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Implementation of phenols recovered from olive mill wastewater as UV booster in cosmetics

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ABSTRACT

The current study investigates the application of different concentrations of phenols (recovered from olive mill wastewater) as UV booster in cosmetics. The spectrums (220–400 nm) of 0–15 mg olive phenols/L combined with physical (30 mg TiO_2/L) and chemical (5 mg Benzophenone-3, 5 mg Uvinol A, 2 mg Octocrylene, 1 mg OMC and 0.5 mg OC-PABA/L) sunscreen agents were obtained and the *in vitro* SPF of respective solutions were calculated. In both UVB and UVA regions, absorption of synthetic UV filters increased as a function of olive phenols concentration, whereas the relationship between SPF increase and olive phenols concentration was linear. The corresponding equations could be used to estimate the amount of added olive phenols in order to reach a desirable SPF value and partially replace the amount of synthetic filters in the final product. The entrapment of olive phenols in silica particles and/or liposomes prior their emulsification in cosmetics was also investigated and resulted in an increase of phenols' water resistance. The results of the current study reveal the potentiality of using olive mill wastewater as a source for the recovery of phenols and their application as UV booster in cosmetics.

1. Introduction

Ultraviolet (UV) light is electromagnetic radiation with a wavelength between visible light and x-rays in the range of 10–400 nm. UV-light is found in sunlight, especially UVB (280–320 nm) and UVA (320–400 nm). Most of the rays that reach earth are UVA (98.7%), but also UVB is present. UVA rays are responsible for the skin tanning but can damage the skin and also increase the risk of skin cancer. UVA rays penetrate deeper into the skin compared the UVB rays. Both radiations lead to free radicals, toxic elements for skin cells and provoke skin ageing (Matsumura and Ananthaswamy, 2004). Sunscreen compounds (*e.g.* benzophenon derivatives, parabens etc) include typically single or multiple aromatic structures, conjugated or not with carbon-carbon double bonds or carbonyl moieties, and thus are able to attenuate the transmission of energetic solar photons (Giokas et al., 2007). Indeed, they absorb light in both UVA and UVB wavelength regions and thus are widely used as active substances in sunscreen products.

Nowadays, as UV filters of cosmetics and particularly sunscreens are becoming widespread available, questions have been raised concerning their long-term usage and the resulted skin damage in the presence of UV radiation (Gasparro et al., 1998; Nohynek and Schaefer, 2001). For instance, synthetic UV filters may penetrate the skin resulting in systemic exposure to potentially harmful xenobiotic and allergic chemicals as well as estrogenic effects (Boehm et al., 1995; Nohynek and Schaefer, 2001). Moreover, *in vitro* studies have shown that some sunscreen ingredients cause DNA damage (inflected by free radicals) and subsequently may be carcinogenic (McHugh and Knowland, 1997).

Antioxidants are typically used in sunscreens to complement UV filter protection, as they are able to reduce the damage induced by the free radicals generated by solar irradiation (Damiani et al., 2006). For instance, Afonso et al. (2014) referred that antioxidants like vitamin C (ascorbic acid), vitamin E (α-tocopherol) and coenzyme Q10 (ubiquinone) decreased UV-related skin damage by increasing the photostability and *in vitro* SPF of avobenzone. Natural phenols have also been proposed for their valorization as active agents in sunscreen formulations (Fang and Bhandari, 2010) since they have similar structures with chemical UV filters and thus could act with the same mechanism. A typical example is quercetin, which has been referred to enhance the photo-stability of methoxy dibenzoylmethane (UVA) and octyl methoxy cinnamate (UVB) filters, respectively (Scalia and Mezzena, 2010). Likewise, hydroxytyrosol has been referred to have a protective role against UVA-induced protein (D'Angelo et al., 2005) and UVB-induced DNA damages. Hydroxytyrosol (100 μM) reduced intracellular reactive oxygen species formation and attenuated the expression of p53 and NF-

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ƙB in a concentration dependent manner, proposing a positive effect as topical use (Guo et al., 2010).

Olive oil industry generates annually significant amounts of olive mill wastewater together with other residues like biomass from olive tree pruning, olive kernel and olive pomace (Souilem et al., 2017; Galanakis, 2017). Lignocellulosic-rich residues from different sources are nowadays considered as potential substrates for the generation of several high-added value products within integrated biorefinery concepts (Pietarinen et al., 2006; Villaverde et al., 2010, 2013). For instance, low moisture residues are considered for heat and power generation as well as the production of bioethanol and bio-based products, *e.g.* oligosaccharides, pectin and antioxidants (Galanakis et al., 2010; Menon and Rao, 2012; Villaverde et al., 2016). High-moisture residues are examined for the recovery of polyphenols, the production of biofuels, animal feed and potential agricultural uses (Belaqziz et al., 2016; Regni et al., 2017; Galanakis and Kotsiou, 2017). Other applications (*e.g.* production of biosorbents and biopesticides) have also been proposed (Villaverde et al., 2016; Galanakis, 2017). Olive mill wastewater is a rich source of bioactive compounds and natural phenols like hydroxytyrosol (Galanakis, 2011, 2012; Rahmanian et al., 2014). In our previous work (Galanakis, 2014), we showed that phenols (recovered from olive mil wastewater) are more active UV filters compared to ascorbic acid and α-tocopherol in both UVB and UVA regions, probably due to their higher antioxidant capacity. The fact that olive phenols absorb in both UV regions of interest allowed their application as UV booster in particular cases, *i.e.* to enhance the absorption of TiO_2 solutions in both UVB and UVA region, the absorption of Tinosorb M and Uvinul A solutions in the UVB region and the absorption of Octocrylene, OD-PABA and OMC in the UVA region.

