Effects, Quenching Mechanisms, and Kinetics of Carotenoids in Chlorophyll-Sensitized Photooxidation of Soybean Oil†

Sang-Hwa Lee and David B. Min*

Department of Food Science and Nutrition, The Ohio State University, 122 Vivian Hall, 2121 Fyffe Road, Columbus, Ohio 43210

The effects of 0, 1.75×10^{-5}, 3.50×10^{-5}, and 5.25×10^{-5} M lutein, zeaxanthin, lycopene, isozeaxanthin, and astaxanthin which contain 10, 11, 11, 11, and 13 conjugated double bonds, respectively, on the photooxidation of soybean oil containing 4.4×10^{-9} M chlorophyll were studied by measuring peroxide values of the oil. The antioxidant effectiveness of the carotenoids increased as the number of conjugated double bonds of carotenoid increased. The peroxide value of oil containing the carotenoid with 10 conjugated double bonds was significantly higher ($P < 0.05$) than the oil containing carotenoids with 11 or 13 conjugated double bonds at the concentration of 5.25×10^{-5} M. The quenching mechanisms and kinetics of the above carotenoids in the photooxidation of soybean oil containing 3.3×10^{-9} M chlorophyll were studied by measuring the headspace oxygen depletion of oil bottle using gas chromatography. The carotenoids quenched singlet oxygen to reduce the chlorophyll-sensitized photooxidation of soybean oil. The total singlet oxygen quenching rate constants of lutein, zeaxanthin, lycopene, isozeaxanthin, and astaxanthin were 5.72×10^9, 6.79×10^9, 6.93×10^9, 7.39×10^9, and 9.79×10^9 M^{-1} s^{-1}, respectively.

INTRODUCTION

Soybean oil is susceptible to oxidation due to the presence of a large amount of unsaturated fatty acids (Warner and Frankel, 1987). Lipid oxidation is mainly responsible for the deterioration of flavor stability (Frankel, 1985; Awl et al., 1987). The lipid oxidation is due to a combination of triplet oxygen and singlet oxygen oxidations (Frankel, 1985). Triplet oxygen lipid oxidation has been extensively studied during the past 50 years (Labuza, 1971; Frankel, 1984). However, it does not fully explain the initiation step of lipid oxidation (Korycka-Dahl and Richardson, 1978; Frankel, 1985; Whang and Peng, 1988).

The participation of singlet oxygen at the initiation step of lipid oxidation was suggested because singlet oxygen can react directly with the double bonds of fatty acids (Rawls and Van Santen, 1970). Singlet oxygen can be formed by chemical, enzymatic, photosensitization, and physical methods (Foote, 1968; Krinsky, 1977; Korycka-Dahl and Richardson, 1978). Singlet oxygen formed by photosensitization is due to the energy transfer from light to a sensitizer and then to triplet oxygen (Foote, 1979). Chlorophylls in vegetable oils are known to be efficient sensitizers for singlet oxygen formation in the presence of light and triplet oxygen (Clements et al., 1973; Usuki et al., 1984; Lee and Min, 1988).

Singlet oxygen reacts directly with the unsaturated fatty acids of vegetable oils to produce a mixture of conjugated and nonconjugated hydroperoxides (Terao and Matsushita, 1977; Frankel et al., 1982). The decomposition of hydroperoxides produces off-flavor volatile compounds in vegetable oils (Neff et al., 1983; Frankel, 1985).

The undesirable photosensitized lipid oxidation can be reduced by quenching singlet oxygen and/or sensitizer physically and chemically (Foote and Denny, 1968; Foote, 1979). β-Carotene has been reported to be an efficient quencher to reduce the photosensitized oxidation of organic compounds (Foote and Denny, 1968; Foote, 1979; Lee and Min, 1988). However, the detailed antioxidant effects, quenching mechanisms, and kinetics of different carotenoids in photosensitized oxidation of vegetable oils have not been studied.

The objective of this research was to study the effects, quenching mechanisms, and kinetics of carotenoids having different numbers of conjugated double bonds in the photooxidation of soybean oil containing chlorophyll.

MATERIALS AND METHODS

Materials. Soybean oil was obtained from Capital City Products Co. (Columbus, OH). Chlorophyll, lutein, and lycopene were purchased from Sigma Chemical Co. (St. Louis, MO). Zeaxanthin, isozeaxanthin, and astaxanthin were obtained from Hoffmann-La Roche Inc. (Nutley, NJ).

