

## **A new long-chain UV absorber derived from 4-*tert*-butyl-4'-methoxydibenzoylmethane: Absorbance stability under solar irradiation**

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### **Synopsis**

A new UV filter, the 1-(4-*tert*-butylphenyl)-2-decanyl-3-(4'-methoxyphenyl)-propane 1,3-dione called C10-DBM, was prepared by grafting a ten-carbon aliphatic chain to the  $\alpha$ -carbonyl position of 4-*tert*-butyl-4'-methoxydibenzoylmethane (BM-DBM).<sup>1</sup> UVA absorption efficiency of a cosmetic preparation containing this new filter, called C10-DBM, was tested and compared to an identical preparation containing BM-DBM. The two preparations were irradiated under a 150-W xenon lamp or exposed to natural sunlight. The originality of this new filter resided in that its UVA absorbance appeared during the irradiation of the molecule. Moreover, although the molar absorption coefficient of C10-DBM in the UVA domain was lower than that of BM-DBM, its absorption showed much more photostable behavior under both methods of irradiation. After two hours of sunlight exposure, the preparation containing the BM-DBM lost 85% of its UVA absorbance, whereas the UVA absorbance of the preparation containing C10-DBM showed a decrease of 3% in comparison to the maximum absorbance obtained after 30 minutes of irradiation. Also, after two hours of exposure to natural sunlight, the UVA absorbance of the preparation containing C10-DBM remained above its initial value (before the irradiation began).

### **INTRODUCTION**

Exposure to ultraviolet (UV) radiation plays a causal role in acute and chronic skin damage. Skin photoaging has been connected with UVA light. Moreover, UVA irradiation generates free radicals, inducing different types of degradation to cellular DNA, lipids, and proteins. It is now commonly recognized that UVA as well as UVB irradiation is involved in the development of skin cancer. This is particularly clear for squamous cell carcinomas (SCCs) and basal cell carcinomas (BCCs) in Caucasian people (1). Fur-

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<sup>1</sup> Patent: FR 2 857 663 (17 July 2003, France (PCT request)).

thermore, the action spectrum of skin SCC and BCC carcinogenesis in the albino hairless mouse established by de Gruijl *et al.* (2) shows two maximum-efficiency wavelengths: the main one in the UVB and a second in the UVA region. The relative efficiency of the second maximum is approximately 10,000 times lower than that of the first, but it is increased by the higher doses of UVA received. UVA represents 98% of the total UV received at the earth's surface, and so it can be considered that the difference in the effectiveness of cancer induction between UVB and UVA is only 100 times. For these reasons, the cosmetics industry has had to improve UVA sunscreen protection (indeed, the first generation of sunscreens did not provide any protection against UVA). Unfortunately, there are relatively few UVA absorbers currently available for sunscreens. One of the most commonly used, 4-*tert*-butyl-4'-methoxydibenzoylmethane (BM-DBM), belongs to the dibenzoylmethane family, as shown in Figure 1. However, it has been established that such molecules can undergo photochemical degradation (3,4).

4-*tert*-butyl-4'-methoxydibenzoylmethane (BM-DBM) absorbs solar energy and filters UVA rays with a maximum efficiency near 340 nm (5). Its absorbance is due to resonance throughout a large part of the molecule owing to a hydrogen bond that creates a six-bond pseudocycle between the carbonyl group and the enol (Figure 1). BM-DBM undergoes a rapid keto/enol photoisomerization by a proton transfer. The keto form absorbs UVB and UVC rays. This induces a shift in the preparation absorbance and a loss of efficiency in UVA. For longer irradiation times, the keto form undergoes photocleavage according to the Norrish I mechanism (6–8). The degradation products obtained are

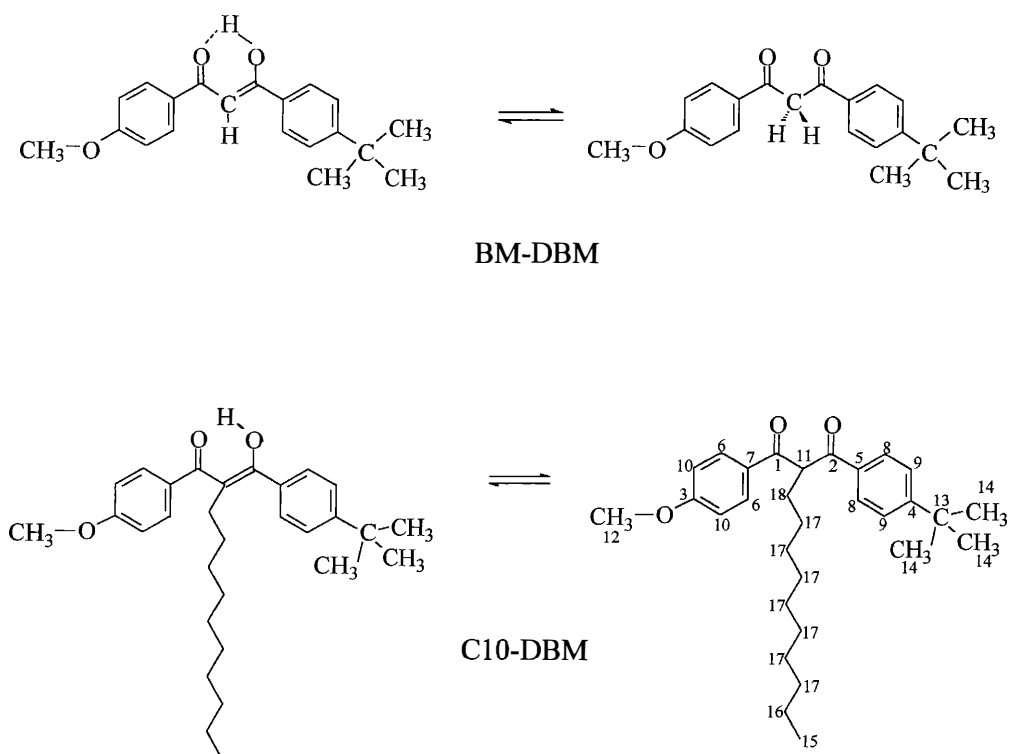


Figure 1. Structure of the two UV filters studied (H and C are numbered for NMR assignments).

