


Measurements of the photodegradation of PABA and some PABA derivatives

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The photodegradation of 4-aminobenzoic acid, 2-ethylhexyl N,N-dimethyl 4-aminobenzoate (Escalol 507[®]) and 1-glyceryl 4-aminobenzoate (Escalol 106[®]), resulting from irradiation by sun lamps, was examined by UV spectroscopy. 2-ethylhexyl N,N-dimethyl 4-aminobenzoate showed the longest half-life, indicating the highest photostability.

Key words: PABA - escalol - photodegradation.

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Photodegradation of UV-absorbing sunscreens has been regarded as a possible carcinogenic risk factor because of the often enhanced reactivity of electronically excited molecules in biological systems (1-6). The implications of these findings have led us to investigate the photostability of some sunscreen agents.

In this study we compared the photodegradation of 4-aminobenzoic acid (PABA), 2-ethylhexyl-N,N-dimethyl 4-aminobenzoate (Escalol 507[®]) and 1-glyceryl 4-aminobenzoate (Escalol 106[®]) following exposure to a Philips TL 40 W/12 light source.

Material and methods

PABA was purchased from Merck (FRG); Escalol 507 and Escalol 106 were obtained from Malinckrodt (FRG) and Hermal Industries (USA),

respectively. The purity of the chemicals was investigated with high-performance liquid chromatography, high-performance gas chromatography, thin-layer chromatography and mass spectroscopy. The products used here were purified according to the above measurements (7,8).

Dilute ethanolic solutions (5×10^{-5} M) of PABA, Escalol 507 and Escalol 106 in sealed standard quartz cuvettes ($1 \times 1 \times 4$ cm) were exposed to the radiation from a Philips TL 40 W/12 light source (emission spectrum shown in Fig. 1). The UV intensity, measured with a UV meter (Waldmann, FRG) was 2.5 mW/cm^2 at the sample position. The UV spectra were recorded at regular intervals with a Perkin-Elmer Lampda 14 UV-VIS spectrophotometer interfaced to a Perkin-Elmer 3700 data station.

Results

The UV absorption spectra are shown in Fig. 1. The curves represent the absorption before irradiation and after 1 h and 3 h of irradiation, corresponding to doses of 9 J/cm² and 27 J/cm², respectively. The concentrations of the sunscreens studied according to exposure time are presented in Fig. 2.

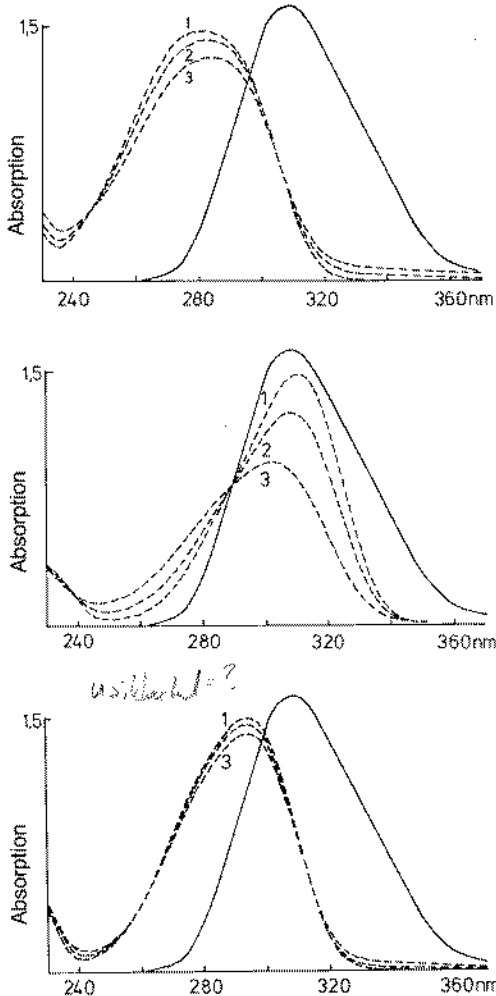


Fig. 1. Photodegradation of sunscreens. A: PABA; B: Escalol 507; C: Escalol 106. The dotted line indicates the absorption spectra: 1: before irradiation; 2: after 1 h; 3: after 3 h. The continuous line shows the emission spectrum of the lamp.

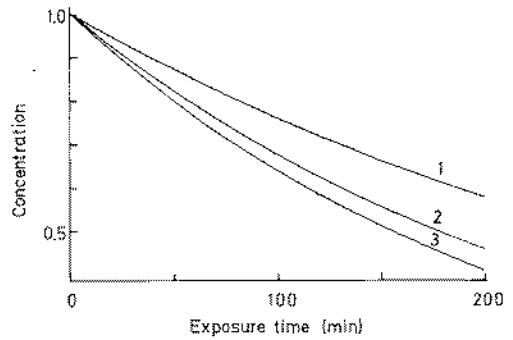


Fig. 2. The concentration of sunscreens during irradiation with the light source. 1: Escalol 507; 2: PABA; 3: Escalol 106. One hundred minutes of UV exposure correspond to 15 J/cm².