Purification of Soybean Oil. Soybean oil was purified according to the method of Lee and Min (1988). The oil was passed through a chromatographic column (60 cm × 4 cm) packed with a series of 120 g of activated silicic acid (100 mesh, Mallinkrodt), 40 g of a 2:1 mixture of activated charcoal (J. T. Baker Chemical Co.) and Celite (Sargent Welch), 120 g of a 2:1 mixture of powdered sugar and Celite, and 120 g of activated silicic acid. The chromatographic column was wrapped with aluminum foil to prevent light effects on the soybean oil during the purification process. The flow rate of oil through the column was 2 mL/h by the application of a vacuum of 635 mmHg. The soybean oil that passed through the column was referred to as purified soybean oil.

Chemical Analysis of Purified Soybean Oil. Tocopherols were determined by high-pressure liquid chromatography (Carpenter, 1979), and carotenoids were analyzed by the spectrophotometric method of Proctor and Snyder (1987). Phospholipids and free fatty acids in the oil were determined according to the AOCS (1980) methods.

Sample Preparation and Storage To Determine the Effects of Carotenoids on the Chlorophyll-Sensitized Photooxidation of Purified Soybean Oil. To study the effects of

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* To whom correspondence should be addressed.

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Table I. Effects of Carotenoids on the Peroxide Value of Soybean Oil Containing 4.4×10^{-9} M Chlorophyll under Light Storage at 20 °C

carotenoids in soybean oil ($\times 10^{-5}$ M)	peroxide value, mequiv/kg of oil							
	0 h	4 h	8 h	12 h	16 h	20 h	24 h	mean[a]
lutein (0)	0	3.62	5.51	6.48	7.50	8.09	9.03	5.75[a]
lutein (1.75)	0	3.14	4.79	5.89	6.53	6.80	7.51	4.95[b]
lutein (3.50)	0	2.43	4.16	5.23	5.64	6.31	6.69	4.35[bc]
lutein (5.25)	0	1.58	3.44	4.61	5.09	5.46	6.12	3.76[c]
zeaxanthin (0)	0	3.62	5.51	6.48	7.50	8.09	9.03	5.75[a]
zeaxanthin (1.75)	0	2.62	4.48	5.48	5.98	6.43	6.90	4.56[b]
zeaxanthin (3.50)	0	2.14	3.75	4.93	5.34	5.76	6.24	4.02[bc]
zeaxanthin (5.25)	0	1.41	3.24	4.17	4.79	5.22	5.71	3.31[c]
lycopene (0)	0	3.62	5.51	6.48	7.50	8.09	9.03	5.75[a]
lycopene (1.75)	0	2.50	3.61	4.78	5.23	5.53	6.05	4.38[b]
lycopene (3.50)	0	2.02	3.61	4.78	5.23	5.53	6.05	3.89[bc]
lycopene (5.25)	0	1.30	3.13	4.03	4.50	5.04	5.45	3.35[c]
isozeaxanthin (0)	0	3.62	5.51	6.48	7.50	8.09	9.03	5.75[a]
isozeaxanthin (1.75)	0	2.39	4.19	5.10	5.51	5.89	6.45	4.22[b]
isozeaxanthin (3.50)	0	1.89	3.46	4.49	4.94	5.38	5.89	3.72[bc]
isozeaxanthin (5.25)	0	1.19	3.01	3.77	4.34	4.85	5.24	3.20[c]
astaxanthin (0)	0	3.62	5.51	6.48	7.50	8.09	9.03	5.75[a]
astaxanthin (1.75)	0	2.12	3.59	4.71	5.01	5.39	5.93	3.82[b]
astaxanthin (3.50)	0	1.59	3.23	4.01	4.57	4.93	5.47	3.40[bc]
astaxanthin (5.25)	0	1.06	2.83	3.52	4.03	4.45	4.81	2.96[c]

[a] Means in a column of the same carotenoid with different superscripts are significantly different at $P < 0.05$.

different carotenoids on the photooxidation of purified soybean oil, soybean oils containing 0, 1.75×10^{-5}, 3.50×10^{-5}, or 5.25×10^{-5} M lutein, zeaxanthin, lycopene, isozeaxanthin, or astaxanthin and 4.4×10^{-9} M chlorophyll were prepared (Lee and Min, 1988).

A 15-mL oil sample was transferred into a 30-mL serum bottle, and the sample bottles were prepared in duplicate. The serum bottles were placed in the light storage box, which was described in detail by Lee and Min (1988), at 20 °C. The light intensity was 4.000 lx. The oxidative stability of soybean oil was determined by measuring the peroxide value every 4 h for 24 h according to the AOCS (1980) method.

