Food Sci. Biotechnol. Vol. 18, No. 2, pp. 526 ~ 532 (2009)

Food Science and Biotechnology

Quenching Mechanisms and Kinetics of α-, β-, γ-, and δ-Tocopherol in Photosensitized Oxidation of Lard

Robert King, Hyung Ok Lee, and David B. Min*

Department of Food Science and Technology, The Ohio State University, 2015 Fyffe Road, Columbus, OH 43210, USA

Abstract Quenching mechanisms and kinetics of α-, β-, γ-, and δ-tocopherol in photosensitized oxidation of lard were studied. Lard at 0.03, 0.07, 0.11, and 0.3 M in methylene chloride containing 4.4×10^{-6} M chlorophyll and 0, 0.1, 0.3, and 0.6 mM α-, β-, γ-, and δ-tocopherol were stored under light for 4 hr, respectively. Oxidation was determined by headspace oxygen and peroxide value. Tocopherols prevented the photosensitized oxidation of lard ($p<0.05$). Steady state kinetic study showed that α-, β-, γ-, and δ-tocopherol prevented the photosensitized oxidation of lard by quenching singlet oxygen. Singlet oxygen quenching rates of α-, β-, γ-, and δ-tocopherol by headspace oxygen depletion were 1.86, 2.39, 2.47, and 2.11×10^{7}/M/sec, respectively. The quenching rates of α-, β-, γ-, and δ-tocopherol by peroxide value were 1.42, 1.11, 0.97, and 0.42×10^{7}/M/sec, respectively. The quenching rates of tocopherols were slightly different depending on the measurements of oxidation.

Keywords: lard, photosensitized oxidation, quenching rate, singlet oxygen, tocopherol

Introduction

Singlet oxygen is a highly reactive and non-radical compound with a very short lifetime, 2 μsec in water (1,2). It is different from atmospheric diradical triplet oxygen in its electron configuration. Singlet oxygen is an electrophilic compound due to its empty outer orbital. Electrophilic singlet oxygen can directly react with electron-rich compounds containing double bonds without the formation of free-radical intermediates (2). The reaction between singlet oxygen and unsaturated fatty acids occurs very rapidly in foods. The reaction rates of oleic, linoleic, and linolenic acid with singlet oxygen are 30,000, 1,500, and 900 times greater than the rates of triplet oxygen oxidation, respectively (3). Singlet oxygen can be formed several different ways; however, the photosensitized mechanism is predominant in food systems (4). Photosensitizer such as chlorophyll, riboflavin, pheopytins, porphyrins, myoglobin, and synthetic colorants in foods can absorb energy from light and transfer it to triplet oxygen to form singlet oxygen (2).

Singlet oxygen oxidation in foods is very important because the rate of singlet oxygen oxidation is much greater than the triplet oxygen oxidation. Singlet oxygen rapidly increases the oxidation rate of foods even at very low temperature and produces new compounds, which are not found in ordinary triplet oxygen oxidation in foods (5). Singlet oxygen quenchers are added to foods to prevent the singlet oxygen oxidation. Tocopherol has been reported to prevent the singlet oxygen oxidation (6,7). Tocopherol can quench singlet oxygen either chemically or physically. The chemical quenching of singlet oxygen results in the destruction of tocopherol and the production of oxidized products. During physical quenching, tocopherol forms a charge transfer complex with singlet oxygen and donates electrons to singlet oxygen (8-10). The transfer complex undergoes an intersystem crossing to form triplet oxygen and the starting tocopherol. Physical quenching is predominant, with chemical quenching accounting for 0.1 to 1.5% of physical quenching (10,11).

There are 4 isomers of tocopherol, α-, β-, γ-, and δ-tocopherol which differ in the number and location of methyl groups in the chromanol ring. The quenching rate of α-tocopherol in the chlorophyll photosensitized oxidation of soybean oil was 2.7×10^{7}/M/sec by peroxide value and 2.6×10^{7}/M/sec by headspace oxygen depletion (6). Yang *et al.* (7) reported that the quenching rate of α-tocopherol in the food colorant FD&C Red No. 3 photosensitized oxidation of soybean oil was 4.1×10^{7}/M/sec. Only α-tocopherol quenching rate was studied among 4 types of tocopherol in foods. There is no information on the quenching mechanisms and kinetics of β-, γ-, and δ-tocopherol in foods. The objectives of this study were to determine the quenching activities, mechanisms, and kinetics of α-, β-, γ-, and δ-tocopherol in the photosensitized oxidation of lard.

Materials and Methods

Materials α-Tocopherol (95%) and chlorophyll b were obtained from Sigma-Aldrich (St. Louis, MO, USA). β-Tocopherol (50 mg/mL hexane), γ-tocopherol (96%), and δ-tocopherol (95%) were obtained from Supleco Inc. (Bellefonte, PA, USA). Pork fat was provided from the Department of Animal Science at The Ohio State University (Columbus, OH, USA). Glacial acetic acid, potassium iodide, and methylene chloride were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Chloroform and sodium thiosulfate (0.1 N in water) were obtained from Mallinckrodt Chemicals (Phillipsburg, NJ, USA) and Sigma-Aldrich, respectively. Headspace vials, Teflon-coated rubber septa, and aluminum caps were obtained from Supelco Inc.

