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The photoisomerization of the sunscreen ethylhexyl *p*-methoxy cinnamate and its influence on the sun protection factor

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Abstract

The photoisomerization of the sun filter ethylhexyl *p*-methoxycinnamate (OMC) was studied under various conditions, (i) by irradiating diluted solutions using various solvents, (ii) by irradiating thin layers of concentrated solutions in non-volatile solvents, and (iii) by irradiating thinly applied commercial sunscreen products. The spectroscopic characteristics of the Z isomer were determined, along with its response factor in HPLC analysis. The ratio of the two isomers was measured under each condition of irradiation. The incidence of photoisomerization in the sun protection factor (SPF) was evaluated on the basis of calculations deduced from the concept of irregular film developed by O'Neill. The decrease in SPF, which can exceed 30%, is primarily dependent upon the rate of isomerization of OMC but also on the composition of sunscreen products. As isomerization of OMC is rapid and its rate unpredictable, it is in theory impossible to obtain good correlation between measurements of SPF in vivo and those in vitro, if measurements in vitro are not preceded by the process of irradiation precipitating isomerization of OMC.

Keywords: Octyl methoxycinnamate; Sunscreen; Photoisomerization; Sun protection factor

1. Introduction

The photostability of commercial sunscreen products is considered a key parameter for effective in vitro evaluation of their effectiveness [1]. A sunscreen product, which loses its capacity to block UV radiation during exposure to the sun, provides a clear risk of damage to the user and its use may be more harmful than the protection it affords. The terms photounstable, photolabile, photodegradable and photoinactive are well defined by Bonda [2]. They refer to any molecule (sun filter in this instance) that, when subjected to a given dose of light energy, will reach an excited state causing its original structure to be altered. Two filters are particularly unstable under light: the UVB filter, ethylhexyl-methoxycinnamate (OMC) and the UVA filter, butylmethoxy dibenzoylemethane (BMDBM). Both filters are widely used commercially because in combination they cover a wide range of those wavelengths of concern, specifically 290–400 nm. A significant volume of research has focused on the degradation of DBM [3–5] as well as on its photostability [6–8]. This remarkably effective filter has justifiably long been of commercial interest, being the only viable UVA filter known.

It is probable that OMC is the active component most used worldwide in cosmetic products. The legal maximum content of OMC is 10% in Europe and 7.5% in USA. As a sunscreen, it is intended for covering the largest possible area of exposed skin and it is recommended that sufficient lotion be applied and reapplied regularly. In recent years, the campaign against skin cancers, particularly melanomas, has become a major public health issue and there has been considerable drive by governments to increase public awareness not to stay too long under the sun and to encourage the use of sunscreen products.

The behaviour of OMC in light has been the subject of several papers referenced by Bonda [2]. In relation to the well known E–Z isomerization of cinnamates, the degradation by dimerization of the molecular structure of cinnamate has also been described [9]. The Z isomer of cinnamic acid has been prepared through irradiation of the E isomer [10]. Numerous studies describe this isomerization from a physico chemical point of

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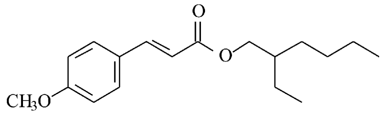
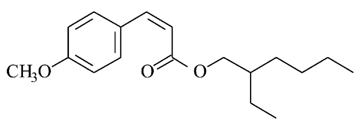
view [11,12]. The E–Z transformation has also been observed during the stocking of E-OMC solution in ethanol [13].



E-OMC



Z-OMC

A research group from a consortium of major European cosmetic companies studied isomerization of OMC using both spectroscopy and HPLC [14]. The relationship between the two isomers was not reported: the Z isomer was merely stated to have a UV spectrum close to that of the E isomer, although with reduced extinction. In their analysis, however, the authors combined the concentrations of both isomers. Similar imprecision has also been encountered in recent studies [4,15]. In the first of these investigations, the photostability of OMC was defined on the basis of the combined responses of the two isomers and not their individual responses. In the second, more recent study, the residual amount of E-OMC after irradiation was specified and it appeared variable as a function of the formulation in which the filter was introduced. Furthermore, the authors did not consider isomerization of OMC a true degradation but rather an effective way to disperse absorbed light energy.

