

Changes in Ultraviolet Absorption of Sunscreens After Ultraviolet Irradiation

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The incidence of skin cancer is increasing rapidly and sunscreens have been recommended in order to reduce damage from sunlight. In this investigation we have studied the change in the absorption spectrum of some photoactive organic species in sunscreens after ultraviolet A and ultraviolet B irradiation in a dose normally encountered during a full day in the sun. Samples of a number of photoactive compounds commonly used in sunscreens were irradiated with ultraviolet A and ultraviolet B light. A UVASUN 2000 MUTZHAS sunlamp was used for ultraviolet A irradiation and an Esshå Corona mini, equipped with two Philips TL12 20 W lamps, was used as the ultraviolet B source. The ultraviolet A dose was 100 J per cm². The ultraviolet B dose corresponded to 20 minimal erythema doses. The absorption spectra of the compounds were recorded before and after irradiation. The absorbance of 2-ethylhexyl 4-methoxycinnamate was reduced significantly, whereas 3-(4-methylbenzyl-

iden)camphor seemed to be rather stable. The benzophenones studied seemed to be relatively stable. In the case of 4-tert-butyl-4'-methoxy-dibenzoylmethane there was a rapid decrease in the ultraviolet A absorption leading to unsatisfactory protection in the ultraviolet A region. 4-Isopropyl-dibenzoylmethane also lost most of its ultraviolet protective capacity after irradiation with ultraviolet A. Ultraviolet B seemed to have a minor effect on all the samples. It is important for the clinician not only to know the initial absorption spectrum in the ultraviolet region for a specific sunscreen substance, but also whether it is altered during irradiation and in what way. This study including gas chromatography and mass spectrometry analysis indicates that some of the photoactive organic species commonly used today in sunscreens are unstable following ultraviolet irradiation. *Key words: decomposition/gas chromatography and mass spectrometry/ultraviolet A/ultraviolet B. J Invest Dermatol 113:547-553, 1999*

Skin cancer has become a threat to the population in recent years. The incidence of malignant melanoma in Sweden is increasing at a rate of 5% per year (Cancer Incidence in Sweden, 1991). Other forms of skin cancer are also increasing rapidly. The most important etiologic factor is generally believed to be exposure to sunlight. The action spectra and dose-response curves are, however, probably different for squamous cell carcinomas, basal cell carcinomas, and malignant melanomas (Setlow *et al*, 1993; Armstrong *et al*, 1997; Urbach, 1997).

The action spectrum for squamous cell carcinomas seems to be fairly similar to that for the induction of erythema, i.e., primarily in the ultraviolet (UV) B region. The incidence increases exponentially with increasing dose of UV radiation (Armstrong *et al*, 1997; Urbach, 1997). Regarding malignant melanoma, the situation is much less clear. It has been argued that small increments in dose at low doses lead to a rapid increase in the incidence of malignant

melanoma, whereas the increase in incidence levels off at higher cumulative doses (Armstrong *et al*, 1997). Also, the action spectrum has been argued to be shifted towards the UVA (Setlow *et al*, 1993). It has been questioned whether or not sunscreens protect against melanoma, as several studies have failed to show a protective effect of sunscreens against this type of malignant melanoma (Westerdahl *et al*, 1995). Sunscreens, however, seem to work against basal cell carcinomas and actinic keratoses (Thompson *et al*, 1993).

Furthermore, there has previously been some discussion regarding possible breakdown products of sunscreens (Kammeyer *et al*, 1987; Roscher *et al*, 1994; Schwack and Rudolph, 1995; Dunlap *et al*, 1998). The presence of such products may lead to different protection spectra for different sunscreens and hence affect their protection against skin cancer.

Consequently, we have investigated the UV spectrum of some photoactive organic species common in sunscreens (Fig 1) before and after irradiation with UVA and UVB light. Possible existence of breakdown products of the sunscreen compounds after irradiation has also been measured using a gas chromatography mass spectrometer.

MATERIALS AND METHODS

The lamps For UVA irradiation a UVASUN 2000 (MUTZHAS, Germany) was used. This unit emits almost exclusively in the UVA region

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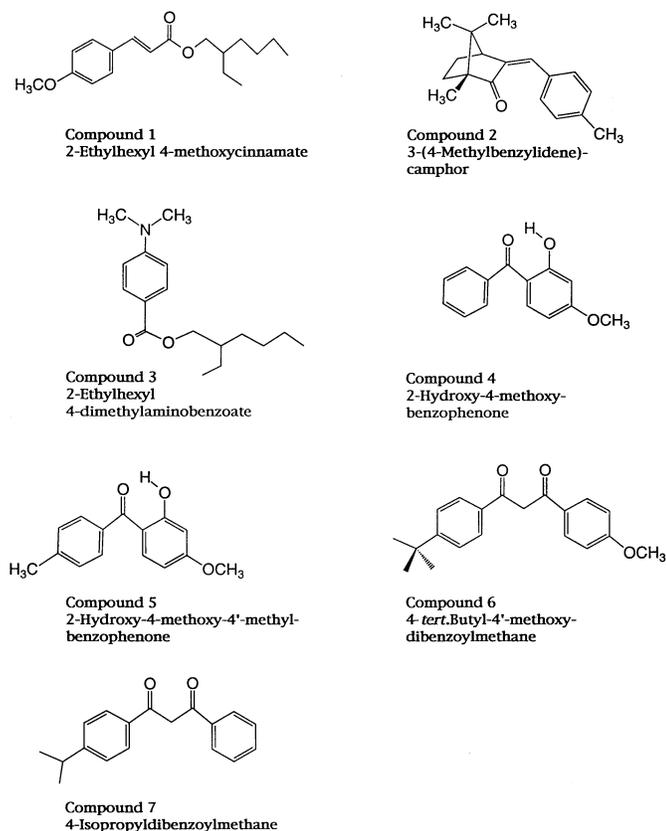


Figure 1. Compounds 1–7. The molecules investigated.

