Industrial Crops & Products 112 (2018) 305–312

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Synergistic photoprotective activity of nanocarrier containing oil of *Acrocomia aculeata* (Jacq.) Lodd. Ex. Martius—Arecaceae

Michelli F. Dario[a], Fernanda F. Oliveira[a], Debora S.S. Marins[a], André R. Baby[a,*], Maria V.R. Velasco[a], Raimar Löbenberg[b], Nádia A. Bou-Chacra[a]

[a] *Faculty of Pharmaceutical Sciences, University of São Paulo, São Paulo, Brazil*
[b] *Faculty of Pharmacy and Pharmaceutical Sciences, University of Alberta, Alberta, Canada*

ARTICLE INFO

Keywords:
Bocaiúva
Photoprotection
Nanostructured lipid carriers
Avobenzone
Octocrylene
Characterization

ABSTRACT

Nanostructured vegetable oils have played a key role towards a major shift in sunscreen formulation. The organic ultraviolet filters, present in conventional products, can be absorbed through the skin resulting in systemic exposure with unpredicted effects. Thus, the long-term exposure to these chemical agents may pose a risk to consumer safety and health. Additionally, structural change or degradation of organic filters such as avobenzone may occur by the ultraviolet radiation (UVR) decreasing its absorption capacity. Nevertheless, the use of these products, at daily basis, is highly recommended for skin cancer and photoaging prevention. The bocaiúva oils contain a high content of fatty acids, polyphenols, oligo-elements and β-carotene. This feature has potential application as a natural effective strategy against the UVR. In the present study, nanostructured lipid carriers (NLCs) have been prepared by high-pressure homogenization technology using bocaiúva almond (BAO) and pulp (BPO) oils and cetyl palmitate, as liquid and solid lipids, respectively. The designed NLCs showed average diameters between 106.9 ± 1.6 and 188.4 ± 2.2 nm and zeta potential higher than 30 mV (in module). The NLC containing BAO (NLC-BAO) and BPO (NLC-BPO) presented avobenzone (AVO) entrapment efficiency (EE) of 75.2 and 33.3% w/w, respectively. Both NLCs presented similar EE for octocrylene (OCT): 82.3 and 82.5% w/w. NLC-BAO, co-loaded with the UV filters, allowed the increase in sun protection factor (SPF) of approximately 2-fold, from 14.1 ± 0.7 to 31.8 ± 0.6, after its incorporation into a hydrophilic cream base SPF 14. Surprisingly, NLC-BAO, without AVO and OCT, shifted the SPF of this cream base to 27.7 ± 0.8. Thus, NLC-BAO has the potential to replace organic filters preserving the photoprotection. This study shows a successful development of a nanocarrier containing bocaiúva almond oil to improve the formulation photoprotective activity. It can be a potentially superior alternative adjuvant to sunscreen products allowing the use of the renewable vegetable source.

1. Introduction

Solar radiation, mainly the ultraviolet (UV) wavelength ranging from 280 to 400 nm, is the main factor responsible for high rates of skin cancer in the world (Narayanan et al., 2010), by indirect or direct features. UVB radiation (290–320 nm) causes burns, is erythematogenous, promotes late and long-term tanning by stimulating melanin synthesis and has a high carcinogenic potential, since it has direct action in both DNA and mutation repair proteins, such as p53 (Reichrath and Rass, 2014). UVA radiation (320–400 nm) induces the formation of several reactive oxygen species (ROS) and lipid peroxidation in cell membranes (Ryu et al., 2014), contributing to the premature aging and appearance of wrinkles, sagging and dry skin (Arakane and Naru, 2015), and indirectly contributes to the photocarcinogenesis (Reichrath and Rass, 2014).

Daily basis application of photoprotective formulations is highly recommended for skin cancer and photoaging prevention. However, organic UV filters, present into conventional products, can be absorbed through the skin and the long-term exposure to these chemicals may result in risk to consumer safety and health (Hojerová et al., 2017).

