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Potential of antioxidant extracts produced by aqueous processing of renewable resources for the formulation of cosmetics

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ABSTRACT

The performance of natural extracts obtained from underutilized and residual vegetal and macroalgal biomass processed with food-grade green solvents was compared with that of commercial antioxidants. Selected extracts were obtained from two terrestrial sources: winery byproducts concentrate (WBC) and chestnut burs hydrothermally fractionated extract (CBAE), and from two underutilized seaweeds: *Sargassum muticum* extracts, either extracted with ethanol (SmEE) or after alginate extraction and hydrothermal fractionation (SmAE) and from *Ulva lactuca* processed by mild acid extraction and membrane concentration (UlAE). These extracts showed *in vitro* antioxidant properties comparable to commercial antioxidants and were safe for topical use based on the absence of skin-irritant effects at 0.1% on reconstructed human tissues. The stability of several cosmetic model emulsions was assessed during accelerated oxidation assays. The incorporation of natural extracts produced from renewable underutilized resources at 0.4–0.5% in an oil-in-water emulsions reduced lipid oxidation during storage.

1. Introduction

The growing demand for natural additives is being incentivized by the restricted use of synthetic antioxidants to prevent lipid oxidation in food and cosmetic products (Andreassi and Andreassi, 2004). Agro-industrial by-products are cheap, abundant and sustainable resources, which contain compounds with antioxidant, cytotoxic and antimicrobial activities that could be proposed as a natural preservative in cosmetic products (Vinardell et al., 2008; Rodrigues et al., 2013). In addition, formulations enriched in antioxidants administered topically by cosmetics or by diet supplements, could exert an antioxidant/protective effect in skin by decreasing the oxidative stress (Morganti et al., 2002), which is one of the major mechanisms for skin aging.

An important concern related to the extraction of natural ingredients for cosmeceutical uses is the desired limitation of toxic solvents (Chaudhari et al., 2011). Water is an abundant solvent, but not suited to extract non-polar compounds. However, hot pressurized water under subcritical conditions possesses dielectric properties similar to some apolar solvents. One of the available technologies operating with subcritical water is autohydrolysis or hydrothermal treatment at temperatures in the range 150–250 °C. This autocatalyzed reaction has been proposed for the environmentally friendly fractionation of vegetal biomass (Conde et al., 2011).

Natural phenolics from terrestrial sources, including benzoic acids, cinnamic acids and flavonoids, possess antioxidant, cardioprotective, neuroprotective, anticancer, anti-inflammation, antiaging and antimicrobial properties (Boudet, 2007; Vinardell et al., 2008). Phlorotannins are phenolic compounds exclusive of marine seaweeds, but these organisms, particularly brown algae, also contain a variety of components with antioxidant action (such as polyunsaturated fatty acids, proteins, pigments, vitamins, polysaccharides and carotenoids). The phlorotannins and algal polysaccharides exhibit anticoagulant, antiviral, antioxidative, anticancer, antiinflammatory and immunomodulatory actions, and could have potential for the development of nutraceutical, pharmaceutical and cosmeceutical products (Batista González et al., 2009; Balboa et al., 2013a; Thomas and Kim, 2013). Valorization and

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utilization of the constituents of the brown macroalga *Sargassum muticum* was proposed, since the solvent extracts (Kim et al., 2007) and the soluble fractions obtained after autohydrolysis (González-López et al., 2012) were active *in vitro* antioxidants. The green alga *Ulva lactuca* does not possess an important phenolic fraction, but contains other components such as polysaccharides and steroids showing bioactive properties (Lahaye and Robic, 2007).

The aim of this work was to evaluate the cosmetic potential of extracts produced from biorenewable underutilized sources using green solvents: two concentrated and refined fractions from terrestrial sources and three crude extracts from seaweeds. The absence of skin irritating properties and the protection against oxidation of model cosmetic products were assessed.

2. Materials and methods

2.1. Extracts

A winery byproducts concentrate (WBC) was prepared from distillery wastes produced in December 2009 (Cooperativa Vitivinícola Ribeiro, Ourense, Spain). The liquid stream separated by pressing was centrifuged to remove suspended solids and phenolic compounds were recovered and concentrated to obtain a light colored powder extract (Díaz et al., 2012).

Chestnut (*Castanea sativa*) burs, collected in Autumm 2006 in Ribeira Sacra (Ourense, Spain), were processed by non-isothermal autohydrolysis (using water as the only reagent). The liquid phase was further refined by extraction with ethyl acetate, washing with ethanol/water solutions, adsorption onto a non-ionic polymeric resin (Sepabeads SP700, Resindion S.R.L., Mitsubishi Chemical Corp.) and elution with ethanol. The dark brownish powder extract (CBAE) was prepared by freeze-drying (Conde et al., 2011).

