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Short communication

Study of the photostability of 18 sunscreens in creams by measuring the SPF in vitro

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Abstract

The target of this research was to evaluate the photostability of various sunscreen agents incorporated into an O/W emulsion. The concept of photostability is very important in the field of solar protection. The effectiveness of the anti-solar products is quantified using a universal indicator: the sun protection factor (SPF). This number which can be found on packaging can be given in two different ways: by methods in vivo (Colipa method) and in vitro. It is this last method which was adopted for this study. According to selected filter UVB (currently directive 76/768/EEC modified authorized 18 filters UVB), we can obtain more or less effective creams. We chose the irradiation of sun lotions formulated using the authorized filters, used with their maximum amount of employment, in a Suntest, with an irradiance of 650 W/m^2 throughout variable time. With interval of regular time, one carries out a measurement of SPF in order to establish for each filter the kinetics SPF = *f*(time). An indicator of stability (t_{90}) is then given. In this way, we could classify the filters by order of increasing photostability.

Keywords: Sunscreens; Photostability; In vitro test

1. Introduction

It is a well-known fact that an over exposure of human skin to ultraviolet light may lead to sunburn cells, premature skin aging and an increased risk for skin cancers [1–4]. The steady increase in the incidence of melanoma, non-melanoma cutaneous neoplasia and preneoplasic disorders has contributed to the demand for more effective protection from the sun. Sunscreen products are intended to protect the skin from the deleterious effects of the sun. In order to guarantee constant efficacy of sunscreen products, the UV filters used should be photostable [1–3]. In this work, we studied the kinetics of photostability of 18 UV filters authorized in European Union [5] by determination of SPF of O/W emulsion containing each sunscreen agent.

2. Experimental

2.1. Materials

The sunscreens and their characteristics are presented in Table 1. Dimethicone (Abil® WE 09) was obtained from Goldschmidt (Montigny-le-Bretonneux, France). Cetiol® HE, stearic acid, glycerin, parabens and triethanolamine (TEA) were purchased from Cooper (Melun, France). Xanthan gum (Keltrol® BT) was obtained from Kelco (Lille Skensved, Denmark). Polymethylmethacrylate (PMMA) plates were purchased from Helioscience (Creil, France).

2.2. Preparation of sunscreen creams

An O/W emulsion was prepared in the laboratory by adding known concentrations of each sunscreen into the formulation components. O/W emulsions tested (Table 2) were manufactured by the authors. Hydrophilic phase and oil-phase were heated separately to 78–82 °C, until the contents of each part are solubilized. The oily preparation was added slowly to hydrophilic

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Table 1
Characteristics of sunscreens studied

INCI name	Suppliers	λ_{max} (nm)	Solubility	Maximum concentration authorized (%)
PABA	Merck, Fontenay sous Bois, France	290.0	Hydrosoluble	5
Homosalate	Merck, Fontenay sous Bois, France	306.0	Liposoluble	10
Oxybenzone	BASF, Levallois Perret, France	287.5	Liposoluble	10
Phenylbenzimidazole sulfonic acid	Merck, Fontenay sous Bois, France	305.5	Hydrosoluble after neutralisation with NaOH	8
Octocrylene	BASF, Levallois Perret, France	304.0	Liposoluble	10
Octylmethoxycinnamate	BASF, Levallois Perret, France	310.0	Liposoluble	10
PEG-25 PABA	BASF, Levallois Perret, France	307.0	Hydrosoluble	10
Isoamyl *p*-methoxycinnamate	Symrise, Neuilly sur Seine, Paris	310.0	Liposoluble	10
Octyltriazone	BASF, Levallois Perret, France	314.5	Liposoluble	5
Diethylhexylbutamidotriazone	Créations couleur, Dreux, France	310.5	Liposoluble	10
4-methylbenzylidene camphor	Merck, Fontenay sous Bois, France	301.0	Liposoluble	4
3-benzylidene camphor	Unipex, Rueil Malmaison, France	291.5	Liposoluble	2
Octylsalicylate	Alzo, Helsinki, Finland	306.0	Liposoluble	5
Octyl dimethyl PABA	Merck, Fontenay sous Bois, France	312.0	Liposoluble	8
Benzophenone-5	BASF, Levallois Perret, France	287.5	Hydrosoluble	5
Methylene bis-benzotriazolyl tetramethylbutylphenol	Ciba, Grenzach-Wyhlen, Germany	305.5	Hydrosoluble	10
Anisotriazine	Ciba, Grenzach-Wyhlen, Germany	310.0	Liposoluble	10
Polysilicone 15	Roche, Fontenay sous Bois, France	312.5	Liposoluble	10

