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International Journal of Pharmaceutics 240 (2002) 85–94

international journal of pharmaceutics

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Vitamin A and vitamin A palmitate stability over time and under UVA and UVB radiation

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Received 9 January 2002; received in revised form 25 March 2002; accepted 26 March 2002

Abstract

Vitamin A and vitamin A palmitate photostability were tested in different media. Ethanol and octyl octanoate solutions of these two vitamins, as such and with the addition of sunscreens (3,4 methylbenzilidencanfora, butyl methoxy dibenzoylmethane and octyl methoxycinnamate) or β-carotene and butylated hydroxy toluene, were analysed spectrophotometrically after UVB or UVA irradiation. An O/W fluid emulsion with 0.5% w/w of retinyl palmitate, with and without butylated hydroxy toluene, was prepared. The oil containing the vitamin was extracted with HCl and aluminium sulfate and analysed spectrophotometrically after UVB or UVA irradiation. The fluid emulsion containing retinyl palmitate with and without butylated hydroxy toluene was stored at different temperatures and analysed every week spectrophotometrically for a month. Of the sunscreens tested butyl methoxy dibenzoylmethane showed the strongest protective action towards vitamin A and vitamin A palmitate, whereas β-carotene did not protect either vitamin. Butylated hydroxy toluene inhibited the photodegradation of both vitamins dissolved in octyl octanoate, suggesting that oxygen may be involved in their degradation. O/W emulsion promoted slightly the degradation of vitamin A ester. Butylated hydroxy toluene protected retinyl palmitate from degradation induced by light and heat. © 2002 Published by Elsevier Science B.V.

Keywords: Vitamin A; Vitamin A palmitate; Photostability; O/W emulsion; Solutions; Wrinkled skin

1. Introduction

Skin becomes thin, dry, pale and finely wrinkled with age. The normal stages of epidermal differentiation are maintained over time, but epidermal thinning, associated with a decreased numbers of keratinocytes, is observed histologically (Varani et al., 2000).

Retinoids are a large class of compounds that are important in modern therapy for dermatological treatment of wrinkled skin (Guénin and Zatz, 1995).

Retinol and its congeners are present in all living organisms, either as preformed vitamin A

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0378-5173/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0378-5173(02)00128-X

or as carotenoids, some of which are provitamins A (Vahlquist, 1999).

The concentration of all-*trans*-retinol in the dermis or epidermis is about 200 pmol/g, and that of the long-chain fatty acyl esters of retinol about 2000 pmol/g.

The percentage of retinyl esters in epidermal tissue is higher than in the blood or dermis, and they are precursors of all known biologically active forms of vitamin A (Sorg et al., 1999).

Of the retinoids, retinol and retinyl palmitate are thought to induce thickening of the epidermis and to be effective for treatment of skin diseases (Tsunoda and Takabashy, 1995).

These functional substances, however, are known to be unstable if exposed to light or heat.

A characteristic feature of retinoids is their sensitivity to ultraviolet radiation. UVB and UVA radiation reduce the vitamin A content of the human epidermis (Andersson et al., 1999).

Although retinol and retinyl palmitate are less dangerous than retinoic acid (which, due to its irritative properties, is acceptable only for therapeutic treatment) the effect of ultraviolet on these compounds makes their use in dermatology more difficult.

To increase the stability and decrease the toxicity of retinoic acid, its precursors retinol and retinyl esters (such as palmitate) are employed in formulations for dermatological use (Song et al., 1999).

The aims of this study were to evaluate the best solvent for retinol and retinyl palmitate for use in preparations similar to those commercially available, and to estimate the photostability of vitamin A alcohol and its ester in different solvents and at different initial concentrations to evaluate the influence of these factors on the photostability of these molecules.

Moreover, the protection that sunscreens and antiradicals could offer to the formulations was investigated and cosmetic preparations (O/W emulsions) were formulated with retinyl palmitate; the influence of a vehicle such as an O/W emulsion on the photostability of retinyl palmitate was examined.

2. Materials and methods

2.1. Materials

All-*trans*-retinol, all-trans retinol palmitate and β-carotene were purchased from Sigma. Absolute ethanol and BHT® (butylated hydroxy toluene) were from Carlo Erba. Dragoxat® EH (octyl octanoate) was from Dragoco. Eusolex® 6300 (3,4 methylbenzilidencanphor) and Eusolex® 9020 [butyl methoxy dibenzoylmethane, 1-(4-terzbutilfenil)-3-(4-metossifenil)-1,3-propandione] were from Merk, and Parsol® MCX (octyl methoxycinnamate) was from Guardian Roure S.A. Hydrochloric acid was from Fluka and aluminium sulfate was from Schiapparelli. Montanov® 68 EC (cetearyl alcohol and cetearyl glucoside), Sepigel® 305 (polyacrylamide, C_{13-14} isoparaffin, Laureth 7) were from Seppic, sodium hydroxide was from A.C.E.F. S.p.A., glyceryl monostearate was from Henkel, Gram® 1 (imydazolidinyl urea) and Kathon® CG were from Sinerga S.r.l.

