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Effects of molecular configurations of food colorants on their efficacies as photosensitizers in lipid oxidation

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Abstract

Effects of twelve commercially available synthetic food colorants, including tartrazine, rose bengal, brilliant blue FCF, new coccin, amaranth, erythrosine B, phloxine B, indigo carmine, acid red, fast green FCF, allura red AC and sunset yellow FCF, on photosensitized oxidation of methyl linoleate (MeLe) were investigated. Rose bengal, erythrosine B and phloxine B accelerated oxidation of MeLe under light exposure and their pro-oxidative effects were concentration-dependent. Light exposure of MeLe with added colorants induced generation of hydroperoxide isomers, including 10-*cis*,*trans*- and 12-*cis*,*trans*-MeLe hydroperoxide, suggesting that the food colorants served as photosensitizers under the present conditions. The addition of α-tocopherol or β-carotene effectively suppressed the oxidation of MeLe, and their antioxidative effects were concentration-dependent. Neither α-tocopherol nor β-carotene altered the distributions of hydroperoxide isomers of MeLe. This study showed that the food colorants containing a xanthene skeleton increased their potential as photosensitizers with increase in both the number and atomic mass of halogen substituents on the xanthene skeleton.

Keywords: Food colorants; Lipid hydroperoxide distributions; Methyl linoleate; Photooxidation; Photosensitizer; α-Tocopherol; β-Carotene

1. Introduction

Lipid oxidation, occurring in food processing and preservation, is one of the main chemical pathways of food quality deterioration due to undesirable flavour volatiles (Frankel, 1998). Physical or chemical parameters that influence the deterioration of unsaturated lipids of foodstuffs in the presence of light have been studied (Andersson & Lingnert, 1998; Kristensen, Orilien, Mortensen, Brockhoff, & Skibsted, 2000; Lennersten & Lingnert, 1998, 2000; Thron, Eichner, & Ziegleder, 2001). The light-induced oxidation of lipids in foods and foodstuffs is not only due to absorption by chromophoric groups present in lipids but can also be a consequence of photosensitized oxidation. Light absorption, either by naturally occurring pigments or synthetic food additives, are particularly relevant in food products that are displayed in transparent containers under illuminated conditions.

Certain food colorants serve as pro-oxidants of lipid when the peroxide value is measured as an oxidation index (Bradley & Min, 1992; Chan, 1975; Kajimoto, Yamaguchi, Kasutani, Yoshida, & Shibahara, 1994; Umehara, Terao, & Matsushita, 1979). Rose bengal is an effective singlet oxygen generator (Barclay, Crowe, & Edwards, 1997; Fukuzawa & Tokumura, 2001; Montenegro, Nazareno, Durantini, & Borsarelli, 2002; Ohtani, Nishida, Nishimoto, & Kagiya, 1986; Stratton, Schaefer, & Liebler, 1993; Wrona, Korytowski, Roanowska, Sarna, & Truscott, 2003; Yasaei, Yang, Warner, Daniels, & Ku, 1996). α-Tocopherol (α-toc) and β-carotene (β-car) serve as the singlet oxygen quenchers when

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lipid oxidation is sensitized by rose bengal (Fukuzawa & Tokumura, 2001; Montenegro et al., 2002; Stratton et al., 1993; Wrona et al., 2003; Yasaei et al., 1996). However, little information is available about the effects of food colorants on the distributions of lipid oxidation products in the presence or absence of α-toc and β-car. It is necessary to make a complete evaluation and comparison of the effects of food colorants on the formation of lipid oxidation products, with or without α-toc and β-car.

The aim of this study was to investigate the effects of artificial food colorants on the oxidation of linoleic acid methyl ester (MeLe) and its oxidation products. The relationship between molecular configuration of food colorants and their efficacies as photosensitizers is also considered.