*Corresponding author: Tel: +1-614-292-7801; Fax: +1-614-292-0218
E-mail min.2@osu.edu
Received February 19, 2009; Accepted February 23, 2009

Sample preparation Lard was prepared from pork fat in a water bath at 70°C for 2 hr. Samples of 0.03, 0.07, 0.11, and 0.3 M lard in methylene chloride containing 4.4×10^{-6} M chlorophyll b were prepared. α-, β-, γ-, and δ-Tocopherol were added to lard samples to obtain the concentration of 0.1, 0.3, and 0.6 mM. Three mL of sample was transferred to a 10-mL headspace vial and sealed airtight with a rubber septum and an aluminum cap. Samples were prepared in duplicate and placed in a plastic carousel in a wooden mirrored light box (70×50×60 cm) as described by King and Min (12). The carousel was motorized and samples were rotated above a 100 W tungsten light bulb so that there was uniform light exposure for each sample. Samples were stored for 4 hr and analyzed for headspace oxygen and peroxide value.

Determination of headspace oxygen Headspace oxygen in a sample vial was measured by injecting 100 mL of headspace gas into a HP 5890 gas chromatograph (Hewlett Packard, Wilmington, DE, USA) equipped with a thermal conductivity detector. A stainless steel column (1.8 m× 0.32 cm) packed with 80/100 Molecular Sieve 13X (Alltech Associates, Inc., Deerfield, IL, USA) was used. High purity (99.995%) helium gas was used as a carrier gas at 20 mL/min. The temperature of the injection, oven, and detector were 120, 40, and 150°C, respectively. The gas chromato-graphic peak was measured by electronic count using a HP 3396A integrator (Hewlett Packard). Depleted headspace oxygen was expressed as μmol O_2/mL headspace. One mL of air is made up of 20.946%, which is equal to 9.35 μmol of oxygen (13).

Determination of peroxide value Peroxide value was determined using a modified AOCS method Cd-8-53 (14). Two g of sample was weighed out and 15 mL of a 3:2 acetic acid:chloroform solution was added. The sample solution was mixed and 0.25 mL of saturated potassium iodide solution was added. The solution was allowed to stand for 1 min, with occasional shaking, and then 15 mL of distilled water was added. The solution was titrated with 0.05 N sodium thiosulfate until the yellow color had almost disappeared. One mL of starch indicator was added and titration continued. Titration was stopped when the blue/purple color had just disappeared. Peroxide value was expressed as milliequivalent (meq) peroxide/kg sample.

Statistical analysis Samples were prepared in duplicate. Analysis of variance and Tukey's test were used to analyze data using SAS 9.1 (SAS Institute Inc., Cary, NC, USA) at $\alpha=0.05$. Regression analysis was performed using Microsoft Office Excel 2003 (Microsoft Corp., Redmond, WA, USA).

Results and Discussion

Properties of lard The initial peroxide value of lard was 2.5 meq/kg lard. The fatty acids composition of lard was 26% palmitic acid, 14% stearic acid, 44% oleic acid, and 10% linoleic acid. Lard has less unsaturated fatty acids than soybean oil which has 25% oleic acid, 55% linoleic acid, and 7% of linolenic acid (4). Lard does not contain chlorophyll, a photosensitizer and is commonly used in foods as an ingredient. Food can contain photosensitizers such as chlorophyll, myoglobin, riboflavin, and synthetic colorant. It is possible that singlet oxygen oxidation occurs in lard when added to foods containing photosensitizer during light storage. Therefore, lard was chosen to study the quenching mechanisms and kinetics of tocopherols in chlorophyll photosensitized oxidation.

Reproducibility of headspace oxygen and peroxide value analyses The coefficients of variation for headspace oxygen and peroxide value analyses for 5 replicates were 0.9 and 1.9%, respectively (data not shown). The low coefficients of variations indicated that headspace oxygen and peroxide value analyses were reproducible and acceptable methods to study the photosensitized oxidation of lard.

Effects of α-, β-, γ-, and δ-tocopherol in chlorophyll photosensitized oxidation of lard The effects of α-, β-, γ-, and δ-tocopherol at 0.1, 0.3, and 0.6 mM in chlorophyll photosensitized oxidation of lard are shown in Table 1. A preliminary study showed that the headspace oxygen and peroxide value of lard sample without chlorophyll under light or with chlorophyll in the dark for 4 hr did not change (data not shown). The headspace oxygen depletion and peroxide value increased only in the presence of chlorophyll during storage under light.