well identified (3,9). The most abundant are benzaldehydes, benzoic acids, and acetophenone. The importance of this phenomenon increases with the duration of the exposure and is one of the reasons why it is recommended to reapply sun cream every two hours or so (other solar filters present the same drawback (10)). It is important to find a way to photostabilize preparations containing BM-DBM in order to improve UVA photoprotection. Two possibilities can be considered. The first, already widely exploited, consists in adding another molecule to the preparation. This molecule has to stabilize the BM-DBM via various mechanisms, most of which are unknown. For example, Thorel (11) added a trimellitic acid derivative, Allard and Forestier (12) incorporated a 3,5-triazine-derived compound and an alkyl ( $\alpha$ -cyano)- $\beta,\beta'$ -diphenylacrylate, and Hansenne and De Chabannes (13) tested a polysaccharide alkylether in order to prepare a photostable composition with a dibenzoylmethane derivative. Some research has also been done to define synergic mixtures of filters (14,15). The second possibility, to our knowledge not yet explored, consists in making chemical modifications of BM-DBM itself. These modifications must keep the UV absorption capacity but must augment the resistance to photodegradation. According to the literature (3,16), photodegradation occurs via the keto form. Our strategy was then to avoid ketonization by stabilizing the enol form.

Dibenzoylmethane derivatives exist as a keto/enol mixture where the keto/enol ratio depends on the nature of the environment. Tobita *et al.* (16) showed that dibenzoylmethane exists mainly in the chelated enol form in both non-polar and polar solvents, although the enol content is higher in non-polar solvents. It seems that a non-polar environment would favor strong intramolecular hydrogen bonding. Thus a long aliphatic chain chemically grafted onto BM-DBM should induce the migration of the molecule to a more apolar environment in complex preparations.

In this study, we present a new UV filter, the 1-(4-*tert*-butylphenyl)-2-decanyl-3-(4'-methoxyphenyl)-propane-1,3-dione called C10-DBM, derived from BM-DBM by grafting a ten-carbon aliphatic chain on the  $\alpha$ -carbonyl position (Figure 1). The chain length is above eight carbons, giving amphiphilic properties to the molecule (17). This filter was incorporated in a water-in-oil preparation, and the UVA absorption efficiency was tested under a 150-W xenon lamp or natural sunlight. The absorbance capacity and stability of preparations containing C10-DBM alone, BM-DBM alone, and a BM-DBM/C10-DBM mixture were compared.

## MATERIALS AND METHODS

### CHEMICAL PRODUCTS

Tetra-*n*-butylammonium fluoride, 75% w/w aq. soln. and 1-bromodecane 98% were obtained from Avocado (Heysham, Lancashire, England). BM-DBM (Parsol<sup>®</sup> 1789) was obtained from Givaudan-Roure (Switzerland). Dichloromethane and acetonitrile, HPLC grade, were obtained from SDS (Peypin, France), and tetrahydrofuran was from Carlo Erba RPE (Val de Reuil, France). Dodecyl sulfate sodium salt 98% was an Aldrich product (Steinheim, Germany) and used as supplied. Silica gel (0.063–0.200 mm) was obtained from Merck (Darmstadt, Germany).

### INSTRUMENTATION

<sup>1</sup>H N.M.R. and <sup>13</sup>C were recorded with a Bruker ARX-400 MHz. Infrared spectra were

recorded with a Perkin-Elmer FT-IR 1760 X. UV spectra were recorded on a HP 8452A diode array spectrometer. Irradiance measurements were performed with UVmeter 70380 from Oriel Instruments (response between 280 nm and 400 nm, with a maximum sensibility at 370 nm). Irradiation was carried out (a) using a 150-W xenon lamp (the xenon lamp emits a continuous spectrum of light, ranging from ultraviolet through visible to infrared (Figure 2), and the lamp output was sent through a water filter (5-cm pathlength) to remove most of the radiations), or (b) under natural sunlight from 12:00 h to 15:30 h (solar time) in May and June 2002 in Toulouse (at latitude 43° North), France.

Molecules were modelled by the software *Pimms Molecular Modelling System VI.47.a*. The predicted log (P) values, partitioning ratio between water and octanol, were calculated using *Tsar* software (Silicon Graphics, Iris Indigo X524/4000).

#### PREPARATION OF C10-DBM

According to the procedure described by Clark and Miller (18,19) and Marzinzik and Felder (20), an aqueous solution of tetra-*n*-butylammonium fluoride (0.017 mol) was added to BM-DBM (0.010 mol). By heating this mixture to 80°C, under reduced pressure (evaporator) for three hours, water escaped, leaving an anhydrous yellow residue. This residue was dissolved in THF (25 ml), and 1-bromodecane (0.030 mol) was added. Then, the mixture was stirred at 70°C for two hours. The solution was evaporated, giving a yellow viscous residue. This was purified on a silica column, with dichloromethane as eluent (42% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ ,  $J_{\text{Hz}}$ : 8.00 (m, 2H,  $J = 8.8$ ;  $\text{H}_6$ ); 7.93 (m, 2H,  $J = 8.4$ ;  $\text{H}_8$ ); 7.46 (m, 2H,  $J = 8.4$ ;  $\text{H}_9$ ); 6.94 (m, 2H,  $J = 8.8$ ;  $\text{H}_{10}$ ); 5.11 (t, 1H,  $J = 6.6$ ;  $\text{H}_{11}$ ); 3.87 (s, 3H,  $\text{H}_{12}$ ); 2.12 (m, 2H,  $\text{H}_{18}$ ); 1.34 (s, 9H,  $\text{H}_{14}$ ); 1.28 (m, 16H,  $\text{H}_{16}$  and  $\text{H}_{17}$ ); 0.89 (t, 3H,  $J = 6.7$ ;  $\text{H}_{15}$ ).  $^{13}\text{C}$  NMR assignments were ascertained with the help of  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HSQC and HMBC spectra.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{ppm}}$ : 196.1 ( $\text{C}_2$ ); 195.1 ( $\text{C}_1$ ); 163.9 ( $\text{C}_3$ ); 157.3 ( $\text{C}_4$ ); 133.9

