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Efficacy of antioxidants in human hair

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ABSTRACT

Hair is exposed every day to a range of harmful effects such as sunlight, pollution, cosmetic treatments, grooming practices and cleansing. The UV components of sunlight damage human hair, causing fibre degradation. UV-B attacks the melanin pigments and the protein fractions (keratin) of hair and UV-A produces free radical/reactive oxygen species (ROS) through the interaction of endogenous photosensitizers. Hair was dyed and the efficacy of two antioxidant formulations was demonstrated after UV exposure by evaluating, surface morphology, protein and amino acid degradation, lipidic peroxidation, colour and shine changes and strength/relaxation properties. UV treatment resulted in an increase in protein and lipid degradation, changes in colour and shine and in adverse consequences for the mechanical properties. Natural antioxidants obtained from artichoke and rice applied to pretreated hair improved mechanical properties and preserved colour and shine of fibres, coating them and protecting them against UV. Furthermore, the lipidic peroxidation of the protein degradation caused by UV was reduced for some treated fibres, suggesting an improvement in fibre integrity. This was more marked in the case of the fibres treated using the artichoke extract, whereas the rice extract was better preserving shine and colour of hair fibres.

1. Introduction

It is well known that the UV components of sunlight damage human hair. This observation has been reported using a laboratory simulation of sunlight [1]. UV irradiation (mainly UV-B) attacks both the melanin pigments and the protein fractions (keratin) of hair [2]. The effects of UV-B irradiation can be severe, resulting in the breakdown of disulfide bonds inside the hair fibre and on the surface of the cuticle. However, UV-A irradiation mainly produces free radical/reactive oxygen species (ROS) through interaction with endogenous photosensitizers. Studies have shown that photo-oxidation of hair fibre involves the fracture of C–S linkages from proteins [3], oxidation of internal lipids, [4] and melanin granules [5] and tryptophan degradation of keratin [6]. Moreover, exposure to sunlight leads to hair decoloration due to melanin oxidation via free radicals, [7,8]. Melanin is a homogeneous biological polymer containing a population of intrinsic, semiquinone-like radicals. There are two types of melanin, the brown–black pigments (eumelanins) and the less prevalent red pigments (pheomelanins) [9]. Melanin granules selectively absorb radiation and offer photoprotection but become degraded or bleached in the process [10].

The lipid and protein fractions play a major role in the structure and integrity of the hair fibre, protecting it against external agents. Therefore, aggressions to the proteic and lipidic fraction [3,4] and the degradation of amino acids susceptible to photodegradation such as tryptophan, [6,9,11] can help us to evaluate the decomposition of hair fibre [12].

The most harmful effect of sunlight on hair is cystine oxidation to cisteic acid, which alters its mechanical properties (long UV exposure) [13]. Shorter irradiations cause unwanted effects such as a decrease in hydration, increased permeability, leading to a loss of colour and shine and to an increase in combing resistance [10,14].

The rapid increase in hair treatments (bleaching, dyeing, etc.) has led to a proliferation of hair cosmetics that facilitate repair and prevent adverse effects on the capillary structure. Vitamins and antioxidants have been included in cosmetic formulations specially designed to reduce the adverse effects on hair fibre. The most effective ingredients are antioxidants that can interrupt radical-chain processes, help to repair skin/hair systems, protect against oxidative damage and are frequently used in food and cosmetics [15]. For instance, vitamin B5 has been used for many years in hair care products because it functions as humectant, increases the water content and improves the elasticity of hair [15]. Incorporation of antioxidants, at low concentrations, in cosmetics can better protect and possibly correct the damage by neutralising free radicals and retard lipid oxidation.

The aim of this work is to study the efficacy of different antioxidant formulations after application on hair subjected to UV radiation and to the most common capillary treatments (dyeing). Two

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natural antioxidant active ingredients were selected to evaluate their effect on hair fibres; a *Cynara scolymus* L. extract obtained from the leaves of artichoke (KERACYN tm) and an *Oryza sativa* L. extract obtained from rice grain (KERARICE tm).

The leaves of artichoke (*C. scolymus* L.) contain the greatest concentration of active principles. Hydroxycinnamic acids (Fig. 1) in artichoke have the general C6–C3 structure with the same aromatic ring and hydroxyl group as phenolic compounds, and a carboxylic function. These hydroxycinnamic acids are rarely free. They are usually found in the form of derivatives, e.g., caffeic acid is esterified with quinic acid, resulting in chlorogenic acid, isochlorogenic acid and neochlorogenic acid. Shahidi and Chandrasekara conducted an extensive review of the antioxidant activity [16], both in vitro and in vivo, of hydroxycinnamic acids (ferulic, caffeic, coumaric, sinapic and derivatives). Flavonoids, which are other molecules present in Artichoke leaves, act as antioxidant agents by inactivating free radicals generated by irradiation.

