Effects of Paprika Pigments on Oxidation of Linoleic Acid Stored in the Dark or Exposed to Light

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We examined the antioxidant effects of paprika pigments on oxidation of linoleic acid and on decoloration of the sample when stored at 37 °C in the dark or exposed to fluorescent light for 8 h per day. ^{1}H nuclear magnetic resonance with dioxane as an external proton reference was used to estimate the oxidative deterioration of linoleic acid. Oxidation was estimated by observing the ratio of the divinylmethylene proton signal area in linoleic acid vs the proton signal area in dioxane. The addition of paprika pigments suppressed the oxidation of linoleic acid during storage in the dark, and the effect was markedly increased with increasing concentrations (0.02, 0.2, and 2%). When the linoleic acid with added paprika pigments was exposed to light, only a slight suppression of oxidation was observed, and the color of the sample disappeared more rapidly than that in the dark. At the time of decoloration of the sample with added pigments, considerable oxidation of linoleic acid occurred. As the color change is due to degradation of the pigment, an increase in oxidation at the time of discoloration is consistent with the pigments functioning as antioxidants. The addition of α-tocopherol to paprika pigments stabilized degradation of the pigments by light. Although the addition of α-tocopherol to linoleic acid with added paprika pigments prolonged the decoloration of the sample under light, the prevention of oxidation under the light condition was not as effective as for the samples stored in the dark.

KEYWORDS: Paprika; carotenoid; antioxidant; oxidation; decoloration; NMR

INTRODUCTION

Oxidative deterioration of fats and oils in food not only lowers the nutritional quality of the food but also leads to the formation of potentially toxic degradative compounds. To prevent deterioration, antioxidants such as butylated hydroxyanisole, butylated hydroxytoluene, and propyl gallate are added. The increasing awareness of consumers regarding the safety of food additives has created the current demand for synthetic antioxidants to be replaced by natural ones, such as tocopherols (*1*).

Numerous studies on antioxidants derived from fruit and vegetables have revealed that ascorbic acid, tocopherols, polyphenols, and carotenoids have a high antioxidant activity (*1−3*). The ripe fruit of paprika (*Capsicum annuum*) is a good source of carotenoid pigments and is widely used as a vegetable and food colorant. Studies of the composition of paprika extracts show that the red color is mainly due to capsanthin (30−60% of all pigments in fully ripe fruit) and capsorubin (*4−7*). Capsanthin is either partially or totally esterified with fatty acids such as lauric, myristic, and palmitic acids. In our previous report (*8*), capsanthin and its esterified forms were shown to be more effective free radical scavengers than β-carotene, a finding also reported by Perez-Galvez and Minguez-Mosquera

(*9*). Capsorubin has a higher antioxidant activity than capsanthin (*9*, *10*). In addition to these carotenoids, ripe paprika contains moderate to high levels of vitamins C and E and flavonoids (*11*, *12*) and thus increasing interest has been shown in the antioxidant properties of paprika powder and its extracts.

In the present study, the oxidation of linoleic acid was investigated using nuclear magnetic resonance (NMR). The antioxidant activities of paprika pigments on the oxidation of linoleic acid stored in the dark or exposed to light were examined.

MATERIALS AND METHODS

Materials. The paprika pigment (paprika oleoresin DN-933) was obtained from San-Ei Gen F. F. I. Inc. (Osaka, Japan). It was used without further purification. Linoleic acid and α-tocopherol were purchased from Wako Pure Chemical Co. Ltd. (Osaka, Japan). Chloroform-*d* was obtained from Aldrich Japan (Tokyo, Japan). Other reagents were of analytical grade and used without further purification.

