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Poly(Phenol Red)-Based Voltammetric Sensor for the Simultaneous Quantification of Hydroxycinnamic Acids †

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Abstract: Hydroxycinnamic acids are one of the most widely distributed classes of natural phenolics in plants. Their coexistence requires selective methods for quantification. Voltammetry on chemically modified electrodes is one of the approaches to solving this problem. Electrodes based on electropolymerized triphenylmethane dyes give sensitive and selective responses to natural phenolic antioxidants of different classes. In this work, a combination of polyaminobenzene sulfonic acid functionalized single-walled carbon nanotubes (f-SWCNTs), and poly(phenol red) was used as an electrode surface modifier. The polymeric coverage was obtained by potentiodynamic electropolymerization, the conditions of which were optimized on the basis of the voltammetric response of the hydroxycinnamic acid mixture. Poly(phenol red)-based electrodes provided well-resolved peaks of caffeic, ferulic, and *p*-coumaric acids, and a significant increase in the oxidation currents compared to bare glassy carbon (GCE) and f-SWCNTs-modified electrodes. Simultaneous voltammetric quantification of caffeic, ferulic, and p-coumaric acids was performed for the first time. Two linear dynamic ranges of 0.10–2.5 µM for all acids, 2.5–100 µM for caffeic acid, and 2.5–50 µM for ferulic and *p*-coumaric acids were achieved using differential pulse voltammetry in a Britton–Robinson buffer with a pH of 2.0. The limits of detection were 47.6, 22.4, and 38.0 nM for the caffeic, ferulic, and *p*-coumaric acids, respectively.

Keywords: voltammetry; modified electrodes; electropolymerization; triphenylmethane dyes; natural phenolics; hydroxycinnamic acids; simultaneous quantification

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1. Introduction

Hydroxycinnamic acids (*p*-coumaric, caffeic, ferulic, 5-hydroxyferulic, and sinapic acids) are one of the most widely distributed classes of natural phenolics in plants [1]. Biosynthesis pathways lead to the coexistence of these acids in plants, fruits, vegetables, and whole grains [1,2]. Therefore, sensitive and selective methods for the quantification of hydroxycinnamic acids are required. Various types of chromatography [1,3] and capillary electrophoresis [4,5] are traditionally used to solve this problem. Nevertheless, these methods are often needed in the preliminary extraction of hydroxycinnamic acids and are characterized by tedious procedures, high consumption rates of organic solvents, and relatively expensive equipment.

Electrochemical methods are simple, cost-effective, and sensitive, but the insufficient selectivity of response to structurally related compounds is a major limiting factor. This problem is partially solved using chemically modified electrodes that allow simultaneous determination of hydroxycinnamic acids in binary and even ternary mixtures [6]. Thus, carbon nanofiber-based screen-printed electrodes allow a simultaneous determination of ferulic and caffeic acids [7]. Glassy carbon electrodes (GCE) modified with multi-walled carbon nanotubes and electropolymerized sunset yellow have been developed for the simultaneous quantification of chlorogenic and ferulic acids in coffee [8]. WS_2

flakes/catechin-capped Au nanoparticles/carbon black-based nanocomposite sensors successfully provided a full resolution of the oxidation peaks of caffeic, sinapic, and *p*-coumaric acids [9]. The analytical characteristics achieved are sufficient for the quantification of hydroxycinnamic acids in real samples. Further development of modified electrodes for the voltammetric analysis of ternary mixtures of hydroxycinnamic acids is of practical interest.

A novel chemically modified electrode was developed in the current work for the simultaneous quantification of caffeic, ferulic, and *p*-coumaric acids (Figure 1) for the first time. A combination of polyaminobenzene sulfonic acid functionalized single-walled carbon nanotubes (f-SWCNTs) and electropolymerized phenol red was used as an electrode surface modifier.

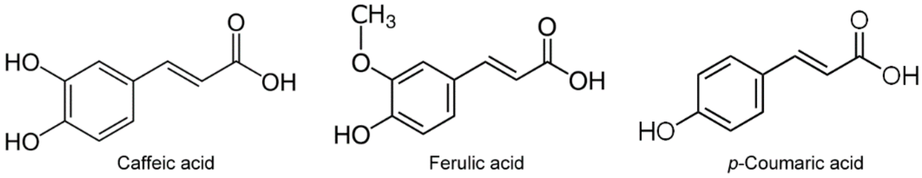

Figure 1. Hydroxycinnamic acids under investigation.

