

PHOTOSTABILITY OF 2-ETHYLHEXYL-P-METHOXY CINNAMATE USED IN SUNSCREEN PREPARATIONS MARKETED IN TURKEY

TÜRKİYE PİYASASINDA BULUNAN GÜNEŞ PREPARATLARINDAKİ 2-ETİLHEKZİL-P-METOKSİ SİNNAMATIN FOTOSTABİLİTESİ

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In this study, photostability of the most widely used ultraviolet (UV) absorber namely 2-ethylhexyl-p-methoxy cinnamate (2-EHMC) in sunscreen preparation marketed in Turkey was investigated by keeping in light stability test cabinet and photodegradation was determined by thin layer chromatography (TLC) and UV spectroscopy. A photoproduct was detected by TLC and data obtained from UV spectroscopy has revealed the changes in spectrum. Since UV chemical absorbers are widely used in sunscreen preparations to protect human skin from UV radiations, it is important to conduct research further on their various properties, especially photostability.

Bu çalışmada, Türkiye piyasasında bulunan güneşten koruyucu preparatlarda UV absorplayıcı olarak kullanılan 2-etilhekzİL-p-metoksi sinnamat (2-EHMC)'nin fotostabilitesi ışık stabilite kabininde bekletilerek incelenmiş ve oluşan fotoparçalanma ince tabaka kromatografisi (İTK) ve UV spektroskopisi ile tayin edilmiştir. İTK ile fotoparçalanma ürünü saptanmış ve UV spektroskopisi yöntemi ile elde edilen veriler, maddenin spektrumunda değişiklik olduğunu göstermiştir. Güneşten koruyucu preparatlar, insan derisini UV radyasyonunun zararlı etkilerinden korunak amacı ile kullanıldığından kimyasal UV absorplayıcı maddelerle ilgili olarak özellikle fotostabilite konusunda araştırmaların derinleştirilmesi önemli bir konu olarak ortaya çıkmaktadır.

Keywords : UV absorber; Photostability, Antioxidants; Thin layer chromatography; UV spectroscopy

Anahtar kelimeler: UV absorplayıcı madde; Fotostabilite; Antioksidanlar; İnce tabaka kromatografisi; UV spektroskopisi

Introduction

It has been known for decades that sunscreens are capable of protecting man from harmful effects of solar radiation such as actinic aging or cutaneous cancer(1). Research regarding to sun protection has become a major concern. Today, several UVabsorbing chemicals are available for sunscreen preparations which need a high degree of resistance to photodecomposition on exposure to sunlight. A sunscreen must be effective in absorbing erythemogenic radiation in the 280-315 nm range without breakdown which would reduce its efficiency or give rise to toxic or irritant compounds (2). Although most aspects of these compounds have been fully investigated, there has not been much information about the photostability of UV absorbers. In recent years, it was reported that spectral stability of some UV absorbers were investigated on stratum corneum sheets and photochemical stability was determined by examining the changes in absorption spectra of the substances (3). There was also information about photostability

of benzylidene camphor, dibenzoyl methane and cinnamate derivatives (4-7). It has also been known that photodegradation may be inhibited by addition of antioxidants (8,9).

In this study, photostability of the most widely used UV absorber, 2-EHMC in sunscreen preparations marketed in Turkey was investigated by TLC and UV spectroscopy after keeping in accelerated light stability test cabinet designed according to the study of Lachman et al. (10, 11) for 10 weeks.

Materials and Methods

Materials and apparatus: Eight sunscreen preparations available in Turkish market which were coded as A-H. 2-EHMC (Haarman&Reimer), diisopropyl ether, n-hexane, acetic acid, sulphuric acid, methanol, ethyl acetate, 25% ammonia, anisaldehyde (E.Merck).

Accelerated light stability test cabinet (Aymes Inc., İstanbul), which is 160x125x110 cm in dimension and radiated with 1000 watt fluorescent tubes (Philips).

Method

1. Light stability test

Eight sun preparations of various manufacturers marketed in Turkey and a reference substance (2-EHMC) in a glass bottle were put into the light stability test cabinet and investigated for their UV absorber degradation at weekly intervals by TLC.

2. Extraction and identification of the UV absorbers

Method used here was the same as in our previous study (12). One gram of the sample was extracted with 4 ml methanol and shaken for 1 hour by using horizontal shaker (B.Braun Mini-Shaker). 0.5 g sodium sulphate

was then added and the mixture left overnight. 5 μ l of the clear supernatant layer was used for identification in TLC (Silicagel HF 254). After elution with solvent systems **a**. (diisopropyl ether/n-hexane/acetic acid 20:80:1) **b**.(ethyl acetate/methanol/25% ammonia 65:30:5), reagent (anisaldehyde/acetic acid/sulphuric acid 0.5:50:1) was sprayed and the plate heated at 100°C for 10 min. Reference sunscreen agent was dissolved in 96% ethanol (1% conc.) and 1 μ l applied to the same plates for identification. UV absorption spectra of 2-EHMC was taken before the experiment and also after 10 weeks. The UV absorption spectrum of the spots in the plates were also used to confirm the results. After elution with an appropriate solvent system and location by visualising under UV light, the spot was scraped off, an 10 ml of 96% ethanol was added. The

