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SERS spectroscopy of kaempferol and galangin under the interaction of human serum albumin with adsorbed silver nanoparticles

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ABSTRACT

Raman and surface-enhanced Raman scattering (SERS) spectroscopy were employed to probe the interaction of the flavonol drugs, kaempferol and galangin, with human serum albumin (HSA). SERS spectra of both flavonol derivatives were obtained from a colloidal silver surface in physiological condition, based on the high performance of the enhanced substrate, the most enhanced modes of kaempferol and galangin were those with certain motions perpendicular to the metal surface. The SERS spectra were allowed to predict similar orientation geometry for both of the drugs on the colloidal surface with minor difference. In addition, both flavonols–HSA complexes were prepared in different concentration ratios and the orientated differences between kaempferol and galangin were investigated by SERS.

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1. Introduction

Kaempferol and galangin (structures shown in Fig. 1), which are the flavonols isolated from traditional Chinese medicines. In medical aspects, they have been found to have anti-inflammatory [1,2], antibacterial [3] and antiviral [4] activities in vivo and in vitro. Kaempferol and galangin share the common mother nucleus structure called 2-phenyl chromone. The structural distinction is the substituent group C(4′) hydroxyl, and this kind of difference [5] will be found in functional activity. Human serum albumin (HSA), the most abundant and prominent protein in plasma, has the function to transport a wide range of endogenous and exogenous compounds like fatty acids [6], amino acids [7], bile acids [8], hormones [9], as well as an extraordinarily broad of medicines [10]. This remarkable ability of HSA is closely linked to its spatially tertiary structure. The crystallographic analysis [11,12] of HSA reveal that it is a globular protein composed of three homologous alphahelical domains (I–III), each of which is composed of two subdomains A and B. The protein is stabilized by 17 disulfide bridges. According to Sudlow nomenclature, the principal regions of ligand binding sites in HSA are located in hydrophobic cavities in subdomains IIA and IIIA, which are known as Sudlow I and II respectively, and the sole tryptophan (Trp 214) residue in HSA is located in Sudlow I [13,14].

In previous works, people studied the interaction between pharmaceutical molecule and HSA mainly by ultraviolet–visible, fluorescence, and Fourier transform infrared spectroscopy [15–19]. From that, the binding site of HSA was located in the hydrophobic pocket of subdomain IIA. In this work, we present surface-enhanced Raman spectroscopy (SERS) to study the interaction between pharmaceutical molecules and HSA [20–22]. This unique feature allows recognition studies containing highly fluorescent pharmacological molecules at trace concentration in solution and in physiological condition [23–26]. We further confirm the information related to the binding orientations of kaempferol/galangin to HSA, and extrapolate the probable trend in different concentrations when the interaction takes place spontaneously.

2. Experimental

2.1. Material

Kaempferol and galangin were purchased from National Institute for Control of Pharmaceutical and Bioproducts, HSA was purchased from Sigma–Aldrich, they are all used without further purification. The buffer Tris had a purity of no less than 99.5% and NaCl, HCl, and so on were all of analytical purity. HSA was dissolved in Tris–HCl buffer solution (0.05 mol/L Tris, 0.15 mol/L NaCl, pH 7.4). The pH values were checked with a suitably standardized pH meter. Kaempferol and galangin were dissolved in 50% ethanol. Glassware

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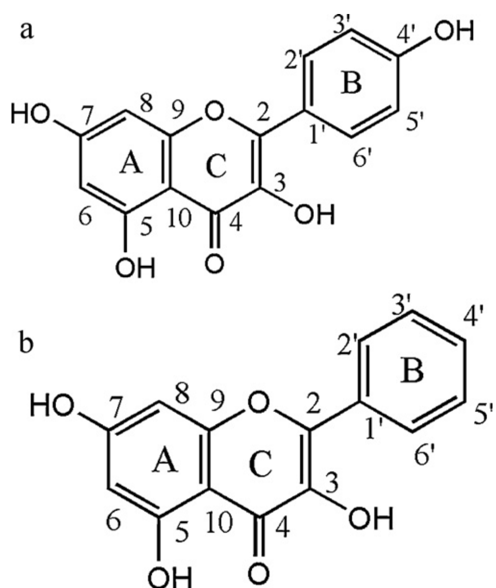

Fig. 1. Molecular structure of kaempferol (a) and galangin (b).

was thoroughly cleaned by washing with detergent, immersion in aqua regia (HNO_3–HCl 1:3, v/v) and then in piranha mixture (H_2SO_4–H_2O_2 3:1, v/v) and rinsing in ultrapure water. Ag colloid was prepared following the method of Lee and Meisel [27] by reduction of silver nitrate with sodium citrate. The Lee–Meisel colloid was preconcentrated by centrifugation prior to aggregation (5 min at 5000 rpm). The final concentration of flavols and flavonols–HSA compound is 10^{-5} mol/L.

