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Formation Kinetic Study of Thermal Products of Tocopherols

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Abstract

The kinetic analyses for thermal products of alpha-, gamma- and delta-tocopherols during heating as functions of temperature and time were studied. Alpha-, gamma- and delta-tocopherols dissolved in glycerol were heated at 100～200°C for 5～60 min. The thermal products were separated by hexane extraction and analyzed by HPLC using a reversed phase μ-Bondapak C_{18}-column with two kinds of elution solvents in a gradient mode. The formation kinetics of thermal products of tocopherols followed a first-order kinetic model. The formation rate of thermal products of tocopherols was dependent on heating temperatures and heating times. The activation energy and enthalpy for the thermal products of γ-and δ-tocopherols were higher than those for α-tocopherol as in the case of the oxidative degradation kinetics of tocopherol. The magnitude order of the activation energy was γ->δ-> α-tocopherol.

Key words: tocopherols, thermal degradation products, kinetics

INTRODUCTION

Tocopherols, as antioxidants, not only quench singlet oxygen (physical quenching) but also react with singlet oxygen (chemical quenching). The proportion of physical quenching vs. chemical quenching is dependent on structure and solvent system. Physical quenching is the major mechanism for tocopherols (1,2). The studies of tocopherols have been mainly focused on their effect as antioxident (3-10).

Many studies have been conducted to investigate the kinetic parameters and kinetics for degradation of food components during heating (11-13) or storage (14,15). Jensen (14) showed that the rate of α-tocopherol degradation in seaweed meal was accelerated by increasing the storage temperature or the moisture content. Rim et al. (15) studied the kinetic parameters for the texture changes in sweet potatoes during heat treatment.

In previous studies (16-18), the separation and formation pattern of thermal degradation products of tocopherols during heating were elucidated. Major thermal degradation products of alpha-tocopherol were identified by LC-MS, and the structures of thermal products were proposed. The degradation products were combined with an oxidized product (tocopherylquinone) to make thermal products through dimerization (19).

The objectives of the present study were to investigate the kinetics, and to evaluate the kinetic parameters for formation of thermal products of α-, γ- and δ-tocopherols during heating.

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MATERIALS AND METHODS

Materials

Tocopherols were obtained from Sigma Chemical Co. (St. Louis, MO, USA). Glycerol was purchased from Junsei Chemical Co. (Tokyo, Japan) and membrane filter from Acrodisc Gelman (Gelman LC13, 0.45 μM, Ann Arbor, MI, USA) was used. All other chemicals were the same as in the previous studies (16-18), unless otherwise specified.

Extraction of thermal degradation products

To study the formation kinetics of degradation products of α-, γ- and δ-tocopherols during heating, all experimental systems were prepared as described by Chung et al. (16-18). A mixture of 50 mg α-tocopherol and 10 mL glycerol in a crucible were placed in a temperature controlled muffle furnace (Thermolyne 6000, Dubuque, IA, USA) and heated at 100, 150 and 200°C for 5, 15, 30 and 60 min. After cooling the mixture for 30 min at room temperature, the thermal degradation products of α-tocopherol were extracted from glycerol with hexane. The hexane layer containing the thermal products of tocopherols was filtered through a membrane filter (Gelman LC13, 0.45 μM, Ann Arbor, MI, USA) to prepare them for analysis of the components. The same method was applied for 2 mg of γ-tocopherol and 4 mg of δ-tocopherol.

Separation of thermal degradation products

The extracted thermal degradation products of toco-

pherols were separated by HPLC under the same analytical conditions as described in the previous studies (16-18). The HPLC system consisted of a Waters 501 and 510 HPLC pumps, and a Waters 745B Data Module integrator (Millipore, Milford, MA, USA). The peaks of thermal degradation products of tocopherols were observed at 295 nm using a Waters 484 UV detector. Hexane-extracted thermal products were separated by HPLC using a reversed phase μ-Bondapak C_{18}-column with two kinds of elution solvents in a gradient mode. The injection volume was 3 μL.

Kinetic data analysis

The formation kinetic analysis of thermal degradation products of α-, γ- and δ-tocopherols was analyzed with the same methods as in the oxidative degradation kinetics of tocopherols (20). The regression coefficients were 0.70～0.78 for zero-order kinetics and 0.87～0.98 for first-order kinetics in the preliminary study. Thus, the formation kinetics of thermal degradation products of tocopherols was modeled as first-order (Table 1) as follows:

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

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

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

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

$$\ln[C] = [C_0] - k_d t \quad (5)$$

where, v and $[P]$ are the initial velocity and product concentration, respectively, $[C]$ = thermal products content during heating, $[C_0]$ = thermal products content at the beginning of heating ($t=0$), t = heating time, k_d = rate constant of the first-order kinetics.