preparation while stirring (Yellow line OST basic mixer, IKA, Staufen, Germany). It was necessary to continue stirring until the emulsion formed was cooled to room temperature (20 °C). In addition, sunscreen agents were incorporated at various concentrations into this emulsion. A cream without any filter is used as blank.

2.3. Photodegradation study

Thirty milligram of product exactly weighed were spread on PMMA plates over the whole surface (25 cm^2) using a cot-coated finger. Polymethylmethacrylate (PMMA) plates were purchased from Helioscience (Creil, France). Fifteen milligram remains on the finger cot. The plates were irradiated for various times with a solar simulator (Suntest CPS+; Atlas, Moussy le Neuf, France) apparatus equipped with a xenon arc lamp (1500 W) and special glass filters restricting transmission of light below 290 nm. The temperature of the samples was kept low and constant using a tap water cooling circuit to the walls of the reactor. In order to eliminate the turbulence inside the Suntest chamber, we have developed in our laboratory a system where the plates are blocked between two rails and covered with quartz plate. The light source emission was maintained at 650 W/m^2 in accordance to global solar spectral irradiance at sea level measured in accordance with CIE [6]. Before and after irradiation, the SPF of the creams was measured in vitro. Three plates were prepared for each product to be tested and nine measures were performed on each plate. Transmission measurements between 290 and 400 nm were carried out using a spectrophotometer equipped with an integrating sphere (UV Transmittance Analyzer UV1000S, Labsphere, North Sutton, US). The standard used was the 8% homosalate standard mandated by the US Food and Drug Administration Sunscreen Monograph. The calculations for either term use the same relationship [7]:

$$\mathrm{SPF} = \frac{\sum_{290}^{400} E_\lambda S_\lambda d_\lambda}{\sum_{290}^{400} E_\lambda S_\lambda T_\lambda d_\lambda} \quad (1)$$

where E_λ is CIE erythemal spectral effectiveness, S_λ the solar spectral irradiance and T_λ is the spectral transmittance of the sample [8,9].

Table 2
Composition of emulsion

Ingredients	Percent by weight
Abil® WE 09 (polyglyceryl-4-isostearate; cetyl PEG/PPG-10/1 dimethicone; hexyl laurate)	5
Paraffin oil	12
Cetiol® HE (PEG-7 glyceryl cocoate)	5
Butylhydroxytoluene	0.01
Stearic acid	5
Eumulgin® B1 (Ceteareth-12)	1.5
Eumulgin® B2 (Ceteareth-20)	1.5
Glycerine	4
Sodium propylparaben	0.05
Sodium methylparaben	0.1
Keltrol® BT (xanthan gum)	0.9
TEA	0.3
Distilled water	qsp 100.0

3. Results and discussion

To fulfil the requirements of sunscreen formulation a silicon cream was chosen [10].