2.2. Instruments

The homogenisers used were Silverson SL 2 and Ultra Turrax 'T 25 basic' (IKA Labortechnik). UVB lamp TL 40/12 RST40T12 and UVA Lamp TL K0540W were used for the radiation tests. Spectrophotometer lambda 2 UV–vis spectrophotometer (Perkin Elmer) and centrifuge 5417 (Eppendorf), were used for the analyses.

2.3. Determination of solubility and molar absorbivity (ε)

To evaluate the possibility of using retinol and retinyl palmitate in cosmetic preparations, the solubility of these two substances in solvents with different lipofilicities and polarities was determined, in order to estabilish the maximum concentration that can be employed.

Concentrated solutions (1.0×10^{-4} M) of retinol and retinyl palmitate in absolute ethanol and in octyl octanoate were prepared to obtain the calibration curves and determine values of ε for both substances in these solvents.

The spectra of diluted solutions: (3.30×10^{-5}, 2.00×10^{-5}, 1.43×10^{-5} and 1.00×10^{-5} M) were recorded over the range 260–400 nm. All measurements were repeated thrice and the means were calculated to plot the graph. The ε value for retinol at 325 nm in absolute ethanol was 54445; in octyl octanoate it was 31434. The ε value for retinyl palmitate at 328 nm in absolute ethanol was 53627; in octyl octanoate it was 55928.

2.4. Radiation tests

To compare solar radiation with that emitted by the lamps, the MED values (minimum dose that produces sunburn) of solar UVB and UVA were compared with the maximum dose of radiation per unit surface (D_R) emitted by the UVB and UVA lamps. In the literature, the UVB solar MED has been evaluated at about 0.020–0.050 J/cm^2 and the UVA solar MED at about 20–50 J/cm^2 (Harry's Cosmetology, 7th edn., 1982, J.B. Wilkinson, R.J. Moore (Eds.), p. 226).

The following equations were used to calculate D_R and P_R:

$$P_R = \frac{P_L}{S} = \text{W/cm}^2 \quad (1)$$

$$D_R = P_R t = \text{J/cm}^2 \quad (2)$$

Eq. (2) was used to calculate D_R, where P_R is the power of the radiation per unit surface (W/cm^2) and t is the maximum time of radiation (s).

P_R was obtained from Eq. (1), where P_L is the power of the lamp declared by the manufacturer and S is the lateral surface of the emission cylinder, whose length is that of the lamp, and whose height is the distance of the container from the light source.

P_L for the UVB lamp was 4.5 W and for the UVA lamp was 40 W. The length of the UVB lamp was 120 cm and that of the UVA lamp was 60 cm.

The distance of the container from the lamp was in both cases 10 cm and the maximum time of radiation was 12000 s.

For the UVB lamp, P_R was calculated to be 5.97×10^{-4} W/cm^2 and D_R was calculated to be 7.165 J/cm^2.

For the UVA lamp, P_R was calculated to be 1.066×10^{-2} W/cm^2 and D_R was calculated to be 127.39 J/cm^2.

The MED value was below the radiation dose per unit of surface caused by both lamps.

Comparing the power of radiation per unit surface of both lamps with that of solar radiation (1.3×10^{-4} W/cm^2 for UVB and 1.08×10^{-3} W/cm^2 for UVA) it was clear that the lamps were stronger than the sun's radiation.

Samples of retinol and retinyl palmitate in different solvents were irradiated with the UVB and with the UVA lamps. The samples were analysed spectrophotometrically at pre-determined times, after dilution, to detect changes of absorbance, peak structure and molar concentrations.

Five millilitres of a 1.0×10^{-3} M retinol solution in ethanol (95% w/w) were irradiated in closed pyrex containers without stirring under the UVB lamp for 3 h. Set sample amounts diluted 1:30 were analysed spectrophotometrically every 40 min. Similar solutions of retinol with the addition of 0.5×10^{-4} M β-carotene, or of sunscreens (Parsol® MCX (1.6×10^{-4} M and 3.2×10^{-4} M), Eusolex® 6300 (1.6×10^{-4} M and 3.2×10^{-4} M) or Eusolex® 9020 (3.0×10^{-4} M)), were irradiated in the same conditions.