Composition of Paprika Pigment. The pigment used in this study is a natural oleoresin extract of paprika originating from Spain (*C. annuum* var. *cuneatum* Paul) with hexane. Main carotenoids in the pigment were analyzed by the high-performance liquid chromatography (HPLC) method of Goda et al. (*13*, *14*) and determined using the esterified capsanthin isolated previously (*8*). The pigment was injected onto a 250 mm × 4.6 mm i.d. Wakosil II 5C18-AR column. Elution was performed using a solvent system consisting of a mixture of solvent

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A (acetonitrile/2-propanol/water, 70/26/4) and solvent B (acetonitrile/2-propanol/water, 39/57/4): 0% B (0−10 min), 0−10% B (10−30 min), 10% B (30−60 min), and then 10−100% B (60−100 min) at a flow rate of 1.0 mL/min. HPLC analysis revealed that the main carotenoids in the pigment were β-carotene (14% of total carotenoids), lauroyl-myristoylcapsanthin (11%), dimyristoylcapsanthin (7%), 3′-O-myristoyl-capsanthin (4%), and 3′-O-lauroylcapsanthin (2%). On the other hand, HPLC analyses of the saponified pigment revealed that it contained 183 μg/mg of capsanthin, 43.5 μg/mg of capsorubin, 47.8 μg/mg of β-carotene, and 7.1 μg/mg of α-tocopherol. The HPLC condition for carotenoids was the following: column, 250 mm × 4.6 mm i.d. Wakosil II 5C18-AR; solvent, 70% acetone (0−5 min), 70−90% acetone (5−10 min), and then 90−100% acetone (10−30 min); flow rate, 0.8 mL/min; column temperature, 40 °C; and detection, 460 nm. For α-toco-pherol, the conditions were as follows: column, 250 mm × 4.6 mm i.d. Shodex SIL 5B; elution, 1% 2-propanol in hexane; flow rate, 1.0 mL/min; fluorescence detection, 290 and 320 nm as the excitation and detection wavelengths, respectively.

Oxidation of Linoleic Acid. Linoleic acid (50 g) with or without the paprika pigments added was placed into a 200 mL Pyrex Erlenmeyer flask. Samples were then stored under light or dark conditions. Under the dark condition, samples were wrapped in tin foil and stored at 37 °C in air. Under the light condition, samples were exposed to light (fluorescent light, 5000 lx; a photo period of 8 h light/16 h dark) in an incubator (Hitachi CT-30) at 37 °C. An aliquot of the sample was periodically withdrawn for NMR analysis and for measurement of its absorbance. Three replicate experiments were performed. Throughout the storage period, the samples were randomly interchanged once every few days to minimize the effects of unequal light exposure.

^{1}H NMR Analysis. Oxidative deterioration of linoleic acid with added paprika pigments was measured by the modified ^{1}H NMR method of Matsui et al. (15) and Miyake et al. (16). NMR spectra were recorded by a JEOL EX-270 NMR spectrometer. The oxidized sample (0.5 mL) was added to chloroform-*d* with 0.03% tetramethylsilane as an internal reference (0.8 mL) and dioxane as an external reference (0.05 mL). The resulting solution was placed in a 5 mm NMR tube. The accumulation was set at 32 scans without spinning and with a 15° pulse angle and a 2.5 s pulse delay.

Residual Paprika Color. The paprika pigment content was deter-mined by measuring the absorbance at 460 nm. A small aliquot of the sample with added paprika pigments was withdrawn periodically, dissolved in isooctane, and then measured. As a control in this experiment, we used oleic acid instead of linoleic acid, because some organic solvents evaporated during storage.

Peroxide Value (POV). The determination of the POV for linoleic acid was performed according to the Standard Methods for the Analysis of Fats, Oils, and Related Materials (16).

