

# Highly sensitive voltammetric method in electrochemistry for the determination of jateorisin with a modified electrode

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A highly sensitive sensor, poly(L-aspartic acid)/GCE, was fabricated by electrochemical deposition of L-aspartic acid on a glassy carbon electrode. A new voltammetric method for the determination of ateorizin has been proposed. The advantages of this method are high sensitivity, good accuracy and simplicity. In practical applications, the poly(L-aspartic acid)/GCE sensor allows a fully selective quantitative analysis of jateorisin without any other interfering signal. The results of the analysis are satisfactory.

**Keywords:** Jateorhizine, poly(L-aspartic acid), voltammetric sensor, liner sweep voltammetry.

**Високочутливий вольтамперометричний метод електрохімії для визначення жатеоризину з модифікованим електродом.** *Xiaobo Wang, Yi Zhang*

Високочутливий сенсор, полі(L-аспарагінова кислота)/GCE, був виготовлений шляхом електрохімічного осадження L-аспарагінової кислоти на скловуглецевому електроді. Запропоновано новий вольтамперометричний метод визначення жатеоризину. Достоїнствами даного методу є висока чутливість, хороша точність та простота. У практичних прикладних дослідженнях сенсор полі(L-аспарагінова кислота)/GCE дозволяє проводити повністю селективний кількісний аналіз жатеоризину без будь-якого іншого інтерференційного сигналу. Результати аналізу задовільні.

## 1. Introduction

Jateorhizine (structure shown in Fig. 1) is an isoquinoline alkaloid and most commonly found in many herbs, such as *Tinospora capillipes* Gagnep [1], *Coptidischinensis* [2], *Cortex phellendri*, and *Berberis vulgaris* [3]. As a kind of isoquinoline alkaloid, jateorhizine possess activities such as anti-tumor [4], antimalarial [5], anti-inflammatory [6], and have been used for the treatment of gastrointestinal diseases and bacterial diarrhea [7]. Moreover, Jatorrhizine has shown the functions of decreasing the blood glucose level in alloxan-diabetic mice and an acetylcholinesterase inhibitory property [8, 9]. It also exhibited inhibitory activity against animal pathogens including *Staphylococcus aureus*, *Staphylococcus albus*, *Staphylococcus epidermidis*, *Proteus*

*vulgaris*, *Acinetobacter lwoffii* and *Sarcina lutea* [10]. In view of these critical pharmacological activities, it is necessary to determine the content of jateorhizine in traditional Chinese medicine (TCM) for the assessment of quality control for TCM products, which is crucial for their therapeutic effect. A variety of separation and detection techniques for jateorhizine have been proposed, such as high-performance liquid chromatography coupled with diode array detection (HPLC-DAD) [11], reversed-phase high-performance liquid chromatography (RP-HPLC)[12], high performance liquid chromatography coupled with diode array detection and mass spectrometry (HPLC-DAD-MS) [13], ultra high performance liquid chromatography with tandem mass spectrometry (U-HPLC-MS/MS) [14] ultra high-performance liquid chromatogra-

phy-electrospray ionization-tandem mass spectrometry (UHPLC-ESI-MS/MS) [15], high performance liquid chromatography-tandem mass spectrometry(LC-MS/MS) [16], liquid chromatography-tandem mass spectrometry (LC-MS/MS) [17], capillary electrophoresis (CE) with acidic potassium permanganate chemiluminescence (CL) [18]. However, these methods are time-consuming, solvent-usage intensive, highly expensive, and require expert handling. Nevertheless, electrochemical methods have attracted much attention with their rapidity, simplicity and sensitivity, and electrochemical techniques also help in identifying the redox characteristics of drug compounds and provide important information about their pharmacological action. Therefore it is necessary and valuable to develop an electroanalytical method for the analysis of jateorizine. To the best of our knowledge, so far there has been only one report on the study of the electrochemical characteristics and electroanalytical methods for jateorizine [19]. Nevertheless, the proposed electrochemical method for analysis of jateorizine in this article allows one to obtain a lower detection limit.

Nowadays, chemically modified electrodes have been proved to be a successful strategy to circumvent this problem, and various materials and techniques have been used. Among these modified electrodes, amino acids modified electrodes have many merits such as good biocompatibility, stability, easiness of the preparation and easily available materials [20–22], except for some limitations that are common to all modified electrodes, such as dependence on the coating method and durability. To date, polymerizations of amino acids have attracted considerable attention and the poly amino acids modified electrodes were extensively applied in the analysis of pharmaceutical drugs owing to their excellent electrocatalytic properties [23–25]. L-aspartic acid (isoelectric point is 2.77), as one of the naturally occurring amino acids, possesses two carboxyl groups and one amine group [26]. It can be electrochemically polymerized on the GCE by cyclic voltammetry and form a membrane surface rich in carboxyl and amino groups [27].

In this work, an electrochemical sensor based on a glassy carbon electrode modified with poly(L-aspartic acid) was fabricated and used to determine jateorizine. Compared with the bare glassy carbon electrode (GCE), an enhanced electrochemical re-

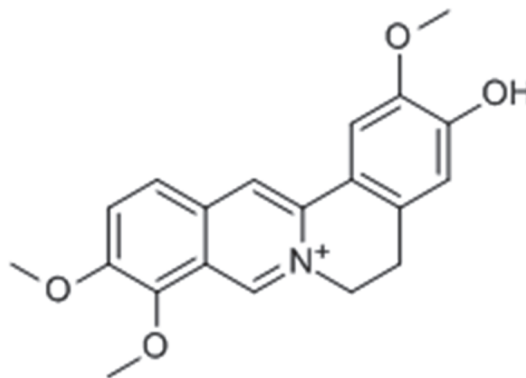


Fig. 1. Chemical structure of Jateorhizine.

sponse of jateorhizine was demonstrated on the modified electrode and a highly-sensitive electroanalytical method for jateorhizine was established. The proposed method was also successfully applied to the detection of jateorhizine in the Chinese herb *Tinospora capillipes* Gagnep with satisfactory results.

