

Evaluation of singlet oxygen quenching by spice pungent compounds in aqueous media

(Received October 21, 2024)

(Accepted January 15, 2025)

Keishi Ohara^{a)}, Nahoko Hiraoka^{b)}

a) Graduate School of Science and Engineering, Ehime University

b) Faculty of Science, Ehime University

Abstract

The singlet oxygen ($^1\text{O}_2$) quenching ability of pungent *o*-methoxyphenols (OMPs) such as capsaicin and zingerone found in spices was evaluated by measuring the time evolution of $^1\text{O}_2$ phosphorescence. The $^1\text{O}_2$ quenching rate constants (k_Q) for poorly water-soluble OMPs in aqueous media were estimated using cyclodextrin (CD) as a solubility enhancer. The k_Q values obtained for the tested compounds in aqueous media were $10^7 \sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which were 20 ~ 100 times larger than those in ethanol, indicating that the quenching reaction is essentially electrophilic. In aqueous media, addition of CD caused a large decrease in k_Q . This was likely due to a kinetic inhibition effect caused by encapsulation and an increase in viscosity. Dispersion into aqueous media using CD is applicable to antioxidant evaluations of poorly water-soluble compounds even for fast reactions such as $^1\text{O}_2$ quenching.

Keywords : spice, capsaicin, antioxidant, singlet oxygen, cyclodextrin

I Introduction

The bioactivities and health effects of natural constituents in spices and herbs have been of great interest¹⁻³⁾. For example, capsaicin (Fig. 1) and its structural analogues are pungent components of chili peppers^{1, 4)}, while gingerol, shogaol, and zingerone (Fig. 1) are found in ginger^{5, 6)}. Such pungent compounds are also used for pharmaceutical and industrial purposes because of their valuable activities; they have antibacterial effects, repellent effects on insects and animals, and antioxidative effects¹⁻⁸⁾. A considerable portion of plant-originated pungent compounds are *o*-methoxyphenol (OMP) derivatives. OMPs are known to exhibit inhibition of lipid peroxidation, a cancer-preventive effect, and antioxidant activity against reactive oxygen species (ROS)⁷⁻¹¹⁾. For such functional compounds contained in spices, foods and beverages, evaluations of their activities in aqueous media are valuable. However, such evaluations are often difficult because of the poor solubility of the target compounds in water. One possible way of making such an evaluation is to disperse target molecules into water by using a solubility enhancer.

Cyclodextrin derivatives (CDs) are cyclic oligosaccharides

consisting of 6 – 8 D-glucopyranose units¹²⁻¹⁴⁾. CDs often make it possible to disperse lipophilic compounds into aqueous solutions through making inclusion complexes. The structures and properties of such inclusion complexes and their usage in dispersing and delivering guest functional molecules have been intensively studied¹²⁻²¹⁾. It is also known that CDs protect guest molecules from oxidative degradation and other reactions through a capsulation effect^{12, 22)}. The masking and sustained release effects of CD on guest molecules are used in the food industry. CDs are also used as a solubility enhancer for target organic molecules in aqueous dispersions. While some applications using CDs in antioxidant assays in aqueous media have been reported²³⁻²⁷⁾, they are not used often. One reason for this may be that the effect of CD on each assay has not been quantitatively clarified. The addition of CD to evaluation systems must affect significant chemical processes in assays such as generating and scavenging steps of ROS. In many cases, it would be difficult to separate and evaluate each contribution.

Singlet oxygen ($^1\text{O}_2$) is molecular oxygen in the electronically lowest excited $^1\Delta_g$ state, and it induces and accelerates oxidation of materials. Thus, $^1\text{O}_2$ quenching by natural