A study by Serpone [16] reports new findings: OMC isomerization was studied both in diluted solution of the pure product, and in the product incorporated in finished products. A solar simulator was used for the irradiations, after dispersal of the sunscreens in various solvents. The relative proportions of the two isomers are not mentioned.

It was not until 2001 [17] that a research group in Thailand successfully isolated the Z isomer (Z-OMC) and determined its characteristics using NMR and LC/MS. The team subsequently published its findings on the spectral characteristics of Z isomer in 2004 [18]. In this latest research, the photostability of OMC was studied in diluted solutions using various solvents and irradiation was achieved by natural sunlight.

Thus, we have focused our attention firstly, on the precise behaviour of OMC towards light under various conditions, namely in diluted solutions as described in [18], in concentrated form within non-volatile solvents, and in commercial sunscreen products. Secondly, we have evaluated the theoretical impact of photoisomerization of the solar protection factor (SPF) through use of home-made software based on the model of irregular film of O'Neill [19].

2. Materials and methods

2.1. HPLC analysis

The HPLC system consisted of a quaternary pump (Model E600) and diode array detector (DAD 996), both from Waters (Saint Quentin-en-Yvelines, France), and controlled by Millenium^{32} software. Solutions were injected via a Rheodyne valve with a 20 μL injection loop. The column (125 cm × 0.4 cm) was a Nucleosil 100-5 C18 from Macherey–Nagel. Solvents used were methanol (A) and a mixture 90/10 of water containing 0.1% H_3PO_4 and methanol. The gradient was as follows: $t = 0$: $A = 30\%$, $B = 70\%$; $t = 3$ min: $A = 100\%$ (linear gradient); $t = 10$ min: $A = 100\%$; $t = 10.1$ min: $A = 30\%$, $B = 70\%$; $t = 15$ min: $A = 30\%$, $B = 70\%$; $t = 15.1$ min stop flow. The flow rate was 1 ml/min. Analyses were performed at room temperature (19–21 °C). The range of the detector extended from 220 to 400 nm. One spectrum was recorded every second with a resolution of 1.2 nm. E-OMC and Z-OMC were both detected at 300 nm. The spectral data (absorbance versus wavelength) for both isomers were obtained using the Spectrum Point function of the Millenium software and were converted into Excel® format.

2.2. Spectroscopy

Spectra were recorded using an Uvikon 922 machine (Serlabo, Entraigues sur la Sorgue, France) with Teflon® stopper 1 cm quartz cuvettes. The wavelength range extended from 220 to 400 nm. The resolution was 1 nm and the scanning rate was 100 nm/min. Spectral data were converted into Excel® format for processing.

2.3. Irradiations

Irradiations were achieved using the solar simulator Suntest CPS+ (Atlas Material Testing Technology, Moussy Le Neuf, France). The working life of the Xenon lamp was 300 h at the beginning of the study. Irradiations of diluted solutions were carried out in spectroscopic 1 cm quartz cuvettes closed by Teflon® stoppers. The cuvettes were placed horizontally in the irradiation chamber and were fixed at their extremities by two bands of Transpore® (adhesive commonly used in SPF determination), because of the strong ventilation in the irradiation chamber. The Transpore masks less than one mm on each extremity of the cuvettes.

The absence of evaporation was confirmed by weighing each cuvette before and after irradiation. Irradiations of concentrated solutions and commercial sunscreen products were achieved using rough glass slides measuring 2.5 cm × 7.5 cm on which a specified quantity of product was placed (15–18 mg equivalent to 0.8–1 mg/cm^2). This quantity was recommended in [1]. During irradiations, the temperature was regulated automatically and varied from 25 to 45 °C according to the length of irradiation. The slides were placed horizontally and were fixed as previously by two bands of Transpore®. Times and energies are specified herein. Energy of irradiation was not measured. It was calculated from the power (P in W/m^2) set on the Suntest and the time of irradiation (t in second) by the formula $E = Pt$. For example, a 250 W/m^2 irradiation during ten minutes (600 s) gives an energy of 150,000 J/m^2 or 150 kJ/m^2.

