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ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 196 (2008) 106–112
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photoreactivity of the sunscreen butylmethoxydibenzoylmethane (DBM) under various experimental conditions

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Received 3 September 2007; received in revised form 23 November 2007; accepted 26 November 2007
Available online 4 December 2007

Abstract

The photoreactivity of the sunscreen butylmethoxydibenzoylmethane (DBM) was studied in three specific environment types: (i) by irradiating diluted solutions in solvents of various polarities; (ii) by irradiating concentrated solutions in non-volatile solvents; (iii) by irradiating thinly applied commercial sun products. The behaviour of DBM clearly showed that its sensitivity to light is dependent on experimental conditions. DBM is stable in a polar solvent such as alcohol, whereas in a non-polar solvent, DBM is undergoing a reversible displacement of tautomeric equilibrium. This unexpected phenomenon is inhibited by a very small modification of polarity. The photodegradation products were detected using liquid chromatography–mass spectroscopy (LC/MS), to detect their molecular masses and thus obtain a broad idea of their identity. The incidence of photodegradation on the sun protection factor (SPF) value was measured. Because the degradation of DBM appears unpredictable, given that sunscreen products are marketed as supplementary health protectors against pathologies related to the harmful effects of sun exposure, the photostability of sun products should be a major safety criterion. There are two reasons for concern: firstly, reduction of protection as a function of progressive irradiation and secondly, the appearance of photodegradation products on the skin surface.

Keywords: Butylmethoxydibenzoylmethane; Sunscreen; Photostability; Sun protection factor

1. Introduction

In a recent paper [1] refining the methodology of the previous work carried out by Pattanaargson et al. [2] by the present authors, the photoisomerization of the sunscreen octylmethoxycinnamate was described. It was demonstrated that *E–Z* photoisomerization brings about a substantial loss of the absorbing power of this specific sunscreen, leading to a loss of effectiveness of the sun product in which it is incorporated.

The sunscreen butylmethoxydibenzoylmethane (DBM) is also known for its photo-instability. Its tautomeric structures are presented in Fig. 1. DBM was, for a long time, the only UVA-blocking product available commercially, until other UVA sunscreens, such as Uvinul A+ (DHHB, diethylamino hydroxybenzoyl hexylbenzoate) or Tinosorb M and S (BEMT, bis-ethylhexyloxyphenol methoxyphenyltriazine and MBBT, methylene bis-benzotriazolyl tetrametylbutylphenol, respectively) became available on the market. DBM does, however, offer a unique absorption spectrum, as well as a very high absorption coefficient, and so remains extensively used world-wide.

Due to the major role played by DBM in protection against UVA, a considerable amount of research has been devoted to its photostabilization. A computer search in the Chemical Abstracts database on the DBM Registry Number provides 1735 references. A first glance at the listing suggests that the majority of these abstracts refer to patents and focus on the stabilization of DBM either by various compounds such as ethylhexylnaphthalenate [3], or by sunscreens, such as octocrylene [4] or

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doi:10.1016/j.jphotochem.2007.11.023

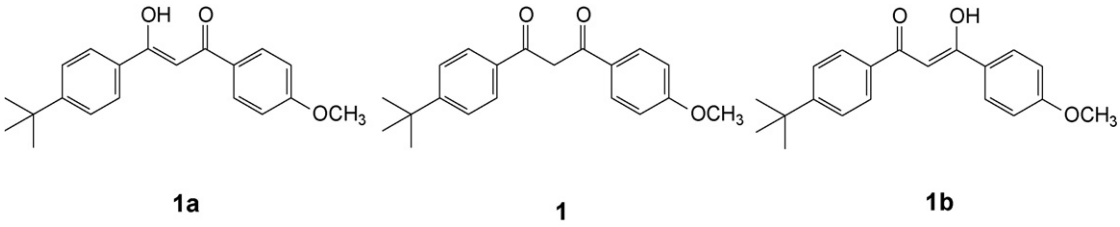

Fig. 1. Tautomeric structures of DBM: **1a** = enol form 1, **1** = 1,3-diketone form, **1b** = enol form 2.

