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The enhanced electrochemiluminescence of lucigenin by some hydroxyanthraquinones

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Abstract

Several hydroxyanthraquinones (emodin, rhein and physcion) were found to strongly enhance the cathodic electrochemiluminescence (ECL) of the lucigenin by scanning under the mode of differential pulse voltammetry. The enhanced intensity was linear with the concentrations of rhein, emodin and physcion. The linear calibration ranges of 8.0×10^{-8} to 2.0×10^{-6}, 3.0×10^{-7} to 8.0×10^{-6} and 1.0×10^{-7} to 1.0×10^{-6} mol/L, the detection limits of 2.1×10^{-8}, 1.6×10^{-7} and 5.2×10^{-8} mol/L were obtained for rhein, emodin and physcion, respectively. Potential-resolved ECL was used to study the possible mechanism of the enhancement effect. An electron transfer pathway was found to be involved in the ECL process. It has been confirmed that the reduced hydroxyanthraquinones reacted with dioxygen to give superoxide radical anion which increased the ECL of the lucigenin. Furthermore, these three hydroxyanthraquinones revealed the different enhanced ECL efficiency in the following order: rhein > physcion > emodin.

Keywords: Electrochemiluminescence; Lucigenin; Hydroxyanthraquinone

1. Introduction

Rhubard is an important Chinese traditional medicine. It has very strong antibacterial action and is used for the treatment of bacterial dysentery. The major active constituents of this herb are hydroxylated anthraquinones, including chrysophanol, emodin, physcion, aloe-emodin and rhein and their glucosides. Hydroxylated anthraquinones are considered to be potential antitumour agents. Especially rhein, emodin and physcion (see Fig. 1) have showed antineuroectodermal tumor activity in vitro and in vivo [1,2]. Therefore, the determination of the hydroxyanthraquinones has been attracted much attention. Previous determination methods of hydroxyanthraquinones were usually based on chemiluminescence (CL) [3], electrochemical detection with mercury and glass carbon electrodes [4], capillary electrophoresis (CE) [5–9] and high-performance liquid chromatography (HPLC) [10–16].

Chemiluminescence (CL) has been used widely to detect many analytes due to its simplicity and high sensitivity. A CL technique for determination of emodin has been reported [3], which is based on the quenching effect of emodin in the CL system of luminol–H_2O_2–Cr^{3+} due to the reaction of emodin and H_2O_2. Electrochemiluminescence (ECL), in contrast to CL, is a process in which light is emitted only when an appropriate voltage is applied to the electrode contacting with the solution containing a proper compound. In most cases, this technique not only has the same advantages of CL analysis, but also performs some other advantages, such as less reagent requirement, more information for mechanism study. However, so far to the best of our knowledge, ECL method has been never applied to determine hydroxylanthraquinones.

The main purpose of this study was to establish a sensitive and rapid ECL method for determination of hydroxylanthraquinones and to explore the possible mechanism of this reaction.

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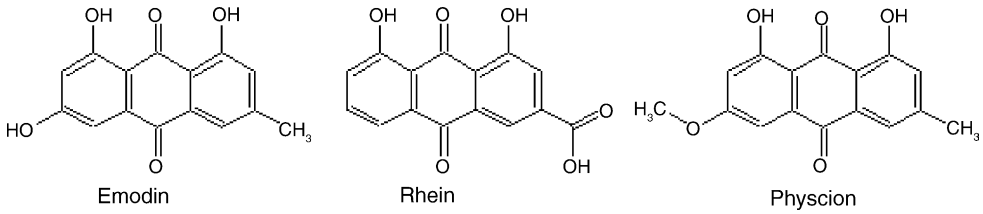

Fig. 1. The molecular structure of the three hydroxyanthraquinones.

2. Experimental

2.1. Chemicals

Lucigenin was purchased from Sigma Chemical Co. (USA) and used without further purification. Rhein, emodin and physcion were purchased from the national institute for the control of pharmaceutical and biological products (Beijing, China). Stock solution of 1.0×10^{-3} mol/L for each hydroxyanthraquinone was prepared and stored at 4 °C in a refrigerator with a tight cover to minimize exposure to light and air. The rhein, emodin and physcion working solutions were made by appropriate dilution with 0.01 mol/L KCl. The Britton–Robinson (B.R.) buffer (pH 2.0–12.0) was prepared by titrating a stock solution containing 0.04 mol/L acetic acid, 0.04 mol/L phosphoric acid, 0.04 mol/L boric acid with 0.2 mol/L sodium hydroxide to the desired pH value.

All other chemicals used in this study were analytical reagent or better. Double-distilled water was used throughout.

2.2. Apparatus

The experimental equipment for ECL measurement including a BPCL ultra-weak chemiluminescence analyzer controlled by a personal computer with BPCL program (Institute of Biophsics, Academia Sinica, China) and a electrochemical analyzer (CHI660a, Shanghai Chenghua instrument Co., China).

A conventional three-electrode system was used as the electrolytic system, which was composed of a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (saturated KCl) electrode as the reference electrode. A commercial 5 mL cylindroid's glass cell was used as ECL cell. Before each measurement, the working electrode was fixed in the same position and directly faced the window of the pohotomultiplier tube. ECL spectrum was monitored by a 970CRT fluorescence spectrometer (Shanghai, China). The working electrode was pretreated by polishing its surface with aqueous slurries of alumina powders (1.0 and 0.3 μm α-Al_2O_3) on a polishing cloth and then carefully washed with water to give a smooth and clean electrode surface. The ECL cell was washed with 0.2 mol/L nitric acid and water in sequence before use.

2.3. Procedure

A 100 μL of sample solution, 1 mL of 1.0×1.0^{-4} mol/L lucigenin and 1 mL of 0.10 mol/L KCl were added successively to a 10 mL volumetric flask, and then diluted with double-distilled water to required volume. 2.5 mL of the diluted solution was transferred to the ECL cell. A potential between 0.0 and −1.0 V was applied to the working electrode and the ECL signal was recorded simultaneously. The emission at −0.55 V was used to the quantitative analysis, based on the net ECL intensity changes (ΔI, $\Delta I = I_s - I_0$), where I_0 was the background signal (ECL intensity) of the lucigenin system without hydroxyanthraquinones, and I_s was the signal obtained with addition of hydroxyanthraquinones.

3. Results and discussion

3.1. The enhanced ECL of lucigenin by hydroxyanthraquinones

The ECL of lucigenin was primarily examined at a glassy carbon electrode (GCE) by differential pulse voltammetry in neutral aqueous solution. When the applied potential was scanned in the range of 0.0 to −1.0 V, a broad ECL peak of lucigenin was observed (see Fig. 2, curve A). The ECL intensity was greatly enhanced by addition of emodin, physcion or rhein (see Fig. 2, curves B–D). Among these three hydroxyanthraquinones, the highest luminescence intensity was obtained in the presence of rhein, and the lowest in emodin.

3.2. Selection of electrochemical parameters

In our previous work [17], the linear sweep voltammetry (LSV), square wave voltammetry (SWV) and differential pulse voltammetry (DPV) were used to examine the effect of excitation waveform on the ECL of licigenin by using the anodic potential sweep. The results showed that the most stable ECL could be obtained by using DPV.

In this paper, LSV and DPV were selected to examine the effects of electrochemical techniques on this ECL system. The result showed that, when DPV was used, a stronger net ECL intensity was obtained. So DPV mode was selected for the subsequent investigation. To establish the optimal conditions, the luminescent intensity was measured as a function of