

## Ultraviolet protective performance of photoprotective lipsticks: change of spectral transmittance because of ultraviolet exposure

H. Maier<sup>1</sup>, G. Schaubberger<sup>2</sup>, B. S. Martincigh<sup>3</sup>, K. Brunnhofer<sup>4</sup>, H. Hönigsmann<sup>1</sup>

<sup>1</sup>Division of Special and Environmental Dermatology, Medical University of Vienna, Vienna, Austria, <sup>2</sup>Institute of Medical Physics and Biostatistics, University of Veterinary Medicine Vienna, Vienna, Austria, <sup>3</sup>School of Pure and Applied Chemistry, University of KwaZulu-Natal, Howard College Campus, Durban, Republic of South Africa, and <sup>4</sup>Austrian Consumers' Association, Vienna, Austria

**Background:** Photoinstability of sunscreens because of ultraviolet (UV) exposure is a well-known and common phenomenon. Recently, it was also shown that sunscreens with complex filter combinations are photo-inactivated by UV exposures, which can easily be acquired by solar exposure over several hours.

**Objectives:** To assess the change of the spectral transmission after UV exposure (UV-challenged protective performance) of 27 commercially available photoprotective lipsticks.

**Methods:** Quartz slides were covered with a lipstick layer (area density  $1.0 \pm 0.1 \text{ mg/cm}^2$ ) and irradiated with increasing doses of solar-simulated radiation. The spectral transmission ( $T$ ) was measured spectrophotometrically before and after 5, 12.5, 25, and 50 standard erythema doses (SED) of exposure. We calculated the change in transmission (photoinstability) as the difference between the spectral transmission before and after a defined UV exposure,  $\Delta T$ , and the arithmetic mean, for both the UVA ( $\Delta T_A$ ) and UVB ( $\Delta T_B$ )

ranges. A product was labelled as photounstable if the mean photoinstability in the UVA,  $\Delta T_A$ , or UVB range,  $\Delta T_B$ , was higher than 5% for an UV exposure of 12.5 SED.

**Results:** Eleven products showed a significant photoinstability in the UVA range ( $\Delta T_A$  between 6% and 27%), only one product in the UVB range ( $\Delta T_B = 13\%$ ), and one product in both the UVA ( $\Delta T_A = 31\%$ ) and UVB ( $\Delta T_B = 9\%$ ) range. In one product photoinstability became significant in the UVA range at higher UV exposures.

**Conclusions:** Out of 27 lipsticks only 13 products showed a photostable performance ( $\Delta T_A < 5\%$  and  $\Delta T_B < 5\%$  for 12.5 SED). We propose therefore that only products, which fulfil these UV photostability criteria should be marketed.

**Key words:** lipstick; photoinactivation; photoprotection; photostability; solar-simulated radiation; sunscreen; ultraviolet radiation; UV; UVA; UVB.

The importance of photoprotective lipsticks as part of a comprehensive sun avoidance strategy appears to be underestimated at present. For example, in the report of the International Agency for Research on Cancer (IARC) no recommendations concerning the use of photoprotective lipsticks were included (1) although it is well known that ultraviolet (UV) radiation is a major risk factor for the development of lip malignancies and premalignant labial lesions (2–5). Because of the upright position of man the vermilion of the lower lips receives the highest irradiances of all facial regions (6). People who spend a lot of time outdoors are therefore at an increased lip cancer risk (3, 7–11) especially when they live and/or work at places with low latitudes (2, 4, 12, 13) and/or high above sea level (although no epidemiological

data are available at present). Other risk factors (pesticides) (14), engine exhaust fumes (15), immunosuppression (16–18), and a history of non-melanoma skin cancer in other locations (19, 20, 21) increase the susceptibility of the carcinogenic potential of solar radiation (13, 22).

It has been shown that regular use of (photoprotective) lipsticks reduces lip cancer frequency (3). At present, epidemiological data are available only for farmers (3, 7–11). An issue of minor importance is UV-induced herpes labialis. In an experimental setting, relapse of herpes solaris could be prevented in all patients who applied photoprotective lipsticks before exposure to solar-simulated radiation (23).

Modern photoprotective lipsticks should therefore fulfil the quality criteria that are demanded for

modern sunscreens (lotions, creams) such as broad-spectrum protection, high protective capacity for both the UVB and the UVA range, and photostability. Nevertheless, despite these criteria it has been shown that, in a high percentage of commercially available broad-spectrum sunscreens, the assessed UV protective performance does not correspond with the claims made by the producers. The UV absorptive capacity before UV exposure is not adequate (24–26) and many sunscreens are significantly photounstable (26–32).

Until now, the UV protective performance of a large number of commercially available photoprotective lipsticks has not been investigated. The objective of our study was to assess the spectral behaviour of photoprotective lipsticks after exposure to increasing doses of solar-simulated UV radiation.

## Materials and methods

### Materials

We purchased 27 photoprotective lipsticks. Before purchasing the products we conducted a market analysis in order to select lipsticks which were widely used among the population. The products of the first series (a–p) were obtained in Austria while the lipsticks of the second series (A–K) were products available on the Italian market. The samples were stored at room temperature and in the dark and opened only immediately before the test procedure. One sample of the same lot of each lipstick analysed was stored under standardized conditions.

### Experimental procedure

The spectrophotometric measurements of the UV transmittance were conducted according to the published *in vitro* test protocol (24), which we modified in certain respects (26). In the present investigation all lipsticks were applied onto quartz glass slides as a layer of  $1.0 \pm 0.1 \text{ mg/cm}^2$  which is only half of the area density ( $2.0 \pm 0.2 \text{ mg/cm}^2$ ) recommended by the COLIPA guidelines to measure the sun protection factor (SPF) of sunscreens (33). We decided to reduce the area density because our own study (34) showed that in practice lipsticks are applied in a much thinner layer than required by the COLIPA guidelines. The application thickness will change the absolute height of the absorbance curve but not its shape. In this work changes in transmittance before and after irradiation were evaluated; these differences are independent of application thickness. Each product was applied to a field of  $10 \text{ cm}^2$  on the quartz slides by circular movements of a gloved finger. The correct quantity was checked immediately after

application by a laboratory balance (with a resolution of 0.01 mg). The samples were dried for 30 min at constant temperature ( $26^\circ\text{C}$ ) and relative humidity (50%), and then irradiated with a solar simulator (COLIPA Dermasun Dr Hönle 400F/5, Dr Hönle Lichttechnik GmbH, Planegg, Germany) at a radiometrically-defined homogeneous field of irradiance (Solar Light SL 5D, Solar Light, Philadelphia, PA, USA).