Tinosorb-S [5]. Many references, although mainly patents, focus on the synergetic effect gained from using DBM in combination with other sunscreens. More elemental research studies concerning the photostability of DBM remain scarce; those in existence are reported in the essential reading review of Bonda [6]. Many of these papers merely describe instability by observing changes in UV absorption [7]. In others, although more refined techniques have been used, i.e. NMR [8] or HPLC [9,10], investigations were performed under highly variable experimental conditions: DBM incorporated into cosmetic formulations; DBM within concentrated or diluted solutions; irradiations with specific or non-specific UV wavelength; employing variable degrees of irradiation power, etc. To date, only two papers appear to focus on the products of DBM photolysis. Roscher et al. [11] described the breakdown of DBM into *t*-butyl and methoxy-benzene derivatives, while Schwack and Rudolph [12] identified unsymmetrical 1,2- and 1,4-diketones as products of DBM photolysis. These two classes of compounds appear to have no greater UVA protection capacity. It should be noted, however, that the experimental conditions used in these two studies differed greatly.

The current authors, however, conjecture that the stability of DBM and its degradation products are highly dependent on their chemical environment, as was the case for octylmethoxycinnamate [1]. Clearly, a more precise understanding of this phenomenon of DBM degradation is required in order to bring about its inhibition/inactivation. The present authors have, therefore, undertaken this investigation to define the types of environment which may bring about one or more structural modifications of DBM under irradiation, according to the Bonda's definition of photo-instability [6].

The stability of DBM was studied in three distinct environment types: (i) diluted solutions in solvents of various polarity; (ii) concentrated solutions in non-volatile solvents; (iii) in commercial sun products. Irradiations were performed in volume in the first of these assays, and using a thin-layer technique in the other two environment types. The light source was derived from the Suntest® CPS+ apparatus, which is easy to use and dispenses a reproducible level of irradiation.

2. Material and methods

2.1. Chemicals

The solvents isopropanol (iPro), tetrahydrofuran (THF), heptane (Hept), hexane (Hex), dioxane (Diox), acetonitrile (ACN), ethyl acetate (AcOEt) of HPLC quality were obtained from Sigma–Aldrich (L'Isles d'Abeau, France), along with methanol for HPLC. Mineral oil (MO), alkyltartarate (AT), capric caprylic triglyceride (CCT), isostearyle isostearate (ISOS), alkyllactate (AL), glycerol (GLY) are industrial products kindly provided by Shadeline sarl (Mouans-Sartoux, France). DBM was an industrial sample from Roche. Water was purified by reverse osmosis. Sunscreens are referenced as follows—MBC: methylbenzyliden camphor; OCR: octocrylene; OMC: octylmethoxycinnamate (both isomers), T150: octyltriazone (Uvinul T150); Tino-S and -M: Tinosorb S and M.

2.2. 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 (12.5 cm × 0.4 cm) was a Nucleosil 100-5 C18 from Macherey–Nagel (Hoerdt, France). Solvents used were methanol (A), and a mixture 90/10 of water containing 0.1% H_3P0_4 and methanol (B). The gradient which was used for the analysis of the simple mixtures, was as follows—t = 0–3 min: A = 30%, B = 70% to A = 100% (linear gradient); t = 3–10 min: A = 100%; t = 10.1–15 min: A = 30%, B = 70%; t = 15.1 min stop flow. For the creams analysis, the following gradients were used with dioxane (C). Gradient 1—t = 0–2 min: A = 30%, B = 70% to A = 100% (linear gradient); t = 3–10 min: A = 100%; t = 10–13 min: A = 100% to C = 100% (linear gradient); t = 13–20 min: C = 100%; t = 20.1 to 25 min: B = 100%. Gradient 2— t = 0 to 5 min: A = 30%, B = 70% to A = 100% (linear gradient); t = 5 to 10 min: A = 100%; t = 10 to 13 min: A = 100% to C = 100% (linear gradient); t = 13–20 min: C = 100%; t = 20.1–25 min: B = 100%.

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 per second with a resolution of 1.2 nm. DBM was detected at 360 nm. Products of photodegradation were detected at 270 nm.