Table 1. Reaction rate constants and correlation coefficients for thermal degradation products of tocopherols[1)]

Tocopherols	Temperature (°C)	Rate constant ($M^{-1}min^{-1}$)	R^2
α-tocopherol	100	0.0480	0.815
	150	0.0645	0.953
	200	0.0839	0.812
γ-tocopherol	100	0.0081	0.618
	150	0.0308	0.929
	200	0.0799	0.932
δ-tocopherol	100	0.0182	0.781
	150	0.0426	0.979
	200	0.0654	0.935

[1)]Values obtained from linear regression data of ln plot of thermal degradation products content of tocopherols.

The activation energy (E_a) and frequency factor (ln A) were determined from the Arrhenius model (21):

$$\ln A = \ln k + E_a/RT \quad (6)$$

where R is the gas constant and T is absolute temperature (K).

The enthalpy of activation (ΔH) was obtained by plotting ln (k/T) vs. $1/T$, and the entropy of activation (ΔS) was obtained from the expression of rate constants based on the transition state theory:

$$\ln(k/T) = \ln(k_b/h) + \Delta S/R - \Delta H/RT \quad (7)$$

where k_b is Boltzmann's constant and h is Planck's constant.

RESULTS AND DISCUSSION

Formation kinetics of thermal degradation products

Oxidized tocopherol and corresponding tocopherylquinone, and their degraded fragments formed various kinds of thermal degradation products during heating (19). The kinetic analysis for thermal degradation products of α-, γ- and δ-tocopherols as functions of temperature and time was performed. The parameters were as follows: times of 5, 15, 30 and 60 min; temperatures of 100, 150 and 200°C. At 200°C, however, the content for thermal degradation products of tocopherols increased until 30 min and thereafter sharply decreased. The thermal degradation products of tocopherols were not easily extracted from glycerol with hexane, because those could be burned to form unextractable substances (18). For all the experimental conditions except heating for 60 min at 200°C, the formation rate constant of the thermal products of tocopherols was described by the first-order kinetics, i.e., ln $[C] = [C_0] - k_d t$. The formation rate of thermal products depended on temperatures. The activation energies were obtained from the values calculated from the slope of an Arrhenius plot by using the experimental data.

Widicus et al. (22) reported that the storage stability of α-tocopherol in a model food system containing no fat could be modeled by first-order kinetics. On the other hand, Widicus and Kirk (23) reported the storage stability of α-tocopherol in a model food system containing methyl linoleate was expressed by zero-order kinetics. The zero-order reaction occurred if the reaction of product was so small in the time period studied that the content of product did not change significantly (24).

The formation rate constants of the degradation products of α-tocopherol, were estimated from the linear regression data as 0.0480, 0.0645 and 0.0839 $M^{-1}min^{-1}$ at

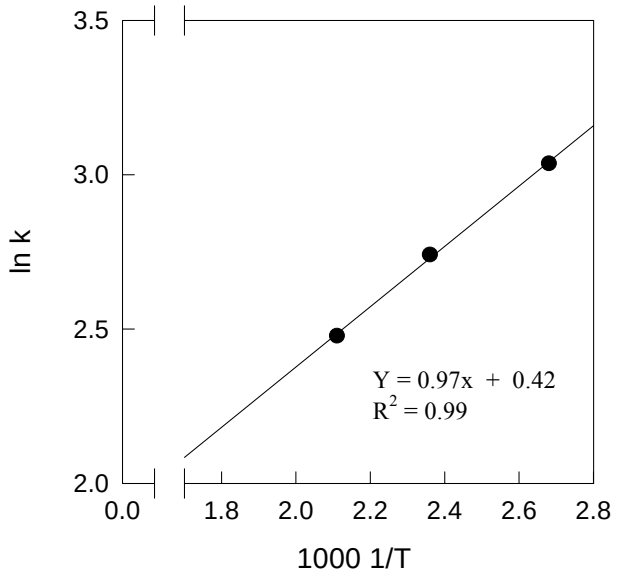

Fig. 1. Arrhenius plot of thermal degradation products of α-tocopherol.

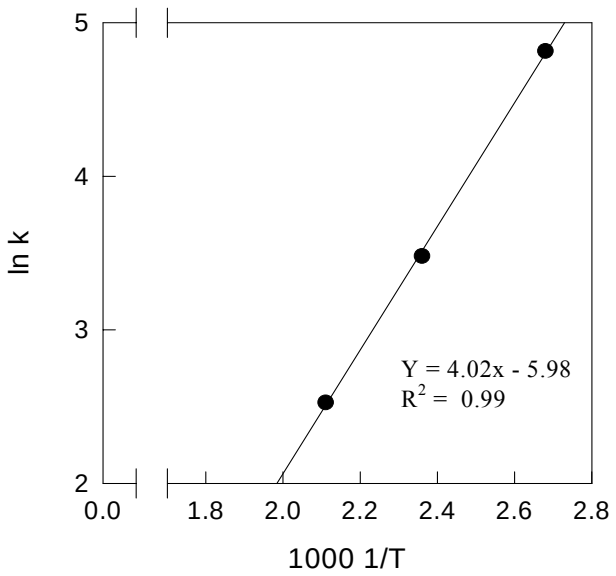

Fig. 2. Arrhenius plot of thermal degradation products of γ-tocopherol.

