Journal of Photochemistry and Photobiology C: Photochemistry Reviews 13 (2012) 91–110

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology C: Photochemistry Reviews

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

Review

Photostability of sunscreens

Jutta Kockler, Michael Oelgemöller, Sherryl Robertson, Beverley D. Glass*

School of Pharmacy and Molecular Sciences, James Cook University, Townsville 4811, QLD, Australia

ARTICLE INFO

Article history:
Received 17 October 2011
Received in revised form
23 December 2011
Accepted 26 December 2011
Available online 6 January 2012

Keywords:
Sunscreens
Photostability
Chemical UV-filters
Physical UV-filters
UV-protection

ABSTRACT

Sunscreens were originally designed to include mainly UVB-filters. Because of the deeper penetration of UVA light, causing photoaging and DNA damage, there has been a shift towards broad spectrum sunscreens. These broad spectrum sunscreens now include both UVA- and UVB-filters and other ingredients which possess antioxidant activity. Although sunscreens are regulated in most countries, photostability testing is not mandatory. Because of the ability of sunscreen ingredients to absorb UV-light and the complexity of most of these formulations, which may include more than one UV-filter, antioxidants and other formulation excipients, it is important that their photostability in combination is determined.

Contents

* Corresponding author. Tel.: +61 7 4781 6423; fax: +61 7 4781 5356.
E-mail address: beverley.glass@jcu.edu.au (B.D. Glass).

1389-5567/$20.00 © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochemrev.2011.12.001

Jutta Kockler completed her Pharmacy degree at the Goethe University in Frankfurt/Main (Germany) and spent six months as visiting researcher at James Cook University in Townsville (Australia) during her degree program. In 2010 she commenced her MPharm in photostability and formulation of sunscreens at James Cook University, Townsville (Australia).

Michael Oelgemöller received his Diploma from the University of Münster (Germany) in 1995 and his PhD from the University of Cologne (Germany) in 1999. He was a researcher at the Inoue Photochirogenesis project in Osaka and at Bayer CropScience Japan in Yuki. He held a position as a Lecturer in Organic and Medicinal Chemistry at Dublin City University (Ireland). Currently he is an Associate Professor in Organic Chemistry at James Cook University (Australia). His research activities include synthetic organic photochemistry, solar photochemistry, the development of new photochemical synthesis tools and photochemical water treatment. He received the Kurt-Alder award of the University of Cologne in 2000.

Sherryl Robertson completed her BAppSc Honours degree in Chemistry at Central Queensland University in Rockhampton (Australia) and PhD from Murdoch University, Perth (Australia). After a research career in hydrometallurgy, she joined the School of Pharmacy and Molecular Sciences at James Cook University as a Senior Technical Officer.

Beverley D. Glass obtained her BSc Honours degree in Chemistry from Nelson Mandela Metropolitan University in Port Elizabeth (South Africa) and her Bachelor of Pharmacy and PhD degrees from Rhodes University, Grahamstown (South Africa). Currently she is the Chair and Professor of Pharmacy in the School of Pharmacy and Molecular Sciences at James Cook University. Her research interests include the stability, especially photostability of drug substances and drug products with a focus on in-use stability and photosensitivity effects in patients.

1. Introduction

Exposure to ultraviolet (UV)-light can be potentially dangerous and as such result in adverse health outcomes [1]. UV-light may be subdivided into the following regions: UVC (100–290 nm); UVB (290–320 nm); UVAI (320–340 nm) and UVAII (340–400 nm). While the UVC-light is filtered to a large extent by the atmosphere and thus does not reach the surface of the earth [2], UVB-light, although mainly restricted to penetration of the upper layers of the skin, can cause DNA-damage and sunburn. Since UVA is not absorbed by the DNA molecule to any great extent, damage caused by UVA-light is largely attributed to photosensitized oxidation, which may occur by two different mechanisms, Type 1 and 2: Type I process results in the substrate reacting with the excited state of the sensitizer to yield radicals or radical ions, by hydrogen atom or electron transfer, while the Type II process occurs when an excited sensitizer reacts with oxygen to form singlet molecular oxygen. UVA-light does penetrate to the deeper skin layers causing photoageing and DNA-damage mainly by generation of reactive oxygen species (ROS) [3,4]. However, DNA damage has also been shown to occur by a Type 1 mechanism involving an intramolecular electron transfer in folic acid and its photodegradation product, pterine-6-carboxylic acid [5].

