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# Determination of photodegradation of UV filters in sunscreens by HPLC/DAD and HPLC/MS

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## Introduction

Sun protection cosmetics are intended to protect us from hazardous UVB and UVA radiation which can provoke skin cancer and premature skin ageing. UV filters must not only absorb irradiation energy, but also release this energy as heat before they decay or react with molecules in their vicinity. Especially older filters need to be used in combination with other sunscreen filters to improve their photostability.

Review of literature shows, that photostability of UV filters is often tested on pure filters or combinations of them in solution (1–7, 12, 13). Only few studies analyzed UV filter stability in ready-to-use cosmetic formulations (8–10). Benzylidene camphor filters are known to undergo E/Z isomerisation in irradiated solutions, but no degradation was observed (2). The same is reported for cinnamates (4). Diluted solutions of five UV-filters were irradiated and the remaining content analyzed by HPLC/DAD (3). Stability decreased in the following order: benzophenone-3 (B3) > butylmethoxy dibenzoylmethane (BMDBM) > octyl dimethyl PABA > PEG-25 PABA > methyl benzylidene camphor (MBC). The stability of some filters can be improved by combining them with others as is shown for BMDBM (1). An *in vivo* study with one sunscreen confirmed *in vitro* results that EHMC is not photostable (8). Another study measured the change of ultraviolet absorbance of 16 sunscreens under solar-simulated radiation by means of UV spectroscopy (11). Seven of the samples had a reduced UVA absorption. The out-dated filter para amino benzoic acid (PABA) is known for a long time to degrade when irradiated. A survey of the photochemical behavior of this compound can be found in (12).

These photodegradation data consequently raise the question about photoreaction products. Only few papers however deal with this issue. Photodimerisation of cinnamate UV filters in solution was reported for EHMC (6) and for IMC (7). EHMC produces a photoadduct with the DNA component thymidine-5'-monophosphate (14). PABA photosensitises thymine dimerisation in DNA (15). Photolysis products of dibenzoyl methane filters were identified in two irradiated suntan lotions (9). The

most comprehensive study so far dealt with the photochemical behavior of EHMC, BMDBM and MBC in solution and in a few sunscreens (10). EHMC was degraded up to 80% and BMDBM up to 100% after five hours of sunlight exposure. Several photochemical reaction products, mainly cycloaddition adducts, have been observed and identified. They accounted for about 30% of the degraded filter substances. 70% of the degradation products of the filters EHMC and BMDBM remained unidentified. In vivo testing revealed even higher degradation rates for MBC and EHMC compared to in vitro testing (irradiation time: 30 minutes) (10).

Photostable sunscreens are a prerequisite for reliable sun protection. Degradation of UV filters would not only lead to insufficient protection from UV radiation (11), but may also expose consumers to potentially toxic degradation products, e.g. free radicals. Up to this date no comprehensive work on the photostability of all approved organic UV filters (over 20) exists. Data concerning their fate in sunscreens is also scarce. Published analytical methods either lack separation power (2, 3, 8) or are rather tedious (10) compared to our HPLC/DAD method (16) which separates 21 organic UV filters in 35 minutes.

In this study we tested a representative range of samples which covered all currently used filters with our HPLC/DAD method (16) and a newly developed HPLC/DAD/MS method.

## Experimental

### *Materials and instruments*

Analytical balance (AT 200, Mettler Toledo, Greifensee), thermostated ultrasonic bath (Branson 3510, Merck, Zürich), centrifuge (Heräus Biofuge Primo, BGB, Anwil), cooling plate (LKB Multiphor II Electrophoresis Unit, Pharmacia, Dübendorf), UV lamp (Osram Ultra Vitalux 300 W)

Quaternary gradient HPLC/MS system consisting of a low pressure mixing quaternary gradient pump (Surveyor MS Pump), an autosampler (Surveyor AS), a photo diode array detector (UV 6000LP fitted with 10 µl 50 mm flowcell), a MS detector (Thermo Finnigan LCQ Duo) and a data station (Excalibur), all from Spectronex, Birsfelden.

Quaternary gradient HPLC/DAD system consisting of a low pressure mixing quaternary gradient pump (Thermo Finnigan P4000), an autosampler (Thermo Finnigan AS3000), a photo diode array detector (UV 6000LP fitted with 2 µl 10 mm flowcell) and a data station (ChromQuest), all from Thermo Finnigan, Allschwil.

Analytical column for LC/DAD/MS: XTerra MS C18, 3 µm, 100×2.1 mm (Waters, Rapperswil).

Analytical column for LC/DAD: Kromasil C18, 3.5 µm, 125×3 mm (Macherey-Nagel, Oensingen), precolumn: Kromasil C18, 3.5 µm, 8×3 mm (Macherey-Nagel, Oensingen).

Nylon syringe filters for HPLC, 13 mm diameter, 0.45 µm pore size (Titan Filtration Systems, Schmidlin, Neuheim).

## Chemicals

Acetic acid p.a. (Merck), acetonitrile gradient grade for HPLC (Merck), methanol gradient grade for HPLC (SDS), methanol for LC/MS (RdH), tetrahydrofuran (THF) for HPLC (Merck), demineralised water for HPLC (J.T. Baker), methanol p.a. (Merck), acetone p.a. (Merck), ammonium acetate p.a. (Merck).