(320–400 nm). Very little radiation is emitted below 350 nm. A dose of 100 J per cm², which corresponds to the amount of UVA irradiation that reaches the surface of the earth in Scandinavia during one full day, was used. The samples were irradiated for 20 min and accordingly the power was 83 mW per cm². For UVB irradiation (290–320 nm), an Eshå Corona Mini (Sweden), equipped with two fluorescent light bulbs, Philips TL 12 (20 W), was used. The emission spectrum of this light source is primarily in the UVB with a peak at 313 nm. The irradiation was measured with an International Light IL 1350 Radiometer/Photometer using an SED 240 probe for UVA and an SED 015 probe for UVB radiation. The irradiance was found to be 0.79 mW per cm² for UVB radiation. A dose of 20 minimal erythema dose (MED), corresponding to the maximum dose during 1 d close to the equator, was applied. A sunscreen compound stable at these conditions will give a sufficient UVB protection.

Compounds studied Instead of investigating commercial sunscreens, the photoactive ingredients (Fig 1) were mixed with petroleum jelly (petrolatum) in about the same concentrations as in commercial sunscreens. The reason for using petroleum jelly was to avoid interference from substances such as perfume, etc. (Saino, 1995). The sunscreen compounds we studied were: 2-ethylhexyl 4-methoxycinnamate (Parsol MCX, Givaudam, Switzerland); 3-(4-methylbenzylidene)camphor (Eusolex 6300, Merck, U.S.A.); 2-ethylhexyl-4-dimethylaminobenzoate (Escalol 507, Merck; Eusolex 6007); 2-hydroxy-4-methoxybenzophenone (Escalol 567, Fluka, Switzerland; Eusolex 4360, Oxybenzone); 2-hydroxy-4-methoxy-4'-methylbenzophenone (Mexenone, Lancaster, U.K.); 4-tert-butyl-4'-methoxy-dibenzoylmethane (Parsol 1789, Givaudam); and 4-isopropylidibenzoylmethane (Eusolex 8020, Pfaltz & Bauer, U.S.A.).

Sample preparation The samples were squeezed on to quartz glass plates by means of a syringe. The volume of the cylinder of sample thus obtained was easy to measure. Another quartz glass plate was placed on top of the sample and squeezed until the sample had attained the corresponding diameter. As the density and volume of the sample were known, the amount per square unit could be easily determined. The amount applied was 2 mg per cm².

Instruments used After exposure the samples were analyzed in a Cary 4 spectrophotometer from Varian (U.S.A.). Absorption spectra in some of

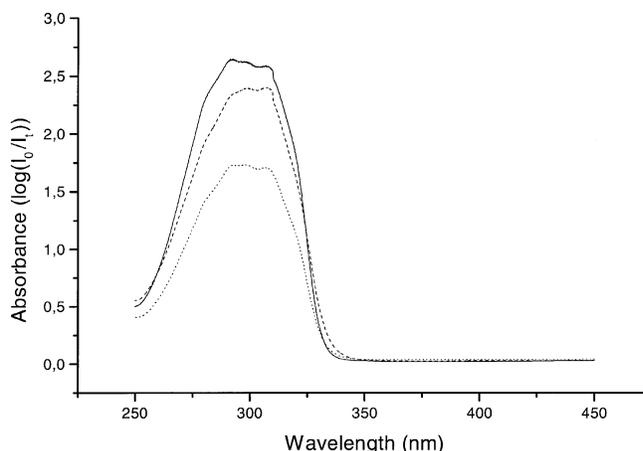


Figure 2. Absorption spectra of 2-ethylhexyl 4-methoxycinnamate (Parsol MCX). The spectra are taken before (straight line) and after irradiation with 20 MED of UVB (dashed line) followed by irradiation with 100 J per cm² of UVA (dotted line).

the experiments were collected every second minute to investigate the time dependence of the degradation. The existence of possible new photo-induced molecules was analyzed by gas chromatography and mass spectrometry. The instrument used was a magnetic sector mass spectrometer (VG7070E, Great Britain) coupled to a gas chromatograph (Hewlett-Packard 5890). A capillary column, internal density 0.25 mm (30 m, coated with DB-Xlb (J. and W. Scientific, U.S.A.)) was temperature programmed from 70 to 320°C at 10°C per min. Samples investigated with gas chromatography and mass spectrometry were taken before and after 20 min exposure of pure sunscreen compounds to the UVA lamp. The samples were dissolved in chloroform and injected on to the gas chromatography column using a split/splitless injector at 250°C.