The efficacy of bioactive compounds in cosmetics is related to their diffusion through the skin. Small soluble molecules with lipophilic and hydrophilic properties have greater ability to cross the stratum corneum than polymers or highly lipophilic substances (Rawlings and Matts, 2005). However, if they are very soluble in water, there is always the problem of being removed from the skin during seawater immersion. This is a common problem with the applications of phenols. Following these considerations, the aim of the current study is to investigate the implementation of phenols (recovered from olive mill wastewater) as UV booster in cosmetics, using different concentrations. In addition, the encapsulation of olive phenols prior their emulsification in cosmetics was investigated with the final purpose of increasing their water resistance.

2. Experimental

2.1. Materials

Olive mill wastewater was collected from a local three-phase olive mill production unit (Chania, Greece). Olives (Olea europaea L.) were mature black. The used extraction process requires 15 L fresh water/100 kg of olives processed to separate the olive oil from the crushed olive cake and the wastewater. Crushing and kneading temperature was kept below 30 °C, while the residence period of the OMW in the sequential extractor was 40 min. Fresh sample (30 °C) was collected from the output of the decanter and kept in plastic containers in the freezer (20 °C) until usage.

Seawater was collected from a local beach in Chania (Greece). Tinosorb M (99%) was purchased from BTC Europe GmbH (Germany). Uvinul A (95%), TiO_2 (99%) and Octocrylene (99%) were purchased from CareCreations BASF (Germany). Liposome base (Pro-Lipo Neo) was purchased from LUCAS MEYER COSMETICS (France). Octyl dimethyl PABA (OD-PABA) (99%) was purchase from Esperis S.P.A. (Italy), whereas Octyl Methoxy Cinammate (OMC) (99%) and Benzophenone-3 (99%) were obtained from Bonne Bell Company (USA) and AGRAR S.R.L. (Italy), respectively. Base Cream (containing water, glycerine, alcohols and others) was provided by Yellow Rose SA (Athens). Levasil 200E/20 was purchased from AkzoNobel Pulp (Sweden).

2.2. Pilot scale recovery of olive phenols

Olive mill wastewater (2 tn) was concentrated for 15 h (26–30 °C) in an electrical vacuum filter concentrator AES-35-70-140 (VELO, Italy) until reaching a final weight of 280 kg. The concentrated olive mill wastewater was mixed with 96% EtOH (1:1 *per* weight) and the alcohol insoluble residue was removed with a SG2-700 ethanol decanter (Alfa Laval, Sweden) under vacuum. The supernatant liquid (10% ethanol) was mixed with maltodextrin and dried with an Anhydro Lab S3 spray drier (capacity of 35 kg water/h). The generated powder kept in air-tight plastic bags in the freezer (20 °C) until analysis and usage. Before usage, samples were defrosted and analysed for total phenols according to the method referred by Galanakis et al. (2010). The initial samples contained 5 g of total phenols/g powder.

2.3. Spectrum experiments

Synthetic UV filters (Benzophenone-3, Uvinul A, Tinosorb M, TiO_2, Octocrylene, OMC and OC-PABA) were diluted alone or in combination with different concentrations of olive phenols in several solvents (water, ethanol or hydroethanolic mixtures). Thereafter, the respective spectrums of the resultant solutions were obtained in the wavelength range of 220–400 nm, using a UV–vis spectrophotometer (Hitachi, Model V-2000) and each solvent as a blank.

2.4. Experiments of entrapped olive phenols in different cosmetic formulations

Formulation Number 1: 200 mg olive phenols powder emulsified with 25 g base cream using blender for 1 min. *Formulation Number 2*: 200 mg olive phenols mixed with 136 μL Levasil (silica gel) and 136 μL deionised water in a tube, using Vortex for 10 min. The resultant mixture emulsified with 24.5 g base cream using a blender for 1 min. The weight of the final cream was equal to 25 ± 0.2 g. *Formulation Number 3*: 200 mg olive phenols powder emulsified with 1200 μL of deionised water in a tube using Vortex from 2 min. Thereafter, 360 μL Pro-Lipo Neo (liposome base) added and the resultant mixture homogenized using Vortex for 10 min. Finally, 23.5 base cream were added and the cream was homogenized using a blender for 1 min. *Formulation Number 4*: 200 mg olive phenols mixed with 136 μL Levasil and 840 μL deionised water in a tube and mixed with Vortex for 2 min. Thereafter, Pro-Lipo Neo and base cream were added subsequently as noted in the formulation Number 7.

2.5. Determinations

2.5.1. Sun protection factor (SPF)

SPF was determined *in vitro* following a modification of the procedure described by Dutra et al. (2004). More specifically, spectrums of diluted sunscreen formulations (1 g in 25 mL isopropanol) were taken using the UV spectrophotometer in the UVB wavelength range of 290–320 nm. SPF was calculated from the following equation:

$$SPF_{spectrophotmetric} = CF \times \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda) \quad (1),$$

where *EE* (λ) – erythemal effect spectrum; *I* (λ) – solar intensity spectrum; *Abs* (λ)- absorbance of sunscreen product; *CF* – correction factor (=10). The values of *EE* × *I* are constant given by Sayre et al. (1979).

2.5.2. Water resistance

Water Resistance (%) of sunscreen formulations was determined using the corresponding SPF:s of the formulations before and after their