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Oxidative spectroelectrochemistry of two representative coumarins

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ABSTRACT

Electrochemical oxidation of two isomeric coumarins, umbelliferone (UF, 7-hydroxycoumarin) and benzotertonic acid (BA, 4-hydroxycoumarin), were comparatively studied in aqueous buffer solutions by cyclic voltammetry, *in situ* long-path-length thin-layer UV–vis spectroelectrochemistry and *ex situ* ATR-FTIR spectrometry. Both the coumarins undergo the completely irreversible oxidation but following totally different oxidation mechanisms. The 7-OH but not the 4-OH group can contribute to antioxidative activity of coumarin *via* an electron transfer mechanism. Electro-oxidation of UF occurs at the 7-OH position and produces an insulating polymer film at the electrode surface, which probably consists of a poly(ethylene oxide) backbone with coumarin side groups. The toxicity-related coumarin 3,4-epoxide is a possible intermediate in the UF oxidation. Electro-oxidation of BA occurs at the $C_3{=}C_4$ double bond, also yielding a non-conductive film at the electrode surface. In this process salicylaldehyde as the possible intermediate undergoes further oxidation to form the poly(aryl ether) film. The knowledge of the mechanisms of UF and BA oxidation should be helpful in understanding the roles and conversion of coumarins in their biological and chemical processes.

1. Introduction

Coumarin (5,6-benzo-α-pyrone) is among the best known oxygen heterocyclics with a δ-lactone ring and has over 1300 derivatives found throughout the plant kingdom [1–3]. Numerous coumarin derivatives have been chemically synthesized, mainly motivated by their multiple biological activities including disease prevention, growth modulation and antioxidant properties [1,4]. Coumarin has shown anti-tumour activity *in vivo*, with the effect believed to be due to its metabolites, e.g., 7-hydroxycoumarin (umbelliferone, UF) [1]. UF is also considered to be the effective chemical structure in the treatment of high-protein edema [2]. Many 7-substituted coumarins are used as sunscreen agents and optical brighteners for textiles due to their UV-activity [5]. 4-Hydroxycoumarin (benzotertonic acid, BA) is used as a precursor in the synthesis of pharmaceuticals especially for anticoagulants [6] and inhibitors against human NAD(P)H quinone oxidoreductase-1 [7]. On the other hand, the toxicity of coumarins as flavouring ingredients in foods has raised some concerns and food safety authorities have set a maximum limit of $2\,\mathrm{mg\,kg^{-1}}$ for foods and beverages in general, and a maximum level of $10\,\mathrm{mg\,L^{-1}}$ for alcoholic beverages [8]. Some reports have indicated that coumarin-induced toxicity is dependent on the formation of coumarin 3,4-epoxide under enzymatic catalysis [9–11]. It is noticeable that coumarin and its derivatives participate in redox regulation in some biological systems [4,7,9–14].

Electrochemical studies have been carried out in different coumarin-containing systems, mostly for the purpose of preparing novel functionalized compounds [3,15–22]. A partly halogenated coumarin phthalonitrile and corresponding metal-free, cobalt and zinc phthalocyanines were synthesized, and the redox processes of the complexes were studied by voltammetry and *in situ* spectroelectrochemistry [3]. A coumarin dye with a side ring was prepared and characterized with respect to photophysical and electrochemical properties for its application in dye-sensitized solar cells [15]. A series of Co(II), Ni(II), and Cu(II) complexes with Schiff bases of formyl coumarin derivatives were synthesized and subjected to electrochemical and *in vitro* antimicrobial studies [16]. Anodic oxidation of UF derivatives was performed in anhyd acetonitrile-lithium perchlorate for the synthesis of oxazolocoumarin derivatives [17]. Two novel photoreversible poly(ferrocenylsilanes) with coumarin side groups were synthesized and their photochemical reactivity and electrochemical behavior were investigated [18]. Copolymerization of polytriphenylamine with coumarin was carried out to improve the oxidation potential and $LiFePO_4$ battery overcharge tolerance [19]. The natural compound scopoletin (7-hydroxy-6-methoxy-coumarin) was electropolymerized onto the electrode surfaces as an immobilization matrix of nucleic acids or proteins [20]. BA was used for

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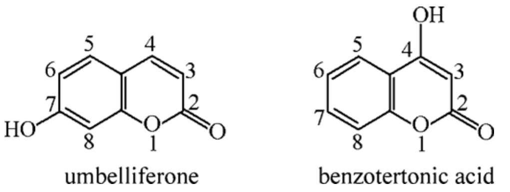

Scheme 1. Chemical structures of umbelliferone (UF) and benzotertonic acid (BA).

electro-organic synthesis of coumestan derivatives [21,22]. Electrochemiluminescence of coumarin derivatives induced by hot electrons was studied at thin insulating film-coated aluminium electrodes in aqueous electrolyte solution [23]. The voltammetric characterization of several structurally similar coumarins has been reported for the potential use in developing methods for liquid chromatography with electrochemical detection of coumarins [24]. Recently, a spectroelectrochemical and chemical study on oxidation of 7,8-dihydroxy-4-methylcoumarin and some related compounds was conducted in aprotic medium [25].