## 2. Experimental

### 2.1 Apparatus and reagents

All electrochemical experiments were carried out using an RST5000 electrochemical system (Zhengzhou Shiruisi Instrument Co. Ltd., Zhengzhou, China). A conventional three-electrode system consisted of an Ag/AgCl reference electrode, a platinum wire auxiliary electrode, and a bare or modified GCE working electrode ( $d = 3$  mm).

Jateorhizine ( $\geq 98\%$ ) was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China) and was configured to a standard solution ( $1 \cdot 10^{-3}$  mol·L $^{-1}$ ) using a methanol solution (stored in a dark refrigerator). L-aspartic acid was also purchased from Aladdin and was configured to a standard solution ( $2.0 \cdot 10^{-3}$  mol·L $^{-1}$ ) using a phosphate buffer solution (pH 6.5). Phosphate buffer solutions (PBS) ( $0.1$  mol·L $^{-1}$ ) were prepared by mixing stock solutions of NaH $_2$ PO $_4$  and Na $_2$ HPO $_4$ ,  $0.1$  mol·L $^{-1}$  each, and the lower pH of PBS was adjusted with  $0.1$  mol·L $^{-1}$  H $_3$ PO $_4$ . All other chemicals were of analytic grade and used as received. Double-distilled water was used throughout, and all the experiments were performed at room temperature.

### 2.2 Preparation of a modified electrode

Prior to the modification, the bare GCE was mechanically polished to a mirror-like surface alternately with a suspension of aluminum oxide  $0.3$  and  $0.05$   $\mu\text{m}$ , successively

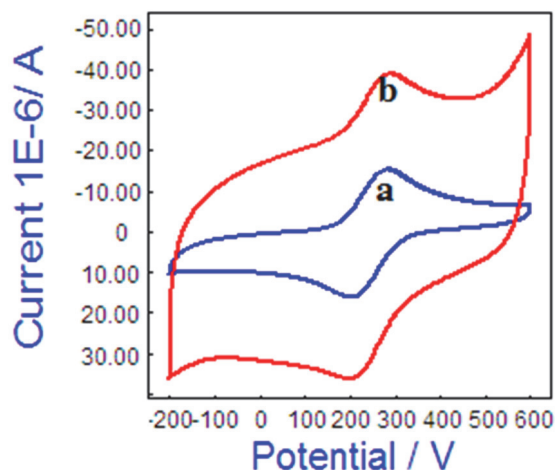


Fig. 2. Cyclic voltammograms of  $[\text{Fe}(\text{CN})_6]^{3-}$  ( $1.0 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ ) containing  $0.1 \text{ mol}\cdot\text{L}^{-1}$  KCl in bare GCE (a) and in poly(L-aspartic acid)/GCE (b). Scan rate:  $0.1 \text{ V}\cdot\text{s}^{-1}$ .

sonicated in bidistilled water, anhydrous ethanol, and was air dried naturally. Then the polished electrode was immersed in L-aspartic acid ( $2.0 \cdot 10^{-3} \text{ mol}\cdot\text{L}^{-1}$  in PBS, pH 6.5) and the poly(L-aspartic acid) was obtained on the bare GCE by cycling potentials from  $-1.5 \text{ V}$  to  $2.5 \text{ V}$  at a rate of  $0.1 \text{ V}\cdot\text{s}^{-1}$  for four circles. The modified electrode was air dried naturally and named poly(L-aspartic acid)/GCE.

### 2.3 Analytical procedure

The poly (L-aspartic acid)/GCE was scanned by cyclic voltammetry from 0.2 to 1.1 V at a of  $0.05 \text{ V}\cdot\text{s}^{-1}$  in PBS (pH 2.0), until a steady state was reached. Then, an appropriate volume of jateorhizine was added into the electrochemical cell. Due to the adsorption property of jateorhizine on the proposed electrode, the concentration step was carried out in an open cycle with stirring of the solution for 210 s. Quantitative determination of jateorhizine was performed using cyclic voltammetry (CV) or linear sweep voltammetry (LSV).

### 2.4 Sample solution preparation

For the analysis of the real sample, 1.0 g of *Tinospora capillipes* Gagnep was accurately weighted after being triturated in a mortar. The mixture was then transferred to a beaker with 10 ml of methanol and sonicated for 3 hours, followed by transfer of the extracting solution to another beaker. The above step was repeated three times and the entire extraction solution was collected together, evaporated by

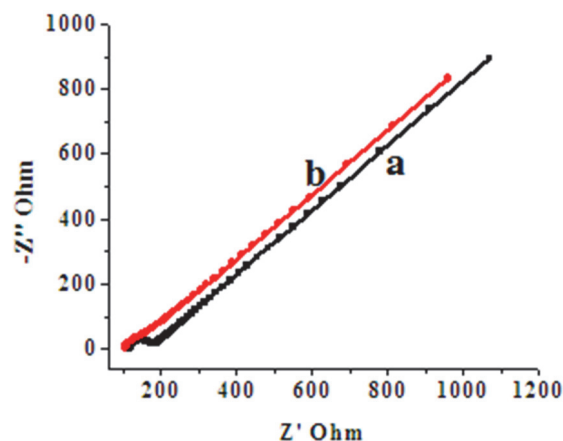


Fig. 3. Nyquist plots of EIS with different electrodes: bare GCE (a), poly(L-aspartic acid)/GCE (b); Solution:  $5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$   $[\text{Fe}(\text{CN})_6]^{3-4-}$  +  $0.1 \text{ mol}\cdot\text{L}^{-1}$  KCl; Frequency range: 1.0 MHz to 0.01 Hz.