The biologically effective irradiance was 12.75 SED/h (SED, standard erythema dose; 1 SED =  $100 \text{ J/m}^2$  of erythemally-effective radiation). An irradiance of 12.5 SED/h<sub>34</sub> corresponds to an UV index of 13.9, which can be expected even outdoors. For a radiation time of 24, 59, 118, and 235 min we obtained a radiant exposure of 5, 12.5, 25, and 50 SED. Under the assumption of a daily UV exposure of about 75 SED (35) the maximum UV exposure of 50 SED would be equivalent to an exposure time of about 2/3 of a day. The variability of the radiation field (5.3%) was significantly below the COLIPA guidelines (33). The spectral irradiance of the solar simulator fulfilled the requirements of the COLIPA guidelines (33) and is shown in Maier et al. (26). Relative humidity (50%) and temperature ( $26^\circ\text{C}$ ) were kept constant during the entire irradiation time.

Two independent replicate samples of each product were prepared and evaluated as described below. We measured the spectral transmittance,  $T_\lambda$ , for both the UVB (280–320 nm) and the UVA range (320–380 nm) before and after 5, 12.5, 25, and 50 SED of solar-simulated radiation with a resolution of 1 nm by means of a UV/visible spectrophotometer (Varian Cary 3E, Varian Australia Pty Ltd, Mulgrave, Victoria, Australia) connected to an integrating sphere (Labsphere DRA-CA-30, Labsphere, North Sutton, NH, USA). In order to eliminate fluorescence effects the sphere was armed with a Schott UG 11 filter (Schott, Mainz, Germany) (26). A tight-fitting steel frame was added to the spectrophotometer sample holder in order to keep the quartz slide in a fixed position during the measurement procedure. This guaranteed that a constant area of approximately  $6 \text{ cm}^2$  of the field on the quartz glass slide, which was covered by the sun care product, was illuminated (26). Furthermore, the sample could not move during the measurement procedure because the sample holder was screwed into the transmittance sample port.

### Data analysis

The change in the spectral transmittance of the investigated lipsticks for a defined UV dose,  $D$ , at a

particular wavelength  $\lambda$ ,  $\Delta T_{\lambda,D}$ , was calculated from the difference between the spectral transmittance before UV exposure,  $T_{\lambda,0}$ , and the spectral transmittance,  $T_{\lambda,D}$ , for the defined UV dose,  $D$  (Eq 1) at that wavelength. This value is called spectral photoinstability  $\Delta T_{\lambda,D}$ .

$$\Delta T_{\lambda,D} = T_{\lambda,0} - T_{\lambda,D}. \quad (1)$$

In addition to the spectral photoinstability,  $\Delta T_{\lambda,D}$ , the arithmetic mean of the  $\Delta T_{\lambda,D}$  values for both the UVA (320–380 nm),  $\Delta T_A$ , and the UVB (280–320 nm) range,  $\Delta T_B$ , for UV doses of 5, 12.5, 25, and 50 SED were calculated. We chose to describe the lipsticks as photostable or photounstable in the UVA range according to whether, at a dose of 12.5 SED,  $\Delta T_A$  was less than, or greater than or equal to, 5%, respectively. The same rule was applied in the UVB range. This limit value of 5% was selected arbitrarily.

## Results

### Characterization of photoprotective lipsticks

The information that appeared on the labels of the 27 photoprotective lipsticks investigated is collected in Table 1. In 23 products broad-spectrum protection was claimed on the package, either by labelling *UVB and UVA protection* or by the use of the word *block*. In four products (d, i, m, and K) no broad-spectrum protection was claimed. The SPF value was given for 21 of the products. Surprisingly, for six lipsticks (B, E, G, H, J, and K) no indication of the SPF was provided. Although the method of assessing the UVA protection factor was shown in only two products (n, D), which were produced by the same company, a UVA protection factor was shown on none of the lipsticks. For all but four lipsticks (g, i, F, and G) a list of the sunscreen active ingredients was available. Four lipsticks contained one UV filter, nine lipsticks two UV filters, five products contained three, and another five contained four different UV filters (inorganic filters included). A total of 13 different filter combinations could be identified. The most common UV filter combinations were: titanium dioxide (TiO<sub>2</sub>), methylbenzylidene camphor (MBC), octyl methoxycinnamate (OMC) and butyl methoxydibenzoylmethane (BMDBM) in three products; OMC and BMDBM (four products); and OMC and an inorganic filter (either TiO<sub>2</sub> or ZnO) in another three products.