100, 150 and 200°C, respectively (Table 1). The experimental activation energy for the degradation products of α-tocopherol was 1.94 kcal/mole (Table 2). A plot of ln *k* vs. absolute temperature (1000 1/*T*) (Fig. 1) was used to fit a kinetic model. Widicus et al. (22) reported that the degradation of α-tocopherol was described by the first order rate kinetics model and experimental activation energies ranged from 8.85～13.05 kcal/mole.

The formation rate constants of the thermal products of γ-tocopherol ranged from 0.0081 to 0.0799 $M^{-1}min^{-1}$ (Table 1). The experimental activation energy for the formation of thermal products of γ-tocopherol was 7.99 kcal/mole (Table 2). Fig. 2 also shows the plot of ln *k* vs. absolute temperature (1000 1/*T*). The formation rate constants of thermal degradation products of δ-tocopherol ranged from 0.0182 to 0.0654 $M^{-1}min^{-1}$ (Table 1). From the plot of ln *k* vs. absolute temperature (1000 1/*T*) (Fig. 3), the activation energy for the thermal degradation products of δ-tocopherol was 4.51 kcal/mole (Table 2). Labuza and Tannenbaum (24) studied the kinetics of various reactions and reported experimental activation energies of 10～25 kcal/mole for lipid oxidation, 10～15 kcal/mole for enzyme reactions, 15 kcal/mole

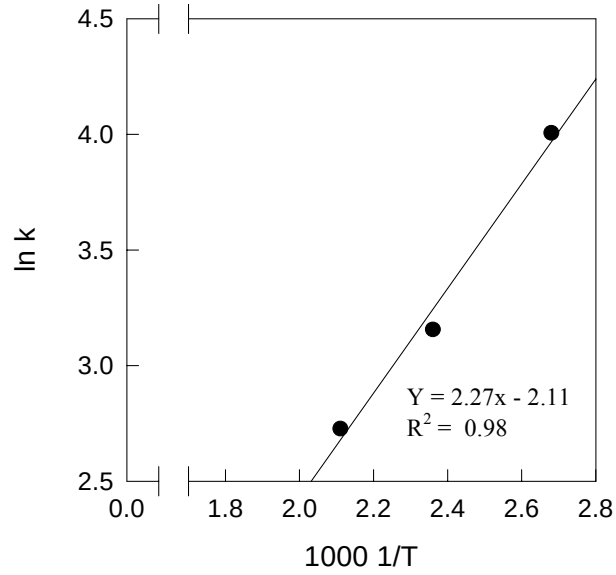

Fig. 3. Arrhenius plot of thermal degradation products of δ-tocopherol.

for hydrolysis. Chung (20) reported the activation energies for the oxidative degradation of α-, γ- and δ-tocopherols ranged from 2.51～6.05 kcal/mole. Higher temperatures and longer heating times increased the for-

Table 2. Activation energies and thermodynamic properties for thermal degradation products of tocopherols

Tocopherols	Activation energy (kcal/mole)[1)]	Intercept ln A[1)]	R^2	Enthalpy of activation (kcal/mole)[2)]	Entropy of activation (kcal/mole · K)[2)]	R^2
α-tocopherol	1.94	0.42	0.998	1.12	-32.40	0.998
γ-tocopherol	7.99	5.98	0.999	7.17	-45.12	0.998
δ-tocopherol	4.51	2.11	0.986	3.67	-37.40	0.977

[1)]Values obtained from slope, intercept and linear regression of Arrhenius plot.
[2)]Values obtained from slope, intercept and linear regression of transition state theory equations.

mation of thermal degradation products from tocopherols (Figs. 1～3).

Kinetic parameters

Table 1 and Table 2 are the kinetic analysis results for the thermal degradation products of α-, γ- and δ-tocopherols. The formation rate of thermal products was dependent on the heating temperatures and heating times. The rate constants become larger as the temperature gets higher. As heating temperature and heating time increased, the formation of thermal products of tocopherols increased accordingly.

The Arrhenius model and transition state theory were used to investigate the influence of temperature on the formation reaction rates. The activation energy (E_a) and frequency factor (ln A) were determined from the Arrhenius equation, and enthalpy (ΔH) and entropy (ΔS) were obtained from transition state theory. The activation energy and enthalpy for the thermal products of γ-and δ-tocopherols were higher than those for α-tocopherol as in the case of the oxidative degradation kinetics of tocopherol (20).

