Note

Photostability of Lycopene Dispersed in an Aqueous Solution

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Lycopene dispersed in aqueous solutions with different dissolved oxygen contents was photo-irradiated by using a xenon weather meter, and the contents of lycopene and dissolved oxygen were measured. Both the degradation of lycopene and the consumption of dissolved oxygen followed a first-order kinetics model. There was a proportional relationship between the degradation content of lycopene and the consumption of dissolved oxygen. These results indicate that dissolved oxygen would also be involved in the photolysis of lycopene.

Key words: carotenoid; lycopene; photostability; dissolved oxygen; aqueous solution

Lycopene is a carotenoid found in tomato, guava, watermelon and pink grape fruit. It is a substance which contributes to the expression of the red color of these fruits. It has been reported that the majority of lycopene in the human body was derived from tomato and the processed food from tomato.1–3 Lycopene derived from tomato is approved as a food color in Japan, and tomato lycopene is widely used for soft drinks, jelly, candy and processed food made from seafood paste.

The color degradation during manufacturing, distribution and consumption decreases the quality of food, and stabilizing the food color to prevent such degradation is necessary. There have been several studies reporting findings on the stability of carotenoids against light and heat,2–4) and on the stability of lycopene in tomato powder.5–9) Water is a major component of the food system, so it is important to obtain knowledge on the degradation stability of carotenoids in an aqueous solution, although most carotenoids are not soluble in water. Studies on the behavior of carotenoids to control degradation in an aqueous solution have been very limited, except for the temperature dependence. The photostability of lycopene in an aqueous solution was evaluated in this study to clarify the degradation factor for lycopene in the food system. It was found that dissolved oxygen was involved in the photolysis of lycopene in an aqueous solution.

The tomato lycopene dispersion (San-Ei Gen F.F.I., Osaka, Japan) consisted of the following materials: 1% of lycopene with 95% purity, 27.5% of gum arabic (as a dispersing agent), 12.5% of propylene glycol (as a solvent), 0.5% of phosphoric acid (as a pH adjuster), and 59% of water. Its average particle size was adjusted to 0.24 μm in diameter which was measured with an MT-3000II laser diffraction particle size analyzer (Microtrac, Largo, Florida, USA), using water as the measurement solvent.

The tomato lycopene dispersion was diluted to become 10 ppm as the lycopene content with ion-exchanged water of two different dissolved oxygen contents (6.15 mg/L and 4.58 mg/L), and with ion-exchanged water of 100 ppm l-ascorbic acid content (1.26 mg/L). Each lycopene solution was irradiated at 600 W/m² (300–700 nm) in a 200-mL glass bottle by using an XWL-75R xenon weather meter (Suga Test Instruments, Tokyo, Japan).

Lycopene was extracted with n-hexane to determine the residual content of lycopene in each aqueous solution. The extracted solutions before and after photo-irradiation were analyzed by high-performance liquid chromatography (HPLC) according to the analytical conditions specified by Joint FAO/WHO Expert Committee on Food Additives (JECFA).10) The photolysis treatment decreased the content of lycopene, whereas the peak patterns detected at 470 nm were no different before and after irradiation. We calculated the degraded lycopene after irradiation in this study by measuring the absorbance of the extracted solution. The absorbance of a test solution at the wavelength for maximum absorption (455–465 nm) was measured with a V-560 spectrophotometer (Jasco, Tokyo, Japan), using n-hexane as the reference, and the lycopene content was calculated by means of the molecular extinction coefficient (E1%1cm of 3450). The lycopene degraded by irradiation was calculated. The dissolved oxygen content was measured with a D25 dissolved oxygen meter (Horiba, Tokyo, Japan), which detects the oxygen molecules passing through a semipermeable membrane by diffusion, and the dissolved oxygen consumption due to irradiation was calculated.

The residual lycopene content in each aqueous solution was plotted against the irradiation time (Fig. 1A). Both solutions with different dissolved oxygen content exhibited a reduction in lycopene content dependent on the photo-irradiation time. In contrast, no significant

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reduction in lycopene content was apparent in the
100 ppm l-ascorbic acid-added aqueous solution.
The plots in Fig. 1A were fitted to the first-order
kinetic model,
\[ R(t) = R(0) \exp(-kt) \]
where \( R(t) \) is the content of lycopene in the aqueous solution at time \( t \).
The rate constant \( (k) \) that was obtained from these
results is shown in Table 1. The constant of lycopene in
the higher initial dissolved oxygen solution (6.18 mg/L)
was significantly larger than that in the lower initial
dissolved oxygen solution (4.58 mg/L). The rate con-
stant and the initial content of dissolved oxygen in the l-
ascorbic acid-added solution were lowest
among those aqueous solutions. These results suggest
that the degradation rate of lycopene might have been
dependent on the initial dissolved oxygen content in the
aqueous solution.