Similar solutions of β-carotene or sunscreen alone in ethanol were irradiated in the same conditions.

Five millilitres of 2.0×10^{-3} M solution of retinol (95% w/w) in octyl octanoate, alone or with 0.01% w/w BHT®, were irradiated (without stirring) in closed containers under the UVB or UVA lamp for 200 min. Aliquots diluted 1:50 were analysed spectrophotometrically every 50 min.

Five millilitres of 1.5×10^{-3} M solution of retinyl palmitate (88% w/w) in ethanol, alone or with Eusolex® 9020 (3.0×10^{-4} M), were irradiated in closed containers without stirring under the UVB or UVA lamp for 200 min. Aliquots diluted 1:50 were analysed spectrophotometrically.

Five millilitres of 5.5×10^{-2} M of retinyl palmitate solutions (88% w/w) in octyl octanoate, alone or with 0.01% w/w BHT®, were irradiated and analysed in the same conditions.

To study the relation between retinyl palmitate degradation rate under radiation and the initial concentration, 1.0×10^{-3}, 1.0×10^{-2}, 3.0×10^{-2} and 5.5×10^{-2} M vitamin A palmitate solutions in octyl octanoate were irradiated under the UVB or UVA lamp as above.

The results enabled us to determine the behaviour of retinol and retinyl palmitate under light, with and without sunscreens or antiradicals, in different solvents and at different initial concentrations, and to establish a relation among additives, solvents, concentrations and photostability of the two vitamins. The irradiation tests were also performed on an emulsion (O/W fluid emulsion with Montanov® 68 EC). Containers with 5 g of emulsion (with 0.5% w/w of retinyl palmitate corresponding to 5.5×10^{-2} M) with and without 0.01% w/w BHT® were irradiated with UVB or UVA. Every 30 min, for a maximum of three hours, aliquots were analysed spectrophotometrically ($\lambda = 328$ nm) after extracting the oil solution of retinyl palmitate from the O/W emulsion.

2.5. Extraction of retinyl palmitate from the emulsion

Aluminum sulfate (0.75 g), 14.25 g of HCl (37% w/v) and 5 g of emulsion were placed in a test tube. The tube was shacken under vortex, then centrifuged at 6000 rpm for 30 min and then at 13000 rpm for 10 min. The oil was taken out, washed twice with water and centrifuged twice at 13000 rpm for 5 min, diluted 1:1800 and analysed spectrophotometrically to determinate the retinyl palmitate percentage actually extracted; the extraction percentage was calculated to be about 99%.

2.6. Preparation of O/W fluid emulsion with Montanov® 68 EC

Vitamin A palmitate (0.568 g) was dissolved in 9.432 g of octyl octanoate using a magnetic stirrer. Three grams of Montanov® 68EC was added to 10 g of octyl octanoate and heated to 60–70 °C. Two-thirds of the total water was warmed at about 80 °C. The lipid phase was then added under homogenizer to the hot water. The preservative (0.05 g of Kathon® CG) was added to the remaining cold water. The emulsion was brought to 25 °C under stirring and solutions of vitamin A and Kathon CG were added.

Composition of O/W emulsion:

	O/W fluid emulsion with Montanov® 68 EC
Octyl octanoate	19.432 g
Retinyl palmitate	0.568 g
Montanov® 68 EC	3.0 g
Kathon® CG	0.05 g
Water	q.s. to 100 g

2.7. Stability over time of O/W fluid emulsion

Three containers with 100 g of O/W emulsion (O/W fluid emulsion with Montanov® 68 EC) were stored under different conditions: 25 °C with 0.01% w/w BHT®, 25 °C without BHT® (0.01% w/w) and 3–5 °C without BHT® (0.01% w/w).

Every 7 days for 1 month, 5 g of emulsion were taken from each container, and the octyl octanoate solution extracted from the emulsion was analysed spectrophotometrically. The stability of retinyl palmitate over time and the influence of temperature on the protection of vitamin A palmitate without and in the presence of antioxidant were thus investigated.

3. Results

3.1. Vitamin A photostability

Fig. 1 shows the difference between the initial

concentration (C_0) and that measured at different times (C_t) in a 1.0×10^{-3} M retinol solution in ethanol irradiated under UVB as such, and with the addition of 0.5×10^{-4} M β-carotene or sunscreens: 1.6×10^{-4} or 3.2×10^{-4} M 3,4 methylbenzilidencanfora; 3.0×10^{-4} M butyl methoxy dibenzoylmethane; 1.6×10^{-4} or 3.2×10^{-4} M octyl methoxycinnamate.

