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Determination of four lipophilic phenolics in o/w emulsions as well as their stability

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Abstract

Phenolic compounds are promising candidates for use in cosmetic formulations thanks to their characteristics such as antioxidant activity, UV-absorbing and melanogenesis inbibition. But most of them have been shown to be light sensitive with a decrease in their efficacy due to photo-degradation. Therefore, for optimizing the efficacy of functional cosmetics, it is important to recognize the unstable profiles of phenolic compounds in cosmetic products upon ambient sunlight exposure. Four of the most common used phenolic compounds, ellagic acid (EA), ferulic acid (FA), caffeic acid (CA), and chlorogenic acid (CHA), were examined. The phenolic compounds, as a single one and a combination, were formulated into o/w emulsion. And then the chemical stability of each of the phenolic compounds in o/w emulsions with and without the sunlight was investigated. Their different stability was evaluated by a high performance liquid chromatography using an isocratic mobile phase consisting of methanol:acetonitrile:water (10:19:71, v/v/v; pH 3.5). The results demonstrated that the developed mobile phase is very suitable for the simultaneous determination of the four phenolic compounds in emulsions without the interference with the corresponding oxidation products from the phenolic compounds or the excipients from cosmetic emulsions. Moreover, the degradation rate of the phenolic compounds in o/w emulsion is much lower than in solvent, indicating the ability of o/w emulsion to protect the phenolic compounds from rapid degradation. In all cases EA is the most stability due to no degradation product, while CHA has the least stability. In addition, stability of CA was improved markedly when it combined with FA, CHA and EA. This suggests that a suitable combination of phenolic compounds would be required to optimize their efficacy in final products.

Keyword: Phenolic compounds; Ellagic acid (EA); ferulic acid (FA); caffeic acid (CA); chlorogenic acid (CHA); Stability; Degradation; o/w emulsion; isocratic HPLC method

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1. Introduction

Phenolic compounds are abundant in naturally occurring plants. Significant amounts of phenolic compounds have been isolated from them. Pharmacological studies showed that they are able to enrich blood, activate blood circulation, regulate menstruation, relieve pain and resax bowels, stimulate smooth muscle, or even inhibit the multiplicity of tumors [1]. Moreover, they also possess anti-inflammatory, anti-carcinogenic, anti-allergic, antimicrobial, antimelanogenic, and antioxidant activities [2-4]. Therefore, using them in cosmetics as functional ingredients has been studied extensively. It is demonstrated, for example, that the use of skin care products including phenolic compounds, such as ferulic acid (FA), ellagic acid (EA), caffeic acid (CA), and chlorogenic acid (CHA) is efficacious in the treatment of skin conditions such as rosacea, sensitive skin and in the prevention of skin photodamage [5,6]. Some authors have even reported the transdermal delivery of ferulic acid and chlorogenic acid out of different cosmetic formulations [7]. In addition, it have been suggested that they are also used as UV-protective enhancer, UV protector and skin-whitening agents in cosmetic products [8-10].

In order to make sure the effectiveness of cosmetic products during the shelf life, the phenolic compounds incorporated into cosmetics should be stable. Unfortunately, most phenolic compounds exhibit unstable properties because they would take place the isomerization of trans-form to cis-form[11,12]. They alsohave been shown to be high sensitive upon light exposure, and their oxidation products were identified as various quinines, dimmers and aldehydes by using LC-MS method [13]. Whether the isomerization of phenolic compounds may induce adversely effect on human skin is unknown, but various reports on photocontact sensitization and on less UV-protecting efficacy induced by the photo-isomerization of typical UV-filters have been issued [14,15]. We wondered if maybe instability of phenolic compounds can result in less efficacious product like those UV-filters. In order to satisfy both effective and healthy requirements, the phenolic compounds used should have a longer useful life in cosmetic formulations and be limited at a suitable level to be safe for application to the skin. In our country the use of ellagic acid is allowed up to a maximum limit of 3% in cosmetic formulations, but the others has not yet been issued. On the other hand, using the phenolic compounds, either alone or as a complex, has become quite popular. Actually, more than two ingredients present in one emulsion will influence or change their stability each other due to their different antioxidant activity [16]. Therefore, it is important to look at the stable profile of each phenolic compound while the phenolic compounds were formulated into cosmetic emulsions by alone or a combination.

