J. Soc. Cosmet. Scientists Korea
Vol.33, No. 3, September 2007, 197-201

화장품 중 유용성감초추출물의 유통기한 예측을 위한 가속수명 시험연구

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(2007년 7월 20일 접수, 2007년 8월 15일 채택)

A Study on the Accelerated Life Test for the Estimation of Licorice Durability in Cosmetics

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(Received July 20, 2007; Accepted August 15, 2007)

요 약: 유용성감초추출물(oil soluble licorice extract)은 미백에 효능이 있는 원료로서, 미백 효과가 최적으로 유지되는 유통기한을 알아야 할 필요가 있다. 실온 상태에서의 화장품 유통기한을 측정하는 것이 제품의 개발 기간에 비해 상대적으로 길기 때문에 가혹 조건하에서의 성분 변화 실험을 통해 실제 유통기한을 예측하고자 하였다. 이를 위해 유용성감초추출물의 수명과 가속 온도 스트레스와의 관계를 아레니우스식에 의해 분석하였다. 가속 온도 스트레스 설정 시 화장품 제형이 변하지 않는 온도 범위 내인 50, 55 및 60 ℃로 설정하였고, 이 구간 내에서 일정 스트레스 부과 방식을 설정하여 실험을 수행하였다. 본 연구에서 화장품 중 유용성감초추출물의 수명은 초기함량의 10 %가 감소되는 시간으로 정의하였으며, 각 온도에서의 유용성감초추출물의 수명은 50 ℃에서 580 h, 55 ℃에서 319 h, 60 ℃에서 166 h로 측정되었다. 실험 결과값을 아레니우스 모델에 적용하여 유용성감초추출물의 수명과 온도 사이의 수명 관계식[log(수명) = − 35.0243 + 1.15322 × (11604.83/온도)]을 도출하였고, 이 식에 의해 25 ℃에서 유용성감초추출물의 수명은 26 개월로 예측할 수 있었다. 예측 결과는 유용성감초추출물을 실온에서 측정한 결과로 검증하였으며 95 % 신뢰수준에서 수명 예측값과 실제값은 유의하지 않았다. 이 연구 방법은 주름 및 미백개선용 기능성 화장품들의 유통기한을 빠르고 정확하게 예측하는데 기여할 것으로 기대된다.

Abstract: Oil soluble licorice extract (licorice extract) is an officially approved cosmetic component as a whitening ingredient in Korea. The durability of licorice, during which the whitening effect can be maintained in optimum condition, must be accurately defined. Since the cosmetics durability under real condition is relatively longer than its development time. It is needed to predict the real durability interval from the experimental measurement under simulated operating conditions. We analyzed the relationship between the licorice lifetime and the high temperature condition by using Arrhenius equation. We have established the constant stress test with temperature of 50 ℃, 55 ℃, and 60 ℃ condition, within which no formulation change of licorice products is expected for the accelerated stress test. In this paper, the lifetime of licorice in cosmetics was defined as time period for its 10 % contents reduction. We observed that the lifetime of licorice is 580 h at 50 ℃, 319 h at 55 ℃ and 166 h at 60 ℃. Using the above experimental data, we obtained the equation for the relationship between the licorice lifetime and temperature as follows; log (lifetime)= − 35.0243 + 1.15322 × (11604.83/temperature). From this equation, the lifetime of licorice at 25 ℃ can be estimated as 26 months. The estimated result was verified by measuring full lifetime of licorice. In fact, there was no significant difference between the estimated lifetime and real measurement within 95 % significance level. This study can be applied to other useful cosmetic components for the fast estimation of the exact durability.

Keywords: *cosmetics durability, accelerated life test, licorice, Arrhenius equation, whitening*

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1. Introduction

Cosmetics durability has been a controversial issue for a long time. The law which became effective from March 11, 2005 in EU (European Union) regulates the indication of cosmetic lifetime like below: lifetime dating for cosmetics under 30 months lifetime and period after opening (PAO) for cosmetics more than 30 months should be marked. The regulation leads customers to use cosmetics more safely[1,2].