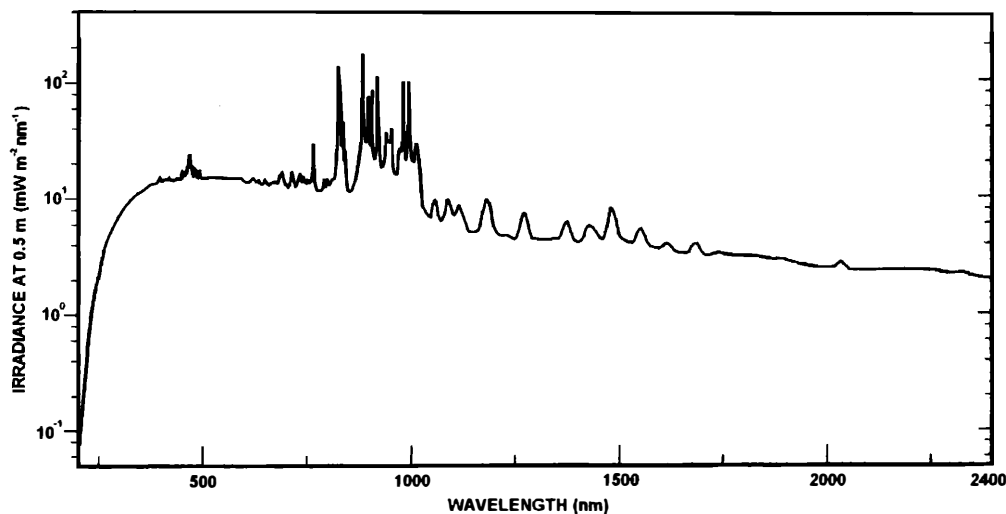


Figure 2. Spectral irradiance of 150-W xenon lamp, showing percentage of total irradiance in specific UV, visible, and near infrared spectral ranges.

(C<sub>5</sub>); 131.2 (C<sub>6</sub>); 129.5 (C<sub>7</sub>); 128.8 (C<sub>8</sub>); 125.9 (C<sub>9</sub>); 114.2 (C<sub>10</sub>); 57.7 (C<sub>11</sub>); 55.7 (C<sub>12</sub>); 35.3 (C<sub>13</sub>); 32.1–28.6 (C<sub>17</sub>); 31.2 (C<sub>14</sub>); 29.9 (C<sub>18</sub>); 22.9 (C<sub>16</sub>); 14.3 (C<sub>15</sub>). IR (KBr),  $\nu_{\text{cm}^{-1}}$ : 2924; 1692; 1663; 1602–1464; 1262; 1171; 844. MS (ES, MeOH, positive mode)  $m/z = 451 [M + H^+]$ . Anal. Calcd for C<sub>30</sub>H<sub>42</sub>O<sub>3</sub>: C, 79.96; H, 9.39; O, 10.65%. Found: C, 80.07; H, 9.69; O, 10.87%.

#### PREPARATION OF THE CREAM

We used a water-in-oil preparation obtained from Dipta (Aix-en-Provence, France) in which we incorporated 1% in weight of each molecule: BM-DBM and/or C10-DBM. The preparation contained dicaprylyl carbonate (10%), beeswax (4%), PEG-30 dipolyhydroxystearate (3%), polyglyceryl-3 diisostearate (1.5%), disodium EDTA (0.2%), sodium chloride (1%), methylparaben (0.2%), xanthan gum (1%), butylparaben (0.3%), glycasil L (0.2%), and water (78.6%).

#### PHOTOSTABILITY ASSAYS

The method used was inspired by that of Rudolph (21) and Allen *et al.* (10). Assays for photostability were performed on small, smooth, quartz plates of 16 cm<sup>2</sup>. The preparations were spread on the plates as thin films (1 mg cm<sup>-2</sup>). The average film thickness was calculated from the sample weight, the sample area, and the specific gravity of the sunscreen preparation. The plates were exposed either to the xenon lamp or natural sunlight irradiation. Irradiance measurements were done with the UVmeter at the distance the quartz plates had been irradiated. Irradiation of the samples was done at room temperature. The reference background used for UV spectra measurement was the water-in-oil preparation with no sunscreen. This preparation was irradiated under the same conditions as the samples. Tables I and II show the irradiation characteristics.

## RESULTS

#### SOLVATOCHROMISM STUDY

C10-DBM was obtained according to the procedure described by Clark and Miller (18,19). The C10-DBM isolated at the end of the purification was in its beta-diketone form (Figure 1). No trace of the enol form was detected by NMR, IR, or HPLC analyses.

**Table I**  
Irradiation Conditions under 150-W Xenon Lamp for Preparations Containing 1% w/w Absorbers

Absorbers	Total concentration (mmol l <sup>-1</sup> )	UV intensity* (mW cm <sup>-2</sup> )	Irradiation experiments	Sample weight (mg cm <sup>-2</sup> )	Film thickness (μm)
BM-DBM	29	10.6	P1	1	11
			P2	0.75	8
			P3	1	11
C10-DBM	21	10.5	C1	1	11
BM-DBM/C10-DBM (7:3)	19	10.8	M1	0.9	10

Preparation specific gravity = 0.934 g cm<sup>-3</sup> and irradiated area = 16 cm<sup>2</sup>.

\* Radiometer: Oriel Instruments.