The absorbance of β-carotene or sunscreen was obtained spectrophotometrically at 325 nm, without irradiation and under UVB and UVA irradiation and then was subtracted from that of vitamin A before calculating the molar concentrations. Fig. 2 shows the absorbance of these additives versus time.

The results of UVB and UVA irradiation of a 2.0×10^{-3} M retinol solution in octyl octanoate, as such and with 0.01% w/w BHT®, are shown in Fig. 3, where the difference between the initial concentration (C_0) and those measured at different times (C_t) is reported versus time. The straight-line equations for the data in Figs. 1 and 3 are in Table 1.

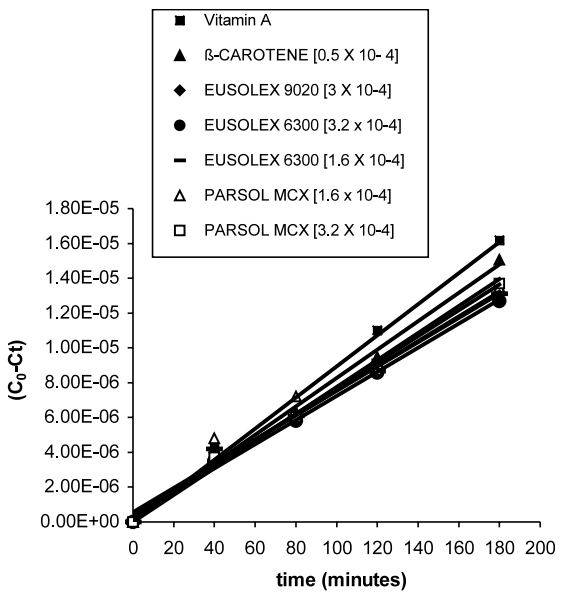

Fig. 1. C_0-C_t vs. time for a solution 1.0×10^{-3} M of retinol in ethanol irradiated under UVB as such, and with: 0.5×10^{-4} M β-carotene; 1.6×10^{-4}, 3.2×10^{-4} M 3,4 methylbenzilidencanfora; 3.0×10^{-4} M butyl methoxy dibenzoilmethane; 1.6×10^{-4}, 3.2×10^{-4} M octyl methoxycinnamate, under UVB radiations.

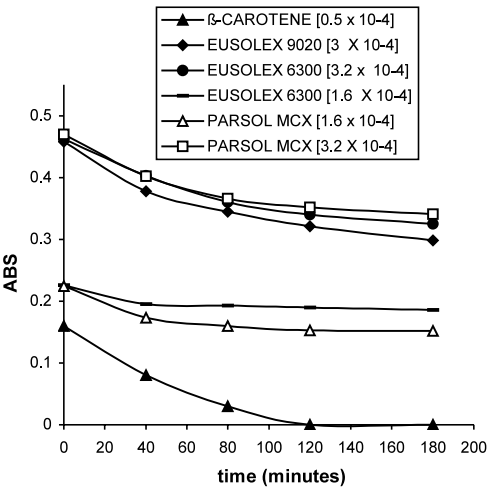

Fig. 2. Absorbance versus time of ethanol solutions of β-carotene (0.5×10^{-4} M); 3,4 methylbenzilidencanfora (1.6×10^{-4}, 3.2×10^{-4} M); butyl methoxy dibenzoylmethane (3.0×10^{-4} M); octyl methoxycinnamate (1.6×10^{-4}, 3.2×10^{-4} M), under UVB radiations.

3.2. Vitamin A palmitate photostability

Fig. 4 shows the plot of C_0-C_t versus time for a 1.5×10^{-3} M solution of retinyl palmitate in ethanol irradiated under UVB or UVA, as such or with the addition of 3.0×10^{-4} M butyl metoxy

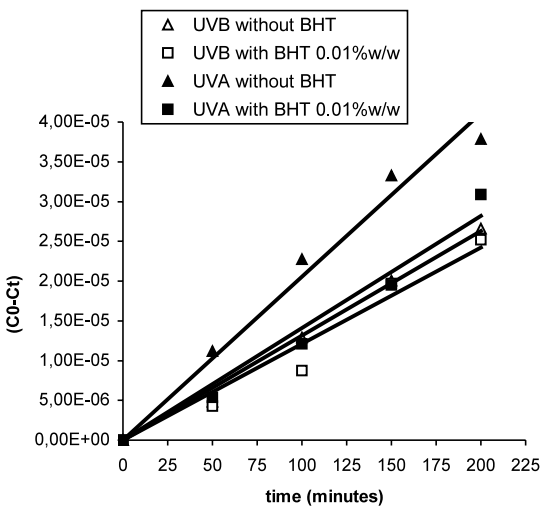

Fig. 3. C_0-C_t vs. time for a 2.0×10^{-3} M retinol solution in octyl octanoate, as such and with 0.01% w/w BHT®, under UVB or UVA radiations.