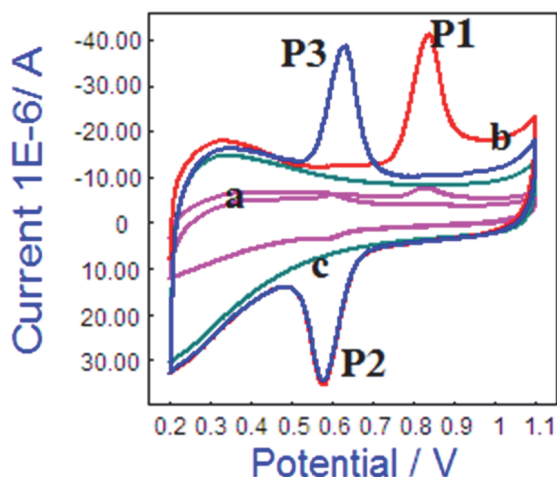


Fig. 4. Cyclic voltammograms of jateorhizine ( $3.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ ) in bare GCE (a) and poly(L-aspartic acid)/GCE (b) and blank voltammograms of poly(L-aspartic acid)/GCE (c). Supporting electrolyte:  $0.1 \text{ mol}\cdot\text{L}^{-1}$  PBS (pH 2.0). Scan rate:  $0.1 \text{ V}\cdot\text{s}^{-1}$ ; open-circuit accumulation time: 210 s.

heating on a water bath and transferred to a 10 ml volumetric flask, diluted to the exact volume with ethanol. The sample solution was stored in the dark and diluted quantitatively using the supporting electrolyte. For the content determination of jateorhizine in *Tinospora capillipes* Gagnep, a certain volume of methanol extract was mixed with 10 mL  $0.1 \text{ mol}\cdot\text{L}^{-1}$  PBS (pH 2.0).

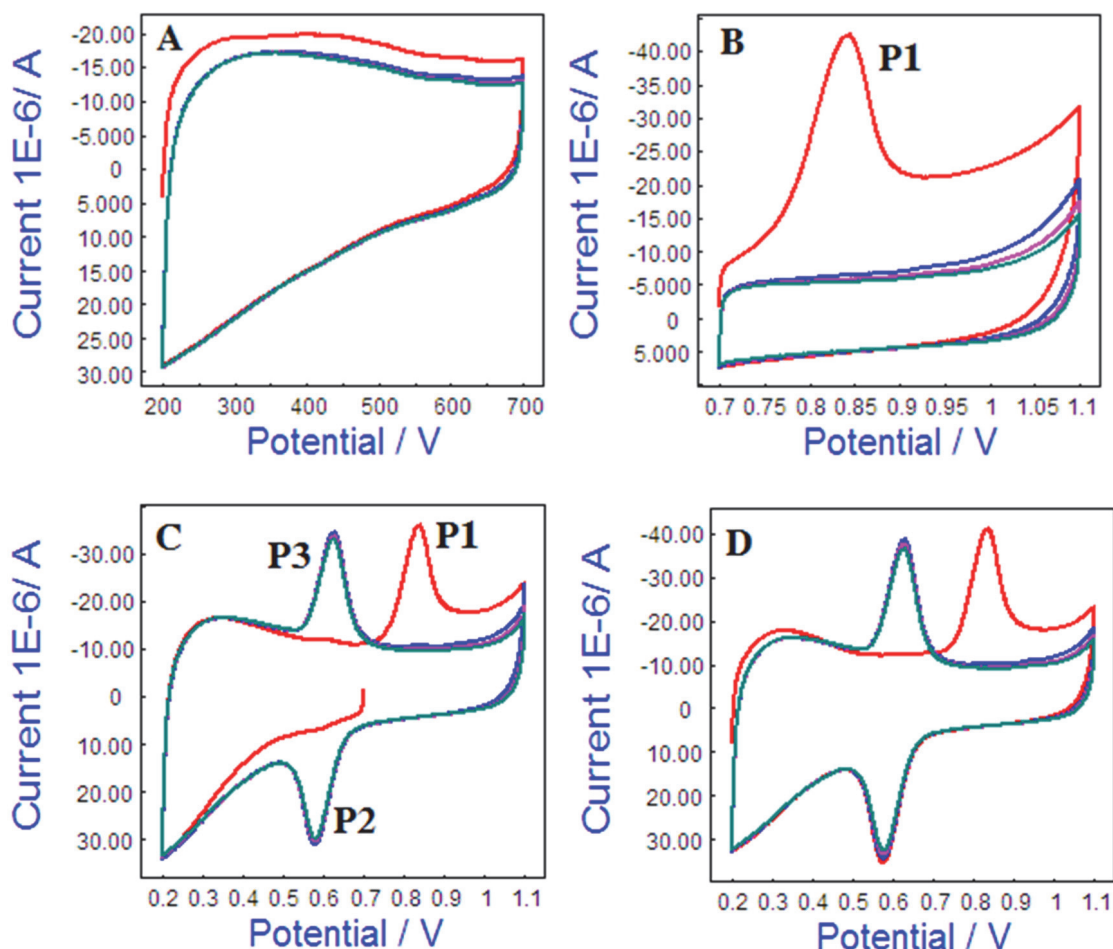


Fig. 5. CVs of jateorhizine ( $3.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) for various potential windows. A: between 0.1 V and 0.7 V; B: between 0.7 V and 1.0 V; C and D: between 1.0 V and 0.1 V. Other conditions are same as in Fig. 4.