Table 1  
Reference substances

<i>Abr.</i>	<i>INCI Name</i>	<i>EC Nr.<sup>1)</sup></i>	<i>Producer</i>	<i>Molecular weight</i>
BP3	Benzophenone-3	1.4	Fluka	228
PBSA	Phenylbenzimidazole sulfonic acid	1.6	Aldrich	274
TDSA	Terephthalylidene dicamphor sulfonic acid	1.7	Chimex	562
BMDBM	Butyl methoxydibenzoylmethane	1.8	Merck	310
OC	Octocrylene	1.10	Aldrich	361
EHMC	Ethylhexyl methoxycinnamate	1.12	Merck	290
IMC	Isoamyl methoxycinnamate	1.14	H & R	248
OT	Octyl triazone	1.15	BASF	822
DTS	Drometrizole trisiloxane	1.16	Chimex	501
DEBT	Diethylhexyllbutamidotriazone	1.17	Sigma 3V	765
MBC	Methyl benzylidene camphor	1.18	Merck	254
EHS	Ethylhexyl salicylate	1.20	Aldrich	250
MBBT	Methylene bis-benzotriazolyl tetramethylbutylphenol	1.23	CIBA	659
BEMT	Bis ethylhexyloxyphenol methoxyphenyl triazine	1.25	CIBA	627

<sup>1)</sup>Classification according to the European Cosmetic Directive 76/768/EC Annex VII part 1 and 2

The composition of the tested sunscreens is given in table 2.

## Procedures

### *Irradiation experiments and sample preparation*

Approximately 500 mg of sample were spreaded as evenly as possible on a 10 cm I.D. petri dish (resulting in a layer of approximately 6 to 7 mg sample/cm<sup>2</sup>).

UV lamp assay: An UV lamp was placed 50 cm above the dishes and irradiation experiments were performed for 30 minutes (which corresponds to the maximum recommended exposure time for humans).

Daylight assay: The plates were exposed to sunlight on a lattice at an angle of approximately 45°. One experiment was conducted with temperature control at

**Table 2**  
**Composition of the analyzed products**

<i>Sample</i>	<i>Type</i>	<i>SPF</i>	<i>Analysis results of organic sunscreen filters</i>						
1	Day Cream	+	3.0% EHMC						
2	Sun Gel Lotion	12	5.1% EHMC	2.1% MBC	2.0% OT	1.3% BMDBM			
3	Sun Cream Gel	20	5.3% EHMC	3.9% MBC	1.4% BMDBM	1.7% OT	1.7% PBSA	0.5% OC	
4	Sun Milk	30	5.5% EHMC	3.1% MBC	3.2% EHS	3.1% MBBT	1.3% BMDBM	0.5% OC	
5	Sun Milk Baby	30	3.1% EHMC	3.0% MBC	2.1% PBSA	2.1% IMC	1.2% BMDBM		
6	Sun Cream	15	3.0% IMC	3.1% MBC					
7	Anti ageing Face Cream	20+	5.7% EHMC	5.6% OC	2.0% DEBT	2.0% BEMT			
8	Sun Cream Sensitive	60	10.0% OC	2.7% DTS	1.7% TDSA	1.1% BMDBM			
9	Sun Lotion	16	7.6% EHMC	5.1% B3	3.0% EHS				
10	Sun Lotion	35	4.0% MBC	2.7% OT	1.7% BMDBM				

SPF: Sun protection factor

40°C by placing petri dishes on a cooling plate. The cooling plate was held at an angle of 45°.

The irradiated sample was transferred to a 200 ml measuring flask by repeatedly rinsing with several milliliters of acetone/THF. The flask was filled up to the mark with acetone/THF=1/1 (v/v) and then put into an ultrasonic bath for 15 minutes, followed by 5 minutes stirring at 60°C in a waterbath.

## Methods

### LC/DAD/MS parameters

LC/DAD/MS analysis was performed with the two gradient elution programs described in tables 3 and 4. Column temperature was 30°C, the injection volume 1 ml. UV spectra were recorded between 220 and 400 nm with a resolution and a bandwidth of 1.2 nm and a sampling rate of 1 Hz. Discrete channels were recorded at 300 and 350 nm with a bandwidth of 5 nm and a sampling rate of 5 Hz.

**Table 3**  
**LC/MS gradient time table**

<i>Time (min)</i>	<i>Flow (µl/min)</i>	<i>0.1 % HCOOH in water</i>	<i>0.1 % HCOOH in acetonitrile</i>
0	300	90%	10%
2	300	90%	10%
3	300	40%	60%
18	300	0%	100%
18.1	600	0%	100%
26	600	0%	100%
26.1	300	90%	10%
31.1	300	90%	10%

**Table 4**  
**LC/MS gradient time table for cycloaddition adducts**

<i>Time (min)</i>	<i>Flow (µl/min)</i>	<i>0.05 % HCOOH in water</i>	<i>0.05 % HCOOH in methanol</i>	<i>0.05 % HCOOH in acetonitrile</i>
0	400	30	25	45
3	400	25	30	45
10	400	25	55	20
10.9	400	25	55	20
16	400	0	55	45
24	400	0	55	45
24.1	400	30	25	45
28	400	30	25	45

Mass spectra were recorded between 100 and 1000 m/z in the APCI positive mode. The heated capillary temperature was set at 155°C and the APCI vaporizer temperature at 300°C. The nitrogen sheath gas flow rate was set at 41 and the auxiliary gas flow rate at 17 arbitrary units. The capillary voltage was 35 V and the spray voltage 5 kV.

