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Effective Protection and Repair of the Hair from Daily Weathering

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abstract

Hair weathering is the deterioration of the hair shaft from root to tip and is the result of a series of cosmetic and environmental factors. Cosmetic practices such as brushing, combing, dyeing, straightening, perming, etc., as well as environmental factors such as exposure to UV light and polluted air can induce structural damage to the F-layer and the hair fiber. The cuticle becomes raised and porous, which exposes the cortex to further damage. A decrease in hair shine, color, elasticity and strength is observed, which eventually leads to hair damage. In different studies measured utilizing state-of-the-art technologies, a hair care ingredient that combines tara tannins derived from *Caesalpinia spinosa* pods and organic sunflower sprout extract (trade name KeraGuard), revealed a capacity to protect hair against free radicals and physical stresses. It was also shown to protect dyed hair from color fading and heat damage as well as to repair chemically treated hair.

Introduction

The Hair Unit

Hair is an integrated system with a peculiar chemical and physical behavior that acts as a unit. It consists of two distinct structures: the part beneath the skin, which is called the follicle, and the visible hair shaft (the part above the skin surface).

The hair shaft configuration is the same for all ethnicities and is formed by cuticle, cortex and medulla. Even though the shape of the hair change enormously, chemical analysis shows that its basic component is invariably keratin [1]. Indeed, studies indicate that not the composition but rather the shape of the hair follicle and its position on the scalp define the shape and thickness of the hair [2].

Each healthy hair is fenced by a protective cuticle which is comparable to the overlapping shingles on a roof, oriented from root to tip. Inside the cuticle, the cortex of the hair contains keratin and melanin. Keratin strengthens the hair while melanin provides the color to the hair. Melanin also protects the hair shaft from sun damage by acting as a barrier for UV radiation. The medulla is the core of the hair and might even be absent. The cuticle is responsible for the luster and texture of human hair. The normal cuticle is smooth, which allows for light reflection and the limiting of friction between the hair shafts. Generally speaking, it is formed by 6–8 scales for Asians, slightly less for Caucasians and even less so in African hair [1]. A thinner cuticle layer makes the hair more prone to breakage. In spite of the hydrophobicity surface of the cuticle, the hair absorbs moisture. This contradictory behavior, which is known as the “hair paradox”, is the result of the interior of the fiber containing hydrophilic amino acid residues.

The F-layer

Each cuticle cell comprises a thin proteinaceous membrane, the epicuticle, which is shielded by an invisible, water-resistant lipid layer that acts as a natural conditioner. This outer lipid layer, which is known as the fatty layer or F-layer, mostly consists of 18-methyleicosanoic acid (18-MEA) and is what naturally gives human hair its smooth and silky feel (**Fig. 1**) [3].

The Hair is Constantly Exposed to Stress Factors

Hair weathering is the progressive hair damage that results from external stress factors, which are basically the ‘wear and tear’ from the environment and cosmetic procedures that mainly affect the hair fiber. Among these factor are the environmental pollutants such as smog, cigarette smoke, radiation, etc. that generate free radicals and ROS. These

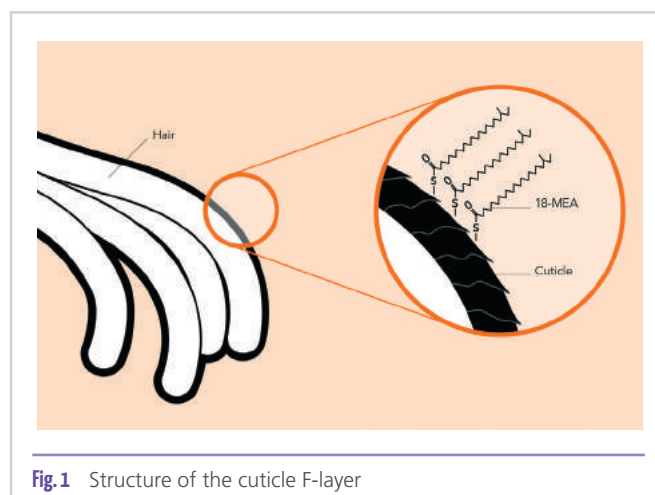


Fig. 1 Structure of the cuticle F-layer

molecules oxidize and degrade the proteins and lipids of the hair surface. Sun exposure, wind and salt water are likely to dehydrate the hair. Oxygen radicals created by UVR break down the disulfide bonds of structural units which reduces the integrity of the hair fiber. Thus, the hair is prone to breakage and to color fading. Moreover, physical stress (such as combing, blow drying, excessive heat from strengthening or curling irons) is likely to dehydrate and degrade the proteins of the hair surface. Also drastic procedures such as perming, relaxing and bleaching cause structural and chemical damage, and are also a source of free radicals and ROS. In addition, shampoos and styling products can in the long run cause dehydration of the hair [4].