RESULTS

Estimation of Oxidative Deterioration by ^{1}H NMR. As it is difficult to measure the oxidative deterioration of linoleic acid with added paprika pigments by conventional methods based on titration, measurement by NMR was attempted in this study. **Figure 1** shows a typical ^{1}H NMR spectrum of linoleic acid. The relative intensity of divinylmethylene protons (DP value) in linoleic acid is determined by the ratio of the integral value of divinylmethylene protons to that of methylene protons in dioxane. **Figure 2** shows the relationship between the DP value and the POV of linoleic acid at different stages of oxidation. The plot shows a linear relationship with a correlation coefficient of −0.993, indicating that a reduction in the relative divinyl-methylene signal correlates with oxidation of the linoleic acid. The NMR spectrum of the 2% paprika solution showed no proton signal in the methylene proton region of dioxane (δ 3.4−3.6 ppm) or in the divinylmethylene proton region (δ 2.7−2.9 ppm) (data not shown). These results suggest that ^{1}H NMR measurement allows for estimation of the oxidative deterioration of linoleic acid with added paprika pigments.
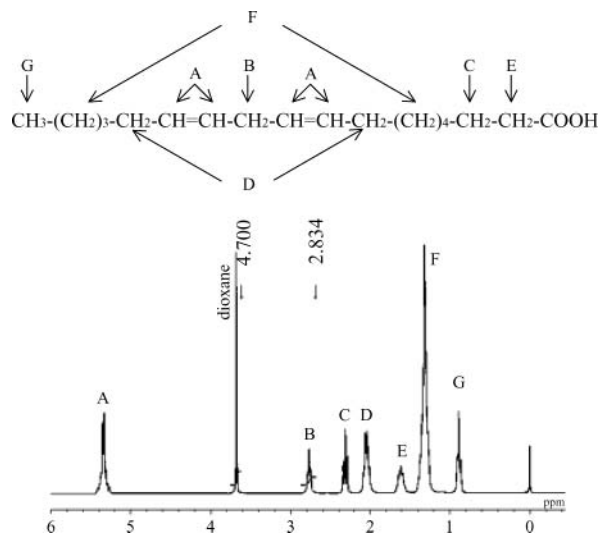
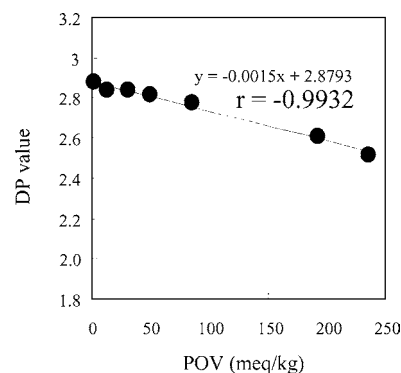**Figure 1.** Typical ^{1}H NMR spectrum of linoleic acid.

Figure 2. Relationship between DP measured by NMR and POV values.

Antioxidant Effect of Paprika Pigments Stored in the Dark. Figure 3A shows the antioxidant effect of paprika pigments on the oxidation of linoleic acid during storage at 37 °C in the dark. In the absence of paprika pigments (control), the DP value of linoleic acid decreased after 5 days in storage. In contrast, the samples with paprika pigments show a concen-tration-dependent effect on oxidation of linoleic acid, with 0.2 and 2% additions particularly effective. For the 0.02, 0.2, and 2% samples, large decreases in DP values were observed after 5, 19, and 40 days in storage, respectively. For the sample with only α-tocopherol (0.02%) added, the behavior was similar to that of the control. Because the paprika pigments used in this study contained 1% α-tocopherol, these findings suggest that the antioxidant effect of the paprika pigments is not due solely to α-tocopherol but instead to the carotenoid pigments and/or their synergistic effect. The measurement of color absorption during storage showed a gradual decrease in the quantity of paprika pigments over time (**Figure 3B**). When the paprika pigments were added to oleic acid, the pigment amount decreased more slowly than for the linoleic acid sample. Oleic acid oxidizes more slowly than linoleic acid, and our result therefore suggests that pigment degradation is related to the oxidation process. When most of the linoleic acid had been oxidized, little pigments remained (0.0073, 0.0102, and 0.0138% paprika pigments remained in 0.02, 0.2, and 2% samples, respectively), and the colors ranged from very pale orange to yellow. This indicates that considerable oxidation of linoleic acid occurred at the same time as decoloration of the sample.

