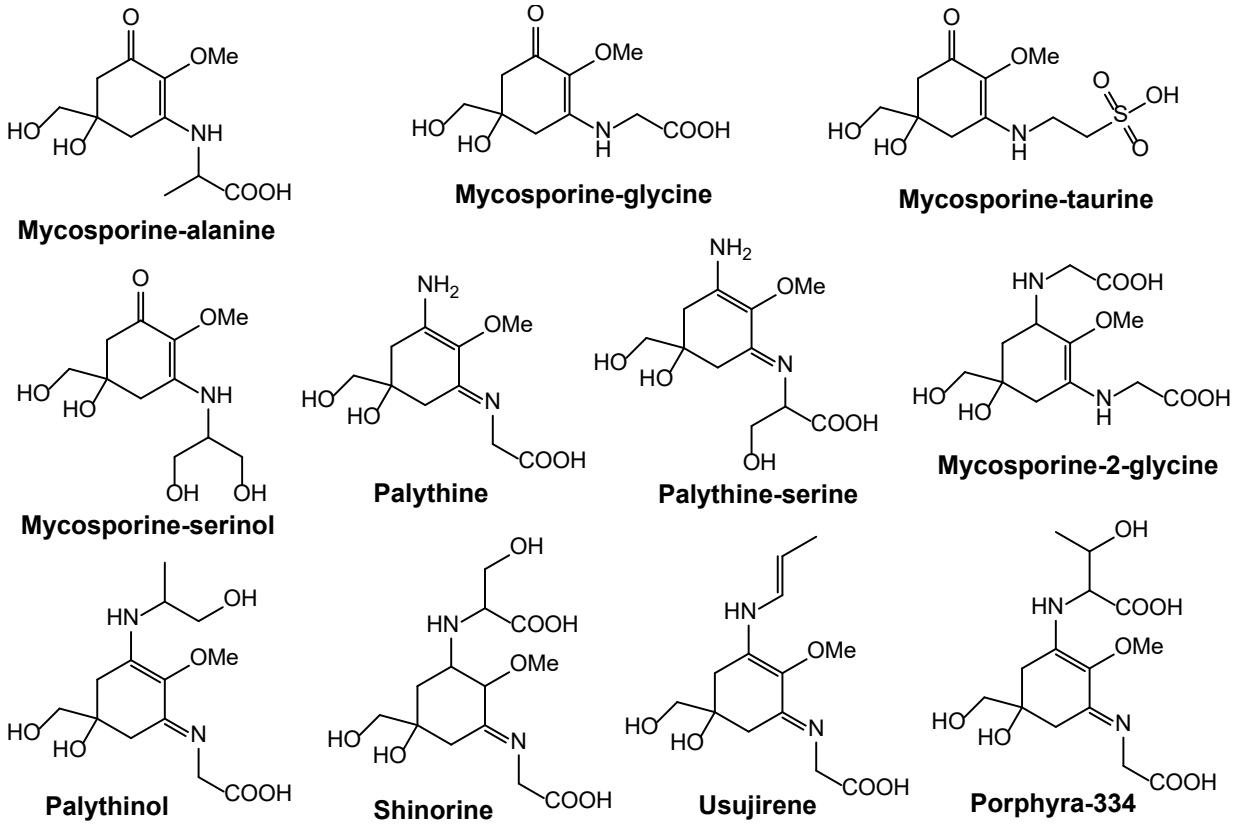


Figure 4. Structures of some MAAs.

4. Conclusion

In conclusion, the natural UV filters are increasingly used in sunscreen for their multifunctional photoprotection activities. Besides the direct UV-absorption, they offer different indirect biological protections. They can function as antioxidants, anti-inflammatories, cell proliferation activators, skin cell renewal stimulators, and even anti-cancer agents. Particularly, natural UV filters attract the attention of environmentalists for their biodegradability and friendliness to coral reefs and marine ecosystems. Recent research on perilla seed extract, pollen-derived microgels, and mycosporine amino acids-based sunscreens is among the notable research findings. Although isolated natural extracts often provide low to medium intrinsic SPF values, they are effective as booster agents. Incorporating them into formulations allows for a significant reduction in the concentration of synthetic chemical filters, which minimizes the risk of skin irritation, systemic absorption, and environmental toxicity. The main limitation of natural UV filters lies in their stability over time and other environmental factors, such as temperature, pH, and chemical oxidation. Therefore, future development should focus on advanced delivery systems, such as nanocarriers and microencapsulation, to promote the use of natural sunscreen in the cosmetic industry.

Author declaration

The author used AI-assisted imaging in this article.

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