Table 1
Straight-line equations for the data in Figs. 1 and 3

Ethanol solution UVB straight-line equations	
Vit. A 1.0×10^{-3} M	$y=8.93\times10^{-8}x$, $R^2=0.989$
Vit. A 1.0×10^{-3} M, β-carotene 0.5×10^{-4} M	$y=8.23\times10^{-8}x$, $R^2=0.995$
Vit. A 1.0×10^{-3} M, parsol MCx, 1.6×10^{-4} M	$y=7.75\times10^{-8}x$, $R^2=0.955$
Vit. A 1.0×10^{-3} M, parsol MCX 3.2×10^{-4} M	$y=7.64\times10^{-8}x$, $R^2=0.996$
Vit. A 1.0×10^{-3} M, eusolex 9020 3.0×10^{-4} M	$y=7.45\times10^{-8}x$, $R^2=0.989$
Vit. A 1.0×10^{-3} M, eusolex 6300 1.6×10^{-4} M	$y=7.40\times10^{-8}x$, $R^2=0.983$
Vit. A 1.0×10^{-3} M, eusolex 6300 3.2×10^{-4} M	$y=7.15\times10^{-8}x$, $R^2=0.995$
Octyl octanoate solution UVA straight-line equations	
Vit. A 2×10^{-3} M	$y=2.05\times10^{-7}x$, $R^2=0.977$
Vit. A 2×10^{-3} M, BHT 0.01% w/w	$y=1.41\times10^{-7}x$, $R^2=0.972$
Octyl octanoate solution UVB straight-line equations	
Vit. A 2×10^{-3} M	$y=1.31\times10^{-7}x$, $R^2=0.993$
Vit. A 2×10^{-3} M, BHT 0.01% w/w	$y=1.21\times10^{-7}x$, $R^2=0.960$

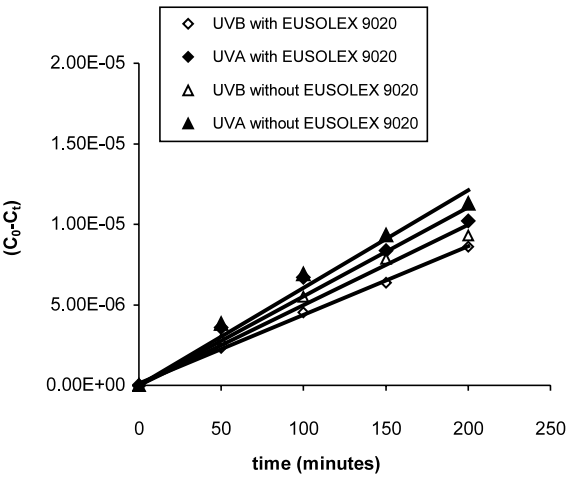

Fig. 4. C_0-C_t vs. time for a 1.5×10^{-3} M solution of retinyl palmitate in ethanol as such or with 3.0×10^{-4} M butyl methoxy dibenzoylmethane, under UVB or UVA radiations.

from the straight lines equations in Table 3) is as follows:

$$\log_{10} K = m \log_{10}\frac{1}{c} + a$$

where K is the kinetic constant obtained as the slope of the straight-line graphs for the different concentrations, c is the molar concentration of

benzoilmethane. Fig. 5 reports C_0-C_t versus time for a 5.5×10^{-2} M solution of vitamin A palmitate in octyl octanoate, under UVB or UVA radiations, as such or with the addition of 0.01% w/w BHT®.

The straight-line equations for the data in Figs. 4 and 5 are in Table 2.

3.3. Dependence of degradation rate of vitamin A palmitate on the initial concentration of the solution

Fig. 6 reports C_0-C_t versus time for solutions of retinyl palmitate in octyl octanoate at four different concentrations irradiated under UVB or UVA.