Although many authors have published the stability for phenolic compounds in solution with different pH values, in medicinal materials, and in extracts [17-20], there are no data available about the stability of the phenolic compounds in cosmetic emulsions. Aiming at a determination of chemical stability of phenolic compounds in cosmetic emulsions upon sunlight exposure, we established an isocratic- HPLC method. For this purpose the four most wildly used phenolic compounds-ellagic acid, ferulic acid, caffeic acid and chlorogenic acid, were selected as functional ingredients. And an o/w emulsion, one of the most popular personal care formulations, is prepared following the procedure used in commercial practice for o/w emulsions.

During the emulsification each single one and the combination of the four phenolic compounds were separately mixed with oil phase, and then the mixtures were added into water phase for producing o/w emulsions with different phenolic compound. For comparison, these phenolics were also prepared in methanol solvent. The stability of each phenolic compound both in methanol solvent and in o/w emulsion was evaluated.

2. Experimental

2.1. Materials and reagents

All the four active phenolic compounds were purchased from Merck (Germany). Span 80and Tween 60, as emulsifiers, were obtained from First Chemical Co(Taiwan). Carbopol 940, glycerin, and mineral were also from First Chemical Co(Taiwan). U-13 and phenoxy ethanol were obtained from Induchem.Co.(Switzerland). The rest of cosmetic materials were purchased by Lipo Co.(USA). HPLC grade methanol and acetonitrile (Sigma-Aldrich, Cermany) were used for the preparation of mobile phase. Analytical grade of phosphoric acid and sodium hydroxide was purchased from Toyao (Japan). Deionized water was obtained from a Milli-Q water system (Millipore, USA).

2.2. Formulations studied

An o/w emulsion was chosen and tested in this work. Six emulsions (Table 1) were formulated in a Ika Eurostar Digital/P1 mixer. The active phenolic compound is first mixed with oil phase. The o/w emulsion was prepared by a dropwise addition of the aqueous phase into the oil phase containing active agents followed by agitation for 15min at high speed (1000rpm) and room temperature, and then given by a low speed (300rpm) until a homogenous emulsion was formed. Emulsion A dose not contain any phenolic compound. Emulsion B-E (with individual phenolic compound) and emulsion F (with a combination) are obtained, respectively.

Table 1 Compositions of the o/w emulsions

Compositions	Percentage of components in each emulsion					
	A	B	C	D	E	F
(I) Oil phase						
Span80	3.0	3.0	3.0	3.0	3.0	3.0
Tween60	2.0	2.0	2.0	2.0	2.0	2.0
Finsolv TN	2.0	2.0	2.0	2.0	2.0	2.0
Squalane	3.0	3.0	3.0	3.0	3.0	3.0
Mineral oil	1.0	1.0	1.0	1.0	1.0	1.0
Finsolv TN	2.0	2.0	2.0	2.0	2.0	2.0
Caprylic/capric Triglyceride	5.0	5.0	5.0	5.0	5.0	5.0
(II)Active agents						
Ellagic acid	-	1.0	-	-	-	0.25
Chlorogenic acid	-	-	1.0	-	-	0.25
Caffeic acid	-	-	-	1.0	-	0.25
Ferulic acid	-	-	-	-	1.0	0.25
(III)Weter phase						
U-13	0.4	0.4	0.4	0.4	0.4	0.4
Pheoxyethanol	0.4	0.4	0.4	0.4	0.4	0.4
Carbopol 940	0.5	0.5	0.5	0.5	0.5	0.5
Glycerin	3.0	3.0	3.0	3.0	3.0	3.0
Distilled water to	100	100	100	100	100	100

2.3 Instrumentation

An Model I-7100 HPLC-UV system consisting of a single pump, a degasser, an injection valve with 25ul sample loop (Model 7725, Rheodyne, Cotati, US), and UV detector was used. And a Mightysil RP-18CP column was used for chromatographic analysis. The mobile phase consisted of the mixture

of methanol:acetonitrile:water (10:19:71, v/v/v), and its pH value was adjusted to 3.5 by phosphoric acid. The isocratic separation was performed and the flow rate was 0.8mL/min at ambient temperature. VU detector was set at 320nm for acquiring the chromatogram. Data acquisition and processing were accomplished with a personal computer including Sisc software (Taiwan).

