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Detection of UV Induced Free Radicals in Hair and their Prevention by Hair Care Products

Keywords: melanin, free radicals, UV, UV-filters, antioxidants

Abstract

Solar UV exposure is one of the most important factors that leads to photoageing and photodamage of the hair. The melanin pigment in the hair protects from UV-induced free radicals, since melanins are efficient radical scavengers. The amount of UV induced free radials can be quantified by measuring the melanin radicals. The new Radical Hair Protection Factor (RHF) presented in this paper allows to characterize the protection effect of hair care products containing UV filters and/or antioxidants.

Introduction

Photoprotection of hair is not a common topic addressed by the dermatologist, but it is an important part of maintaining the cosmetic value of the hair shaft. Even so the whole science of hair and photoprotection is currently in its infancy and an area of focused research within the hair care product and salon industries. There are many reasons why hair condition can deteriorate; the sources of possible degradation can be grouped into three categories: (a) mechanical (i.e. brushing, friction); (b) chemical (i.e. perms, oxidative colouring, lipid-depleting surfactants); and (c) environmental (i.e. solar radiation, heat from hot blow drying, chlorine from swimming pools) (1,2).

Solar exposure and oxidative coloring are the most common and important factors that can lead to color fading and loss in hair manageability, caused by alteration of the hair surface. The hair encounters more damage as it becomes more hydrophilic, the cuticles of the hair surface are lifted and the hair shows more split ends (3-5). In fact, ultraviolet (UV) radiation is cosidered to be the most damaging of all environmental factors. Hair has natural protection against the sun's rays. UV rays cause major changes in the mechanical ultra-structural and sensorial properties of hair, such as change of texture, a dry appearance, increase in porosity, loss of suppleness, ecc. (6). UV rays also effect the color and brillance of hair. The UV induced damage involves deep changes in the structure of keratin caused by 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 (7,8).

In conclusion, oxidative damage is the main reason for hair condition changes and the most important contributor to oxidation is UV radiation. Oxidative reactions in biological systems lead to the generation of free radicals. An efficent approach to alleviate the damage is the use of UV filters and antioxidants able to reduce the amount of free radicals. The present study is aimed to quantify the protection factor of UV filters and antioxidant containing hair care products. Most of the techniques used to define oxidative damage to hair structures are focused on the macromolecular hair structure properties.

Table 1 lists some of the most widely used endpoints to measure oxidative damage and UV protection in hair care.

Color is perhaps the most obvious characteristic of human hair. The color of hair is due to the presence in the cortex of granules of a pigment called melanin. Biopolymers from the melanin family of molecules are known to be semiconducting and photoconductive. These materials are heteropolymers of indolequinones such as 5,6-dihydroxyindole **(Fig. 1)**. Biologically, the melanins perform a variety of roles. Predominantly, they are photoprotectants and pigments, but it is thought that they also function as antioxidants, free radical scavengers, and charge transport mediators.

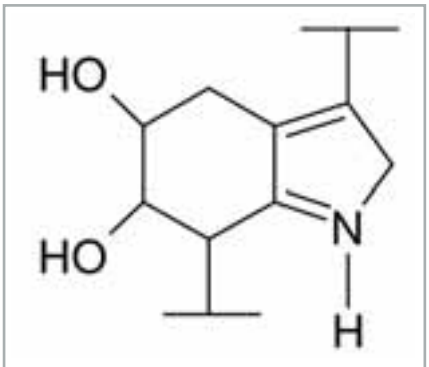

Fig. 1 Structure of 5,6-dihydroxyindole, one monomer of the melanin family

ROVISOME Q10

The right combination makes the difference. ROVISOME Q10 are specially developed liposomes which transport Coenzyme Q10 as highly active Ubiquinol into the deeper skin layers. The liposomal encapsulation is cell-identical and leads to an increase in the skin's natural anti-oxidative potential by 22 %.