Liquid chromatography–mass spectroscopy (LC/MS) analyses were performed using a 3200 QTrap (Applied Biosystems, Concord, ON, Canada) equipped with an atmospheric pressure ionization source. Positive-mode electrospray ionization (ESI) was performed at 5.0 kV and the orifice voltage was set to 20 V. In negative mode ESI, these voltages were set to −4.5 kV and −20 V, respectively. Air was used at 40 psi pressure as the nebulising gas. The HPLC system coupled with mass

spectrometry was an Agilent Series 1100 instrument (Agilent Technologies, Palo Alto, CA) equipped with a quaternary pump and an automatic sampler. Chromatographic separation was performed using the same column as for UV detection and the column oven was maintained at 25 °C. The elution gradient was the same as in the UV detection method but the H_3PO_4 used in eluent B was replaced by acetic acid, which is more ESI compatible. Mass spectra were acquired using a quadrupole as the mass analyzer on a 150–380 *m/z* range. The Analyst software (version 1.4.1) was used for instrument control, data acquisition and data processing.

2.3. Spectroscopy

Spectra were recorded using an Uvikon 922 spectrophotometer (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 500 nm/min.

SPFs were measured with this machine equipped with an integrating sphere (Serlabo, Entraigues sur la Sorgue, France). Sun products (29–30 mg) were spread onto polymethylmethacrylate (PMMA) rough plates from Europlast (Aubervilliers, France). Plates used were 5 cm × 5 cm × 0.2 cm, with a roughness of 5–7 μm. The studied product is put in several plots and uniformly spread by a circular movement of one finger with a latex glove. The obtained preparation should be a 12 μm film if the plates were without roughness.

The wavelength range extended from 290 to 400 nm. The resolution was 1 nm and the scanning rate was 200 nm/min. Four plates were spread with each product and ten scans were realized per plate. Spectral data were converted into Excel® format for processing.

2.4. Irradiation

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 550 h at the beginning of the study. Irradiations of diluted solutions were carried out in spectroscopic 1-cm quartz cuvettes capped by Teflon® stoppers. 4.5 ml of the solution are put into the cuvettes. The absence of evaporation was confirmed by weighing each cuvette before and after irradiation. The cuvettes were horizontally placed in the irradiation chamber, the transparent face turned to the luminous source. Irradiations of concentrated solutions were achieved using rough PMMA plates horizontally placed. Cuvettes and plates were fixed with the Patafix® gum. Irradiations of commercial sun products were carried out with two of the four plates used for SPF determination. SPFs were measured after irradiation and then the plates were washed with a predetermined volume of iPro and the concentrations of sunscreen determined by HPLC.

During irradiations, the temperature was regulated automatically and varied from 25 to 45 °C according to the time of the irradiation. Times and energies are specified herein.

3. Results and discussion

3.1. Irradiation of DBM in diluted solutions

The core results obtained in these conditions of irradiation were first reported by Bonda's team from the company CP Hall [13]. Unfortunately, their results were presented at a symposium and are not readily available. The current authors repeated these experiments and the results obtained fully confirmed those of Bonda. DBM was found stable in dioxane, acetonitrile, ethyl acetate, THF, ethanol and isopropanol. Irradiation was performed at 4-min interval at 250 W/m^2, corresponding to a dose of 60 kJ/m^2. After five successive periods of irradiation no change in the UV spectrum was observed. At the most, a 1–2% loss in absorbance could be detected, which the authors considered insignificant.

In non-polar solvents (hexane, heptane, cyclohexane) Bonda demonstrated unexpected behaviour of DBM. This specific result is mentioned only in his review. The current authors repeated this experiment under their own irradiation conditions. After each irradiation a change in UV spectrum was observed as shown in Fig. 2 (left panel).

It could be inferred on observing such behaviour that DBM is photo-unstable under these irradiation conditions. However, Bonda also demonstrated that when the irradiated "photodegraded" solution of DBM was kept in the dark, the initial absorption was gradually and fully recovered. The present