Mean values of headspace oxygen contents were calculated from 0.03, 0.07, 0.11, and 0.3 M lard in methylene chloride containing 4.4×10^{-6} M chlorophyll b and 0, 0.1, 0.3, and 0.6 mM α-, β-, γ-, and δ-tocopherol under light for 4 hr (Table 1). The headspace oxygen of sample without tocopherol decreased from 20.9 to 17.0% after 4 hr of

Table 1. Effects of α-, β-, γ-, and δ-tocopherol at 0, 0.1, 0.3, and 0.6 mM on headspace oxygen and peroxide value of 0.03, 0.07, 0.11, and 0.3 M lard in methylene chloride containing 4.4×10^{6} M chlorophyll b under light for 4 hr

Tocopherol	Concentration (mM)	Headspace oxygen (%)	Peroxide value (meq/kg)
α-	0	17.02a[1)]	6.95a
	0.1	17.10a	6.20b
	0.3	17.56b	5.15c
	0.6	18.30c	4.78c
β-	0	17.02a	6.95a
	0.1	17.77b	5.72b
	0.3	18.03bc	5.70b
	0.6	18.54c	5.05c
γ-	0	17.02a	6.95a
	0.1	17.43b	6.94a
	0.3	18.60c	5.92b
	0.6	18.32d	4.98c
δ-	0	17.02a	6.95a
	0.1	17.33b	6.97a
	0.3	17.74c	5.91ab
	0.6	18.22d	5.48b

[1)]Different letters followed by data indicate significant differences among concentrations of each tocopherol at $p<0.05$.

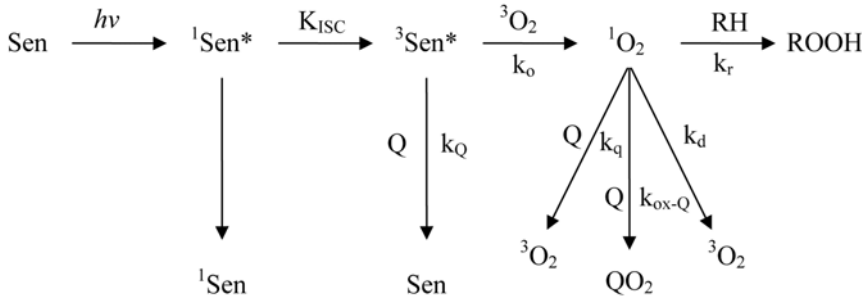

Fig. 1. Schematic diagram of photosensitized oxidation and quenching.

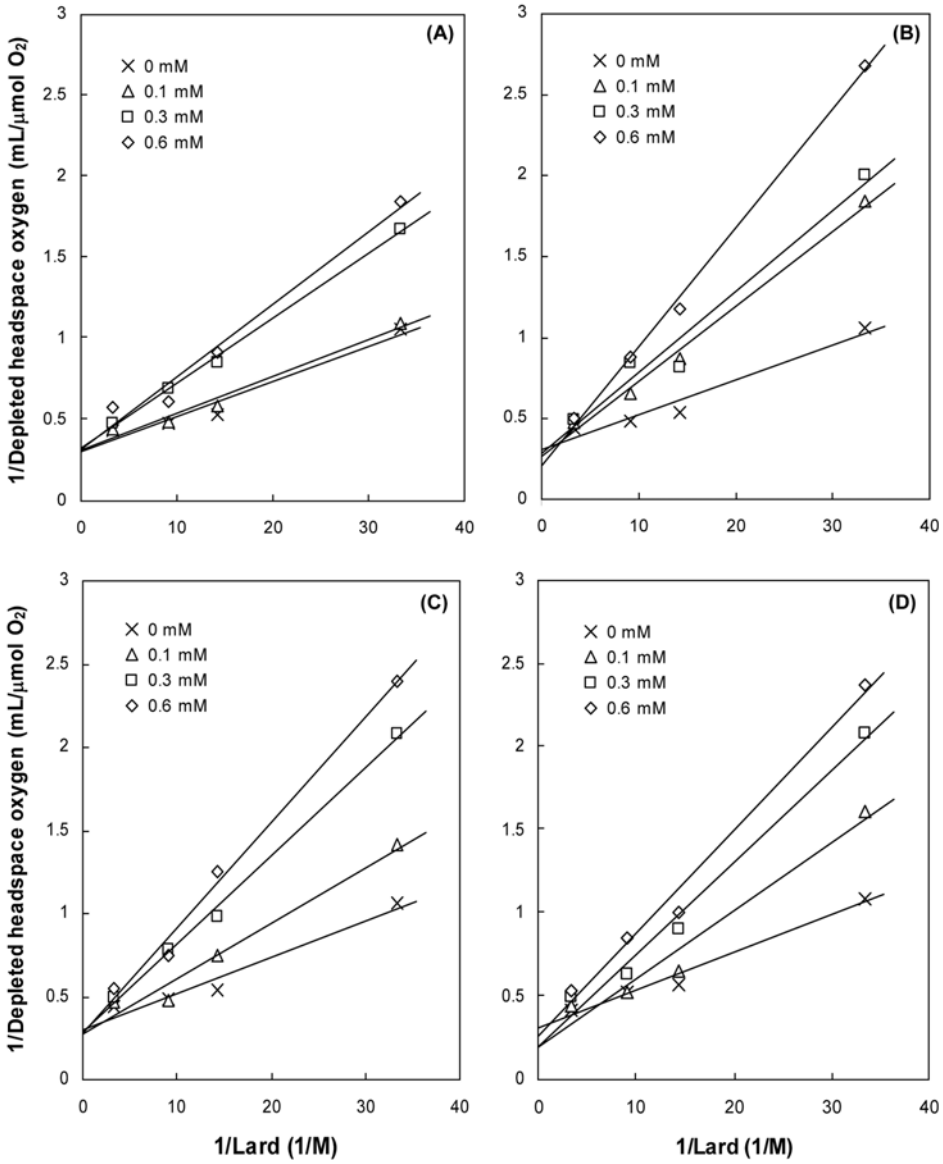

Fig. 2. Effects of 0.1, 0.3, and 0.6 mM α-tocopherol (A), β-tocopherol (B), γ-tocopherol (C), and δ-tocopherol (D) on the headspace oxygen depletion of lard in methylene chloride containing 4.4×10^{-6} M chlorophyll b under light for 4 hr. The reciprocal plot of depleted headspace vs. lard concentration.