2.4. Chemicals

The solvents isopropanol (iPro), tetrahydrofuran (THF), heptane (Hept), dioxane (Diox), acetonitrile (ACN), ethylacetate (AcOEt) of highest grade were obtained from Sigma Aldrich (L'Isles d'Abeau, France), along with methanol for HPLC. Mineral oil (MO), alkyltartrate (AT), octyldodecanol (OD), C12–C15 alkylbenzoate (CAB), capric caprylic triglyceride (CCT), isostearyl isostearate (ISOS), alkyllactate (AL), and ethylhexyl *p*-methoxycinnamate (OMC) are industrial products kindly provided by DIPTA (Aix-en-Provence, France). Water was purified by reverse osmosis.

3. Results and discussion

The response factor of Z-OMC using HPLC in relation to E-OMC was determined at a specified wavelength of 300 nm. Thereafter, the spectroscopic characteristics of Z-OMC were determined. Although these characteristics were available [18], spectrum data (SD = absorbance versus wavelength) in Excel® format was required in order to calculate the SPF using our software. The ratio of the two isomers was subsequently determined after irradiation of diluted solutions, concentrated solutions and commercial products. Irradiations were performed using the solar simulator Suntest CPS+, allowing better reproducible operating conditions than described in [18]. The results were not simply based on variations in UV spectra as documented in [16], but obtained through HPLC analysis and calculation of the percentages of both isomers. Finally, the variation in SPF induced by photoisomerization of OMC was determined using the SD of Z-OMC and the range of values of the E–Z ratio obtained under various conditions of irradiation.

3.1. Spectrum characteristics of Z-OMC

The SD of Z-OMC were determined through a combination of spectroscopy and HPLC analysis. A diluted solution of E-OMC in iPro was irradiated with a dose of 150 kJ/m^2 equivalent to 10 min at 250 W/m^2. This power value is the minimum one delivered by the machine. The UV spectrum was recorded before and after irradiation and the solution was analysed by HPLC before and after irradiation.

The results of spectroscopy appeared to indicate a decrease in absorbance and the analysis by HPLC demonstrated the appearance of a new peak, of shorter retention time, attributed to Z-OMC. The UV spectra and the chromatogram are presented in Fig. 1. It was assumed that with low energy irradiation, all the E-OMC lost was recovered in the Z-OMC form. The area of the peak of E-OMC measured after irradiation in relation to the area before irradiation indicated a residual rate of this isomer of 34.3%. Thus, the concentration of isomer Z (65.7%) and the area of its peak were known, and its response factor ($k = 0.56$) was deduced by comparing it to E-OMC. This response factor was only valid at 300 nm, the analysis wavelength. Following numerous assays, the response coefficient was calculated as 0.56 ± 0.02.