2. Materials and methods

2.1. Materials

Twelve kinds of artificial food colorants, approved by the Food Sanitation Law of Japan (a part of these colorants has been approved by FDA), including tartrazine, rose bengal, brilliant blue FCF, new coccin, amaranth, erythrosine B, phloxine B, indigo carmine, acid red, fast green FCF, allura red AC and sunset yellow FCF, as well as authentic pigments, such as methylene blue, flurorescein and eosine, were purchased from Sigma (St. Louis, MO, USA) and Tokyo Kasei Kogyo, Co., Ltd. (Tokyo, Japan) as characterized in Table 1. *cis*-9,*cis*-12-Octadecadienoic acid methyl ester of >99% purity was purchased from Sigma, and purified with Sep-pak® Silica Cartridges (Waters Co., MA, USA) prior to use. α-Toc and β-car were secured from Sigma and Tokyo Kasei Kogyo Co., Ltd, respectively. *n*-Hexane, of reagent grade, was used after glass-distillation. Diethyl ether was purified by a combination of first washing with ferrous-sulfuric acid solution to remove peroxide, followed by glass-distillation.

2.2. Photosensitized oxidation of linoleic acid methyl ester by food colorants

A purified portion of 250 mg of MeLe was dissolved in 50 ml of methanol with 0.1 mg of food colorants in a 100 ml beaker. The beaker was exposed to a 100 W tungsten light source (4500 lux) through a 3 cm layer of water in an acryl tank to filter out infrared radiation in a cold room set at 5 °C. The sample without added colorant was kept under the same light-exposure conditions and was used as control. At appropriate intervals, a 200 μl portion of the solution was used for peroxide value measurement. A 4 ml portion of the solution was taken in a flask and flushed under a nitrogen stream. Subsequently, 2 ml of *n*-hexane was added and the hexane solution was filtered through a polytetrafluroethylene (PTFE) membrane filter (0.2 μm, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) to remove pigment. A 20 μl portion of the filtrate was subjected to high-performance liquid chromatography (HPLC) to analyze hydroperoxide isomers.

A portion of 400 mg of purified MeLe was mixed with α-toc or β-car. α-Toc and β-car were dissolved in methanol and *n*-hexane, respectively. The photosensitized oxidation of MeLe was carried out in a 2 ml of methanol solution with 50 μg of food colorants under similar conditions to those described above. The sample without added α-toc and β-car, treated under similar conditions, was used as control. At appropriate inter-

Table 1
Synthetic food colorants permitted by the Food Sanitation Laws of Japan and USA

Japanese name	Chemical name	FDA name	Color index name	CI name	Use in foods
Yellow no. 4	Tartrazine	FD&C yellow no. 5	Acid yellow 23	CI 19140	Foods generally
Yellow no. 5	Sunset yellow FCF	FD&C yellow no. 6	Food yellow 3	CI 15985	Foods generally
Red no. 2	Amaranth	D&C red no. 2	Acid red 27	CI 16185	Confectionery, beverage, wine and whisky
Red no. 3	Erythrosine	FD&C red no. 3	Acid red 51	CI 45430	Foods generally
Red no. 102	New coccin		Acid red 18	CI 16255	Confectionery, beverage, agricultural food products and seafood products
Red no. 104	Phloxine	D&C red no. 28	Acid red 92	CI45410	Confectionery,beverage, agricultural food products and seafood products
Red no. 105	Rose bengal		Acid red 94	CI 45440	Confectionery,beverage, agricultural food products and seafood products
Red no. 106	Acid red		Acid red 52	CI 45100	Confectionery, beverage, agricultural food products and seafood products
Blue no. 1	Brilliant blue FCF	FD&C blue no. 1	Food blue 2	CI 42090	Foods generally
Blue no. 2	Indigo carmine	FD&C blue no. 2	Acid blue 74	CI 73015	Foods generally
Green no. 3	Fast green FCF	FD&C green no. 3	Food green	CI 42053	Confectionery and candy
Red no. 40	Allura red AC	FD&C red no. 40	Food red 17	CI 16035	Foods generally

*FD&C represent usage for food, drug and cosmetic, respectively.

vals, a 50 μl portion of solution was used for chemical and instrumental analyses.

