

PHOTOSTABILITY OF SOME VEHICLES AND ANTIOXIDANTS IN COSMETIC
PREPARATIONS

KOZMETİK PREPARATLAR İÇİNDEKİ BAZI TAŞIYICI VE ANTIOKSİDANLARIN
FOTOSTABİLİTESİ

GÜLGÜN YENER, YALÇIN TOPALOĞLU

Department of Pharmaceutical Technology, Faculty of Pharmacy, University of İstanbul, Beyazıt 34452,
İstanbul, Turkey

Vehicles and antioxidants generally used in sunscreen preparations were tested for their photostability since they are exposed to intensive sunlight for long time. It has been found out that among tested vehicles only vaseline had undergone degradation and in case of antioxidants butylated hydroxytoluen (BHT) was found to be the most stable followed by α -tocopheryl acetate, butylated hydroxyanisol (BHA), α -tocopherol and cysteine respectively. The results showed that proper choice of antioxidants related to vehicles for especially sunscreen preparations is of prime importance.

Güneşten koruyucu preparatların terkinde bulunan bazı taşıyıcı ve antioksidanların uzun süre yoğun güneş ışığına maruz kalmaları nedeniyle fotostabiliteyi araştırılmıştır. Teste tabi tutulan taşıyıcılardan sadece vazelinin parçalandığı saptanmış, antioksidanlar arasında ise butil hidroksitoluen en dayanıklı olmak üzere, α -tokoferil asetat, butil hidroksianisol (BHA), α -tokoferol ve sistein dayanıklılık açısından sıralanmışlardır. Elde edilen sonuçlar, özellikle güneşten koruyucu preparatlar açısından kullanılan antioksidanların uygun şekilde seçilmesinin büyük önemini ortaya koymaktadır.

Keywords: *Vehicles in sunscreens; Antioxidants; Thin layer chromatography*

Anahtar kelimeler: *Güneşten koruyucu preparatlardaki taşıyıcılar, Antioksidanlar; İnce tabaka kromatografisi*

Introduction

Photostability of various vehicles and antioxidants used in cosmetic creams and lotions (especially sunscreen preparations) were investigated by storing in light stability test cabinet for 14 weeks. Among vehicles used in cream and lotions, it has been reported that vaseline (also called petrolatum) may contain a suitable stabilizer (1) and should be protected from light (2,3). In pharmacopeias, it has been reported that vehicles as paraffin, polyethylene glycol(1), cetyl alcohol (1,2) and propylene glyco (1,2,4) should be kept in well-closed containers. In case of antioxidants, butylated hydroxyanisol (BHA) (2), α -tocopherol (1,2) and α -tocopheryl acetate (1-4) should be protected from light. However butylated hydroxytoluen (BHT) was reported as to be kept in well-closed container (1), there is no record for light protection of BHT in pharmacopeias.

It has been reported that additives used in dermatologic and cosmetic preparations might be transformed due to chemical effects of ultraviolet (UV) light which would penetrate even through clothes covering the body. There was suggestion that additives used in micronized

form should be tested for their UV stability and the changes in their structure should be revealed (5).

In this study, the light stability of some vehicles and antioxidants used in sunscreen preparations were investigated in light stability test cabinet by using thin layer chromatography (TLC).

Materials and Methods

Materials: Vaseline, cetyl alcohol, paraffin, polyethylene glycol (PEG) 400 and 4000, propylene glycol (Henkel). BHA and BHT (Merck), α -tocopherol, α -tocopheryl acetate (Hoffmann La Roche), cysteine (Fluka). All reagents and solvents were of analytical grade.

Apparatus: Accelerated light stability test cabinet (Aymes Inc., İstanbul) 160x125x110 cm in dimension with 1000 watt fluorescent tubes (Philips).

Methods

TLC analysis of vehicles

All vehicles subjected to stability test were dissolved in methylene chloride (1%). Samples of 10 μ l applied to the Kieselgehl HF 254 (Merck) plates for detection,

eluted with methanol (12) and were visualised under UV light at 254 nm.