The relationship between the kinetic constants obtained at different concentrations and the initial concentration of vitamin A palmitate (derived

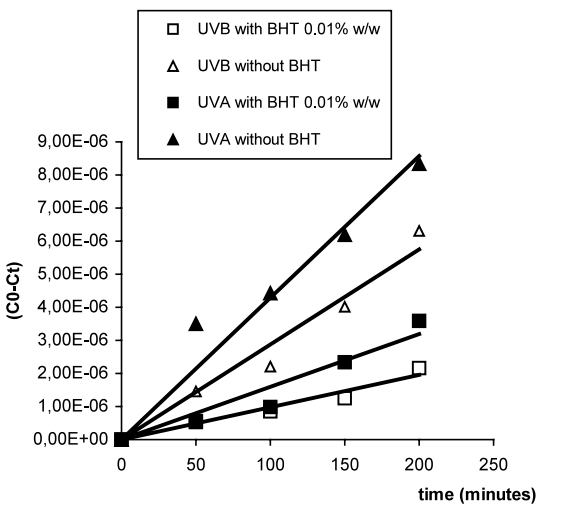

Fig. 5. C_0-C_t vs. time for a 5.5×10^{-2} M solution of vitamin A palmitate in octyl octanoate as such or with 0.01% w/w BHT®, under UVB or UVA radiations.

Table 2
Straight-line equations for the data in Figs. 4 and 5

Ethanol solution UVA straight-line equations	
Vit. A palm. 1.5×10^{-3} M	$y=6.05\times10^{-8}x$, $R^2=0.974$
Vit. A palm. 1.5×10^{-3} M, eusolex 9020 3.0×10^{-4} M	$y=5.53\times10^{-8}x$, $R^2=0.957$
Ethanol solution UVB straight-line equations	
Vit. A palm. 1.5×10^{-3} M	$y=4.8\times10^{-8}x$, $R^2=0.983$
Vit. A palm. 1.5×10^{-3} M, eusolex 9020 3.0×10^{-4} M	$y=4.33\times10^{-8}x$, $R^2=0.998$
Octyl octanoate solution UVA straight-line equations	
Vit. A palm. 5.5×10^{-2} M	$y=4.28\times10^{-8}x$, $R^2=0.949$
Vit. A palm. 5.5×10^{-2} M, BHT 0.01% w/w	$y=1.59\times10^{-8}x$, $R^2=0.929$
Octyl octanoate solution UVB straight-line equations	
Vit. A palm. 5.5×10^{-2} M	$y=2.88\times10^{-8}x$, $R^2=0.964$
Vit. A palm. 5.5×10^{-2} M, BHT 0.01% w/w	$y=9.77\times10^{-9}x$, $R^2=0.955$

Table 3
Straight-line equations for the data in Fig. 6

Octyl octanoate solution UVA straight-line equations	
Vit. A palmitate 1×10^{-3} M	$y=7.07\times10^{-8}x$, $R^2=0.972$
Vit. A palmitate 1×10^{-2} M	$y=5.72\times10^{-8}x$, $R^2=0.981$
Vit. A palmitate 3×10^{-2} M	$y=4.75\times10^{-8}x$, $R^2=0.988$
Vit. A palmitate 5.5×10^{-2} M	$y=4.28\times10^{-8}x$, $R^2=0.949$
Octyl octanoate solution UVB straight-line equations	
Vit. A palmitate 1×10^{-3} M	$y=7.47\times10^{-8}x$, $R^2=0.936$
Vit. A palmitate 1×10^{-2} M	$y=5.37\times10^{-8}x$, $R^2=0.938$
Vit. A palmitate 3×10^{-2} M	$y=3.62\times10^{-8}x$, $R^2=0.988$
Vit. A palmitate 5.5×10^{-2} M	$y=2.88\times10^{-8}x$, $R^2=0.964$

vitamin A, m is the slope of the logarithmic graph and a is its interception on the x axis.

Fig. 7 plots the $\log_{10}$ of the kinetic constants against $\log_{10}$ of the inverse concentrations of solutions of retinyl palmitate in octyl octanoate at the four different concentrations irradiated under UVB or UVA. The equations of the straight-line relating the degradation constants measured for the vitamin A ester to the initial concentrations are:

$$\log_{10} K = 0.1234\ 1/c - 7.511\ (R^2=0.975)\ \text{under UVA}$$

$$\log_{10} \mathrm{K} = 0.2312\ 1/c - 7.794\ (R^2=0.941)\ \text{under UVB}$$

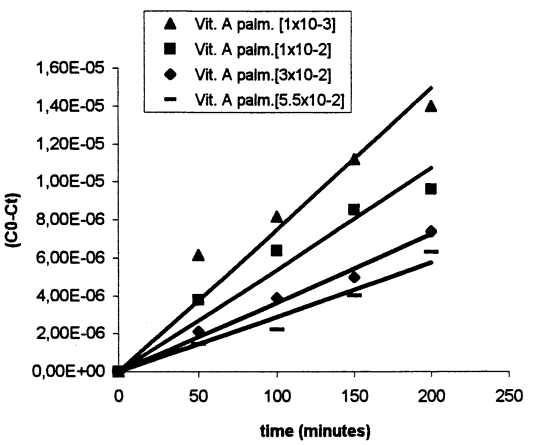

Fig. 6. C_0-C_t vs. time for solutions of retinyl palmitate in octyl octanoate at four different concentrations (1.0×10^{-3} M, 1.0×10^{-2} M, 3.0×10^{-2} M and 5.5×10^{-2} M), under UVB or UVA radiations.