The experimental conditions were determined by correlating the results obtained in vitro with the creams manufactured by the authors with the results obtained in vivo with the same creams, using the protocol recommended by the Colipa (the European Cosmetic Toiletry and Perfumery Association) in the SPF range

Table 3
Photodegradation of the sunscreens incorporated into an O/W emulsion

Sunscreen	SPF_0	Standard deviation	$t_{50\%}$ (half-life) (min)	$t_{90\%}$ (min)	k (min^{-1})
PABA	3.36	0.12	7500	1600	0.0001
Homosalate	3.91	0.44	300	45	0.0023
Oxybenzone	3.22	0.18	1500	320	0.0005
Phenylbenzimidazole sulfonic acid	9.63	0.24	1390	215	0.0005
Octocrylene	13.82	1.08	515	95	0.0014
Octylmethoxycinnamate	11.16	0.41	225	35	0.0031
PEG-25 PABA	4.11	0.11	115	20	0.0061
Isoamyl *p*-methoxycinnamate	13.00	1.92	115	15	0.0059
Octyltriazone	7.41	0.54	300	35	0.0022
Diethylhexylbutamidotriazone	13.94	0.20	8850	1520	0.00008
4-methylbenzylidene camphor	4.81	0.27	345	65	0.0021
3-benzylidene camphor	2.36	0.05	225	35	0.0031
Octylsalicylate	2.70	0.19	85	10	0.0075
Octyl dimethyl PABA	8.64	0.26	85	20	0.0062
Benzophenone-5	3.97	0.13	1150	180	0.0006
Methylene bis-benzotriazolyl tetramethylbutylphenol	5.25	0.23	1700	240	0.0004
Anisotriazine	25.64	2.08	155	20	0.0044
Polysilicone 15	4.48	0.45	180	25	0.0038

[1–30] [11]. Furthermore, there is no difference of anti-solar efficacy of homosalate 8% into the FDA preparation and our excipient [10]. The photodegradation of various sunscreens for our specific formulation and under the given experimental conditions was expressed as the rate of change of SPF (Table 3). The photodegradation followed apparent first order kinetics and is described by the following equation:

$$\frac{SPF}{SPF_0} = e^{-kt} \quad (2)$$

where SPF and SPF_0 are the sun protection factor after and before irradiation, respectively, and k is the apparent first order degradation rate constant.

Fig. 1 demonstrates the gradual decrease in SPF during photodegradation of various filters. The degradation rate constant k was calculated from the slope of the line of SPF versus time. According to the drugs stability testing we consider that a product is stable when it preserves 90% of its effectiveness [12]. The $t_{90\%}$ and the half-live ($t_{50\%}$) are, respectively, the time necessary to obtain a decrease of 10 and 50% of initial SPF. In the event of exposure, it is recommended to the users to apply a sunscreen every 2 h. This recommendation led us to classify the filters in two categories, those whose $t_{90\%}$ is higher than 2 h (good photostability) and those whose $t_{90\%}$ is lower than 2 h (poor photostability).

The PABA known to be very photostable [13] proves not interesting because of the allergic reactions which it is likely to cause [14,15]. Benzophenone-3, phenylbenzimidazole sulfonic acid, benzophenone-5 and methylene bis-benzotriazolyl tetramethylbutylphenol present a very good comparable photostability. This is confirmed for benzophenone-3 in mixture [16]. Besides methylene bis-benzotriazolyl tetramethylbutylphenol is proposed to increase the photostability of other filters [16]. With a half-life of approximately 150 h, diethylhexylbutamidotriazone is the best of filters tested. Homosalate, octocrylene, octylmethoxycinnamate, octyltriazone and 4-methylbenzylidene camphor have a good photostability. OMC undergoes a *cis–trans* isomerization mechanism and we can consider it as a very efficient way of dispersing the absorbed energy [17]. So we can consider that PEG25-PABA, isoamyl *p*-methoxycinnamate,