Sample Preparation for the Studies of Quenching Mechanisms and Kinetics of Carotenoids. The quenching mechanisms and kinetics of different carotenoids in chlorophyll-sensitized photooxidation of the purified soybean oil were studied by using the steady-state kinetic method (Foote and Denny, 1968; Foote et al., 1974; Yamauchi and Matsushita, 1977; Foote, 1979). Samples of 0.025, 0.05, 0.067, 0.10, or 0.20 M soybean oil in methylene chloride containing 3.3×10^{-9} M chlorophyll and 0, 0.25×10^{-5}, 0.50×10^{-5}, 0.75×10^{-5}, or 1.0×10^{-5} M lutein, zeaxanthin, lycopene, isozeaxanthin, and astaxanthin were prepared (Foote and Denny, 1968; Yamauchi and Matsushita, 1977; Foote, 1979; Lee and Min, 1988). Molar concentration of soybean oil was obtained from the average molecular weight of soybean oil triglycerides, which was calculated from the fatty acid composition of the purified soybean oil (Lee and Min, 1988).

A 15-mL oil sample was transferred into a 30-mL serum bottle. Sample bottles were prepared in duplicate. The oil bottles were sealed with Teflon septa and aluminum caps so as to be airtight and placed in the light storage box for 2 h (Lee and Min, 1988). The quenching mechanisms and kinetics of carotenoids in chlorophyll-sensitized photooxidation of soybean oil were studied by measuring the headspace oxygen depletion in the serum bottle using a Hewlett-Packard 5880A gas chromatograph equipped with a thermal conductivity detector and Hewlett-Packard 3390A electronic integrator (Fioriti, 1977; Fakourelis et al., 1987; Lee and Min, 1988). Oxygen concentration in the headspace gas of the serum bottles was expressed as micromoles of O_2 per milliliter of headspace and was calculated according to the following formula: μmol of O_2/mL of headspace gas = 9.35 × (electronic units of oxygen peak in 1-mL headspace of serum bottle)/(electronic units of oxygen peak in 1 mL of air). A conversion factor of 9.35 was used because 1 mL of air = 9.35 μmol of O_2 when the atmospheric air contains 20.946% oxygen (Parker, 1982).

Statistical Analyses. The peroxide values and headspace oxygen contents reported in this paper are the mean value of duplicate samples. Tukey's range test (SAS, 1982) was used to ascertain the effects of different levels of various carotenoids on the peroxide value of soybean oil during storage.

RESULTS AND DISCUSSION

Purified Oil. The purified oil obtained by column chromatography was colorless and did not contain any detectable quantities of peroxides, free fatty acids, phospholipids, tocopherols, or carotenoids.

Quantitative and Qualitative Effects of Carotenoid on the Chlorophyll-Sensitized Photooxidation of Soybean Oil. The effects of 0, 1.75×10^{-5}, 3.5×10^{-5}, and 5.25×10^{-5} M lutein, zeaxanthin, lycopene, isozeaxanthin, and astaxanthin on the peroxide value of purified soybean oil containing 4.4×10^{-9} M chlorophyll during storage are shown in Table I. The coefficient of variation for the peroxide value analysis of oil was 2% (Fakourelis et al., 1987). Lutein has 10 conjugated double bonds, zeaxanthin, lycopene, and isozeaxanthin have 11 conjugated double bonds, and astaxanthin has 13 conjugated double bonds. As the carotenoid concentration in soybean oil increased, the peroxide value of the soybean oil decreased. The oils containing 1.75×10^{-5} M carotenoid had significantly lower ($P < 0.05$) peroxide values than the control oil containing no carotenoid (Table I). Foote and Denny (1968) and Lee and Min (1988) reported that β-carotene reduced photosensitized oxidation of organic compounds.

Tukey's range test for the effects of number of conjugated double bonds of carotenoids on the peroxide values of soybean oil (Table II) demonstrated that as the number of conjugated double bonds increased from 10 to 11 and 13, the peroxide value of soybean oil decreased significantly ($P < 0.05$) at the concentration of 5.25×10^{-5} M.