TLC analysis of antioxidants

BHA and BHT were dissolved in ethanol (0.02%) (10). Samples of 10 µl were applied to Silicagel 25/ Kieselguhr 5 plates and eluted with hexane/acetic acid (80:20) visualised with molybdophosphoric acid (5%) and after spraying, heated at 120°C (13).

α-tocopherol was dissolved in ethanol (0.05%) and 5 µl applied to the Silicagel G (Merck) plates, eluted with petroleum ether/diisopropyl ether (80:20) and visualised by fluorescein (0.01%) reagent. Under UV light at 254 nm, yellow spots occurred (13).

α-tocopheryl acetate was dissolved in chloroform (0.05%). 5 µl were applied to Silicagel G plates, eluted with cyclohexane/diethyl ether (4:1), visualised with concentrated sulphuric acid, heated at 105°C (7).

Cysteine was dissolved in ethanol (0.1%). 10µl were applied to Kieselgehl G plates, eluted with butanol/acetic acid/water (48:12:20) and visualised under UV light (14).

Results and Discussion

According to monographs of active ingredients and vehicles in pharmacopeias, there are statements concerning "should be kept in well-closed containers" which might be due to oxidation reasons but in our study, it has been thought that light would also influence the stability of tested antioxidants and vehicles

due to its oxidative effects. Therefore it was investigated to determine whether the "light protection" condition should be added or not. In our study, among tested vehicles, degradation was observed only with vaseline in 4 weeks. It could be concluded from these results that for vehicles except vaseline, there is not any necessity for light protection in the test conditions.

In pharmacopeias, BHA and BHT (1), α-tocopherol (since USP XXI-1985) were registered as antioxidants but there is no record for α-tocopheryl acetate and cysteine. However in many cosmetic preparations including sunscreen preparations, they find use as antioxidants (15). Among these substance, α-tocopherol and α-tocopheryl acetate are often used due to their skin repair effects in sunscreen preparations. Therefore these substances were also investigated in our study for their photostability and antioxidant effectiveness.

It was shown that in case of antioxidants except cysteine, others were degraded. α-tocopherol, BHA, α-tocopheryl acetate and BHT gave degradation products in 2,7,8,11 weeks respectively. The Rf values of the antioxidants and their degradation products

Table 1. Photodegradation of antioxidants in 14 weeks

Antioxidants	BHA	BHT	Cysteine	α-Tocopherol	α-Tocopheryl acetate
Degradation time (week)	7	11	-	2	8
Rf	55	32	16	50	70
Color	Blue	Blue	Brown	Yellow	Yellow
Rf (Degradation product)	29	96	-	90	90

Table 2. Photodegradation of vehicles in 14 weeks

Vehicles	Vaseline	Cetyl alcohol	Paraffin	Propylene glycol	PEG 4000	PEG 400
Degradation time (week)	4	-	-	-	-	-
Rf	0	70	0	77	80	80
Rf(Degradation product)	68	-	-	-	-	-

in various solvent systems and the colors obtained were shown in Table 1. α -tocopheryl acetate is practically unaffected by the oxidizing influence of air and UV light (6). When it is refluxed in acidic and basic solutions in the absence of oxygen, the molecule is hydrolyzed to the free α -tocopherol. Since it was cited as α -tocopheryl acetate is not affected by UV light (7), in our study it was shown that there was degradation in 8 weeks. All vehicles and antioxidants were subjected to light stability tests in a cabinet designed according to Lachman et al.(8,9). TLC analysis were performed to detect the degradation products.