2.4 Recovery study in o/w emulsion

Emulsion A (without phenolic compound) shown in Table 1 was used as a control in the recovery study. To test the recovery, each of the four phenolics standards was formulated into the control emulsion at low and high concentrations (0.25 and 2.5 %, w/v) during the emulsification. For the assay of the phenolic compounds, about 1g of each of the formulated emulsion was weighed into a glass flask and 25 ml of methanol was added and then the flask was immersed in an ultrasonic bath for 20 min at ambient temperature. The extraction samples were centrifuged for 1min. Of each of the centrifuged samples, 1 ml were taken, and then diluted to 10 ml with methanol before injecting onto the HPLC system. Table 2 summarized the recovery of the phenolic compounds in the type of o/w emulsion using various extraction solvents.

2.5 Stability studies

The difference in stability of each phenolic compound in emulsion (B-F) without or with sunlight exposure was evaluated by HPLC analysis with isocratic separation during the study period. For comparison, the tested phenolic compounds, as a single one or the combination of the four phenolic compounds, is separately prepared into methanol solvent. Approximately 10-ml of aliquots of each sample were kept in glass vials and placed in sunlight at ambient temperature (30-36℃). After either exposing them to the sun or protecting from the sun by covering with aluminum foil during a period of 28 days, these samples were assayed at the following time points: 0, 1, 7, 14, 21, and 28 days. For the assay of phenolic compounds, each of the emulsion and solution samples is treated as the same with those described in section 2.4.

3. Results and Discussion

3.1. Chromatography and resolution

The structure of the four phenolic compounds, ferulic acid (FA) , ellagic acid (EA), caffeic acid (CA), and chlorogenic acid (CHA), is shown in Figure 1. Containing carboxylic acid group or phenolic hydroxyl group in each molecular structure, they are all weak acidic substances with a strong hydrophobicity. Two of major factors, mobile phase and pH value, which affect the separation performance, are examined in order to optimize chromatographic conditions with no interference with matrix in cosmetic samples. When the mixture of methanol:water with vary pH value was used as mobile phase, peak overlap and poor symmetry appeared (not displayed). Instead, the use of isocratic elution with a methanol:acetonitrile:water (10:19:71, v/v/v) adjusted to a pH value of 3.19 by phosphoric acid gave good results in separation of the four phenolic compounds either in solvent or in emulsion without and with sunlight exposure, as shown in Figure 2. The HPLC chromatograph showed good resolution and separation with retention time of less than14 min. In Figure 2(a)(sample treated with dark conditions), it can be seen that the retention time of CHA, CA, EA and FA appear at 4.8 min, 6.3 min, 8.7 min and 10.3 min, respectively. Figure 2(d) resulted

from a control emulsion. On the other hand, the changes of the phenolic compounds in methanol and in emulsion with sunlight exposure are shown in Figure 2(b) and 2(c), respectively. The results of Figure 2(c) are similar to those in Fig 2(b). It is clear that there were extra three peaks to appear by comparing them with Fig 2(a), suggesting all the tested phenolic compounds could cause decomposition but EA by sunlight exposure.

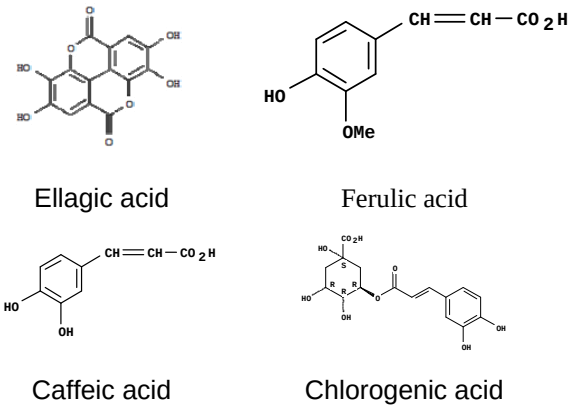
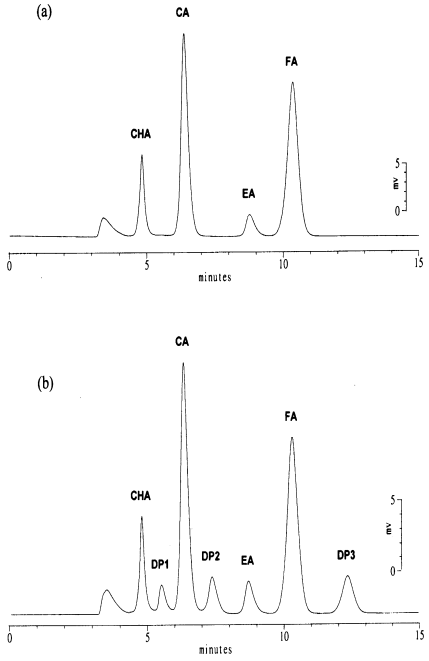