## LC/DAD parameters

LC/DAD was performed as described in (16). However, instead of a 4 mm column, a 3 mm I.D. column was used. Flow rate was therefore reduced by 40%.

## Results and discussion

### Sample preparation

Under the presented irradiation conditions several filters, such as PBSA (5, 12), OC (12), EHS or OT, proved to be photostable and were, therefore, used as points of reference. Three irradiation assays (UV lamp) of two samples showed a relative standard deviation of about 2% for MBC, about 5% for IMC, about 3% for BMDBM and about 5% for EHMC. Day to day variations of sun-irradiated samples are higher because of varying weather conditions. Some experiments were carried out under temperature control at 40°C in order to discern effects caused by irradiation from those caused by heat. No heat effect was observed.

### Chromatography and detection

HPLC/DAD was used to determine the photostability of the UV filters and the generation of photoisomerisation products. The only problem encountered with our HPLC/DAD method (16) was coelution of an IMC degradation product (Z-IMC) with a byproduct of BMDBM.

LC/MS was used to detect reaction products with poor UV chromophores and to obtain information on their molecular weight and structure. MS conditions were optimized for cinnamates and MBC, for which high degradation rates were observed by HPLC/DAD. Salicylates were not detectable with this method. The sulfonic acids TDSA and PBSA gave only poor signals with the present method. The vaporisation temperature of 300°C is far below the optimum for the high molecular weight filters DTS, BEMT, MBBT, OT and DEHT, but signal intensities were still acceptable. An overview chromatogram of a reference solution is shown in figure 1.

### UV Irradiation experiments

Eight products with different UV filters (table 2) were tested with a UV lamp as described. A HPLC/DAD chromatogram of an irradiated sample versus the original product is shown in fig. 2.

Table 5 shows that decomposition rates depend on the combination of UV filters used in the specific product. EHMC degradation rates varied by a factor of 30 depending on the sample. Furthermore products containing only IMC, EHMC, MBC or BMDBM alone or in combination (samples 1, 5 and 6) generally have high decomposition rates. In samples containing MBC in combination with EHMC and/or IMC, those with the highest degradation of EHMC and IMC also have the highest degradation of MBC. Our data clearly show that stabilization of UV filters can be achieved with an adequate formulation.

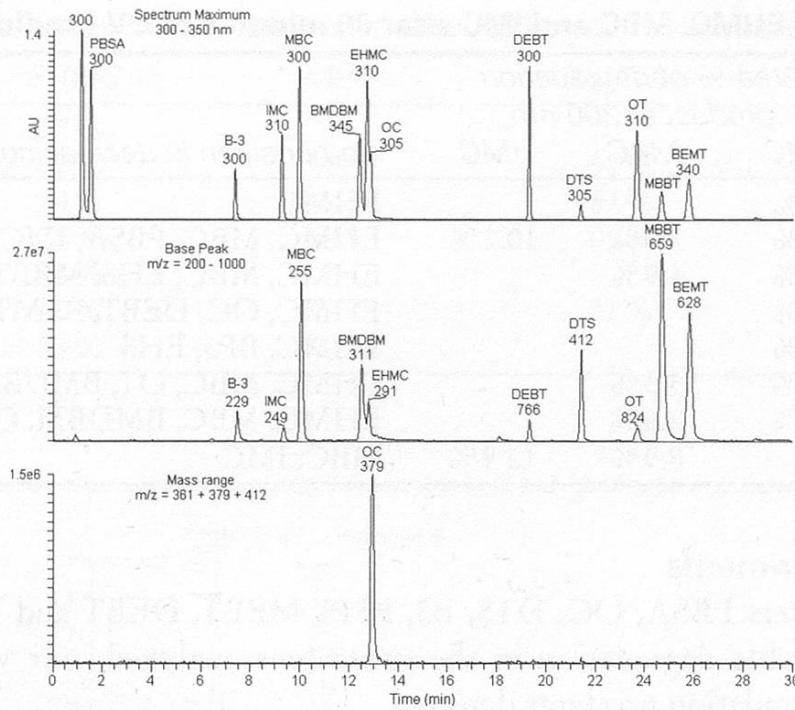


Figure 1 **HPLC/DAD/MS screening chromatogram of a reference solution.** LC conditions as described in table 3. LC/DAD notation: spectrum maximum (nm); LC/MS notation: m/z of most intense ion (base peak).

