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The role of melanin as protector against free radicals in skin and its role as free radical indicator in hair

Thomas Herrling [a,*], Katinka Jung [b], Jürgen Fuchs [c]

[a] *Department of Medical Physics, University of Applied Sciences TFH Berlin, Luxemburger Straße 10, 13353 Berlin, Germany*
[b] *GEMATRIA TEST LAB, Pestalozzistr. 5–8, 13187 Berlin, Germany*
[c] *Department of Dermatology, University Clinic Frankfurt, Frankfurt, Germany*

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Abstract

Throughout the body, melanin is a homogenous biological polymer containing a population of intrinsic, semiquinone-like radicals. Additional extrinsic free radicals are reversibly photo-generated by UV and visible light. Melanin photochemistry, particularly the formation and decay of extrinsic radicals, has been the subject of numerous electron spin resonance (ESR) spectroscopy studies. Several melanin monomers exist, and the predominant monomer in a melanin polymer depends on its location within an organism. In skin and hair, melanin differs in content of eumelanin or pheomelanin.

Its bioradical character and its susceptibility to UV irradiation makes melanin an excellent indicator for UV-related processes in both skin and hair.

The existence of melanin in skin is strongly correlated with the prevention against free radicals/ROS generated by UV radiation. Especially in the skin melanin (mainly eumelanin) ensures the only natural UV protection by eliminating the generated free radicals/ROS. Melanin in hair can be used as a free radical detector for evaluating the efficacy of hair care products.

The aim of this study was to investigate the suitability of melanin as protector of skin against UV generated free radicals and as free radical indicator in hair.

Keywords: Skin; Hair; Melanin; UV irradiation; Free radical; ESR spectroscopy

1. Introduction

The sun emits a wide spectrum of electromagnetic waves of which ultraviolet light (UV) is the most aggressive towards cellular compounds. Large amounts of UVB and UVC are screened out by ozone, the major photoprotective agent formed in earth's atmosphere. Hence, solar UV radiation that reaches the earth as well as our skin, is composed of 5–10% highly energetic UVB (280–320 nm) and 90–95% UVA (320–400 nm) which is less energetic, but penetrates the skin deeper (Fig. 1) due to its longer wavelength. In contrast, hair is fully penetrated by both UVA and UVB.

Both UVA and UVB irradiation are very damaging to skin and hair. Depending on wavelength, UV damage occurs via different mechanisms. UVA mainly produces free radicals (FR)/reactive oxygen species (ROS) though interaction with endogenous photosensitizers. These ROS will cause indirect damage to DNA, proteins and membranes. ROS is believed to be involved in photodamage of dermal connective tissue cells and proteins. On the contrary, DNA with its aromatic, heterocyclic bases is a strongly absorbing chromophore for UVB (absorption maximum at 260–265 nm). Direct absorption of the UVB photons leads to disruption of DNA, with cyclobutane pyrimidine dimmers (CPD) and pyrimidine pyrimidone photoproducts as a result.

Hence, both UVA and UVB play a role in the pathogenesis of photosensitive diseases such as polymorphic light eruption (PLE), sunburn, immunosuppression, photoaging and even photocarcinogenesis.

So, free radical reactions in the skin are one of the most interesting subjects of skin research because they are involved in various skin diseases, including skin tumors, skin wrinkling and

* Corresponding author. Tel.: +49 30 43737764; fax: +49 30 43737765.
E-mail address: email@gematria-test-lab.de (T. Herrling).

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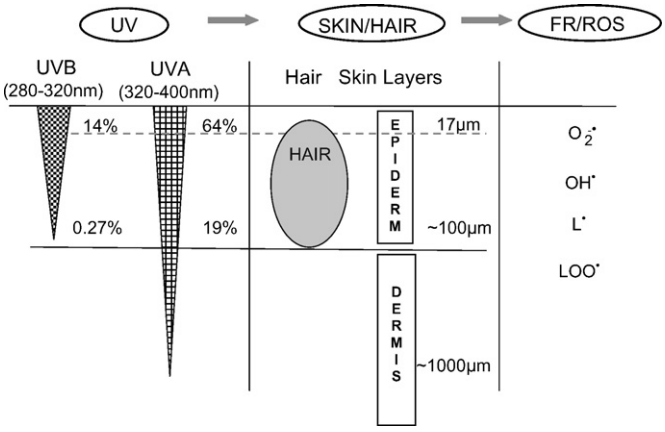

Fig. 1. Schematic exposition of the penetration depth of UVA and UVB radiation in the different layers of the skin and the hair and the presentation of the types of free radicals which are involved in this process.

skin aging [1]. Following UV-exposure, free radicals (FR) and reactive oxygen species (ROS) play a major role in producing lipid radicals ($L^{\bullet}$) that seem to be responsible for the destruction of the cell membrane and ultimately the cell [2,3].