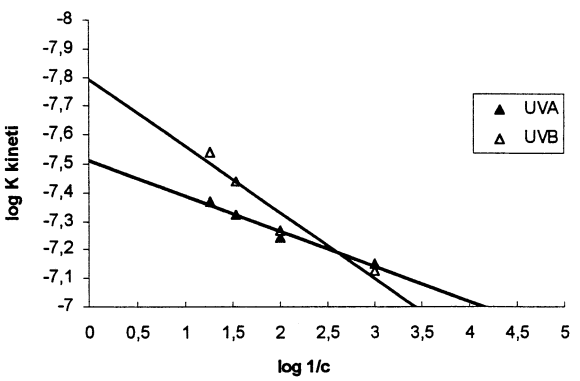

Fig. 7. Log_{10} of the kinetic constants against $\log_{10}$ of the inverse concentrations of solutions of retinyl palmitate in octyl octanoate at four different concentrations (1.0×10^{-3} M, 1.0×10^{-2} M, 3.0×10^{-2} M and 5.5×10^{-2} M), under UVB or UVA radiations

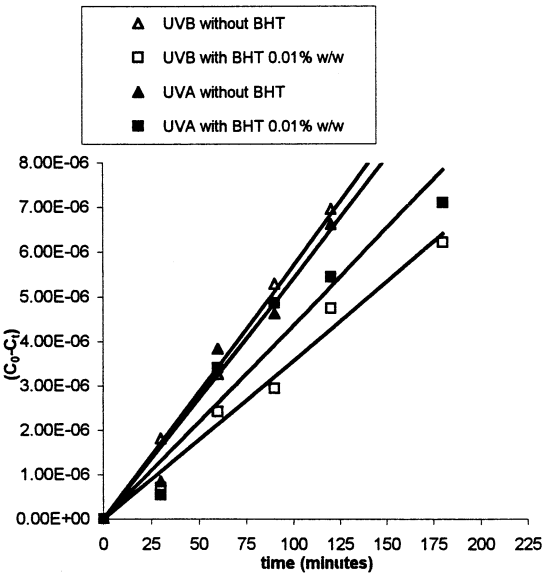

Fig. 8. C_0-C_t vs. time of 5.5×10^{-2} M retinyl palmitate in octyl octanoate solution, in the presence or in the absence of 0.01% w/w BHT®, extracted from an O/W fluid emulsion, under UVA or UVB radiations.

The vitamin degradation-rate depends inversely on the initial concentration.

3.4. Photostability of the O/W fluid emulsion with retinyl palmitate

Fig. 8 shows the plot of C_0-C_t of retinyl palmitate extracted from an O/W fluid emulsion with 0.5% w/w vitamin A ester (5.5×10^{-2} M octyl octanoate extracted solution) versus time under UVA or UVB radiation, in the presence or in the absence of 0.01% w/w BHT®.

Table 4
Straight-line equations for the data in Fig. 8

Octyl octanoate solution UVA straight-line equations	
Vit. A palm. 5.5×10^{-2} M	$y=5.24\times10^{-8}x$, $R^2=0.984$
Vit. A palm. 5.5×10^{-2} M, BHT 0.01% w/w	$y=4.36\times10^{-8}x$, $R^2=0.932$
Octyl octanoate solution UVB straight-line equations	
Vit. A palm. 5.5×10^{-2} M	$y=5.71\times10^{-8}x$, $R^2=0.999$
Vit. A palm. 5.5×10^{-2} M, BHT 0.01% w/w	$y=3.57\times10^{-8}x$, $R^2=0.984$