The isobestic points for the sunscreen/photoproduct UV spectra are well defined. Hence, the data can be analyzed in terms of a single, although possibly very complicated, process: sunscreen → photoproduct. The photoproduct (P) may be one or several chemical compounds that do not (or very slowly) undergo further photochemical reaction. For optically thin (very dilute) solutions, the UV spectrum of the sunscreen/photoproduct mixture versus photolysis time, $A(\lambda, t)$, can then be analyzed by:

$$A(\lambda, t) = e^{-kt} S(\lambda) + (1 - e^{-kt}) P(\lambda)$$

where $S(\lambda)$ is the absorption spectrum of the pure sunscreen and $P(\lambda)$ is the absorption spectrum of the photoproducts formed. λ is the wavelength and t is the time. The 2 unknown parameters (the rate constant to photodegradation of the sunscreen (k) and the spectrum of the photoproducts $P(\lambda)$) were determined by a least squares curve fitting procedure. The derived half-lives of the sunscreen agents under our experimental

Table 1. Half-life times of sunscreen agents

Sunscreen agent	Half-life (minutes)
Escalol 507	253
PABA	177
Escalol 106	155

Udled g av $A(\lambda, t)$
+ usikkerhed på konstant!

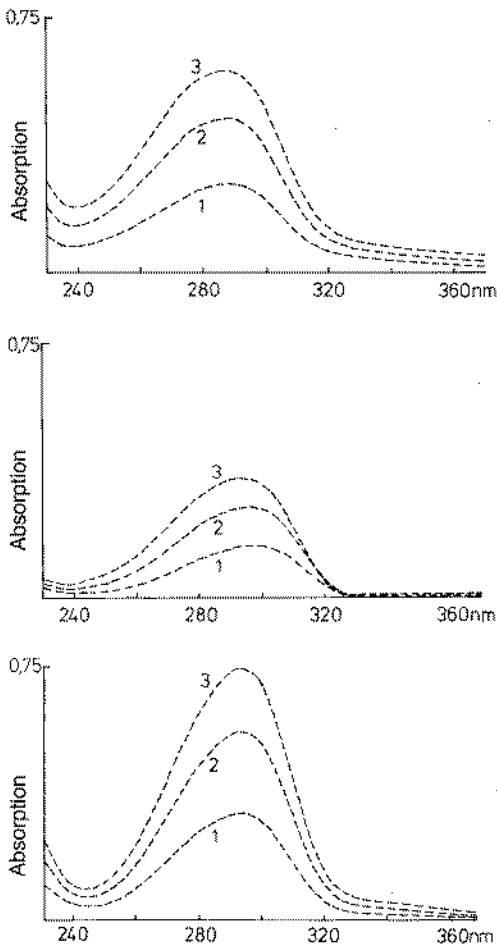


Fig. 3. The absorption spectra of the photoproducts after irradiation of the sunscreens. A: PABA; B: Escalol 507; C: Escalol 106. 1: the absorption spectra after 1 h; 2: after 2 h; 3: after 3 h.

conditions are shown in Table 1; the calculated UV spectra of the photoproducts formed by UV irradiation are presented in Fig. 3.

Discussion

The spectrum of the light source must be considered in evaluating the degradation of the sunscreen agents. We have included the emission

spectrum of the sunlamp (arbitrary units) in Fig. 1. The absorption profile of Escalol 507 is almost overlapped by the emission spectrum, whereas only a partial overlap is found for PABA and Escalol 106. Despite this, Escalol 507 had the longest half-life (Table 1). This seems surprising because the peak absorption of Escalol 507 decreases more rapidly than for PABA and Escalol 106 (Fig. 1). However, this can be explained by the fact that the photoproducts of Escalol 507 are weaker UV absorbers than the photoproducts of PABA and Escalol 106 (Fig. 3).

The emission spectrum of the sunlamp differs from the spectrum of natural sunlight because the sunlamp emits wavelengths beyond 290 nm. The UV intensity used in our laboratory was higher than the irradiance levels measured at southern latitudes (28°N) at solar noontime under clear sky conditions (9). Therefore, the sunscreens studied would have reacted slower in natural sunlight. It should also be emphasized that the UV exposure doses we applied in this experiment were extremely high and that only a minor degree of photodegradation took place after exposure to doses comparable to outdoor conditions.

Escalol 507 is the most widely used sunscreen agent among the compounds studied here. It had a higher degree of photostability than either PABA or Escalol 106.

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References

- Hodges N D M, Moss S H, Davies D J G. The sensitizing effect of a suncreening agent, p-aminobenzoic acid, on near UV-induced damage in a repair deficient strain of *Escherichia Coli*. *Photochem Photobiol* 1977; **26**: 493-498.
- Osgood P J, Moss S H, Davies D J G. The sensitization of near-ultraviolet radiation killing of mammalian cells by the sunscreen agent para-aminobenzoic acid. *J Invest Dermatol* 1982; **79**: 354-357.
- Sutherland B M. p-aminobenzoic acid - sunlamp sensitization of pyrimidine dimer formation and transformation in human cells. *Photochem Photobiol* 1982; **36**: 95-97.

4. Sutherland J C, Griffin K P. p-aminobenzoic acid can sensitize the formation of pyrimidine dimers in DNA: direct chemical evidence. *Photochem Photobiol* 1984; **40**: 391-394.
5. Gasparro F P. PABA: friend or foe? *Photodermatol* 1986; **3**: 61-63.
6. Gasparro F P. UV-induced photoproducts of para-aminobenzoic acid. *Photodermatol* 1985; **2**: 151-157.
7. Bruze M, Gruvberger B, Thune P. Contact and photocontact allergy to glyceryl para-aminobenzoate. *Photodermatol* 1988; **5**: 162-165.
8. Bruze M, Fregert S, Gruvberger B. Occurrence of para-aminobenzoic acid and benzocaine as contaminants in sunscreen agents of para-aminobenzoic acid type. *Photodermatol* 1984; **1**: 277-285.
9. Wester U. Solar ultraviolet radiation on the Canary Islands and in Sweden - a comparison of irradiance level. In: Passhler W F, Bosnjakovic B F M, eds. Human exposure to ultraviolet radiation: risks and regulations. Amsterdam: Elsevier, 1987: 275-279.

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