2.3. Determination of hydroperoxide isomers

Positional isomers of hydroperoxides were analyzed by HPLC equipped with a post-column fluorescence detection system using diphenyl-1-pyrenyphosphine (DPPP), as described previously (Ohshima, Hopia, German, & Frankel, 1996; Ohshima, Ushio, & Koizumi, 1997). Briefly, the hydroperoxide isomers were separated through a Supelcosil LC-Si silica column (2.1 mm i.d. × 250 mm, 5 μm; Supelco, Bellefonte, PA) using a mixture of 500 ml of *n*-hexane and 30 ml of diethyl ether as mobile phase with a flow rate of 0.6 ml/min. The eluate from the column was monitored at 234 nm with a Shimadzu model SPD-10A UV spectrophotometric detector and subsequently mixed with a DPPP solution (3 mg in a mixture of 200 ml of 1-butanol and 200 ml of methanol) pumped with a Shimadzu model LC-9A HPLC pump with a flow rate of 0.3 ml/min to form DPPP oxide in a post-column reaction coil kept at 89 °C in a hot-water bath. The fluorescence intensity of the DPPP oxide was monitored at the emission wavelength of 380 nm and excitation wavelength of 352 nm, using a Shimadzu model RF 535 fluorescence spectrophotometer.

2.4. Identification of hydroperoxide isomers

The hydroperoxide positional isomers were identified by gas chromatography–mass spectrometry (GC–MS) as described previously (Ohshima et al., 1996, 1997). Briefly, each of the hydroperoxide isomers fractionated by HPLC was reduced to the corresponding hydroxy ester by addition of $NaBH_4$, hydrogenated and subsequently converted to the trimethylsilyl (TMS) ether derivative. The TMS derivative was separated by GC using a Shimadzu model GC 17A instrument equipped with a Supelcowax-10™ fused silica open-tubular column (0.25 mm i.d. × 25 m, 0.25 μm) and the outlet of the column was directly connected to a Shimadzu mass spectrometer model QP 5000. The column temperature was programmed from 150 to 180 °C at a rate of 5 °C/min, and then from 180 to 240 °C at a rate of 2 °C/min. Sample injection port temperature was 250 °C. Helium was used as carrier gas. Mass spectra were acquired using 3 kV accelerating energy, 70 eV electron beam energy and a source temperature of 250 °C by using a computer system (Shimadzu Class-5000).

2.5. Determination of peroxide value

The peroxide value (PV) of the oxidized lipids was determined photometrically by the ferric thiocyanate method (Hapman & Mackay, 1949).

3. Results and discussion

3.1. Effects of food colorants on oxidation rates of linoleic acid methyl ester

Changes in PV of MeLe, with and without certain food colorants as well as typical photosensitizers, are shown in Fig. 1. The PV of MeLe with each of the added food colorants (4 ppm each), including rose bengal, erythrosine B and phloxine B, increased with an increase in the period of exposure to light. In contrast, the other 9 food colorants, including tartrazine, brilliant blue FCF, new coccin, amaranth, indigo carmine, acid red, fast green FCF, allura red AC and sunset yellow FCF, did not accelerate the oxidation of MeLe. When rose bengal, erythrosine B and phloxine B were used at the same concentrations (4 ppm), their potentials as photosensitizers increased in the following order: Phloxine B < erythrosine B < rose bengal.

Rose bengal was more effective than erythrosine B at the same concentrations, erythrosine B being more effective than phloxine B. These results strongly suggested that rose bengal, erythrosine B and phloxine B served as photosensitizers when MeLe was oxidized (Fig. 2).

