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Electrochemical characteristics of *cis*-jasmone in acid media at multi-wall carbon nanotube-Nafion composite film modified electrode and its analytical application

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ABSTRACT

cis-Jasmone is a plant activator in terms of production of defence-related volatile semiochemicals. The redox and quantitative analysis of *cis*-jasmone are practically significant for the investigation of physiological processes in plants. In this work, the electrochemical characteristics of *cis*-jasmone in different acid media were investigated at a multi-wall carbon nanotube/Nafion composite film modified glassy carbon electrode (MWNT/Nafion/GCE) by cyclic voltammetry, chronocoulometry and infrared spectroscopy. The redox mechanism of *cis*-jasmone in strong acid media, i.e., a remarkable catalytic oxidation process for the reduction product of *cis*-jasmone at MWNT/Nafion/GCE, was demonstrated to be completely different from the cases in weakly acidic or neutral solution. The standard rate constant k^0, the diffusion coefficient D and the surface coverage Γ were calculated and discussed. The sensitive anodic stripping voltammetric response of *cis*-jasmone was employed to determine its content in the extract of rice spikelet. The electrochemical redox and quantitative analysis of *cis*-jasmone are therefore of great significance for studying not only the physiological processes of *cis*-jasmone in plants but also the electrochemical redox mechanism of other α,β-unsaturated ketones.

1. Introduction

The groups of jasmonates (JAs), which are cyclopentanone derivatives, originate biosynthetically from linolenic acid. JAs are important phytohormones distributed throughout higher plants, which can regulate or co-regulate a wide range of processes in plants, such as fruit ripening, production of viable pollen, root growth and tendril coiling [1–3]. Upon exposure to stress (e.g., wounding and pathogens), JAs are produced in plants and cause the induction of a proteinase inhibitor. The level of JAs concentration in plants is relatively low, usually 10–1500 ng/g [4], which also varies as a function of tissue and cell type, developmental stage and in response to several different environmental stimuli [5–7]. Quantitative analysis of endogenous JAs is important for its physiological processes in plants.

Currently the most available methods for determining JAs in plant extracts are chromatographic methods, such as gas chromatography (GC) [8], liquid chromatography (LC) [9,10] and high performance liquid chromatography (HPLC) [11], usually coupled with mass spectrometry (MS). Capillary electrophoresis with laser-induced fluorescence detection was also reported [12]. For instance, Han et al. established a normal phase liquid chromatography–quadrupole time-of-flight mass spectrometry (NPLC–QTOF-MS) method for the simultaneous discrimination and direct analysis of all the four JA stereoisomers [13]. The detection limit for single JA stereoisomer was 0.5 ng mL^{-1} (2.4 fmol). These chromatographic methods have some advantages, such as simultaneous multicomponent quantitative analysis, higher sensitivity and lower detection limit, but they are costly, time-consuming, and require specialized equipments and skilled technicians. Electrochemical methods, with many advantages of low cost, easy operation, fast response and compatibility with other technologies, have been widely used for the determination of various phytohormones, such as gibberellins acid [14], indole-3-acetic acid [15] and salicylic acid [16]. Recently, methyl jasmonate was determined based on self-assembling of different phosphotungstic acid nanohybrid, such as montmorillonite and graphene oxide on graphite electrode [17,18].

cis-Jasmone, a member of the jasmonate family, is known to be a plant activator in terms of production of defence-related volatile semiochemicals that repel aphids and increase the foraging activity of aphid parasitoids. *cis*-Jasmone can induce selective production of secondary metabolites that are capable of directly reducing

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development of pests, diseases and weeds [19,20]. *cis*-Jasmone has a structure of α,β-unsaturated ketone, which can be reduced by electrochemical method to a variety of products [21,22]. The ketone function may be reduced to the corresponding alcohol or saturation of the carbon–carbon double bond may occur. We have found that the reduction of *cis*-jasmone in weak acidic solution and neutral solution takes place at the unsaturated carbon–carbon double bond on its branched chain in the presence of cetyltrimethylammonium bromide (CTAB) [22]. In this paper, we report the electrochemical characteristics and determination of *cis*-jasmone in strong acidic solutions. The redox mechanism of *cis*-jasmone in this kind of media was studied by voltammetry, chronocoulometry and Fourier transfer IR spectroscopy. A multi-wall carbon nanotubes/Nafion film modified glassy carbon electrode (MWNT/Nafion/GCE) was employed to determine *cis*-jasmone in the extract from spikelet of rice by stripping voltammetry.

2. Experimental

2.1. Chemicals

cis-Jasmone (purity ≥ 99.0%, GC) was purchased from the Sigma–Aldrich Chemie GmbH, Germany. A stock solution of 0.05 M *cis*-jasmone was prepared with 1:1 ethanol–water and sealed and stored at 4 °C in darkness to prevent evaporation, which was diluted to desired concentrations with 1:1 ethanol–water before use. The Nafion solution (5% solution (w/v), Sigma) was also diluted to a final concentration of 0.02% (w/v) by 1:1 ethanol–water before use. MWNTs (Nanotimes Co., Chengdu, China) were dispersed into 70% HNO_3 with sonication and refluxed at 120 °C for 14 h to eliminate impurities such as metal catalyst and amorphous products. MWNT/Nafion suspensions were prepared by sonicating MWNTs in a 0.02% Nafion solution to form a final concentration of 0.5 mg/mL. Potassium ferricyanide ($K_3Fe(CN)_6$) was obtained from Beijing Reagent Co., China. Other reagents were of analytical grade and used as received. All aqueous solutions were prepared with doubly distilled water.

