



ELSEVIER

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Immobilization of kojic acid in ZnAl-hydrotalcite like compounds

Valeria Ambrogi^{a,*}, Luana Perioli^a, Morena Nocchetti^b, Loredana Latterini^c, Cinzia Pagano^a, Elena Massetti^a, Carlo Rossi^a^a Dipartimento di Chimica e Tecnologia del Farmaco, Università di Perugia, Via del Liceo 1, 06123 Perugia, Italy^b Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy^c CEMIN-Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

ARTICLE INFO

Article history:

Received 23 July 2011

Received in revised form

18 September 2011

Accepted 5 October 2011

Available online 12 October 2011

Keywords:

A. Inorganic compounds

B. Chemical synthesis

C. Infrared spectroscopy

C. Thermogravimetric analysis

C. X-ray diffraction

ABSTRACT

Kojic acid (KOJ) is a melanin synthesis inhibitor widely used as skin lightening agent in topical preparations. Unfortunately it is easily susceptible to photo-oxidation, phenomenon responsible for chemical and organoleptic modifications. The aim of this work was the intercalation of KOJ in hydrotalcite-like compounds (HTlc) in order to stabilize KOJ and to reduce its photolability. Hydrotalcite containing Zn and Al (ZnAl-HTlc) was used as host to obtain the final compound ZnAl-HTlc-KOJ. The intercalation was carried out, after many attempts, by ionic exchange mechanism by means of the strong base EtO⁻ in anhydrous ethanol/dimethylsulfoxide (DMSO) mixture as solvent in order to generate KOJ⁻ anions. The final product was characterized by the X-ray powder diffraction (XRPD), FT-IR spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and elemental analysis. The intercalated compound was formulated in a siliconic water free self-emulsifying ointment and the in vitro release profile was evaluated. All samples (intercalation compound and its formulation) were submitted also to spectrophotometric assays in order to evaluate the matrix protective effect towards ultraviolet rays.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Recently a gradual increase in the realization of skin lightening [1] products has been observed. This is strictly connected to the growth of skin hyperpigmentation problems. Actually, many products such as on prescription, over-the-counter (OTC) and cosmetics, are on the market for the treatment of this kind of skin conditions. Unfortunately, among the available formulations, it is not easy to find a topical regimen that fits with the requirements of safety and efficacy [2].

Hydroquinone is one of the most effective agents in the hyperpigmentation therapy. Actually, this molecule is not employed in UE and USA cosmetic market because of its side effects, namely allergies, irritant dermatitis, acneiform eruptions, telangectasias and fungal and bacterial infections (folliculitis and impetiginous lesions). However, the hydroquinone is still used in Africa, although it is the cause of frequent cutaneous complications [3,4]. Because of these side effects, studies on alternative depigmenting agents have been encouraged; one of the most promising is KOJ (Fig. 1). It is a fungal metabolite produced by many species of *Aspergillus*, *Acetobacter* and *Penicillium*. It is used

* Corresponding author. Tel.: +39 0755855135; fax: +39 0755855135.
E-mail address: valeria.ambrogi@unipg.it (V. Ambrogi).

as a food additive for preventing enzymatic browning and, as a cosmetic agent, for skin whitening because of its excellent inhibitory activity on the polyphenol oxidase (tyrosinase) [5]. It is the most popular agent employed for the treatment of melasma and it can be combined with other skin lighteners. Unfortunately, it is easily susceptible to oxidation after sunlight exposure, pH and temperature variations [6,7]. KOJ both in solution and in cosmetic formulations browns because of its oxidation or it turns red because of its complexation with metal ions like iron. This behavior is responsible for its chemical and organoleptic modifications, while skin-lightening efficacy decreases [6]. Recently, KOJ has been evaluated also as potential radioprotective agent that can improve the tolerance of normal tissue to radiation [8].