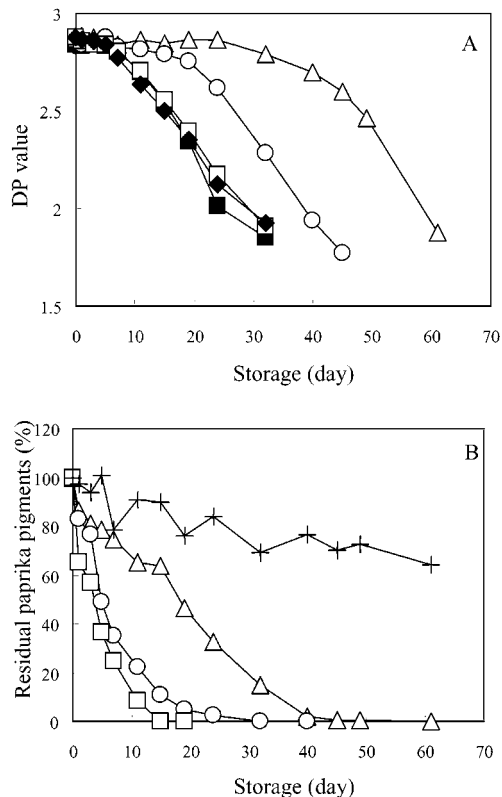**Antioxidant Effect of Paprika Pigments Exposed to Light.** The antioxidant effect of paprika pigments (0.2%) on the

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Figure 3. Changes in DP value (**A**) and quantity of paprika pigments (**B**) for oxidation of linoleic acid at 37 °C in the dark. Linoleic acid: ■, no paprika pigments (control); ◆, 0.02% α-tocopherol; □, 0.02% paprika pigments; ○, 0.2% paprika pigments; △, 2% paprika pigments. Oleic acid: +, 2% paprika pigments.

oxidation of linoleic acid while exposed to light was investigated. The antioxidant effect of paprika pigments in samples stored under light is smaller than that in samples stored in the dark (**Figure 4A**). A large decrease in DP value was observed after 10 days in storage. The amount of paprika pigments in the samples exposed to light decreased faster than those in the dark, with the color disappearing after 10 days in storage (**Figure 4B**). These results show that linoleic acid oxidizes faster under light than in the dark and that significant oxidation occurs when there is little of the pigment remaining.

Stability of Paprika Color to Light. In this experiment, the paprika pigments (0.2%) were added to oleic acid. Samples with more α-tocopherol added were prepared and then exposed continuously to light at 37 °C. As shown in **Figure 5**, the quantity of paprika pigments rapidly decreased in the sample without added α-tocopherol and the color disappeared after only 18 h. For samples of paprika pigments with added α-tocopherol, the color of the sample disappeared more slowly, consistent with suppression in photodegradation of the paprika pigments. The degradation time of the sample with 0.2% added α-tocopherol was similar to the degradation time of the sample stored in the dark.

Antioxidant Effect of Paprika Pigments Exposed to Light. Samples with paprika pigments (0.2%) with added α-tocopherol were prepared in order to examine the antioxidant effect on the oxidation of linoleic acid when exposed to light. The oxidation of linoleic acid in the sample with paprika pigments with 0.2% α-tocopherol added was suppressed slightly in comparison to the sample without added α-tocopherol (**Figure 6A**). However, the effects were smaller than for the sample stored in the dark. The addition of α-tocopherol more effectively suppressed the
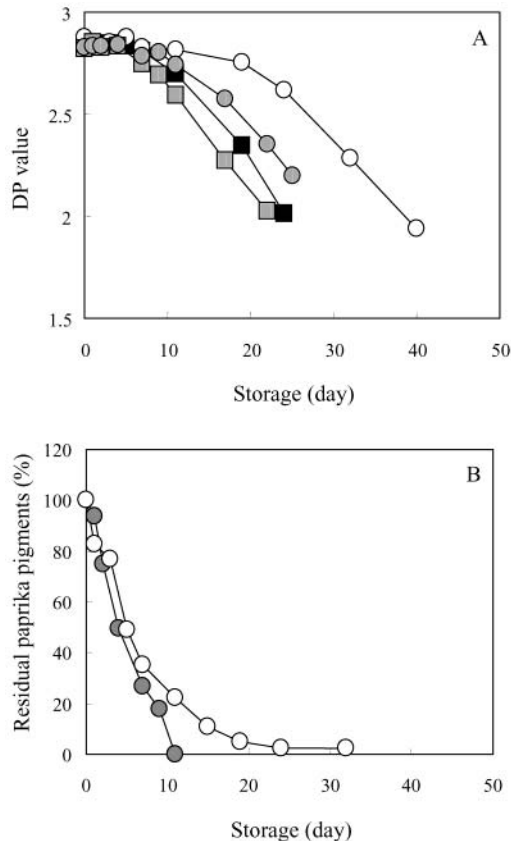