Generally speaking, daily weathering and chemical cosmetics procedures might damage hair by removing the F-layer and drastically reducing the hydrophobicity of the hair surface. All of these stress factors make the hair more porous and therefore more brittle, rough feeling as well as dull looking. Consequently, the hair needs to be reinforced, repaired and protected on a daily basis.

Methods

Determination of the Antioxidant Power

Electron spin resonance (ESR) spectroscopy (X-band ESR spectrometer Miniscope MS300, Magnettech, Germany) was used to analyse the antioxidant activity of KeraGuard (from now on referred as "active ingredient"). The method measures the reducing activity against the stable test radical diphenyl-picryl-hydrazyl (2,2-diphenyl-1-picryl-hydrazyl, Sigma Aldrich, Germany). The method allows for the analysis of the reduction potential, as well as the reaction time: the kinetic component. The result is called 'antioxidative power' (AP). The resulting AP is expressed in antioxidative units (AU), where 1 AU corresponds to the activity of a 1 ppm solution of pure vitamin C (ascorbic acid) as benchmark.

Analysis of the Radical Scavenging Properties by ESR Spectroscopy

Natural brown-auburn human Caucasian hair was cut in pieces of 1.0 cm length and samples of 10 mg hair were incubated in water (placebo) or in 0.5 % and 2 % active ingredient diluted in H₂O for 10 minutes. The hair samples were then washed twice in deionized water (with washing step) or left unwashed (without washing step). The first Electron Spin Resonance (ESR) spectrum was recorded (X-band ESR Spectrometer Miniscope MS300, Magnettech, Germany) before irradiation (Sun Simulator SOL2, Honle GmbH, USA). Then, the samples were exposed to 5 minutes UV radiation (28,3 mW/cm² UVA and 9,6 mW/cm² UVB). The melanin signal intensity was measured by ESR and the intensity after irradiation was normalized to the intensity before irradiation (= relative Melanin increase).

Electron Spin Resonance (ESR) Spectroscopy on Bleached Hair

Natural brown human Caucasian hair and bleached hair were used for the measurements. The hair was cut in pieces of 1.5 cm length and samples of 10 mg hair were incubated with 0.5 % and 1 % active ingredient (in water) for 10 minutes followed by 2 washes with water. The hair was afterwards incubated with a 40 mM solution of CuSO₄ for 10 minutes, washed once and inserted into the ESR spectrometer (X-band ESR Spectrometer Miniscope MS300, Magnettech, Germany). All hair samples were analysed in three replicas (N=3).

Hair Color Protection

Hair tresses of natural, dark brown, straight human hair were bleached and dyed red. The hair colour mixture (amber col 645) was applied homogeneously to the dry hair tresses with a brush. At room temperature, the colour mixture was left on the hair tresses for 20 minutes and then rinsed under water. The baseline Chromameter measurements (Skin Colorimeter CL400, C+K electronic GmbH, Germany) for hair lightness L* were carried out 5 times per each red-dyed hair tress.

The tresses were then pre-treated with 0.5 % active ingredient or placebo and washed. Afterwards, the hair tresses were stretched 10 times with straightening plates at 175°C (Rowenta, Germany). 20µl of Hair serum (placebo) or 0.5 % active ingredient in Hair serum per gram of hair tress were applied with a syringe from the top to the bottom of each hair tress. Then, hair tress was massaged manually for 30 seconds and let set for 15 minutes.

A-pre-treatment simulating 2 weeks of product application (3 product applications per week) and washing before UV exposure was performed.

After the pre-treatment, 12 product's applications are performed intercalated by UV exposure cycles (SPF-290AS, Solarlight, USA), simulating 15 days of intense sun exposure.

After drying (for 48 h, at room temperature) and combing, Chromameter measurements were carried out 5 times per each hair tress.