Hydrotalcite-like compounds [9] have been proposed as matrices able to increase sunscreen photostability such as p-aminobenzoic acid (PABA), 4-benzophenone and phenylbenzimidazole sulfonic acid [10,11]. Therefore, these matrices may represent a new strategy to improve KOJ stability. Hydrotalcites are natural anionic lamellar solids with positively charged layers balanced by exchangeable anions [9]. They have the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_n^{n-}]^x-m S$, where M(II) is a bivalent metal cation, M(III) is a trivalent metal cation (usually Al), Aⁿ⁻ is an exchangeable inorganic or organic anion that compensates the positive charge of the layer, m are the moles of solvent S, usually co-intercalated water for mole of compound.

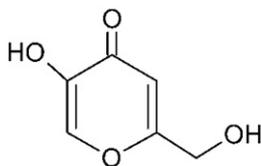


Fig. 1. KOJ (5-hydroxy-2-hydroxymethyl-4H-pyran-4-one) chemical structure.

An intercalated anion can be replaced by another via ion-exchange mechanism and for this reason the interlayer region of a lamellar host can be considered a microvessel where an anionic molecule may be stored [12,13].

The aim of this research work was to store the KOJ anions (KOJ^-) in the HTlc interlayer region. For this purpose, ZnAl-HTlc was chosen as lamellar host because for its good photoprotection [11].

Al and Zn are metals largely used both in pharmaceutical and cosmetic formulations, the first as salt for astringent activity, the second as oxide (ZnO) for sun photoprotection [14] and dermatologic treatments, as zinc ions are known to have a critical and important role in overall skin health [15].

This paper proposes KOJ^- intercalation into HTlc to improve its photostability and release.

2. Experimental

2.1. Materials

Well crystallized $[\text{Zn}_{0.69}\text{Al}_{0.31}(\text{OH})_2](\text{NO}_3)_{0.31} \cdot 0.4\text{H}_2\text{O}$ was obtained by co-precipitating ZnCl_2 (obtained dissolving ZnO with HCl 12 M) and AlCl_3 , from 'homogeneous solution' using urea as precipitant reagent [16]. The obtained Zn(II) and Al(III) hydroxycarbonate (HTlc-CO_3) was converted into nitrate form by ion exchange with HNO_3 0.1N titration [16].

KOJ, liquid paraffin and silicon oil were provided by Comifarm, (Perugia, Italy). Hydrochloric acid, nitric acid, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, ZnO, NaOH and metallic sodium were purchased from Carlo Erba (Milano, Italy). Cetylstearyl alcohol and cetomacrogol 1000 were purchased from ACEF (Firenze, d'Arda Piacenza, Italy). Other chemicals and solvents were of reagent grade and were used without further purification.

2.2. Intercalation of KOJ into HTlc- NO_3 (HTlc-KOJ)

Metallic sodium (0.93 g) was slowly added to a mixture of dry ethanol (200 ml) and DMSO (150 ml) in order to obtain a stoichiometric amount of ethoxy anions and then KOJ (5.62 g; molar ratio $\text{ethoxy}^-/\text{KOJ}^-$ 1/1) was added giving rise to a light yellow solution. After few minutes, HTlc- NO_3 (4.95 g) was added (molar ratio $\text{NO}_3^-/\text{KOJ}^-$ 1/1.5) and the resulting suspension was stirred at room temperature for 24 h. The solid was filtered and washed three times with a mixture of dry ethanol/DMSO 1/1). The product was dried at ca. 40 °C under vacuum and was stored in a desiccator over P_2O_5 under vacuum.

2.3. Characterization

XRPD spectra were achieved by a PW 1710 Philips diffractometer (Philips, Almelo, The Netherlands), using the Ni-filtered $\text{Cu K}\alpha$ radiation.

DSC analyses were carried out using an automatic thermal analyzer (Mettler Toledo DSC 821^e, Italy). Temperature calibrations were performed with indium as standard. Sealed and holed aluminum pans were used for all samples and an empty pan prepared in the same way was used as a reference. Samples of 3–6 mg were

weighted directly into the aluminum pans and thermal analyses were conducted at a scanning rate of 5 °C/min from 25 to 200 °C.

FT-IR spectra were recorded in KBr dispersion on a Jasco model FT-IR-410, 420 Herschl series (Jasco Corporation Tokyo, Japan) using the EasiDiff Diffuse Reflectance Accessory. Samples were prepared by gently grinding the powder with KBr.