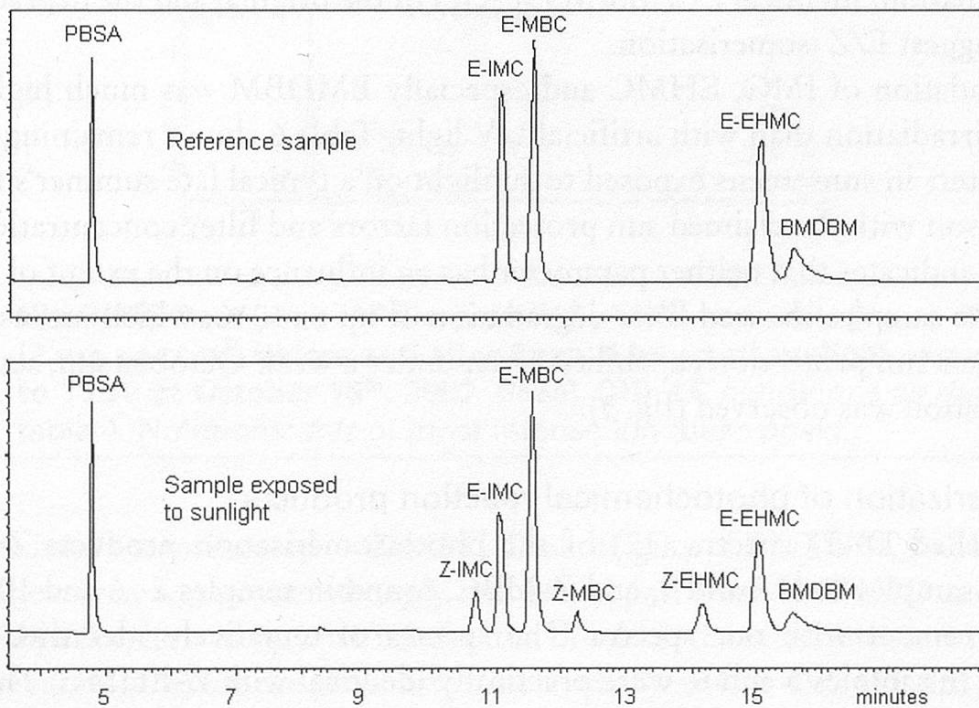


Figure 2 **HPLC/DAD chromatograms of sample 5 before and after 2.5 hours of sunlight exposure (10:00 am to 0:30 pm at August 26<sup>th</sup>, 2003).** LC conditions according to (16).

Table 5

**Degradation of EHMC, MBC and IMC after 30 minutes of UV irradiation**

Sample	Area-% of degradation product at 300 nm			Composition in decreasing order
	EHMC	MBC	IMC	
1	15.0%			EHMC
5	8.1%	7.0%	10.2%	EHMC, MBC, PBSA, IMC, BMDDBM
4	4.8%	4.9%		EHMC, MBC, EHS, MBBT, BMDDBM, OC
7	3.3%			EHMC, OC, DEBT, BEMT
9	2.5%			EHMC, BP3, EHS
2	1.1%	3.3%		EHMC, MBC, OT, BMDDBM
3	0.5%	2.6%		EHMC, MBC, BMDDBM, OT, PBSA, OC
6		8.9%	12.9%	MBC, IMC

**Daylight experiments**

The UV filters PBSA, OC, DTS, B3, EHS, MBBT, DEBT and BEMT showed neither measurable degradation in the sunscreens analyzed, nor were additional peaks from degradation products detected.

For MBC and TDSA, degradation after sunlight exposure was about as high as after artificial UV irradiation. TDSA as a camphor derivative, although described as photostable (17), is expected to show E/Z isomerisation upon irradiation, as seen with MBC or described for benzylidene camphor and benzylidene camphor methosulfate (2). DAD and MS data revealed one additional peak with higher intensity after irradiation. Identical LC/MS/MS spectra of the original and the degraded compound suggest E/Z isomerisation.

Degradation of IMC, EHMC and especially BMDDBM was much higher upon sunlight irradiation than with artificial UV light. Table 6 shows remaining contents of UV filters in sunscreens exposed to sunlight on a typical late summer's morning. Comparison with the claimed sun protection factors and filter concentrations listed in table 2 indicates that neither parameter has an influence on the extent of degradation. Some samples showed filter degradation of up to 40%, which means a partial loss of their sun protection capability. Even under a weak October sun, severe photodegradation was observed (fig. 3).

**Characterization of photochemical reaction products**

Published DAD spectra (12) of the photoisomerisation products Z-EHMC, found in samples 1–5, 7 and 9, and Z-MBC, found in samples 2–6 and 10, were in good agreement with our spectra. The spectra of tentatively identified Z-IMC, observed in samples 5 and 6, were practically identical with Z-EHMC. These findings were confirmed by mass spectrometry. Using LC/MS, additional photodegradation products were found in sunscreens. Figure 3 shows the base peak chromatogram of a sample before and after exposure to two and four hours of daylight in October. While PBSA proved to be stable under these conditions, small amounts

Table 6

**Remaining content of sunscreen filters after 2.5 hours of exposure to sunlight**

Sample	<i>EHMC</i>	<i>MBC</i>	<i>BMDBM</i>	<i>IMC</i>
1	57 %			
5	62 %	96 %	58 %	61 %
4	73 %	96 %	82 %	
3	78 %	94 %	65 %	
7	78 %			
2	80 %	97 %	71 %	
9	83 %	103 %		