Abbreviations: AA, antioxidant activity; AE, antiradical efficiency; AVO, avobenzone; BAO, bocaiúva almond oil; BPO, bocaiúva pulp oil; CB, cream base; CP, cetyl palmitate; DPPH, 2,2-diphenyl-1-picrylhydrazyl; EC, efficient concentration; EE, entrapment efficiency; FA, free acidity; FAME, fatty acid methyl ester; GAE, gallic acid equivalents; LMMP, poloxamer; NLC, nanostructured lipid carriers; OCT, octocrylene; ORAC, oxygen radical absorbance capacity; PdI, polydispersity index; ROS, reactive oxygen species; SLP, soybean lecithin; SLS, sodium lauryl sulphate; SLN, solid lipid nanoparticle; SPF, sun protection factor; TCCA, triglycerides of capric/caprylic acid; UV, ultraviolet; UVR, ultraviolet radiation; Z-average, average diameter; ZP, zeta potential; λ_c, critical wavelength

* Corresponding author at: 580 Prof. Lineu Prestes Avenue, Bl-15, 05508-900, São Paulo, SP, Brazil.
E-mail address: andrerb@usp.br (A.R. Baby).

https://doi.org/10.1016/j.indcrop.2017.12.021
Received 12 September 2017; Received in revised form 16 November 2017; Accepted 9 December 2017
0926-6690/

Additionally, these UV filters can be degraded by the radiation, reducing their efficacy and generating photo-degradation products that may cause skin irritation or photodermatosis, including phototoxicity/photoirritation and photoallergic reactions (Nash and Tanner, 2014). Therefore, antioxidants from vegetable oils have been extensively studied in order to reduce UV filters concentrations in sunscreens, maintaining or elevating the efficacy, or even, to obtain photostable systems, safer to the consumer (Badea et al., 2015).

As alternative to reduce photoinactivation and skin permeation of UV filters, preserving photoprotective efficacy and safety (Morabito et al., 2011), it has been proposed nanotechnology-based system loaded with organic filters as solid lipid nanoparticles (SLN) (Lacatusu et al., 2011), nanoemulsion (Puglia et al., 2014; Silva et al., 2013), nanostructured lipid carriers (NLC) (Xia et al., 2007), polymeric nanoparticles (Vettor et al., 2008), and cyclodextrin complexation (Scalia et al., 2011). SLN and NLC have been investigated in sunscreens as UV filter carriers and scattering particles. SLNs are composed of solid lipids, which can form relatively perfect lipid crystals. On the other hand, NLCs are prepared from a mixture of solid with liquid lipids, which produces imperfect crystals. This property allows NLCs to have a loading capacity even more than SLN, as an advantage, since active molecules can occupy the additional space provided by the imperfections in the crystal (Xia et al., 2007).

In addition to the interesting properties of NLC, nanostructured vegetable oils have been successfully used in sunscreens aiming to improve photoprotective activity (Badea et al., 2015). Vegetable oils present several advantages over isolated synthetic compounds due to their complex composition. Triglycerides, fatty acids, phenolics, and carotenoids are among the bioactive compounds usually found in seed, almond and pulp oils. Most of these substances, with antioxidant properties, have demonstrated impressive effects in providing protection of skin against ROS, synergistically improving the photoprotective properties of sunscreens (Lubbe and Verpoorte, 2011; Mukherjee et al., 2011).

Bocaiúva palm (*Acrocomia aculeata* (Jacq.) Lodd. Ex Martius), also known as macaúba, is an oleaginous palm tree from the Arecaceae family abundant in Brazil, mainly in Southeast and Midwest regions, whose oil is rich in fatty acids, triglycerides phenolic compounds, terpenes, β-carotene and oligo elements (Basso et al., 2013; del Río et al., 2016; Moura et al., 2010; Vieira et al., 2012), revealing its potential use in photoprotective formulations (Ferreira et al., 2011; Silva and Andrade, 2013).

In this study, innovative sunscreen formulations containing lipid nanocarriers were prepared aiming to reduce the organic filters concentration without compromising the photoprotective efficacy. Bocaiúva pulp (BPO) and almond (BAO) oils were obtained by the cold-pressing method and characterized. The NLCs containing the oils, without and with avobenzone (AVO) and octocrylene (OCT), were prepared by high-pressure homogenization. In addition, NLC-BPO and NLC-BAO were characterized and their photoprotective property investigated.