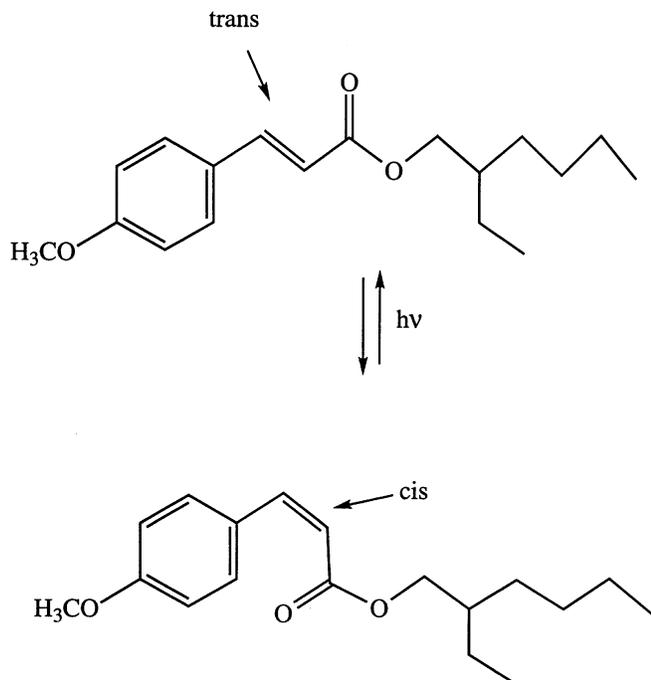
RESULTS

Some of the photoactive ingredients in sunscreens were found to be relatively stable, whereas others decomposed rather quickly. The amount of sunscreen was chosen so as to follow the recommendations of the accepted standards. This meant that very little light penetrated the sunscreens at their absorption maxima. In several cases, the initial absorbance was greater than 3, corresponding to a transmission of just 0.1% of the incoming light. Thus, photo-decomposition must start at the upper surface and then progress through the layer in order to give the observed spectrum after irradiation. The results of irradiation of the sunscreens are presented below for sunscreens claimed to protect against mainly UVB and mixed UVA and UVB radiation.

UVB sunscreen compounds

Compound 1 – UVA and UVB unstable The UVB content (290–320 nm) of normal sunlight is approximately 5% of the UV radiation whereas the remaining 95% is UVA radiation (320–400 nm). The three UVB-protecting compounds studied in this investigation have very different chemical structures and they were found to have different stability. The cinnamate (compound 1) decomposed slightly after exposure to 20 MED of UVB radiation and then a little more rapidly upon additional exposure to UVA light (Fig 2). The light/heat converting photochemical reaction is a *cis-trans* photoisomerization (Scheme 1), which can change the UV spectrum slightly before photo-equilibrium is established. The result from the gas chromatograph showed an additional peak but its mass spectrum is very similar to the original substance, assigned as the *cis*-isomer.

Compound 2 – UVA and UVB stable The camphor derivative (compound 2) is more stable. It too undergoes a *cis-trans* photoisomerization upon irradiation and thus its absorption spectrum may be expected to change initially, as was also observed experimentally (Fig 3). The two isomers have very similar spectra and their protective power does not change significantly after photo-equilib-



Scheme 1. Photoreaction of 2-ethylhexyl 4-methoxycinnamate.

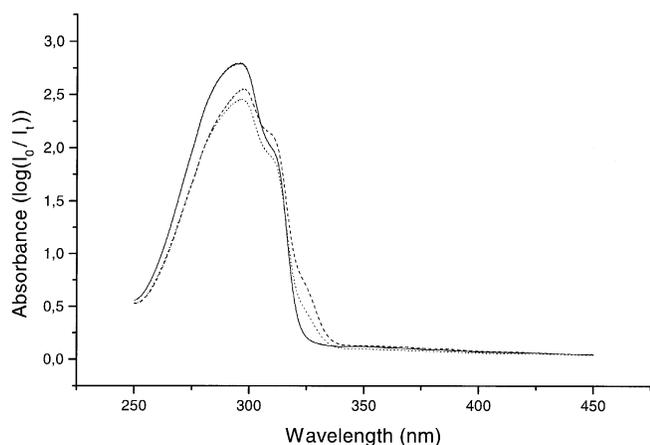
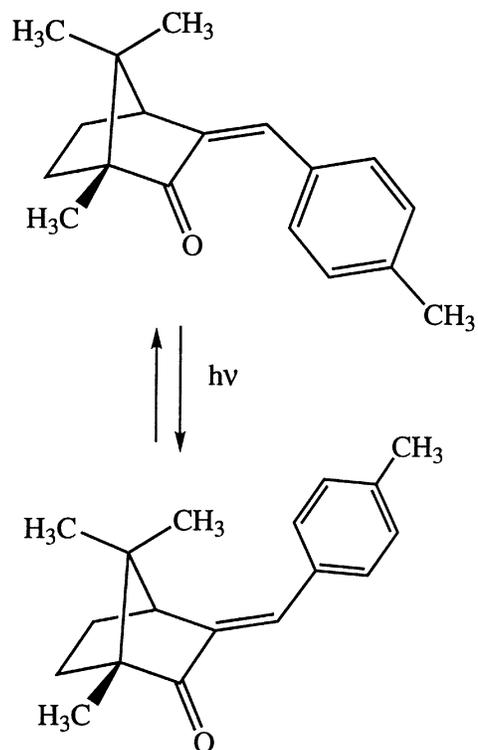


Figure 3. Absorption spectra of 3-(4-methylbenzylidene)camphor (Eusolex 6300). The spectra are taken before (straight line) and after irradiation with 20 MED of UVB (dashed line) followed by irradiation with 100 J per cm² of UVA (dotted line).

rium has been established (Scheme 2). An extra peak appears in the gas chromatogram of the exposed compound but its corresponding mass spectrum is also very much like the original substance and thus assigned as the photoisomer.