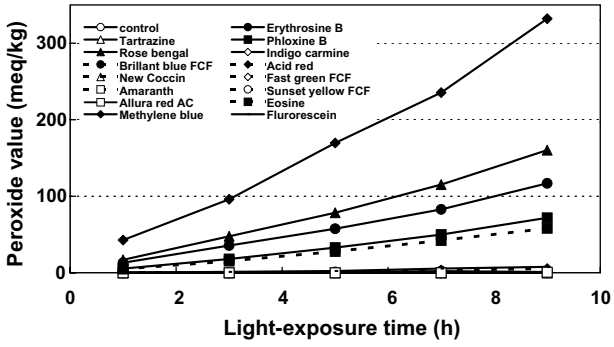

Fig. 1. Changes in peroxide values of methyl linoleate (5 mg/ml methanol) with added food colorants and authentic photosensitizers (4 ppm each) during exposure to light (4500 lx) at 5 °C.

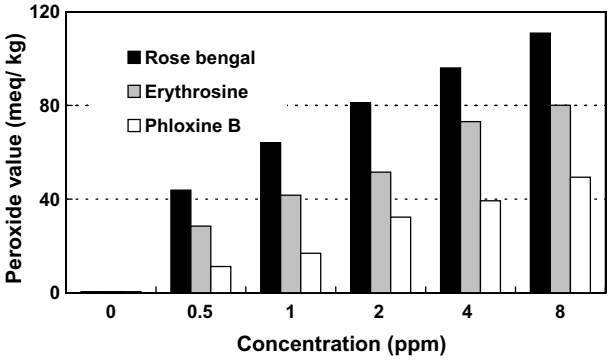

Fig. 2. Changes in peroxide values of methyl linoleate (5 mg/ml methanol) with different concentrations of rose bengal, erythrosine B and phloxine B during exposure to light (4500 lx) for 7 h at 5 °C.

3.2. Effects of added food colorants on the distributions of isomeric hydroperoxides of linoleic acid methyl ester

Typical HPLC chromatograms of isomeric hydroperoxides generated by exposure of MeLe with added phloxine B to light for 1 and 3 h are shown in Fig. 3. Partially separated (five) peaks of isomeric hydroperoxides of MeLe were detected by fluorescent detection (Fig. 3(a)). After 3 h of light exposure, the relative ratios of peaks Nos. 2 and 5 became larger than that of peak No. 3 (Fig. 3(c)). The isomers of peaks Nos. 2 and 5 did not absorb UV light at 234 nm, suggesting that the peak components include non-conjugated dienes (Fig. 3(b) and (d)).

Mass spectrometry of the fractionated hydroperoxide isomers (data not shown) confirmed the identification of the positional isomers as follows: Peak No. 1, 13-hydroperoxy-*cis*-9,*trans*-11-octadecadienoate (13-*cis*,*trans*-18:2-OOH); peak No. 2, 12-hydroperoxy-*cis*-9,*trans*-13-octadecadienoate (12-*cis*,*trans*-18:2-OOH); peak No. 3, 13-hydroperoxy-*trans*-9,*trans*-11-octadecadienoate (13-*trans,trans*-18:2-OOH); peak No. 4, 9-hydroperoxy-*trans*-10,*cis*-12-octadecadienoate (9-*cis*,-*trans*-18: 2-OOH); peak No. 5, a mixture of 10-hydroperoxy-*trans*-8, *cis*-12-octadecadienoate (10-*cis*,*trans*-18: 2-OOH) and 9-hydroperoxy-*trans*-10,*trans*-12-octadecadienoate (9-*trans,trans*-18:2-OOH). These results for hydroperoxide isomers coincided well with previous results (Ohshima et al., 1996, 1997).