2. Materials and methods

2.1. Materials

The following materials have been used from the indicated sources without further purification procedures. Triglycerides of capric/caprylic acid (TCCA), cetyl palmitate (CP) and soybean lecithin (SLP) were provided by Mapric (São Paulo, Brazil). Sodium lauryl sulfate (SLS) was acquired from Merck (São Paulo, Brazil). Poloxamer (Lutrol micro 68 MP®) (LMMP) was donated by BASF (São Paulo, Brazil). Tween® 80 (polyoxyethylene sorbitan monooleate) was acquired from J.T. Baker (São Paulo, Brazil). Avobenzone and octocrylene were purchased from Volp (São Paulo, Brazil). Ultra-purified water was obtained from a Milli-Q Plus system (Gradient 10, Millipore®). The vegetable oils, bocaiúva pulp oil (BPO) and bocaiúva almond oil (BAO), were obtained from Cocal Óleos Specials Ltda (rural community) from Abaeté, Minas Gerais (Brazil). The bocaiúva almond and pulp oils were prepared by a mechanical press procedure (Piratininga R-158). For the pulp, aiming to increase the efficiency in extraction, a vapor generator boiler (Sathel, Brazil) was used. The temperature was increased from 30 to 50 °C to maintain the integrity of the compounds. A total of 100 kg of pulp resulted in 40 kg of oil and from 100 kg of almond, 60 kg of oil was extracted.

2.2. Quantification of antioxidant compounds

2.2.1. Total phenolic compounds

Total phenols were analyzed by spectrophotometry (Shimadzu UV–vis, 2100) at 725 nm using Folin-Ciocalteau method (Singleton and Rossi, 1965). The content was expressed as gallic acid equivalents (GAE) in milligrams per gram of sample, using a standard curve generated with gallic acid.

2.2.2. Total carotenoids

Quantification was performed in a spectrophotometer (Shimadzu UV–vis 2100), covering a wavelength interval from 300 to 550 nm (Rodrigues-Amaya, 1999). The total amount of carotenoids was expressed in β-carotene equivalent (μg β-carotene g^{-1} oil).

2.3. Analysis of fatty acids

Fatty acid profile was determined according to EU Regulation (UE Regulation 702, 2007). The methyl esters (FAME-fatty acid methyl ester) were obtained by cold alkaline transesterification with methanolic potassium hydroxide solution and extracted with n-heptane. The fatty acid profile was analysed by gas chromatography (Varian® GC, 430 GC) equipped with a CP 8713 (Chrompack) silica column (100 m × 0.25 mm ID × 0.2 μm film thickness), a flame ionization detector with helium as the carrier gas (29 mL/min), and a temperature range from 140 to 240 °C. The Galaxie software was used to quantify and identify the peaks. A control sample of fatty acid methyl ester standard mixture (Supelco 37 FAME Mix) was used for calibration and for the identification of the FAME by their retention times (Sigma-Aldrich®, Brazil).

2.4. Free acidity (FA), iodine value and refraction index

FA was determined by an acid-base titration using 0.1 M KOH of free fatty acids in an oil sample previously dissolved in ethanol/ether 2:1 (v/v) (UE Regulation 702, 2007). FA was expressed as a percentage of oleic acid. The iodine value was determined using AOAC Official Method 993.2 and the refractive index was determined using an ABBÉ® refractometer maintained at 40 °C, according to the method proposed by American Oil Chemists' Society (AMERICAN OIL CHEMISTS' SOCIETY, 1990).

2.5. Antioxidant activity of bocaiúva pulp oil

2.5.1. DPPH method

The antioxidant activity was determined by the scavenging activity evaluation of the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH·), according to the method described by Kalantzakis et al. (Kalantzakis et al., 2006). The antiradical efficiency (AE) of oils was determined according to Eq. (1) (Brand-Williams et al., 1995) where AE is the antiradical efficiency, EC is the efficient concentration

$$AE = 1/EC_{50} \quad (1)$$

2.5.2. ORAC antioxidant assay

ORAC (Oxygen Radical Absorbance Capacity) procedure was