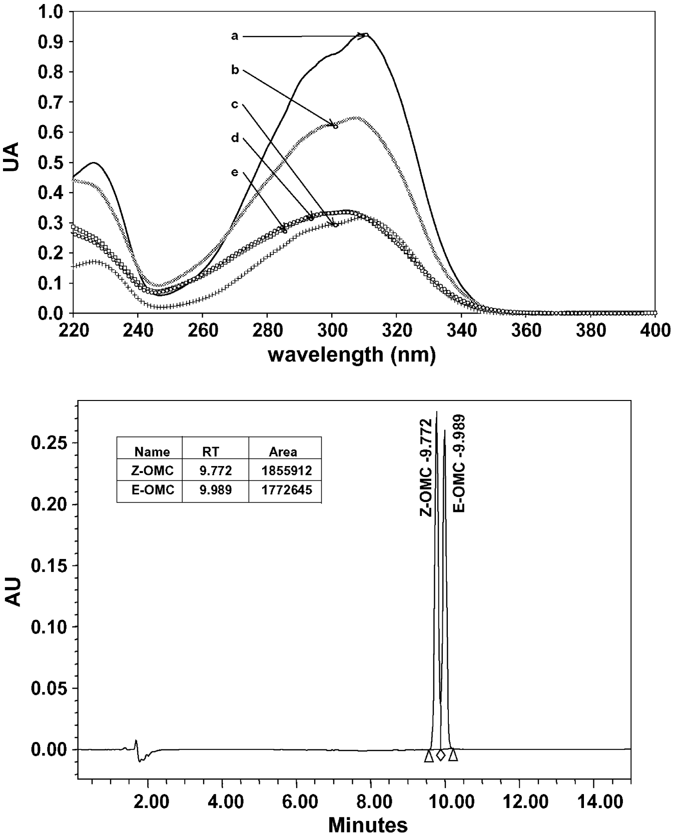


Fig. 1. Up: (a) E-OMC spectrum before irradiation; (b) spectrum of mixture E, Z-OMC after irradiation in iPro; (c) calculated spectrum of residual E-OMC; (d) calculated spectrum of formed Z-OMC; (e) Z-OMC spectrum using the diode array detector. Down: chromatogram of mixture E, Z OMC corresponding to the b spectrum.

The UV spectrum obtained following irradiation constituted 34.3% of the original UV spectrum and 65.7% of unknown UV spectrum of Z-OMC. For each wavelength, 34.3% of the original value of the absorbance was subtracted to give the absorbance value of Z-OMC. The results of these calculations are represented graphically in Fig. 1.

The accuracy of this mathematical process was demonstrated when the spectrum calculated for Z-OMC was compared with the Z-OMC spectrum obtained from the diode array detector. Although the wavelength scales differed, visual comparison of the spectrums suggested a marked similarity between the two spectra (d and e) as shown in Fig. 1.

The theoretical spectra of Z-OMC and E-OMC were standardized at the same arbitrary concentration. The residual spectrum of E-OMC thus corresponded to the arbitrary concentration of 34.3, and Z-OMC to the arbitrary concentration of 65.7. Standardization at 100 for both spectra represented the spectra of both isomers at the same concentration. The two spectra are presented in Fig. 2.

As it is shown from normalized spectral data of both isomers, the ratio of absorbance at 300 nm of Z and E form is 0.58, a value closely related to the relative response factor. As noted qualitatively in [14] and quantitatively in [18], Z-OMC exhibits an absorbance capacity inferior to that of E-OMC. This absorbance capacity was evaluated by calculating the area

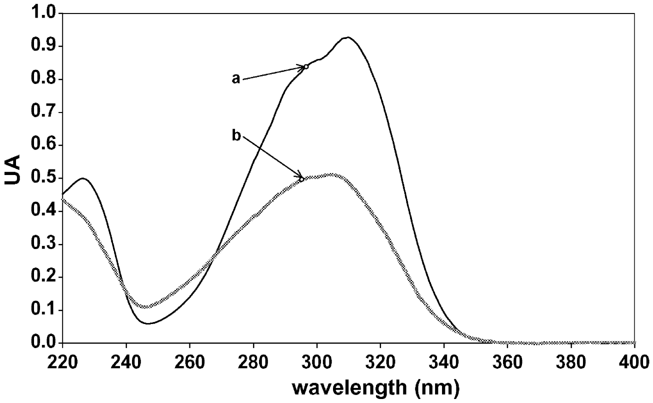


Fig. 2. Spectra of E-OMC (a) and Z-OMC (b) standardized at the same arbitrary concentration.

under the absorption curve between 290 and 400 nm, namely the wavelength range regarding sun protection, in relation to the area under the curve of E-OMC. The calculation indicated that the absorbance capacity of Z-OMC was 54.5% of that of E-OMC.