Compound 3 – UVA unstable and UVB stable The least stable compound among the pure UVB absorbents is 2-ethylhexyl 4-dimethylaminobenzoate (compound 3). It shows a very sharp UV-absorbing edge at 320 nm (Fig 4). The light/heat converting mechanism is very different from that of the aforementioned compounds, and involves the formation of a very polar excited state. UVA radiation was found to decompose the sunscreen fairly rapidly. Two new peaks are shown in the gas chromatogram of the exposed compound (Fig 5). The mass of the first eluting one corresponds to the loss of a methyl group from the original molecule; the new molecule is 2-ethylhexyl 4-methylaminobenzoate. The mass spectrum of the other new peak shows a molecule with an extra 14 atomic mass units to the original one. Of the fragments



Scheme 2. Photoreaction of 3-(4-methylbenzylidene) camphor.

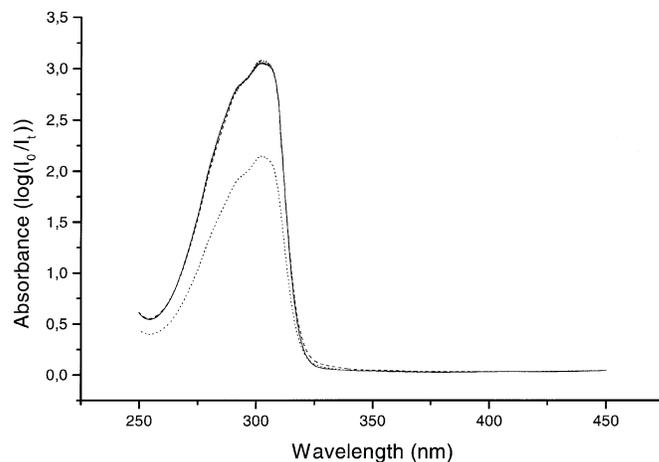


Figure 4. Absorption spectra of 2-ethylhexyl 4-dimethylaminobenzoate (Escalol 507, Eusolex 6007). The spectra are taken before (straight line) and after irradiation with 20 MED of UVB (dashed line) followed by irradiation with 100 J per cm² of UVA (dotted line).

in the mass spectrum we presume that this extra mass arises due to an oxidation of the amine part (see also Futamura and Kamiya, 1988).

UVA and UVB sunscreen compounds Four common compounds with both UVA and UVB protecting properties were tested; two benzophenones (compounds 4 and 5) and two dibenzoyl-methanes (compounds 6 and 7). The light/heat converting reactions of these compounds involve a hydrogen shift from an alcohol to a carbonyl group in the excited state, followed by a dark reaction in which the hydrogen returns to its original position.

Compounds 4 and 5 – UVA and UVB stable It is quite clear that the two benzophenones (compounds 4 and 5) are fairly stable against UVA and UVB irradiation. The small difference in their structure is reflected in their UV spectra; compound 4 with a better

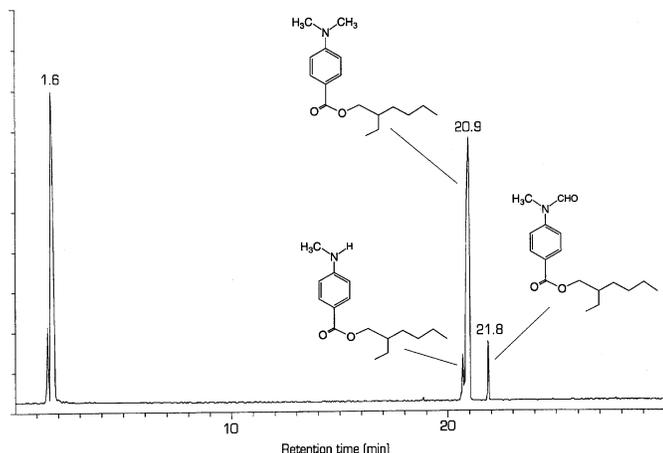


Figure 5. Gas chromatogram of 2-ethylhexyl 4-dimethylamino-benzoate. The chromatogram is taken after irradiation with 100 J per cm^2 of UVA. The peaks at 20.7 and 21.8 min correspond tentatively to 2-ethylhexyl 4-methylaminobenzoate and 4-(formylmethylamino) benzoate, respectively, and arise after irradiation. Also seen is the original molecule (20.9 min).

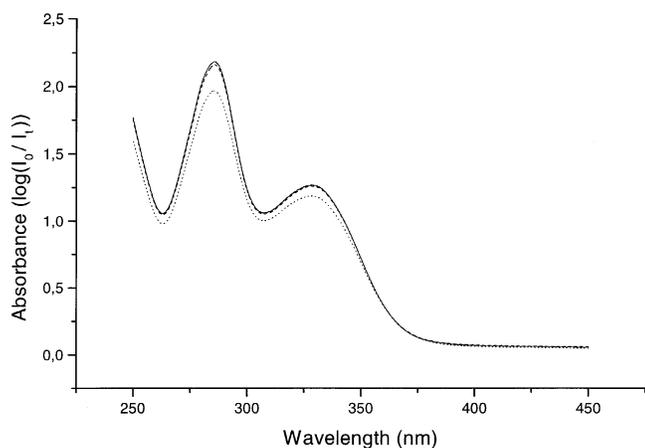


Figure 6. Absorption spectra of 2-hydroxy-4-methoxybenzophenone (Escalol 567, Eusolex 4360, Oxybenzone). The spectra are taken before (straight line) and after irradiation with 20 MED of UVB (dashed line) followed by irradiation with 100 J per cm^2 of UVA (dotted line).

absorption (Figs 6 and 7). Although these compounds are effective light/heat converters in nonpolar media, where the molecule is fixed in the most effective conformation by a strong hydrogen bond to the alcohol group, the conformation can be different in polar media (Scheme 3). Then the benzophenone can act as a sensitizer and catalyze photo-decomposition reactions (Calvert and Pitts, 1967).