### Change in spectral transmittance because of UV exposure

In order to distinguish between photostable and photounstable products we selected a mean photoinstability of 5% for an UV exposure of 12.5 SED either in the UVB ( $\Delta T_B$ ) or in the UVA range ( $\Delta T_A$ ) as the threshold value (Table 2). This UV exposure corresponds to a minimal erythemal dose (MED) for skin type II (1 MED = 250 J/m<sup>2</sup> of erythemally-effective UV radiation) of about five MED, which is a realistic value for the application of a lipstick. In the case of 11 lipsticks (a, b, c, j, n, B, E, G, H, J, and K), photoinstability in the UVA range,  $\Delta T_A$ , for 12.5 SED was significantly above 5%, whereas only one lipstick (m) exhibited photoinstability in the UVB range,  $\Delta T_B$ , and one product (l) showed photoinstability in both spectral ranges above the threshold value of 5%. Lipstick D ( $\Delta T_A$  for 12.5 SED = 4.4%) showed significant photoinstability in the UVA range with higher UV doses and is therefore also regarded

Table 1. Details of the photoprotective lipsticks investigated. Products a–p were available on the Austrian market and products A–K were available on the Italian market

Suncare product	Made in*	SPF	Broad-spectrum protection labelled†	UV filters‡
<b>a</b>	D	10	+	OMC, MBC, BMDBM
<b>b</b>	D	25	+	TiO <sub>2</sub> , OMC, MBC, BMDBM
<b>c</b>	D	18	+	TiO <sub>2</sub> , OMC, MBC, BMDBM
d	F	4	–	OMC
e	S	7	+	BP, ODM-PABA
f	F	15	+	BP
g	E	20	+	ND
h	B	15	+	OMC, OS
i	D	15	–	ND
j	D	15	+	BP, OMC, BMDBM
k	D	12	+	TiO <sub>2</sub> , MBC, IAMC
<b>l</b>	UK	20	+	TiO <sub>2</sub> , OMC, MBC, BMDBM
<b>m</b>	ND	4	–	OMC
<b>n</b>	CH	20	+	ZnO, TiO <sub>2</sub> , OMC, BMDBM
o	ND	16	+	OS, OT, MBC, BMDBM
p	USA	15	+	TiO <sub>2</sub> , OMC
<b>A</b>	F	25	+	TiO <sub>2</sub> , OMC
<b>B</b>	F	ND	+	TiO <sub>2</sub> , OMC, BMDBM
<b>C</b>	I	10	+	ZnO, OMC
<b>D</b>	CH	20	+	OMC, MBC, BMDBM
<b>E</b>	I	ND	+	OMC, BMDBM
<b>F</b>	Mon	30	+	ND
<b>G</b>	I	ND	+	ND
<b>H</b>	I	ND	+	OMC, BMDBM
<b>I</b>	F	30	+	BP
<b>J</b>	I	ND	+	OMC, BMDBM
<b>K</b>	I	ND	–	OMC, BMDBM

Photounstable products, shown in bold; SPF, sun protection factor; ND, not declared.

\*postal code for country.

†UVB/UVA protective capacity declared on package or product name containing the word “block”.

‡abbreviations for UV filters: BP, benzophenone-3 (oxybenzone); BMDBM, butyl methoxydibenzoylmethane (avobenzene); IAMC, isoamyl p-methoxycinnamate; MBC, methylbenzylidene camphor; ODM-PABA, octyl dimethyl para-aminobenzoic acid (padimate-O); OMC, octyl methoxycinnamate; OS, octyl salicylate; OT, octyl triazone; TiO<sub>2</sub>, titanium dioxide; ZnO, zinc oxide; UV, ultraviolet.

ability of 5% for an UV exposure of 12.5 SED either in the UVB ( $\Delta T_B$ ) or in the UVA range ( $\Delta T_A$ ) as the threshold value (Table 2). This UV exposure corresponds to a minimal erythemal dose (MED) for skin type II (1 MED = 250 J/m<sup>2</sup> of erythemally-effective UV radiation) of about five MED, which is a realistic value for the application of a lipstick. In the case of 11 lipsticks (a, b, c, j, n, B, E, G, H, J, and K), photoinstability in the UVA range,  $\Delta T_A$ , for 12.5 SED was significantly above 5%, whereas only one lipstick (m) exhibited photoinstability in the UVB range,  $\Delta T_B$ , and one product (l) showed photoinstability in both spectral ranges above the threshold value of 5%. Lipstick D ( $\Delta T_A$  for 12.5 SED = 4.4%) showed significant photoinstability in the UVA range with higher UV doses and is therefore also regarded

Table 2. Mean photoinstability in the UVA (320–380 nm) range,  $\Delta T_A$  (%), and the UVB (280–320 nm) range,  $\Delta T_B$  (%), for an UV exposure of 5, 12.5, 25, and 50 SED\*

Lipstick	Mean photoinstability (%) in the UVA and in the UVB range for different UV exposures (in SED)							
	UV exposure (in SED*)							
	50		12.5†		25		50	
	$\Delta T_B$	$\Delta T_A$	$\Delta T_B$	$\Delta T_A$	$\Delta T_B$	$\Delta T_A$	$\Delta T_B$	$\Delta T_A$
a	0.04	3.01	0.91	<b>15.01</b>	0.98	31.35	1.06	48.66
b	-0.05	6.28	0.97	<b>18.87</b>	1.44	26.76	1.77	27.99
c	0.21	9.98	0.64	<b>20.59</b>	1.00	25.33	1.58	27.03
d	0.94	-0.65	1.63	-1.09	2.04	-1.87	3.74	-1.62
e	-0.16	0.84	-0.07	1.13	0.01	0.52	0.38	-0.34
f	0.03	0.27	-0.01	-0.21	0.15	1.41	0.12	1.14
g	0.05	0.60	-0.63	0.16	-0.58	2.02	-0.29	7.11
h	0.94	-2.97	2.29	-2.29	4.06	-0.70	9.62	3.45
i	0.33	1.45	0.44	0.30	0.46	-0.27	0.79	0.51
j	0.08	4.07	0.21	<b>12.94</b>	0.07	18.61	0.25	21.75
k	0.36	-2.08	0.53	-1.85	0.75	-1.70	1.26	-0.86
l	1.52	9.87	<b>8.72</b>	<b>30.77</b>	10.69	44.33	13.04	48.28
m	8.07	1.65	<b>13.34</b>	3.73	12.83	3.70	17.06	5.18
n	0.87	16.50	1.49	<b>19.98</b>	2.29	20.57	4.71	22.67
o	0.17	0.69	0.21	1.77	0.34	4.16	0.45	7.66
p	0.81	-2.03	1.04	-2.42	1.73	-1.10	4.26	1.40
A	0.18	-0.02	0.30	-0.06	0.31	-0.07	0.52	0.80
B	0.38	1.38	1.04	<b>5.93</b>	2.40	19.89	8.21	51.38
C	1.38	0.98	1.81	1.23	2.66	2.05	4.04	3.74
D	0.05	1.17	0.08	4.41	0.19	12.16	0.28	34.69
E	2.23	9.92	3.36	<b>26.84</b>	5.26	46.19	9.19	51.99
F	-0.06	-0.07	0.04	0.02	-0.03	0.14	-0.02	0.48
G	0.88	4.20	2.78	<b>17.64</b>	5.77	43.23	12.03	57.97
H	0.12	5.76	0.39	<b>26.21</b>	1.06	53.75	2.70	63.00
I	0.03	0.38	0.06	0.58	0.05	0.84	0.10	1.08
J	1.33	7.11	4.07	<b>24.74</b>	6.21	41.09	10.31	49.56
K	1.39	3.20	3.48	<b>10.21</b>	6.27	26.06	12.29	52.83