Figure 4. DP value (**A**) and residual paprika pigments (**B**) for oxidation of linoleic acid stored in the dark or under light. Linoleic acid stored in the dark: ■, no paprika pigments; ○, 0.2% paprika pigments. Linoleic acid stored under light: ■, no paprika pigments; ●, 0.2% paprika pigments.
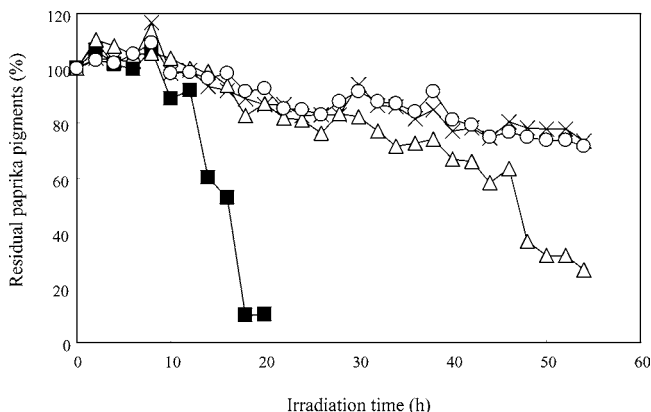

Figure 5. Effect of α-tocopherol on photodegradation of paprika pigments. Paprika pigments samples stored under light: ■, no α-tocopherol; △, 0.02% α-tocopherol; ○, 0.2% α-tocopherol; ×, the paprika pigments stored in the dark.

photodegradation of paprika pigments than for the sample in the dark (**Figure 6B**). However, despite pigments remaining in the sample for a longer time, a weaker antioxidant effect was observed.

DISCUSSION

It is well-known that the integral value of a spectrum obtained by ¹H NMR is proportional to the number of the protons present in the sample. Several researchers have applied NMR measurements to lipid oxidation (*18−20*). Matsui et al. (*15*) reported a
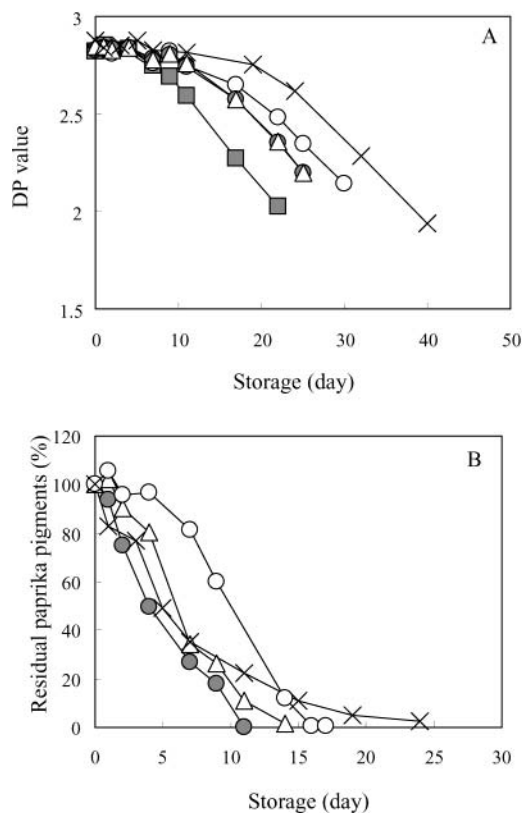
Figure 6. Changes in DP value (**A**) and paprika pigments (**B**) for oxidation of linoleic acid containing paprika pigments with or without α-tocopherol stored under light. Linoleic acid: ■, no paprika pigments; ●, 0.2% paprika pigments without added α-tocopherol; △, 0.2% paprika pigments with 0.02% α-tocopherol added; ○, 0.2% paprika pigments with 0.2% α-tocopherol added; ×, 0.2% paprika pigments stored in the dark.

