



Toward a high added value compound 3, 4-dihydroxyphenylacetic acid by electrochemical conversion of phenylacetic acid



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ABSTRACT

The development of the effective procedure to recover the potentially high-added-value phenolic compound, 3,4-dihydroxyphenylacetic acid (3,4-DHPAA) was investigated using electrochemical conversion of phenylacetic acid (PAA). The proposed mechanism is based on the hypothesis of two-electron oxidation of PAA molecule leading to 3-hydroxyphenyl acetic acid. The latter underwent a second bi-electronic transfer by means of a radical cation, thus leading to the formation of the 2,5 dihydroxyphenylacetic (2,5-DHPAA) acid and 3,4-DHPAA as major products. The 3,4-DHPAA was synthesized by anodic oxidation of PAA at lead dioxide electrode and identified by cyclic voltammetry and spectrophotometry UV-visible. It was also confirmed by mass spectrophotometry using LC-MS/MS apparatus. According to their voltammetric behavior during electrolysis, the oxidation potential of 3,4-DHPAA was lower than that of PAA. The antioxidant activity was measured by DPPH assay, showing that the strongest antiradical activity was detected when the 3,4-DHPAA concentration was higher during electrolysis experiments.

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1. Introduction

Olive oil is a rich source of mono-unsaturated fatty acids and phenolic compounds from simple to very complex structures [1]. Water-soluble simple phenols of lower molecular weight, including 3,4-dihydroxyphenylacetic acid (3,4-DHPAA), are lost during the production of oils. They pass into the water phase which is called "Olive Mill Waste Water" (OMWW) [1–3]. Such water contains a great amount of phenolic compounds, especially hydroxytyrosol, tyrosol, 3,4-DHPAA, caffeic, p-coumaric, ferrulic, gallic acids.... Among these compounds, the orto-dihydroxylated aromatic products exhibit higher antioxidant activity [2,4–6]. Hydroxytyrosol and 3,4-DHPAA are shown to have the highest radical-scavenging effect on DPPH (2,2-diphenyl-1-picrylhydrazyl free radical), especially 3,4-DHPAA which has the highest protective effect against oil oxidation. This compound may potentially be used as an alternative to butylated hydroxyanisol (BHA) and butylated hydroxytoluene (BHT), which are natural antioxidants, to stabilize edible oils. At the same time it can appease a major concern of consumers over the use of synthetic antioxidants in food products [2].

In this context, several methods have been developed to produce 3,4-DHPAA which has the highest antioxidant power. In fact, it is produced by biological method [7,8] and by chemical reaction [9].

Different attempts have been used to evaluate the antioxidant activity of different compounds [10,11] using an accelerated test [12,13], radical species such as ABTS⁺ (2,2 azinobis (3-ethylbenzthiazoline-6-sulfonic acid) [14], DPPH[•] [15] and ESR (electron spin resonance) spin trapping technique [16]. However, all these procedures have some drawbacks since they require the use of specific reagents and tedious and time consuming sample preparation.

Recently, electrochemical measurements have been established for the determination of antioxidant activity [17], such as their use as a rapid proof of the antioxidant capacity of a lot of organic materials. The oxidation potentials measured by cyclic voltammetry have been used to compare the antioxidant strength of compounds such as phenolic acids, flavonoids, cinnamic acids,... [17–21]. Low oxidation potentials are associated with a greater facility or strength of a given molecule for the electrodonation, and thus acting as antioxidant. Cyclic voltammetry has been successfully applied to analyze antioxidants present in wine [22], plant extracts [21], phenolic standards [17,23,24], and even human plasma [25].

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Cyclic voltammetry at platinum oxide is used to follow the degree of antioxidant activity during the electrochemical conversion of PAA. Platinum is often regarded as the ideal solid electrode for fundamental electrochemical investigation due to its chemical and electro-catalytic properties in the oxidation reaction by electronic transfer between the reagent and the anode [26,27]. The electro-catalytic properties of Pt oxides electrode was characterized by the charge Q corresponding to the electrochemical formation of the Pt oxides. Besides, we showed in a previous works that the charge Q allows control of electro-catalytic properties of the Pt oxides electrode [28].

In this work, we developed the galvanostatic electrolysis method using an electrode material characterized by a high oxygen over-potential such as lead dioxide (PbO_2), in order to convert PAA into 3,4-DHPAA as a product with important biological activities. On the other hand, the antiradical ability of PAA and its oxidation products was assessed by DPPH assay. The structure of the converted products was confirmed using Liquid Chromatography–Mass Spectrometry (LC-MS) analysis.

2. Experimental

2.1. Reagents and chemicals

Sodium molybdate dehydrate and organic solvents were purchased from Merck (Darmstadt, Germany). PAA, 3,4-DHPAA, DPPH, and all other chemicals were purchased from Sigma–Aldrich (St. Louis, MO). All used reagents and chemicals were of analytical grade.

2.2. Apparatus

A potentiostat type PJT Tacussel was used for electrochemical measurements and the data was recorded using a GSP4 Tacussel X-Y recorder. The amount of electricity was measured using an IG6-N Tacussel integrator. In this investigation, all the potentials refer to $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ electrode ($E^\circ = +0.61$ vs SHE/V).

The electronic absorption spectra of PAA solutions under investigation and their treated solutions by anodic oxidation were recorded within the wavelength range of 200–400 nm, using a Shimadzu model UV-1650 PC spectrophotometer.