### 3. Results and discussion

#### 3.1 The electrochemical characters of poly(L-aspartic acid)/GCE

Cyclic voltammetry is an efficient, well-accepted analytical method to monitor surface modification [28]; thus, the electrochemical features of the prepared poly(L-aspartic acid)/GCE were characterized by cyclic voltammetry with potassium ferricyanide as an electrochemical probe. As shown in Fig. 2, both anodic and cathodic peak currents remained unchanged with both poly(L-aspartic acid)/GCE (b) and bare GCE (a). However, the charging current increases significantly, which may be due to the fact that poly(L-aspartic acid)/GCE has a large effective surface area. In addition, the electrochemical impedance spectroscopy (EIS) has also been used to investigate the interfacial properties of the surface-modified electrode. According to the EIS results

(Fig. 3), the semicircle of poly(L-aspartic acid)/GCE (b) in the high-frequency region was smaller than that of bare GCE (a), which was consistent with the CV analysis. The  $R_{ct}$  values of the bare GCE and the poly(L-aspartic acid)/GCE were  $56.01 \Omega$  and  $36.26 \Omega$ , respectively.

#### 3.2 Electrochemical behavior of jateorhizine at the poly(L-aspartic acid)/GCE

Fig. 4 displayed the cyclic voltammograms for bare GCE (a) and poly(L-aspartic acid)/GCE in 0.1 M PBS (pH = 2.0) with (b) or without (c) jateorhizine ( $3.0 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) with a scan rate of  $0.1 \text{ V} \cdot \text{s}^{-1}$ . Obviously, no redox peaks were observed in the blank solution (curve c) and three redox peaks were observed after addition of jateorhizine in the PBS (curve b). In comparison, three redox peaks for the bare GCE (curve a) were lower than those for the modified electrode, suggesting that the current response of jateorhizine was improved significantly

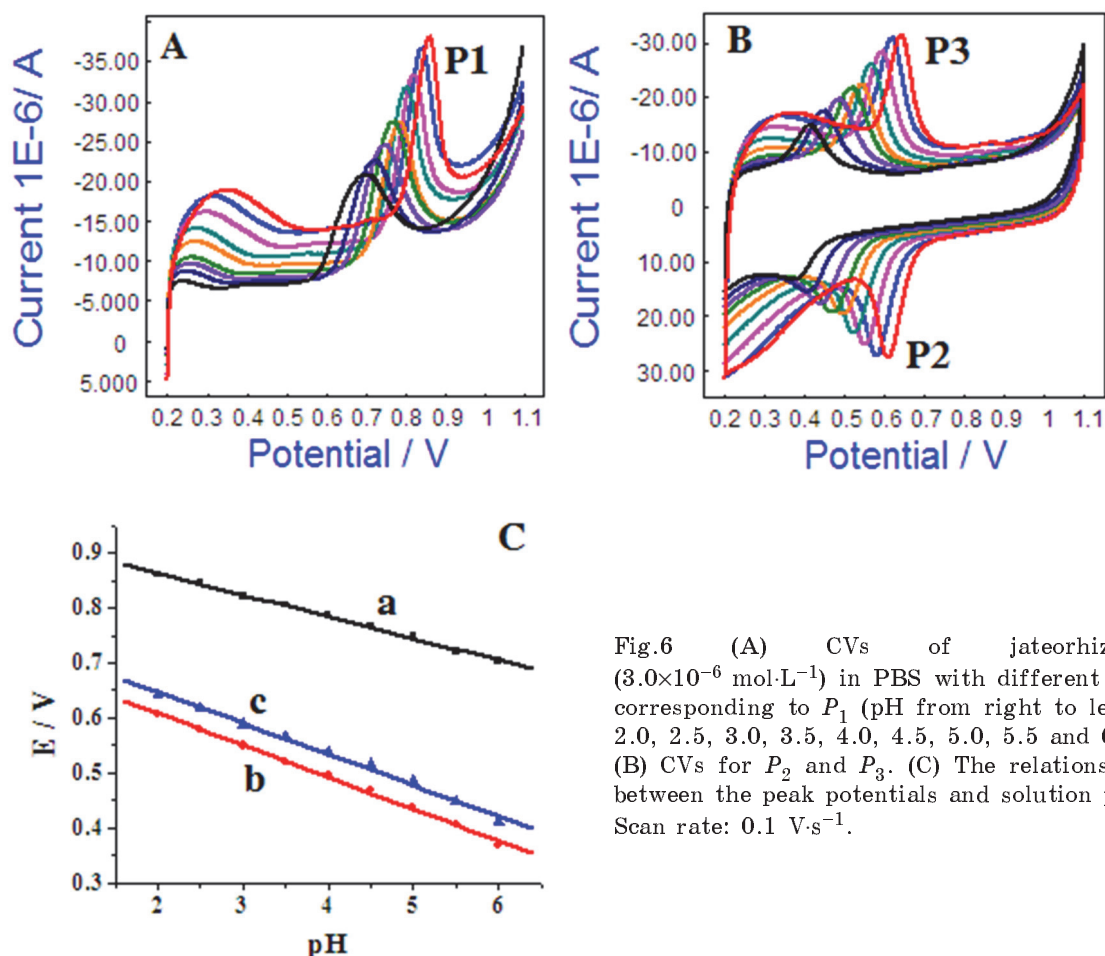


Fig.6 (A) CVs of jateorhizine ( $3.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) in PBS with different pH corresponding to  $P_1$  (pH from right to left): 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0. (B) CVs for  $P_2$  and  $P_3$ . (C) The relationship between the peak potentials and solution pH. Scan rate:  $0.1 \text{ V} \cdot \text{s}^{-1}$ .

after the electrode was modified with a poly(L-aspartic acid) film. At the same time, it can be observed that an anodic peak (P1) and a cathodic peak (P2) appear on the modified electrode in jateorhizine in the first cycle. When the potential scan continued to the second cycle, a new anodic peak (P3) appeared and the P1 disappeared, but the P2 did not change. According to the experimental data, we preliminarily predicted that P1 was an irreversible anodic peak and the P2, P3 were a pair of redox peaks whose active group came from the product of P1 reaction.