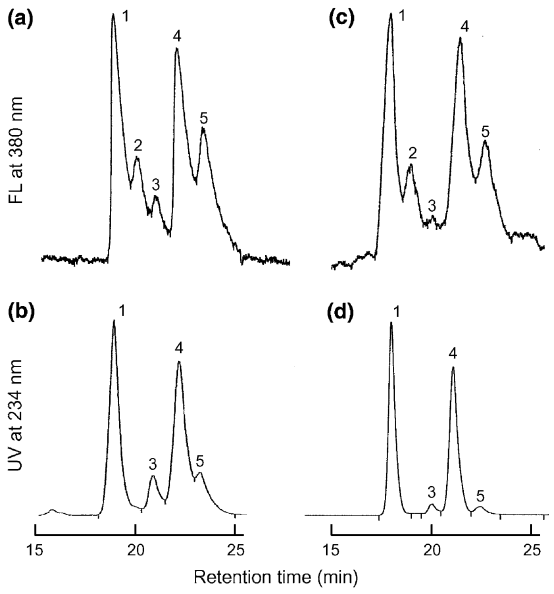

Fig. 3. Typical HPLC chromatograms of isomeric hydroperoxides of linoleic acid methyl ester photosensitized with phloxine B (4 ppm) in methanol at 5 °C. (a) and (c), detected by fluorescence after 1 and 3 h of light-exposure, respectively; (b) and (d), detected by UV at 234 nm after 1 and 3 h of light-exposure, respectively. Peak No. 1, 13-*cis*,*trans*-18:2-OOH; peak No. 2, 12-*cis*,*trans*-18:2-OOH; peak No. 3, 13-*trans*,*trans*-18:2-OOH; peak No. 4, 9-*cis*,*trans*-18:2-OOH; peak No. 5, a mixture of 10-*cis*,*trans*-18:2-OOH and 9-*trans*,*trans*-18:2-OOH.

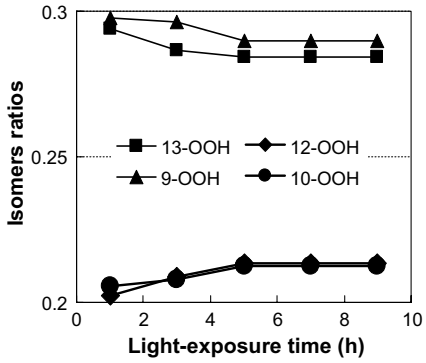

Fig. 4. Changes in the distributions of hydroperoxide isomers of methyl linoleate generated by phloxine B (4 ppm) in methanol (5 mg/ml). ■, 13-*cis*,*trans*-18:2-OOH; ◆, 12-*cis*,*trans*-/13-*trans*,*trans*-18:2-OOH; ▲, 9-*cis*,*trans*-18:2-OOH; ●, 10-*cis*,*trans*-/9-*trans*,*trans*-18:2-OOH.

Changes in the distributions of the isomeric hydroperoxides of MeLe during light-exposure are shown in Fig. 4. During up to 5 h of light-exposure, the area ratios of peaks No. 2 (non-conjugated 12-*cis*,*trans*-18:2-OOH) and No. 5 (non-conjugated 10-*cis*,*trans*-18:2-OOH), increased gradually, and the area ratios of peaks No. 1 (13-*cis*,*trans*-18:2-OOH) and No. 4 (9-*cis*,-*trans*-18:2-OOH) decreased gradually. Longer light-exposure periods (over 5 h) did not alter the area ratios of peaks. These results revealed that 12-*cis*,*trans*-18:2-OOH and 10-*cis*,*trans*-18:2-OOH, which are both characteristic hydroperoxide isomers generated only by the singlet oxygen oxidation of MeLe, increased in accumulated amounts during exposure of samples to light. Other hydroperoxide isomers, due to the radical oxidation of MeLe with added phloxine B for up to 5 h, were negligible in this particular case. After 5 h of light-exposure, the amounts of radical oxidation products, 13-*trans*,*trans*-18:2-OOH (peak No. 3 in Fig. 3(c)) and 9-*trans*,*trans*-18:2-OOH (peak No. 5 in Fig. 3(c)), were relatively small, suggesting that photooxidation dominated the oxidation of MeLe. No detectable amounts of hydroperoxides were generated in the control sample, showing that lipid oxidation proceeded slowly in the control.