Figure1.Chemical structures of four phenolic compounds



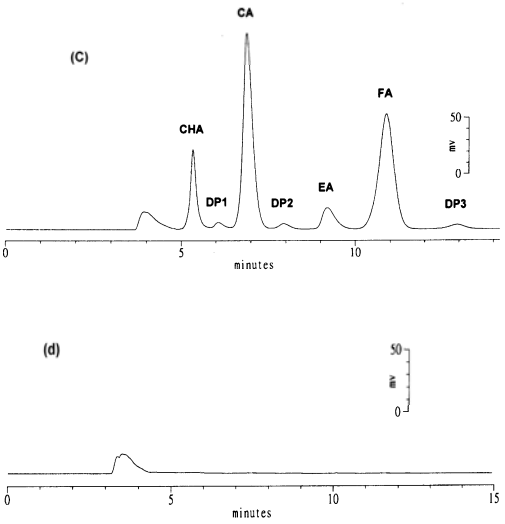


Figure 2. HPLC chromatographic analysis of the four tested phenolic compounds (a) in methanol solvent with dark conditions (b) in methanol solvent with 7 days sunlight exposure (c) in o/w emulsion F with 7 days sunlight exposure, and chromatogram of (d) placebo(emulsion A) with 7 days sunlight exposure. Peaks: EA=ellagic acid; CHA= chlorogenic acid; DP1= degradation product of CHA; CA=caffeic acid; DP2= degradation product of CA; FA=ferulic acid and DP3= degradation product of FA.

3.2. Linearity and Assay precision

Our results were validated in terms of linearity and precision. Excellent linearty was obtained over the range 1~ 200 ug / ml for all compounds except EA for which the range was 5~200 ug / ml. The coefficients were all above 0.998. The precision (CV) was between 0.9~ 4.5. The minimum detectable limits, calculated as greater than three times the baseline noise level in the assay, were below 0.02 ug / ml for all the phenolic compounds.

3.3. Recovery study

It was necessary to evaluate the influence of the different solvent on the recovery of the four phenolic compounds. Table 2 summarizes recovery of the four phenolic compounds in the o/w emulsion when they

were treated with tetrahydrogenfuran (THF), menthanol (MeOH) and ethanol (EtOH) as the extraction solvents, respectively. It was found that at the low and high concentrations their recoveries were at a range of 68.5~102.3 % with regard to different kinds of solvents and the coefficients of variance calculated from three replicates were all less than 8.0 %. However, some problems would occur when using EtOH or THF as extraction solvent. In the use of THF, the interference peak was observed and results in wide broad peak by which the peak of the tested analytes were overlapped. Regarding the use of EtOH, there were low recovery and the ease of filtration is troublesome. As a consequence, an accepted recovery for all the four analytes and no matrix interference were observed in the use of MeOH. Therefore, MeOH is a suitable choice as solvent for the treatment of cosmetic samples.

Table 2 Recovery of the phenolic compounds in o/w emulsion using various extraction solvents

Compound	AmountsAdded (w/w%)	MeOH		EtOH		THF	
		Recovery	CV	Recovery	CV	Recovery	CV
EA	0.25	96.3	2.3%	68.5	3.4%	80.3	5.2%
	2.50	94.5	1.5%	70.5	2.8%	85.9	6.9%
FA	0.25	96.8	1.2%	82.1	2.6%	87.8	4.6%
	2.50	97.5	0.7%	80.6	3.1%	79.1	8.0%
CA	0.25	102.3	1.8%	83.2	2.8%	82.8	5.8%
	2.50	100.5	2.1%	81.9	3.2%	92.4	6.9%
CHA	0.25	98.6	1.6%	69.4	2.6%	83.2	7.2%
	2.50	97.3	1.9%	71.8	1.6%	91.6	6.7%