Products a–p were available on the Austrian market and products A–K were available on the Italian market

\*SED, standard erythema dose; UV, ultraviolet.

†A photoinstability of  $\geq 5\%$  for an UV exposure of 12.5 SED was used to distinguish between photostable and photounstable products (shown in bold).

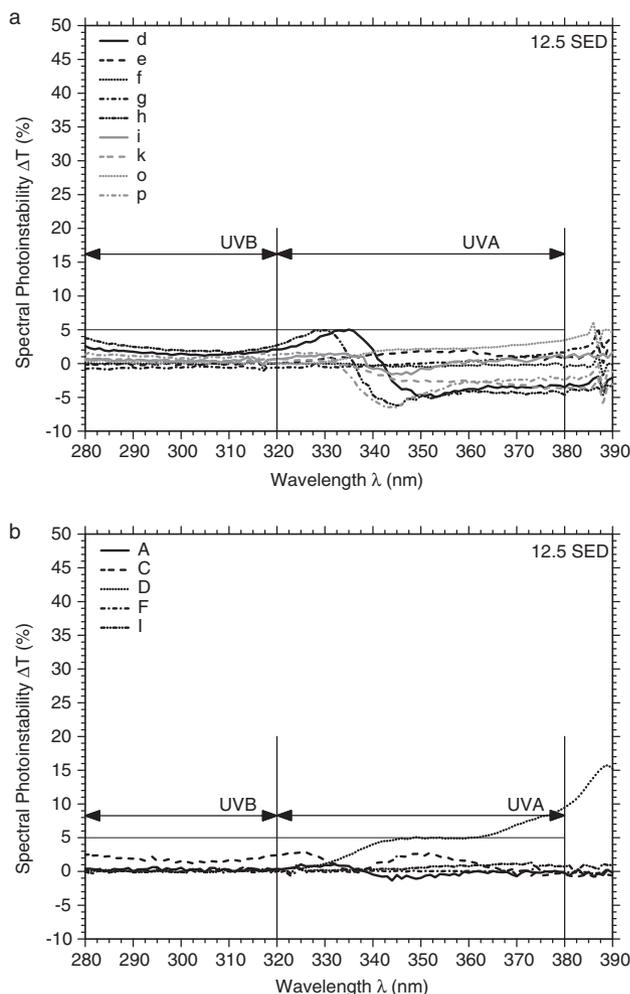
(but not labelled in the tables) as a photounstable product. In addition to products l and m with significant instability in the UVB range, several lipsticks (E, G, J, and K) showed an increase in the UVB transmittance of about 3–4%. In these four products a moderate photoinstability in the UVB range was induced by higher UV exposures (Table 2). For UV exposures of 5, 12.5, 25, and 50 SED, respectively, the numbers of photounstable products were 8, 13, 14, and 17. Photoinstability in both wavelength ranges of all photounstable lipsticks increased with UV dose. The change in spectral transmittance (here referred to as spectral photoinstability) for a UV exposure of 12.5 SED is depicted in Fig. 1 for the photostable lipsticks and in Fig. 2 for the photounstable products. This is the UV exposure, which was used to distinguish between photounstable products (Table 2,  $\Delta T_A > 5\%$  or  $\Delta T_B > 5\%$  highlighted in bold) and photostable products. Most photounstable products show a steep increase in the

spectral photoinstability in the range between 330 and 350 nm, except for product j, which shows an increase beyond 350 nm.

#### UV protective performance and UV filter system

We correlated the UV protective performance of the lipsticks investigated with the UV filter substances (Table 1). Seven combinations of UV filters (either singly or in combination) were present in the 14 photounstable products of our test series. These ranged from one active ingredient present to four. For one unstable product (G) the active ingredients were not specified.

What is evident is that all lipsticks, which contain the UV filter combination BMDBM and OMC, irrespective of the other active sunscreen ingredients, are unstable. Only one photostable product (o) contained BMDBM, but not in combination with OMC. Apart from products d and m, all other identical filter combinations exhibited the same behaviour. Products