3.2. Irradiation of E-OMC in diluted solutions

Preliminary results were obtained after 10 min of irradiation. They were similar to those previously described [18], although the solvent employed was different (iPro substituting ethanol) and the irradiations were achieved by artificial means. The isomerization of E-OMC in iPro, therefore, occurs rapidly. To determine whether the steady state is reached after this period of irradiation, the same solution of E-OMC was irradiated for 10 s, 1, 2, 4, 10 and 60 min. The proportions of both isomers did not vary following 4 min of irradiation, nor until at least 60 min. Therefore subsequent assays were carried out using an irradiation time of 10 min. Irradiations were performed using the following solvents classified in increasing order of their dielectric constant (ε): Hept; Diox; AcOEt; THF; ACN; iPro; and Water. The percentages of both isomers were calculated using the initial area of E-OMC arbitrarily fixed at 100, from the area of residual E-OMC and the area of Z-OMC formed, corrected by the response factor of 0.56. These values are recorded in Table 1 together with their respective sums, which should theoretically equate to 100.

Table 1
Composition of mixtures of E-OMC and Z-OMC obtained by irradiation of E-OMC in diluted solutions in different solvents

	ε	[c] (mg/l)	% E-OMC	% Z-OMC	Sum
Hept	1.9	15	53.0	47.4	100.4
Diox	2.2	18	41.5	59.0	100.5
AcOEt	6	13	43.5	57.1	100.6
THF	7.6	15	40.6	60.0	100.6
iPro	20	15	34.2	68.1	102.3
ACN	38	14	33.6	66.6	100.2
Water	78	10	55.4	16.3	71.7

These results corroborate entirely with those described in [18]. It should be noted that the E isomer was the major constituent in those solvents with the lowest and highest polarity (Hept and Water). In those aprotic solvents of intermediate polarity (Diox, AcOEt and THF), the proportions of E-OMC were relatively similar constituting 40–43% of the mixture The proportion of E-OMC was lowest in the aprotic or protic polar solvent ACN and iPro. Hence it appears that the polarity of medium plays a preponderant role on the isomerization rate. Finally in water, a protic and highly polar solvent, proportions were reverse to that of iPro, although it should be noted that the sum of both isomers was lower than 100 and, thus, implied a degradation of the structure of cinnamate. The progression of the reaction in water was observed as a function of the length of irradiation by recording the UV spectrum after each successive 4 min period at 250 W/m^2 and analysing the mixture by HPLC. The results are shown in Fig. 3.

In aqueous solution E-OMC was very rapidly isomerized as it was in other solvents. The steady decrease in absorbance observed was attributed to the degradation of the structure of cinnamate. This behaviour was also demonstrated using HPLC by the decrease in the sums of the percentages of the two isomers. The degradation of cinnamate structure implies the appari-

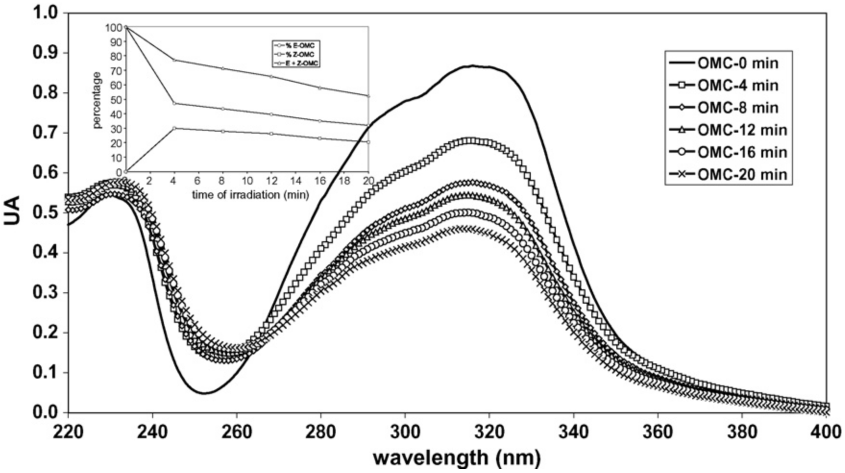


Fig. 3. Progression of the OMC UV spectrum in water as a function of irradiation time; insert: succession of percentages of both isomers and sum values.