Table II

Irradiation Conditions under Natural Sunlight (12:00 h–15:30 h solar time, in May–June, Toulouse, 43° North, France) for Preparations Containing 1% w/w of Absorbers

Absorbers	Total concentrations (mmol l <sup>-1</sup> )	UV intensity* (mW cm <sup>-2</sup> )	Irradiation experiments	Sample weight (mg cm <sup>-2</sup> )	Film thickness (μm)
BM-DBM	27	3.6–4.7	P'1	0.9	10
C10-DBM	19	3.6–4.7	C'1 and C'2	0.8	9
BM-DBM/C10-DBM (7:3)	19	3.4–4.4	M'1	0.9	10

Preparation specific gravity = 0.934 g cm<sup>-3</sup> and irradiated area = 16 cm<sup>2</sup>.

\* Radiometer: Oriel Instruments.

The solvatochromic properties of the molecule were first investigated in organic solvents. In acetonitrile, the molecule absorbed in the UVB-UVC domain (Figure 3), with a maximum absorption at 263 nm. UV spectra of the diketone C10-DBM were recorded in dichloromethane, hexane, ether, pentanol, isopropanol, and methanol. We noted that the wavelength of maximum absorbance ( $\lambda_{\max}$ ) did not fluctuate much (between 262 nm in hexane and 268 nm in dichloromethane), and the molar absorption coefficient at  $\lambda_{\max}$  ranged from 20 000 M<sup>-1</sup> cm<sup>-1</sup> in acetonitrile to 25 000 M<sup>-1</sup> cm<sup>-1</sup> in hexane.

When C10-DBM was incorporated in an organized environment, a micellar solution of SDS ( $5 \times 10^{-2}$  mol l<sup>-1</sup>), the UV spectrum (Figure 4) showed two absorption bands: a first band corresponding to the diketone form, with a maximum absorbance at 271 nm, and a second corresponding to the enol form at 361 nm. An organized environment seemed to favor the enol form, which absorbed UVA rays.

#### BEHAVIOR UNDER IRRADIATION WITH A 150-W XENON LAMP

*In organic solvents.* Figure 5 shows the absorption spectrum recorded before (dotted curve)

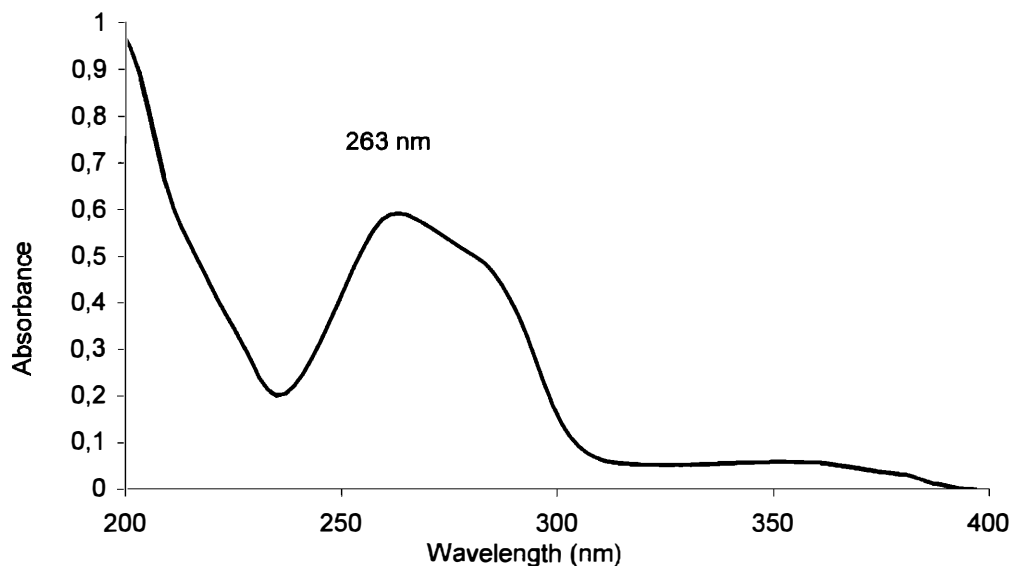


Figure 3. UV spectrum of C10-DBM in acetonitrile ( $2.9 \times 10^{-5}$  M).



Figure 4. UV spectrum of C10-DBM in an aqueous micellar solution of SDS ( $5 \times 10^{-2}$  M).

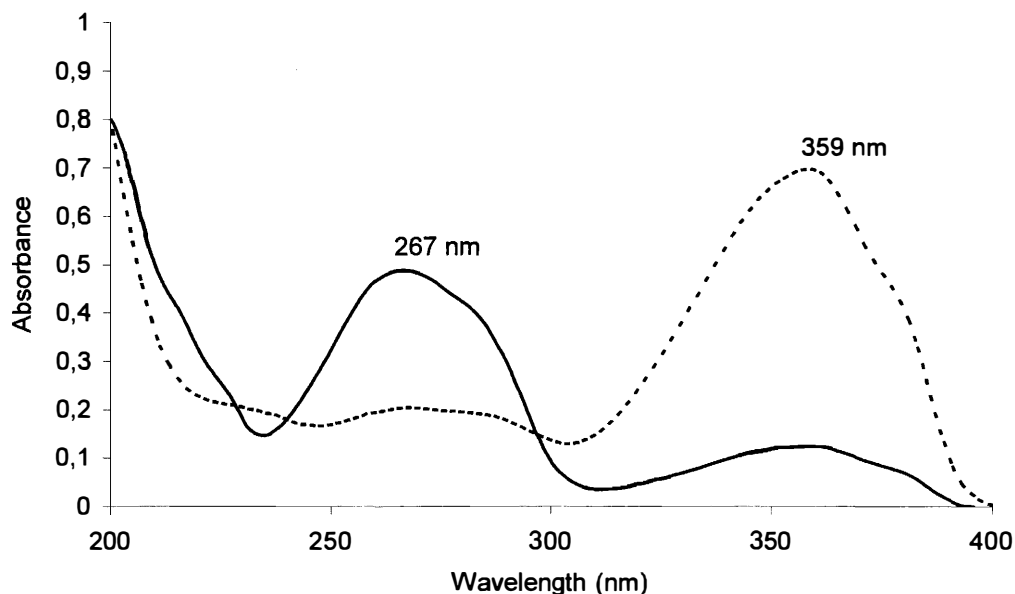


Figure 5. UV spectra of BM-DBM in acetonitrile ( $2.2 \times 10^{-5}$  M) before irradiation (dotted line) and after five minutes of irradiation (full line) with a 150-W xenon lamp ( $P = 20 \text{ mW cm}^{-2}$ ).

and after (full curve) five minutes of irradiation of BM-DBM in acetonitrile. When a solution of BM-DBM in acetonitrile was irradiated for five minutes (xenon lamp,  $P = 20 \text{ mW cm}^{-2}$ ), a strong fall in the UVA absorbance at 359 nm was observed, while the UVB absorbance increased, with a maximum at 267 nm.