storage under light. The depletion of headspace oxygen was due to the oxidation of lard. As the concentration of α-, β-, γ-, and δ-tocopherol increased, the headspace oxygen depletion decreased. Tukey's test showed that the effect of α-tocopherol at 0.3 and 0.6 mM and β-, γ-, or δ-tocopherol at 0.1, 0.3, and 0.6 mM was significantly different compared to the control without tocopherol ($p<0.05$). Headspace oxygen analysis showed that α-, β-, γ-,

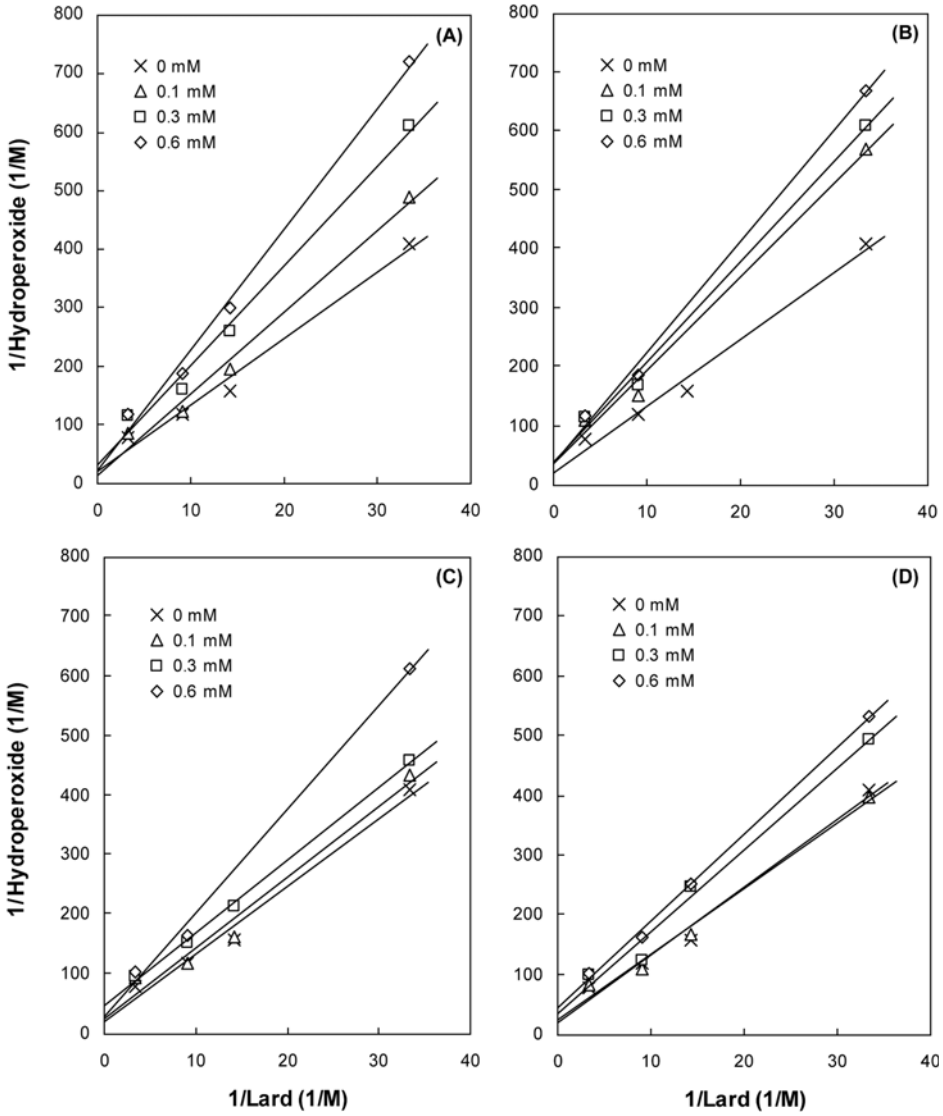

Fig. 3. Effects of 0.1, 0.3, and 0.6 mM α-tocopherol (A), β-tocopherol (B), γ-tocopherol (C), and δ-tocopherol (D) on the peroxide value of lard in methylene chloride containing 4.4×10^{-6} M chlorophyll b under light for 4 hr. The reciprocal plot of hydroperoxide concentration vs. lard concentration.

and δ-tocopherol prevented the chlorophyll photosensitized oxidation of lard.