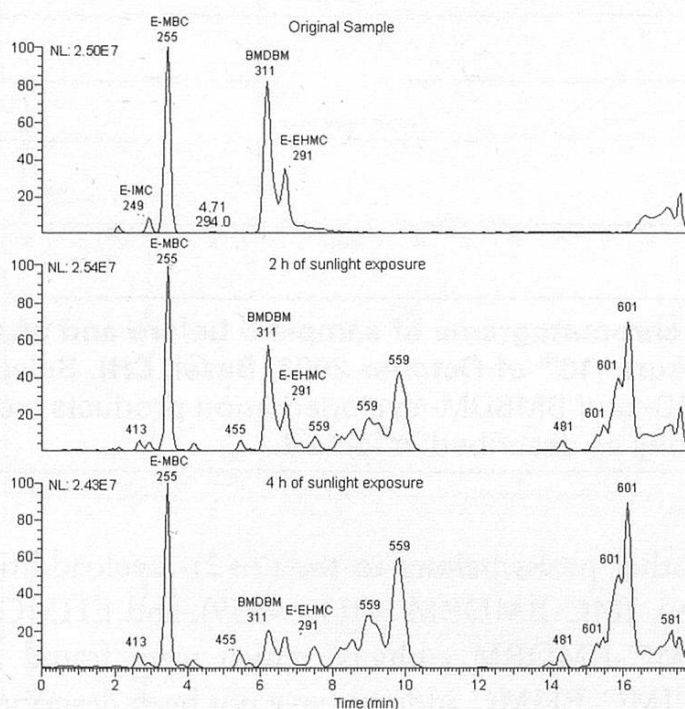
Layers of 7 mg sample/cm<sup>2</sup>

Figure 3 **HPLC/MS Base peak (APCI+,  $m/z$ : 200–1000) chromatograms of sample 5 (2 mg per cm<sup>2</sup>) before and after 2 resp. 4 hours of sunlight exposure (9:30 to 13:30 at October 16<sup>th</sup>, 2003, Basel, CH). LC conditions as described in table 4. Notations:  $m/z$  of most intense ion (base peak).**

of E-MBC were transformed to Z-MBC. Peak heights of BMDBM, E-EHMC and E-IMC, however, were more strongly reduced. Apart from Z-EHMC and Z-IMC, additional peaks showed up after irradiation, of which the most intense with a mass-to-charge ratio ( $m/z$ ) for the protonated molecule were 413, 439, 455, 481, 497, 539, 559, 581 and 601. For  $m/z=497$  to 601 multiple peaks are observed (fig. 4). Some of these might represent IMC-IMC dimers ( $MH^+=497$ ) and EHMC-EHMC dimers ( $MH^+=581$ ), which were already detected in irradiated solutions of the pure substances (6, 10). Several EHMC-EHMC dimers were also detected in sunscreens

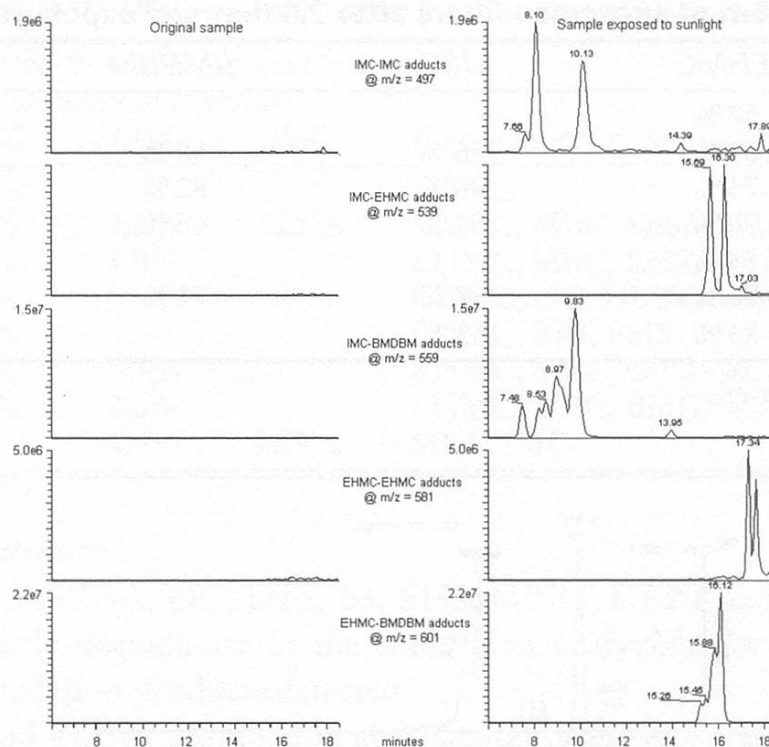


Figure 4 HPLC/MS chromatograms of sample 5 before and after 4 hours of sunlight exposure (16<sup>th</sup> of October 2003, Basel, CH). Selected ion traces for EHMC-, IMC- and BMDDBM- cycloaddition products (see text for details). LC conditions as described in table 4.