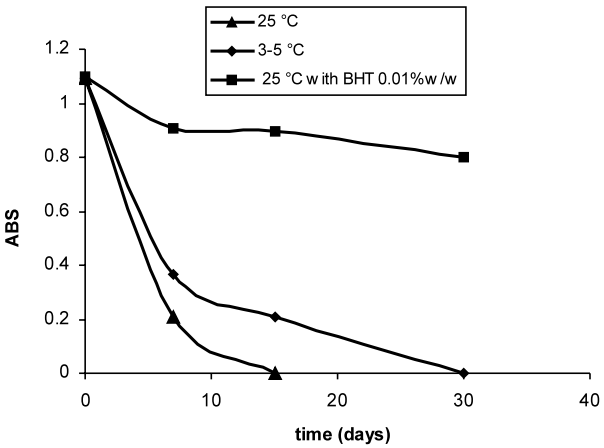

Fig. 9. Absorbance versus time of 5.5×10^{-2} M solution of vitamin A palmitate in octyl octanoate extracted from an O/W fluid emulsion stored under three different conditions: 3–5 °C as such, 25 °C as such and 25 °C with the addition of 0.01% w/w BHT®.

The straight-line equations for the data in Fig. 8 are in Table 4.

3.5. Stability over time

Fig. 9 reports the absorbance versus time of 5.5×10^{-2} M solution of vitamin A palmitate in octyl octanoate extracted from an O/W fluid emulsion stored under three different conditions: 3–5 °C as such, 25 °C as such and 25 °C with the addition of 0.01% w/w BHT®.

4. Discussion

4.1. Photostability of vitamin A

The sunscreens and β-carotene do not protect the vitamin A ethanol solution very well, probably due to the low initial vitamin concentration (1×10^{-3} M), which might increase the speed of retinol degradation. β-Carotene provides least protection of vitamin A, while 3,4 methylbenzilidencanfora (3.2×10^{-4} M ethanol solution) provides the best, but, after 150 min of irradiation it shifts the maximum λ of retinol from 325 to 311 nm, suggesting a modification of the molecular structure of vitamin A. The best sunscreen, which

does not shift the maximum λ, is butyl metoxy benzoilmethane (3.0×10^{-4} M ethanol solution).

The sunscreens used, irradiated as such as solution in ethanol, showed an initial higher degradation, after which they remained constant over time. The absorbance of β-carotene decreased more than that of the sunscreens, which might explain the low protection it gives to the vitamin by this substance.

The concentration of the solutions of retinol in octyl octanoate decreased more under UVA than under UVB possibly since the ABS maximum (325 nm) of the vitamin has only a tail in the UVB range but is centred within the UVA range.

BHT® provides good protection for retinol, which might suggest that the photodegradation mechanism is an oxidative one. BHT® provides better protection under UVA than under UVB.

Comparing the data relative to solutions in ethanol and in octyl octanoate, vitamin A degrades more quickly in oil than in alcohol.

4.2. Photostability of vitamin A palmitate

Buthyl metoxy benzoilmethane was also found to provide protection for retinyl palmitate under UVB and UVA irradiation. The protection given by this substance to vitamin A ester is similar to that given to vitamin A. Retinyl palmitate solution in octyl octanoate also decrease more under UVA than under UVB. BHT® provides better protection to vitamin A ester than it does to vitamin A.

4.3. Dependence of the degradation-rate of vitamin A palmitate on the initial concentration of the solution

The degradation rate of vitamin A ester varies inversely with its initial molar concentration.

More concentrated systems have greater stability; this tendency is more marked under UVB than under UVA irradiation.

4.4. Photostability of O/W fluid emulsion with retinyl palmitate

Vitamin A palmitate is slightly less stable under irradiation (especially under UVB) when in O/W emulsion as a solution than in octyl octanoate, possibly because it is located at the O/W interface and the aqueous medium could negatively influence the stability of vitamin A palmitate (Tsunoda and Takabashy, 1995). BHT® protects the solution better than it does the O/W emulsion containg retinyl palmitate.

4.5. Stability over time

BHT is important for the correct protection of O/W emulsions over time. The degradation curve of vitamin A palmitate in the emulsion with the addition of 0.01% w/w of BHT® shows an initial slight decrease and then remains constant over time.

An antioxidant, such as BHT®, thus appears essential for the protection of emulsions containing retinyl ester. Temperature also influences the degradation over time. Heat is a possible factor responsible for retinyl palmitate degradation.

5. Conclusions

Vitamin A palmitate is more stable than vitamin A; thus, in dermatological formulations it is better to use, retinyl ester than retinol. Under irradiation, ethanol solutions are more stable than oil solutions, but oil solutions are more stable than O/W emulsions. The degradation process of these two molecules has an oxidative mechanism, thus the use of an antioxidant is necessary for their proper storage over time. Sunscreens are not good protectors for either vitamins, under UVB or under UVA irradiation.

Degradation of vitamin A palmitate solutions depends inversely on their initial molar concentration.

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