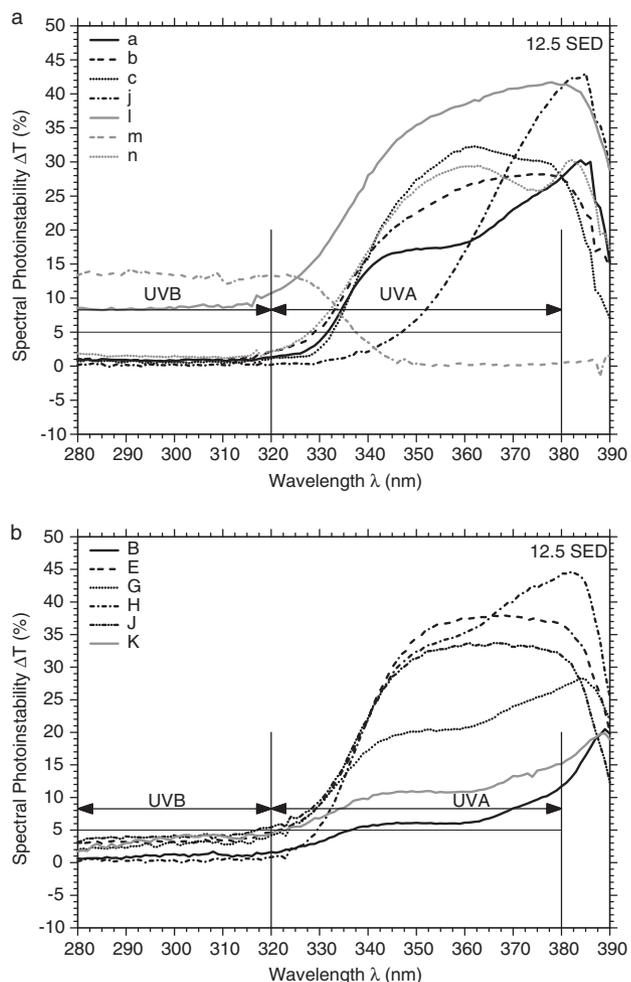
*Fig. 1.* Photostable photoprotective lipsticks on the Austrian market (a) and the Italian market (b) shown by the spectral photoinstability  $\Delta T_{\lambda}$  for an ultraviolet (UV) exposure of 12.5 standard erythema doses (SED). The photounstable products were selected based on a mean photoinstability  $\Delta T$  in the UVB or in the UVA range of equal to or greater than 5% (thin line).

d and m contained the same UV filter, namely OMC, but d was photostable and m was photounstable.

The spectral transmittance curves (Figs 1 and 2) for lipsticks with the same UV filters in the formulation are essentially the same in shape but are shifted on the y-axis because of different amounts of the active substances in each formulation.

## Discussion

Photoinstability of sunscreen active ingredients is a well-known phenomenon (31, 32, 36–42), which is closely related to the photophysical mechanism by



*Fig. 2.* Photounstable photoprotective lipsticks on the Austrian market (a) and the Italian market (b) shown by the spectral photoinstability  $\Delta T_{\lambda}$  for an ultraviolet (UV) exposure of 12.5 standard erythema doses (SED). The photounstable products were selected based on a mean photoinstability  $\Delta T$  in the UVB or in the UVA range of equal to or greater than 5% (thin line).

which these compounds absorb radiant energy. A significant body of research exists that describes the photoinstability of single UV filters (31, 36–42) and demonstrates the change in the spectral absorbance (39, 40) which occurs on UV exposure, as well as identifying the resulting photolysis products (37, 39–42). A modern sun care product consists of a number of different ingredients besides UV filters and vehicles (43). Photochemical reactions between excited UV filter molecules and other sunscreen ingredients are therefore highly likely. There are only few studies, however, which assess the UV behaviour of finished sun screening products (26–30, 32). To the best of our

knowledge this study is the first report on the photostability of a representative sample of commercially available photoprotective lipsticks.

Sunscreen producers attempt to stabilize sunscreen formulations by using complex combinations of organic and inorganic UV filters (44), and the addition of stabilizers (45, 46). Our study, which is in agreement with the results of our previous work (26) and of other study groups (27–30, 32), shows that these methods are not always successful. Furthermore, our present study confirms the findings of our previous work (26) and of other working groups (27, 29, 30, 32) that inorganic filters as part of the filter system do not guarantee photostability. The addition of TiO<sub>2</sub> may accelerate photodegradation of organic UV filters, and even sunscreens which contain only inorganic compounds may show significant photoinstability (32). In contrast to the UV behaviour of the sunscreens of our previous test series (26) in which some of the sunscreens with a particular UV filter combination were photounstable whereas other products which contained identical filters were photostable, all lipsticks other than d and m with identical filter combinations showed a unidirectional performance. This is not a discrepancy but emphasizes the importance of solvent vehicle and type of emulsion (W/O, O/W) (47–49). It has been shown that the photostability behaviour changes significantly in solvents with different polarity (32, 37, 49).

Photoprotective lipsticks are ideal study objects for photostability tests. First, because of their solid consistency and low water content they can be applied in a homogeneous layer, which may not be possible for other photoprotective preparations, such as creams and lotions (50–52). Second, in all of them the active ingredients are dissolved in an oily phase (O). The use of one type of emulsion (O) appears to be the reason why lipsticks, which contain identical filters show the same UV behaviour.

In our previous study (26) photoinstability could be demonstrated only for the UVA range whereas all sunscreens were photostable in the UVB range. In the present test series of lipsticks, however, 12 products were photounstable in the UVA range, one lipstick showed a significant photoinstability in the UVB range, and one was photounstable in both the UVB and the UVA range. This corresponds with the results of other studies, which show that photoinstability occurs in both the UVA and UVB ranges, and that photoinstability is more significant in the UVA range (27–29, 32). All these investigations indicate that photoinstability is a common phenomenon in sun-screening products, which can be purchased over the

counter (26, 27, 29, 30, 32), and is induced by UV exposures of a magnitude which can easily be acquired by sunbathers (26–30).

It is interesting to note that all lipsticks containing the UV filter combination BMDBM and OMC, irrespective of the other active sunscreen ingredients, are photounstable. It is well-known that BMDBM undergoes photodegradation in a non-polar environment (39), such as the oily phases used in lipsticks, and that in all environments OMC undergoes *trans-cis* photoisomerization and thereby loses some of its absorbing ability. In combination BMDBM can further photodegrade OMC as it can act as a photosensitizer to the photoisomerization reaction (27, 49). BMDBM is one of the few organic suncreening agents, which afford particular protection in the longwave UVA range. It absorbs maximally at about 356 nm and its photoinstability can be seen in the sharp increase in spectral photoinstability between 330 and 350 nm exhibited by the photounstable products. The fact that product j, although unstable, shows this rapid change at a longer wavelength can be accounted for by the fact that it contains benzophenone-3 (oxybenzone), a photostable absorber, which absorbs in the short wavelength UVA region and hence masks part of the BMDBM photoloss. Although products d and m are apparently identical in terms of UV filter (only OMC) and SPF they behaved differently. Neither of these products can afford UVA protection as they do not contain a UVA filter, but the change in spectral photoinstability for product m can be explained by the fact that, upon UV irradiation, OMC photoisomerizes to its *cis*-isomer which is a less efficient absorber of UVB radiation. Why this did not occur with product d is not evident, but it emphasizes the importance of the vehicle, since OMC in different sun-care products has been shown to lose between 20% and 46% of its absorptive capacity for the same UV exposure of 12 J/cm<sup>2</sup> (30).