The MeLe hydroperoxides, generated in the samples with added rose bengal or erythrosine B by exposure to light, were similar to those with added phloxine B. The characteristic hydroperoxide isomers, 12-*cis*,*trans*-18:2-OOH and 10-*cis*,*trans*-18:2-OOH, generated solely by the photosensitized oxidation of MeLe, were detected (data not shown). In contrast, no detectable amounts of hydroperoxides were detected in the control or samples with the other 9 added food colorants, tartrazine, brilliant blue FCF, new coccin, amaranth, indigo car-

mine, acid red, fast green FCF, allura red AC on sunset yellow FCF, under the present conditions. Generation of non-conjugated hydroperoxide isomers clearly indicated that photosensitized oxidation proceeded in the samples with added rose bengal, phloxine B or erythrosine B, and these colorants served as photosensitizers. The other 9 food colorants did not serve as photosensitizers.

3.3. Inhibitory effects of α-tocopherol and β-carotene on the oxidation of methyl linoleate photosensitized with food colorants

Changes in PV of MeLe with added α-toc and/or β-car are shown in Fig. 5. The addition of α-toc, in concentrations up to 240 ppm, to MeLe with 20 ppm of added erythrosine B effectively suppressed photosensitized oxidation of MeLe. The antioxidative effects of α-toc increased with the increase in concentration. At all tested concentrations of β-car up to 240 ppm, β-car effectively suppressed photosensitized oxidation of MeLe with 20 ppm of added erythrosine B. The antioxidative effects of β-car increased with the increase of concentrations. β-Car exhibited a better antioxidative effect than α-toc at the same concentration. When α-toc and β-car were used as a mixture, significant increase in antioxidative effects was achieved, suggesting a synergistic antioxidative effect of α-toc and β-car.

The analysis of hydroperoxide isomers by HPLC confirmed that the addition of α-toc and β-car did not affect the distributions of hydroperoxide isomers generated by oxidation of MeLe sensitized with erythrosine B (Table 2). There were no significant differences in the distributions of hydroperoxide isomers between the control and the samples containing β-car, α-toc or both of them. The conjugated hydroperoxides were much more dominant (60%) than nonconjugated hydroperoxides (40%) during the photosensitized oxidation treatment. The addition of α-toc and β-car also did not affect the distributions of hydroperoxide isomers generated by oxidation of MeLe sensitized with rose bengal or phloxine B. These results indicate that antioxidative effects of α-toc and β-car did not involve hydrogen donation and only served as singlet-oxygen quenchers under the present experimental conditions.

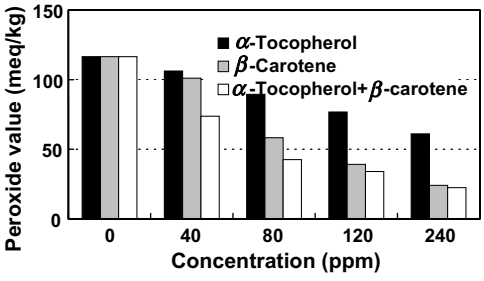

Fig. 5. Comparison of concentration-dependent inhibition effects of α-tocopherol and β-carotene on oxidation of methyl linoleate in methanol (0.2 g/ml) photosensitized with erythrosine B after 5 h (20 ppm).

The present study clearly demonstrates that rose bengal, erythrosine B and phloxine B have singlet-oxygen generation ability. As shown in the chemical structures of certain food colorants (Fig. 6), rose bengal, erythrosine B, phloxine B, eosine and fluorescein have similar chemical structures with a common xanthene skeleton. The differences between these compounds are the substituents of halogen or hydrogen atoms attached to the xanthene skeleton. As confirmed in the present study, the efficacies as photosensitizers increased in the following order: Fluorescein < eosine < phloxine B < erythrosine B < rose bengal < methylene blue. Consequently, it is possible to conclude that phloxine B, erythrosine B and rose bengal increased their efficacies as photosensitizers with increase in the number and atomic mass of halogen substituents on the xanthene skeleton.