Mean values of peroxide value were determined from 0.03, 0.07, 0.11, and 0.3 M lard in methylene chloride containing 4.4×10^{-6} M chlorophyll b and 0, 0.1, 0.3, and 0.6 mM α-, β-, γ-, and δ-tocopherol under light for 4 hr (Table 1). As the concentration of α-, β-, γ-, and δ-tocopherol increased, the peroxide value decreased. Tukey's test showed that α- and β-tocopherol at 0.1, 0.3, and 0.6 mM and α- and δ-tocopherol at 0.3, and 0.6 mM had significant effect to decrease peroxide value compared to the lard sample without tocopherol ($p<0.05$). Peroxide value analysis indicated that α-, β-, γ-, and δ-tocopherol prevented the chlorophyll photosensitized oxidation of lard.

The average headspace oxygen contents of lard containing 0.1, 0.3, and 0.6 mM α-, β-, γ-, and δ-tocopherol were calculated to compare the activity of tocopherols and were 17.65, 18.11, 18.12, and 17.76%, respectively. The antioxidative activities in chlorophyll photosensitized oxidation of lard were β=γ>δ>α-tocopherol. The overall means of peroxide value of lard samples containing α-, β-, γ-, and δ-tocopherol were 5.38, 5.49, 5.95, and 6.12 meq/kg lard, respectively. The antioxidative activities were α>β>γ>δ-tocopherol. While both headspace oxygen and peroxide value analyses showed the antioxidant activity of tocopherols in the chlorophyll photosensitized oxidation of lard, these analyses were not in total agreement (Table 1). It is well known that the results of oxidation evaluation in foods are different depending on the analytical method. The headspace oxygen analysis measures the depletion of oxygen which is a reactant in the oxidation reaction, while peroxide value measures the hydroperoxide which is the intermediate compound of oxidation and decomposed during storage.

Quenching mechanisms and kinetics of α-, β-, γ-, and δ-tocopherol in chlorophyll photosensitized oxidation of lard Chlorophyll is a photosensitizer for singlet oxygen

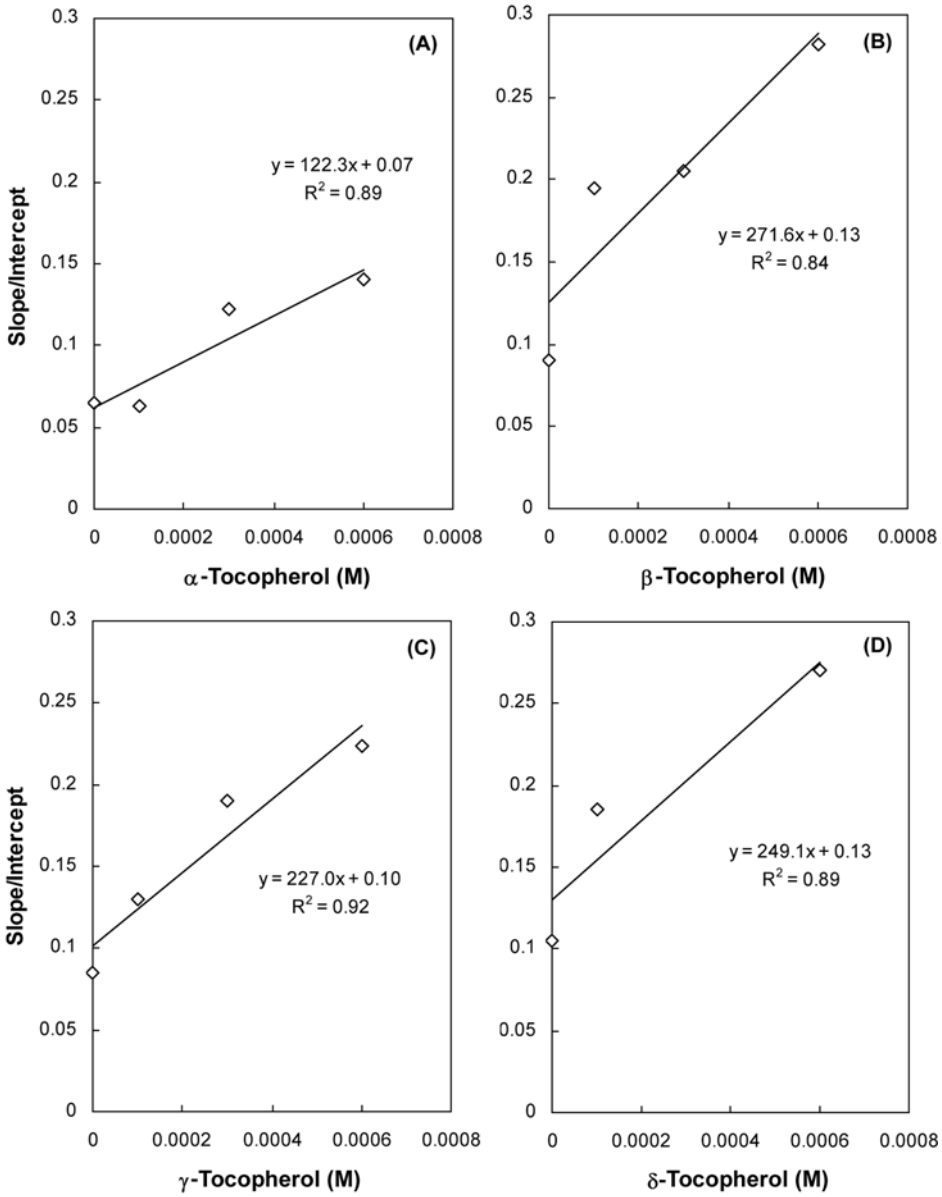

Fig. 4. Relationship between the slope-intercept and the concentration of α-tocopherol (A), β-tocopherol (B), γ-tocopherol (C), or δ-tocopherol (D) as determined by headspace oxygen depletion.