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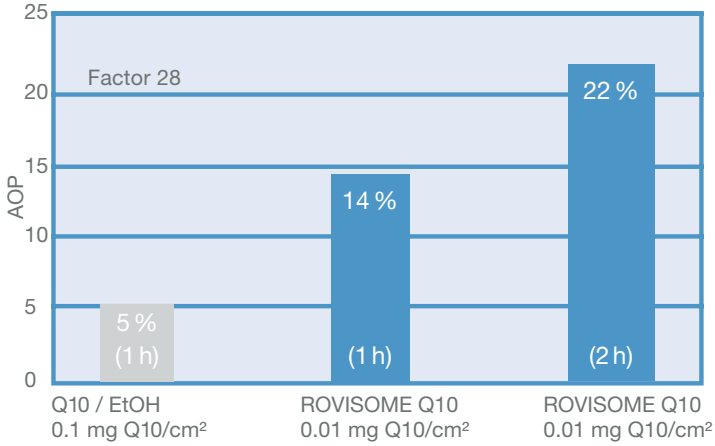

Cosmetic efficacy

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ROVI COSMETICS

Melanins are biological polymers which are responsible for the pigmentation of many animals and plants. Melanins are present in human hair with different concentrations ranging from very black to blond hair.

One remarkable characteristic of the melanins is the presence of free radicals in their structure, both in the solid state and in suspension. Electron Spin Resonance (ESR) is therefore a suitable technique to study melanins. The characteristics of the ESR spectrum of melanins are known (g-factor, line-width, number of spins per gram). Effects of temperature, hydration, pH, and light on the ESR signal have been investigated (9). In particular, it is shown, that only wavelength lower than 360 nm induce stable intrinsic radicals in the melanin structure.

The intrinsic free radicals are sensitive to light, leading to an increased ESR signal after UV radiation **(Fig. 2)**.

Melanin + UV → Melanin *

Using this effect it is possible to measure not only the UV protection of hair care products but also the efficacy of antioxidants present in a hair care product.

Endpoints	Technique of measurements	Assessment of hair degradation
Combing force	Combability testing	Increase of combing force
Hair strength / integrity	Tensile testing Flexabrasion test	Decrease in hair strength Decrease in yield slope Decrease in flexabration cycles
Scale Thickness **Porosity** **Split Ends**	SEM, microscopy imaging	Decrease in scale thickness Increase in porosity Increase in number of split ends
Hair Shine	Panel evaluation Photogoniometry measure Image analysis	Decrease in shine scoring, Decrease in lustre value
Degradation of proteins and lipids	Amino acid analysis Colorimetric reactions (i.e. with Merbromin)	Decrease in amino acid content (i.e. cysteine, tryptophan) Increase of cysteic acid content (degradation product of cysteine) Increase in thiol content Decrease in lipid content Increase in alkaline solubility Increase in copper uptake
Discoloration of hair (natural or artificial color)	Colorimetric, i.e. L*a*b* measurements	Loss in color Fading

Table 1 Some of the most common techniques for characterizing hair damage

■ Materials and Methods

Non-colored, natural brown hair from one female person was used for all experiments. Hair was washed, dried and cut into pieces of 1.5 cm. 10 mg of hair was fixed into a special ESR flat cell and the melanin signal intensities were measured using a Magnettech ESR spectrometer Miniscope 200. Hair was irradiated using a solar simulator (Hönle AG, SOL 200) with 28,3 mW/cm² UVA and 9,6 mW/cm² UVB for different times, corresponding to different UV doses. Following products were applied to the hair samples prior to UV irradiation:

Biotherm Sunfitness anti aging body sunscreen SPF 6

Wella System Professional Sunshine Lotion SPF 15

ROVI GmbH & Co. ROVISOME Q10 containing 0.5% coenzyme Q10 encapsulated in ROVISOME liposomes.

ROVI GmbH & Co. ROVISOME Defence containing 2% green tea extract encapsulated in ROVISOME liposomes.