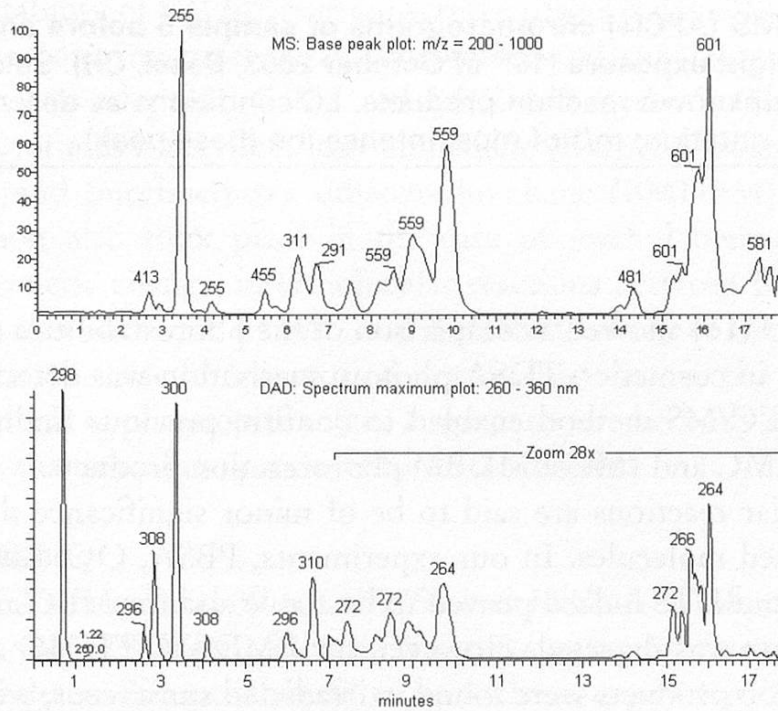
(10). Three of the other peaks belong to the (2+2)- cycloaddition adducts IMC-EHMC ( $MH^+=539$ ), IMC-BMDBM ( $MH^+=559$ ), and EHMC-BMDBM ( $MH^+=601$ ). Unlike EHMC-BMDBM adducts, which were found in cosmetics (10), IMC-BMDBM and IMC-EHMC adducts have not been described so far.

Table 7 shows that the described reaction products are found in all products containing these filters. Thus, none of the sunscreens analysed proved to be stable. For further verification, solutions containing different combinations of IMC, EHMC and BMDDBM were exposed to sunlight. The reaction products found were the same as in the sunscreen samples and confirmed that excited molecules of EHMC, IMC and BMDDBM have a long enough lifespan to react with suitable molecules in their vicinity. The above mentioned peaks were also detectable with HPLC/UV, but their UV maxima were all below 280 nm (fig. 5). This means that they lost their capability to absorb UVB or even UVA rays.

We have no explanation for the peaks with  $MH^+$  of 413, 439, 455 and 481 (fig. 6). Data of three samples with different combinations of IMC, EHMC and BMDDBM showed that the masses ( $MH^+$ ) of 413 and 439 probably belong to reaction products of IMC with BMDDBM and the masses of 455 and 481 to reaction products of EHMC with BMDDBM.

**Table 7**  
**Intermolecular reaction products**

Sample	Sunscreen filters contained	masses (MH <sup>+</sup> ) found				
		m/z 497	m/z 539	m/z 559	m/z 581	m/z 601
1	EHMC	-	-	-	+	-
2	EHMC, BMDBM	-	-	-	+	+
3	EHMC, BMDBM	-	-	-	+	+
4	EHMC, BMDBM	-	-	-	+	+
5	EHMC, BMDBM, IMC	+	+	+	+	+
6	IMC	+	-	-	-	-
7	EHMC	-	-	-	+	-
8	BMDBM	-	-	-	-	-
9	EHMC	-	-	-	+	-



**Figure 5 Comparison of HPLC/DAD with HPLC/MS of sample 5 after 4 hours of sunlight exposure (16<sup>th</sup> of October 2003, Basel, CH). LC conditions as described in table 4. LC/DAD notation: spectrum maximum (nm); LC/MS notation: m/z of most intense ion (base peak).**