Figure 6 shows the absorption spectrum recorded before (dotted curve) and after (full curve) five minutes of irradiation of C10-DBM in acetonitrile. Irradiation of a solution

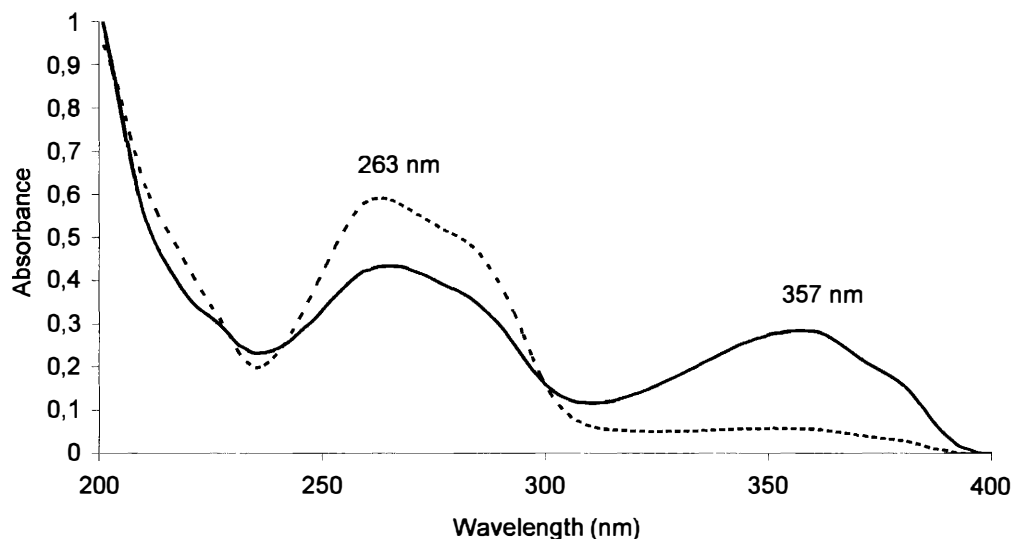


Figure 6. UV spectra of C10-DBM in acetonitrile ( $2.9 \times 10^{-5}$  M) before irradiation (dotted line) and after five minutes of irradiation (full line) with a 150-W xenon lamp ( $P = 20 \text{ mW cm}^{-2}$ ).

of C10-DBM in acetonitrile for five minutes (xenon lamp,  $P = 20 \text{ mW cm}^{-2}$ ) led to a strong diminution of the UVB absorbance at 263 nm, while the UVA absorbance increased, with a maximum at 357 nm. The same phenomenon was observed in other organic solvents such as hexane or dichloromethane. When irradiation was continued for a further five minutes, absorbance in the UVA region decreased.

*In cosmetic preparations.* First of all, BM-DBM was incorporated in a water-in-oil preparation (1% w/w). The preparation was then spread on a quartz plate (three dosages were assayed, all around  $1 \text{ mg cm}^{-2}$ ), and the absorbance of the plates was followed under irradiation (see P1, P2, and P3 in Table I).

Figure 7 shows the variations of absorbance of the cream with 1% w/w BM-DBM versus the duration of irradiation (xenon lamp, 150 W). The curves were normalized in order to correct for the variation of the amounts of preparations spread on the plates. The evolution of the three assays was identical, and so we can conclude that the method is reproducible.

Thus, we investigated preparations containing 1% w/w C10-DBM and the C10-DBM/BM-DBM mixture. Three preparations were examined: water-in-oil emulsion + BM-DBM 1% w/w; water-in-oil emulsion + C10-DBM 1% w/w; and water-in-oil emulsion + 1% w/w of a mixture (BM-DBM/C10-DBM, molar ratio 7:3). Each cream was tested in the conditions described above. Figure 8 shows the variation of absorbance at 358 nm of preparations under xenon lamp irradiation.

A strong decrease in the absorbance of the cream containing 1% w/w BM-DBM (diamonds in Figure 8, referred to as P1 in Table I) was observed during the irradiation. Indeed, after five, ten, and 20 minutes of irradiation, it lost 50%, 80%, and 96%, respectively, of its UVA absorbance.

Initially, the cream containing 1% w/w C10-DBM (squares in Figure 8 corresponding to C1 in Table I) presented very low absorbance in UVA (OD at 358 nm: 0.14). On