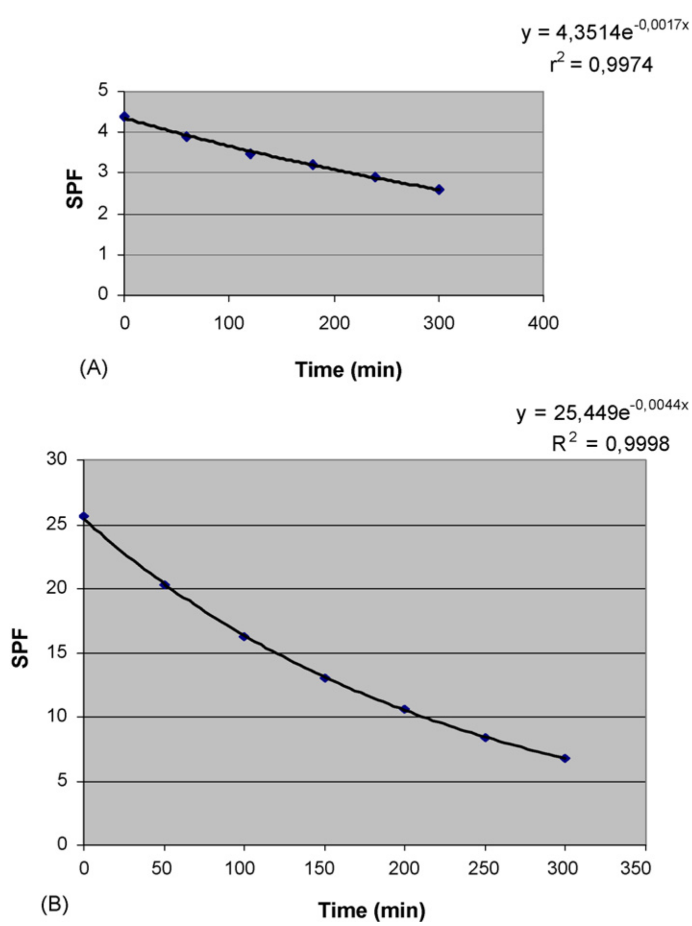

Fig. 1. Photodegradation of homosalate (A) and anisotriazine (B) into O/W emulsion.

octylsalicylate, octyldimethyl PABA and the anisotriazine present a poor photostability.

References

[1] E. Chatelain, Photochem. Photobiol. 74 (2001) 401–406.
[2] V. Vanquerp, C. Rodriguez, C. Couteau, L.J.M. Coiffard, J. Chromatogr. A 832 (1999) 273–277.
[3] K.C. Farmer, M.F. Naylor, Ann. Pharmacother. 30 (1996) 662–673.
[4] B.L. Diffey, P.R. Tanner, P.J. Matts, F. Nash, J. Am. Acad. Dermatol. 53 (2000) 1024–1035.
[5] Council Directive 76/768/EEC of 27 July 1976 on the approximation of the laws of the Member States relating to cosmetic products.
[6] CIE Pub. 85, Tab. 4.
[7] B.L. Diffey, J. Robson, J. Soc. Cosmet. Chem. 40 (1989) 127–132.
[8] R.M. Sayre, P.P. Agin, D.L. Desrochers, E. Marlowe, J. Soc. Cosmet. Chem. 31 (1980) 133–143.
[9] L. Perioli, V. Ambrogi, B. Bertini, M. Ricci, M. Nocchetti, L. Latterini, C. Risi, Eur. J. Pharm. Biopharm. 62 (2006) 185–193.
[10] C. Couteau, M. Pommier, E. Paparis, L.J.M. Coiffard, Pharmazie, in press.
[11] Comité de Liaison des Industries de la Parfumerie (Colipa) Guidelines for International Sun Protection Factor Test Method, 2006.
[12] J. Meunier, Sci. Techn. Pharm. 10 (1981) 375–381.
[13] H. Flindt-Hansen, C.T. Nielsen, P. Thune, Photodermatology 5 (1988) 257–260.
[14] P. Tornero, M. De Barrio, M.L. Baeza, T. Herrero, Contact Dermatitis 51 (2004) 57–62.
[15] W. Uter, H. Lessman, J. Geier, D. Becker, T. Fucks, G. Richter, Allergy 57 (2002) 319–322.
[16] L.R. Gaspar, M. Campos, Int. J. Pharm. 307 (2006) 123–128.
[17] S.T. Butt, T. Christensen, Radiat. Prot. Dosim. 91 (2000) 283–286.