quantitative method for evaluating lipid oxidation using dioxane as an external reference. Miyake et al. (*16*) also examined in detail properties that have an effect on quantitative and rapid analysis by NMR, particularly T_1 relaxation time (*21*), and proposed the use of the rapid NMR method. NMR allows us to rapidly evaluate the oxidation of linoleic acid (3 min per sample), and results from NMR measurements have confirmed that paprika pigments show an antioxidant effect on the oxidation of linoleic acid. Taken together, the present results and those of previous studies suggest that it is possible to estimate antioxidant activity of natural pigments on the oxidation of various oils using the NMR method.

In the present study, it was found that considerable oxidation of linoleic acid occurred after or at the same time as the decoloration of the added paprika pigments (**Figures 3** and **4**). These results imply that the paprika pigments exert an antioxidant effect and suggest that they could be used as an indicator to visually judge the oxidative deterioration of oils. Many reports have demonstrated that paprika pigments and other extracts show antioxidant activity, for example, in the inhibition of lipid oxidation. These extracts are thought to prevent oxidation by scavenging radicals (*3, 12, 22*). Asai et al. (*23*) reported that lipid peroxidation in mice was suppressed by a dietary supplement that contained paprika extract. Oshima et al. (*24*) and Etoh et al. (*25*) reported that dietary capsanthin was absorbed in the body after the ingestion of paprika juice in human subjects. Once absorbed by the human body, this pigment may have an antioxidant effect. Therefore, edible oils with added paprika pigments could act as both a source of antioxidants and a potential indicator for the deterioration of the oils. Studies to

elucidate the relationship between antioxidant effect and residual paprika pigments in edible oils are needed. Currently, there is little information about the degradative compounds of paprika pigments and the mechanism by which they prevent oxidation. Although paprika extract is one of the oldest and most widely used natural food colors, further studies regarding the safety of its degradative compounds are needed.

It is well-known that carotenoids are unstable toward light. The paprika pigments showed some antioxidant ability under light, although the effect was smaller than for samples stored in the dark. The addition of another antioxidant provides a stabilizing effect on degradation of carotenoid pigments (*26, 27*). Also, carotenoids and tocopherols act synergistically as antioxidants (*28*–*30*). In the present study, we used α-tocopherol as an antioxidant to stabilize the paprika pigments, and the addition effectively suppressed the photodegradation of paprika pigments. However, when the paprika pigments with added α-tocopherol were exposed to light, the antioxidant effect was not as great as for the samples stored in the dark, despite more pigments remaining in the samples (**Figure 6**). Goda et al. (*14*) reported that in paprika, cis-esterified capsanthin isomerized completely to the all trans isomer during photoirradiation. Although there are no reports of the antioxidant abilities of different capsanthin isomers, Levin et al. (*31*) have reported that *cis-β*-carotene was a more effective antioxidant than the all trans isomer. Furthermore, it has been suggested that the reaction mechanism of cis/trans isomers of *β*-carotene on free radicals is different (*32*). Because edible oils such as vegetable oil and dressings are exposed to light during retail display or in the kitchens of consumers, further investigation is needed of the application of paprika pigments as an antioxidant or indicator to edible oils.

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JF035319S