Artificial pigments, such as eosin and methylene blue, are effective photosenstizers since they possess triplet states of appropriate energies for sensitization of oxygen. Methylene blue is a phenothiazinium dye with strong absorption bands in the green area of the visible spectrum (480–550 nm) and produces singlet oxygen in high yields (DeRosa & Crutchley, 2002; Gutierrez & Norman, 1998). Increasing the number and atomic mass of halogen substituents on the xanthene skeleton causes the peak maximum to undergo a red shift. Likewise, the presence of heavier halogens increases the yield of intersystem crossing to the triplet state of a pigment, which is an important criterion for a photosensitizer (DeRosa & Crutchley, 2002; Gutierrez & Norman, 1998). For this reason, tetraiodo xanthene derivatives, such as rose bengal and erythrosine B, are generally more effective photosensitizers than other halogenated derivatives. For flurorescein, the photosenstizing ability becomes very weak, probably because there is no halogen substituent on the xanthene skeleton.

Many workers (Cillard, Cillard, Cormier, & Girre, 1980; Edge, McGarvey, & Truscott, 1997; Evans, Kodali, & Addis, 2002; Haila & Heinonen, 1994; Kamal-Eldin & Appelqvist, 1996; Palozza & Krinsky, 1992; Viljanen, Sundberg, Ohshima, & Heinonen, 2002; Yoshida, Kajimoto, & Emura, 1993; Young & Gordon, 2001) evaluating the antioxidative and pro-oxidative properties of α-toc and β-car have reported complicated results. This might be due to different experimental conditions used. The concentrations of α-toc or β-car, solvent, oxygen and the nature of the environment are important in assessing the anti-/pro-oxidant properties

Table 2
Effects of α-tocopherol and β-carotene on the distribution of hydroperoxide isomers (%) from methyl linoleate in methanol (0.2 g/ml) photosensitized with erythrosine B (20 ppm)

	Concentration (ppm)	PV (meq/kg)	Hydroperoxide isomers (%)*			
			13-OOH	9-OOH	12-OOH	10-OOH
1 h						
α-Tocopherol	0	29.1	29.4	29.8	20.2	20.6
	40	25.7	28.5	29.6	20.9	21.0
	80	21.2	28.5	29.3	21.2	21.1
	120	16.8	28.4	29.0	21.3	21.3
	240	15.7	28.4	29.0	21.5	21.2
β-Carotene	40	18.8	29.3	29.4	20.3	20.9
	80	13.0	28.7	29.4	20.8	21.1
	120	10.9	28.7	29.2	20.9	21.2
	240	9.9	28.3	29.2	21.0	21.6
α-Tocopherol + β-carotene	20 + 20	18.8	28.1	29.0	21.0	21.9
	40 + 40	12.3	29.6	29.8	19.2	20.2
	60 + 60	10.3	28.5	29.2	20.3	22.0
	120 + 120	8.9	28.6	29.5	21.1	20.9
2 h						
α-Tocopherol	0	50.1	29.9	30.6	18.9	20.6
	40	42.5	29.2	30.4	19.7	20.7
	80	33.9	29.0	30.1	20.2	20.7
	120	30.8	29.0	30.0	20.2	20.7
	240	25.7	29.0	29.6	20.3	21.1
β-Carotene	40	33.2	29.9	30.6	18.9	20.6
	80	23.6	29.2	30.4	19.7	20.7
	120	16.8	29.0	30.1	20.2	20.7
	240	13.0	29.0	30.0	20.2	20.7
α-Tocopherol + β-carotene	20 + 20	30.5	29.0	29.6	20.3	21.1
	40 + 40	19.9	29.3	30.3	19.8	20.6
	60 + 60	15.7	29.1	30.0	20.3	20.6
	120 + 120	12.3	29.2	30.4	20.3	20.0
3 h						
α-Tocopherol	0	70.6	28.5	29.3	21.2	21.1
	40	63.8	30.4	29.9	19.0	20.7
	80	52.5	29.7	29.8	19.7	20.8
	120	44.6	29.0	29.7	20.4	20.8
	240	37.0	28.9	29.7	20.5	20.9
β-Carotene	40	55.3	28.7	29.6	20.7	21.0
	80	31.2	30.8	31.4	17.7	20.2
	120	22.9	30.5	29.6	21.0	18.9
	240	16.5	31.4	31.1	18.3	19.3
α-Tocopherol + β-carotene	20 + 20	42.8	30.1	29.6	20.1	20.3
	40 + 40	27.5	29.7	30.9	20.1	19.3
	60 + 60	21.2	31.9	30.1	19.6	18.3
	120 + 120	16.8	30.4	30.7	18.7	20.1