Sargassum muticum, collected in Mourisca Beach, Alcabre (Pontevedra, Spain) in Summer 2010, was separated from other species, washed with tap water, oven dried at 50 °C, milled and stored at room temperature in sealed plastic bags until use. Ground *S. muticum* was further extracted with 96% ethanol. After filtration to separate solids and vacuum evaporation of the liquid phase to remove the solvent, a dark green solvent extract named SmEE was obtained. The ground *S. muticum* biomass was also processed by conventional technology for the solubilization of alginate, with sequential extractions using 1% formaldehyde, 0.2N sulphuric acid, 1% sodium carbonate and intermediate washings with tap water. Alginate was recovered from the sodium carbonate soluble fraction and the solid residue remaining after alginate extraction was treated with water, at a liquid:solid ratio of 30:1 g:g, in a batch reactor (Parr Instr. Co., Moline, IL) under non-isothermal conditions until the equipment temperature reached 190 °C. The liquid phase or autohydrolysis liquors were recovered by filtration and freeze-dried, this dark brown powder product was named SmAE and contained both phlorotannins and fucoidan fractions (González-López et al., 2012).

Ulva lactuca, removed during cleaning of shellfish banks in February 2011 in Vilagarcía de Arousa (Pontevedra, Spain), was manually separated from other species, washed with tap water, oven dried at 50 °C, milled to a particle size of less than 1.0 mm and stored at room temperature before processing. Algal biomass was subjected to an acid hydrolysis with 1.25% H_2SO_4 in glass bottles in an autoclave using a liquid:solid ratio of 60:1 at 120 °C during 1 h. The liquid obtained after filtration was neutralized adding $CaCO_3$. A second filtration to remove $CaCO_3$ was necessary. This liquid phase was concentrated thrice by a Prep/Scale spiral membrane (Millipore, TFF6, 1 kDa, 0.54 m^2 filtration area, made of regenerated cellulose) operating with 200 L/h at 4 bar and 22 °C. The retentate was freeze-dried to obtain a slightly yellow powder extract (UlAE) and stored until use.

2.2. Cosmetic model products

Two creams, avocado cream and suncream and two cosmetic oils, massage oil and shower oil, were chosen for the experiments. The extracts were added as antioxidants in the cosmetics preparations.

Avocado cream (AC) was formulated with the following components (g): avocado oil (25), sorbitan monolaurate (5), water (100) and antioxidant (0.4). All the ingredients were mixed, homogenized with sonication and neutralized with triethanolamine (if the mixture had acid pH), to form the emulsion. The extracts tested in this cream were: tocopherol (T), *Sargassum muticum* ethanol extract (SmEE) and autohydrolysis extract (SmAE), chestnut burs autohydrolysis extract (CBAE) and winery byproducts concentrate (WBC).

Sun cream (SC) was prepared with an *oil phase* containing (g): cream basis (o/w) (18), dimethicone 350 (6), avocado oil (3), sunscreen (8), titanium dioxide (18), antioxidant (0.75), Fenonip (0.35) and a *water phase* containing propylene (6), carbopol ultrez 10 (1.5), triethanolamine (1.5), demineralized water (80). The melted oils were mixed in a water bath, until the water temperature achieved 70 °C. When the mixture raised 40 °C, 0.45 mL of bergamot oil and 3 mL of tetramer cyclomethicone were added. The carbopol and the propylene were separately added to the water, sonicated and neutralized with triethanolamine to form a gel. The oily phase was mixed with the aqueous one with constant stirring. The compounds and extracts tested in this cream were T, tea extract (TE) (Guinama, Valencia, Spain), commercial vine extract (VE, Guinama, Valencia, Spain), WBC and *Ulva lactuca* powder extract (UlAE).

Massage oil (MO) was composed of the following ingredients (g): glyceryl tricapryl-caprate (42.5), octyldodecanol (25.5), isopropyl myristate (22), almond oil (6), menthol (1.5), camphor (1.5) and antioxidant (0.5). The oil was prepared by adding the camphor and the menthol to the almond oil, the mixture was stirred with a spatula and after the addition of the other components, it was sonicated for 4 min. The extracts tested in this oil were T, TE, SmEE and *Fucus* extract (FE) (Guinama, Valencia, Spain).

Shower oil (SO) was formulated by mixing and homogenizing the following components (g) in the proposed order: octyldodecanol (35), isopropyl myristate (20), antioxidant (0.5), essence of roses (0.3), glyceryl tricapryl-caprate (44). The extracts tested in this oil were: T, TE, SmEE, and FE.

The antioxidant extracts were added to the oil dissolved in ethanol. Control samples without any extract added were also prepared and analyzed.

2.3. Analytical methods

Total phenolic content was colorimetrically determined using the Folin-Ciocalteu reagent (Sigma-Aldrich, St. Louis, USA) and expressed as gallic acid (Sigma-Aldrich, St. Louis, USA) equivalents. All analyses were performed at least in triplicate and are reported on a dry matter basis. Ash content was gravimetrically determined. The monomeric sugars were measured by HPLC in samples previously hydrolyzed with 4% sulfuric acid at 121 °C for 20 min (Balboa et al., 2013b).

2.4. Antioxidant activity

Ferric reducing antioxidant power (FRAP), reducing power and the scavenging capacity of DPPH (*α,α-Diphenyl-β-picrylhydrazyl*) *and ABTS* (ABTS$^{\bullet+}$, 2,2′-azinobis (3-ethyl-benzothiazoline-6-sulfonate))