formation (6). A schematic diagram of chlorophyll photosensitized oxidation is shown in Fig. 1. Chlorophyll (Sen) can absorb light energy and become an excited singlet chlorophyll (^{1}Sen*), which can then be convert to an excited triplet chlorophyll (^{3}Sen*) by an intersystem crossing (K_{ISC}) mechanism. Excited triplet chlorophyll may interact with a quencher (Q) to become ground state chlorophyll or with triplet oxygen ($^3O_2$) to produce singlet oxygen ($^1O_2$). Singlet oxygen may naturally decay, react with food components, or be quenched, physically or chemically, by quenchers (4).

The inhibition of photosensitized oxidation by a quencher can be described with the steady state kinetic equation as following (6,15,16):

$$1/\{-d[O_2]/dt\}=1/\{d[ROOH]/dt\}=(1/K)\{(\{k_O[^3O_2]+k_Q[Q]\}/k_O[^3O_2])(k_{ox\text{-}Q}[Q]+k_q[Q]+k_d)/k_r[RH]\}$$

where $\{-d[O_2]/dt\}$ is the derivative of headspace oxygen depletion over time, $\{d[ROOH]/dt\}$ is the derivative of oxidized product concentration over time, K is the rate of $^1O_2$ formation, k_O is the reaction rate constant of photosensitizer with $^3O_2$, k_Q is the reaction rate constant of photosensitizer quenching, $k_{ox\text{-}Q}$ is the reaction rate constant of chemical $^1O_2$ quenching, Q is the quencher concentration, k_Q is the reaction rate constant of physical $^1O_2$ quenching, k_d is the $^1O_2$ decay rate constant, k_r is the reaction rate constant of the substrate with $^1O_2$, and RH is the concentration of the substrate. In this study, Q and RH represents α-, β-, γ-, or δ-tocopherol and lard, respectively. When only singlet oxygen quenching is occurring, the steady state kinetic equation can be simplified to (6,15,16):

$$1/\{-d[O_2]/dt\}=1/\{d[ROOH]/dt\}=(1/K)\{1+(k_{ox\text{-}Q}[Q]+k_Q[Q]+k_d)/k_r[RH]\}$$