Although skin cancer is the worst outcome of excessive exposure to UV-light [6,7], sunburn, eye conditions such as cataract or ocular melanoma, premature skin ageing such as wrinkles or irregular pigmentation of the skin and a compromised immune system may also result from this exposure [8]. It is noteworthy that Australia and New Zealand have the highest rates of skin melanoma in the world [9].

Sunscreens are photochemical systems containing UV-filters, which absorb or reflect light and can be divided into two types: chemical and physical UV-filters. The chemical UV-filters can be further subdivided into UVA-filters which only absorb UVA-light, UVB-filters (only absorbing UVB-light) and broad spectrum filters which absorb both UVA- and UVB-light. The available physical UV-filters are broad spectrum filters, which absorb and reflect UV-light. Besides these UV-filters, sunscreens may contain other additives such as antioxidants, which are also thought to play a role in protecting the skin from the effects of exposure to UV-light [10].

Regular application of sunscreens to the skin is the most effective protection against the dangerous effects of UV-light. The first modern sunscreens merchandised in the 1930s [11] were characterized by the Sun Protection Factor (SPF), which is a laboratory measure of the effectiveness of a sunscreen. The higher the SPF, the more protection the sunscreen offers against UVB radiation [12]. The SPF-testing method is an in vivo method, where protected and unprotected skin-areas of subjects are exposed to artificial sunlight for various time periods. The SPF is defined as the minimum erythemal dose (MED = UVB-dose when redness of the skin is visible) on protected skin divided by the MED on unprotected skin (Eq. (1)) [13].

$$\mathrm{SPF} = \frac{\mathrm{MED}_{\mathrm{protected}}}{\mathrm{MED}_{\mathrm{unprotected}}} \quad (1)$$

Since the harmful and photoageing effects of UVA have been reported, UVA-filters are now included in sunscreens, which are classified as broad spectrum [6,14–17]. The UVA-protection factor (UVA-PF) can be measured in vivo or in vitro. The in vivo test-method, also called the Persistent-Pigment Darkening (PPD) method was developed by the Japanese industry and modified by the French health agency (Afssaps = Agence française de sécurité sanitaire des produits de santé) and measures the minimal darkening effect of UVA-radiation on the skin before and after exposure to UVA-light. The UVA-PF is defined as minimal pigmenting dose (MPD = UVA-dose when darkening of the skin is visible) on protected skin divided by the MPD on unprotected skin (Eq. (2)) [18,19].

$$\mathrm{UVA-PF} = \frac{\mathrm{MPD}_{\mathrm{protected}}}{\mathrm{MPD}_{\mathrm{unprotected}}} \quad (2)$$

Because of their role in protecting the skin from the harmful effects of UV-light, sunscreens are required to be regulated. The regulation of sunscreens differs, depending on the particular country and/or the requirements of the relevant regulatory agency. These regulations include in general a list of approved UV-filters, the appropriate labelling of sunscreens and requirements for the measuring of SPF, UVA-PF and water resistance.

In Australia, although most sunscreens are 'listed' medicines under the *Therapeutic Goods Act 1989*, some can be 'exempt' and others are required to be 'registered' [19]. In the USA, sunscreens are regulated as over-the-counter (OTC) drugs under the supervision of the FDA (Federal Drug Administration). The *Federal Register of 1999* contains the final monograph with regulations for sunscreens, entitled: *Sunscreen drug products for over-the-counter human use*. Besides the list of allowed sunscreen active ingredients (UV-filters), their required maximum concentration and the allowed combinations of UV-filters, this monograph contains requirements for labelling and testing of the SPF and water resistance, but not for UVA-protection. In contrast to Australia and the USA, in Europe sunscreens are regarded as cosmetics. The European Commission publishes a *Commission Recommendation on the efficacy of sunscreen products*, where they provide advice regarding the hazards of UV-radiation, the need of sunscreens and recommendations about labelling and testing. An industry association, namely Colipa (European Cosmetic, Toiletry and Perfumery Association) was founded to develop the industry standards on testing, labelling and consumer education [18,20].