Heat Damage Test

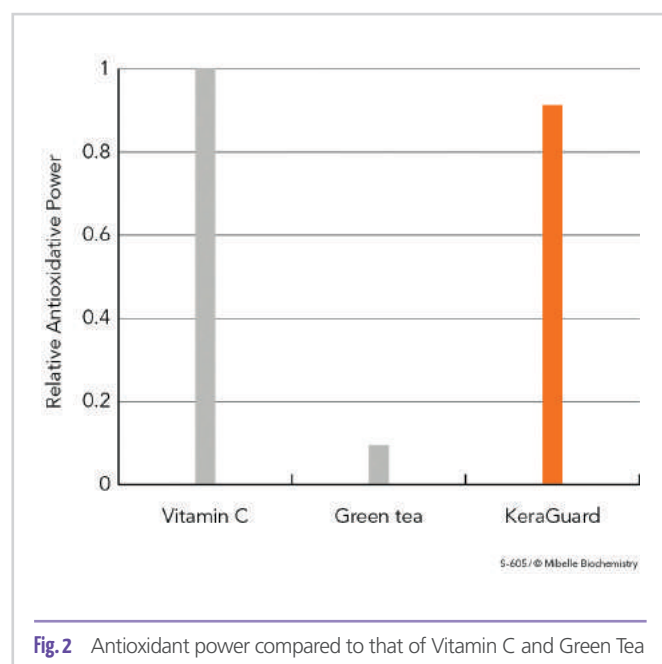
Hair tresses of natural dark brown human hair were washed with an aqueous solution of SLES 12 %. Hair fibers were then rinsed with tap water for 30 seconds, with a constant water flow, in order to completely remove the SLES. The test products were then applied (a placebo hair serum and a hair serum containing 0.5 % active ingredient). Hair fibers were dipped in the test products for a period of 5 seconds then massaged manually for 30 seconds in order to spread the product homogeneously. All hair tresses were rinsed with tap water with a constant water flow. The baseline was determined after two cycles of washing and test products application. Thereafter, the hair fibers were submitted to eight

cycles of heat damage induced with a flat iron (Rowenta® for Elite model Look) at 200°C for 1 minute and 30 seconds intercalated with the application of the test products and the corresponding washing step. The degree of hair damage was evaluated by Scanning Electron Microscopy (FEI Quanta 400 FEG_ESEM/EDAX Pegasus X4M) at the baseline and after eight cycles of heat damage.

Results

Antioxidant Power Compared to that of Vitamin C

The antioxidant power (AP) of the active ingredient was determined by evaluating its capacity to reduce DPPH (a stable and well-known radical) by using ESR spectroscopy. This technique is used to detect unpaired electrons in radicals. The AP indicates the quantity of free radicals that are neutralized according to time and therefore this value provides information about both the intensity of the reaction and its speed. A high AP corresponds to a strong capacity to neutralize free radicals correlated to a short reaction time. The AP of the active ingredient (dry matter) was benchmarked against pure vitamin C (ascorbic acid) and compared to known values of other substances in their pure form, such as green tea.

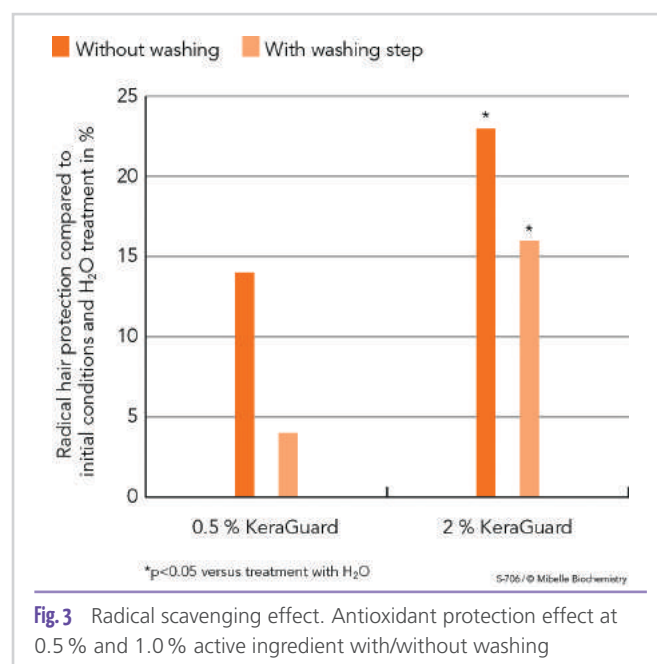


As shown in the **Fig. 2**, the active ingredient has a high AP, which indicates that it neutralizes antioxidants and free radicals both in a robust and quick manner. It is therefore an effective and efficient antioxidant. Furthermore, the active ingredient was shown to be almost as active as vitamin C and much more efficient than green tea.