3.4. Stability study

Due to photo unstable property, the phenolic compounds present in cosmetic products would greatly influence the effectiveness and the safety of final products. Hence, using them as UV-protector in emulsions will exhibit less UV-protecting capacity due to isomerization. Therefore, it is important to know if any degradation or isomerization occurs in phenolics-containing emulsions. Although many reports on decomposition and isomerization of phenolic compounds in solution following the elevated temperature or UV irradiation have been issued, there is little documentation related to their chemical stability in cosmetic emulsions upon sunlight exposure. We present the isocratic HPLC method that simultaneously determines the different amounts of the four phenolic compounds both in solvent and o/w emulsion during exposing them to the sunlight. As the mention above, only four separated peaks for the four phenolic compounds in methanol are observed in Figure 2(a), indicating no degradation to occur in the dark. When compared to Fig 2(a), three extra peaks appear in figure 2(b) under sunlight exposure. After confirmed alone, the three extra peaks are degradation product of CHA, CA and FA. It is obvious that only EA did not undergo degradation either in methanol or in emulsion upon exposed to sunlight. The difference in stability can be attributed to their different molecular structure. Unlike CA or CHA or FA, EA does not include double bond having the ability of isomerzation in its molecular structure. That is the reason why EA's degradation product is not found. Based on the findings, we deduce that these extra peaks should be degradation products resulted from isomerzation of phenolic compounds upon sunlight exposure. Table 3 summarizes the degradation of the four tested compounds as a single one in methanol. The degradation was observed in the samples as a decrease in the level of the active component or as an increase in the level of degradation product. The unidentified degradation product, is presented as the

ratio of $A_{D.P}$ and A_{Ph} and is expressed as a percentage: $\%A = A_{D.P}/A_{Ph} \times 100\%$, where $A_{D.P}$ is area of the degradation product peak and A_{Ph} is area of its phenolic compound peak. The more the degradation is, the less the stability. Table 3 showed that among these phenolic compounds EA has the most stable behavior without any degradation product. In contrast, after 28 days sunlight exposure CHA is worse- its concentration was decreased by up to 24.1% of the initial concentration, and its degradation product increases rapidly in peak area with time, up to 17.7% of area ratio. In addition, Figure 3 and Figure 4 illustrate the degree of phenolics degradation in methanol and emulsion, respectively. Degradation extent of each of the assayed phenolic compounds, either alone (Figure 3(a), Figure 4(a)) or a combination (Figure 3(b), Figure 4(b)), was represented as percent remaining,

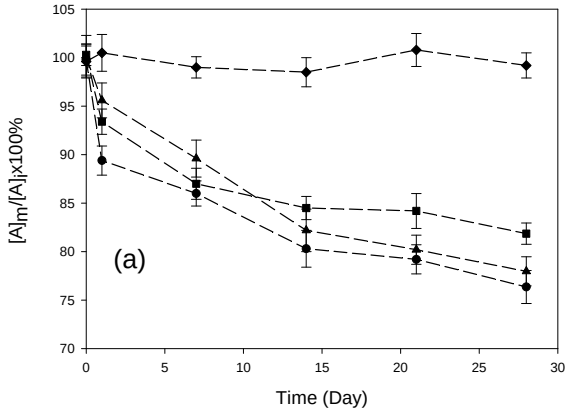
$[Pheno]_{mt} / [Pheno]_{mo} \times 100\%$, where $[Pheno]_{mt}$ is the measured concentration of phenolics at any time, t. and $[Pheno]_{mo}$ is the concentration of phenolics at initial time, t = 0. All the cases, EA is among the most stable phenolic compounds with no change in amounts during the study period, but it has a smaller recovery than the other assayed phenolic compounds (table 2). The stability profile of EA in emulsions is similar to that of EA present in natural fruits and nuts published by Daniel, Elaine M and his coworkers [21]. The rest of them are in different decline because the percent remaining decrease with time. Importantly, FA, CHA, and CA, have a better stability in emulsion than in methanol solvent whenever they exist as a single one or a combination. By comparing Figure 3(a) with Figure 4(a) at 28 days sunlight exposure, the percent remaining of CHA, CA, and FA in methanol solvent drop to 77%, 78%, and 83%, respectively, but be maintained on 82%, 85% and 90% in emulsion (C, D E), respectively. Moreover, by comparing Figure 3(b) with Figure 4(b), it is clear that the percent remaining of FA, CHA, and CA in emulsion do increases, too. Especially, CA and FA in emulsion F reach to a high level of 95% and 93%, respectively. In summarizes, these results suggest that emulsions seem to provide an environment protecting them from a rapid degradation induced by exposed to sunlight. This could be attributed to the less concentration of oxygen in the media of emulsions or the less radiation-dose due to the sunlight absorbed by the excipients in emulsions.