2.2. Equipment and spectral measurement

The fluorescence spectra were measured with RF-5301PC spectrofluorophotometer (Shimadzu, Japan) equipped with 1.0 cm quartz cells. The widths of the excitation slit and the emission slit were set to 5 nm and 3 nm, respectively. An excitation wavelength of 295 nm was chosen and the emission wavelength range was 300–500 nm. Ag colloid was characterized (Fig. 2) by field emission scanning electron microscope (FE-SEM) using JEOL JSM-6700F FE-SEM with an accelerating voltage of 3 kV.

The normal Raman (NR) and SERS spectra were conducted with a HORIBA Jobin Yvon T64000 micro-Raman spectrometer. Radiation of 514.8 nm from a Ar^+ laser was used for excitation. The output laser power was 6 mW at sample. The NR spectra were obtained from pure powdered compounds on a glass. The liquid sample for SERS measurement was prepared simply by adding 10 μL of the sample solution to a 30 μL of the Ag colloid in a U-type glass tube.

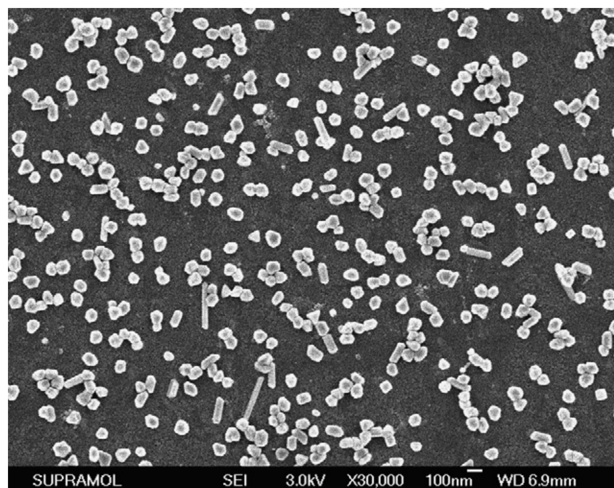

Fig. 2. SEM of Ag particles.

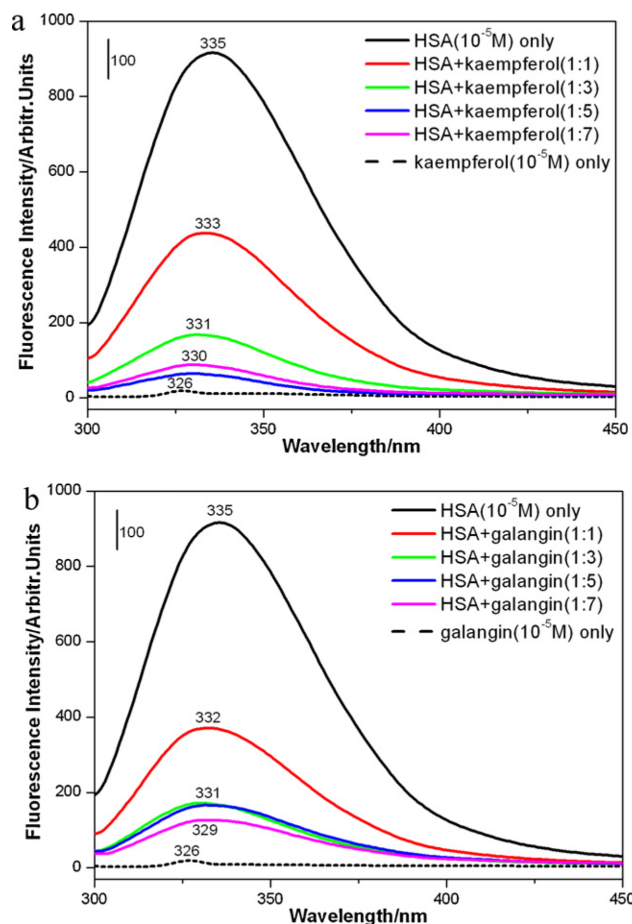

Fig. 3. Fluorescence emission spectra of HSA in the presence of various concentrations of kaempferol (a) and galangin (b).

3. Results and discussion

3.1. Fluorescence spectra of flavonols–HSA complex

The fluorescence spectra of HSA in the absence and presence of flavonols in the pH 7.4 Tris–HCl buffer are obtained with the excitation wavelength at 295 nm in Fig. 3. HSA exhibits a strong fluorescence emission with a peak at 335 nm owing to the single tryptophan residue (Trp 214), and flavonols are almost non-fluorescence under the same experimental conditions. With the addition of a solution of flavonols to HSA, it is observed that a progressive decrease in the fluorescence intensity of tryptophan residue is caused by quenching, accompanied by a hypsochromic shift. The result probably indicates that the binding of flavonols to HSA can easily quench the intrinsic fluorescence of the single tryptophan. This also suggests an increased hydrophobic environment surrounding the tryptophan site. As seen from fluorescence emission spectra of flavonols–HSA complexes, the changing tendency of kaempferol (Fig. 3a) and galangin (Fig. 3b) with increasing concentration are in accordance with reported literatures [28,29]. Consequently, it shows that kaempferol and galangin have the same binding site to HSA, which has been confirmed definitely in hydrophobic cavity in subdomain IIA.

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