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Characteristics of curcumin using cyclic voltammetry, UV–vis, fluorescence and thermogravimetric analysis

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ABSTRACT

Curcumin, the yellow, primary bioactive component of turmeric, has recently received attention from chemists due its wide range of potential biological applications as an antioxidant, anti-inflammatory, and anti-carcinogenic agent. The electrochemical behaviour of curcumin at a platinum electrode has been studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The oxidation of curcumin is an irreversible process that proceeds in two steps in 0.1 M $(C_4H_9)_4NClO_4$ in acetonitrile. The process of oxidation and its kinetics have been investigated. The rate constant, electron transfer coefficient and diffusion coefficients for the electrochemical oxidation of curcumin were determined. A mechanism for the oxidation of curcumin is proposed. The data obtained are consistent with the current literature and suggest that voltammetric studies on mechanically transferred solids may be a convenient method for elucidating the electrochemical oxidation mechanisms of compounds in anhydrous media. Theoretical calculations regarding the optimization of curcumin, electronic properties like highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated using with HyperChem software by AM1 semi-empirical method. The properties of curcumin in a homogeneous environment were investigated using spectroscopic techniques and thermogravimetric analysis.

1. Introduction

Electrochemical methods are an important class of diagnostic techniques which were widely used for the investigation of biological properties of electroactive species [1,2]. One of the most important groups of electroctive species is phenolic compounds. Polyphenols, flavonoids, and tannins are widely found in plants, primarily fruits and vegetables, and contribute to their flavour and colour [3,4]. One of the bioactive compound is curcumin. The polyphenol curcumin (1,7-bis (1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadione-3,5-dione) is an important natural phytochemical found in the rhizomes of Curcuma longa or turmeric, which is known for its medicinal properties [5,6].

Curcumin is an important component of the spices turmeric and chilli. These spices are very popular, especially in Indian and Mexican cuisine [7–9]. Curcumin, which has been found to be nontoxic in humans at dose up to 10 g/day, [10] shows only slight side effects and possesses a variety of remarkable pharmacological properties [10,11]. Due to its high medicinal potential with virtually no side effects, this compound has attracted considerable interest in recent years [7–9,12–15]. Curcumin has been shown to possess antioxidant [16], anti-inflammatory, antiviral, antibacterial, antifungal, immunomodulatory, and antitumor activities [17,18]. It has been shown that curcumin regulates classic and alternative pathways in the nervous system, and it is being used to treat Alzheimer's disease, multiple sclerosis, and dementia [19–21]. The complex mechanism for the action of curcumin involves various biological targets including signal transducers and activators, DNA and several kinases [22–24]. Hence, the main activities of curcumin can be attributed to its potent antioxidant [25] and free-radical quenching properties, which result in the interception and neutralisation of potent chemical carcinogens, such as ROS (superoxide anions, peroxyl radicals, and hydroxyl radicals) and NOS (nitric oxide and peroxynitrite compounds). The biological activity of curcumin and its remarkable antioxidant properties are thought to result from the hydroxyl groups in the aromatic side chains or from the CH_2 group of the β-diketone moiety [26]. Curcumin exhibits keto–enol tautomerism in solution [27,28] (Fig. 1).

Electrochemical techniques are excellent methods for the sensitive determination of organic molecules, including drugs and related molecules in pharmaceutical dosage forms and biological fluids [29–33]. Advantages of experimental electrochemical techniques for the analysis of compounds are their simplicity, low

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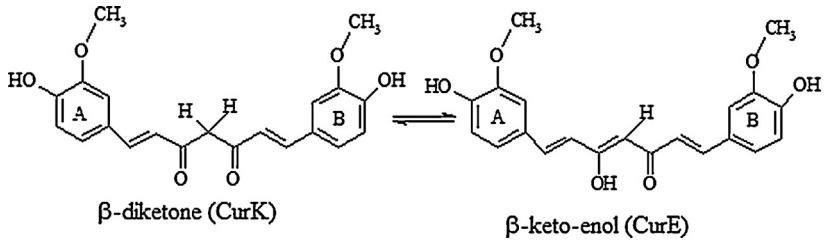

Fig. 1. Keto-enol tautomerism of curcumin.

cost, and shorter analysis time compared to other techniques. Cyclic voltammetry is frequently used for the characterization of electroactive systems. Half-wave potential ($E_{1/2}$) is a useful parameter that provides information about the antioxidant activity of the compound under study [34]. It has been shown that organic molecules with a less positive oxidation potential or a higher susceptibility to electrochemical oxidation possess higher radical scavenging activities [35–37]. Electrochemical characterisation under different conditions is a promising tool for understanding the behaviour of polyphenolic compounds [38,39] and the electrochemical properties of curcumin have been described in previous research [28,40–43].