Compounds 6 and 7 – very unstable to UVA and slightly unstable to UVB In contrast to the benzophenones, the dibenzoylmethanes (compounds 6 and 7) are not stable against UV irradiation (Figs 8–10). The light/heat converting reactions of compound 6 are shown in Scheme 4 and require keto-enol isomerization prior to the photoreaction. Of the two dibenzoylmethanes compound 6 with the tertiary butyl group, is the more stable one. Following the decomposition of this substance, mass spectroscopy reveals that the photoproduct appears to be a well-defined product with strong absorption in the UVB region. The isopropyl derivative (Fig 10) undergoes a similar decomposition but much less cleanly. Gas chromatogram of compound 7 after irradiation is shown in Fig 11 together with a tentative identification of the decomposition products: benzil (retention time 16.1 min), isopropylbenzil (19.4 min), 1-phenyl-3-(4-*iso*-propylphenyl)-propane-1,2,3-trione (23.0 min), and 1,3-di(4-*iso*-propylphenyl)-propane-1,2,3-trione

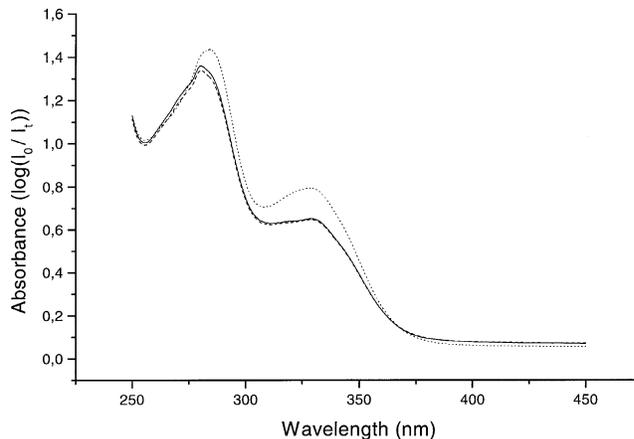
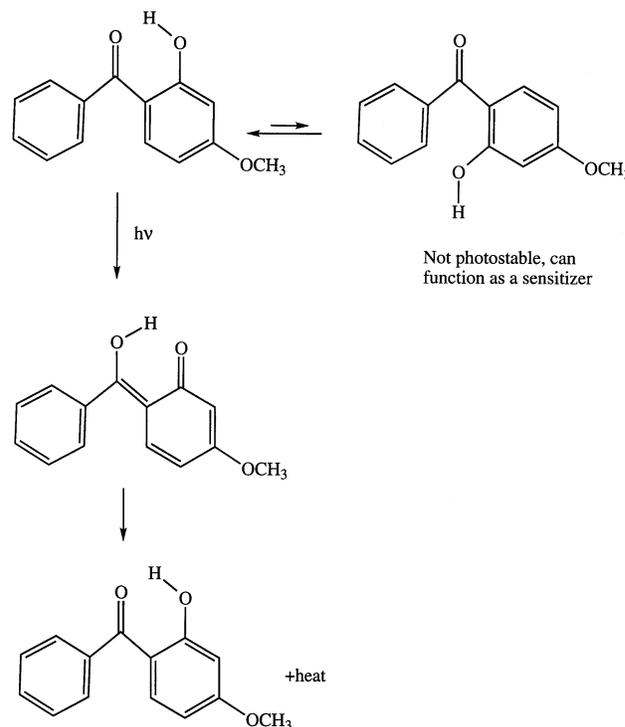


Figure 7. Absorption spectra of 2-hydroxy-4-methoxy-4'-methylbenzophenone (Mexenon). The spectra are taken before (straight line) and after irradiation with 20 MED of UVB (dashed line) followed by irradiation with 100 J per cm^2 of UVA (dotted line).



Scheme 3. Photoreaction of 2-hydroxy-4-methoxybenzophenone.

(25.5 min) and minor amounts of dibenzoylmethane (19.2 min), 1-phenyl-3-(4-*iso*-propylphenyl)-propane-1,3-dione-2-hydroxyl (23.8 min), and di(*iso*propylbenzoyl)methane (24.7 min).

DISCUSSION

Sunscreens have been recommended by dermatologists for a long time as a protective measure against excessive amounts of sunlight. The sun protection factor is defined as the quotient between the MED of a protected vs. an unprotected area. For UVA, there is no generally accepted standard for the protection capacity. Some years ago, a survey revealed that there were several sun protection factor standards (Kivisäkk et al, 1994).