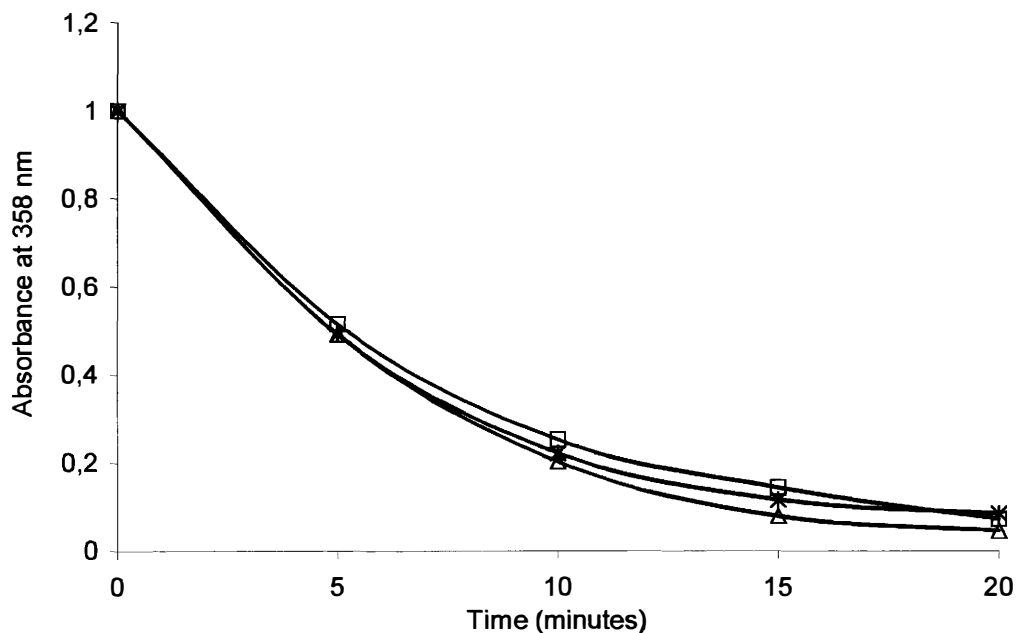


Figure 7. Absorbance of preparations containing 1% w/w BM-DBM under xenon lamp irradiation for three identical experiments (P1: stars; P2: squares; P3: triangles).

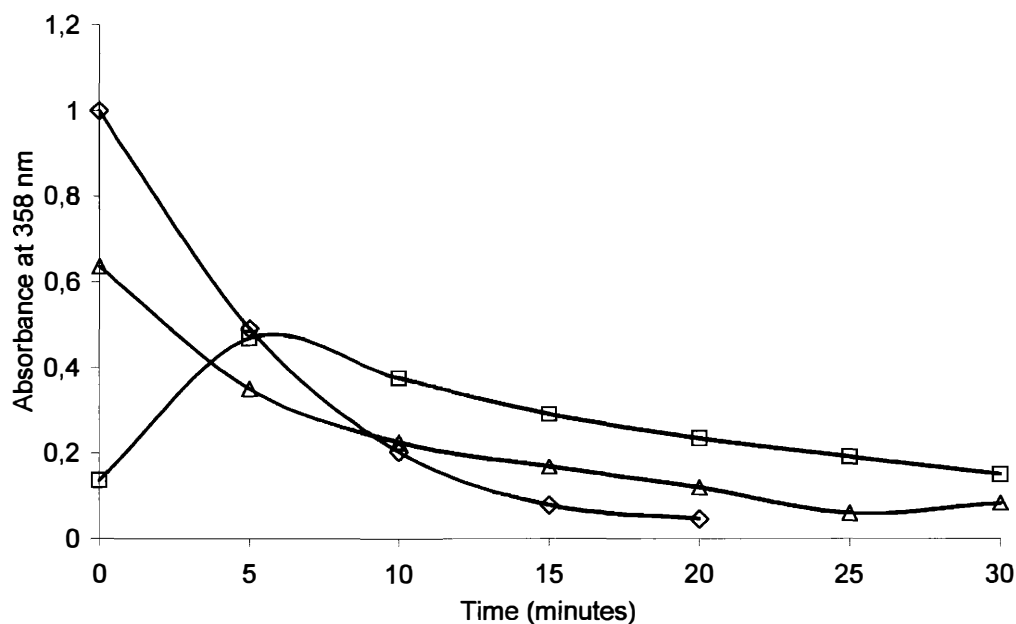


Figure 8. Absorbance of preparations containing 1% w/w BM-DBM (P1: diamonds), C1-DBM (C1: squares), and BM-DBM/C1-DBM mixture, 7:3 molar ratio (M1: triangles) under xenon lamp irradiation.

irradiation, UVA absorption appeared. After five minutes of irradiation, an increase of 71% in the absorbance at 358 nm was noted. Then a slow decrease began. After 10 minutes, the absorbance fell by 16%. After 30 minutes of irradiation, absorbance had

returned to the values noted before irradiation (OD at 358 nm: 0.15). The UVA absorbance decrease was slower for the preparation with the C10-DBM than for that of the preparation with BM-DBM.

The triangles in Figure 8 (corresponding to M1 in Table I) plot the variation of the absorbance of the cream containing 1% w/w of a BM-DBM/C10-DBM mixture (molar ratio 7:3). Absorbance at 358 nm decreased progressively. After five, ten, and 20 minutes of irradiation, the cream had lost, respectively, 45%, 65%, and 80% of its absorbance in the UVA (compared to 50%, 80%, and 96% for the preparation with BM-DBM alone). The rate of absorbance diminution was slower than that of the preparation containing BM-DBM.

#### BEHAVIOR UNDER IRRADIATION WITH NATURAL SUNLIGHT

The same preparations were exposed to solar light. Each cream was tested under the conditions described above (see Table II). Figure 9 shows the variations of absorbance of creams with 1% w/w C10-DBM versus time of exposure to natural sunlight. Two assays (C'1 and C'2 in Table II) were carried out and confirmed the reproducibility of the method. Figure 10 shows the variation of absorbance at 358 nm of preparations containing 1% w/w of filter under natural sunlight.

We observed a strong decrease in the absorbance of the cream containing 1% w/w BM-DBM (diamonds in Figure 10, corresponding to P'1 in Table II). Indeed, after one hour, two hours and three hours of irradiation, the cream lost 64%, 85%, and 92%, respectively, of its UVA absorbance.

