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Photodegradation of avobenzone: Stabilization effect of antioxidants

S. Afonso [a], K. Horita [a], J.P. Sousa e Silva [a,*], I.F. Almeida [a], M.H. Amaral [a], P.A. Lobão [a], P.C. Costa [a], Margarida S. Miranda [b], Joaquim C.G. Esteves da Silva [b], J.M. Sousa Lobo [a]

[a] Laboratory of Pharmaceutical Technology, Department of Drug Sciences, Faculty of Pharmacy, University of Porto, Rua Jorge de Viterbo Ferreira, n.° 228, 4050-313 Porto, Portugal
[b] Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, P-4169-007 Porto, Portugal

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ABSTRACT

Avobenzone is one of the most common UVA-filters in sunscreens, and is known to be photounstable. Some of the strategies used to stabilize this filter present some drawbacks like photosensitization reactions. Antioxidants are widely used as cosmetic ingredients that prevent photoageing and complement the photoprotection offered by the UV-filters preventing or reducing photogenerated reactive species. The purpose of this work was to study the effect of antioxidants in the photostabilization of avobenzone. The filter dissolved in dimethyl sulfoxide or incorporated in a sunscreen formulation was irradiated with simulated solar radiation (750 W/m^2). The tested antioxidants were vitamin C, vitamin E, and ubiquinone. The area under the curve of the absorption spectrum for UVA range and the sun protection factor (SPF) were calculated. Vitamin E (1:2), vitamin C (1:0.5) and ubiquinone (1:0.5) were the more effective concentrations increasing the photostability of avobenzone. In sunscreen formulations, the most effective photostabilizer was ubiquinone which also promoted an increase in SPF.

This knowledge is important to improve effectiveness of sunscreen formulation. Antioxidants can be valuable ingredients for sunscreens with a triple activity of filter stabilization, SPF boosting and photoageing prevention.

1. Introduction

Nowadays, there is a need to develop more effective sunscreens to ensure optimal photoprotection. Chemical UV-filters are compounds incorporated on sunscreen formulations to absorb specific wavelengths of ultraviolet radiation, UVA (320–400 nm), UVB (290–320 nm) or both. The high capacity of UV-filters to absorb UV should remain stable for the entire period of sun exposure in order to achieve the expected photoprotection for commercial sunscreen products [1]. Some UV-filters are photochemically unstable, which impair their absorbance after UV exposure. UV-filters molecules absorb the incoming UV radiation and reach an excited state. However, the excited molecules return to the basal state by different mechanisms. These mechanisms can lead to the formation of new compounds or photoproducts which can be inactive, decreasing sunscreen effectiveness [2], can interact with skin biocomponents causing photoallergy and phototoxicity reactions [2–4] or even interact with other UV-filters [5] or other ingredients present in sunscreen formulations leading to the formation of another compounds with unknown toxicity [1,2,6].

Avobenzone (4-*tert*-butyl-4′-methoxydibenzoylmethane) is one of the most common UVA-filters in sunscreens, and is known to be photounstable. The photochemical behaviour of this filter has been extensively studied and it has been found that its photostability is highly dependent on the polarity and proticity of the solvent [7–9]. Photoallergic and cytotoxic reactions have often been associated to avobenzone due to the photodegradation products such as arylglyoxals and benzils [4].

Several strategies have been explored in order to improve avobenzone-containing sunscreens. For example, it is well known that avobenzone–octocrylene association improves avobenzone photostability [2]. Octocrylene, among other triplet quenchers like methylbenzylidene camphor, is the most effective at stabilizing avobenzone [10] but it is expensive and difficult to incorporate into sunscreens [11]. Such as octocrylene, there are many available molecules stabilizing avobenzone but unable to quench reactive species generated due to photofragmentation [12]. Actually, safety issues have arisen regarding octocrylene and such as the generation of reactive oxygen species (ROS) in human epidermis keratinocytes as a result of UV irradiation [13]. Furthermore, reports of positive patch test and photopatch test reactions to octocrylene have increased during the last decade [14,15]. Following these data it is of utmost importance to develop new strategies for avobenzone photostabilization.

* Corresponding author. Tel.: +351 220428620.
E-mail address: paulo.silva@ffup.pt (J.P. Sousa e Silva).

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Antioxidants are often used in the cosmetic industry to reduce skin ageing due to UV radiation and in sunscreen formulations to complement the photoprotection offered by the UV-filters [16], preventing or reducing potentially photogenerated reactive species [17–19]. The question that arises is whether these antioxidants may also be involved in the chemical stabilization of UV-filters.

The aim of this study was to evaluate the photodegradation of avobenzone after exposure to simulated solar radiation and study the effect of antioxidants vitamin C, vitamin E and ubiquinone on its photostability. To the best of our knowledge there are very few research works that addressed the use of antioxidants to photostabilize avobenzone, and this one performed a systematic study of the use of antioxidants. The results of this research can be useful to improve the formulation of sunscreens incorporating avobenzone.

