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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

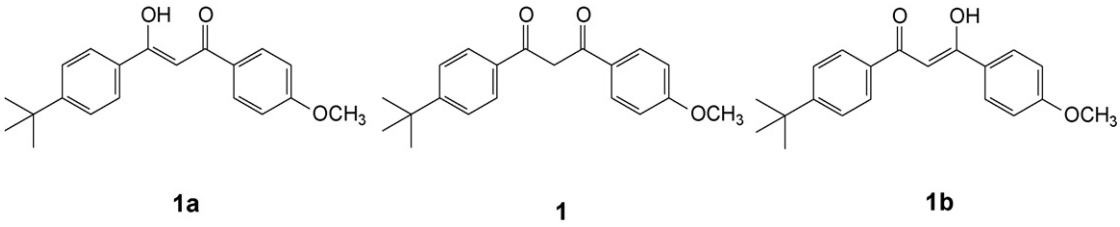

Fig. 1. Tautomeric structures of DBM: **1a** = enol form 1, **1** = 1,3-diketone form, **1b** = enol form 2.

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