Quenching Mechanisms and Kinetics of Carotenoid in Chlorophyll-Sensitized Photooxidation of Soybean Oil. The effects of 0, 0.25×10^{-5}, 0.50×10^{-5}, and 1.0×10^{-5} M lutein, zeaxanthin, lycopene, isozeaxanthin, or astaxanthin on the headspace oxygen depletion of 0.025, 0.05, 0.067, 0.10, or 0.20 M soybean oil in methylene chloride containing 3.3×10^{-9} M chlorophyll during

Table II. Tukey's Range Test for the Effects of the Number of Conjugated Double Bonds of Carotenoids at 5.25×10^{-5} M on the Peroxide Value of Soybean Oil Containing 4.4×10^{-9} M Chlorophyll during Light Storage at 20 °C

carotenoids in soybean oil, 5.25×10^{-5} M	conjugated double bonds	peroxide value, mequiv/kg of oil, mean[a]	grouping[b]
lutein	10	3.76	a
zeaxanthin	11	3.51	
lycopene	11	3.35	
isozeaxanthin	11	3.20	
av[c]		3.35	b
zeaxanthin	13	2.96	c

[a] Mean of peroxide values of soybean oil after 0, 4, 8, 12, 16, 20, and 24 h of storage (peroxide values are from Table I). [b] Means in a column with different letters are significantly different at $P < 0.05$. [c] Average of peroxide values of zeaxanthin, lycopene, and isozeaxanthin having 11 conjugated double bonds.

Table III. Effects of Carotenoids on the Headspace Oxygen Depletion of Soybean Oil in Methylene Chloride Containing 3.3×10^{-9} M Chlorophyll under Light Storage at 20 °C for 2 h

carotenoids in methylene chloride, ($\times 10^{-5}$ M)	depleted headspace oxygen, μmol of O_2/mL of headspace for soybean oil in methylene chloride, M				
	0.025	0.050	0.067	0.10	0.20
carotenoid (0)	1.603	2.556	2.994	3.627	4.589
lutein (0.25)	0.765	1.365	1.697	2.244	3.310
lutein (0.50)	0.493	0.914	1.162	1.592	2.531
lutein (1.00)	0.302	0.577	0.747	1.059	1.815
zeaxanthin (0.25)	0.687	1.240	1.549	2.063	3.097
zeaxanthin (0.50)	0.441	0.824	1.052	1.456	2.360
zeaxanthin (1.00)	0.261	0.505	0.653	0.932	1.626
lycopene (0.25)	0.713	1.283	1.603	2.134	3.195
lycopene (0.50)	0.445	0.830	1.060	1.464	2.374
lycopene (1.00)	0.261	0.502	0.651	0.929	1.617
ixozeaxanthin (0.25)	0.692	1.248	1.561	2.090	3.145
isozeaxanthin (0.50)	0.425	0.796	1.018	1.409	2.296
isozeaxanthin (1.00)	0.248	0.477	0.620	0.887	1.553
astaxanthin (0.25)	0.560	1.026	1.298	1.761	2.744
astaxanthin (0.50)	0.347	0.658	0.849	1.192	2.007
astaxanthin (1.00)	0.192	0.374	0.489	0.760	1.270

storage are shown in Table III. The coefficient of variation of headspace oxygen analysis by gas chromatography was 3% (Min and Schweizer, 1983; Fakourelis et al., 1987), and the correlation coefficient between headspace oxygen disappearance and peroxide value was −0.99 (Fakourelis et al., 1987). The gas chromatographic headspace oxygen analysis was very simple and takes less than 5 min. As the concentration and number of conjugated double bonds of carotenoids increased, the depleted headspace oxygen of the oil bottle decreased (Table III). The carotenoids acted as antioxidants in the chlorophyll-sensitized photooxidation of soybean oil. If carotenoids reduced the chlorophyll-sensitized photooxidation of soybean oil by singlet oxygen quenching, the steady-state kinetic equation

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

is established (Foote and Denny, 1968; Foote, 1979), where K is the rate of singlet oxygen formation; ROOH is oxidized soybean oil; k_r is the reaction rate constant of soybean oil with singlet oxygen; RH is soybean oil; k_q is the reaction rate constant of physical singlet oxygen quenching by carotenoid; $k_{ox\text{-}Q}$ is the reaction rate constant of chemical singlet oxygen quenching by carotenoid; Q is carotenoid; and k_d is the decaying rate constant of singlet oxygen.