BHA, BHT (0.02%) (10), α -tocopherol and α -tocopheryl acetate (0.05%) (11) were added to vaseline and its photostability was investigated. A suitable stabilizer was recommended for vaseline(1). It was observed that three were degradation in vaseline samples containing α -tocopherol and BHA in 10 weeks whereas α -tocopheryl acetate and BHT containing vaselines were not degraded in 12 weeks. According to our expectations, vaseline with α -tocopheryl acetate was not degraded in testing

and α -tocopheryl acetate were added to vaseline and investigated. The results regarding to this test were shown in Table 3. In our study α -tocopheryl acetate and BHT were found to be as suitable stabilizers for vaseline since vaseline samples including these antioxidants were more resistant to photochemical degradation. This situation reveals that since sunscreen preparations containing vaseline are exposed to sun light frequently so they should be added one of these antioxidants for photostabilization. It should have to be pointed out that choice of suitable antioxidants or determination of usage concentration in formulating cosmetic products which might be exposed to sun light is of prime importance. In this study, among tested antioxidants, BHT was degraded in 11 and α -tocopheryl acetate in 8 weeks. Also in determining the photostability of vaseline with four different antioxidants in various concentrations, it was shown that vaseline samples containing BHT and α -tocopheryl acetate were not degraded during testing time. Due to these results, it

Table 3. Photodegradation of vaseline incorporated with antioxidants in 12 weeks

Antioxidants added to vaseline	BHA 0,02 %	BHT 0,02 %	α -Tocopherol 0,05 %	α -Tocopheryl acetate 0,05 %
Degradation time of Vaseline (week)	10	-	10	-

time whereas vaseline with α -tocopherol was. This result could mean that α -tocopheryl acetate and BHT are more effective than BHA and α -tocopherol as antioxidants even in this case for vaseline. Taking in to account all the results, it could be concluded that the most suitable antioxidant for vaseline might be BHT.

According to the tables of results, among tested antioxidants, only cysteine showed no degradation in 14 weeks. In case of vehicles, only vaseline was found to be photoinstable in 4 weeks and other vehicles were not degraded in testing time of 14 weeks. For this reason, most widely used antioxidants of sunscreen preparations namely BHA, BHT, α -tocopherol

could be concluded that the most photostable and suitable antioxidants in the test conditions are BHT and α -tocopheryl acetate respectively.

References

1. The United States Pharmacopeia (USP XXIII), United States Pharmacopeial Convention Inc. Rockville, MD 20852 USA, 1995
2. British Pharmacopeia, Her Majesty's Stationery Office at the University Press, Cambridge, 1993
3. Deutsches Arzneibuch 9. Ausgabe, Deutscher Apotheker Verlag Stuttgart, Govi-Verlag GmbH Frankfurt, 1986
4. European Pharmacopeia, Council of Europe, Maisonneuve S.A. 57, Sainte Ruffine France, 1975

5. Fiedler, H.P.: Pharm. Ind. 45, 521 (1983)
6. The Merck Index. Eleventh Edition, Merck and Co., Inc., Rahway, N.J., USA, 1989
7. Fluorey, K.: Analytical Profiles of Drug Substances Vol.3, Academic Press, New York, London, 1974
8. Lachman, L., Swartz, C.J.: J.Am.Pharm.Assoc. 49, 213 (1960)
9. Lachman, L.:ibid 48, 226 (1959)
10. Handbook of Pharmaceutical Excipients, American Pharmaceutical Association, Washington DC, 1986
11. Nowak, G.A.: Cosmetic Preparation Vol.1, verlag für chem. Industric H. Ziolkowsky K.G. Augsburg G., 1985
12. Kovar, K.A.: Identifizierung von Arzneistoffen, Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, 1985
13. Stahl, E.: Dünnschicht Chromatographic, Springer-Verlag, Berlin, Heidelberg, New York, 1967
14. Bonker, G.J., Tongue, B.L.: J.Chrom. 12, 52 (1963)
15. Wenniger, J.A.: CTFA Cosmetic Ingredient Handbook, Second Edition, The Cosmetic, Toiletries, and Fragrance Association, Washington D.C. 20036, 1992

Accepted: 25.11.1996