In order to further verify the initially prediction about the electrochemical behavior of jateorhizine in poly(L-aspartic acid)/GCE, the electrode response of jateorhizine within different potential windows were recorded. First, by setting the window from 0.2 to 0.7 V for 4 cyclic scans, no peaks were observed (Fig. 5A). By setting the potential window from 0.7 to 1.1 V for 4 cyclic scans, the P1 appeared in the first cycle and then disappeared in the

following cycles (Fig. 5B). Then the initial potential was set up at 0.7 V turning negative, and the integral potential window was controlled between 0.2 and 1.1 V for 4 cycles (Fig. 5C). As we predicted, the P2 was not observed in the first cycle, and then the three peaks were obtained, as in the curve in Fig. 4 during subsequent cycles. All these experimental data confirmed the above assumption. Finally, the next 4 cyclic scans were performed between 0.2 V and 1.1 V (Fig. 5D). The P1 disappeared after the first cycle and the peak currents and potentials corresponding to P2 and P3 did not change much in the next 3 scan cycles.

### 3.3 Optimization conditions and dynamic parameters

#### 3.3.1 The influence of supporting electrolyte

The responses of jateorhizine ( $3.0 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) at poly(L-aspartic acid)/GCE were examined by CV in different supporting electrolytes, including PBS, HAc-NaAc, and the  $0.1 \text{ mol} \cdot \text{L}^{-1}$  Britton-Robinson buffer solution (B-R). Taking into account the sensitivity and shape of the

jateorhizine peak, PBS was chosen as the optimized supporting electrolyte and was used throughout in following experiments.

### 3.3.2 The effect of solution pH

To understand the reaction pathway and evaluate the ratio of electrons and protons participating in the redox of jateorhizine, it is necessary to investigate the effect of the pH of the solution. Fig. 6 showed the superimposed voltammograms of jateorhizine ( $3.0 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) in poly(L-aspartic acid)/GCE with the PBS pH varied from 2.0 to 6.0. It can be seen that the potentials of all three peaks are shifted in the negative direction, and the current has also changed. The maximum value of current was found at pH 2.0. Therefore pH 2.0 was chosen as the optimum pH value for PBS. Plots of peak potentials versus solution pH were found to be linear over the pH range of 2.0–6.0. The linear regression equations were  $E_{p1}(\text{V}) = -0.0395 \text{ pH} + 0.9424$  ( $R = 0.9983$ ),  $E_{p2}(\text{V}) = -0.0582 \text{ pH} + 0.7251$  ( $R = 0.9990$ ),  $E_{p3}(\text{V}) = -0.0563 \text{ pH} + 0.7594$  ( $R = 0.9964$ ) (Fig. 6C). According to the slopes of  $-0.0395 \text{ V pH}^{-1}$  ( $P_1$ ), the number of electrons transferred in the  $P_1$  process was twice that of protons. The slopes of  $-0.0582 \text{ V}$  ( $P_2$ ) and  $-0.0563 \text{ V}$  ( $P_3$ ) per pH unit were close to the theoretical value  $0.059 \text{ V}$ , which means that protons and electrons are involved in the processes  $P_2$ ,  $P_3$  in a ratio of 1:1.

### 3.3.3 Influence of scan rate

The effect of the scan rate on the electrochemical properties of jateorhizine at poly(L-aspartic acid)/GCE was studied by varying the scan rate ( $v$ ) from  $0.06$  to  $0.7 \text{ V} \cdot \text{s}^{-1}$  in PBS at pH 2.0. Fig. 7A showed the superimposed voltammograms of jateorhizine with different scan rates. As can be seen, the currents of three peaks were increased and the potentials of  $P_1$ ,  $P_3$  shifted positively, while  $P_2$  shifted negatively with increasing the scan rate. For  $P_1$ , a good linear relationship between the peak potential ( $E_{p1}$ ) and  $\ln v$  was obtained with a regression equation of  $E_{p1} = 0.0287 \ln v + 0.9286$  ( $E_p$  in V,  $v$  in  $\text{V} \cdot \text{s}^{-1}$ ,  $R = 0.9890$ ) (Fig. 7B, curve a). According to Laviron's theory [29] for an irreversible electrode process, the following equation exists:

$$E_p(\text{V}) = E^0 - \frac{RT}{\alpha n F} \ln \frac{RT k_s}{\alpha n F} + \frac{RT}{\alpha n F} \ln v. \quad (1)$$

where  $E^0$  is the formal standard potential;  $k_s$  is the standard heterogeneous reaction rate constant;  $n$  is the number of transfer