Antioxidant Protection Effect on Hair

Analysis of the radical scavenging properties of the active ingredient was assessed by the Radical Hair Protection method (RHP). RHP is based on the measurement of the Electron Spin Resonance (ESR) spectrum of melanin in the human hair. Brown and black hair possess a defined and stable melanin signal (Melanin I). UV irradiation of the hair generates free radicals that are scavenged by the melanin polymer and this leads to a re-organization of its electron structure. This new structure emits a different melanin signal (Melanin II). The increase of Melanin II signal is directly proportional to the UV dose; in other words, to the oxidative damage on the hair.

Results showed that the active ingredient significantly increased the hair protection against UV stress in a dose dependent manner (**Fig. 3**). The active ingredient also exerts its antioxidant protection power after being washed off.



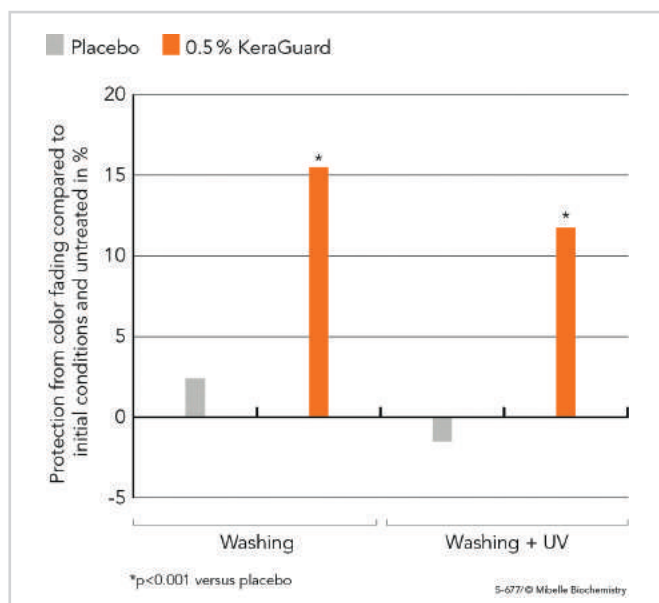


Fig. 4 Hair color protection effect against washing and UV exposure in comparison to the placebo

Hair Color Protection against Sequential Washing and UV Exposure

One of the most perceptible changes is on fibre colouration, as a result of a photoreaction of the hair’s natural pigments, as well as a result of photodecomposition of artificial hair dyes.

The goal of this study was to evaluate the efficacy of the active ingredient in protecting the colour of hair tresses from fading by washing procedures and UV radiation. Results showed a significant hair color protection with the hair serum containing 0.5 % active ingredient compared to the placebo, following the washing procedure as well as after washing and UV irradiation (**Fig. 4**).

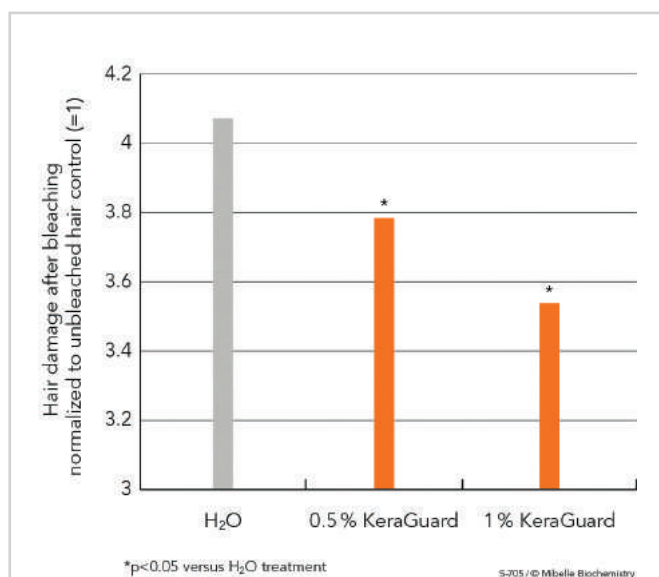


Fig. 5 Repair of bleached hair. Restoration effect of the hair after bleaching using 0.5 % and 1.0 % active ingredient