On the other hand, stability of CA is different from that of CHA and FA. An improvement in stability of CA could be achieved easily by combination with other phenolic compounds, but not for FA and CHA. For example, Figure 3(a) showed that when existed as alone in solvent 28 days sunlight exposure, CA drop to 82%, but existed as a combination in solvent (Figure 3(b)), it is maintained on 86%. Moreover, as shown in Figure 4(a) and Figure 4(b), CA in emulsion F also exhibited also higher percent remaining (95%) than in emulsion E (85%). In other words, in the presence of FA and CHA and EA can markedly improve stability of CA. Some reports on stability study of antioxidants have been issued. Lin, Fu-Hsiung and his coworkers have reported on the increasing stability of antioxidants vitamins (C +E) by combination with Ferulic acid[22] and A.Segall and his colleagues have studied stability of lipoic acid in the presence of vitamins A and E[23]. Unlike CA, percent remaining of FA in emulsion F do not change much, when compared to that in emulsion E over time. However, stability of CHA is different from FA. At the beginning CHA in emulsion F exhibited slighter decline than in emulsion C, but 21 days after sunlight exposure the degree of CHA decline in emulsion F and in emulsion C stay the same.

Table 3 Stability of phenolic compound as a single one in solvent upon sunlight exposure

Time (days)	FA (ppm)	D.P. (%A)	EA (ppm)	D.P. (%A)	CA (ppm)	D.P. (%A)	CHA (ppm)	D.P. (%A)
0	100.3±1.2	0	99.5±1.5	0	100.0±2.1	0	99.9±1.6	0
1	99.8±1.4	1.0	99.9±1.6	0	100.2±1.8	0.8	95.6±1.8	5.0
7	97.2±1.9	2.7	100.1±1.3	0	98.3±1.9	2.3	91.8±1.2	9.3
14	93.9±1.7	4.8	100.1±1.2	0	95.7±2.2	4.0	88.0±1.7	12.3
21	88.1±1.7	6.8	99.8±1.9	0	90.4±1.5	5.4	84.2±1.1	15.2
28	78.1±2.1	10.3	100.0±1.9	0	81.9±1.5	7.8	75.9±1.1	17.7

* The data is a percentage of the ratio of the peak of degradation product to phenolic compound: % A $=A_{D.P.}/A_{Ph} \times 100\%$



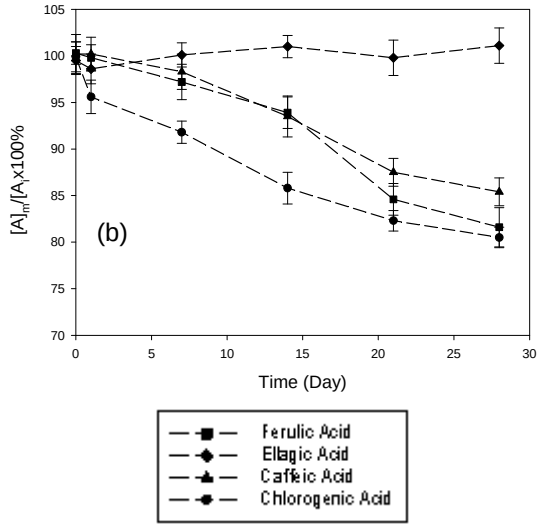
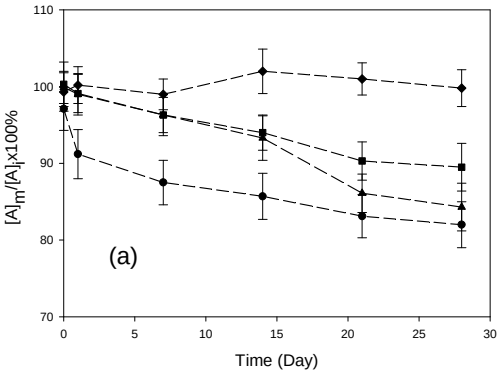


Figure 3. In methanol solvent stability change of the four tested phenolic compounds, as (a) individual single one and (b) a combination. Measurement was performed at time, t=0, 1, 7, 14, 21, and 28 days after sunlight exposure



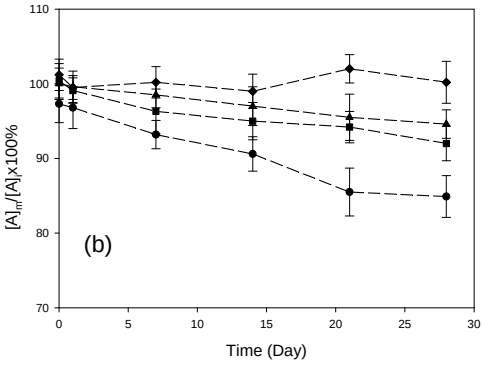


Figure4. In o/w emulsion stability change of the four tested phenolic compounds, (a) as individual single one (emulsion B-E) and (b) as a combination (emulsion F). Measurement was performed at time, t=0, 1, 7, 14, 21, and 28 days after sunlight exposure

