Lignin-Based Sunscreens

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In light of recent research, a vast majority of the commonly-used broad-range sunscreens fail to provide adequate protection against portions of sunlight that age and otherwise damage the skin, including visual light. In addition, many of their UV-active synthetic components that easily pass through effluent wastewater treatment plants have been linked to coral bleaching and other negative effects on marine ecosystems. These compounds may also penetrate the skin and are suspected of causing allergies and acting as hormone disruptors. Technical lignins are phenolic biopolymers obtained in large quantities as by-products of chemical pulping and biomass refinery processes that have been found to be of low toxicity to normal mammalian cells. Because of their polymeric nature, they should be much easier to remove from wastewater than the small synthetic UV-active compounds used in chemical sunscreens. Provided that they have the right chemical structure and are converted to nanoparticles, they display significant absorbance in the UV- and visual wavelength areas of sunlight. Most commercial sunscreens are whitish because of perceived consumer preference and for this reason, contain only compounds that have insignificant absorbance in the visual region of sunlight. Coupled with their ability to act as antioxidants and preservatives, lignin-based sunscreens offer themselves as a bio-based and safe multi-functional additive for high-SPF (Sun Protection Factor) sunscreens and cosmetics. This review addresses the state-of-the art of lignin-based sunscreens.

sunscreen | Lignin | UV light | antioxidant | antimicrobial | preservative | nanoparticles

1. Background

Sunlight is the portion of solar electromagnetic radiation that reaches the Earth's surface and includes ultraviolet (UVB, 290–320 nm and UVA, 320–400 nm), visual (VIS, 400–700 nm) and infrared (IR, 700–1000 nm) wavelengths, all of which induce photoaging and can cause skin cancer [1][2][3]. While limited exposure to sunlight is beneficial [4], clinical investigations support the application of broad-spectrum (UVB + UVA) sunscreens to mitigate the damage associated with prolonged or frequent sun exposure [3].

The effectiveness of sunscreens in preventing UVB-induced sunburn is denoted by their Sun Protection Factor (SPF). For example, an individual wearing the recommended dose of SPF 15 sunscreen is able to stay in the sun without suffering sunburn 15 times as long as they could if not wearing sunscreen [5]. The UVB absorbance of sunscreens increases non-linearly with an increase in their SPF and those with moderate-to-high SPFs of 15–50 block 93–98% of UVB radiation when applied as recommended [3]. Broad-spectrum sunscreens also block a significant portion of the skin-aging UVA radiation. In the US and EU, sunscreens claiming broad-spectrum UV protection must have a so-called critical wavelength of 370 nm or more, meaning that 10% of the protection that the sunscreen offers has to be for UVA wavelengths above 370 nm. This ability is represented by the UVA Protection Factor (UVA-PF). The EU also requires that the UVA-PF offered by a broad-spectrum sunscreen be at least one third of the labelled SPF.

SPF is determined in vivo based on the UV energy required to produce a minimal erythemal dose (MED) in sunscreen-protected skin (applied at 2 mg/cm^2) divided by the UV energy required to produce a MED on unprotected skin [3][6]. To determine sunscreen SPF in vitro, UVB transmittance is measured through a layer of sunscreen spread at a standard dose (2 mg/cm^2) on a UV-transparent slide. UVA-PF can be determined by similar in vivo and in vitro methods.

Broad-spectrum chemical sunscreens of SPF 15 or higher typically contain over 20% of various UVB- and UVA-absorbing synthetic organic compounds [5][7], while mineral-based (physical) sunscreens usually have somewhat lower levels of titanium dioxide (TiO_2) and/or zinc oxide (ZnO) nanoparticles that scatter, reflect and absorb UV rays. It should be noted that the so-called herbal or natural sunscreens [8][9], formulated without synthetic chemical UV absorbers, usually contain these metal oxides as the main UV active component while their plant-based components mainly act as antioxidants and emollients.

An estimated 14,000 tons of sunscreen originating from wastewater effluent discharges, water-based recreational activities and other sources [10] end up in the world's oceans every year. Chemical UV absorbers such as oxybenzone and octinoxate commonly used in chemical sunscreens have come under increased scrutiny because of their deleterious effects such as coral bleaching on marine ecosystems and their high environmental persistence [11][12][13][14]. In consequence, the sale of sunscreens containing these UV active components has already been banned in ocean-bordering countries such as Australia and island regions such as Hawaii [13][14]. The fact that chemical UV absorbers are small molecules that are poorly captured by wastewater treatment plants aggravates the problem. Regarding the environmental impact of physical sunscreens, ZnO (but not TiO_2) nanoparticles have been found to be detrimental to coral reefs [15].