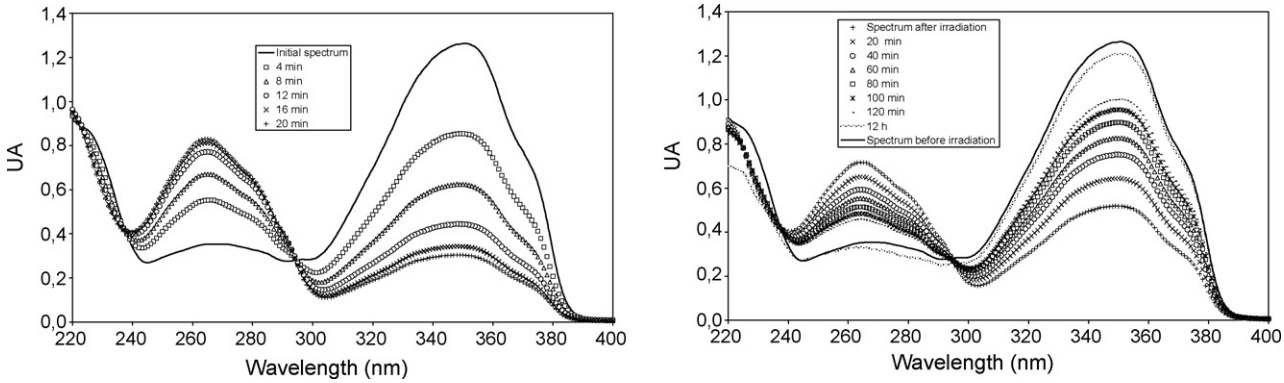

Fig. 2. Left panel: UV spectra of DBM in heptane recorded after each irradiation time of 4 min. Right panel: recovery of initial spectrum *vs.* time by keeping the irradiated solution of DBM in the dark.

authors, too, clearly observed this unexpected phenomenon. After a sequence of five irradiations, the cuvette was maintained in the dark and a spectrum was recorded every 4 min and again after 12 h. The evolution of the spectrum is represented in Fig. 2 (right panel).

Bonda's team made another rather interesting observation. In the presence of 1% iPro the phenomenon was fully inhibited. This was fortuitously observed when the isopropanol solution of DBM is diluted a 100-fold with hexane.

These results concerning the behaviour of DBM clearly showed that the light-sensitivity of DBM is highly dependent on experimental conditions. Under light in non-polar medium, DBM is not degraded, but the tautomeric equilibrium is strongly displaced to the inactive diketone form **1**, the active enol forms **1a** and/or **1b** being recovered in the dark. It should be noted that a very small modification in polarity (1% iPro in HEX) is sufficient to inhibit the phenomenon. Work is in progress in order to explain this stabilizing effect, particularly with the NMR analysis of the keto-enol equilibrium in different conditions.

As a complement to the work of Bonda, we observed a further feature of the behaviour of DBM. Adding water to iPro had no effect up to 75%, DBM remaining stable as stated by Shaath. With 90% water or with pure water, changes in UV spectra were observed after each irradiation but in this case the phenomenon was not reversible: a breakdown of DBM occurred. Spectra obtained after each five-irradiation step are shown in Fig. 3.

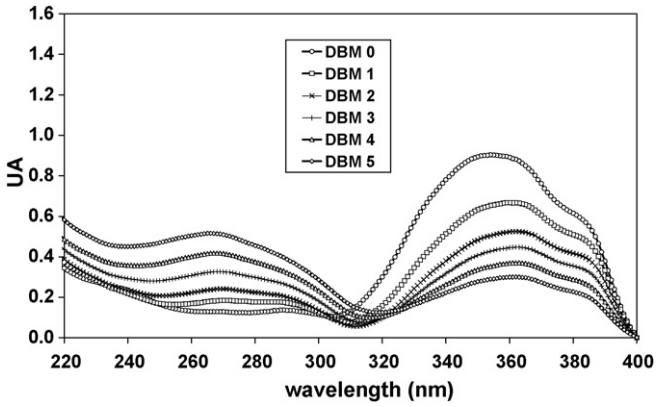

Fig. 3. Spectra of DBM in water recorded after each of the five-irradiation step.

The photodegradation of DBM in aqueous medium can be found in a recent work of Damiani et al. [14,15]. Those authors irradiated DBM liposomal suspensions only in UVA. With those experimental conditions, it is difficult to know if DBM was in aqueous solution or in the phospholipidic membranes of the liposomes.

HPLC analysis of the solution before and after the five-irradiation step showed 36% DBM recovery and the appearance of a large number of products. The chromatogram at 270 nm is shown in Fig. 4 (top panel).