UV rays cause major changes in the mechanical ultrastructural and sensorial properties of hair, such as change of texture, a dry appearance, increase in porosity and loss of suppleness [4]. UV rays also affect the color and brilliance of hair. The UV induced damage involves deep changes in the structure of keratin including the photo-oxidation of amino acids, sterols and fatty acids, resulting in rupture of sulfur bridges, decomposition of lipids, decrease in melanin as well as numerous micro-molecular lesions [5,6].

Multiple lines of defense have evolved, aimed to protect skin and hair from oxidative stress, including prevention, interception, and repair. The first defense line against UV generated free radicals in skin and hair is caused by melanin contained in different qualities and concentrations in human skin and hair, characterizing different skin types including the corresponding hair color. Both skin and hair are characterized by their different melanin content determining the different skin types (Table 1).

Biopolymers from the melanin family of molecules are known to be semiconductive and photoconductive. These materials are heteropolymers of indolequinones such as 5,6-dihydroxyindole (Fig. 2). Biologically, the melanin performs a variety of roles. Predominantly, it is a photoprotective pigment,

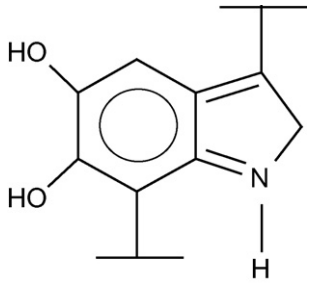

Fig. 2. Structure of 5,6-dihydroxyindole, one monomer of the melanin family.

but it is thought that it also functions as an antioxidant, free radical scavenger, and charge transport mediator.

Melanin is a biological polymer which is responsible for the pigmentation of many animals and plants.

Throughout the body, melanin is a homogenous biological polymer containing a population of intrinsic, semiquinone-like radicals. Additional extrinsic free radicals are reversibly photo-generated by UV and visible light. Melanin photochemistry, particularly the formation and decay of extrinsic radicals, has been the subject of numerous electron spin resonance (ESR) spectroscopy studies [7–9]. ESR can allow the identification of an unknown organic radical as well as provide insights into the chemistry of radical formation and degeneration.

Several melanin monomers exist, and the predominant monomer in a melanin polymer depends on its location within an organism. In skin and hair, melanin differs in eumelanin or pheomelanin while in the eye it is exclusively eumelanin. These different melanin types are distinguishable by ESR studies, where the signals of the photo generated extrinsic radicals are distinct. ESR spectroscopy enables highly accurate and sensitive non-destructive analysis and differentiation of natural melanin and has been the most powerful method to investigate melanin.

What is the functionality of melanin in skin and hair and what can we apply for skin and hair testing?

The existence of melanin in skin and hair is strongly correlated with the prevention from free radicals/ROS generated by UV radiation. Especially in the skin melanin (mainly eumelanin) ensures the only natural UV protection by eliminating the generated free radicals/ROS.

The aim of this study was to investigate the suitability of melanin as protector/radical scavenger against free radicals in skin and as a detector of UV-generated free radicals in hair.

Table 1
Skin and hair types concerning the duration of their maximum sunlight exposure time without detrimental effect on skin

Skin type	Constitutive color of unexposed skin	Hair color	Typical ethnicity	Exposure duration (min)
I	White	Red	Celtic	5–10
II	White	Blonde to light brown	Northern European, Scandinavian	10–20
III	White	Dark blond to brown	Average Caucasian	20–30
IV	Pale brown	Dark brown	Mediterranean, Oriental, Hispanic	40
V	Brown	Dark brown Black	American, Indian, East Indian, Hispanic	60
VI	Dark brown black	Black	African, Australian and South Indian, Aborigine	>60