As durability test needs long time while development cycle of cosmetic product is relatively short, it is difficult to evaluate the durability of cosmetics with its full lifetime. Even though the accelerated stability test does not provide strong reliability on the accuracy of the result, it is preferred as it costs relatively short time. In this study, a method to test the durability of whitening cosmetics was proposed by the accelerated life test with 'Arrhenius model' formulation.

'Arrhenius model' can be applied to the accelerated test model in case that there is relationship between temperature and rate of reaction. The rate of reaction depends on temperature as follows

$$rate\ (v) = A' \exp[-\frac{\triangle H}{kT}] \qquad (Eq.\ 1)$$

ΔH is the activation energy of the reaction, usually in electron volts. K is Boltzmann's constant, 8.617 × 10^{-5} electron volts per ℃. T is the absolute Kelvin temperature. A is a constant that is characteristic of the product failure mechanism and test conditions.

The following relationship is based on a simple view of failure due to such a chemical reaction. The product is assumed to fail when some critical amount of the chemical has reacted; a simple view of this is

(critical amount) = (rate) × (time to failure)

Equivalently,

(time to failure) = (critical amount) / (rate)

This suggests that nominal time τ to failure is inversely proportional to the rate. This yields the Arrhenius life relationship

$$\tau = A \exp\ [\frac{\triangle H}{kT}] \qquad (Eq.\ 2)$$

Here A is a constant that depends on product, test method and other factors. Products with more than on failure mode have different A and ΔH values for each mode.

The Arrhenius acceleration factor between life τ at temperature T and life τ' at reference temperature T′ is

$$AF = \frac{\tau}{\tau'} = \exp\ [\frac{\triangle H}{k}(\frac{1}{T} - \frac{1}{T'})] \qquad (Eq.\ 3)$$

By equation 3, the lifetime in room temperature (T) can be estimated from the lifetime in test temperature (T′). This quantitative formulation enables accurate and fast estimation of cosmetics durability which takes relatively long time[3,4].

2. Materials and Methods

2.1. Materials

Glabridin standard was purchased from Kanto (Japan). Acetic acid was purchased from Sigma-Aldrich (Denmark). All solvent was analytical grade. Cosmetic sample which contains licorice were prepared by Amore-Pacific (Korea).

2.2. Instrumentation

HPLC analyses were performed on Waters Alliance system (Waters Co., USA) with PDA detector, column oven enabling temperature control of analytical column. Data were collected and processed by chromatographic software Empower II.

Constant temperature oven of JASCO (Japan) was used in this test.

2.3. Storage Method

Several samples with same contents were prepared. And then, they were stored in the oven with constant temperature (50 ℃, 55 ℃ and 60 ℃) under the constant-stress accelerated condition, respectively.

2.4. Sample Preparation

Each sample (6 g) was taken from the oven and left to cool to room temperature. The product (ca. 6.0 g)

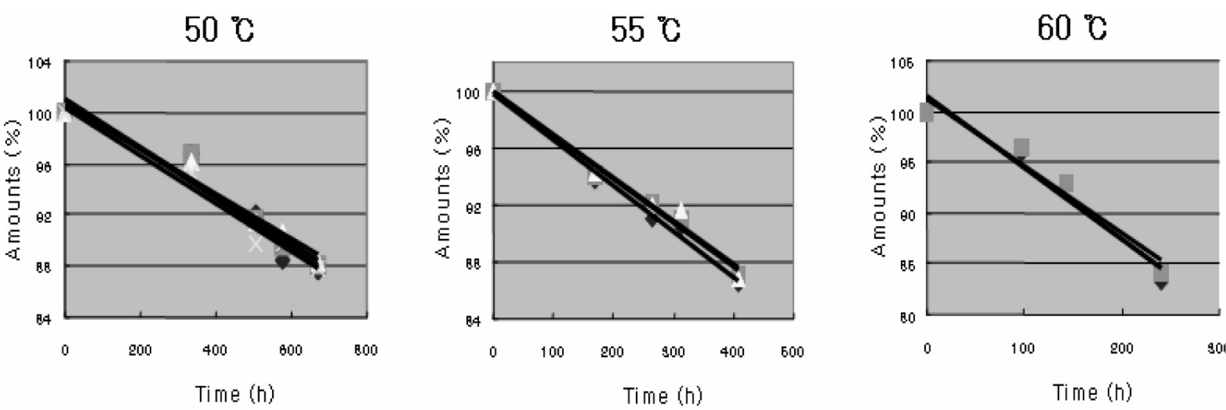

Figure 1. The quantity change of licorice versus time in cases of 50 ℃, 55 ℃ and 60 ℃.