2. Materials and Methods

Caffeic (98%) and 98% *p*-coumaric acids from Sigma (Steinheim, Germany) and 99% ferulic acid from Aldrich (Steinheim, Germany) were used. Their standard 10 mM solutions were prepared in ethanol (rectificate). Phenol red (ACS grade purity) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Its 10 mM solution was prepared in ethanol (rectificate). Exact dilution was applied for the preparation of less concentrated solutions.

f-SWCNTs ($d \times l$ is 1.1 nm × 0.5–1.0 μm) were purchased from Sigma-Aldrich (Steinheim, Germany). Their 1.0 mg mL^{-1} homogeneous suspension in dimethylformamide was prepared by sonication for 30 min in an ultrasonic bath (WiseClean WUC-A03H) (DAIHAN Scientific Co., Ltd., Wonju-si, Republic of Korea).

Other reagents were c.p. grade. Distilled water was used for the measurements. The laboratory temperature was (25 ± 2 °C).

Electrochemical measurements were conducted on the potentiostat/galvanostat Autolab PGSTAT 302N with the FRA 32M module (Eco Chemie B.V., Utrecht, The Netherlands) and NOVA 1.10.1.9 software. A glassy electrochemical cell of 10 mL volume was used. The three-electrode system consisted of the working GCE of 3 mm diameter (CH Instruments, Inc., Bee Cave, TX, USA) or a modified electrode, an Ag/AgCl reference electrode, and a platinum wire was used as the auxiliary electrode.

pH measurements were carried out using the "Expert-001" pH meter (Econix-Expert Ltd., Moscow, Russian Federation) with a glassy electrode.

3. Results and Discussion

3.1. Voltammetry of Hydroxycinnamic Mixture at the Bare and Polymer-Modified Electrodes

Caffeic, ferulic, and *p*-coumaric acids were oxidized at bare GCE (Figure 2a) at 0.53, 0.76, and 0.94 V, respectively. The peak potential separation allows their simultaneous detection. Nevertheless, low oxidation currents, especially for *p*-coumaric acid, make this task impossible. Therefore, an electrode surface modification with f-SWCNTs and electropolymerized phenol red was performed. The application of f-SWCNTs as a support for the electrodeposition of poly(phenol red) provides a higher surface area available for polymer deposition, as well as more uniform distribution of polymeric coverage. On the other side, f-SWCNTs increase the conductivity of the electrodes, which is important for effective electron transfer in the case of non-conductive polymeric coverages that are usually formed from phenolic moieties containing triphenylmethane dyes [10,11].

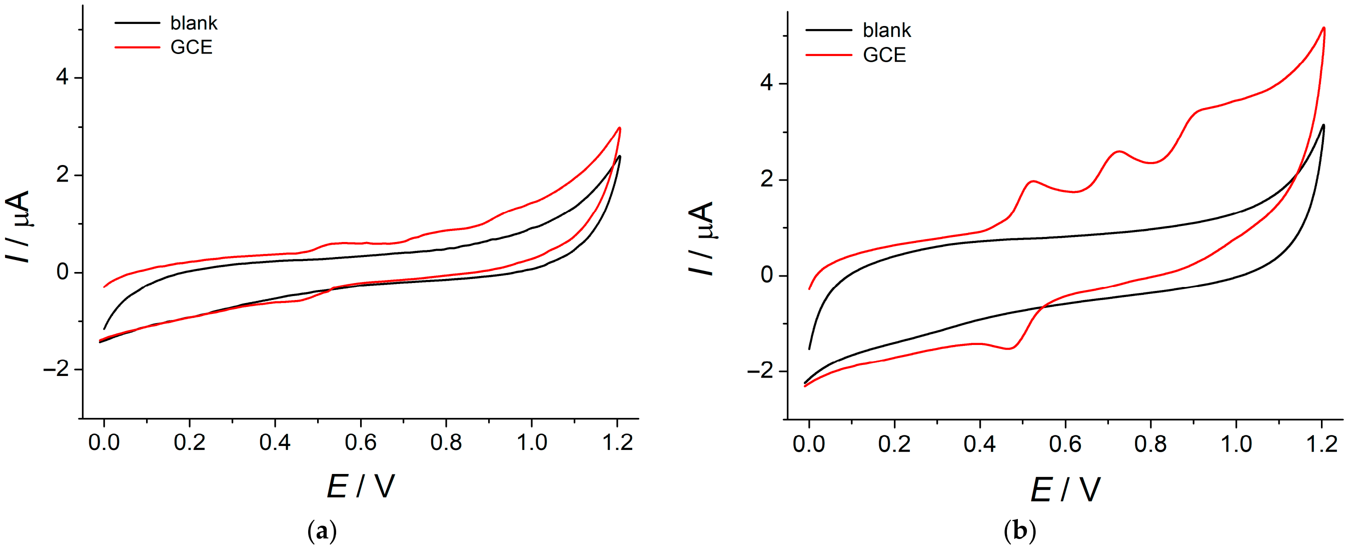

Figure 2. Cyclic voltammograms of 5.0 µM mixture of caffeic, ferulic, and *p*-coumaric acids in Britton–Robinson buffer, pH 2.0: (**a**) at bare GCE; (**b**) at poly(phenol red)/f-SWCNTs/GCE. Potential scan rate is 100 mV s^{-1}.