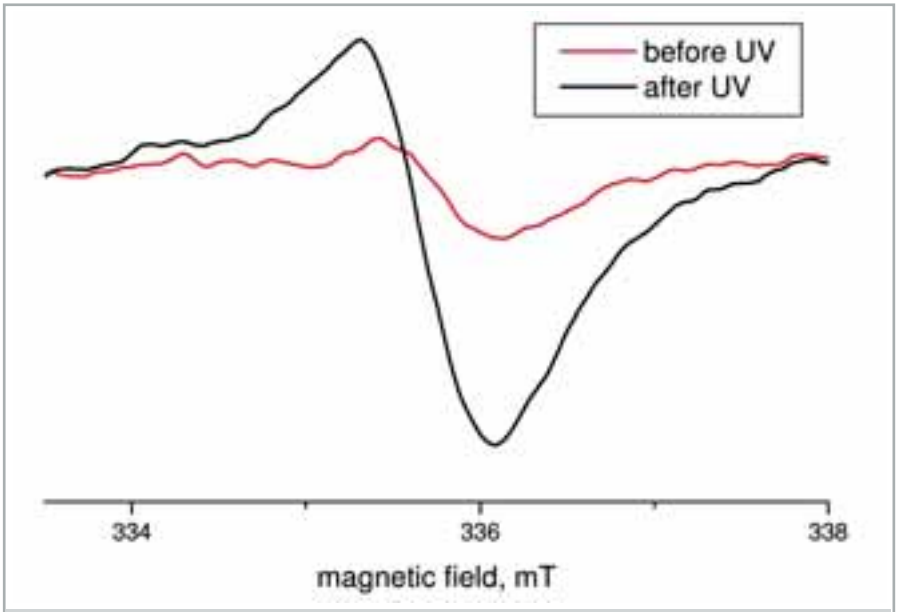

Fig. 2 ESR spectra of hair before and after UV irradiation

The intensity of the melanin ESR signal was measured before UV irradiation and after the irradiation of hair with different UV doses. The melanin signal intensity is directly proportional to the UV dose applied, up to a saturation that depends on the quantity and type of melanin present in the hair. Red hair is

particular rich in pheomelanin, whereas brown and black hair is composed mainly of eumelanin. Different melanin polymers have different response to UV radiation.

Results

Two UV suncare products and two liposomal encapsulated antioxidants were analysed regarding their protective effect against UV induced free radicals in hair. The RHF method quantifies the amount of free radicals that are generated in the hair according to:

$$RHF = \frac{N(\text{free radicals})_{\text{unprotected}}}{N(\text{free radicals})_{\text{protected}}}$$

The RHF is a factor characterizing the protection of a sunscreen against the generation of free radicals and represents the ratio between the number N of generated free radicals in the unprotected and protected skin assuming the same applied UV dose (constant irradiance, variable irradiation time) for both. The RHF is also a measure for the increase of the time staying in the sun by using UV filter protection assuming the generation of the same amount N of free radical/ROS like for the unprotected hair. The results are presented in **Table 2** and **Fig. 3**. The UV filters constitute the first defence line that aims to reduce the amount of free radicals by absorbing or

	Products	Permeation time, min	RHF
UV filters	Biotherm Sunfitness SPF 6	15	**2.64**
	Wella System Professional SPF 15	15	**5.82**
Antioxidants	ROVISOME Q10	60	**3.05**
	ROVISOME Defence	60	**6.43**