was accurately weighed in to a 50 mL volumetric flask and dispersed in methanol by ultra-sonication for 10 min. After dilution to volume, the sample was filtered through 0.2 μm membrane filters (Whatman, USA) and then analyzed by HPLC.

2.5. Method of Analysis

The samples were analyzed through HPLC by using PDA. The operation condition was summarized in Table 1. The assay of licorice (as the glabridin) was measured 5 times with HPLC (Waters Alliance System) during 1 month after storage.

3. Results

Licorice is an officially approved component as a whitening function. In this study, the durability of cosmetic product which contains licorice was estimated by the accelerated life test with 'Arrhenius model' formulation.

For acceleration test, samples were stored in oven with constant temperature (50 ℃, 55 ℃, and 60 ℃) respectively. After each sample was warmed up to the oven temperature during certain period, leave them in the room for 30 min for cooling. And then, the quantity of licorice was determined using HPLC. The quantity changes of licorice in each temperature condition (50 ℃, 55 ℃, and 60 ℃) were like Figure 1. The lifetime of licorice in each temperature case was obtained: 580 h in 50 ℃, 319 h in 55 ℃, and 166 h in 60 ℃.

The relationship between time and the amount of licorice under the constant-stress accelerated condition was most suitably fitted into the Weibull distribution, which was verified with statistical analysis using 'Minitab' software solution[5]. If the lifetime of licorice was defined as a time period when 90 % of initial amount was left (10 % was vanished) during the test, then the lifetime of each temperature condition can be calculated.

Table 1. HPLC Operation Conditions for Determination of Licorice

System	HPLC alliance
Column	Mightysil RP-18 (4.6 mm × 250 mm, 5 m)
Eluent	63 : 37 : 0.1(v/v/v) water/acetonitrile/acetic acid
Elution speed	1.0 mL/min
Column temperature	25 ℃
Injection volume	20 μL
Detector wavelength	282 nm

The relationship between the decreasing rate of licorice and storage temperature was fitted into the 'Arrhenius model' of the lifetime (L) and temperature (T) (Eq. 6).

(critical amount) = (rate) × (time to failure)

The quantity decrease x and its lifetime τ has relationship like $x = \upsilon\tau$. Suppose that if x reaches x_0, the lifetime ends. Lifetime (L) is like below:

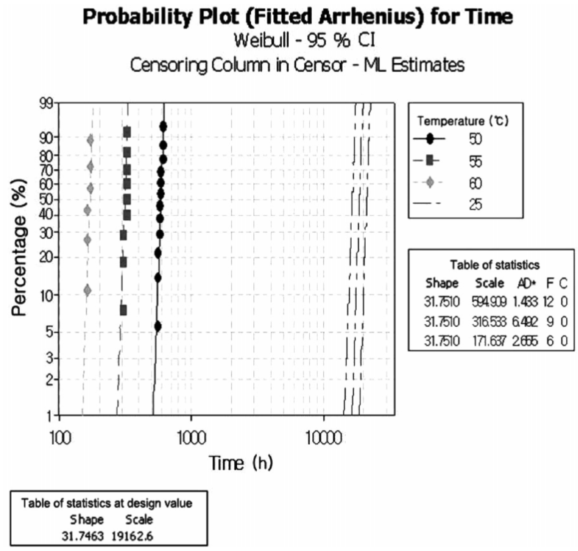

Figure 2. Probability plot versus time in cases of 50 ℃, 55 ℃, and 60 ℃.