4. Conclusion

In the stability studies, the phenolic compounds contained in either solution or an emulsion exhibit much less stability under sunlight exposure than under dark condition. Obviously, this is due to the

occurrence of photo-degradation under sunlight exposure. It seems that molecule itself and the types of media can impact on their stability. In all cases, for example, EA dose not occur degradation due to the lack of double bond to result in isomerization, maintaining the most stability under even sunlight exposure. Based on this finding, when cosmetics need for single phenolic agent to optimize their effectiveness, EA will be the first selected phenolic compound for gaining more effective cosmetics. In addition, we found that it is easy to improve stability of CA using combination with FA and CHA and EA. However, further research on the stability of the phenolic compounds by any combination of two or more phenolic compounds is required to acquire whole acknowledge about what the stability of phenolic compounds in various combinations is different. A right combination of phenolic compounds should be incorporated into functional cosmetic emulsions to optimize their efficacy and to give them longer shelf life. And cosmetic emulsions including phenolic compounds do shield from sunlight during the production, too. Then the selected containers for packing cosmetic emulsions with active phenolic compounds must have the ability to protect them from degradation. Importantly, the HPLC assay developed is simple, rapid and convenient method. It can accurately quantify the four phenolic compounds in different types of media and ensure the quality control.

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References

1. Guang-Hua Lu, Kelvin Chan, Kelvin Leung, Chi-Leung Chan, Zhong-Zhen Zhao, Zhi-Hong Jiang. 1996. **Assay of free ferulic acid and total ferulic acid for quality assessment of Angelica sinensis.** Journal of Chromatography A 1068(2005)209-219.
2. Lanzani, A.; Cardillo, M.; Fedeli, E. 1979. **Study on the antioxidant ability of chlorogenic acid isolated from sunflower seed.** Rivista Italiana delle Sostanze Grasse 57(7), 273-5.
3. Eggensperger, Heinz; Wilker, M.1996. **Multiactivity of gerulic acid and its esters in cosmetics. Part 2.** SOFW Journal 122(4), 210, 212, 215.
4. Chikuno, Takao; Dato, Hiroshi; Kadota, Megumi. 2005. **Skin external use medicine for beauty white.** Jpn.Kokai Tokkyo Koho 10 pp.
5. Facino R M; Carini M; Aldini G; Saibene L; Pietta P; Mauri P. 1995. **Echinacoside and caffeoyl conjugates protect collagen from free radical-induced degradation: a potential use of Echinacea extracts in the prevention of skin photodamage.** Planta medica 61(6), 510-4
6. Smith, Wendy A.; Gupta, Ramesh C.1996. **Use of a microsome-mediated test system to assess efficacy and mechanisms of cancer chemopreventive agents,** Carcinogenesis 17(6), 1285-1290.
7. Ping-Bo, Ma. 2002. **Promotion of ferulic acid transdermal absorption by water-soluble azone in Shengfaling tincture.** Diyi Junyl Daxue Xuebao 22(1), 56-58.
8. Vanessa V. da Silva, Cristina D. Ropke, Rebeca L.de Almeida, Denise V. Miranda, Clarissa Z. Kera, Diogo P. Rivelli, Tania C.H. Sawada, Silvia B.M. Barros 2005. **Chemical stability and SPF determination of Pothomorphe umbellate extract gel and photostability of 4-nerolidycathecol.** International Journal of Pharmaceutics 303, 125-131.