TGA were performed by a Stanton Redcroft STA 781 thermo-analyzer (Stanton-Redcroft, US) at heating rate of 10 °C min^{-1} in airflow 30 ml min^{-1} .

The KOJ content was determined by UV spectrophotometry (spectrophotometer Agilent 8453) at $\lambda_{\text{max}}=269.0$ nm.

$^1\text{H-NMR}$ spectra were recorded by Bruker AC 200 instrument (200 MHz) in deuterium chloride.

Metal analyses were performed by Varian 700-ES series Inductively Coupled Plasma-Optical Emission Spectrometers (ICP-OES, Palo Alto-CA, USA) using solutions prepared by dissolving the samples in concentrated HNO_3 that were then properly diluted.

Elemental analysis were performed using EA 1108 CHN Fisons Instruments.

2.4. Preparation of ZnAl-HTlc-KOJ formulation

A silicone oil ointment (Table 1) containing ZnAl-HTlc-KOJ was prepared as reported below: cetylstearyl alcohol and cetomacrogol 1000 were mixed in a steam bath and then paraffin oil and silicone oil were added slowly under stirring. The mixture was stirred until cooling and finally the intercalation product was added. The final KOJ concentration was 2.5%.

2.5. In vitro release studies

The formulation was submitted to dissolution test using the "Petri disk" method [10,17] in sink conditions: 200 mg of formulations were spread on the Petri disk (50 mm diameter) with a spatula to produce a uniform surface of constant dimensions. The dissolution vessels, closed on the top, were kept in a thermostatically controlled water bath at 32 °C. Phosphate buffer pH 5.5 (100 ml) (F.U.XII) was used as dissolution medium and the paddle rotation speed was kept at 60 rpm [18]. At predetermined times, 2 ml aliquots were removed and analyzed spectrophotometrically at λ_{max} 269.0 nm. The removed aliquots were replaced with the same volume of medium. Tests were made in triplicate and the results were recorded as an average.

2.6. Photostability studies

Absorption spectra of the solid samples were recorded by a Varian (Cary 4000) spectrophotometer, equipped with a 150 mm integration sphere and a barium sulphate tablet was used as reference. The spectra were analyzed by the Kubelka-Munk equation in order to make the comparison possible. Steady state irradiation experiments were performed by a Xenon lamp as light

Table 1

Silicone oil ointment	
Ingredient	amount (% w/w)
cetylstearyl alcohol	16.0
cetomacrogol 1000	4.0
paraffin oil	35.0
silicone oil	35.0
ZnAlHTlc-KOJ	10.0

source and by a monochromator selecting the excitation wavelength (330 nm). Samples were irradiated for a period of 2 h.

3. Results and discussion

3.1. Preparation and characterization of ZnAl-HTlc-KOJ

Synthetic ZnAl-HTlc in the carbonate form, prepared as previously described, was not suitable for KOJ intercalation because it is well known that carbonate ions are strongly held in the interlayer region [19] making very difficult its replacement with other anions. Therefore, since monovalent anions, as NO_3^- , are more easily replaced than carbonates, ZnAl-HTlc- CO_3 was converted into its nitrate form [16,20] and KOJ intercalation was performed via ionic exchange in water at pH 11.0. Unfortunately the first attempt failed, since XRPD spectra (data not reported) showed a peak at 0.76 nm typical of hydroxyl or carbonate forms and KOJ intercalation did not occur probably because of the acid-base properties of KOJ^- anions, which, behaving as relatively strong Brønsted base ($\text{pK}_a=7.9$ [21]), deprotonate the water molecules of the solvent by giving rise to OH^- intercalation. Moreover, despite the intercalation process has been performed using CO_2 -free deionized water and the procedure was conducted under nitrogen atmosphere, the complete absence of CO_2 could not be assured during all steps. However, the intercalation product was successfully prepared by working in anhydrous conditions, generating KOJ^- through the strong base EtO^- in a mixture of ethanol and DMSO suitable to solve the organic acid. In this case ZnAl-HTlc-KOJ XRPD showed an increase of the interlayer distance as a consequence of KOJ^- intercalation. The intercalation product was washed with CO_2 -free deionized water to eliminate the inorganic ions and the organic material eventually adsorbed (KOJ or its anions). Unfortunately, during this process KOJ^- de-intercalation occurred, phenomenon associated to its basic nature. Thus, in order to prevent KOJ^- de-intercalation, instead of water, the anhydrous mixture of ethanol and DMSO was used to wash ZnAl-HTlc-KOJ. Fig. 2 shows the XRPD of ZnAl-HTlc-KOJ wet (Fig. 2b) and dried at 40°C under vacuum compared with that of pristine ZnAl-HTlc- NO_3 (Fig. 2a). The peaks of ZnAl-HTlc- NO_3 were indexed by comparing them with the patterns of ZnAl-HTlc in chloride form, which has already been indexed based on its structural parameters [22]. The pattern of the wet ZnAl-HTlc-KOJ shows two 003 reflections at 1.58 and