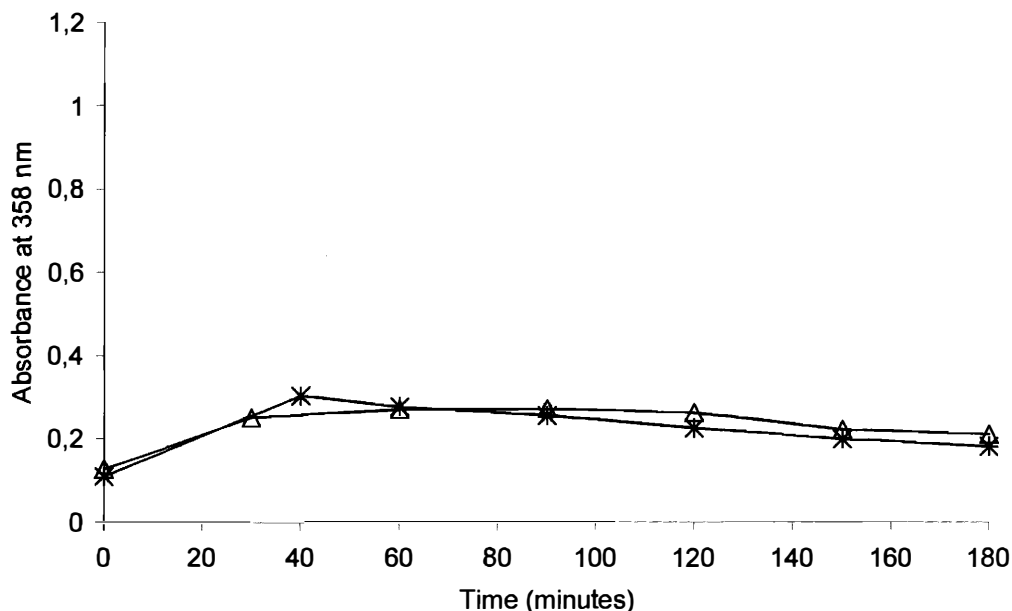


Figure 9. Absorbance of preparations containing 1% w/w C10-DBM under natural sunlight irradiation (C'1: triangles; C'2: stars).

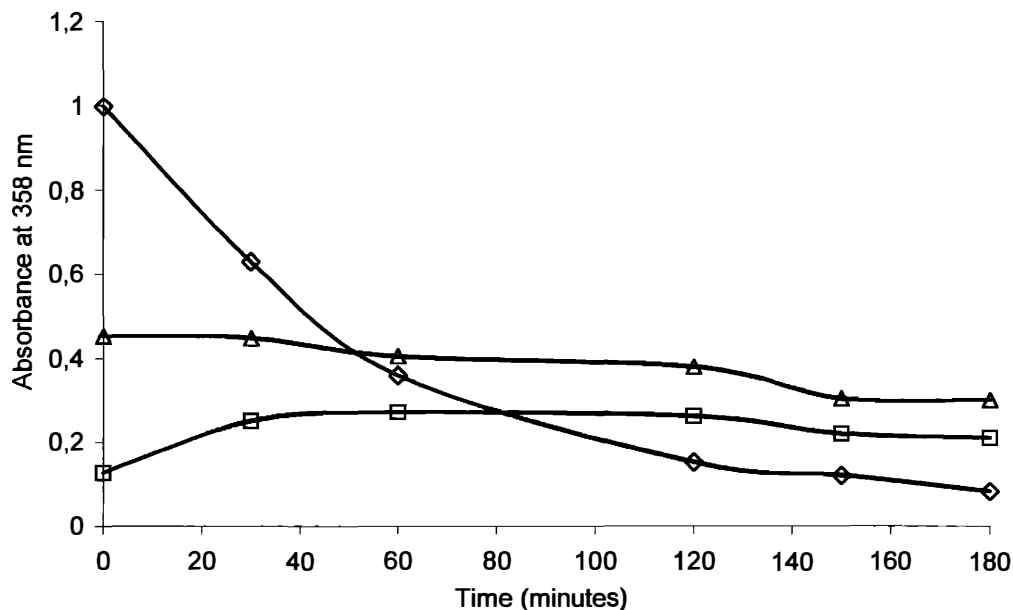


Figure 10. Absorbance of preparations containing 1% w/w BM-DBM (P'1: diamonds) or C10-DBM (C'1: squares) or a BM-DBM/C10-DBM mixture, 7:3 molar ratio (M'1: triangles) under natural sunlight.

Initially, the cream containing 1% w/w C10-DBM (squares in Figure 10, corresponding to C'1 in Table II) presented very low absorbance in UVA (OD at 358 nm: 0.13). Like under xenon lamp irradiation, UVA absorbance increased as irradiation started. After 60 minutes of irradiation, an increase of 58% in the absorbance at 358 nm was noted. The absorbance reached a maximum (OD at 358 nm: 0.27) and remained stable for 30 minutes. Then it began to decrease slowly. After two hours of irradiation, we observed a decrease of 3% in comparison with the maximum absorbance obtained (85% for BM-DBM). After three hours, we noted a decrease of 22% (92% for BM-DBM) in comparison with the absorbance at one hour of irradiation. The absorbance was always above the initial one (OD at 358 nm: 0.21).

Concerning the cream containing 1% w/w of a BM-DBM/C10-DBM mixture (molar ratio 7:3) (triangles in Figure 10, corresponding to M'1 in Table II), the UVA absorbance at 358 nm remained constant during the first 30 minutes of solar exposure. Then it decreased slowly and progressively. After one hour, two hours, and three hours of irradiation, the cream lost 11%, 16%, and 34%, respectively, of its absorbance in UVA. The rate of absorbance diminution was slower than that of the cream containing only BM-DBM.

## DISCUSSION

Beta-diketone compounds exist as keto/enol tautomers. Considerable attention has been focused on the equilibrium populations of each tautomer in various solvents, especially for dibenzoylmethane and its derivatives (16,22–24). The keto/enol tautomer ratio depends on the nature of the  $\alpha$ -substituents, the nature of the solvents, the temperature,

and the presence of traces of proton acceptors and/or donors (25). For most of them, the enol form is the major one. The conjugated system of the enol form spreads further than that of the keto form due to the formation of a pseudo-six-membered ring with OH. This induces a bathochromic shift in absorbance.