We are far from supporting sunscreen phobia 'which has captured the imagination of popular press' (53). Beyond doubt, the benefit achieved through the use of modern sunscreens of high quality far outweighs the damage because of unprotected UV exposure. However, there is strong evidence that photounstable UV filters may be harmful to human skin. Two mechanisms, that in the end are closely related, have been described. First, the decrease of the absorptive capacity because of photoinstability of the absorbers results in an increase of the transmitted radiation and in many cases this happens to be UVA radiation (54), as was shown in this work. The transmittance of great amounts of UVA radiation

may at first sight appear to be inconsequential if one considers the reference action spectrum for UV-induced erythema and the estimated action spectrum for induction of squamous cell carcinomas by UV in the skin of hairless mice (55), since the erythemogenic and carcinogenic effect of a transmitted UVB dose is much more pronounced than the biological effect of a transmitted UVA dose. Furthermore, a recent publication indicated that the vermilion of human lips appears to be less UV-sensitive than the skin in other areas of the body (56). Nevertheless, both UVB and UVA were defined as carcinogenic factors by the IARC (57) and sub-erythemogenic UVA doses are responsible for various biological effects, e.g., induction of photosensitivity diseases (58) and skin photo-damage (59). Second, as a result of photochemical reactions short-lived reactive products form which may react with biomolecules (60–63) and give rise to potentially mutagenic products.

The practical relevance of these *in vitro* studies and the possible health risks induced by photounstable UV filters is not obvious at present. Until an action spectrum for photoaging has been defined, the damaging effect cannot be quantified. Lipsticks are among the most common causes of acute contact cheilitis (64), with UV filters (65) taking third place as causative agents in a retrospective analysis (64). To our knowledge, photoallergic/phototoxic reactions of lip skin have until now not been described. The question of whether photoallergic/phototoxic cheilitis is really a rare disease or only rarely diagnosed is unanswered at present.

The surprisingly bad UV protective performance of commercially available photoprotective lipsticks calls for rigorous guidelines. A specification of the relevant properties of purchasable sunscreens (SPF, UVA protection factor, method of assessment of UVA protection factor, photostability test, complete list of ingredients and amounts of UV filters) should be a minimal requirement. It goes without saying that the labelled features should be demonstrable in reality. There are several good reasons for these demands: firstly, sunscreen producers are subject to product liability; secondly, sunscreens should meet the challenge they are constructed for; thirdly, consumers should not be lulled into a false sense of security; fourthly, photostable products are already available on the market and there is no reason to tolerate sunscreens with insufficient UV protective performance. Our final suggestion is specific to photoprotective lipsticks. International health authorities, e.g. the IARC, should include a recommendation for regular photoprotective lipstick use in the guidelines

as a valuable part of a comprehensive sun avoidance strategy especially for people with increased risk for the development of lip malignancies, such as outdoor workers (7–11) and transplant recipients (16, 17).

#### Acknowledgements

The authors thank Alexander Cabaj, Institute of Medical Physics and Biostatistics, University of Veterinary Medicine Vienna, for critical discussion of the manuscript and CERIES for financial support. BSM wishes to acknowledge financial support from the National Research Foundation and the Cancer Association of South Africa.

#### References

1. Vainio H, Miller AB, Bianchini F. An international evaluation of the cancer-preventive potential of sunscreens. *Int J Cancer* 2000; **88**: 838–842.
2. Moore SR, Allister J, Roder D, Pierce AM, Wilson DF. Lip cancer in South Australia, 1977–1996. *Pathology* 2001; **33**: 167–171.
3. Pogoda JM, Preston-Martin S. Solar radiation, lip protection, and lip cancer risk in Los Angeles county women (California, United States). *Cancer Causes Control* 1996; **7**: 458–463.
4. Swerdlow AJ, Cooke KR, Skegg DC, Wilkinson J. Cancer incidence in England and Wales and New Zealand and in migrants between the two countries. *Br J Cancer* 1995; **72**: 236–243.
5. Lyon JL, Gardner K, Gress RE. Cancer incidence among Mormons and non-Mormons in Utah (United States) 1971–85. *Cancer Causes Control* 1994; **5**: 149–156.
6. Schauburger G, Keck G. Beitrag zur Bestimmung der solaren UV Belastung der Haut: eine epidemiologische Betrachtung zur Ätiologie des Basalioms. *Aktuel Dermatol* 1990; **11**: 289–328.
7. Khuder SA. Etiologic clues to lip cancer from epidemiologic studies on farmers. *Scand J Work Environ Health* 1999; **25**: 125–130.
8. Cerhan JR, Cantor KP, Williamson K, Lynch CF, Torner JC, Burmeister LF. Cancer mortality among Iowa farmers: recent results, time trends and life style factors (United States). *Cancer Causes Control* 1998; **9**: 311–319.
9. Schouten LJ, Meijer H, Huveneers JA, Kiemeneys LA. Urban–rural differences in cancer incidence in the Netherlands 1989–1991. *Int J Epidemiol* 1996; **25**: 729–736.
10. Wiklund K, Dich J. Cancer risks among male farmers in Sweden. *Eur J Cancer Prev* 1995; **4**: 81–90.
11. Fincham SM, Hanson J, Berkel J. Patterns and risks of cancer in farmers in Alberta. *Cancer* 1992; **69**: 1276–1285.
12. Lookingbill DF, Lookingbill GL, Leppard B. Actinic damage and skin cancer in albinos in northern Tanzania: findings in 164 patients enrolled in an outreach skin care program. *J Am Acad Dermatol* 1995; **32**: 653–658.
13. Dardanoni L, Gafa L, Paterno R, Pavone G. A case-control study on lip cancer risk factors in Ragusa (Sicily). *Int J Cancer* 1984; **34**: 335–337.
14. Davies DL, Blair A, Hoel DG. Agricultural exposures and cancer trends in developed countries. *Environ Health Perspect* 1993; **100**: 39–40.
15. van den Eeden SK, Friedman GD. Exposure to engine exhaust and risk of subsequent cancer. *J Occup Med* 1993; **35**: 307–311.
16. Jensen P, Hansen S, Moller B, et al. Skin cancer in kidney and heart transplant recipients and different long-term immuno-