Therefore, the understanding of the redox mechanisms of coumarins is important since their roles and applications in many aspects of biology and chemistry are based on the redox or electron transfer processes. Due to the lack of literature on the electrochemical oxidation mechanisms of coumarins, we carried out a spectroelectrochemical investigation on the oxidation of UF and BA, which are two representative and widely spread coumarins with one hydroxyl group at the benzene ring and the pyrone ring, respectively (Scheme 1). A long-optical-path thin-layer electrochemical cell (LTE-cell) was used for the *in situ* UV–vis measurements, allowing direct observation of the spectral change occurring in the thin-layer solution near the electrode surface. The obtained information and the resulting conclusions should be useful in understanding the roles and conversion of coumarins in their biological and chemical processes.

2. Experimental

2.1. Chemicals and solutions

UF and BA (98% purity each) were purchased from Shanghai Nuotai Chem Company and was used as received. Spectrograde graphite powder (320 mesh) and spectrograde paraffin wax (solidification point 62–65 °C) were purchased from Shanghai Chemical Works for preparing the sCPE. Doubly distilled water was prepared in an all-glass distillatory apparatus for solution preparation. All other chemicals were of analytical grade from China-Reagent group. High pure N_2 was used for solution deaeration. The supporting electrolytes were 0.2 mol dm^{-3} Britton–Robinson buffered solutions (BRS) with various pH values plus 0.5 mol dm^{-3} KCl. The stock solutions of UF and BA both with a concentration of 1.0 mmol dm^{-3} were prepared with ethanol as solvent and stored at 4 °C in a refrigerator. Before use, the stock solution was diluted to various desired concentrations with the buffer supporting electrolytes.

2.2. Electrode preparation

The solid carbon paste electrode (sCPE) was selected in this work with solid paraffin wax as a binder, because of its advantages of low noise and background current, improved reproducibility, robust in operation and better stabilization against organic solvents than oily liquids [26–28]. A disk sCPE with a smaller geometrical area of 3.8 mm^2 was prepared for the voltammetric measurements, while a quadrate sCPE with a larger area of 77 mm^2 was fabricated for the *in situ* spectroelectrochemical experiments. The disk electrode body was a polystyrene hollow tube with inner diameter of 2.2 mm, which was tightly impacted with a copper rod leaving a cavity of 2 mm depth at one end of the tube. The quadrate electrode body was a polystyrene plate with a cavity of 8.0 mm × 9.6 mm, as described previously [29].

The solid carbon paste was made from dry graphite powder and paraffin wax in a ratio of 5:2 (w/w). The wax was heated in an evaporating dish until molten, and then was mixed with the graphite powder to obtain a well blended paste. This paste was pressed firmly into the cavities of the two kinds of electrode bodies, and then the paste surface was polished successively with 800–4000 grit emery papers. The resulting sCPE was washed ultrasonically in doubly distilled water for 5 s to remove the stuck particles, and then stored in the BRSs prior to use.

2.3. Apparatus and procedures

Electrochemical measurements including cyclic voltammetry and spectroelectrochemistry were carried out on a CHI660C electrochemical analyzer (Chenhua, Shanghai, China). The working electrode was the sCPE, used along with a platinum coil counter electrode and a KCl-saturated Ag/AgCl reference electrode (0.195 V vs. SHE, self-made). A conventional single-compartment cell was used for the voltammetric measurements.

The time-dependent thin-layer UV–vis spectra were recorded *in situ* on an UV-2500 spectrophotometer (Shimadzu, Japan), to monitor the redox products of UF and BA at different pHs. The

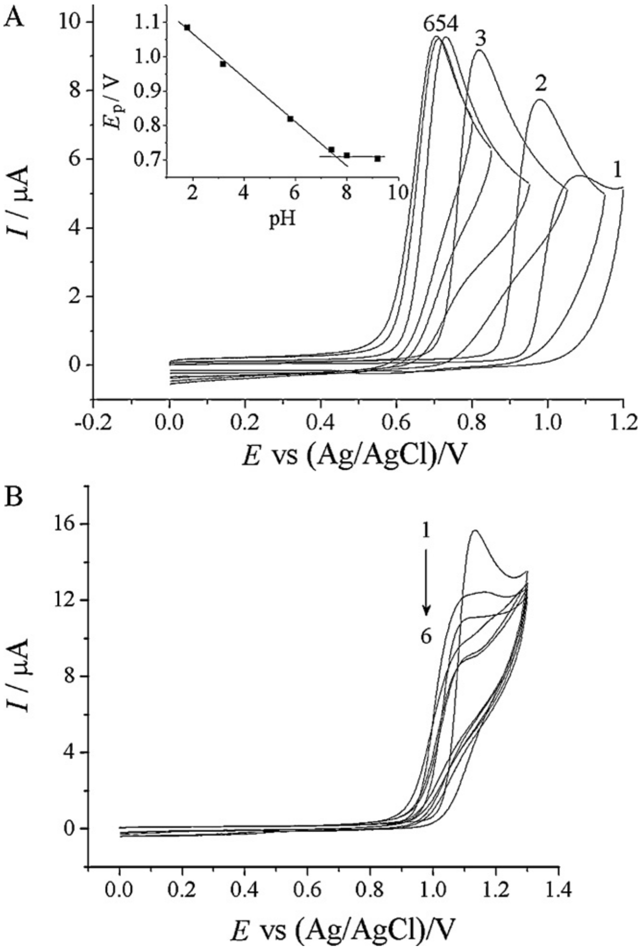

Fig. 1. CVs of UF (A) and BA (B) both of 0.10 mmol dm^{-3}. Buffer pH (1 → 6): 1.8, 3.2, 5.8, 7.4, 8.0, 9.2; scan rate: 100 mV s^{-1}. Inset: the dependences of the peak potential on pH.