The amount of sunscreen applied also plays an important part. Generally, 2 mg per cm^2 is recommended, but in the actual 'beach' situation people apply much less than that (Stenberg and Larkö, 1985; Bech-Thomsen and Wulf, 1992). Concerning sunscreens

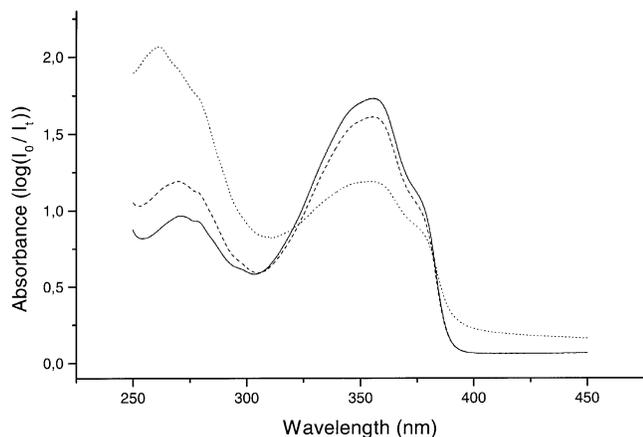


Figure 8. Absorption spectra of 4-tert-butyl-4'-methoxy-dibenzoylmethane (Parsol 1789). The spectra are taken before (straight line) and after irradiation with 20 MED of UVB (dashed line) followed by irradiation with 100 J per cm² of UVA (dotted line).

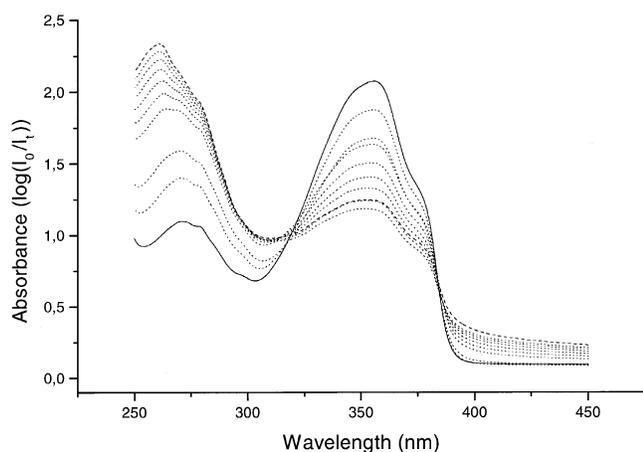


Figure 9. Absorption spectra of 4-tert-butyl-4'-methoxy-dibenzoylmethane. The spectra are taken before (straight line) and after increasing doses of UVA.

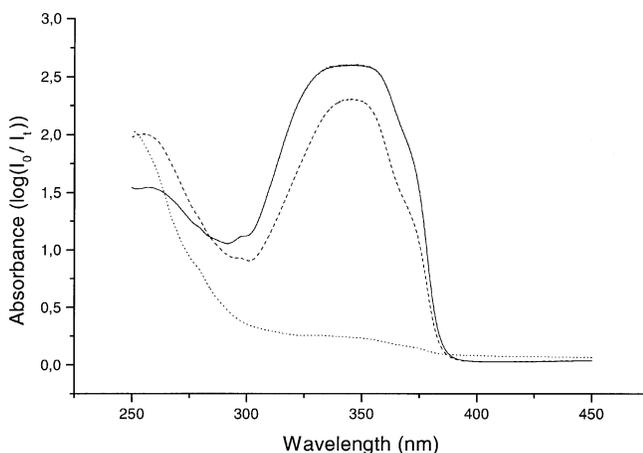
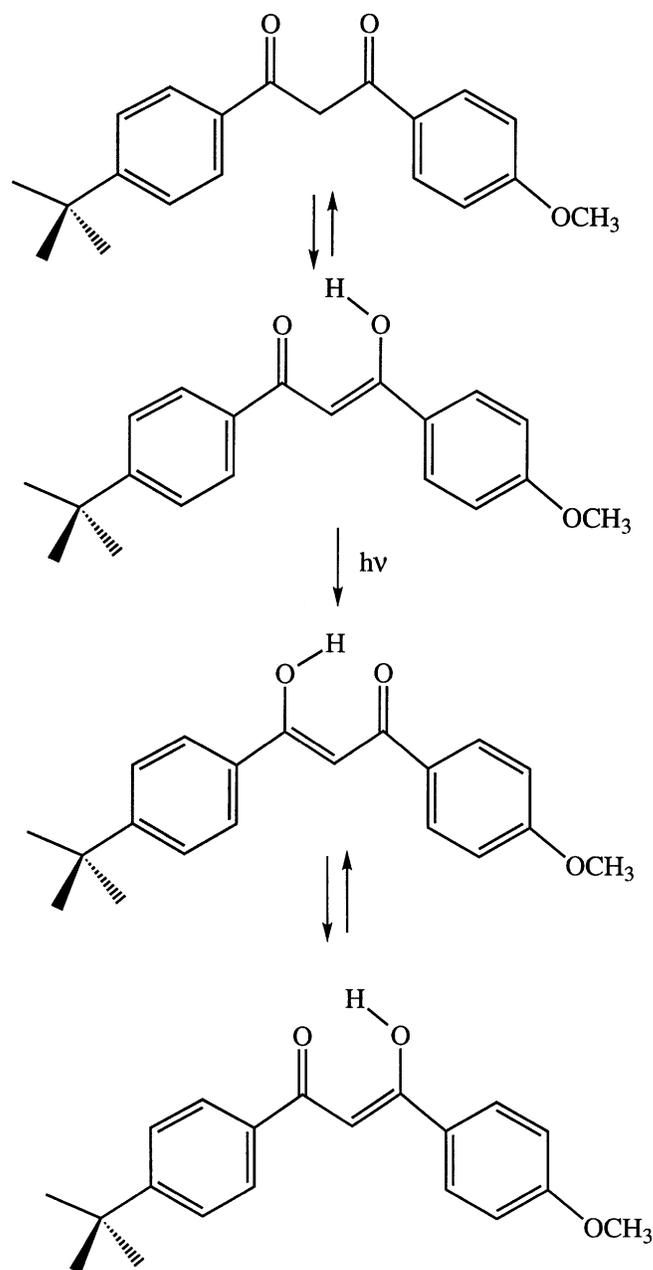