1.29 nm relative to the KOJ^- intercalation. The interlayer distance of 1.58 nm can be attributed to ethanol and KOJ^- co-intercalation. Indeed, in the dried ZnAl-HTlc-KOJ XRPD this 003 reflection greatly decreases whereas the 003 reflection at 1.29 nm increases. The 003 reflection due to the nitrate anions (0.9 nm) decreases remarkably and the basal space became smaller than that of the pristine ZnAl-HTlc- NO_3 indicating the presence of nitrate ions oriented in the interlayer with the plane formed by NO_3^- parallel to the layer [23]. The formula of intercalated product was obtained through many techniques. The content of Al and Zn (determined by ICP) in the intercalation compound showed a Al molar fraction=0.31. Elemental analysis allowed to evaluate the amount of nitrogen (relative to nitrate anion not exchanged), sulphur (relative to DMSO) and hydrogen and carbon. The presence of DMSO was confirmed by ^1H NMR spectrum (data not reported) performed in deuterium chloride. UV KOJ quantification, performed after destruction of the HTlc structure in acidic medium, showed a loading of 25%. This result was confirmed by TGA (Fig. 3), which showed the weight loss as function of temperature and was interpreted as follows: from room temperature to ca. 200°C the sample loses co-intercalated solvents (ethanol and DMSO), then from 200 to ca. 1000°C the weight losses are attributable to KOJ and residue nitrate decomposition and to water loss coming from inorganic layers dehydroxylation, while the pattern of the sample heated at 1000°C is diagnostic for the presence of ZnO and ZnAl_2O_4 . Thus the final ZnAl-HTlc-KOJ formula resulted $\text{Zn}_{0.69}\text{Al}_{0.31}(\text{OH})_2\text{KOJ}_{0.25}(\text{NO}_3)_{0.06} \bullet 0.28\text{EtOH} \bullet 0.04\text{DMSO}$ (percentages of C, H, N, S: experimental values C 18.1, H 3.6, N 0.7, S 0.9; calculated values C 18.2, H 3.8, N 0.6, S 0.9).

FT-IR ZnAl-HTlc- NO_3 spectrum (Fig. 4) shows a broad band between 3200 and 3800 cm^{-1} , due to the stretches of hydrogen-bonded hydroxyl groups of hydroxide layers and interlayer water, an adsorption peak at ca. 1620 cm^{-1} , relative to the co-intercalated water bending and a great peak at 1420 cm^{-1} due to the intercalated nitrate. It is worthy that this band almost disappeared in ZnAl-HTlc-KOJ spectrum, meaning that nitrate anions underwent to almost complete exchange by KOJ anions. The very broad band between 3000 and 3600 cm^{-1} is diagnostic for hydrogen-bonded hydroxyl groups of hydroxide layer stretches with the intercalated compound.