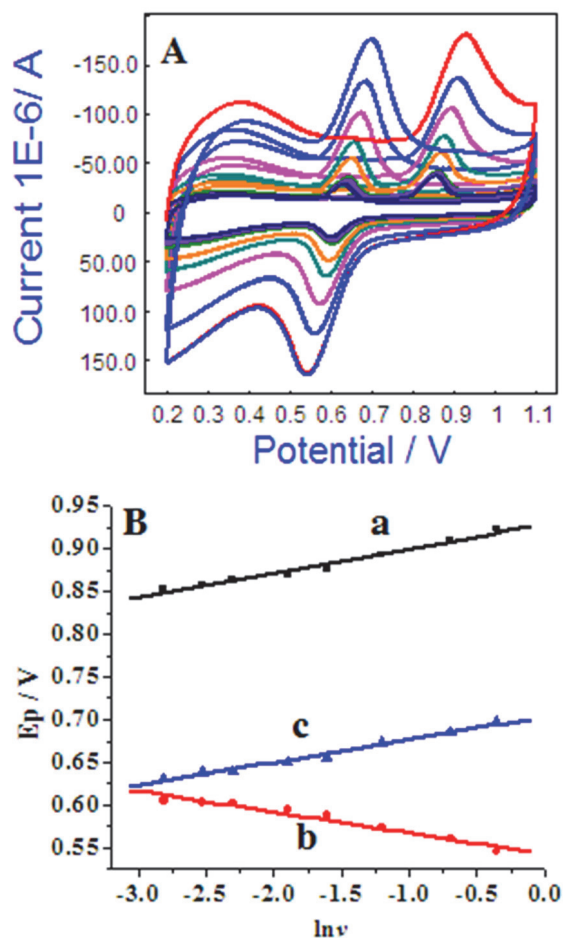


Fig. 7. (A) The superimposed voltammograms of jateorhizine ( $3.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) at different scan rates (from inner to outer):  $0.06$ ,  $0.08$ ,  $0.1$ ,  $0.15$ ,  $0.2$ ,  $0.3$ ,  $0.5$ ,  $0.7 \text{ V} \cdot \text{s}^{-1}$ . (B) The relationship between  $E_{p1/2/3}$  and  $\ln v$ : curve a for  $P_1$ , curve b for  $P_2$ , curve c for  $P_3$ .

electrons;  $\alpha$  is the charge transfer coefficient;  $v$ ,  $R$ ,  $T$  and  $F$  have their usual meaning. Based on the slope of  $E_{p1}$  with  $\ln v$ , we could obtain the  $n = 2$  assuming  $\alpha = 0.5$ . Therefore, there was two electrons and one proton involved in the electrode reaction of  $P_1$ . According to the above equation, we can also obtain the electron transfer coefficient ( $\alpha = 0.45$ ) and the heterogeneous electron transfer rate constant ( $k_s = 2.4 \text{ s}^{-1}$ ). The formal standard potential ( $E^0 = 0.8519 \text{ V}$ ) was calculated from another linear relation of  $E_{p1} - v$  by extrapolating  $v = 0$ . For  $P_2$  and  $P_3$ , the regression equation between  $E_{p2}$  ( $E_{p3}$ ) and  $\ln v$  were  $E_{p2} = -0.0245 \ln v + 0.5430$  ( $E_p$  in V,  $v$  in  $\text{V} \cdot \text{s}^{-1}$ ,  $R = 0.9950$ ) (Fig. 7B, curve b),  $E_{p3} = 0.0269 \ln v +$