Figure 10. Absorption spectra of 4-isopropyl-dibenzoylmethane (Eusolex 8020). The spectra are before (straight line) and after irradiation with 20 MED of UVB (dashed line) followed by irradiation with 100 J per cm² of UVA (dotted line).

that only provide protection against UVB it has been argued that there is a risk of the erythema being blocked out leading to high exposure to UVA. If the action spectrum for the induction of



Scheme 4. Photoreaction of 4-tert-butyl-4'-methoxydibenzoylmethane.

malignant melanoma is shifted towards the UVA compared with the action spectrum for squamous cell carcinomas, the risk of melanoma development can actually be enhanced. With a sunscreen protecting only against UVB there is a risk that the population would be exposed to high amounts of UVA seldom contracted otherwise. Normally, the erythema threshold for UVB would be the limiting factor. It has been argued that the 'warning signal' is blocked out.

Accordingly, sunscreens with a better UVA-protective capacity have been recommended. There is, however, reason to believe that the absorption spectra of some sunscreens change upon irradiation with UV radiation. This has been demonstrated for octyl methoxycinnamate and butyl methoxydibenzoylmethane.^{1,2} If the absorption decreases while the shape of the absorption curve remains the same, there will be an increase in the amount of UV radiation, but of the same spectrum, reaching the basal epidermal cell layers. If the shape of the absorption spectrum also changes, however, the situation becomes more complicated. This can lead

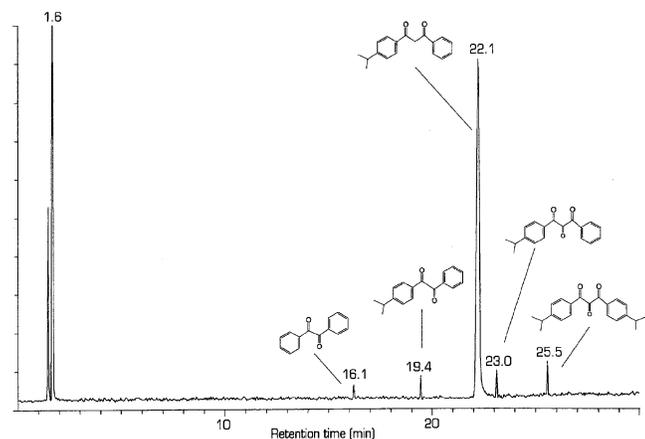


Figure 11. Gas chromatogram of 4-isopropyl-dibenzoylmethane. The chromatogram is taken after irradiation with 100 J per cm² of UVA. The peaks at 16.1, 19.4, 23.0, and 25.5 min correspond tentatively to benzil, isopropylbenzil, 1-phenyl-3-(4-*iso*-propylphenyl)-propane-1,2,3-trione and 1,3-di(4-*iso*-propylphenyl)-propane-1,2,3-trione, respectively, and arise after irradiation. Also seen is the original molecule (22.1 min).

to a higher UVA exposure than expected. In this study we found that both the degree of UV absorption and the shape of the spectrum change for some substances.

It is clear that most of the protective compounds decompose when exposed to UVA and UVB radiation, although the camphor derivative (compound 2) is relatively stable. The light/energy converting photoreactions differ for the different compounds. Reversible *cis-trans* photoisomerization occurs in the cinnamate and the camphor derivative (compounds 1 and 2). Intermolecular hydrogen transfer is the preferred excited state reaction in the benzophenones (compounds 4 and 5) as well as in the dibenzoylmethanes (compounds 6 and 7). In 2-ethylhexyl 4-dimethylaminobenzoate (compound 3) the excited state is a highly polar one.

What are the competing photoreactions that lead to decomposition? Earlier studies on the photo-decomposition of sunscreen agents in solution have shown that dibenzoylmethanes decompose into complex mixtures, whereas benzophenones are rather photostable (Roscher *et al*, 1994; Schwack and Rudolph, 1995). The main decomposition route of *N,N*-dimethylaminobenzoate involves the loss of a *N*-methyl group. Photo-oxidation has been proposed to be a major photodegradation route for dibenzoylmethanes (Roscher *et al*, 1994). Photodimerization of dibenzoylmethanes has been observed by Dubois *et al* (1998).

Our preliminary results on the photodegradation of 2-ethylhexyl 4-dimethylaminobenzoate, compound 3, by mass spectrometry analysis of the photoproducts, show that an oxidation of the amine part and then the loss of the carbonyl is a major photodegradation route. 2-Ethylhexyl esters of 4-methyl-aminobenzoate and 4-(formylmethylamino)benzoate are formed. This would, however, not alter the absorption spectrum of the sunscreen significantly.

All the sunscreens are carbonyl compounds which usually undergo efficient intersystem crossing in the excited state to form triplets. The triplets have enough energy to act as sensitizers towards normal air, if present, and to produce singlet oxygen. Singlet oxygen can then attack the sunscreen dye or any other compound present in the sunscreen mixture (Turro, 1978). When the sunscreen

is applied to the skin, the secondary photoreactions induced by the sunscreen dye can be rather complex.

The photodegradation of sunscreens is solvent dependent. The keto-enol equilibria in dibenzoylmethanes and the hydrogen-bonding schemes, as well as the conformation under realistic conditions, are important for the photostability of common sunscreens and must be further investigated.