Table 2 RHF of sun care products and antioxidants

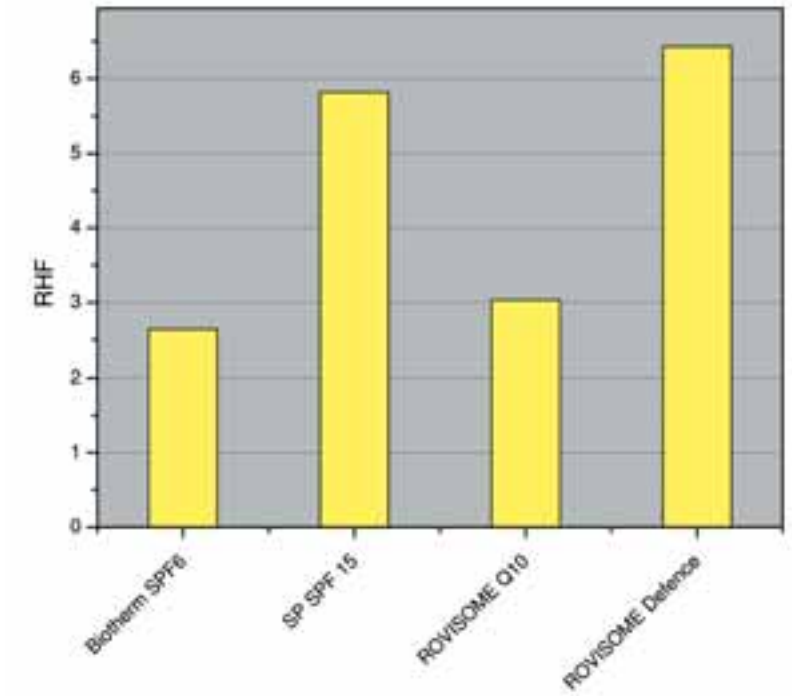

Fig. 3 Radical Hair Protection Factor (RHF) of hair care products containing UV filters or antioxidants

scattering the UV radiation. The second defence line is constituted by antioxidants that can neutralize the free radicals generated during UV radiation. As shown in **Fig. 3** both strategies are successful in reducing the free radical injury. The UV filter products differ in the UV filter content. The Biotherm SPF 6 contains one UVB filter (Ethylhexylmethoxycinnamate), one UVA filter (Terephthalylidene dicamphor sulfonic acid), and one UVAB filter (Drometrizole Trisiloxane). The Wella SP product contains 4 UVB filters (Ethylhexylmethoxycinnamate, 4-Methylbenzilidene camphor, Phenylbenzimidazole sulfonic acid, Ethylhexyltriazone) and one UVA filter (Butyl Methoxydibenzoylmethane). These differences are reflected in the RHF values. Higher concentration in UVB filters and a high photostability results in an efficient protection against free radicals. Also the antioxidants show distinct protection against UV damage. But in contrast to UV filters, antioxidants have to penetrate into the hair structure and must interact with the melanin polymer to be efficient. The encapsulation in suitable carrier systems i.e. liposomes enhances the penetration capacity of actives into the hair and protects the antioxidants against oxidation.

■ Discussion and Conclusion

The new Radical Hair Protection Factor (RHF) method presented in this work bases on the measurement of UV induced free radical production in hair. Melanin is the intrinsic defence system in the hair because it is able to capture free radicals. ESR spectroscopy enables the direct quantification of melanin radicals and allows to analyse the functional properties of melanin as a free radical trapping agent. Using the melanin radical it is also possible to quantify the protection effect of UV filters and antioxidants in hair care products. While the UV filters represent a first defence line, aimed to reduce the amount of UV radiation that reaches the hair structure, antioxidants constitute a second defence line by reducing the amount of free radicals generated inside the hair. The efficacy of UV filters depends mainly on their absorption spectrum. UVB filters are more efficient than UVA filters to avoid the free radical production in hair. The cosmetic formulation of the hair care product should allow the UV filters to adhere on the hair surface for a long period and the UV filters should be sufficiently photostable. The efficacy of antioxidants depends on several parameters. The antioxidant should be an efficient radical scavenger. Furthermore it has to be able to penetrate into the hair shaft and to interact with the melanin. An adequate carrier system is of primary importance for this purpose. Liposomal encapsulation into ROVISOMES helped the antioxidants coenzyme Q10 and green tea extract to penetrate into the hair in shorter times with respect to the non encapsulated actives and protected the antioxidants against photooxidation.

High UV protection effect in hair means to avoid mechanical and chemical damage and therefore to avoid loss in hair structure and fading. The oxidative stress of coloring and the possibility to avoid fading and hair damages by using antioxidants are recently under study.

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