2. Experimental

2.1. Materials

Avobenzone (Eusolex 9020) and EDTA were obtained from Merck®. Vitamin E acetate, vitamin C, ubiquinone, isopropyl myristate, paraffinum liquidum and glycerine were obtained from Acofarma® and tween® 60, sodium benzoate and nipagin® from Vaz Pereira®. Cetostearyl alcohol from Guinama®, span® 60 from Roig Farm® and dimethylsulfoxide (DMSO) from Acrõs Organics®.

2.2. Sample preparation

2.2.1. Avobenzone solutions

Avobenzone solutions (5 μg/mL) with antioxidants (vitamin E, vitamin C, ubiquinone) at different concentrations were prepared in dimethyl sulfoxide using amber volumetric flasks. These solutions were prepared by mixing avobenzone's and antioxidants' stock solutions, so that the final concentrations were those shown in Table 2. A solution of avobenzone was used as control.

2.2.2. Sunscreen formulations

Five formulations were prepared (Table 1): non-ionic emulsion without avobenzone (base) and without antioxidants (1), with avobenzone and without antioxidants (2), with avobenzone associated to vitamin C (3), vitamin E (4) and ubiquinone (5). The creams were prepared by the conventional hot emulsification process with phase inversion. The antioxidants were added after the cooling phase. Vitamin C was previously dissolved in water, vitamin E was directly incorporated into the cream and ubiquinone was previously dissolved in isopropyl myristate. These formulations were characterized for their appearance. The pH of the formulation containing vitamin C was determined.

Table 1
Composition of sunscreen formulations under study (wt%).

Ingredients	1	2	3	4	5
Cetostearyl alcohol	6	5	5	5	5
Isopropyl myristate	17	14	14	14	14
Tween® 60	4.5	4.5	4.5	4.5	4.5
Span® 60	2	2	2	2	2
Liquid paraffin	2	2	2	2	2
Glycerin	2	2	2	2	2
EDTA	0.1	0.1	0.1	0.1	0.1
Sodium benzoate	0.1	0.1	0.1	0.1	0.1
Nipagin®	0.1	0.1	0.1	0.1	0.1
Water q.s.	100	100	100	100	100
Avobenzone	–	4	4	4	4
Vitamin C	–	–	2	–	–
Vitamin E	–	–	–	8	–
Ubiquinone	–	–	–	–	2

2.3. Irradiation

Avobenzone solutions were contained in screw cap quartz cells and formulations were spread in polymethylmethacrylate (PMMA) plates (1 mg/cm^2). The samples were irradiated at 750 W/m^2 using a xenon lamp equipped with a special UV-filter used to simulate UV radiation that reaches the earth and IR-block filter to neutralize temperature effects (Atlas, Suntest CPS+). The irradiation time was 1 h and the incident dose of UV was 2700 kJ/m^2.

2.4. UV measurements

The spectra of avobenzone solutions were obtained in a spectrophotometer (Jasco V-650). To measure the decrease in absorbance of avobenzone the spectra were recorded before and two hours after irradiation, from 250 nm to 400 nm. The area under the curve (AUC) was calculated for UVA range, before and after irradiation.

The AUC ratio (AUC R) was used to calculate the photostability increase (PI) in %. If the AUC ratio was higher than 0.80 the UV-filter was considered photostable [20].

$$\text{AUC R} = \frac{\text{AUC } \textit{after}}{\text{AUC } \textit{before}} \tag{1}$$

$$PI\ (\%) = \frac{\text{AUC R } (\textit{sample}) - \text{AUC R } (\textit{control})}{\text{AUC R } (\textit{control})} \times 100 \tag{2}$$

2.5. In vitro sun protection factor (SPF) measurement

The *in vitro* determination of the SPF of the sunscreen formulations was carried out according to the Diffey and Robson method [21], with minor modifications. The transmission spectrum of the UV radiation (290–400 nm) was measured after application (1 mg/cm^2) of the sunscreen formulation on a roughened PMMA plate. The plate was placed into the spectrophotometer (Jasco V-650) sample compartment, facing the light emission source. A plate with the formulation 1 (base) was used as blank. The spectral data were processed with a personal computer and the SPF calculated according to Eq. (3):

$$\text{FPS}_{\ in\ vitro} = \frac{\int_{\lambda=290\text{ nm}}^{\lambda=400\text{ nm}} E(\lambda) * I(\lambda) * d\lambda}{\int_{\lambda=290\text{ nm}}^{\lambda=400\text{ nm}} E(\lambda) * I(\lambda) * 10^{-A_0(\lambda)} * d\lambda} \tag{3}$$

where $E(\lambda)$ is the spectral irradiance of terrestrial sunlight under defined conditions at wavelength λ, $I(\lambda)$ is the erythemal action spectrum at wavelength λ and $A(\lambda)$ is the monochromatic absorbance of the sample.

AUC ratio and photostability increase (PI) were also calculated as described previously in triplicate.

2.6. Statistical analysis

Statistical analysis of the experimental data (AUC ratio) of sunscreens was performed by Anova followed by Tukey HDS tests using SPSS 20.0 (SPSS Inc., software). Differences were accepted as statistically significant when $p < 0.05$.

3. Results and discussion

Photostability is an important property that impact UV-filters effectiveness and can be evaluated by measuring the decrease in absorption after irradiation.