2.2. Instruments

The electrochemical experiments were carried out with a CHI660 electrochemical workstation (CH Instruments, Shanghai, China). A three-electrode system was used, including a modified glassy carbon working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter electrode. Scanning electron microscopy (SEM) was performed with a Hitachi X-650 microscope. Fourier transfer (FT) IR spectra were measured on a Nicolet Magna-IR 550 spectrometer in reflection mode. Unless noted otherwise, all electrochemical experiments were performed at room temperature.

2.3. Preparation of the modified electrode

A glassy carbon electrode (0.07 cm^2) was polished to a mirror finish with 0.3–0.05 μm alumina slurries on a polish paper, and then cleaned thoroughly in an ultrasonic cleaner with nitric acid water (1:1) solution, alcohol and redistilled water, sequentially. Then, the GCE was coated with 5 μL of the resulting MWNT/Nafion suspension and allowed to evaporate water at room temperature in air, that is, MWNT/Nafion/GCE. The Nafion/GCE was prepared by the same procedure as explained above, but without MWNT. After each measurement, the modified electrode should be washed carefully by doubly distilled water and swept by cyclic voltammetry (CV) for 3 cycles from −1.6 to 1.5 V in 0.1 M H_2SO_4 to remove the residual *cis*-jasmone on the electrode surface.

2.4. Experimental procedure

The electrochemical behavior of *cis*-jasmone was examined by CV in the potential range of 1.5 to −1.8 V in 0.1 M H_2SO_4 solution. Anodic stripping voltammetry and chronocoulometry were performed in the range of 0.7–1.3 V and both were preconditioned at −1.6 V for 80 s with stirring. The electrochemical impedance were tested employing a solution of 5.0 mM $K_3Fe(CN)_6$ in 1.0 M KCl. The frequency range was from 100 mHz to 100 kHz, the dc potential was the average potential of the oxidation and the reduction peaks, and the amplitude was 5 mV. For preparing the IR samples, the electrolysis of 2.5×10^{-3} M *cis*-jasmone was carried out by bulk electrolysis with coulometry on bare GCE with large area of 2.25 cm^2 at −1.6 V in 0.1 M H_2SO_4 solution for 8 h.

2.5. Extraction of cis-jasmone from spikelet samples of rice

The spikelet samples of rice were kindly provided by professor Zeng from Jiangxi Agricultural University in China. They were frozen in liquid nitrogen from the moment they were picked up and have been lyophilized. The spikelet samples were ground in mortar using a pestle to fine powder. 1.0 g of this powder was collected in a vessel and mixed with 5.0 mL of 60% methanol solution. The mixture was completely sealed and placed in an ultrasonic mixer for 45 min ultrasound-assisted extraction. The supernatant was collected after centrifugation at 11,500 rpm for 20 min, which was used for real sample analysis. The extraction procedure was performed in ice bath to prevent the evaporative loss of *cis*-jasmone.

3. Results and discussion

3.1. Electrochemical responses of cis-jasmone in different acid media

cis-Jasmone can be reduced by electrochemical method to a variety of products. Our previous report showed that the reduction of *cis*-jasmone in weak acid or neutral solution takes place at the unsaturated carbon–carbon double bond on its branched chain in the presence of CTAB [22]. Here, the electrochemical responses of *cis*-jasmone were investigated on bare GCE by cyclic voltammetry in different H_2SO_4 solutions from pH 0.9 to pH 4.0. Oxygen had no apparent influence on the electrochemical response of *cis*-jasmone, so the solution used was not deaerated. As shown in Fig. 1, when the potential initially shifts from 1.5 to −1.8 V, two cathodic peaks

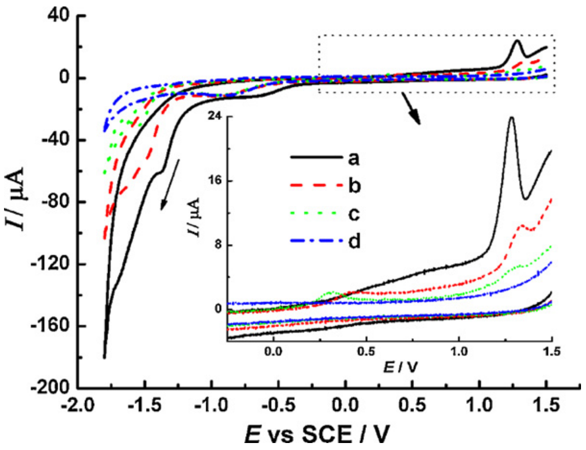

Fig. 1. Cyclic voltammograms of 1.0×10^{-4} M *cis*-jasmone on bare GCE in H_2SO_4 solution with different pHs: (a) pH = 0.9, (b) pH = 2.0, (c) pH = 3.0 and (d) pH = 4.0. Initial potential: 1.5 V; scan rate: 100 mV/s. Inset: enlarged view of the dotted line area.