2.3. Electrolysis

The electrolysis of PAA solutions were carried out in an isothermal reactor using a thermoregulated single compartment cell ($V = 200 \text{ cm}^3$). The cathode was a cylindrical mesh made up of platinum. The initially electrolytic solution contained 8 g L^{-1} PAA in 0.5 mol L^{-1} H_2SO_4 . The Ta/ PbO_2 anode was placed in a coaxial of the cathode. The total surface area of the working electrode was 6 cm^2 . The experimental details for the preparation of Ta/ PbO_2 were described in our previous research work [29]. The solutions of PAA were electrolyzed at 30°C , with magnetic stirring and under different applied current densities 10, 30 and 50 mA cm^{-2} .

2.4. Treatment of the platinum electrodes

The layer of Pt oxides was prepared by cyclic voltammetry between -600 mV and $+890 \text{ mV}$ at a potential scan rate of 300 V min^{-1} using a Pt disc ($\varphi = 1 \text{ mm}$), previously polished with $0.3 \mu\text{m}$ Al_2O_3 then washed several times with distilled water in 0.5 mol L^{-1} sulfuric acid solution. The Pt electrode, initially shining, was progressively covered with a grey and adherent layer of Pt oxides. Fig. 1 (curve 1) shows the electrochemical response of the Pt/Pt oxides electrode in 0.5 mol L^{-1} sulfuric acid aqueous solution. From 143 mV , an anodic wave corresponding to the Pt oxides

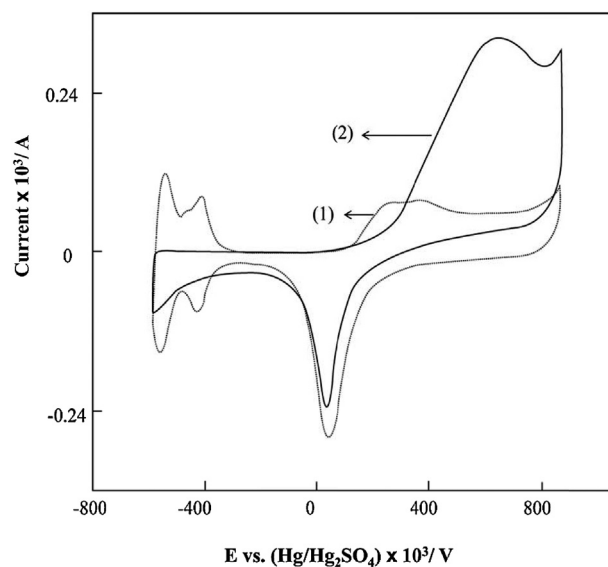


Fig. 1. Cyclic voltammograms of PAA at platinum disk in 0.5 mol L^{-1} H_2SO_4 at Ta/ PbO_2 anode. Potential scan rate 50 mV s^{-1} ; $Q = 0.6 \text{ mC}$; $T = 20^\circ\text{C}$. PAA concentration: (1) 0; (2) 8 g L^{-1} .

formation and a cathodic peak at 43 mV relative to the Pt oxides reduction can be noted. In the present research work, the Pt/Pt oxides electrode was characterized by the amount of electricity (Q) corresponding to the electrochemical reduction of the formed Pt oxides. The Q value was measured during a potential scan between $+843$ and -585 mV at a potential scan rate of 50 mV s^{-1} . The amount of electricity (Q) was considered as the unique parameter that characterizes the surface state of the Pt/Pt oxides electrode. It is worthy to note that the amount of electricity (Q) is a global parameter that does not take into account the heterogeneity of the electrode surface.

2.5. Liquid Chromatography–Mass Spectrometry analysis

The liquid chromatography–mass spectrometry (LC–MS) of the PAA after 16 hours of electrolysis was performed on an Agilent 1100 series LC–MSD. The compounds were separated with a Zorbax 300 A° Extend-C-18 column ($2.1 \times 150 \text{ mm}$, particle size $5 \mu\text{m}$, Agilent Technology, INC, Wilmington, DE, USA). The mobile phase was a mixture of two solvents: (A: formic acid 1% in water) and (B: 89.5% methanol, 9.5% acetonitrile and 1% formic acid). The analysis conditions were as described earlier by Bouaziz et al. [30]. The percentage by volume of (B) varied linearly with time as follows: from 10 to 30% for the first 5 minutes, then from 30 to 40% up to 25 minutes after isocratic during 5 minutes, from 40 to 50% up to 40 minutes and from 50 to 100% up to 50 minutes, after that back to 10% up to 55 minutes and finally isocratic up to 65 minutes. The column outlet was coupled with an Agilent MSD ion trap XCT mass spectrometer (Santa Clara, CA, USA) equipped with an ESI ion source.

2.6. Ortho-diphenolic determinations

Ortho-diphenolic content was determined following the previously modified method described by Cert et al. [31]. This method is based on the formation of a yellow complex between ortho-diphenols and molybdate ions. Briefly, 2 mL of the sample was added to 0.5 mL of the sodium molybdate dihydrate solution (0.5 g L^{-1} in a mixture of ethanol-water (50% ethanol, 50% water)). The mixture was shaken and after 15 min, the absorbance was measured at 370 nm at room temperature. Standards of gallic acid were similarly prepared.

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