Table1. Photodegradation of 2-EHMC in sunscreen preparations (A-H) kept in light stability test cabinet for 10 weeks

| Sunscreen Preparation | | A | B | C | D | E | F | G | H |
|----------------------------------|----------------------------|----|------------------------------|------------------------------|----|----------------------|-----|----|----|
| Antioxidant | | - | α -tocopheryl acetate | α -tocopheryl acetate | - | α -tocopheryl | BHT | - | - |
| UV absorber (2-EHMC) degradation | | x | - | - | x | x | - | x | x |
| a | R _f | 42 | 42 | 43 | 41 | 40 | 41 | 42 | 42 |
| | R _{f_d} | 70 | - | - | 71 | 71 | - | 69 | 70 |
| b | R _f | 74 | 75 | 74 | 72 | 74 | 74 | 72 | 75 |
| | R _{f_d} | 16 | - | - | 18 | 20 | - | 18 | 18 |

R_f : 2-EHMC

R_{f_d}: degradation product

a, b : solvent systems used in TLC



Fig.1. UV absorption spectrum of 100 μ g 2-EHMC in 10 ml ethanol

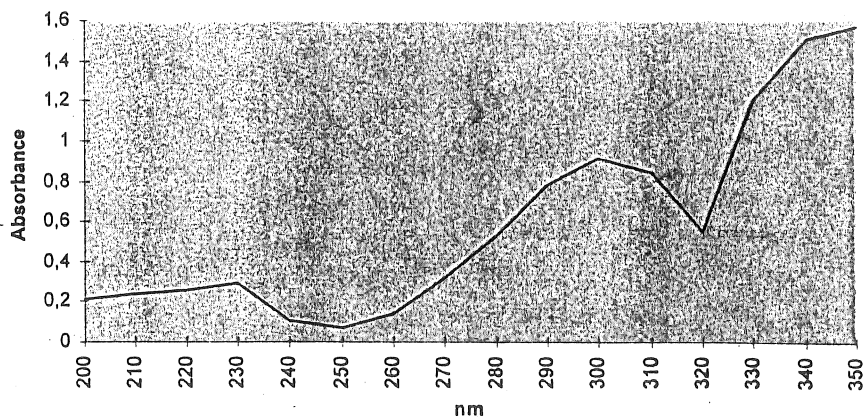


Fig.2. UVabsorption spectrum of 100 µg irradiated 2-EHMC in 10 ml ethanol

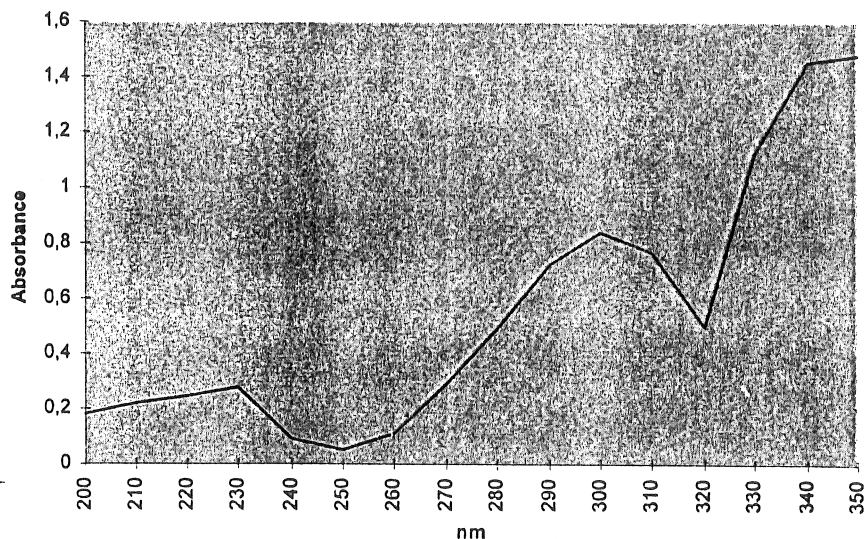


Fig.3. UV absorption spectrum of degraded 2-EHMC in sunscreen preparations

mixture was then vigorously shaken and filtered. The UV spectrum of the filtrate between 200-350 nm was then obtained.

Results and Discussion

In investigating the photostability of 2-EHMC used in sunscreen preparations marketed in Turkey, it has been found out that 5 out of 8 preparations had undergone degradation. As can be seen from the results in Table 1, the most striking point here is that four of these preparations containing degraded UV absorber have been formulated without antioxidants whereas sunscreen preparations containing α - tocopheryl acetate and butylated

hydroxytoluen (BHT) as antioxidants together with UV absorber had not been degraded. In some studies, it was stated that there was increase or decrease in absorption spectra of UV absorbers after exposure to simulated sun light (3,4). It was concluded in this study, as shown in Fig. 2, the absorption spectrum of 2-EHMC had changed after keeping in light stability test cabinet. The degradation product was observed by performing TLC test. UV absorption spectrum of the degraded 2-EHMC in sunscreen preparations has also changed as can be seen in Fig.3. Generally sunscreens were introduced as aqueous, alcoholic, oily solutions and emulsions. It was reported that the type of solvent used as vehicle affects the

UV absorption capacity and the photostability of a sunscreen (13,14). According to our findings, addition and type of antioxidant also affects the photostability where α -tocopheryl acetate and BHT seems to be suitable but α -tocopherol does not in the preparations tested. Since UV damage on skin leads to very serious results, all factors influencing the photostability and proper choice of antioxidants and vehicles should be taken into consideration.

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