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Thermal Degradation Kinetics of Tocopherols during Heating without Oxygen

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무산소 가열시 토코페롤의 열분해 키네틱스

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Abstract

천연 항산화제로 사용되는 토코페롤은 가열 온도가 높을수록, 가열 시간이 길수록 토코페롤의 분해율이 증가하였으며, 무산소 가열의 경우, 토코페롤은 산소가 있을 때 보다 덜 분해되었다. 알파-, 감마-, 델타-토코페롤의 무산소 가열 조건을 만들기 위하여 100~250℃에서 5~60분 가열하는 동안 회화로 속으로 질소를 계속 흘려보내는 실험 방법을 사용하였다. 헥산으로 추출한 토코페롤은 두 종류의 용출 용매와 역상 μ-Bondapak C_{18}-컬럼을 사용한 HPLC로 분리하였고 토코페롤의 분해 패턴과 잔존량을 조사하였다. 토코페롤의 열분해 키네틱스는 온도와 시간의 함수로 분석되었고 열분해 패턴은 1차 반응으로 나타났다. 무산소 가열시 알파-, 감마-, 델타-토코페롤의 열분해 활성화 에너지는 각각 3.47, 5.85 그리고 6.76 kcal/mole 이었다.

색인어: 토코페롤, 열분해, 키네틱스, 무산소.

INTRODUCTION

Lipid foods are deteriorated by oxidation at ambient temperature, and their oxidation becomes more rapidly during heating at high temperatures[1~5]. Oxidation results in undesirable changes affecting the sensory characteristics, nutritional quality and safety of food. The addition of antioxidants to lipid foods is one of the most effective ways to prevent oxidation[6~9].

The tocopherols function as antioxidants in the mode of inhibition of free radicals produced by singlet oxygen oxidation of free fatty acids and in the mode of direct quenching of singlet oxygen[10]. Grams and Eskins[11] reported that α-tocopherol was most reactive with singlet oxygen, followed by β-, γ- and δ-tocopherol.

In previous studies[12~15], the simultaneous separation of α-, γ- and δ-tocopherols and their thermal degradation products by HPLC using a reversed phase μ-Bondapak C_{18}-column was studied. The thermal degradation pattern of tocopherols during heating in the presence or absence of oxygen was also elucidated. These studies on the degradation of tocopherols could be useful to understand the function as antioxidants.

In this study, the thermal degradation kinetics of tocopherols during heating at various temperatures without oxygen was investigated.

MATERIALS AND METHODS

1. Materials

Tocopherols were obtained from Sigma Chemical Co.(St. Louis, MO, USA). Glycerol was purchased from Junsei Chemi-

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cal Co.(Tokyo, Japan) and membrane filter was obtained from Acrodisc Gelman(Gelman LC13, 0.45 ㎛, Ann Arbor, MI, USA). All other chemicals were the same as in the previous studies[12~15], unless otherwise specified.

2. Experimental Methods

To study the thermal degradation kinetics of tocopherols during heating without oxygen, all experimental system was the same methods as described in the previous studies[12~15]. A mixture of 50 ㎎ α-tocopherol and 10 ㎖ glycerol were placed in a crucible in furnace(Thermolyne 6000, Dubuque, IA, USA) and heated at 100, 150, 200 and 250℃ for 5, 15, 30 and 60 min. A furnace was used for controlling the temperature. Especially, a continuous stream of nitrogen was flushed through the furnace to remove oxygen during heating. The same method was applied for 2 ㎎ of γ-tocopherol and 4 ㎎ of δ-tocopherol.

3. Chromatographic Instrumentation

Tocopherols and their thermal degradation products which were extracted with hexane were simultaneously separated by HPLC with the same analytical conditions as described in the previous studies[12~15]. The HPLC system and operation conditions for tocopherols are shown in Table 1.

4. Kinetic Analysis

The degradation kinetics of each tocopherol was analyzed by determining the rate constants of thermal degradation of tocopherols during heating without oxygen. In the preliminary study, it was determined whether the thermal degradation kinetics of tocopherols obeyed zero- or first-order kinetics by calculating the regression coefficient. The regression coefficients were 0.70~0.78 for the zero-order kinetics, and 0.87~0.98 for the first-order kinetics, respectively. Thus, the first-order kinetic equations were employed in this study(data not shown).