Rice can grow in diverse media. It will grow faster and more vigorously in hot and humid environments. The chemical composition of the active ingredient is characterised by the presence of biofunctional peptides and amino acids, polysaccharides and phytic acid.

The amino acid composition of the peptides present in the active ingredient is characterised by a high concentration of glutamic acid (up to 17%) and large amounts of aspartic acid, arginine, leucine, phenylalanine, serine, valine and tyrosine (up to 10%). Approximately 80% of the protein hydrolyzate has a molecular weight between 500 and 3000 Da. The molecular weight of the peptides present is directly related to its function in the hair. Low molecular weight peptides (<1000 Da) can penetrate and repair hair fibres from the inside. Medium molecular weight peptides (1000–3000 Da) can repair the cuticle [17,18], and account for 42% of the extract.

The main polysaccharide present in the rice active ingredient is amylopectin (Fig. 2a).This is a water-soluble branched polymer composed of glucose units connected linearly by bonds α (1 $\rightarrow$ 4). Each molecule of amylopectin can contain between 100.000 and 200.000 glucose units, and each branch is formed by 20–30 glucose units in length. This type of three-dimensional structure prevents an excessive accumulation of the active ingredient and hair matting, compared with normally used linear polymers.

Phytic acid (myo-inositol hexaphosphoric acid, abundant in edible legumes, cereals and seeds) (Fig. 2b) is another key component of rice and acts as an antioxidant agent by inactivating free radicals generated by irradiation. Phytic acid is capable of chelating metals, especially divalent metals. It forms an iron chelate which greatly accelerates Fe^{2+}mediated oxygen reduction yet blocks iron-driven hydroxyl radical generation and suppresses lipid peroxidation [19].

Protein and amino acid degradation, lipid peroxidation, strength, shine and colour measurements were used to evaluate proteic and lipidic photodecomposition in hair fibres subjected to antioxidant action.

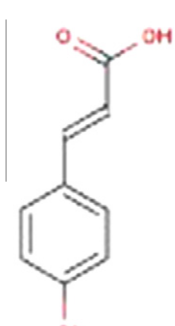

Fig. 1. Hydroxycinnamic acid.

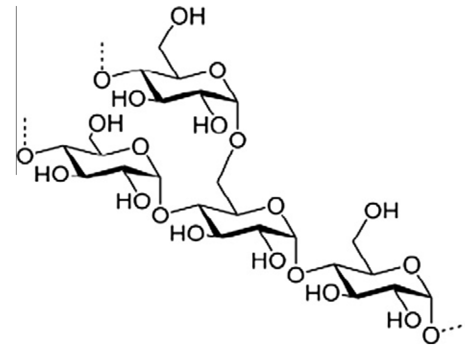

Fig. 2a. Amilopectin.

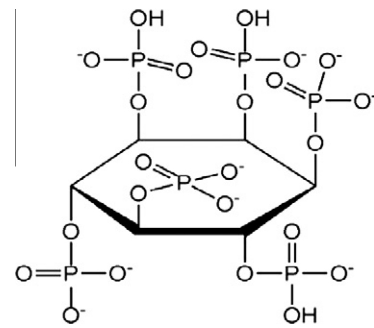

Fig. 2b. Phytic acid.

A Scanning Electron Microscopy (SEM) study was also performed with all hair samples to evaluate the possible changes in the surface morphology of the hair fibres due to the different treatments [20].

All these methodologies were applied to virgin or dyed hair tresses subjected to UV radiation and pre-treated with the two antioxidant formulations in order to achieve a possible protection of hair properties.

2. Materials and methods

2.1. Chemicals

Revlon 7.45 dye was provided by The Colomer Group (Barcelona, Spain). Natural dark brown hair tresses (20 cm in length) were purchased from De Meo Brothers Inc (New York). Hair tresses were treated with a shampoo base formulation (Table 1), placebo and a protective serum which contained *C. scolymus* antioxidant active (Cyn) and *O. sativa* antioxidant active (Rice) (Table 2).

2.2. Hair Treatments

Hair was chemically treated by dyeing and also subjected to antioxidant treatments:

2.2.1. Dyeing procedures

Untreated hair (32 g) was dyed with 70 ml of dye solution containing 50 ml of Revlon 7.45 dye and 20 ml of H_2O_2 (20 vol.%). The hair was covered and maintained for 30 minutes at 25–29 °C. Finally, the hair was washed with neutral shampoo and was dried at 30–40 °C.

2.2.2. Antioxidant treatments

Four dyed (D) hair tresses of 8 g each were prepared. For comparison, four tresses of 10 g untreated (UT) hair (virgin hair) were