The aim of this study was to determine the electrochemical behaviour of curcumin during electrooxidation at a platinum electrode in anhydrous media.

2. Experimental

2.1. Chemicals

Pure curcumin (1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, $C_{21}H_{20}O_6$) was obtained from a commercial source (Sigma–Aldrich) and used as received.

The chemical used for the preparation of the flavonoid solutions was acetonitrile (CH_3CN) pure p.a. (POCh Gliwice, Poland), and tetrabutylammonium perchlorate ($(C_4H_9)_4NClO_4$) (Fluka) was used as a supporting electrolyte. All reagents used were of analytical grade.

2.2. Measurement methods

To assess the electrochemical oxidation mechanism and the kinetics for the compound under investigation, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used with an *Autolab* analytical unit (*EcoChemie*, *Holland*). A three-electrode system was used for the measurements. Platinum was used as the anode and auxiliary electrode. The electrode potential was measured against a ferricinium/ferrocene reference electrode (Fc^+/Fc), whose standard potential is defined as zero, independent of the solvent used. All of the solutions were degassed with argon prior to the measurements. During the measurements, an argon blanket was maintained over the solution. The effect of the scan rate on the electrooxidation of curcumin in an anhydrous medium was assessed. Before measurements, the solutions were purged with argon to remove any dissolved oxygen. During the measurements, an argon blanket was kept over the solutions. All of the experiments were performed at room temperature.

UV–vis spectra were recorded from 190 to 800 nm using a UV-VIS spectrophotometer (Shimadzu UV-24001 PC).

The thermogravimetric analysis of curcumin was performed using a Mettler Toledo TGA/DSC1 apparatus, and the measurements were performed under argon from 25 to 500 °C at a nitrogen flow rate of 1.2–1.4 l/h and a heating rate of 10 °C/min.

Chemiluminescence was examined with a Lumina spectrofluorometer from Thermo Scientific Company using the following parameters:

- Voltmeter voltage, 400 V;
- Integration time, 20 ms;
- Emission channel slit and excitation channel slit, 5 nm;
- Radiation range, 300–420 nm.

The emission was recorded as a function of wavelength.

3. Results and discussion

3.1. The electrochemical behaviour of curcumin

The electrochemical oxidation behaviour of curcumin has been studied to evaluate its electron-transfer potential. Oxidation potentials can be used to study the electron-donating capacity of a molecule and as a general indicator of its radical scavenging ability. Electrochemical cyclic voltammetry allows for the determination of the redox properties of antioxidant molecules in solution. The cyclic voltammograms of curcumin in acetonitrile solution are shown in Fig. 2. The half-wave potential of the electrode reaction, as determined by cyclic voltammetry, corresponds to the peak potential from differential pulse voltammetry. Within the potential range where the compound oxidation peaks appear, the supporting electrolyte (0.1 M $(C_4H_9)_4NClO_4$ in acetonitrile shows no characteristic peaks, (Fig. 2, curve 3).

Voltammograms presented in Fig. 2 (curve 1 and 2) show that curcumin is oxidized probably irreversibly at potentials lower than those of electrolyte decomposition. Irreversibility of this electrode reaction needs to be proved.

The half-wave potential ($E_{1/2}$) of the first step of curcumin oxidation, as determined by cyclic voltammetry, is 0.88 V. This

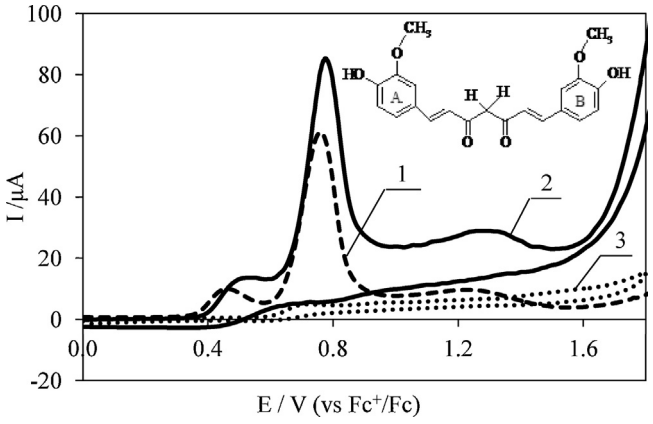

Fig. 2. Voltammograms of curcumin electrooxidation at Pt electrode; curve 1 – differential pulse voltammogram 2 – cyclic voltammogram, 3 – cyclic voltammogram recorded in the supporting electrolyte; $c = 1.0 \times 10^{-3}$ M in 0.1 M $(C_4H_9)_4NClO_4$ in acetonitrile, $\nu = 0.01\ V\ s^{-1}$.