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Dangers of UV Radiation and Melanin as a Photoprotectant: A Review

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Abstract - *Some of the harmful effects of ultraviolet radiation like DNA photodamage, sunburn and erythema, photodamage, photoaging, photocarcinogenesis and damage to the eye are listed and explained in brief in this article. The use of melanin and melanin-infused products that are either already developed or can be developed to overcome these conditions is also presented in this article.*

Key Words: Ultraviolet radiation, sunburn, photodamage, photocarcinogenesis, melanin, photoprotection.

1. INTRODUCTION

Ultraviolet radiation (UVR) from the sun has numerous implications when considering its various effects on the life on earth. However, the adverse effects of this very life sustaining solar radiation have been studied about in great detail and cannot be ignored. With the ozone layer being harmed, the extent of damage caused by UVR has increased greatly in recent times. A number of solutions for this problem have been proposed and melanin is on top among them. Melanin is a naturally found pigment and has been found to have immense importance in various applications. It shows properties like anti-oxidant activity, anti-microbial activity, radioprotective activity as well as the most promising photoprotective properties. These properties when taken into consideration together makes melanin a very promising polymer for various cosmetic, environmental, medical and biomedical uses. The polymer and the materials derived from it are biodegradable and this quality should be given high priority in today's time where anything and everything that is less damaging to the environment than conventional materials should be the go-to option. In this article, we have reviewed some of the damages caused by UVR and have attempted to list some of its solution using melanin and melanin-infused products.

2. LITERATURE REVIEW

To understand the importance of photoprotective properties of melanin, it is first necessary to understand the harm UV radiations can cause to humans as well as other objects.

2.1 Most common damaging effects of UV on humans:

2.1.1 UV induced DNA damage:

In humans, ultraviolet radiation has a number of effects ranging from short-term (acute) to long-term (chronic). Some of the effects are briefly explained below:

UVR exposure damages DNA and this has now been established. UVA penetrates deep into the skin and the damage is done by the Reactive Oxygen Species (ROS), which leads to single-strand break in the DNA crosslinks. UVB causes damage by increasing the chemical energy of molecules causing them to form abnormal bonds between adjacent pyrimidine molecules in the same strand of the double helix. This mainly causes the formation of thymine dimers (also other base pair dimers in small amounts), that are called photoproducts, which forms a bulge in the normal DNA strand structure, thus blocking normal binding with nucleotides on the opposite strand.[1] Photodamage to DNA in critical genes can cause unwanted and harmful mutation in the cells like alteration of the genes associated with cell cycle, apoptosis, etc. can lead to unfit cells not being stopped at cell cycle checkpoints and healthy cells undergoing apoptosis. All of these eventually lead to formation and propagation of cancerous cells.

2.1.2 Sunburn and Erythema:

Erythema is the reddening of the epidermis due to over-exposure in the sunlight. The ultraviolet rays in sun particularly UVB causes this. UVA also has an effect but in significantly higher amounts (800-1000 times as required for UVB). This causes certain blood vessels near the skin surface to dilate, resulting in excess volume of blood being supplied to the skin. This makes the skin look red and inflamed.[2] The induction of erythema brings about a lot of changes at the cell and molecular levels. Apoptotic keratinocytes, also called as, sunburn cells start to appear.[3] These are the keratinocytes that show premature keratinization. Such cells are bound to enter the apoptotic pathway. If this is not done and if the cell skips the checkpoint during cell cycle, it will lead to the formation of melanoma cells.

2.1.3 Photoaging:

Photoaging also called as photodamage is a complicated process in which the primary causative agent is the oxidative stress resulting from UVR generated Reactive Oxygen Species [ROS]. It is mostly caused by UVB radiation. UVA, though permeates deeper into the layers of skin, the harm caused by it is minimal as compared to UVB.[2] Long-term exposure to UVR over many years have been shown to induce changes at the cellular level in human skin. The extent of the damage depends greatly on the degree of exposure and the phototype of skin, i.e. the amount of melanin present in the skin.

Skin Type	Sunburn history	Tanning history
I	always	never
II	always	minimal
III	moderate	gradual & uniform
IV	minimal	always
V	rare	profuse
VI	never	Deep pigmented tan

Tabe 2.1 Phototype of skin as per Fitzpatrick scale (45-60 mins of exposure)

It has been seen that high exposure to UVR affects the production of skin anti-oxidants. It leads to the depletion of endogenous anti-oxidants, which over a period of time leads to signs such as coarse, dry, wrinkly skin and pigmentation spots. This happens as a result of the skin losing its property of elasticity as continuous UVR exposure decreases the amount of mature collagen fibre present in the skin.[4] These effects are much more pronounced in parts that are constantly exposed to the sun such as back of the neck, cheeks, nose and arms.