Restoration of Bleached Hair

Bleaching raises the outer cuticle of the hair, which allows the bleaching agent to penetrate and remove color by oxidation. During such chemical treatments the bond between the F-layer and the keratin cysteine gets severed: the disulfide-bonds (-S-S-) are disrupted and the resulting -SH groups are available for undergoing complex formation with bivalent ions. Cu(II) ions are able to complex with free -SH groups and this is measurable via ESR. The higher the damage of the F-layer of the hair, the more free SH groups are available to complex with copper. The repair action of the active ingredient on bleached hair was analyzed by copper – amino acid complexes formed in human hair and measured using electron spin resonance (ESR) spectroscopy. The active ingredient showed a significant repair action against the damage of the F-layer by hair bleaching (**Fig. 5**).

Protection of the Hair from Heat Damage

The scanning electron microscopy is an appropriate technology for observing the hair shaft following mechanical and chemical damages, providing images of the hair cuticle condition. The condition of the hair surface can be graded according to the degree of the induced damage. This placebo-controlled ex vivo study aimed to evaluate the heat damage protection efficacy of the active ingredient incorporated in a hair serum. Results showed that 0.5 % active ingredient effectively protects the hair cuticle from the heat damage in comparison to the placebo. The high resolution images showed a significant change on the hair surface before and after heating and in the presence or not of the active ingredient (**Fig. 6**). After heating the cuticle scales of the hair treated with the placebo were lifted up. The hair started to fray and appeared jagged edges. The active ingredient, instead, protected the

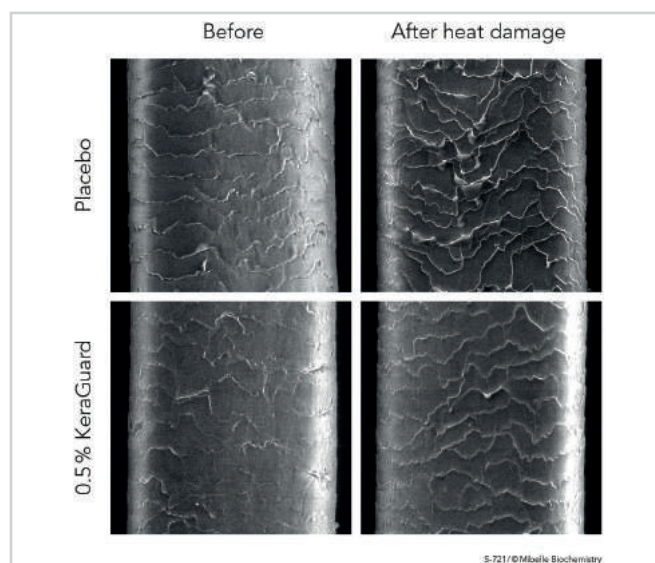


Fig. 6 Protection effect from heat damage. Scanning Electron Microscopy before and after heat treatment with placebo or with 0.5 % active ingredient

hair cuticle from jaggging. After heating the cuticle scales lied flatter on the hair tresses treated with 0.5 % active ingredient than with the placebo.

Summary

Although hair is a physiological phenomenon, it is also a social one. Hair is an object of intense elaboration and preoccupation in almost all societies. Hairstyles and rituals surrounding hair care and adornment tend to carry powerful messages about the beliefs, lifestyles and commitments of a person. Therefore, our hair is regularly subjected to weathering: stresses which damage the hair and make it more sensitive. In different ex vivo studies a hair care ingredient, that combines tara tannins derived from *Caesalpinia spinosa* pods and organic sunflower sprout extract, was shown to repair chemically treated hair and to protect hair against physical stresses. Besides, 0.5 % of the hair active ingredient was shown to protect dyed hair from color fading as well as to reduce the damaging effect of heating on the hair cuticle scales. Thanks to its antioxidant potential, the active ingredient efficiently protected the hair against free radicals.

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