Fig. 5 reports a computer generated model of ZnAl-HTlc-KOJ, obtained with the Hypherchem program, on the basis of the structural data of the host and the interlayer distance of the intercalation compound. The presence in the interlayer region of a

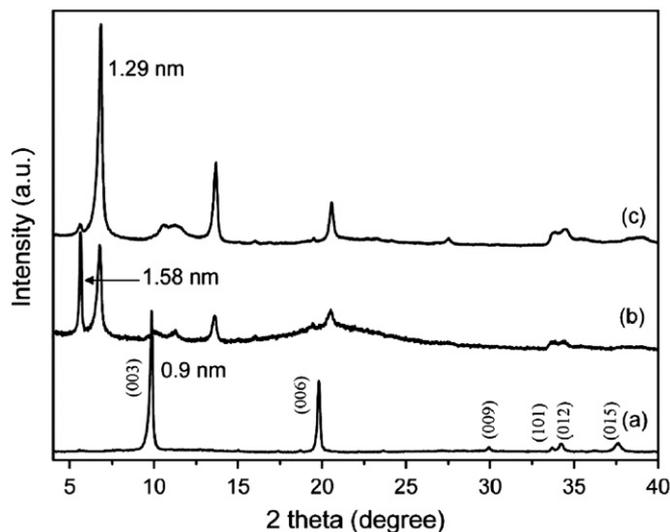


Fig. 2. XRPD patterns of ZnAlHTlc- NO_3 (a), wet (b) and dried (c) ZnAlHTlc-KOJ.

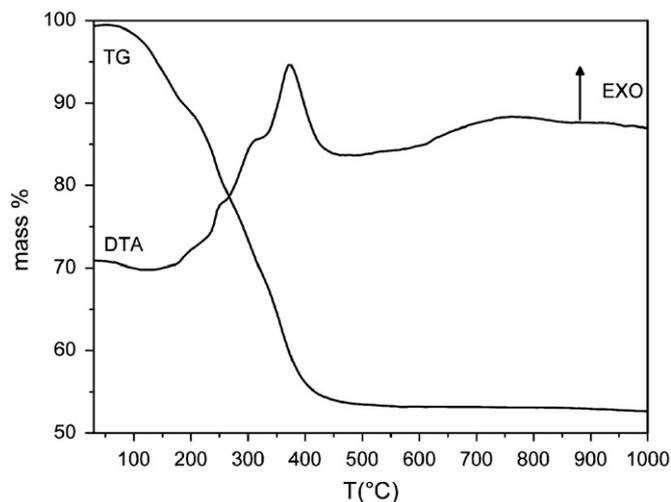


Fig. 3. TGA profile of ZnAlHTc-KOJ.

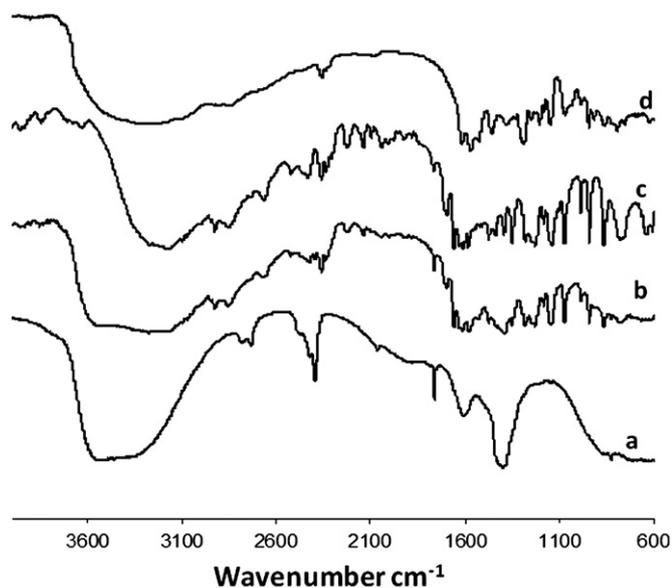


Fig. 4. FT-IR spectra of ZnAl-HTlc-NO₃ (a), ZnAl-HTlc-NO₃/KOJ physical mixture (b), KOJ (c) and ZnAl-HTlc-KOJ (d).