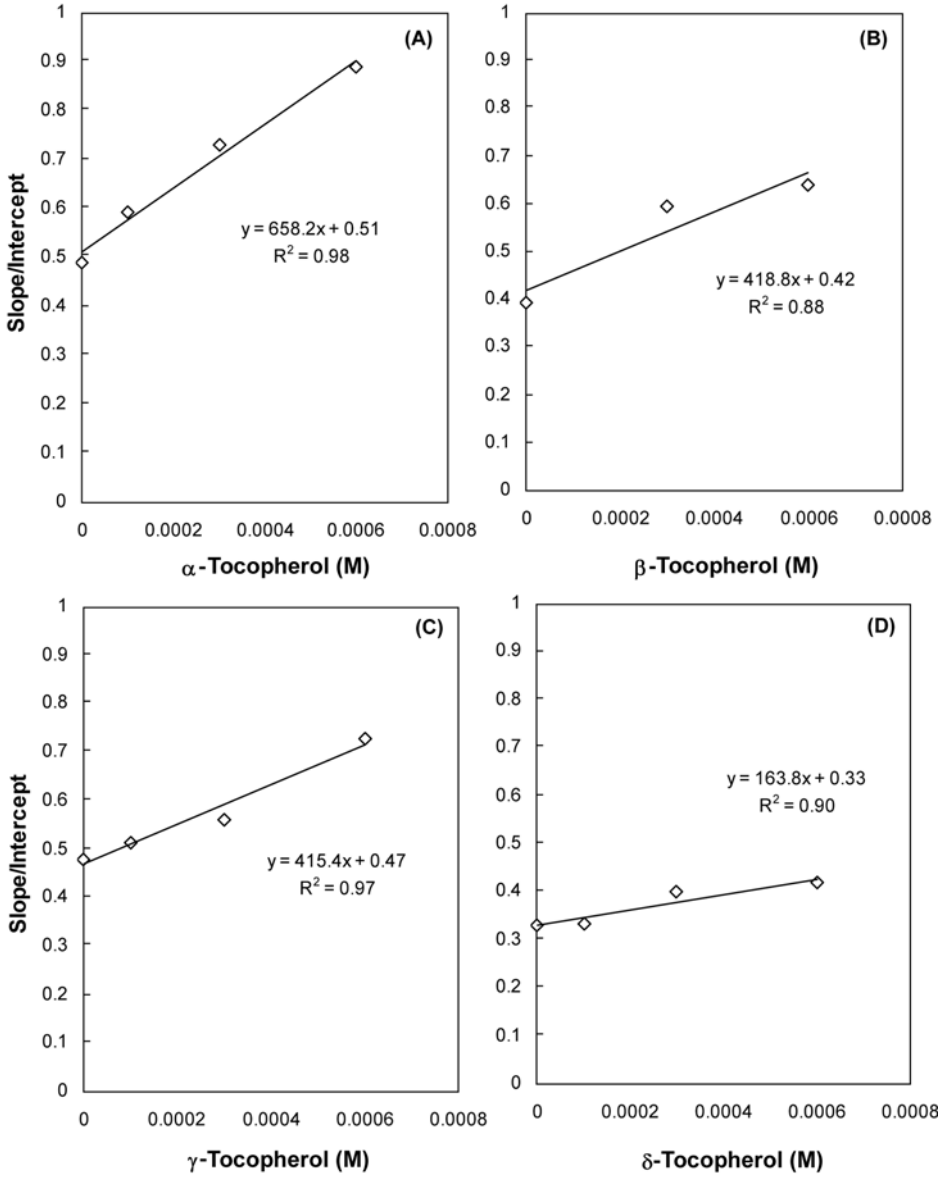

Fig. 5. Relationship between the slope-intercept and the concentration of α-tocopherol (A), β-tocopherol (B), γ-tocopherol (C), or δ-tocopherol (D) as determined by peroxide value.

The slope and intercept of 1/[ROOH] vs. 1/[RH] at various quencher concentration equals to $(1/K)\{k_d+(k_{ox\text{-}Q}+k_Q)[Q]\}/k_r$ and 1/K, respectively. The slopes of the plots are dependent on the concentration of quencher and the intercepts are independent of the concentration of quencher. The ratio of slope to intercept (S/I) equals to $\{k_d+(k_{ox\text{-}Q}+k_Q)[Q]\}/k_r$. A new graph S/I plotted against [Q] results in a line with a slope of $(k_{ox\text{-}Q}+k_Q)/k_r$ and an intercept of k_d/k_r.

The antioxidant mechanism of tocopherol isomers can be determined from the plot of 1/[ROOH] against 1/[RH] at various concentrations of tocopherol ([Q]). The plot of 1/[depleted headspace oxygen] against 1/[lard] and 1/[peroxide value] against 1/[lard] for α-, β-, γ-, and δ-tocopherol are shown in Fig. 2 and 3, respectively. The slopes of all plots were dependent on the concentration of α-, β-, γ-, and δ-tocopherol and the intercepts were independent of the concentration of α-, β-, γ-, and δ-tocopherol. Since the intercepts of various concentration of α-, β-, γ-, and δ-tocopherol were not significantly different and the slopes increased according to the increase of α-, β-, γ-, and δ-tocopherol concentration, tocopherols quenched singlet oxygen to reduce chlorophyll photosensitized oxidation of lard.

The graphs of slope-intercept ratio (S/I) against tocopherol concentration ([Q]) are plotted to determine the total singlet oxygen quenching rate ($k_{ox\text{-}Q}+k_Q$) and shown in Fig. 4 and 5. The total quenching rate for each tocopherol can be calculated if k_d and k_r are determined. The decay rate for singlet oxygen (k_d) varies depending on the solvent (17). The k_d in methylene chloride is 1.1×10^4/sec (18). Since k_d/k_r is equal to the intercept of the plot of S/I against [tocopherol], k_r can be calculated by $k_r=k_d/\text{Intercept}$. Once k_r is determined, total quenching rate can be determined using the slope of the plot of S/I versus [tocopherol]: $(k_{ox\text{-}Q}+k_Q)=\text{Slope}\times k_r$.

For example, the quenching rate of α-tocopherol was

calculated from the headspace oxygen depletion. The plot of 1/[depleted headspace oxygen] against 1/[lard] for α-tocopherol at 0, 0.1, 0.3, and 0.6 mM is shown in Fig. 2A. The slope and intercept from each equation of 0, 0.1, 0.3, and 0.6 mM α-tocopherol was determined by linear regressions. The ratio of S/I versus [α-tocopherol] was plotted as shown in Fig. 4A. The linear regression equation of the plot of S/I against [α-tocopherol] was y=122.32x+0.0723, where y is S/I and x is the concentration of α-tocopherol (M). The slope of this regression line was 122.32, which is equal to $(k_{ox\text{-}Q}+k_Q)/k_r$, and the intercept was 0.0723, which is equal to k_d/k_r. k_r can be calculated to $k_r=k_d/0.0723=1.1\times10^4$/sec/$0.0723=1.52\times10^5$/M/sec. Therefore, the total singlet oxygen quenching rate, $(k_{ox\text{-}Q}+k_Q)$ of α-tocopherol was calculated to $(k_{ox\text{-}Q}+k_Q)=122.32\times k_r=122.32\times1.52\times10^5=1.86\times10^7$/M/sec.