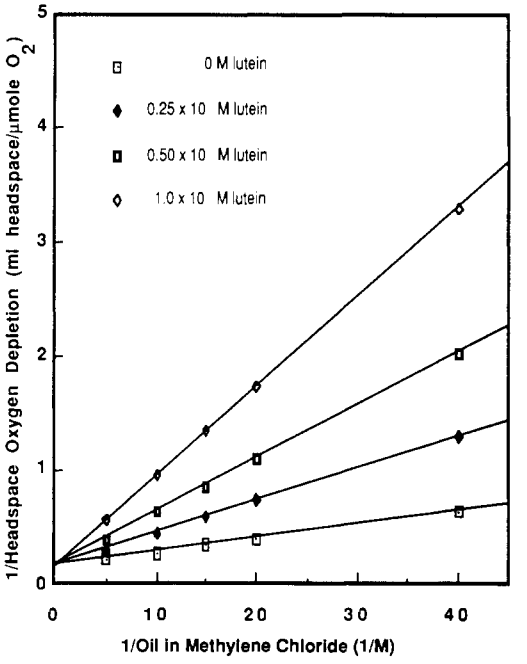

Figure 1. Effects of lutein on the headspace oxygen depletion of soybean oil in methylene chloride containing 3.3×10^{-9} M chlorophyll under light storage at 20 °C for 2 h.

The plots of $(-d[O_2]/dt)^{-1}$ vs $[RH]^{-1}$ at various [Q] have constant intercepts of K^{-1} and the intercepts are [Q] independent. Constant intercepts of the plots of $(-d[O_2]/dt)^{-1}$ vs $[RH]^{-1}$ at various [Q] are diagnostic of singlet oxygen quenching (Foote, 1979). The slope of the plot of $(-d[O_2]/dt)^{-1}$ vs $[RH]^{-1}$ is $K^{-1}(k_q[Q] + k_{ox\text{-}Q}[Q] + k_d)/k_r$. The plot of S_Q/S_0 (slopes of the presence and absence of quencher) vs [Q] is a straight line, and the slope of the straight line is $(k_q + k_{ox\text{-}Q})/k_d$ (Foote et al., 1974; Yamauchi and Matsushita, 1977; Foote, 1979). The rate constants (k_d) of singlet oxygen decay in a number of solvents were determined (Hurst et al., 1982). Therefore, the total singlet oxygen quenching rate constant ($k_q + k_{ox\text{-}Q}$) of quencher can be obtained from the slope of the plot of S_Q/S_0 vs [Q] when the value of k_d is known (Foote, 1979).

The values (Table III) of $(-d[O_2]/dt)^{-1}$ vs [soybean oil]$^{-1}$ at different concentrations of lutein in methylene chloride were plotted, and the plots are shown in Figure 1. The steady-state kinetic equation (Foote, 1979) predicts that if the y intercepts of plots having different levels of quencher are the same and the slopes are different, the reduction of photosensitized oxidation by quencher is due to singlet oxygen quenching. Since the y intercepts of the plots having different levels of lutein are the same, but the slopes are different (Figure 1), lutein quenched singlet oxygen to reduce the chlorophyll-sensitized photooxidation of soybean oil. Similarly, $(-d[O_2]/dt)^{-1}$ vs [soybean oil]$^{-1}$ at various concentrations of lycopene, zeaxanthin, isozeaxanthin, or astaxanthin was plotted. The y intercepts of the plots of $(-d[O_2]/dt)^{-1}$ vs [soybean oil]$^{-1}$ at different levels of lycopene, zeaxanthin, isozeaxanthin, or astaxanthin were the same, but the slopes were different (plots not shown). Therefore, these carotenoids reduced the chlorophyll-sensitized photooxidation of soybean oil by quenching singlet oxygen. The same quenching mechanism has been reported for β-carotene, which quenched singlet oxygen in both chlorophyll-sensitized or methylene blue sensitized photooxidation of

Table IV. Slopes and Ratios of S_Q to S_0 of Plots (Figure 1) of $(-d[O_2]/dt)^{-1}$ vs [Soybean]$^{-1}$ at Various Concentrations of Lutein

lutein in methylene chloride, $\times 10^{-5}$ M	slope, (M - mL of headspace)/ μmol of O_2	S_Q/S_0[a]
0	0.0116	
0.25	0.0287	2.4741
0.50	0.0466	4.0172
1.00	0.0787	6.7845

[a] S_Q and S_0 are the slopes of the plots of $(-d[O_2]/dt)^{-1}$ vs [soybean oil] in the presence and absence of lutein, respectively.