$$x_0 = A_0 L \exp\left(-\frac{\triangle H}{kT}\right) \qquad (Eq.\ 4)$$

$$L = \left(\frac{x_0}{a_0}\right)\exp\left(\frac{\triangle H}{kT}\right) = a\ \exp\ \left(\frac{\triangle H}{kT}\right) \qquad (Eq.\ 5)$$

$$\ln L = \ln a + \left(\frac{\triangle H}{k}\right)\frac{1}{T} \qquad (Eq.\ 6)$$

Let L : lifetime,
a : constant,
ΔH : activation energy,
k : Boltzmann constant,
T : absolute temperature

By the statistical analysis using the 'accelerated life testing' function of Minitab solution, it was found out that the probability plots of 3 different temperature conditions for time are parallel to each other (Figure 2), which means that there are similarities in the lifetime plots of different temperature conditions.

By the 'Arrhenius model' formulation, the relationship between temperature and lifetime can be plotted as (Figure 3) and can be formulated as (Eq. 7).

$$\ln L = -35.0243 + 1.15322 \times \left(\frac{11604.83}{T}\right) \qquad (Eq.\ 7)$$

The lifetime of licorice at any specific temperature and its estimation with the confidence level of 95 % can be calculated by the equation (Eq. 7). The process which was established in this research can contribute to the fast and exact lifetime estimation of other useful components in cosmetics.

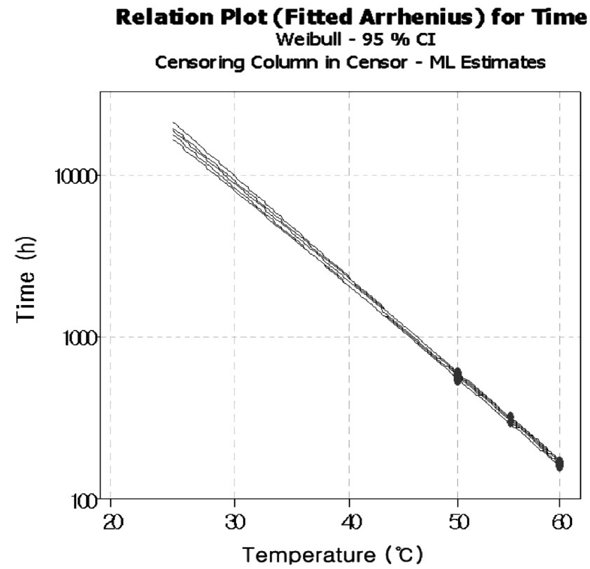

Figure 3. Relation plot for time in cases of 50 ℃, 55 ℃, and 60 ℃.

4. Conclusion

In this study, a method to test the durability of whitening cosmetics which contain licorice was proposed by the accelerated life test with 'Arrhenius model' formulation. The lifetime of licorice was defined as time for its 10 % reduction, which enabled the formulation of the 'Arrhenius equation'. By the equation, the estimated lifetime of licorice at 25 ℃ can be estimated as 26 months. There was no significant difference between the estimation value and real measurement in 95 % significance level.

References

1. L. Rigano and N. Lionetti, The period after opening in the jungle of EU product labeling, *Cosmetics & Tioletries*, **120**(5), 87 (2005).
2. Articles 5 to 7 of the Directive 76/768/EEC (2003).
3. C. Jo, J. Son, M. Shin, and M. Byun, Irradiation effects on color and functional properties of per-

simmon (*Diospyros kaki* L. folium) leaf extract and licorice (*Glycyrrhiza uralensis* Fischer) root extract during storage, *Radiation Physics and Chemistry*, **67**(2), 143 (2003).
4. R. Brown, Ageing of rubber-accelerated heat ageing test results, *Rapra Technology* (2001).
5. S. Seo, 가속수명시험 자료의 분석, MINITAB Reliability Analysis, 219 (2002).
6. J. F. Lawless, Statistical models and methods for lifetime data, 277, John Wiley & Sons, Inc., New York (1982).
7. W. Nelson, Applied life data analysis, 60, John Wiley & Sons, Inc., New York (1990).