2.1.4 Photocarcinogenesis

Photocarcinogenesis is a complex, multistage process that involves numerous sequential steps like initiation, promotion and progression and ultimately results in the cancer of skin. The amount of radiation, its intensity and the duration of exposure, all play a decisive role in the eventual appearance of the condition.[5] It is conventionally believed that the damage to DNA caused by UVR (photodamage) is the initiation and sunburn/erythema helps in its promotion.[6] The mutations caused by UVR are mainly repaired by the cells by Nucleotide Excision Repair.

This repair mechanism is absent in the case of patients with the condition Xeroderma Pigmentosum (XP), characteristics of which include very high photosensitivity and susceptibility to skin cancer.

The mechanism is as follows:

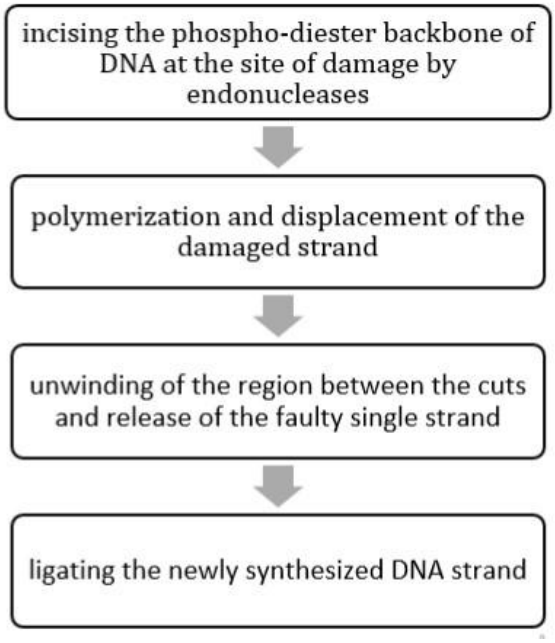

Fig-2.1: Nucleotide Excision Repair (NER) Mechanism

2.1.5 Photodamage to the eye:

Long term exposure in sunlight can have adverse effect on the lids, cornea and retina of the eye. Conditions like cataracts and Welder's flash (photokeratitis or arc eye) are prevalent in people who have history of excessive outdoor work and hence excessive exposure.[7]

2.2 Some of the damaging effects of UV on other objects:

UV, natural and emitting from artificial light sources, such as incandescent lamps, fluorescent lamps and Light Emitting Diodes (LEDs) have a number of derogatory effects on objects illuminated by it such as books kept in libraries, artefacts in museums and genealogical archives, leather and other organically derived fabrics as well as furnishes made of wood. Long term exposure and high intensity leads to discolouration and bleaching of pigments and dyes in the objects and thus decreases the value and networth of the objects. Yellowing of paper and degradation of organic materials are some of the harmful effects of UVR exposure. All of the damage done is cumulative and irreversible as the original items lose their authenticity with frequent restorations.[8][9] Since, the various harmful effects of UVR have been widely studied upon and understood in depth, various photoprotective measures have been proposed to limit the extent of damage caused. We are going to look at one such agent, melanin, which is humans' as well as many other organisms' innate defence mechanism for reducing the effects of UV damage.

2.3 Melanin

Melanins are a group of natural pigments that range from yellow-red (pheomelanin) to dark brown- black (eumelanin) formed by oxidative polymerization found in most organisms. It is synthesized in specialized cells called the melanocytes, which have melanosomes, the organelles that synthesize the pigment.

The pigmentation of human skin can be attributed to 2 factors namely intrinsic skin colour and facultative skin colour. Intrinsic colour is the pigment that is as a result of the genetic constitution of an individual, whereas, facultative colour is the generation of melanin in accordance to the individual's level of exposure to the sun (suntan).[10] The amount of melanin produced on exposure to UVR depends on the skin phototype of individuals.

2.3.1 The mechanism of melanin protection:

In the epidermis, melanin concentration and distribution plays an important role in determining the extent of transmission of the incident radiation through the outer layers. This distribution depends upon the genetically bestowed capacity of an individual's intrinsic and facultative skin colour.[11] The pigment also scavenges light-induced free radicals.

In other objects and on their surfaces, melanin acts as a photo-screen by scattering UV light.