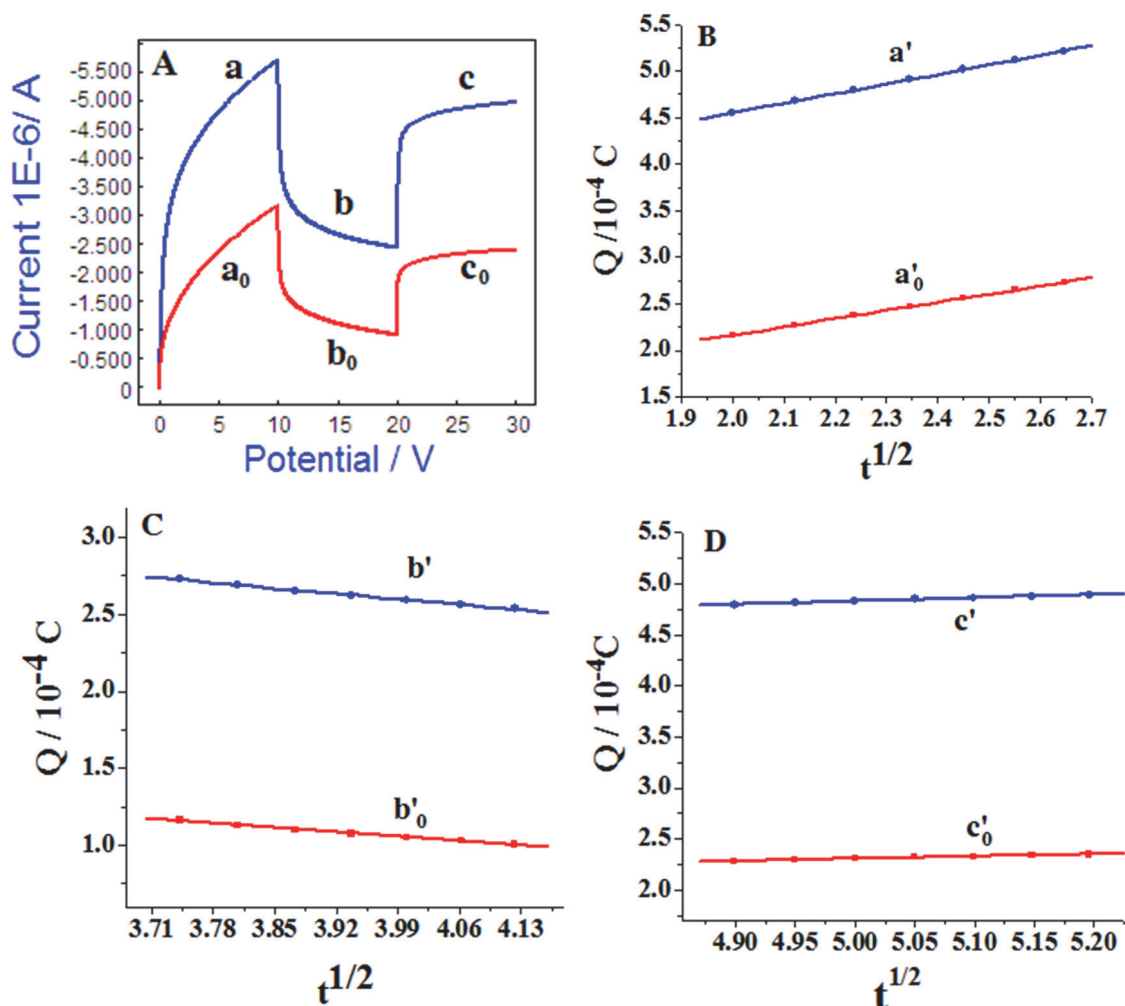


Fig. 8. (A) Chronocoulometric curves obtained for the poly(L-aspartic acid)/GCE in the presence (*a*, *b*, *c*) and absence (*a*<sub>0</sub>, *b*<sub>0</sub>, *c*<sub>0</sub>) of jateorhizine ( $3.0 \times 10^{-6}$  mol·L<sup>-1</sup>). (B, C, D) Dependence of charge *Q* ( $10^{-4}$ ) vs.  $t^{1/2}$ ; the corresponding data were obtained from (A).

0.7039 ( $E_p$  in V,  $v$  in V·s<sup>-1</sup>,  $R = 0.9924$ ) (Fig. 7B, curve *c*). The electron transfer kinetics of  $P_2$  and  $P_3$  could be obtained by using the Laviron equations (2–4) [29]:

$$E_{pc} = E^0 - \frac{RT}{\alpha nF} \ln v, \quad (2)$$

$$E_{pa} = E^0 - \frac{RT}{1 - \alpha} \ln v, \quad (3)$$

$$\lg k_s = \alpha \lg(1 - \alpha) + (1 - \alpha) \lg \alpha - \lg \frac{RT}{nFv} - \alpha(1 - \alpha) \frac{nF\Delta E_p}{2.3RT}, \quad (4)$$

$k_s$ ,  $v$ ,  $n$ ,  $\alpha$ ,  $R$ ,  $F$ , and  $T$  have their usual meaning. A value of 2 could be achieved for  $n$ , and  $\alpha$  was 0.52 contained for  $P_2$  and  $P_3$  redox according to Eq. (2) and Eq. (3).

Based on the Eq. (4), the value of  $k_s$  was further calculated to be  $1.85$  s<sup>-1</sup>. According to the data obtained above, it can be concluded that the electrode reaction of jateorhizine on poly(L-aspartic acid)/GCE is a two-electron and one-proton irreversible electro-oxidation process for  $P_1$  and a two-electron and two-proton quasi-reversible redox process for  $P_2$  and  $P_3$ , which is consistent with the results of [19].

#### 3.3.4. Chronocoulometry studies

The  $Q_{ads}$  of jateorhizine on poly(L-aspartic acid)/GCE was measured in PBS (2.0) using multi-potential step chronocoulometry. Multi-potential step chronocoulometry was employed to do this experiment based on the formula given by Anson [30]:

$$Q = \frac{2nFAc(Dt)^{1/2}}{\pi^{1/2}} + Q^{dl} + Q_{adc}, \quad (5)$$

where  $Q_{dl}$  is the double-layer charge, and  $Q_{ads}$  is the Faraday charge due to the oxidation of adsorbed jateorhizine. In this experiment,  $Q_{dl}$  was considered to be the same in the presence and absence of jateorhizine. As shown in Fig. 8A, the  $Q-t$  curves (curves  $a_0$ ,  $b_0$  and  $c_0$ ) were recorded in blank PBS, and the  $Q-t$  curves (curves  $a$ ,  $b$  and  $c$ ) was recorded in a jateorhizine solution ( $2 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) after stirring for several minutes to achieve saturated adsorption. The markers  $a$ ,  $b$ ,  $c$  corresponded to  $P_1$ ,  $P_2$ ,  $P_3$ . Linear relationships between  $Q$  and  $t^{1/2}$  extracted from Fig. 8A are shown in Fig. 8B, C and D. As shown in Fig. 8B, 8C and 8D, the straight lines of the  $Q-t^{1/2}$  plots were almost parallel in both the presence and absence of jateorhizine, which means that the redox of jateorhizine in  $P_1$ ,  $P_2$  and  $P_3$  was an adsorption-driven electrode process. The corresponding  $Q-t^{1/2}$  curves  $a$ ,  $b$ ,  $c$  and  $a_0$ ,  $b_0$ ,  $c_0$  were calculated with the linear equations of  $Q$  ( $10^{-4}\text{C}$ ) =  $0.8776t^{1/2} + 0.4106$  ( $R = 1$ ) and  $Q$  ( $10^{-4}\text{C}$ ) =  $1.028t^{1/2} + 2.499$  ( $R = 0.9999$ ),  $Q$  ( $10^{-4}\text{C}$ ) =  $-0.4109t^{1/2} + 2.697$  ( $R = 0.9982$ ) and  $Q$  ( $10^{-4}\text{C}$ ) =  $-0.5017t^{1/2} + 4.601$  ( $R = 0.9970$ ),  $Q$  ( $10^{-4}\text{C}$ ) =  $0.2180t^{1/2} + 1.217$  ( $R = 0.9974$ ) and  $Q$  ( $10^{-4}\text{C}$ ) =  $0.3278t^{1/2} + 3.192$  ( $R = 0.9974$ ), respectively. According to the intercepts, the values  $Q_{ads}$  were estimated to be  $2.088 \cdot 10^{-4} \text{ C}$ ,  $1.904 \cdot 10^{-4} \text{ C}$  and  $1.975 \cdot 10^{-4} \text{ C}$  for the redox processes of  $P_1$ ,  $P_2$  and  $P_3$ , respectively. The degree of surface coverage with jateorhizine  $\Gamma^*$  can be determined as  $1.52 \cdot 10^{-8} \text{ mol} \cdot \text{cm}^{-2}$ ,  $1.39 \cdot 10^{-8} \text{ mol} \cdot \text{cm}^{-2}$ ,  $1.44 \cdot 10^{-8} \text{ mol} \cdot \text{cm}^{-2}$  in accordance with Laviron's theory:  $O_{ads} = nFA\Gamma^*$ .