- suppressive therapy regimens. *J Am Acad Dermatol* 1999; **40**: 177–186.
17. King GN, Healy CM, Glover MT, et al. Increased prevalence of dysplastic and malignant lip lesions in renal transplant recipients. *N Engl J Med* 1995; **332**: 1052–1057.
  18. Birkeland SA, Storm HH, Lamm LU, et al. Cancer risk after renal transplantation in Nordic countries, 1964–1986. *Int J Cancer* 1995; **60**: 183–189.
  19. Wassberg C, Thorn M, Yuen J, Ringborg U, Hakulinen T. Second primary cancers in patients with squamous cell carcinoma of the skin: a population-based study in Sweden. *Int J Cancer* 1999; **80**: 511–515.
  20. Frisch M, Hjalgrim H, Olsen JH, Melbye M. Risk for subsequent cancer after diagnosis of basal cell carcinoma. A population based, epidemiologic study. *Ann Intern Med* 1996; **125**: 815–821.
  21. Jaeger AB, Gramkow A, Hjalgrim H, Melbye M, Frisch M. Bowen disease and risk of subsequent malignant neoplasms: a population-based cohort study of 1147 patients. *Arch Dermatol* 1999; **135**: 790–793.
  22. Preston-Martin S, Henderson BE, Pike MC. Descriptive epidemiology of cancers of the upper respiratory tract in Los Angeles. *Cancer* 1982; **49**: 2201–2207.
  23. Rooney JF, Bryson Y, Mannix ML, et al. Prevention of ultraviolet-light-induced herpes labialis by sunscreen. *Lancet* 1991; **338**: 1419–1422.
  24. Marginean G, Fructus AE, Marty JP, Arnaud-Battandier J. New *ex-vivo* method for evaluating the photoprotective efficacy of sunscreens. *Int J Cosmet Sci* 1995; **17**: 233–243.
  25. Diffey BL, Tanner PR, Matts PJ, Nash JF. *In vitro* assessment of the broad-spectrum ultraviolet protection of sunscreen products. *J Am Acad Dermatol* 2000; **43**: 1024–1035.
  26. Maier H, Schauburger G, Brunnhofer K, Hönigsmann H. Change of ultraviolet absorbance of sunscreens by exposure to solar-simulated radiation. *J Invest Dermatol* 2001; **117**: 256–262.
  27. Sayre RM, Dowdy JC. Photostability testing of avobenzene. *Cosmet Toil* 1999; **114**: 85–91.
  28. Kockott D. *In vitro* Bewertung von Sonnenschutzmitteln. *Kosmetische Med* 1998; **19**: 290–293.
  29. Diffey BL, Stokes RP, Forestier S, Mazalier C, Rougier A. Suncare product photostability: a key parameter for a more realistic *in vitro* efficacy evaluation. *Eur J Dermatol* 1997; **7**: 226–228.
  30. Forestier S, Mazalier C, Rougier A. Suncare product photostability: a key parameter for a more realistic *in vitro* efficacy evaluation. Part II: chromatographic analysis. *Eur J Dermatol* 1997; **7**: 6–8.
  31. Jiang R, Hayden CG, Prankerd RJ, Roberts MS, Benson HA. High-performance liquid chromatography assay for common sunscreens agents in cosmetic products, bovine serum albumin solution and human plasma. *J Chromatogr B* 1996; **682**: 137–145.
  32. Serpone N, Salinaro A, Emeline AV, Horikoshi S, Hidaka H, Zhao J. An *in vitro* systematic spectroscopic examination of the photostabilities of a random set of commercial sunscreen lotions and their chemical UVB/UVA active agents. *Photochem Photobiol Sci* 2002; **1**: 970–981.
  33. COLIPA (European Cosmetic Toiletry and Perfumery Association). SPF test method. Brussels: COLIPA, 1994.
  34. Maier H, Schauburger G, Brunnhofer K, Hönigsmann H. Assessment of thickness of photoprotective lipsticks and frequency of reapplication: results from a laboratory test and a field experiment. *Br J Dermatol* 2002; **148**: 763–769.
  35. Schmalwieser AW, Schauburger G, Janouch M, et al. Global validation of a forecast model for irradiance of the solar, erythemally effective ultraviolet radiation. *Opt Eng* 2002; **41**: 3040–3050.
  36. Vanquerp V, Rodriguez C, Coiffard C, Coiffard LJ, De Roeck-Holtzhauer Y. High-performance liquid chromatographic method for the comparison of the photostability of five sunscreen agents. *J Chromatogr* 1999; **832**: 273–277.
  37. Tarras-Wahlberg N, Stenhagen G, Larkö O, Rosen A, Wennerberg AM, Wennerström O. Change in ultraviolet absorption of sunscreens after ultraviolet irradiation. *J Invest Dermatol* 1999; **113**: 547–553.
  38. Berset G, Gonzenbach H, Christ R, et al. Proposed protocol for determination of photostability Part I. Cosmetic UV filters. *Int J Cosmet Sci* 1996; **18**: 167–177.
  39. Schwack W, Rudolph T. Photochemistry of dibenzoylmethane UVA filters Part I. *J Photochem Photobiol B* 1995; **28**: 229–234.
  40. Roscher NM, Lindemann MKO, Kong SB, Cho GC, Jiang P. Photodecomposition of several compounds commonly used as sunscreen agents. *J Photochem Photobiol A* 1994; **80**: 417–421.
  41. Gasparro FP. UV-induced photoproducts of para-aminobenzoic acid. *Photodermatology* 1985; **2**: 151–157.
  42. Chignell CF, Kalyanaraman B, Mason RP, Sik RH. Spectroscopic studies of cutaneous photosensitizing agents-I. Spin trapping of photolysis products from sulphonamide, 4-aminobenzoic acid and related compounds. *Photochem Photobiol* 1980; **32**: 563–571.
  43. Klein K. Sunscreen products. Formulation and regulatory considerations. In: Lowe NJ, Shaath NA, Pathak MA, eds. Sunscreens, development, evaluation, and regulatory aspects, 2nd edn. New York: Marcel Dekker, 1997; 285–311.
  44. Chatelain E, Gabard B. Photostabilization of butyl methoxydibenzoylmethane (Avobenzene) and ethylhexyl methoxycinnamate by bis-ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S), a new UV broadband filter. *Photochem Photobiol* 2001; **74**: 401–406.
  45. Scalia S, Villani S, Casolari A. Inclusion complexation of the sunscreen agent 2-ethyl hexyl-p-dimethylaminobenzoate with hydroxypropyl-(beta)-cyclodextrin: effect on photostability. *J Pharm Pharmacol* 1999; **51**: 1367–1374.
  46. Bonda C, Steinberg DC. A new photostabilizer for full spectrum sunscreens. *Cosmet Toil* 2000; **115**: 37–45.
  47. Agrapidis-Paloympis LE, Nash RA, Shath NA. The effect of solvents on the ultraviolet absorbance of sunscreens. *J Soc Cosmet Chem* 1987; **38**: 209–211.
  48. Marti-Mestres G, Fernandez C, Parsotam N, Nielloud F, Mestres JP, Maillois H. Stability of UV filters in different vehicles: solvents and emulsions. *Drug Dev Ind Pharm* 1997; **23**: 647–655.
  49. Panday R. A photochemical investigation of two sunscreen absorbers in a polar and a non-polar medium. MSc thesis, Durban, South Africa: University of Natal. 2003
  50. Lott DL, Stanfield J, Sayre RM, Dowdy JC. Uniformity of sunscreen product application: a problem in testing, a problem for consumers. *Photodermatol Photoimmunol Photomed* 2003; **19**: 17–20.
  51. Grecis PW, Stokes R. An evaluation of photographic methods to demonstrate the uniformity of sunscreen applied to the skin. *J Audiov Media Med* 1999; **22**: 171–177.
  52. Loesch H, Kaplan DL. Pitfalls in sunscreen application. *Arch Dermatol* 1994; **130**: 665–666.
  53. Nohynek GJ, Schaefer H. Benefit and risk of organic ultraviolet filters. *Regul Toxicol Pharmacol* 2001; **33**: 285–299.
  54. Moyal D, Refregier JL, Chardon A. *In vivo* measurement of the photostability of sunscreen products using diffuse reflectance spectroscopy. *Photodermatol Photoimmunol Photomed* 2002; **18**: 14–22.
  55. deGrujil FR, Sterenborg HJCM, Forbes PD, et al. Wavelength dependence of skin cancer induction by ultraviolet radiation of albino hairless mice. *Cancer Res* 1993; **53**: 53–60.
  56. Gabard B, Ademola J. Lip sun protection factor of a lipstick sunscreen. *Dermatology* 2001; **203**: 244–247.