3. SOLUTIONS PROPOSED TO OVERCOME THE PROBLEMS:

3.1 Photothermal Therapy (PTT):

Melanoma, or cancer in general has become a topic of the highest concern because of the number of people being diagnosed with it worldwide. As a result, many novel clinical measures are being researched upon that can deliver the cure with minimum side effects. PTT is one such approach with high efficiency and low side effects. In this approach, melanins from various sources act as agents to deliver the therapy. The agents possess high light to heat conversion properties and are injected into cancer patients. Then, using target recognition technology, they are assembled at the site of tumour. These agents then kill the cancerous cells by converting light energy to heat energy under the irradiation of a localized near-infrared (NIR) laser.[12]

3.2 Application in Cosmeceuticals:

From the photoprotection of skin against UV radiation point of view, the study of melanin and its extraction from the microbial origin is now being incorporated in research worldwide; especially in the cosmetic industry for its antioxidant properties and ability to absorb UV and visible light.[13][14]A research study carried out by Geng et al[15] on bacteria-derived melanin and its photoprotective ability showed that the melanin so obtained blocked UVA irradiation at a specific concentration range and also displayed efficient scavenging the activity of ROS, thereby making it a promising ingredient to be introduced in sunscreens. Amongst the two main types of melanin; pheomelanin and eumelanin, the latter has exhibited to be a promising physical barrier that can scatter UV and absorb 50% to 70% of UV radiation thereby having an efficiency of about 2-4 sun protective factors (SPF).[3] Topically applied melanins have the potential to provide protection both by absorbing and scattering UV radiation, as well as by neutralizing free radicals.

Also the properties of eumelanin being able to form emulsions with lipids and its water insolubility can be manipulated to make it more or less soluble in water as per product composition; thereby making it a promising ingredient in different formulations of sunscreen. However, the dark colour of the resulting product due to the incorporation of eumelanin has restricted its use sunscreens. This has led to the search of various other sources from which compounds exhibiting similar properties to that of eumelanin and are now being studied extensively.[14]

Apart from the traditional topical sunscreen various forms of non-topical sunscreen in the form of pills and drugs consisting of compounds analogous to melanin are being studied. One such drug is known as Scenesse created by the company Clinuvel Pharmaceuticals based in Melbourne, Australia is chemically similar to α-melanocyte-stimulating hormone (α-MSH) and when ingested, it stimulates melanocytes to synthesize melanin due to sun exposure. Although having the ability to act as a non-topical sunscreen, the drug instead will be only targeted towards the treatment of severe sun damage.[16]

This indicates that even if many ongoing studies are exploring the application of melanin in sunscreen of different formulations, many other factors such as the aesthetic appearance of the product, the efficiency level of its photoprotection, and promising results supplemented by clinical trials are yet to be worked upon.

3.3 Eyewear:

Melanin infused lenses for sunglasses or regular spectacles have been tested and have been found to be efficient in reducing the amount of UV rays exposure to the eyes. The melanin in the lenses filters out the harmful UV rays. This sort of a contraption is especially useful for aged people whose natural synthesis of melanin decrease with old age. It has also been noted that infusion of melanin in lenses increases the perception of true colour by blocking the scattering of blue light.[17]

3.4 Eumelanin infused light bulbs and photoprotective shields:

With a strong photo-protective ability, optical and electrical conductive properties of eumelanin are being explored for its incorporation in organic-based electronic devices and biomaterials. Due to its distinctive broad range UV absorption spectrum, hydration based electrical conductance, easy availability from a wide range of microbial and plant-based sources, and biodegradability, eumelanin can be engineered to form thin, adhesive films that can have a wide range of applications in upcoming electronic devices and biomaterials.[18] However, due to a lack of sufficient information regarding the actual structure of melanin, synthetically derived eumelanin such as 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid derivative (DHICA) are being studied for their UV shielding and electrical conductance properties.[19] Eumelanin derived from cuttlefish Sepia in PVA showed almost 100% blocking ability against UVC and UVB whereas only 30% blocking capacity against UVA. On further suspension in a polycarbonate (PC) matrix, better melanin dispersion and greater transparency of the material was observed at minuscule particle size.[20] In order to obtain a much better shielding ability against UVA without altering the material transparency, Wang et al proposed that PVA- dopamine nanocomposite films infused with polydopamine melanin-hollow(PDA-h) nanoparticles showed better shielding and transparent material properties as compared to polydopamine melanin-solid (PDA-s) nanoparticles.[21] These research findings have paved a way to introduce eumelanin as a component of (Organic light-emitting diodes) OLEDs and UV shields that can be installed in residential buildings, museums, and libraries where it can be used in conjunction with glass sheets to prevent harmful radiations from the sun causing damage to humans as well as objects such as old books, archives, and artefacts of historical, scientific, artistic or cultural importance. Moreover, due to the complexity of the structure of eumelanin and its electrical conductance properties the application of eumelanin in photoprotective UV shields and bioelectrical devices such as light bulbs is still in the research phase so as to gain more concrete evidence to have a robust practical utilization. [20][21][22]

4. SUMMARY:

Melanin is widely available in nature and has abundant sources. Even the synthetic production of melanin is cheap. It is biodegradable as well as highly biocompatible. These are the properties of melanin that have been researched upon to some extent and the results achieved have been quite promising until now. More and in-depth study and research still needs to go into this field of melanin and its derived materials.

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