Table 1. HPLC operation conditions for tocopherols

	Operation conditions			
Instrument	Waters HPLC system(Millipore, USA)			
Column	μ-Bondapak C_{18}(Waters 3.9×300 ㎜, 10 ㎛)			
Detector	Waters 484 absorbance detector(295 ㎚)			
Solvent	A solvent - acetonitrile:methanol=3:2(v/v) B solvent - acetonitrile:methanol:2-propanol :chloroform:methylene chloride =3:2:5:0.5:0.5(v/v/v/v/v)			
Gradient table	Waters 680 gradient controller			
	Time	Flow	%A	%B
	Initial	1:00	100	0
	30.0	1:00	0	100
	39.0	1:00	0	100
	49.0	1:00	0	100
	50.0	1:00	100	0
Injection volume	3 ㎕			

$$v = \frac{d[P]}{dt} = -\frac{d[C]}{dt} \quad (1)$$

$$-\frac{d[C]}{dt} = k_d[C] \quad (2)$$

$$\frac{d[C]}{[C]} = -k_d dt \quad (3)$$

$$\log\frac{[C]}{[C_0]} = -k_d\frac{t}{2.3} \quad (4)$$

$$\log[C] = \log[C_0] - k_d\frac{t}{2.3} \quad (5)$$

where, v and $[P]$ are the initial velocity and product concentration, $[C]$ = residual tocopherol content during heating, $[C_0]$ = tocopherol content at the beginning of heating(t=0), t = heating time, k_d = rate constant of the first-order kinetics. The rate constant k_d was obtained from the slope of the plot(Fig. 1).

Experimental activation energies were determined by the Arrhenius equations[16] :

$$k_d = Ae^{-E_a/RT} \quad (6)$$

Or, in linear form :

$$\log k_d = \log A - \frac{E_a}{2.3R}\frac{1}{T} \quad (7)$$

where, k_d = rate constant, A = pre-exponential factor, E_a = activation energy, R = gas constant, T = absolute temperature(K).

Activation energy was determined from the slope $-\frac{E_a}{2.3R}$ of the $\log k_d$ vs. $\frac{1}{T}$ plot.

RESULTS AND DISCUSSION

The kinetics for the degradation of α-, γ- and δ

-tocopherols in the absence of oxygen was analyzed as a function of temperatures and times. The parameters are : times of 5, 15, 30 and 60 min ; temperatures of 100, 150, 200 and 250℃. For all experimental conditions, the rate constant of the degradation of tocopherols was described by the first-order kinetics. The rate of the degradation of tocopherols in a model food system was dependent on the heating temperatures. The activation energies were obtained from the Arrhenius equation.

Fig. 1 shows the plot of the content of α-tocopherol vs. heating time. The degradation rate constants of α-tocopherol, estimated from the linear regression data, were 0.0015, 0.0015, 0.0018 and 0.0071 $M^{-1}min^{-1}$ at 100, 150, 200 and 250℃, respectively(Table 2). The activation energy calculated for the thermal degradation of α-tocopherol was 3.47 kcal/mole(Fig. 2).

Fig. 3 also shows the plot of the content of γ-tocopherol vs. heating time. The degradation rate constants ranged from 0.0034 to 0.0320 $M^{-1}min^{-1}$(Table 2). The activation energy for the thermal degradation of γ-tocopherol was 5.85 kcal/mole (Fig. 4). At the plot of the content of δ-tocopherol vs. heating time(Fig. 5), the degradation rate constants ranged from 0.0020 to 0.0800 $M^{-1}min^{-1}$(Table 2). The activation energy for the thermal degradation of δ-tocopherol was 6.76 kcal/mole(Fig. 6).

Table 2 summarizes kinetic analysis results for the degradation of α-, γ- and δ-tocopherols without oxygen. The rate of degradation of tocopherols was dependent on the heating temperatures. The rate of degradation of tocopherols became larger as the heating temperature increased. The degradation rate constants for γ- and δ-tocopherols were higher than those for α-tocopherol. Thus, it implied that γ- and δ-tocopherols de-

Table 2. Kinetic analysis for degradation of tocopherols without oxygen

Sample	Reaction kinetics			
	Temperature (℃)	Rate constant ($M^{-1}min^{-1}$)	E_a[1] (kcal/mole)	R^2
α-Tocopherol	100	0.0015	3.47	0.60
	150	0.0015		
	200	0.0018		
	250	0.0071		
γ-Tocopherol	100	0.0034	5.85	0.82
	150	0.0039		
	200	0.0084		
	250	0.0320		
δ-Tocopherol	100	0.0020	6.76	0.77
	150	0.0030		
	200	0.0100		
	250	0.0800		

[1] Values obtained from slope of Arrhenius plot.

