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Antioxidant potential and DPPH radical scavenging kinetics of water-insoluble flavonoid naringenin in aqueous solution of micelles

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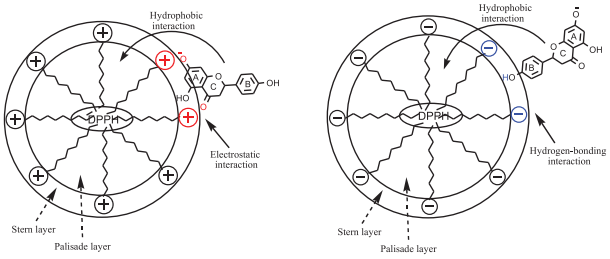
HIGHLIGHTS

- The micellar effects on the antioxidant capacity of naringenin in aqueous micellar solutions of CTAB and SDS have been investigated.

GRAPHICAL ABSTRACT



- The kinetics of DPPH radical reaction with naringenin has been evaluated in micellar media.
- Data process has shown that the activity and rate of DPPH radical scavenging increase by increasing concentration of micelles SDS and CTAB.
- The antioxidant performance of naringenin in SDS solution is higher compared to that in the CTAB micelle.
- The micellar effects on the antioxidant efficiency were explained in terms of interactions between naringenin and the micelle surface.

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ABSTRACT

The antioxidant performance of flavonoid naringenin was investigated in terms of the DPPH free radical scavenging activity (RSA) in different aqueous micellar media using UV–vis spectrophotometric technique. The DPPH assay was done at $(25.0 \pm 0.1)^{\circ}$C and various concentrations of anionic amphiphile of sodium dodecylsulfate (SDS) and cationic amphiphile of cethyltrimethylammonium bromide (CTAB). The kinetics of the antioxidant behavior of naringenin was also evaluated in the micelle systems. The RSA values and kinetic data obtained in the model self-assembled system demonstrate that activity and rate of the DPPH radical scavenging increase with increasing concentration of micelles SDS and CTAB. It was found that these abilities in SDS solution are higher compared to that in the colloidal aggregated CTAB surfactant. Finally, the micellar effects on the antioxidant efficiency were explained in terms of possible interaction modes between naringenin and the micellar surfaces.

1. Introduction

Flavonoids or bioflavonoids, including flavonols, flavanone, flavanols, flavones, isoflavones and anthocyanidins, are natural bioactive polyphenols known as health-promoting, disease-preventing dietary supplements and cancer-preventive agents [1]. Moreover, they are extremely safe and with low toxicity, which

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makes them excellent chemopreventive agents [2]. Many of the pharmacological effects of flavonoids are related to their antioxidant activity, a biological function that is important in keeping the oxidative stress levels below a critical point in the body. This property of flavonoids is supposedly due to their ability to scavenge free radicals and to synergistic effects with other natural antioxidants such as vitamin E, carotenoids etc. The radical scavenging by flavonoids occurs primarily via donation of an electron or a hydrogen atom from the free hydroxyl groups on the flavonoid nucleus, with the formation of a less reactive flavonoid aroxyl radical stabilized by resonance. Therefore it plays a moderate role in the propagation of radical-induced damage in biological systems [3,4].

Naringenin (4′,5,7-trihydroxyflavanone) is one of the most abundant citrus flavonones that possesses a wide range of therapeutic activities such as antioxidant, anti-carcinogenic, antitumor and anti-estrogenic effects. Therefore, it can play a protection role against cancer, cardiovascular and microvascular diseases, hypertension, Alzheimer's disease etc. [5,6]. In addition, this polyphenolic compound is known to reduce hepatitis C virus production by infected hepatocytes (liver cells) in cell culture. This seems to be secondary to naringenin ability to inhibit the secretion of very low density lipoprotein (LDL) by the cells [7]. However, the advantages and potential health benefits of this flavonoid in functional food or pharmaceutical products is limited because of its low water solubility and poor bioavailability [8]. A sketch of molecular structure of naringenin is presented in Scheme 1. Naringenin's polyphenol structure makes it very sensitive to changes in the surroundings, which can alter the planarity, hydrophobicity and electrostatic components, and eventually can lead to changes in its antioxidant properties.

Many surveys have focused on the free radical scavenging assay of flavonoids. Some of them confirmed that the radical scavenging ability of flavonoids in different systems depends not only on the environmental factors like pH, temperature, solvent composition etc. [3,9,10], but also on a number of parameters including hydrophilicity of the compounds and the microenvironment of the reaction media [11–13]. A general methodology for modeling these factors is to employ a microheterogeneous colloidal system like the micellar medium [13]. The micelle is a colloidal assembly of amphiphilic molecules that is formed spontaneously when a surfactant is added to aqueous solution at a concentration higher than the critical micelle concentration (CMC). This specific structure is composed of the hydrophobic tails pointed toward the center and the hydrophilic head groups pointed at the surface of the micelle which makes the micelles capable of establishing chemical and physical interactions with either hydrophilic or lipophilic substances present in a system [14]. Most micelles are spherical and contain some tens of surfactant molecules oriented [15].