The dissolved oxygen content of each aqueous solu-
tion was plotted against the irradiation time (Fig. 1B).
The plots in Fig. 1B were also fitted to a first-order
kinetic model, the rate constant \( (k) \) obtained from these
results being shown in Table 1. There was no apparent
difference in the consumption rate of dissolved oxygen
in relation to the initial dissolved oxygen content.
There was no significant change in dissolved oxygen
content by photo-irradiation in the L-ascorbic acid-added
solution.

Carotenoids are very easy to degrade in the air, and
their stability varies according to the type of carotenoid,
isomer, and degree of esterification.\(^{11} \) Henry et al.
have reported that the degradation kinetics for carotenoids in
an oil model system followed a first-order kinetic model
and that lycopene was the most susceptible to degrada-
tion.\(^{3} \) Furthermore, Ax et al. have reported that the
thermal degradation of lycopene in an aqueous solution
of an oil-in-water emulsion followed a first-order kinetic
model, and suggested that the thermal degradation
would progress easily in the presence of oxygen.\(^{12} \)

The consumption of dissolved oxygen and the
degraded content of lycopene were highly correlated in
our experiment using the tomato lycopene dispersion
system (Fig. 2). The relationship between the degraded
content of lycopene and the consumption of dissolved

<table>
<thead>
<tr>
<th>Initial dissolved oxygen (mg/L)</th>
<th>l-Ascorbic acid (ppm)</th>
<th>Rate constant ( (k) ) (h(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lycopene</td>
<td>6.15</td>
<td>0</td>
<td>0.0464 ± 0.0020</td>
</tr>
<tr>
<td>Lycopene</td>
<td>4.58</td>
<td>0</td>
<td>0.0283 ± 0.0012</td>
</tr>
<tr>
<td>Lycopene</td>
<td>1.26</td>
<td>100</td>
<td>0.0010 ± 0.0007</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>6.15</td>
<td>0</td>
<td>0.0352 ± 0.0026</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>4.58</td>
<td>0</td>
<td>0.0416 ± 0.0016</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>1.26</td>
<td>100</td>
<td>0.0048 ± 0.0026</td>
</tr>
</tbody>
</table>

The rate of constant \( (k) \) is presented as the mean ± standard error.
oxygen could be expressed by the degraded content of lycopene (mg/L) = 1.85 x consumption of dissolved oxygen (mg/L) + 0.1968. These data suggest that the oxygen content in an aqueous solution might play a major role in the photostability of lycopene and that lycopene photodegradation would progress by oxidation. In addition, the content of dissolved oxygen required to degrade 1 mg/L of lycopene (1.86 mmol/L) would be 0.54 mg/L (16.875 mmol/L). Since gum arabic might also affect the photostability of lycopene in an aqueous solution, future efforts will be concerned with a comparison of different dispersion materials for the photodegradation of lycopene. A comparison of the HPLC chromatograms before and after irradiation revealed that only the lycopene content was decreased by photo-irradiation. These findings suggest that oxygen may affect the conjugated double bonds in lycopene which causes degradation and color fading.

As the addition of l-ascorbic acid to the aqueous solution significantly reduced the dissolved oxygen content in the solution (Fig. 1B), it is assumed that lycopene would not be degraded without dissolved oxygen. Ribeiro et al. have reported that emulsions containing lycopene diluted with orange juice were more stable than those diluted with milk or water.13) Considering the fact that orange juice contains a significant amount of l-ascorbic acid, the stability of lycopene in orange juice can be explained by the reduction of dissolved oxygen in the test solution, but not by its antioxidative effect.

In conclusion, the present results provide evidence for a correlation between the photo-induced loss of lycopene and the consumption of dissolved oxygen. This indicates that the most effective way to prevent the photodegradation of lycopene in an aqueous solution would be deoxygenation of the food system.

References