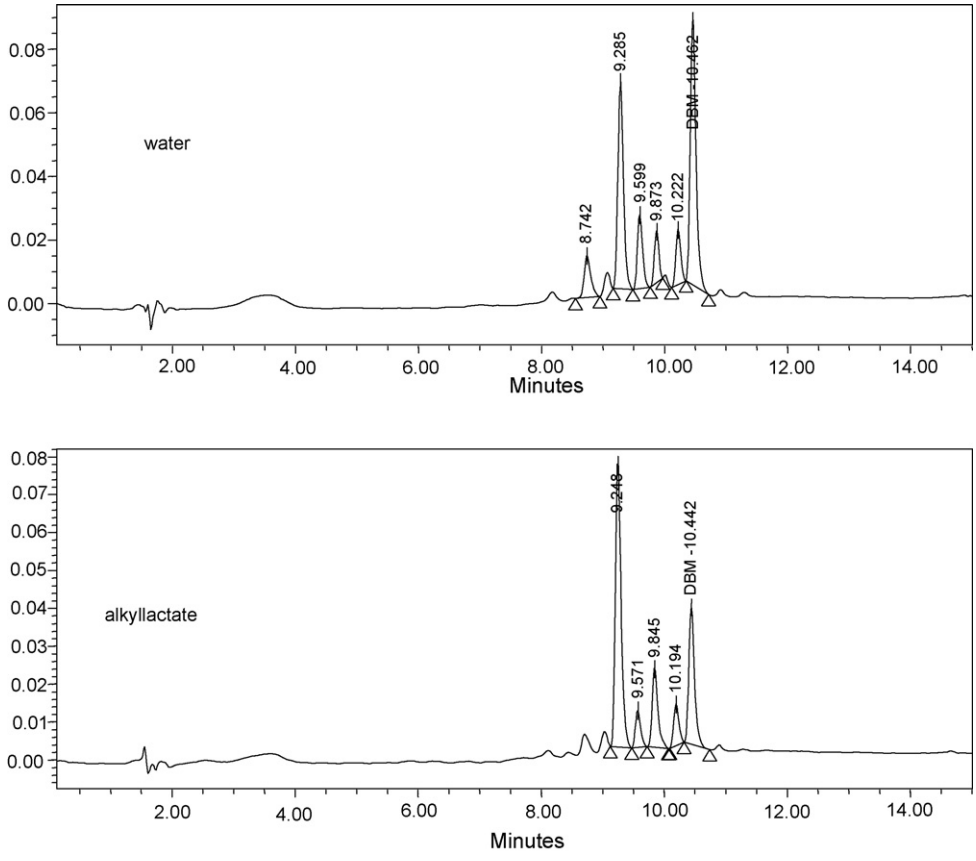

Fig. 4. Chromatogram at 270 nm of the mixture resulting from irradiation of a solution of DBM in water (top panel) and in alkyllactate (bottom panel).