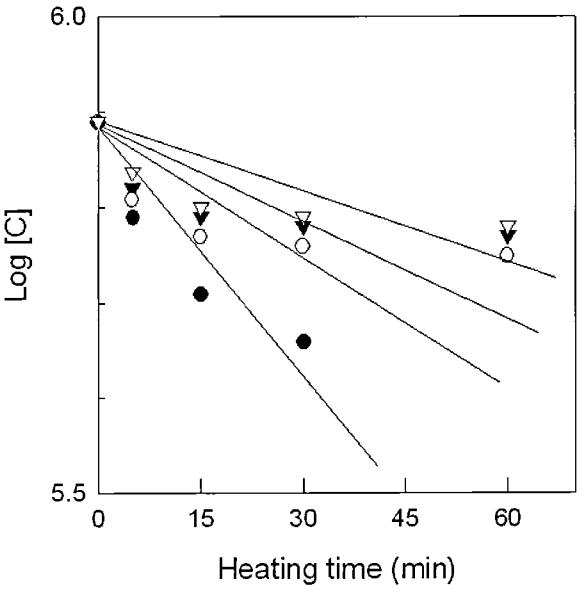

Fig. 1. Semi-logarithmic plot of residual α-tocopherol content during heating at various temperatures without oxygen.

▽: 100℃, ▼: 150℃, ○: 200℃, ●: 250℃.

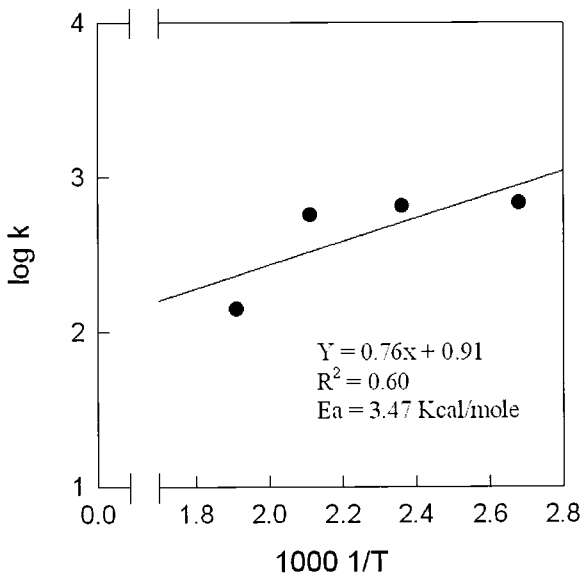

Fig. 2. Arrhenius plot of degradation of α-tocopherol without oxygen.

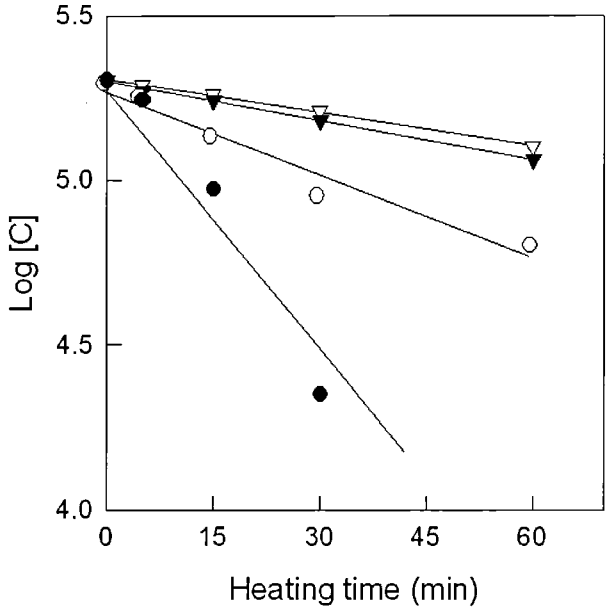

Fig. 3. Semi-logarithmic plot of residual γ-tocopherol content during heating at various temperatures without oxygen.

▽: 100℃, ▼: 150℃, ○: 200℃, ●: 250℃.

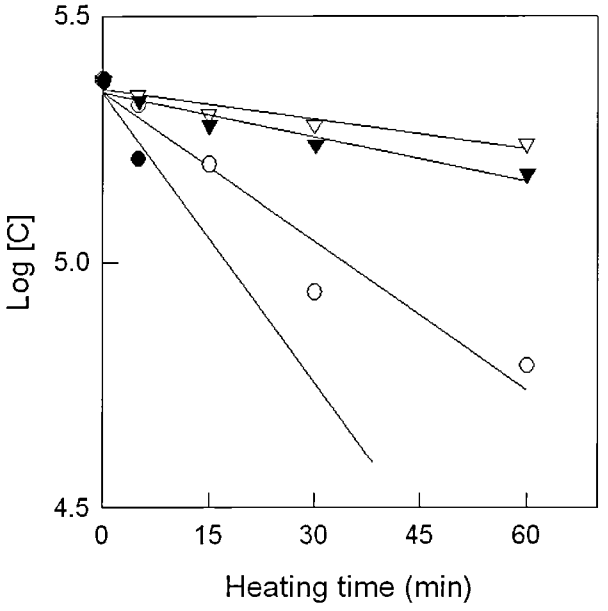

Fig. 5. Semi-logarithmic plot of residual δ-tocopherol content during heating at various temperatures without oxygen.