The total singlet oxygen quenching rates of α-, β-, and δ-tocopherol at 0, 0.1, 0.3, and 0.6 mM were calculated as same way as α-tocopherol. The total singlet oxygen quenching rates of α-, β-, γ-, and δ-tocopherol determined from headspace oxygen depletion were 1.86×10^7, 2.39×10^7, 2.47×10^7, and 2.11×10^7/M/sec, respectively. The total singlet oxygen quenching rates of α-, β-, γ-, and δ-tocopherol determined from peroxide value were 1.42×10^7, 1.11×10^7, 0.97×10^7, and 0.42×10^7/M/sec, respectively. Jung *et al.* (6) reported that the inhibition of chlorophyll photosensitized oxidation of soybean oil by α-, γ-, and δ-tocopherol was the result of singlet oxygen quenching and the total quenching rate of α-tocopherol in purified soybean oil was 2.6×10^7/M/sec by headspace oxygen depletion and 2.7×10^7/M/sec by peroxide value. The quenching rate of α-tocopherol in synthetic colorant FD&C Red No. 3 photosensitized oxidation of soybean oil was 4.1×10^7/M/sec. The rate of singlet oxygen quenching was different depending on a photosensitizer and a substrate for oxidation.

In conclusion, the singlet oxygen quenching rates of 4 types of tocopherols were determined by both headspace oxygen and peroxide value analyses. α-, β-, γ-, and δ-Tocopherol prevented the photosensitized oxidation of lard by quenching singlet oxygen. The order of quenching rates of tocopherols was slightly different depending on the measurements. For the headspace analysis, γ-tocopherol was determined to have the highest quenching rate followed by β-, δ-, and α-tocopherol. For the peroxide value analysis, α-tocopherol had the highest rate followed by β-, γ-, and δ-tocopherol. The literature supports the results determined by peroxide value (6,19).

References

1. Merkel PB, Kearns DR. Radiationless decay of singlet molecular oxygen in solution. An experimental and theroritical study of electronic to vibrational energy transfer. J Am. Chem. Soc. 94: 7244-7253 (1972)
2. Min DB, Boff JM. Lipid oxidation of edible oils. pp. 335-364. In: Food Lipids. Akoh CC, Min DB (eds). Marcel Dekker, New York, NY, USA (2002)
3. Gunstone FD. Reaction of oxygen and unsaturated fatty acids. J. Am. Oil. Chem. Soc. 61: 441-447 (1984)
4. Choe E, Min DB. Chemistry and reactions of reactive oxygen species in foods. J. Food Sci. 70: R142-R159 (2005)
5. Bradley DG, Min DB. Singlet oxygen oxidation of foods. Crit. Rev. Food Sci. 31: 211-236 (1992)
6. Jung MY, Choe E, Min DB. α-, γ-, δ-Tocopherol effects on chlorophyll photosensitized oxidation of soybean oil. J. Food Sci. 56: 807-815 (1991)
7. Yang WT, Lee JH, Min DB. Quenching mechanism and kinetics of α-tocopherol and β-carotene on the photosensitizing effects of synthetic food colorant FD&C red No.3. J. Food Sci. 67: 507-510 (2002)
8. Fahrenholtz SR, Doleiden FH, Trozzolo AM, Lamola AA. On the quenching of singlet oxygen by α-tocopherol. Photochem. Photobiol. 20: 505-509 (1974)
9. Gorman AA, Gould IR, Hamblett I, Standen MC. Reversible exciplex formation between singlet oxygen, $^1\Delta_g$, and vitamin E. Solvent and temperature effects. J. Am. Chem. Soc. 106: 6956-6959 (1984)
10. Kaiser S, Di Mascio P, Murphy ME, Sies H. Physical and chemical scavenging of singlet molecular oxygen by tocopherols. Arch. Biochem. Biophy. 15: 101-108 (1990)
11. Di Mascio P, Devasagayam TPA, Kaiser S, Sies H. Carotenoids, tocopherols, and thiols as biological singlet molecular oxygen quenchers. Biochem. Soc. T. 18: 1054-1056 (1990)
12. King JM, Min DB. Riboflavin photosensitized singlet oxygen oxidation of vitamin D. J. Food Sci. 63: 31-34 (1998)
13. Parker SP. Oxygen. Vol. 12, p. 604. In: McGraw-Hill Encyclopedia of Science and Technology. McGraw-Hill, New York, NY, USA (1987)
14. AOCS. Official Methods and Recommended Practices of the AOCS. 5th ed. Method Cd-8-53. American Oil Chemists' Society, Champaign, IL, USA (2004)
15. Foote CS, Denny RW. Chemistry of singlet oxygen. VII. Quenching by β-carotene. J. Am. Chem. Soc. 90: 6233-6235 (1968)
16. Lee SH, Min DB. Effects, quenching mechanisms, and kinetics of carotenoids in chlorophyll-sensitized photooxidation of soybean oil. J. Agr. Food Chem. 38: 1630-1634 (1990)
17. Hurst JR, McDonald JD, Schuster GB. Lifetime of singlet oxygen in solution directly determined by laser spectroscopy. J. Am. Chem. Soc. 104: 2065-2067 (1982)
18. Salokhiddinov KI, Byteva IM, Gurinovich GP. Lifetime of singlet oxygen in different solvents. Zh. Prikl. Spektrosk. 34: 892-897 (1981)
19. Neely WC, Martin JM, Barker SA. Products and relative reaction rates of the oxidation of tocopherols with singlet molecular oxygen. Photochem. Photobiol. 48: 423-428 (1998)