* 13-OOH, 9-OOH, 12-OOH and 10-OOH refer to, 3-*cis*,*trans*-, 9-*cis*,*trans*-, 12-*cis*,*trans*-, and 10-*cis*,*trans*-18:2-OOH, respectively.

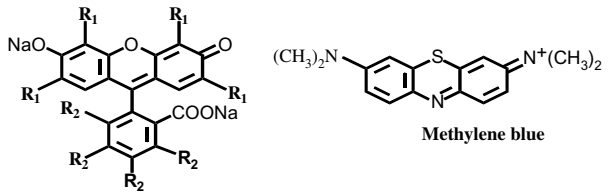

Photo sensitizer		R_1	R_2
Rose bengal	(acid red 94)	I	CI
Erythrosine B	(acid red 51)	I	H
PhloxineB	(acid red 92)	Br	CI
Eosine	(acid red 87)	Br	H
Fluorescein	(acidyellow 73)	H	H

Fig. 6. Chemical configurations of certain food colorants.

of α-toc and β-car. The present study demonstrated that α-toc and β-car prevented the formation of MeLe hydroperoxides and thus they acted as antioxidants in rose bengal-, erythrosine B- or phloxine B-induced photosensitized oxidations of MeLe. No effect of α-toc and β-car on the distributions of isomeric hydroperoxides of MeLe indicated that α-toc and β-car served as singlet-oxygen quenchers under the present experimental conditions. Viljanen et al. (2002) reported that lutein, lycopene and β-car showed similar results when the oxidation was photosensitized with methylene blue and inhibited.

4. Conclusions

Rose bengal, erythrosine B and phloxine B accelerated oxidation of MeLe under light exposure. Their pro-oxidative effects were concentration-dependent, and their potentials were in the following order at the same concentration of 4 ppm: Phloxine B < erythrosine B < rose bengal. Light exposure of the samples with added colorants induced generation of hydroperoxide isomers, including 9-*cis trans*-, 10-*cis*,*trans*-, 12-*cis*,*trans*- and 13-*cis*,*trans*-18:2 Me–OOH. The addition of α-toc or β-car effectively inhibited oxidation of MeLe at the concentrations of 40, 80, 120 and 240 ppm when the concentrations of added food colorants were 20 ppm. Inhibitory effect of α-toc or β-car was concentration-dependent. The addition of α-toc or β-car did not effectively alter the distributions of hydroperoixide isomers of MeLe. In conclusion, the food colorants used in the present study served as photosensitizers under the present conditions. α-Toc or β-car probably served as singlet-oxygen quenchers. The results suggest that the food colorants with a xanthene skeleton had increased efficiencies as photosensitizers with increase in the number and atomic mass of halogen substituents on the xanthene skeleton.

Rose bengal, erythrosine B and phloxine B are widely used in processing of foods, such as confectionery, beverages, agricultural food products and seafood products. Especially, for seafoods containing high percentages of unsaturated lipids with added food colorants, photosensitized lipid oxidation, involving a mechanism different from autoxidation, may shorten shelf life and contribute to their quality deterioration when the light passes through transparent containers under certain conditions.

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