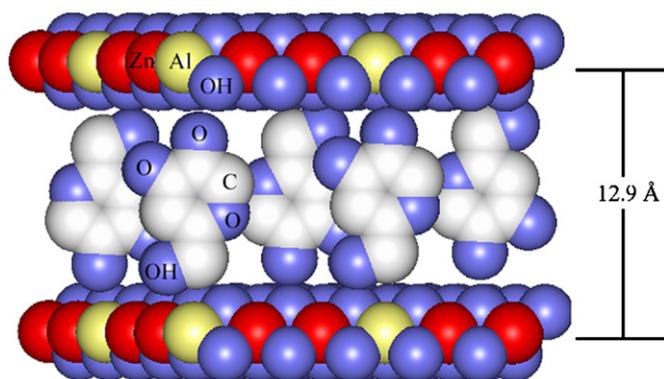


Fig. 5. Computer generated model of ZnAlHTlc-KOJ (without co-intercalated solvents).

KOJ⁻ monolayer, with its principal axis almost perpendicular to the layer plane, was hypothesized. In this model, the anions, after intercalation, point the 2-hydroxymethyl groups towards the hydrotalcite sheets allowing, in this way, the formation of hydrogen bonds.

DSC (Fig. 6) of KOJ shows an endothermic peak at ca. 156 °C relative to the melting point of pure crystalline substance. The thermogram relative to ZnAl-HTlc-KOJ does not show the endothermic peak of KOJ meaning that a new compound was produced and that KOJ⁻ intercalation in HTlc occurred. The physical mixture shows an endothermic peak at ca. 140 °C superimposed with a peak at 156 °C relative to acid fusion. This indicates that some interactions between KOJ and hydrotalcite are present in the physical mixture too.

3.2. Preliminary formulation studies

The ZnAl-HTlc-KOJ formulation was realized taking into account that the presence of water causes immediate KOJ⁻ release from the intercalation compound. Thus, a water free self-emulsifying ointment was proposed in order to prevent KOJ⁻ leakage in storage conditions. In this case, the cosmetic ingredient release can be promoted spreading the formulation on moist skin. With this aim, a silicone oil self-emulsifying ointment was chosen

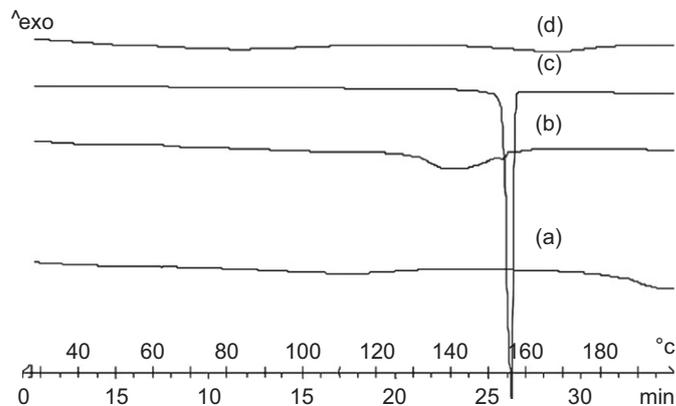


Fig. 6. DSC thermograms of ZnAlHTlc-NO₃ (a), ZnAl-HTlc-NO₃/KOJ physical mixture (b), KOJ (c) and ZnAlHTlc-KOJ (d).

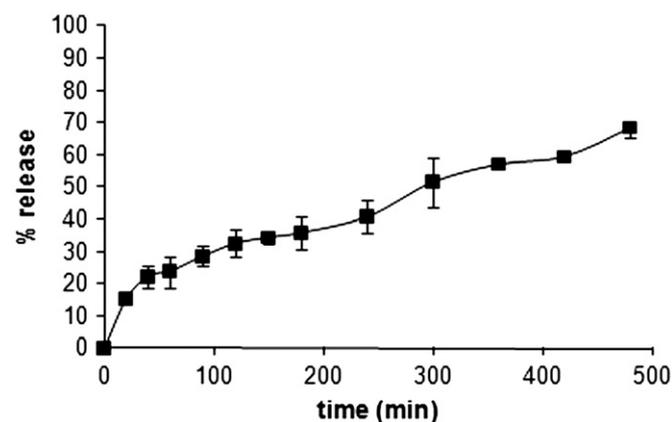


Fig. 7. KOJ release from the ointment at 32 °C ± 0.1, in phosphate buffer pH 5.5.

(Table 1). This formulation, loaded with ZnAl-HTlc-KOJ containing 2.5% of KOJ, was submitted to release studies.