The dibenzoylmethanes lose much of their UV-protective capacity after UV irradiation. Upon irradiation they seem to form new products with distinct UV absorption at shorter wavelengths.

Concerning the dibenzoylmethane derivative (Fig 9) there seems to be a concentration-dependent decrease in absorption in the UVA region, whereas the absorption in the UVC region increases. The latter is of minor importance, as natural sunlight does not contain wavelengths below 290 nm. Also, the decrease in absorption occurs already at rather low UVA doses. UVB alone does not seem to change the absorption spectrum significantly. It is worrying that the UVA-absorbing capacity decreases and that this substance does not afford the kind of protection, which could be expected from the initial absorption curve. As the sun protection factor is a measure of the protection against erythema, mainly caused by UVB, the sun protection factor of this substance does not necessarily change as much as the absorption capacity in the UVA region. Consequently, when this substance is used, much higher levels of UVA reach the basal cell layers of the epidermis than one would expect from the initial absorbance spectrum.

The UVA dose used in this study is comparable with those encountered during a full day in natural sunlight in the summer in southern Sweden. It is also evident that even a small decrease in the UVA absorption capacity leads to a substantial increase in the amount of UVA reaching the basal layers of the skin, due to the high flux of UVA in natural sunlight.

It has been argued lately that the action spectrum for the induction of malignant melanoma lies more in the UVA region (Setlow *et al*, 1993). This means that 4-*tert*-butyl-4'-methoxy-dibenzoylmethane (compound 6) may give a false impression regarding its melanoma-protective capacity.

In conclusion, we have shown that the UV absorption spectra of sunscreen agents following UVA irradiation are changed in many instances. The absorption is generally decreased and the shape of the absorption spectrum is also altered in some cases. It is important to take this into consideration when recommending a specific sunscreen. Generally, we only have data on the initial absorption. As some of the substances are not stable, the resulting protection spectrum can be something entirely different.

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REFERENCES

- Armstrong BK, Kricger A, English DR: Sun exposure and skin cancer. *Australasian J Dermatol* 58 (Suppl.):S1-S6, 1997
- Bech-Thomsen N, Wulf HC: Sunbathers' application of sunscreen is probably inadequate to obtain the sun protection factor assigned to the preparation. *Photodermatol Photoimmunol Photomed* 9:242-244, 1992
- Calvert JG, Pitts JN Jr: *Photochemistry*. New York: Wiley, 1967, p. 534
- Cancer Incidence in Sweden: National Board of Health and Welfare. Stockholm: The Cancer Registry, 1991
- Dubois M, Gilard P, Tiercet P, Defendre A, Lefebvre MA: Photoisomerisation of the sunscreen filter PARSOL® 1789. *J Chim Phys* 95:388-394, 1998
- Dunlap WC, Yamamoto Y, Inoue M, Kashiba-Iwatsuki M, Yamaguchi M, Tomita K: Uric acid photo-oxidation assay: *in vitro* comparison of suncreening agents. *Int J Cosmet Sci* 20:1-18, 1998
- Futamura S, Kamiya Y: Sensitized photooxidation reactions of compounds having activated methylenes. *Stud Org Chem* 33:85-90, 1988
- Kammeyer A, Westerhof W, Bolhuis PA, Ris AJ, Hische EA: The spectrum stability of several suncreening agents on stratum corneum sheets. *Int J Cosmet Sci* 9:125-136, 1987
- Kivisäkk E, Wester U, Larkö O: Testing of the sunscreens on the Swedish market. Report 94-20. Swedish Radiation Protection Institute, Stockholm, 1994

¹Seim J, Christensen T, Johnsen B, Hannevik M: Decomposition of sunscreens by ultraviolet radiation. 6th Congress of the European Society for Photobiology, 1995, p. 69 (abstr.)

²Diffey BL, Stokes RP, Forestier S, Mazilier C, Rougier A: Sunscreen product photostability: A key parameter for a more realistic *in vitro* efficacy evaluation. *Australas J Dermatol* 38 (Suppl. 2): 63-64, 1997 (abstr.)

- Roscher NM, Lindemann MKO, Kong SB, Cho CG, Jiang P: Photodecomposition of several compounds commonly used as sunscreen agents. *J Photochem Photobiol A* 80:417-421, 1994
- Saino EL: The ingredients, safety, efficacy and stability of sunscreens. Helsinki: National Consumers Administration, Publishers Series 16/1995, 1995
- Schwack W, Rudolph T: Photochemistry of dibenzoyl methane UVA filters. *J Photochem Photobiol B* 28:229-234, 1995
- Setlow RB, Grist E, Thompson K, Woodhead AD: Wavelengths effective in induction of malignant melanoma. *Proc Natl Acad Sci USA* 90:6666-6670, 1993
- Stenberg C, Larkö O: Sunscreen application and its importance for the sun protection factor. *Arch Dermatol* 121:1400-1402, 1985
- Thompson SC, Jolley D, Marks R: Reduction of solar keratoses by regular sunscreen use. *N Engl J Med* 329:1147-1151, 1993
- Turro NJ: *Modern Molecular Photochemistry*. Menlo Park, CA: Benjamin/Cummings, 1978, p 187
- Urbach F: Ultraviolet radiation and skin cancer of humans. *J Photochem Photobiol B* 40:3-7, 1997
- Westerdahl J, Olsson H, Måsbäck A, Ingvar C, Jonsson N: Is the use of sunscreens a risk factor for malignant melanoma? *Melanoma Res* 5:59-65, 1995