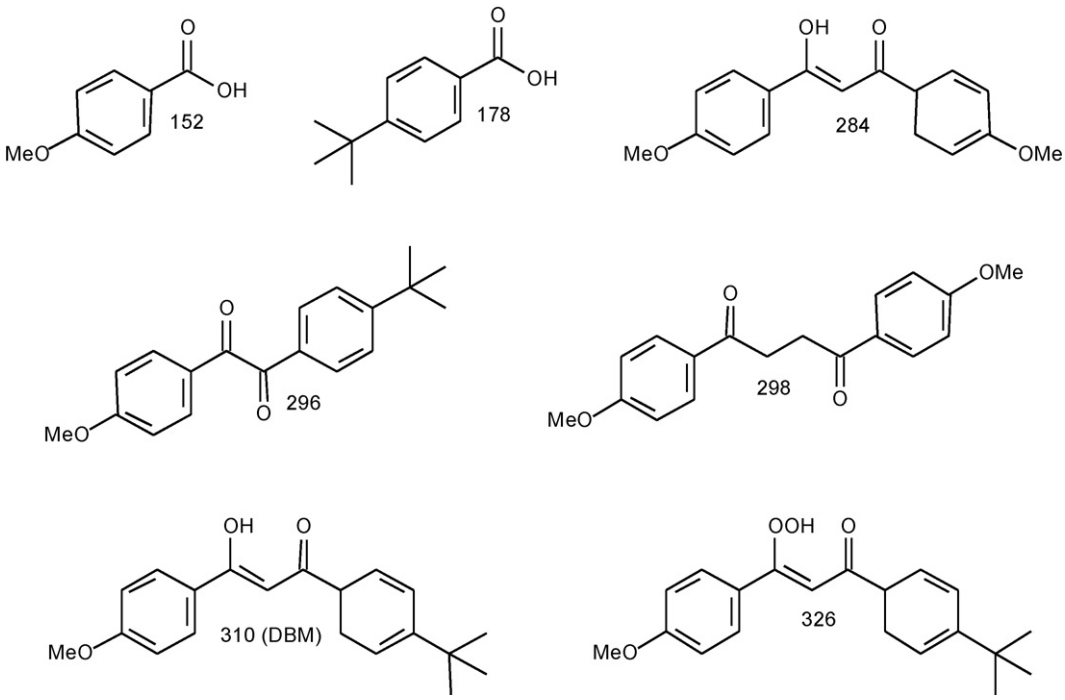

Fig. 5. Possible structures of photodegradation products of DBM in water.

This complex mixture was analyzed by LC/MS to obtain a broad idea of photodegradation products by detecting molecular mass. The following molecular masses were unambiguously obtained: 284, 152, 178, 298, 378, 326, 296 and 310. The structures presented in Fig. 5 comply with these values but it should be kept in mind that these identifications are not completely reliable. These structures were also proposed by Schwack and Rudolph [12] except the structure of mass 326, the supposed dimethoxydibenzoylmethane (mw 284) being an impurity present in the initial DBM.

The molecular mass of 326 was the only one, which was higher than DBM's. This 16 units difference might be connected to the addition of an oxygen atom in the DBM molecule. The experimental conditions were able to produce oxidation reactions with synthesis of a hydroperoxide product.

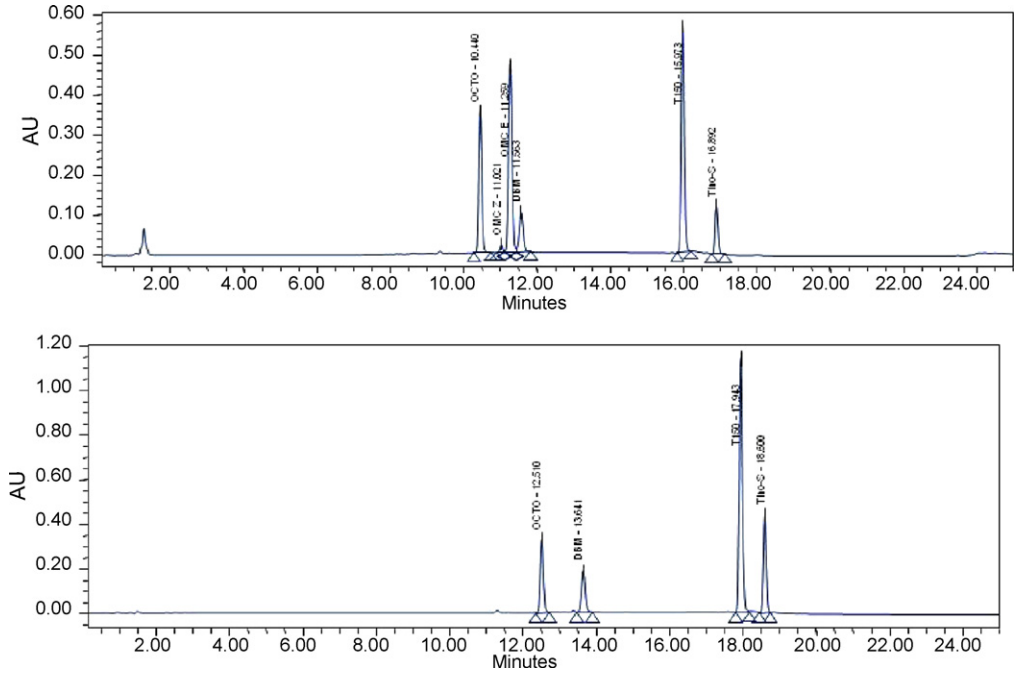

Fig. 6. Top panel: chromatogram (300 nm) of cream A (gradient 1); bottom panel: chromatogram (300 nm) of cream I (gradient 2).