3.3. In vitro KOJ release from the formulation

KOJ release from the ointment was performed at pH 5.5 phosphate buffer employing the “Petri disk method” [10] (Fig. 7) in order to reproduce real use conditions. KOJ release resulted gradual and increased during the test reaching ca. 40% after 4 h and a maximum of 68% after 8 h. In these conditions, KOJ⁻ release occurred by contact between the buffer and HTlc-KOJ dispersed in the ointment.

3.4. Photostability studies

The absorption spectra in 200–600 nm region (Fig. 8) were recorded to investigate the fraction of UV–vis light absorbed by the samples and the effects of the inorganic matrix in preventing KOJ photodegradation. The KOJ spectrum (Fig. 8a) has a maximum at 300 nm and a shoulder in the 330–400 nm region; ZnAl-HTlc-KOJ (Fig. 8c) presents a similar spectrum, although the low energy shoulder is broader and it extends till about 500 nm. The comparison between the spectrum of the intercalated sample and the spectra of KOJ in acidic or salt form (Figs. 8a and b, respectively) revealed evident differences suggesting that the inorganic matrix stabilizes arrangements, like π - π stacking, which lead to spectral broadening in the Vis region. When the compounds were dispersed in the cream no significant spectral changes were observed.

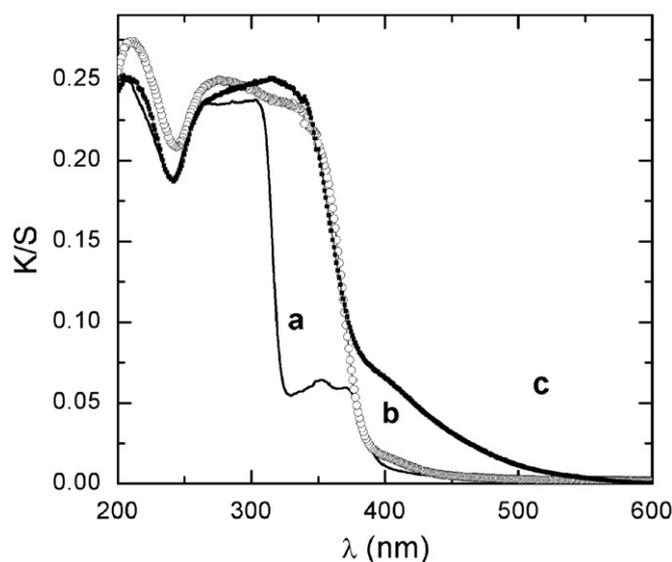


Fig. 8. Absorption spectra of KOJ (a), KOJ-Na (b) and ZnAlHTlc-KOJ (c).

Table 2

Sample	ΔOD [$\lambda_{loss}=400$ nm]	ΔOD [$\lambda_{loss}=300$ nm]
KOJ	52%	8%
KOJ-Na	82%	8%
ZnAlHTlc-KOJ	33%	11%
ZnAlHTlc-KOJ silicone oil ointment	30%	19%

The spectrophotometric analysis of the samples before and after steady state irradiation at 330 nm allowed the evaluation and the comparison of their photostability. Generally, for all samples changes in the absorption spectrum were observed upon irradiation; in particular, an increase of absorbances above 400 nm was detected while in 250–350 region a decrease was observed. In Table 2, the percentage of absorbance change at two wavelengths is reported. Data indicate that the chromophore intercalation in the inorganic matrix leads to an improvement of its photostability in terms of photoinduced oxidation and/or addition processes [24] since the absorbance changes at 400 nm (region where the oxidation and addition products absorb) of the intercalate samples are reduced. The origin of the spectral changes observed at 300 nm, especially for ZnAlHTlc-KOJ silicone

oil ointment, needs to be further investigated and the occurrence of new photochemical reactions cannot be excluded at this stage.

4. Conclusions

In the present work, KOJ was successfully intercalated into a ZnAl-HTlc-like anionic clay by a ion-exchange mechanism performed in anhydrous conditions. The intercalation compound was then formulated in a water free self-emulsifying ointment designed to be spread on the moist skin creating an *in situ* W/O emulsion. The proposed formulation showed good *in vitro* KOJ release profiles. Moreover, photostability studies revealed that KOJ intercalation in the inorganic matrix reduces photo-induced oxidation and addition reactions.