57. IARC (International Agency for Research on Cancer). Solar and ultraviolet radiation. Monographs on the evaluation of carcinogenic risks to humans; **vol. 55**. Lyon: IARC, WHO, 1992.
58. Duguid C, O'Sullivan D, Murphy GM. Determination of threshold UVA elicitation dose in photopatch testing. *Contact Dermatitis* 1993; **29**: 192–194.
59. Lavker R, Kaidberg F. The spectral dependence for UVA-induced cumulative damage in human skin. *J Invest Dermatol* 1997; **108**: 17–21.
60. Damiani E, Carloni P, Biondi C, Greci L. Increased oxidative modification of albumin when illuminated *in vitro* in the presence of a common sunscreen ingredient: protection by nitroxide radicals. *Free Radic Biol Med* 2000; **28**: 193–201.
61. McHugh PJ, Knowland J. Characterization of DNA damage inflicted by free radicals from a mutagenic sunscreen ingredient and its location using an *in vitro* genetic reversion assay. *Photochem Photobiol* 1997; **66**: 276–281.
62. Schallreuter KU, Wood JM, Farwell DW, Moore J, Edwards HG. Oxybenzone oxidation following solar irradiation of skin: photoprotection versus antioxidant inactivation. *J Invest Dermatol* 1996; **106**: 583–586.
63. Dogra A, Minocha YC, Sood VK, Dewan SP. Contact dermatitis due to cosmetics and their ingredients. *Ind J Dermatol Venereol Leprol* 1994; **60**: 72–75.
64. Freeman S, Stephens R. Cheilitis: analysis of 75 cases referred to a contact dermatitis clinic. *Am J Contact Dermatitis* 1999; **10**: 198–200.
65. Aguirre A, Izu R, Gardeazabal J, Gil N, Diaz-Perez JL. Allergic contact cheilitis from a lipstick containing oxybenzone. *Contact Dermatitis* 1992; **27**: 267–268.

*Accepted for publication 1 December 2004*

*Corresponding author:*

Harald Maier, M.D.

Division of Special and Environmental Dermatology

Medical University of Vienna

Währinger Gürtel 18–20

A-1090 Vienna

Austria

Tel: +43 1 4060866

Fax: +43 1 4081278

e-mail: harald.maier@meduniwien.ac.at