In conclusion, the thermal degradation products of tocopherols obeyed a first-order kinetics. The formation rate of thermal products was dependent on the heating temperatures and heating times. The activation energy and enthalpy for the thermal degradation products of γ- and δ-tocopherols were higher than those for α-tocopherol as in the case of the oxidative degradation kinetics of tocopherol. The magnitude order of the activation energy was γ->δ->α-tocopherol.

REFERENCES

1. Min DB, Lee EC, Lee SH. 1989. Singlet oxidation of vegetable oils. In *Flavor Chemistry of Lipids Foods*. Min DB, Smouse TH, eds. The American Oil Chemists' Society, Campaign, IL, USA. p 57-64.
2. Grams GW, Eskins K. 1972. Dye-sensitized photooxidation of tocopherols. correlation between singlet oxygen reactivity and vitamin E activity. *Biochem* 11: 606-608.
3. Hahm TS, King DL, Min DB. 1993. Food antioxidants. *Foods and Biotechnol* 2: 1-18.
4. Lea CH, Ward RJ. 1959. Relative antioxidant activities of the seven tocopherols. *J Sci Food Agric* 10: 537-548.
5. Lehmann JW, Putnam DH, Qureshi AA. 1994. Vitamin E isomers in grain Amaranths (*Amaranthus* spp.). *Lipids* 29: 177-181.
6. Dugan Jr LR, Kraybill HR. 1956. Tocopherols as carry-through antioxidants. *J Am Oil Chem Soc* 33: 527-528.
7. Jung MY, Min DB. 1990. Effects of α-, γ-, and δ-tocopherols on oxidative stability of soybean oil. *J Food Sci* 55: 1464-1465.
8. Jung MY, Choe E, Min DB. 1991. α-, γ- and δ-Tocopherol effects on chlorophyll photosensitized oxidation of soybean oil. *J Food Sci* 56: 807-815.
9. Parkhurst RM, Skinner WA, Sturm PA. 1968. The effect of various concentrations of tocopherols and tocopherol mixtures on the oxidative stability of a sample of lard. *J Am Oil Chem Soc* 45: 641-642.
10. Huang SW, Frankel EN, German JB. 1994. Antioxidant activity of α- and γ-tocopherols in bulk oils and in oil-in water emulsions. *J Agric Food Chem* 42: 2108-2114.
11. Rhim JW, Victor AJ, Kenneth RS. 2002. Texture degradation kinetics of sweet potatoes during heat treatment. *Food Sci Biotechnol* 11: 24-28.
12. Rhim JW. 2002. Kinetic compensation relations for texture changes in sweet potatoes during heating. *Food Sci Biotechnol* 11: 29-33.
13. Rhim JW. 2002. Kinetics of thermal degradation of anthocyanin pigment solutions driven from red flower cabbage. *Food Sci Biotechnol* 11: 361-364.
14. Jensen A. 1969. Tocopherol content of seaweed and seaweed meal. Ⅲ. Influence of processing and storage on the content of tocopherols, carotenoids and ascorbic acid in seaweed meal. *J Sci Food Agric* 20: 622-625.
15. Livingston AL, Nelson JW, Kohler GO. 1968. Stability of α-tocopherol during alfalfa dehydration and storage. *J Agric Food Chem* 16: 492-495.
16. Chung HY, Kwon DY, Yoon SH, Yang CH. 1998. Differential separation of thermal degradation products of tocopherols by HPLC. *Food Sci Biotechnol* 7: 80-83.
17. Chung HY. 1998. Thermal degradation pattern of tocopherols on heating without oxygen in a model food system. *Korean J Food & Nutr* 11: 635-639.
18. Chung HY, Yang CB. 1999. Oxidative degradation pattern of tocopherols on heating. *Food Sci Biotechnol* 8: 168-171.
19. Chung HY. 2004. Characterization of thermal products of alpha-tocopherol. *J Food Sci Nutr* 9: 295-299.
20. Chung HY. 2007. Oxidative degradation kinetics of tocopherols during heating. *J Food Sci Nutr* 12: 115-118.
21. Atkins PW. 1986. The rates of chemical reactions. In *Physical Chemistry*. W.H. Freeman and Company, New York, NY, USA. p 699.
22. Widicus WA, Kirk JR, Gregory JF. 1980. Storage stability of α-tocopherol in a dehydrated model food system containing no fat. *J Food Sci* 45: 1015-1018.
23. Widicus WA, Kirk JR. 1981. Storage stability of α-tocopherol in a dehydrated model food system containing methyl linoleate. *J Food Sci* 46: 813-816.
24. Labuza TP, Tannenbaum SR. 1972. Nutrient losses during and storage of dehydrated foods. *Crit Rev Food Technol* 3: 217-240.

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