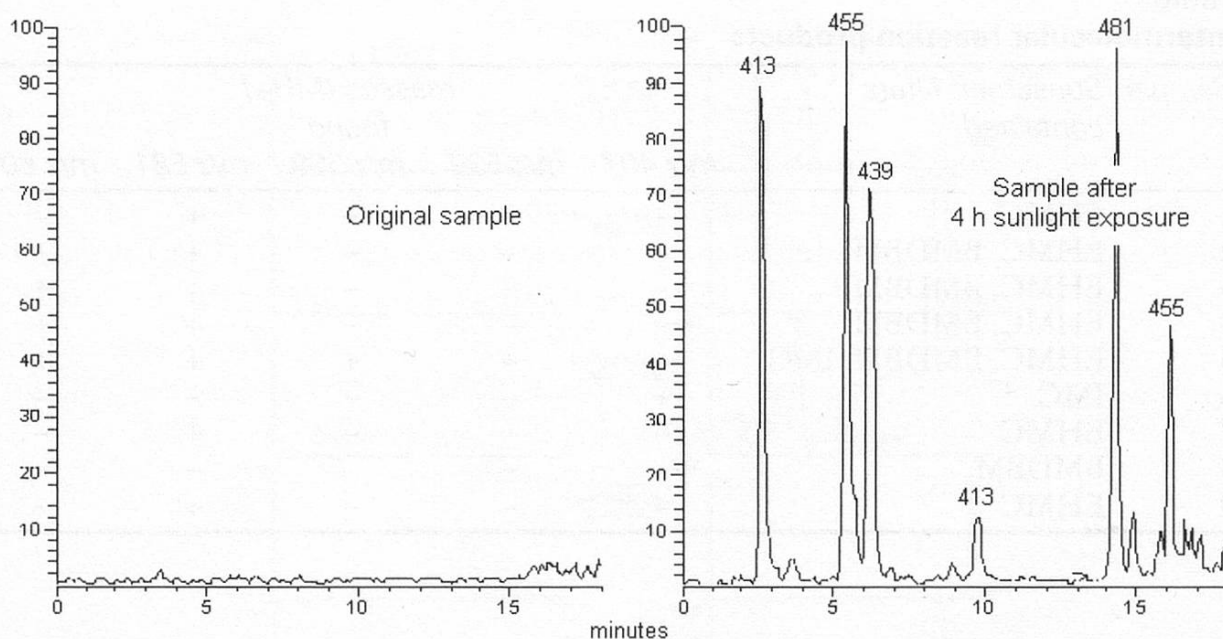


Figure 6 HPLC/MS (APCI+) chromatograms of sample 5 before and after 4 hours of sunlight exposure (16<sup>th</sup> of October 2003, Basel, CH). Selected ion traces of yet unknown reaction products. LC conditions as described in table 4. LC/MS notation: m/z of most intense ion (base peak).

### Conclusions

HPLC/DAD (16) allowed a comparison of the photostabilities of all UV filters currently found in cosmetics. TDSA photoisomerisation was detected for the first time. The new LC/MS method enabled to confirm previous findings (10) and to detect IMC-EHMC and IMC-BMDBM photoreaction products.

Intermolecular reactions are said to be of minor significance due to the short lifespan of excited molecules. In our experiments, PBSA, OC, EHS, OT, BEMT, DEBT, MBBT and DTS indeed proved to be stable and for MBC and TDSA, only E/Z isomerisation was detected. However, for BMDBM, EHMC and IMC intermolecular reaction products were found in irradiated sunscreens, which is in agreement with previous findings (10). Cinnamates and BMDBM seem to react easily with unsaturated molecules in their vicinity, such as squalene, unsaturated fatty acids or DNA bases on our skin. In fact, degradation of EHMC and MBC on skin is higher than on glass plates (10).

Sunscreens are applied as “stay on” products on large parts of the human body. Their contents of organic UV filters can reach a maximum of 25%. If used as recommended (1–2 mg/cm<sup>2</sup>), several grams of sunscreens are applied with one application. Taking into account that BMDBM, IMC and EHMC degraded up to 40% under irradiation (up to 100% in (10)), hereby forming reactive radicals, isomers

and adducts which may (11) or may not (8) penetrate human skin, toxicological aspects certainly need deeper consideration.

EHMC and BMDBM belong to the most often used UV filters (16). According to our market survey on sun protection products in 2001, EHMC and BMDBM were found in about 80% of the sunscreens. EHMC is also frequently used in concentrations up to 5% in other cosmetics, such as day creams, antiageing products and lip sticks. Even higher degradation rates must be expected here, because EHMC is not used in combination with other filters, and photostability of the product may not be of first concern to the producer. In fact a day cream showed the lowest photostability of all products analyzed (sample 1, table 6). Apart from toxicological concerns, the instability of BMDBM, which is often the only UVA filter used in a sunscreen, compromises the important UVA protection.

Given the wide range of approved UV filters of higher photostability, substitution of BMDBM, IMC and EHMC should be considered.

## Summary

The photostability of UV filters in sunscreens towards daylight was investigated in ten products covering most of the currently used sunscreen filters, applying newly developed or adapted LC/MS and LC/DAD methods. The study showed that up to 40% of ethyl-hexylmethoxy cinnamate (EHMC), isoamylmethoxy cinnamate (IMC) and butylmethoxy dibenzoylmethane (BMDBM) were degraded. Photodegradation also took place in the case of methyl benzylidene camphor. Besides E/Z isomeric change, intermolecular reactions between EHMC, IMC and BMDBM were also observed. EHMC and BMDBM belong to the most often used sunscreen filters. As these filters are used in concentrations in the percent range in cosmetics and their application involves large parts of the body's surface, further toxicological evaluation of the products formed is needed.

## Zusammenfassung

Mit zum Teil neu entwickelten LC/MS- und LC/DAD- Methoden wurde die Photostabilität von UV-Filtern in zehn Sonnenschutzpräparaten, welche die am meisten verwendeten Sonnenschutzfilter enthielten, gegenüber Tageslicht untersucht. Die Untersuchungen wiesen einen Abbau von bis zu 40% der ursprünglich vorliegenden Filter Ethylhexylmethoxy Cinnamate (EHMC), Isoamylmethoxy Cinnamate (IMC) und Butylmethoxy Dibenzoylmethane (BMDBM) nach. Auch Methyl Benzylidene Camphor erwies sich als nicht photostabil. Neben E/Z-Isomerisierungen wurden auch intermolekulare Reaktionen zwischen EHMC, IMC und BMDBM beobachtet. Die Reaktionspartner EHMC und BMDBM gehören zu den häufigst verwendeten Sonnenschutzfiltern überhaupt. Da die betroffenen Filter im Prozentbereich in Kosmetika eingesetzt und grossflächig auf den Körper appliziert werden, sind Abklärungen bezüglich der Toxikologie der gebildeten Produkte unumgänglich.