References

- [1] Z.D. Draeos, *Dermatol. Ther.* 20 (2007) 308–313.
- [2] K. Jimbow, Y. Minamitsuji, *Dermatol. Ther.* 14 (2001) 35–45.
- [3] M. Miyajima de Souza, *Clin. Dermatol.* 26 (2008) 27–29.
- [4] O. Faye, S. Keita, F.S. Diakité, H.D. Konaré, H.T. Ndiaye, *Int. J. Dermatol.* 44 (Suppl. 1) (2005) 35–36.
- [5] G.A. Burdock, M.G. Soni, I.G. Carabin, *Regul. Toxicol. Pharm.* 33 (2001) 80–101.
- [6] N. Stefani, P. del Pup, M. De Carli, *Cosmet. Technol.* 4 (2005) 43–52.
- [7] M. Gallarate, M.E. Parlotti, M. Trotta, A.E. Grande, C. Malarico, *J. Cosmet. Sci.* 55 (2004) 139–148.
- [8] S. Emami, S.J. Hosseinimehr, S.M. Taghdisi, S. Akhlaghpour, *Bioorg. Med. Chem. Lett.* 17 (2007) 45–48.
- [9] F. Trifirò, A. Vaccari, *Hydrotalcite-like anionic clays (layered double hydroxides)*, in: G. Alberti, T. Bein (Eds.), *Solid-State Supramolecular Chemistry: Two and Three-dimensional Inorganic Networks*, of *Comprehensive Supramolecular Chemistry*, Pergamon Press, Oxford, 1996, p. 251.
- [10] L. Perioli, V. Ambrogi, B. Bertini, M. Ricci, M. Nocchetti, L. Latterini, C. Rossi, *Eur. J. Pharm. Biopharm.* 62 (2006) 185–193.
- [11] L. Perioli, V. Ambrogi, C. Rossi, L. Latterini, M. Nocchetti, U. Costantino, *J. Phys. Chem. Solids* 67 (2006) 1079–1083.
- [12] V. Ambrogi, G. Fardella, G. Grandolini, L. Perioli, M.C. Tiralti, *AAPS PharmSci-Tech* 3 (3) (2002) article 26.
- [13] V. Ambrogi, G. Fardella, G. Grandolini, M. Nocchetti, L. Perioli, *J. Pharm. Sci.* 92 (2003) 1407–1418.
- [14] S. Lautenschlager, H.C. Wulf, M.R. Pittelkow, *The Lancet* 370 (2007) 528–537.
- [15] J.R. Schwartz, R.G. Marsh, Z.D. Draeos, *Dermatol. Surg.* 31 (2005) 837–847.
- [16] U. Costantino, F. Marmottini, M. Nocchetti, R. Vivani, *Eur. J. Inorg. Chem.* (1998) 1439–1446.
- [17] B.J. Poulsen, E. Young, V. Coquilla, M. Katz, *J. Pharm. Sci.* 57 (1968) 928–933.
- [18] Z.T. Chowhan, R. Pritchard, *J. Pharm. Sci.* 64 (1975) 754–759.
- [19] F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today* 11 (1991) 173–301.
- [20] D.L. Bish, *Bull. Mineral* 103 (1980) 170–175.
- [21] S. Budavari, in: *The Merck Index*, 12th Ed., Version 12:3, Whitehouse Station, NJ, Merck and Co. and Boca Raton, FL, Chapman and Hall/CRC, 2000.
- [22] U. Costantino, M. Casciola, L. Massinelli, M. Nocchetti, R. Vivani, *Solid State Chem* 97 (1997) 203–212.
- [23] N. Iyi, K. Fujii, K. Okamoto, T. Sasaki, *Appl. Clay Sci.* 35 (2007) 218–227.
- [24] J.A. Bartrop, A.C. Day, C.J. Samuel, *J. Am. Chem. Soc.* 101 (1979) 7521–7528.