To date, various methods have been developed to measure antioxidant capacity of natural bioactive compounds. These assays are often performed in pure organic or mixed aquo-organic solvents due to the insolubility of species used in water [16]. Among them, the assay employing the stable N-atom-centered free radical 1,1-diphenyl-2-picryhydrazyl (DPPH, Scheme 1) is the most widely used in vitro test [16,17]. This radical reacts with both electron and hydrogen donors [18], in other words, the DPPH assay is based on both electron transfer (ET) and hydrogen atom transfer (HAT) pathways [3,19]. Very few systematic studies have been reported in the literature about the employment of pure aqueous medium in DPPH radical scavenging assay of the antioxidant agents. Therefore, it is necessary to develop new techniques to overcome this limitation. To this end, the use of micelle systems is a simple alternative because they are known to improve solubilization, dissolution and bioavailability of pharmacologically bioactive molecules in aqueous solution [20,21].

The employment of the DPPH method in presence of various surfactant and micelle systems has been mostly limited to aquo-organic solvent mixtures so far. Thus, in this work, we attempted to use DPPH assay for evaluation of the radical scavenging activity (RSA) of antioxidant flavonoid naringenin in pure aqueous micellar solution without need to an organic co-solvent. We studied also the influences of the surfactant charge, concentration of surfactant and concentration of flavonoid as factors that can affect the antioxidant capacity. In addition, reaction rates of DPPH radical with naringenin in the model micelle systems are evaluated for a deeper study of this flavonoid's antioxidant behavior in aqueous media. The information obtained in the aqueous micellar systems can play a crucial role in understanding the antioxidant activity of the water-insoluble phytochemicals found in food such as flavonoids.

2. Experimental

2.1. Chemicals

Gallic acid (Scheme 1), flavonoid naringenin and the stable DPPH free radical were purchased from Fluka. The anionic surfactant SDS and cationic surfactant CTAB (Scheme 2) of the highest quality available were obtained from Sigma. All chemicals were of analytical reagent grade and used as supplied. The doubly distilled deionized water (conductivity of $1.2 \pm 0.1\ \mu\Omega^{-1}$) was used throughout all experiments.

2.2. DPPH radical scavenging assay

The DPPH assay is a fast, simple, stable and economic method to measure antioxidant capacity of food products or plant extracts. It is based on the decay of the main absorption band in the visible spectrum of DPPH radical. In presence of a hydrogen- or electron-donating compound such as flavonoids, the DPPH radical would be scavenged through hydrogen or electron donation, and its absorbance is decreased. The decreased extent of absorbance is considered as a measure for the antioxidant activity [22]. The DPPH assay was carried out in the micelle system as following procedure. The stock solutions of DPPH (0.03 mM) and naringenin (0.05 mM) were daily prepared in same surfactant concentration and then stored at refrigerator until needed. To a known volume of aqueous micelle solution taken in a 5 mL volumetric flask, 2 mL DPPH solution was pipetted and the reaction was started by adding an aliquot (0.08–0.30 mL) of naringenin to the mixture. Further, this mixture was vigorously shaken by hand and allowed to stand for 5 min at room temperature in the darkness. The same procedure was repeated at least for five different concentrations of the surfactants tested in range 6.50–8.50 mM of CTAB and 15.00–25.00 mM of SDS. In each concentration of the micelle, six different concentrations of naringenin were used. The DPPH in aqueous micelle solution without an antioxidant was used as control of this experiment. After 5 min of starting of reaction, the samples were analyzed using a PerkinElmer (Lambda 25) UV–vis spectrophotometer in the wavelength range of 400–700 nm. The aqueous micelle solutions were used as blank. The radical scavenging potential in each surfactant micelle solution was derived based on the value of the DPPH visible absorbance at the maximum according to the following expression:

$$\%\mathrm{RSA} = \left[\frac{\mathrm{Abs}_{\mathrm{control}} - \mathrm{Abs}_{\mathrm{sample}}}{\mathrm{Abs}_{\mathrm{control}}}\right] \times 100 \quad (1)$$

where $\mathrm{Abs}_{\mathrm{control}}$ and $\mathrm{Abs}_{\mathrm{sample}}$ are the absorbances at maxima wavelength of the control and the sample, respectively. All the assays were performed in three independent runs and the