▽: 100℃, ▼: 150℃, ○: 200℃, ●: 250℃.

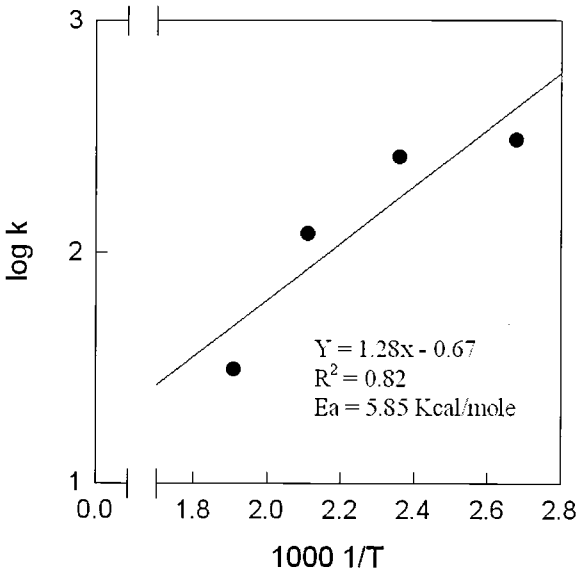

Fig. 4. Arrhenius plot of degradation of γ-tocopherol without oxygen.

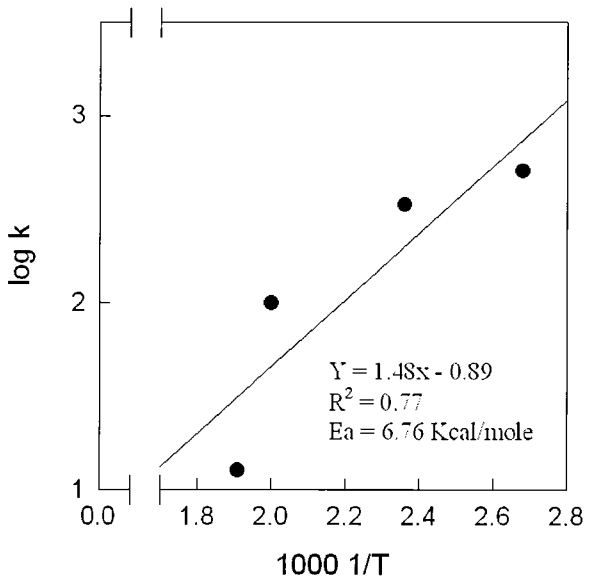

Fig. 6. Arrhenius plot of degradation of δ-tocopherol without oxygen.

graded more rapidly than the α-tocopherol. The activation energies for the thermal degradation of tocopherols without oxygen were described in Table 2. The experimental activation energy for α-tocopherol was smaller than γ- and δ-tocopherols in the absence of oxygen. These results suggest that the degradation of γ- and δ-tocopherols was more affected by the change of heat-

ing temperatures than that of α-tocopherol.

In summary, the degradation of α-, γ- and δ-tocopherols was described by the first-order kinetics in the absence of oxygen. The rate of tocopherols degradation was dependent on heating temperatures. The degradation rate constants for tocopherols showed an increasing trend as the heating temperature increased. The magnitude order of the experimental activation energy was δ -> γ -> α-tocopherol. These results can provide information for the control of the oxidation of foods.

SUMMARY

The thermal degradation kinetics of alpha-, gamma- and delta-tocopherols was studied during heating at 100, 150, 200 and 250℃ for 5, 15, 30 and 60 min in the absence of oxygen. The tocopherols were separated by HPLC using a reversed phase μ-Bondapak C_{18}-column with two kinds of elution solvent system in a gradient mode. The kinetics for degradation of α-, γ- and δ-tocopherols was analyzed as a function of temperatures and times. The degradation of tocopherols was described by the first-order kinetics in the absence of oxygen. The rate of tocopherols degradation was dependent on heating temperatures. The degradation rate constants for α-, γ- and δ-tocopherols showed an increasing trend as the heating temperature increased. The magnitude order of the experimental activation energy was δ -> γ -> α-tocopherol.

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