tion of degradation products. Analysis of the chromatogram obtained after 20 min of irradiation was carried out at 254 nm, and not 300 nm corresponding to the maximum absorbance of E-OMC and Z-OMC. Two significant new peaks with longer retention times were observed, suggesting compounds with a higher lipophilicity and with UV spectra, compatible with non-conjugated benzene nucleus. These two structural indices are compatible with the proposal that products resulting from a cycloaddition [9] of two cinnamate molecules using double bonds effectively cancel the conjugation responsible for the absorption characteristics of cinnamates.

However, as noted by Sayre et al. [4], the study of photostability in very dilute solutions is not representative of what may occur in concentrated solutions or within the complex mixtures that constitute formulations of cosmetic products. So we investigated the behavior of E-OMC in concentrated solutions and in cosmetic products.

Table 2
Percentages of E- and Z-OMC after irradiation of concentrated solutions and commercial products

Solvent	% E-OMC	% Z-OMC	Sum
MO	54.8	45.4	100.2
AT	47.2	52.0	99.2
OD	42.5	57.5	100.1
CAB	50.8	49.1	99.9
CCT	52.1	47.1	99.2
ISOS	49.3	51.0	100.3
AL	48.7	51.4	100.1
A	78.3	21.8	100.1
B	76.9	23.3	100.2
C	67.6	31.1	98.7
D	68.9	32.8	101.7
E	69.1	30.5	99.6
F	63.1	38.7	101.8

3.3. Irradiation of E-OMC in concentrated solutions using different solvents and in commercial products

Irradiations were carried out by applying to rough glass slides (7.5 cm × 2.5 cm) a thin layer of 4% solution of E-OMC in the following non-volatile solvents: MO, AT, OD, CAB, CCT, ISOS and AL. The commercial products: A–F were obtained from local retail outlets. The quantities applied were in the range of 15–18 mg equivalent to a 1 mg/cm^2 [1]. For each assay, a sample slide was kept at 35 °C in the absence of light. Irradiations were timed to last 20 min at 250 W/m^2 of power, the double of the dose used for diluted solutions. The slides were then washed with iPro (30 ml) and the solutions analyzed by HPLC. The results obtained from these solutions were, as previously, expressed by determining the area of E-OMC before and after irradiation and the corrected area for Z-OMC. The results in Table 2 are expressed in terms of the percentage of residual E-OMC. The percentage of Z-OMC was calculated by the ratio of the corrected area of the peak to the initial area of the E-OMC peak of the sample.

The respective sums of the percentages of both isomers were close to 100, indicating no evidence of molecular breakdown under these irradiation conditions. The rate of isomerization in concentrated solutions is approximately 50%. In concentrated solutions rates of isomerization are not significantly different. The rate of E-OMC isomerization in the six commercial products tested was slightly lower. The E isomer remains the major constituent in all cases.

Essentially, this study shows that isomerization is rapid and that the relationship of the two isomers depends more on their chemical environment than on the actual irradiation power. This rapid isomerization very probably occurs at the skin surface under the normal use of the sunscreens. Hence, any sunscreen

Table 3
Calculated values of SPF based on percentage of filters and different rates (τ) of isomerization