9. Shimogaki,H.; Tanaka, Y.; Tamai, H.; Nasuda, M. 2000. In vitro and in vivo evaluation of ellagic acid on melanogenesis inhibition. International Journal of Cosmetic Science 22(4), 291-303.
10. M. Turkoglu and N.Cigirgil, 2007. **Evaluation of black tea gel and its protection potential against UV.** International Journal of Cosmetic Science 29, 437-442.
11. Lorant, Bela., 1968. Thermal degradation of coffee and cocoa constituents of interest to food chemistry**,** Nahrung 12(4), 351-6.
12. Ding Mingyu, Ma Shuaiwu, Liu Delin. 2004. **Stability of ferulic acid and its existing form in Ligusticum chuanxiong and Angelica sinensis.** Zhongcaoyao 35(1), 28-30.
13. Antolovich, Michael; Bedgood, Danny R.,Ju.; Bishop, ndrea G..; Jardine, Daniel; Prenzler, Paul D.; Robards, Kevin, 2004. **LC-MS Investigation of Oxidation Products of Phenolic Antioxidants.** Journal of Agricultural and Food Chemistry 52(4), 962-971.
14. Paola Perugini, Manuela Vettor, Rosanna Tursilli, Santo Scalia, Ida Genta, Tiziana Modena, Franca Pavanetto, Bice Conti. 2005 **Technological strabegies to improve photostability of a sunscreen agent.** J.Appl. Cosmetol. 23,59-69
15. S. Pattanaaargson and P. Limphong, 2001. **Stability of octyl methoxycinnamate and identification of its photo-degradation product.** International Journal of Cosmetic Science 23, 153-160.
16. Oszmianski, Jan; Chang Y.,Lee, 1990. **Enzymic oxidative reaction of catechin and chlorogenic acid in a model system.** Journal of Agricultural and Food Chemistry 38(50), 1202-4.
17. Chen, Gang; Shixiang, Hou; Ping, Hu; Ning, He; Yaning, Zhu; Lun, Cao. 2003. **Studies on stability of chlorogenic acid in extract of flos Ionicerae.** Zhongguo Zhongyao Zazhi 28(3), 223-226.
18. Friedman, Mendei; Juergens, Hella S., 2000. **Effect of pH on the Stability of Plant Phenolic Compounds.** Journal of Agricultural and Food Chemistry 48(6), 2101-2110.
19. Lorant, Bela., 1968. **Thermal degradation of coffee and cocoa constituents of interest to food chemistry,** Nahrung 12(4), 351-6.
20. Boles, Jennifer Snow; Crerar, David A.; Grissom, Grady; Key, Tonalee C., 1988. **Aqueous thermal degradation of gallic acid.** Geochimical et Cosmochimica Acta 52(2), 341-4.
21.Daniel, Elaine M.; Krupnick, Alexander S.; Hiur, Toung Hun; Blinzler, Jane A.; Nims, Raymond W.; Stoner, Gary D.,1989. **Extraction, stability, and quantitation of ellagic acid in various fruits and nuts.** Journal of Food Composition and Analysis 2(4), 338-49.
22.Lin, Fu-Hsiung; Lin, Jing-Yi; Gupta, Ravindra D.; Tournas, Joshua A.; Burch, James A.; Selim, M. Angelica; Monteiro-Riviere, Nancy A.; Grichnik, James M.; Zielinski, Jan; Pinnell, Sheldon R. 2005. **Ferulic acid stabilizes a solution of vitamins C and E and doubles its photoprotection of skin.** Journal of Investigative Dermatology 125(4), 826-832.
23.A. Segall, M.Sosa, A. Alami, C.Enero, F. Hormaechea, M.T.Pizzzorno, C. Bergni, and R. Serrao, 2004. **Stability study of lipoic acid in the presence of vitamins A and E in o/w emulsions for cosmetic application.** J. Cosmet. Sci., 55, 449-461.

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四種親脂性酚性化合物在 O/W 乳化製品中之成份測定與安定性之研究

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摘要

天然來源之酚性化合物由於具有好的抗氧化與美白及安全等特性，已成爲化妝品產品最佳的原料來源。然而由於這些酚性化合物之化性不安定，因此，當添加在化妝品中時會降低化妝品的安定性與有效性。因此爲了獲得健康及優質的功效性化妝品，建立正確的分析方法以及促進酚性物質的安定性是相當重要的。本實驗選擇四種普遍應用在化妝品中的酚性化合物-Ellagic acid(EA)、Ferulic acid(FA)、Caffeic acid(CA) 和 Chlorogenic acid(CHA) 分別以單一添加及四種混合添加在基礎乳液中，利用高效液相色層枌析方法進行成份測定及安定性測試。結果顯示，以爲移動相可以同時成功地定量乳化製品中所存在的四種酚性物質外，各個酚性物質呈現不同的安定性（在照光與暗室的條件）。其中以 EA 最穩定，因爲即使在太陽光照射下也不會有任何分解物;但是 CHA 則是最不穩定的。另外在 FA、CHA 和 EA 同時存在時可以大大地改善 CA 的安定性。因此可知，活性成分被添加在化妝品中時須考慮選擇恰當的組合成分，才能延長活性成分在乳化產品中的安定性與有效性。

關鍵詞：酚性化合物；鞣花酸；安定性；分解；水包油型乳化製品；等位流析液相色層分析法

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