## Résumé

La photostabilité à la lumière du jour des filtres UV utilisés dans des crèmes solaires a été étudiée à l'aide de méthodes nouvelles ou adaptées LC/MS et LC/DAD. Les études ont montré que éthylhexylméthoxy cinnamate (EHMC), isoamylméthoxycinnamate (IMC) et butylméthoxy dibenzoylméthane (BMDBM) atteignent un taux de dégradation jusqu'à 40%. Il s'est avéré que méthyl benzyldène camphre (MBC) n'est pas photostable non plus. A côté des isomérisations E/Z, des réactions intermoléculaires entre EHMC, IMC et BMDBM pouvaient être observées. EHMC et BMDBM appartiennent au groupe des filtres UV les plus souvent utilisés. Au vu des concentrations élevées (de l'ordre du pourcent) dans les cosmétiques et de l'application de ces produits sur une grande surface corporelle, une évaluation toxicologique des substances formées s'avèrent indispensables.

## Key words

Sunscreen Filters, Cosmetics, Photostability, LC/MS, Photoreactions

## References

- 1 Osterwalder, U., Luther H. und Herzog B.: Über den Lichtschuttfaktor hinaus – neue effiziente und photostabile UVA-Filter. Bundesgesundheitsbl. Gesundheitsforsch. Gesundheitsschutz, 5, 463–469 (2001)
- 2 Beck I., Deflandre A., Lang G., Arnaud R. and Lemaire J.: Study of the photochemical behaviour of sunscreens – benzylidene camphor and derivatives. Int. J. Cosmetic Sci., 1981, 139–152 (1981)
- 3 Vanquerp V., Rodriguez C., Coiffard C., Coiffard J.M., De Roeck-Holtzhauer Y.: High-performance liquid chromatographic method for the comparison of the photostability of five sunscreen agents. J. Chromatogr. A, 832, 273–277 (1999)
- 4 Morlière P., Avicet O., Melo T. SA. E., Dubertret L., Giraud M. and Santus R.: A study of the photochemical properties of some cinnamate sunscreens by steady state and laser flash photolysis. Photochem. Photobiol., 36, 395–399 (1982)
- 5 Berset G., Gonzenbach H., Christ R., Martin R., Deflandre A., Mascotto R.E., Jolley J.D.R., Lowell W., Pelzer R., and Stiehm T.: Proposed protocol for determination of photostability Part I: cosmetic UV filters. Int. J. Cosmet Sci., 18 (1996)
- 6 Broadbent J.K., Martincigh B.S., Raynor M.W., Salter L.F., Moulder R., Sjöberg P. and Markides K.E.: Capillary supercritical fluid chromatography combined with atmospheric pressure chemical ionisation mass spectrometry for the investigation of photoproduct formation in the sunscreen absorber 2-ethylhexyl-p-methoxycinnamate. J. Chromatogr. A, 732, 101–110 (1996)
- 7 Schrader A., Jakupovic J. and Baltes W.: Photochemical studies on trans-3-methylbutyl 4-methoxycinnamate. J. Soc. Cosmet. Chem., 45, 43–52 (1994)
- 8 Cambon M., Issachar N., Castelli D. and Robert C.: An in vivo method to assess the photostability of UV filters in a sunscreen. J. Cosmet. Sci., 52, 1–11 (2001)
- 9 Schwack W. and Rudolph T.: Photostabilität und Photoreaktionen von UV-Filtersubstanzen in Kosmetika. GIT Fachz. Lab., 4, 373–376 (1996)
- 10 Köhnlein M.: Untersuchungen zum photochemischen Verhalten des UV-B-Filters Octylmethoxycinnamat in Modellsystemen, Sonnenschutzmitteln sowie auf der Haut. Berichte aus der Chemie. Shaker Verlag, Aachen. 2000

- 11 *Maier H., Schaubberger G., Brunnhofer K. and Hönigsmann H.:* Change of ultraviolet absorbance of sunscreens by exposure to solar-simulated radiation. *J. Investigative. Dermatology*, **117**, 256–262 (2001)
- 12 *Parlar S.:* Untersuchungen zur photochemischen Stabilität mittels Durchflussreaktoren (hv-HPLC). Dissertation, Humboldt Universität, Pharmacy, Berlin (2000)
- 13 *Schwack W. and Rudolph T.:* Photochemistry of dibenzoyl methane UV filters Part I. *J. Photochem. Photobiol. B: Biol.*, **28**, 229–234 (1995)
- 14 *Martincigh B.S., Kowlaser K. and Raynor M.W.:* Photoproducts of 2-Ethylhexyl-para-Methoxycinnamate. 27<sup>th</sup> annual meeting of the american society for photobiology (1999), Washington
- 15 *Aliwell S.R., Martincigh B.S. and Salter L.F.:* Para aminobenzoic acid-photosensitized dimerization of thymine II. In pUC19 plasmid DNA. *J. Photochem. Photobiol. A: Chem.*, **71**, 147–153 (1993)
- 16 *Hauri U., Lütolf B. and Hohl Ch.:* Determination of organic sunscreen filters in cosmetics with HPLC/DAD. *Mitt. Lebensm. Hyg.*, **94**, 80–92 (2003)
- 17 *Osterwalder U. and Herzog B.:* New systems of broad-spectrum UV protection. *IFSCC Magazine*, **5** (3), 1–7 (2002)

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