No.	Percentage of filter					Initial SPF	SPF (% residual)	
	E-OMC	BMDBM	Octocrylene	Uvinul A+	Tinosorb S		$\tau = 20\%$	$\tau = 60\%$
1	8	2				20.3 (19.8)[a]	18.0 (89)	14.0 (69)
2	8		2	2		21.0	18.8 (90)	14.8 (70)
3	8			4		21.2	18.7 (89)	14.3 (68)
4	6	3		4		19.6	17.6 (90)	14.0 (71)
5	5	4		4	1	21.2	19.3 (91)	15.9 (75)
6	8	4		4		31.5	26.3 (83)	20.5 (65)
7	8	1	5	2		30.0	27.0 (92)	21.3 (71)
8	10		2	3		30.5	26.9 (88)	20.4 (67)
9	10			4		29.0	25.3 (87)	18.6 (64)
10	10	2.5				29.3 (28.4)[a]	25.6 (87)	19.0 (65)
11	8	3	5	3	2	59.1	52.6 (89)	41.0 (69)
12	10	3		4	2	59.4	51.2 (86)	37.1 (62)
13	10	4	2	4		60.6	52.6 (87)	38.4 (63)
14	8	4	3.5	4	2	61.2	54.1 (88)	41.4 (67)
15	10	3	1.5[b]	4		60.7	53.6 (88)	40.5 (66)

Uvinul A+ and Tinosorb-S are two recent sunscreens from BASF and CIBA, respectively. The first is a UVA sunscreen based on benzophenon structure, the second is a UVA–UVB sunscreen based on the triazone one.

[a] Value determined by the CIBA Simulator.

[b] In this case Uvinul T150.

products containing OMC lose part of their effectiveness within minutes. This loss of effectiveness was evaluated by calculation of SPF from virtual products containing OMC.

3.4. Incidence of OMC isomerization on SPF

The software developed in-house was based, similarly to that of CIBA [20] and that of Ferrero et al. [21], on the model of irregular film developed by O'Neill [19]. Given the spectrum data of solar filters in standardized concentrations and the predetermined optical path (in this instance 1% for an optical path of 20 μm), it was possible to calculate an absorption spectrum for an individual filter or mixture of filters. The CIBA solar simulator is limited to commercial filters only and absorption spectra cannot be obtained in Excel® format.

The calculation is based on two parameters, which define the geometry of the step film. Parameters used in this work are the same as those used in CIBA simulator [20], namely a thickness of 0.935 for the thinned section of film and 0.269 for the area of this section. The percentages of solar filters were chosen to give three groups of SPFs with values around 20, 30 and 60. Of course E-OMC was present in each formulation. The SPFs were then calculated using our simulator and that of CIBA when possible. For each original formulation, the SPF was recalculated with isomerization rates (τ) of E-OMC of 20% and 60%. These values covered the range of rates observed under different irradiation conditions. The results of the calculations are collated in Table 3.

A decrease in SPFs of approximately 10% was observed for all groups of SPF and an isomerization rate of 20%. Because this value is probably lower than the more precise measurements of SPF in vitro or in vivo, such a decrease can be considered negligible. Formulation No. 6, however, elicited a decrease in SPF of 17% compared to that of 8% for formulation No. 7, a more than two-fold reduction. Perhaps such a decrease cannot be neglected.

If the isomerisation rate is increased to 60%, an acceptable value only obtained in diluted solutions in polar solvent, but not in concentrated solutions nor in commercialized sunscreens, the decrease in SPF regularly exceeded 30%, reaching 38% in formulation No. 12. Clearly a decrease of this magnitude cannot be considered negligible.

4. Conclusion

The isomerization of E-OMC under light is a rapid phenomenon. As it is reasonable to suggest that this process of isomerization occurs at the skin surface, there is a rapid and unavoidable loss of protection with sun products containing OMC. The extent of this loss depends on the filter constituents of the formulations and the chemical environments of cinnamate. If the minimum rate of isomerization is assumed to be 20%, producing a decrease in SPF of approximately 10%, this can be considered negligible. For an isomerization rate of 60%, the decrease in SPF can vary between 29% and 38%, according to the composition of the formulation. If OMC is a constituent of sunscreen products, accurate correlation of measurements of SPF in vitro and in vivo are not possible owing to the fact that measurements in vivo require irradiations that very probably lead to isomerization, which is not the case with those measurements undertaken in vitro using a spectrophotometer. It may thus be considered indispensable to measure SPF in vitro following a period of irradiation, as recommended in [1], to derive an index that reflects the actual chemical characteristics of the product.

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