### 3.4. Analytical application

#### 3.4.1. Calibration curve

The current of response of  $P_1$  was chosen to generate a calibration curve, and the relationship between peak current and the content of jateorhizine was investigated by linear sweep voltammetry (LSV). Fig. 9A shows the superimposed LSV curves of jateorhizine on the poly(L-aspartic acid)/GCE with various concentrations in the PBS solution with pH 2.0. With the addition of a successive amount of jateorhizine, the current of the oxidation peak clearly increased. The oxidation peak current increased linearly with the concentrations of jateorhizine in the range of  $2.0 \cdot 10^{-8}$ – $4.0 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$  (Fig. 9B), and the

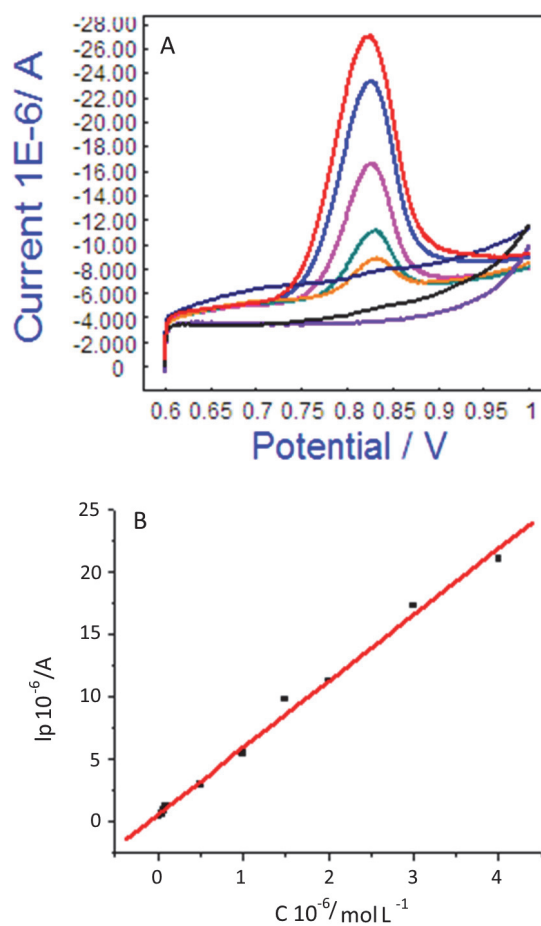


Fig. 9. (A) LSV curves for various amounts of jateorhizine on poly(L-aspartic acid)/GCE; the concentrations of jateorhizine varied from bottom to upper):  $0$ ,  $2.0 \cdot 10^{-8}$ ,  $5.0 \cdot 10^{-8}$ ,  $5.0 \cdot 10^{-7}$ ,  $1.0 \cdot 10^{-6}$ ,  $2.0 \cdot 10^{-6}$ ,  $3.0 \cdot 10^{-6}$ ,  $4.0 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ . (B) Plot of  $i_{pa}$  vs jateorhizine concentration. Supporting electrolyte: PBS, pH 2.0; scan rate:  $0.05 \text{ V} \cdot \text{s}^{-1}$ .

linear regression equation can be expressed as  $I_{pa} = 5.319C$  ( $10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ) +  $0.5623$  ( $R = 0.9978$ ). The detection limit was  $2.0 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ .

#### 3.4.2. Interference, reproducibility and stability

The influence of some possible interfering substances on the determination of jateorhizine at the level of  $1 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$  was evaluated in detail. The test results indicated that the 100-fold concentration of  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , glucose, sucrose, and starch does not influence on the signals of jateorhizine with deviations below 5 %.

The reproducibility and stability of the proposed sensor were also evaluated. In a  $1.0 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$  jateorhizine solution, the



RSD of five interval measurements using one poly(L-aspartic acid)/GCE was 3.8 %, indicating the good reproducibility of the proposed sensor. Meanwhile, the fabrication reproducibility was investigated by constructing three poly(L-aspartic acid)/GCE in parallel under the same conditions. The RSD was 3.1 %, showing that the fabrication procedure was reliable. In addition, the sensor retained about 95.4 % of its original response with  $1.0 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1}$  jateorizine after storage in  $0.1 \text{ mol} \cdot \text{l}^{-1}$  PBS (pH 2.0) at  $4^\circ\text{C}$  for one week, demonstrating its stability during long-term storage.

#### 4. Conclusion

In summary, a simple but highly sensitive voltammetric method for the determination of jateorizine was developed using a poly(L-aspartic acid) modified electrode. The redox character of jateorizine was investigated systematically in details. Using electrochemical techniques, several dynamic parameters of the electrode reaction were calculated and a reasonable mechanism of the reaction of Jateorizine on the L-aspartic modified electrode was also discussed and proposed, which could serve as a guide for the pharmacological action of jateorizine in clinical studies. Under optimum conditions, the linear range was from  $2.0 \cdot 10^{-8}$  to  $4.0 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$  with a low detectable limit of  $2.0 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ . Therefore, the high sensitivity for jateorizine analysis on the proposed electrode was realized.

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