C10-DBM and BM-DBM were modelled, and the predicted log (P) values were calculated. Log (P) for BM-DBM was estimated at 4.0, whereas for the enol form of C10-DBM, log (P) was estimated at 7.9 and the keto form at 8.2. It is, of course, the long aliphatic carbon chain of the C10-DBM that induces its partition toward an apolar environment and hence an original behavior.

When C10-DBM was incorporated in an organized environment, a micellar solution of SDS, absorbance shifted from UVB to UVA. One hypothesis is that the keto–enolic equilibrium was displaced to the enol form (absorbance maximum at 361 nm). The environment has an important influence on this equilibrium: indeed a particular micellar distribution of C10-DBM in the solutions examined can result in the modification of the solute–solvent interactions and of the polarity environment. We can easily imagine the insertion of C10-DBM into micelles, favoring the enol isomer. Indeed, it seems that the keto–enolic equilibrium is shifted towards the enol form in apolar environments.

Watarai *et al.* (26) described the tautomerization of benzoylacetone, benzoyltrifluoroacetone, and 2-naphthoyltrifluoroacetone in anionic, cationic, and non-ionic microemulsions by means of UV spectrophotometry. The ratio of the two absorbance maxima (around 300–350 nm for the enol form and 250 nm for the keto form) reflected the degree of enolization. They studied the effect of dissolving the molecules in SDS micellar media on the absorbance ratio of these  $\beta$ -diketones. They noted an increase in the absorbance ratio ( $A_{\text{enol}}/A_{\text{keto}}$ ) when the SDS is above its critical micellar concentration. They explained this increase by a preferential solubilization of the enol form in micelles. In our case, almost all C10-DBM molecules were in the enol form in the micellar solution of SDS.

C10-DBM seems to have a different behavior from other 1,3-dicarbonyl compounds. Unlike BM-DBM, in organic solvents, C10-DBM is in its keto form. Irradiated for a few minutes, the absorbance shifted from UVB to UVA. Spectral changes can be due to the conversion of the diketone form of C10-DBM ( $\lambda_{\text{max}} = 263$  nm) to the enol form ( $\lambda_{\text{max}} = 357$  nm) or to its photodegradation into UVA-absorbing species. The mechanism of this phenomenon was studied in more detail and is the subject of a second article (27). HPLC-MS indicated the coexistence of two processes:

- in organized media, a shift of the keto–enolic equilibrium towards the enol
- under irradiation, decomposition of C10-DBM leading to BM-DBM (Norrish II photoreaction)

In water-in-oil preparations, the same phenomenon as in micellar solutions of SDS was observed. We noted weak UVA absorbance of the cream containing 1% w/w C10-DBM before irradiation. Irradiation with either xenon lamp or natural sunlight induced an increase in UVA absorbance for five minutes for the xenon lamp or one hour for sunlight (Figures 8 and 10, respectively). Furthermore, UVA absorbance of the preparation containing C10-DBM is more stable than that of the preparation containing BM-DBM. After three hours under natural sunlight, we noted a 22% decrease in the UVA absor-

bance for the preparation containing C10-DBM and an 92% decrease for the preparation with BM-DBM. However, the molar absorption coefficient of C10-DBM is lower than that of the BM-DBM. In the creams, the molar absorption coefficient at 358 nm of C10-DBM in the enol form was estimated at  $17\,000\text{ M}^{-1}\text{ cm}^{-1}$ , whereas that of BM-DBM was estimated at  $40\,000\text{ M}^{-1}\text{ cm}^{-1}$ . Thus C10-DBM should not be used alone in cosmetic preparation, but in association with BM-DBM. High initial UVA absorbance will be given by the presence of BM-DBM and it will be preserved by the presence of C10-DBM, which under irradiation will supply BM-DBM. Therefore, a cream containing a mixture of BM-DBM/C10-DBM (molar ratio 7:3) was prepared. Looking at the triangles in Figures 8 and 10 (preparations M1 and M'1, respectively, in Tables I and II), we can confirm that the UVA absorption of these creams was more stable than the UVA absorption of creams P1 and P'1. C10-DBM, which is a BM-DBM precursor under irradiation, allowed us to preserve the UVA absorption of the preparation containing the mixture. Moreover, creams M1 and M'1 showed an initial absorbance that was higher than the absorbance of creams C1 and C'1. Thus cosmetic preparations containing both C10-DBM and BM-DBM exhibit UVA absorbance that remains at useful levels for longer than cosmetic preparations containing only BM-DBM. Studying the curves in Figure 8 and 10, we note that the efficiency of the C10-DBM molecule was greater under natural sunlight irradiation. Indeed, absorbance of creams C'1 and M'1 (Figure 10) can be considered stable under natural sunlight for three hours, corresponding to the period of strongest light intensity (12:00 h–15:30 h solar time, in May and June, Toulouse, latitude  $43^\circ$  North, France). Irradiation with the 150-W xenon lamp was performed without any UVC filter. Therefore, the xenon lamp emitted short wavelength rays, hence more energetic than natural sunlight. Thus the photodegradation of the filters was much faster under xenon lamp irradiation than under natural light.

## CONCLUSION

In this paper, we present a new UV absorber, the 1-(4-*tert*-butylphenyl)-2-decanyl-3-(4'-methoxyphenyl)-propane-1,3-dione called C10-DBM, derived from BM-DBM by grafting a long alkyl chain. The present work reports the absorbance photostabilities of UVA sunscreen preparations containing BM-DBM and C10-DBM in water-in-oil preparations similar to those currently used in cosmetics. Although C10-DBM shows a weaker molar absorption coefficient in the UVA than BM-DBM, its absorption is more photostable in this domain, especially under natural sunlight. The use of both filters together, BM-DBM and C10-DBM, the first one for its high UVA absorption and the second one for its ability to supply BM-DBM under irradiation, results in good stability in UVA protection.

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