The use of chemical sunscreens results in systemic exposure to their small UV absorbers that are readily absorbed through human skin and remain in the body for extended periods [16]. Many of them are known to cause skin rashes in sensitive individuals and have been shown to act as hormone disruptors in animal trials. However, evidence is lacking on the severity of any hormone-disruptive effects in humans. Nanoparticulate UV filters of physical sunscreens are considered safer to humans than chemical sunscreens despite conflicting evidence regarding their ability to penetrate human skin [12]. In addition, systemic exposure to harmful sunscreen ingredients can occur by inhalation of sprayable sunscreens.

Besides the UV active components of sunscreens, concerns have been raised for the safety of their synthetic antioxidants and preservatives [17][18][19]. There is clearly scope to improve not only the sunlight protection provided by commercial sunscreens but also their environmental and user safety. The benefits and challenges of potentially safer lignin-based sunscreens are addressed below.

2. Technical Lignins as Sunscreen Antioxidants

As mentioned earlier, UV, VIS and even IR wavelengths of sunlight accelerate skin aging by generating ROS that can cause oxidative damage to skin. However, besides protecting the skin by absorbing sunlight across its whole spectrum, lignin also offers a second level of protection from sunlight by neutralizing ROS. By the same token, lignin can help prevent rancidity of lipids and other sunscreen ingredients that are susceptible to oxidation. The antioxidant properties of lignin depend on the substituents of the aromatic ring and side chain structures. Resonance effects (-C=C- and -C=O conjugation with the aromatic ring) and electron-donating functional groups (phenolic hydroxyl and methoxyl) tend to increase antioxidant properties while electron-withdrawing functional groups (carbonyls) display an inductive effect that reduces antioxidant properties [20][21][22][23][24][25][26]. As with UV absorbance, the antioxidant activity of lignin per mass unit can be increased by demethylation of methoxyl groups [27][25] to increase the content of phenolic hydroxyls that may be oxidized to phenoxy radicals. This process is the main antioxidant mechanism of lignin and, depending on the lignin structure, phenoxy radicals may regenerate the phenolic hydroxyl, which can then be oxidized again [25]. Lignin whose phenolic hydroxyls have been etherified has no antioxidant activity [26]. Removal of moieties such as aliphatic hydroxyl that have little direct impact on antioxidant activity can also improve antioxidant activity per mass unit of lignin. In terms of electron-withdrawing structures (-C=C- and -C=O) of the lignin side chains, their deactivating inductive and activating resonance effects clash and the net result is hard to predict [28]. The parameters of alkaline pulp cooking can be optimized to maximize the antioxidant properties of the dissolved lignin [29]. The antioxidant activity of kraft lignin and many other technical lignins is higher or similar to that of the commercial antioxidants butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) [30][31][32][33][34][35]. While these compounds that are used in commercial sunscreens and cosmetics have been found to be non-carcinogenic [36], they have raised health concerns, warranting further investigations into their potential effects on menopause [17]. Because of this radical-scavenging antioxidant activity [31][32], the need for additional and potentially harmful synthetic antioxidants is reduced or eliminated for lignin-based sunscreens.

3. Technical Lignins as Sunscreen Preservatives

Sunscreen lotions are equipped with synthetic preservatives such as phenoxyethanol, hydroxybenzoates and triclosan to inhibit the growth of harmful bacteria that would otherwise spoil the sunscreen [19]. Similar to commercial chemical UV absorbers, some of them have been recognized as environmental pollutants that largely originate from rinse-off skin-care products such as sunscreen lotions and are difficult to remove at wastewater treatment plants [18][19]. However, technical lignins have demonstrated significant antibacterial and antifungal activities against common spoilage and pathogenic microorganisms [37][38][39]. The antibacterial properties are mostly attributed to phenolic hydroxyl groups that damage the bacterial cell walls, inducing lysis and leakage of the cell contents. The antimicrobial activity of technical lignins suggests a reduced requirement for additional synthetic and possibly deleterious preservatives for lignin-based sunscreen products. However, to confirm any preservation effect of lignins in sunscreen and cosmetic formulations, this topic should be directly addressed in a future investigation.

4. Safety of Technical Lignins

Unlike the UV-active, antioxidant and preservative ingredients of commercial sunscreens, most of which are small monomeric molecules passing easily through filtration and other purification stages of wastewater treatment plants [40], the polymeric technical lignins that are insoluble in water at pH levels below 9 would be far easier to remove from wastewater and would thus contribute little to marine pollution caused by effluent discharges of wastewater treatment plants.

Lignins show low cytotoxicity to normal mammalian cells but a certain degree of cytotoxicity to cancerous cells [30][32][34][35][39][41]. However, it was recently reported [30] that mammalian cell proliferation may be negatively impacted with prolonged exposure to high lignin doses.

On balance, lignin sunscreens offer themselves as a relatively safe option for both the environment and consumers of sunscreens and SPF cosmetics.

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