The potentiodynamic electropolymerization of phenol red was performed in 0.1 M NaOH (Figure 3), as electron detachment proceeds easier in a basic medium. The oxidation peak at 0.63 V was decreased on the second and subsequent cycles until full disappearance occurred at the tenth cycle, which confirmed the formation of a non-conductive polymer that agrees well with phenol red electropolymerization at the GCE in phosphate buffer pH 7.4 [12].

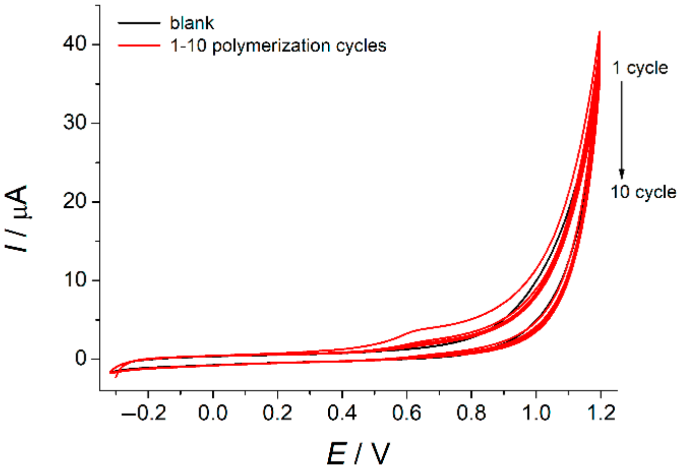

Figure 3. Electropolymerization of 75 µM phenol red at the f-SWCNTs/GCE in 0.1 M NaOH. Potential scan rate is 75 mV s^{-1}.

The electropolymerization conditions strongly affect the properties of the final polymeric coverage and its response to target analytes. Therefore, monomer concentration, number of cycles, and electrolysis parameters (potential scan rate and polarization window) were optimized on the basis of the voltammetric response of the hydroxycinnamic acid mixture. The best voltammetric characteristics of the hydroxycinnamic acid mixture (Figure 2b) were obtained at the polymeric coverage of the 75 µM phenol red after 10 cycles in a polarization window from −0.3 V to 1.2 V at a potential scan rate of 75 mV s^{-1}. Statistically significant increases in the caffeic, ferulic, and *p*-coumaric acid oxidation currents at the polymer-modified electrode confirmed the improvement in the sensitivity of detection.

On the basis of cyclic voltammetry data for individual acids at various pH levels of the Britton–Robinson buffer and potential scan rate, a diffusion-controlled electrooxidation with proton transfer was proved. The diffusion coefficients were equal to $(3.9 \pm 0.1) \times 10^{-5}$, $(2.1 \pm 0.3) \times 10^{-5}$, and $(4.6 \pm 0.2) \times 10^{-5}$ cm^2 s^{-1} for the caffeic, ferulic, and *p*-coumaric acids, respectively. Two electrons were involved in the electrooxidation of all the acids. Anodic transfer coefficients of 0.62, 0.46, and 0.40 were calculated for caffeic, ferulic, and *p*-coumaric acids, respectively.

3.2. Simultaneous Quantification of Hydroxycinnamic Acids

The quantification of caffeic, ferulic, and *p*-coumaric acids was performed under conditions of differential pulse voltammetry. The effect of pulse parameters on the response of the hydroxycinnamic acid mixture was studied. The best results were obtained at a pulse amplitude of 50 mV and a pulse time of 25 ms. The peak area was used as an analytical signal that linearly increased as the caffeic, ferulic, and *p*-coumaric acid concentrations grew. Two linear dynamic ranges of 0.10–2.5 µM for all acids and 2.5–100 µM for caffeic acid (2.5–50 µM for ferulic and *p*-coumaric acids) were achieved. The detection limits at S/N = 3 are equal to 47.6, 22.4, and 38.0 nM for the caffeic, ferulic, and *p*-coumaric acids, respectively.

The accuracy of the method developed was checked by an added-found method. The relative standard deviation did not exceed 2% (3–5% for the low concentrations of hydroxycinnamic acids), indicating the absence of random errors in determination. Recovery values (99.2–100.6%) confirmed the high accuracy of the method developed.

Thus, a simultaneous voltammetric determination of caffeic, ferulic, and *p*-coumaric acids was performed for the first time. GCE modified with f-SWCNTs and poly(phenol red) gives a sensitive response and reliable results, and can be applied in coffee sample screening.

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