Table 1
Irradiation of commercial sunscreen products: incidence on the SPF value and residual rates of sunscreens mainly DBM

	SPF			Sunscreen						
	Label	Before	After	MBC	OCR	Z, E-OMC	DBM	T150	Tino-S	Tino-M
A	30	41	28		99.7	78.3	70.7	98.1	102.2	
B	8	17	9	90.0		96.4	37.6			
C	30	35	31		97.8		85.2			
D	15	40	18			78.2	53.2		100.9	
E	80	40	16	97.0		66.4	26.3			
F	40	45	23			82.0	62.5		98.3	
G	30	29	17	89.8		63.4	40.3			
H	15	23	11	91.3		83.3	9.8			
I	50^+	50^+	50^+		100.2		97.1	100.3		102.7
J	15	19	11				43.0	99.5		98.8
K	15	17	15		99.8		83.2			101.1

50^+ is the SPF written on the I cream.

This behaviour of DBM in aqueous medium is comparable to that of octylmethoxycinnamate, which is irreversibly *E–Z* isomerised in many solvents but chemically degraded in aqueous solution [1].

However, the conditions at this stage, i.e. highly diluted solutions with irradiations carried out in volume, are far removed from the true in vivo conditions for sunscreen products. We, therefore, investigated the behaviour of 4% solutions of DBM in non-volatile solvents when irradiated in thin-layer form.

3.2. Irradiation of DBM in concentrated solutions

As stated by Bonda, the polarity of solvents has a major impact on the photostability of sunscreens. The current authors, therefore, studied the behaviour of DBM in concentrated solutions (2 and 4%, w/w) in the following non-volatile solvents—A: 50–50 mixture of MO and ISOS (2% solution); B: ISOS (4%); C: CCT (4%); D: AT (4%); E: AL (4%). Mixture A was obtained by diluting solution B twofold with MO.

Four plates were coated with 30 ± 0.5 mg of each mixture and for each plate a spectrum was recorded. The four plates were irradiated together at 550 kW/m^2 in 15-min step. The dose was 495 kJ/m^2, corresponding approximately to one MED. After each period, a plate was removed and the spectrum was recorded and then washed using a pre-determined amount ($\sim$20 g for the 4% solutions and $\sim$10 g for the 2% solutions) of iPro. The resulting solutions were analyzed by HPLC. The initial point is determined by analyzing the initial mixture diluted in iPro at the same range of concentration. For each analysis the area of the peak of DBM is divided by the concentration to give the normalized area.

HPLC analysis showed the formation of numerous photoproducts and a residual rate for DBM ranging between 15 and 25% was recorded. The degradation rate appeared relatively independent of the solvent. Only the distribution of photoproducts and their relative abundance were modified. From the experiment in AL we analyzed the irradiated mixture by LC/MS on the basis of the chromatogram shown in Fig. 4.

Some molecular masses detected were the same as measured previously (Fig. 5), i.e. 284, 178, 326 and 310 (DBM). Other masses were also detected: 136, 258, 330, 366, 344, 272, 350, 302 and 334. The 136 mass was compatible with that of *p*-methoxybenzaldehyde and the 350 mass had the same symmetrical structure as 298, although with two *t*-butyl instead of two methoxy groups. The other masses detected were not interpretable under these conditions. An interaction with the solvent, alkyllactate, cannot be precluded. The authors intend to undertake a more thorough study of these photoreactions in future.

The major finding of this part of the authors' current research is that the photodegradation of DBM is largely dependent upon experimental conditions. However, irradiation of thin layers of concentrated solutions of DBM in various solvents does result in a significant degradation of the sunscreen, reaching up to 80%. Most of the photoproducts obtained from these simple solutions are not characterized, which implies a highly complex process of photochemical reaction.

The subsequent stage of this investigation was devoted to the study of the degradation of DBM contained in commercial formulations, under irradiation in thin-layer geometry.

3.3. Irradiation of DBM in commercial sun products

The same protocol as above was applied to sunscreen products. The commercial sunscreen products obtained from European supermarkets—A: Eroski Solar Lotion SPF 30 (Spain); B: Ysiance (France); C: Garnier delial Ambre Solaire Moisturizing Solar Lotion SPF 30, L'OREAL DPGP (Spain); D: Nivea Sun Spray Solaire Hydratante SPF 15 (Spain); E: Arubix SPF 80 Crème Protection Maximale, Laboratoire SICOBEL (France); G: Ysiance Solaire Crème Visage Haute Protection Hydratante* IP 30 (France); H: Dia Sun Lotion 15 (Spain). F: Shadeline Kceutic, is a sun product prescribed medically and is used after skin graft surgery. I: Uriage 50^+, J: Uriage 1, and K: Uriage 2 (France), were products at a development stage at the time of the study. An HPLC analysis was performed as before, by washing the plates with a predetermined amount of iPro. The chromatograms which were obtained with creams A and I before irradiation are presented in Fig. 6.