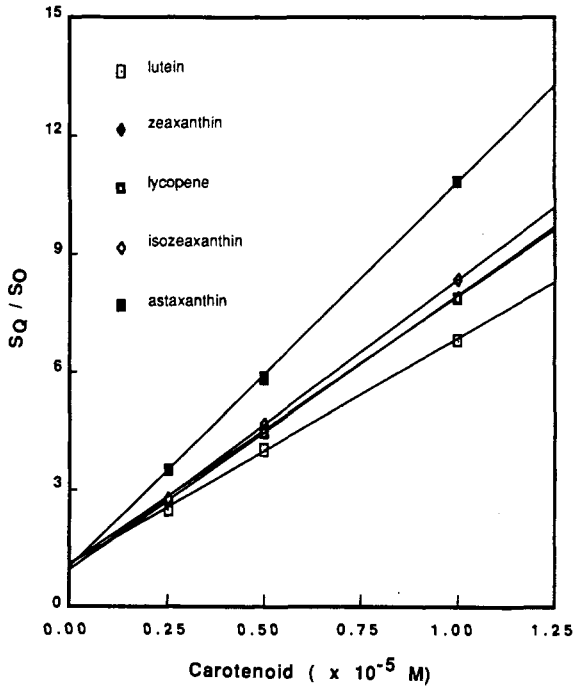

Figure 2. Plots of S_Q/S_0 vs [carotenoid] (see Table IV for lutein).

organic substances (Foote and Denny, 1968; Foote, 1979; Lee and Min, 1988).

The slopes and the S_Q/S_0 of the plots of different levels of lutein shown in Figure 1 are given in Table IV. The S_Q and S_0 are the slopes of the plot $(-d[O_2]/dt)^{-1}$ vs [soybean oil]$^{-1}$ in the presence and absence of quencher, respectively. The ratios of S_Q to S_0 vs [lutein] presented in Table IV were plotted, and the plot is shown in Figure 2. The slope of the plot is 5.72×10^5 M^{-1}. Since the slope of the plot of S_Q/S_0 vs [quencher] is $(k_q + k_{ox\text{-}Q})/k_d$ (Foote and Denny, 1968; Yamauchi and Matsushita, 1977; Foote, 1979) and the k_d value of singlet oxygen in methylene chloride is 1.0×10^4 s^{-1} (Hurst et al., 1982), the total singlet oxygen quenching rate constant $(k_q + k_{ox\text{-}Q})$ of lutein is 5.72×10^9 M^{-1} s^{-1} in methylene chloride. Similarly, the ratios of S_Q to S_0 vs [zeaxanthin], [lycopene], [isozeaxanthin], or [astaxanthin] were plotted, and the plots are shown in Figure 2. The slopes of the plots of S_Q/S_0 vs [zeaxanthin], [lycopene], [isozeaxanthin], and [astaxanthin] are 6.79×10^5, 6.93×10^5, 7.39×10^5, and 9.79×10^5 M^{-1}, respectively (Figure 2). Since the k_d value in methylene chloride is 1.0×10^4 s^{-1}, the total singlet oxygen quenching rate constants $(k_q + k_{ox\text{-}Q})$ of zeaxanthin, lycopene, isozeaxanthin, and astaxanthin are 6.79×10^9, 6.93×10^9, 7.39×10^9 and 9.79×10^9 M^{-1} s^{-1} in methylene chloride, respectively. The quenching rate constants of the carotenoids showed that as the number of conjugated double bonds increased from 10 to 11 and 13, the singlet oxygen quenching rates of carotenoids increased. Foote et al. (1970) reported that the singlet oxygen quenching rate constants of polyene compounds in photosensitized oxidation increased as the number of conjugated double bonds increased from 5 to 7, 9, and 11. The singlet oxygen quenching rate of β-carotene, which contains 11 conjugated double bonds, was 6.5×10^9 M^{-1} s^{-1} in pyridine (Fahrenholtz et al., 1974), 8.5×10^9 M^{-1} s^{-1} in methylene chloride (Carlsson et al., 1972), 1.4×10^9 M^{-1} s^{-1} in methylene chloride (Matheson and Lee, 1972), and 1.3×10^{10} M^{-1} s^{-1} in benzene (Farmilo and Wilkinson, 1973). The total singlet oxygen quenching rates of zeaxanthin, lycopene, and isozeaxanthin with 11 conjugated double bonds are similar to that of β-carotene with 11 conjugated double bonds. Since solvents influence the decaying rate (k_d) of singlet oxygen (Hurst et al., 1982), the singlet oxygen quenching rates of quencher may be different in different solvent systems.

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