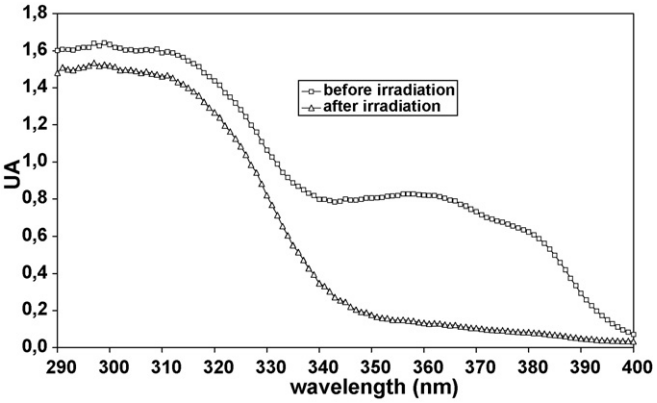

Fig. 7. Absorption spectra of the product H before and after irradiation.

Areas of peaks were divided by concentration leading to a normalized area from which the residual amount of each sunscreen could be calculated. Results are presented in Table 1.

As expected, certain sunscreens were unmodified by irradiation: OCR; T150; and the two Tinosorb. MBC exhibited a slight instability with a loss less than 10% for all products.

With regard to OMC, the value indicated in the table represents the sum of the two isomers E and Z; the area of the latter being compensated by its response factor as described earlier [1]. A 37% loss of this sunscreen was observed in one product (G); and OMC was stable under light in one other product (B).

The behaviour of DBM was highly variable. The loss was maximal (up to 90%) for product H, and did not exceed 3% for product I, the latter being considered as highly photostable. Clearly, the coexistence of Tino-S did not provide complete stabilization of DBM, as would be expected from [5]. The loss rate of DBM in products A, D and F was, respectively 30, 47 and 37%. The stabilizing effect of OCR was more noticeable; the three products containing this sunscreen demonstrating minimal losses of DBM.

Obviously, the photodegradation of DBM had a marked influence on the SPF values. The diminution of SPF reached up to 50% for product H. Absorption spectra of this product before and after irradiation are shown in Fig. 7.

The SPF of product G decreased from 29 to 17, which can be explained by the simultaneous loss of DBM and OMC. Considering the precision of the measurement, the SPF of products A, C, I and K seemed unaffected by irradiation.

4. Conclusion

This study clearly shows that the behaviour of DBM towards irradiation is highly unpredictable. The chemical environment of the sunscreen plays a fundamental role. In diluted solutions, the effect of the solvent is maximal. DBM is stable in polar solvents such as alcohol, whereas in the non-polar solvent DBM is undergoing a reversible displacement of tautomeric equilibrium. This phenomenon is inhibited by a very small modification of the solvent, elicited by adding 1% of polar solvent. Conversely, DBM in aqueous medium is fully degraded by light. When the irradiation is performed on a thin layer of DBM, dissolved in non-volatile solvents, a chemical degradation is regularly observed. The degradation products, well observed by HPLC, are not, on the whole, those expected according to Schwack and Rudolph [12]. Although at this investigative stage, no other attempts of identification were carried out, subsequent studies are anticipated.

In 10 tested commercial sunscreen products, DBM has the same behaviour as in a concentrated solution. For product I which purports an SPF of 50^+, no degradation of DBM is observed with a rate of recovery of 97%. Nevertheless, it is important to note that this present study was performed on 11 commercial products only and so, does not claim to be able to account for the behaviour of all sunscreen products.

In summary, as the degradation of DBM appears unpredictable, and that sunscreen products are marketed as supplementary health protectors, against those pathologies related to excessive sun exposure, the photostability of any relevant sun product should be a major safety criterion. The principal reason for such is the loss of the level of protection as irradiation progresses and secondly, the appearance on the skin surface of photodegradation products, which have not yet been identified. The frequent application of a sun product may overcome this primary effect of photodegradation, but the immediate corollary of applying the sunscreen repeatedly in this manner, will be an increase in those unidentified photoproducts on the skin surface.

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