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

Souhel Kallel Trabelsi, Olfa Dridi Gargouri, Boutheina Gargouri, Ridha Abdelhèdi, Mohamed Bouaziz *

Laboratoire d'Electrochimie et Environnement, Ecole Nationale d'Ingénieur de Sfax, BP 1173, 3038 Sfax. Université de Sfax. Tunisia

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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.

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-ethyl-benzthiazoline-6-sulfonic acid) [14], $DPPH^{\bullet}$ [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].

* Corresponding author. Tel : +21698667581.
E-mail address: mohamed.bouaziz@fsg.rnu.tn (M. Bouaziz).

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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. Appratus

A potentiostat type PJT Tacussel was used for electrochemical measurements and the data was recorded using a GSTP4 Tacussel X-Y recorder. The amount of electricity was measured using an IG6-N Tacussel integrator. In this investigation, all the potentials refer to $Hg/Hg_2SO_4/K_2SO_4$ 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 ($V = 200\ cm^3$). 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 mV at a potential scan rate of $300\ V\ min^{-1}$ using a Pt disc ($\varphi = 1$ mm), previously polished with 0.3 μm 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

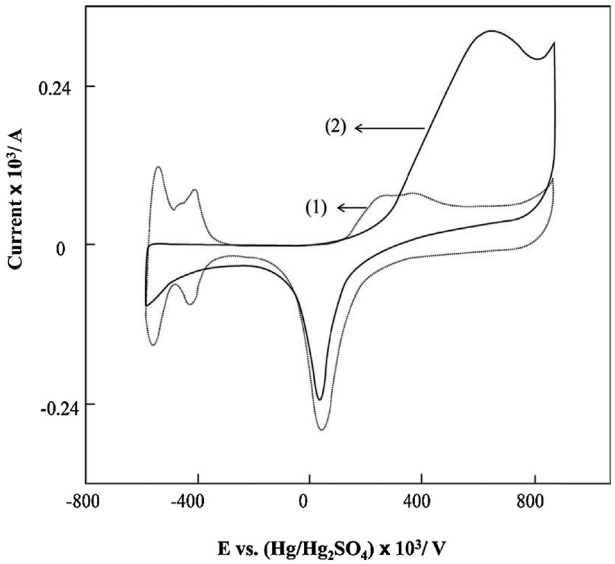

Fig. 1. Cyclic voltamograms of PAA at platinum disk in $0.5\ mol\ L^{-1}\ H_2SO_4$ at Ta/PbO_2 anode. Potential scan rate $50\ mV\ s^{-1}$; Q = 0.6 mC; T = 20 °C. PAA concentration: (1) 0; (2) $8\ g\ L^{-1}$.

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 × 150 mm, particle size 5 μm, Agilent Technology, INC, Wilmingtom, 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.

2.7. Determination of DPPH radical-scavenging activity

The DPPH radical scavenging effect was evaluated following the procedure described in a previous study [30]. The Aliquots (50 μL) of various concentrations (5, 10, 15, 20 and 25 μg/mL) of the test extracts in methanol were added to 5 mL of methanolic solution containing DPPH radicals ($6\ 10^{-6}$ mol L^{-1}). After 30 min incubation period at room temperature and in the dark, the absorbance was read against control at 517 nm. The inhibition percentage of free radical DPPH (%RSA) was calculated using Eq (1):

$$\%RSA = [(A_{blank} - A_{sample})/A_{blank}] \times 100 \quad (1)$$

where %RSA is the percentage radical-scavenging activity, A_{blank} is the absorbance of the control reaction (containing all reagents except the test extract), and A_{sample} is the absorbance of the test extract. The concentration of the test extract providing 50% inhibition (IC_{50}, expressed in mg L^{-1}) was calculated from the graph plotted with inhibition percentage against the extract concentration. The synthetic antioxidant reagent BHT was used as positive control and all tests were carried out in triplicate.

3. Results and discussion

3.1. Effect of current density in the electrochemical conversion of PAA at PbO_2 anode

The electrochemical conversion of PAA was investigated by anodic oxidation under three different current densities (j_{app}) 10, 30, and 50 mA cm^{-2}. In anodic oxidation, organic compounds are directly oxidized by the reaction with hydroxyl radical ($HO^{\bullet}$) formed at the anode surface from water decomposition (Eq. (2)).

$$H_2O \rightarrow HO^{\bullet}_{ads} + H^+ + 1e^- \quad (2)$$

Fig. 2 shows a typical profile of variation of orthodiphenols concentration during the electrolysis essays of 8 g L^{-1} PAA at 10, 30 and 50 mA cm^{-2}. As can be seen in this figure, the orthodiphenolic concentration was weakly influenced by applied current density. When the applied current density increases from 10 to 50 mA cm^{-2}, the maximum of orthodiphenolic concentration passed from 466 to 394 mg L^{-1}. However, the time necessary for the electrochemical conversion was very much influenced by the current density. It was clearly shown that the electrochemical conversion of PAA at 30 mA cm^{-2} was more rapid than at 50 mA cm^{-2}. This behavior could be attributed to the high reactivity of greater amounts of $HO^{\bullet}$, which can be lost by the secondary reaction (Eq. (3)).

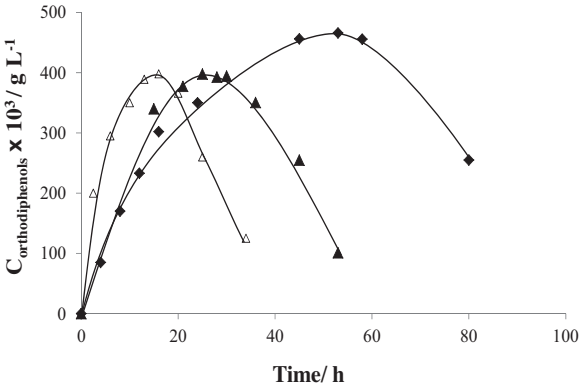

Fig. 2. Effect of current density on the variation of orthodiphenols concentration with electrolysis time of 8 g L^{-1} PAA solutions in 0.5 mol L^{-1} H_2SO_4 at Ta/PbO_2 anode. V = 200 cm^{-3}; T = 30 °C; j_{app}/ mA cm^{-2}: (◆) 10, (Δ) 30 and (▲) 50.

$$2HO^{\bullet}_{ads} \rightarrow \frac{1}{2}O_2 + H_2O \quad (3)$$

Therefore, to have a short-time conversion, the best chosen current density of the subsequent analysis was at 30 mA m^{-2}.

The electrochemical oxidation of PAA at PbO_2 anode under 30 mA cm^{-2} was followed by cyclic voltammetry at the treated platinum electrode. Fig. 3(a) exhibits the cyclic voltammograms at different electrolysis time intervals of 8 g L^{-1} PAA. The initial voltammogram for the untreated solution (Fig. 1 curve 2 or Fig. 3(a) curve 1) shows only the oxidation peak I_1 of PAA at E_{pa1} = 643 mV. The voltammograms (Fig. 3(a) curve 2, 3, 4, 5 and 6) reveal two peaks I_2 and I_3 at E_{pa2} = 100 mV and E_{pa3} = 185 mV, respectively, which are related to the more stable oxidation products of PAA. Peak I_2 is ascribed to the oxidation of 3,4-DHPAA by comparison with its authentic voltammogram recorded under identical experimental conditions. This peak reached its maximum about 0.2 mA after 16 hours of oxidation, and then decreased (Fig. 3(b)). However, the peak I_1 intensity decreased until zero after 34 hours.

3.2. UV-Visible analysis

Fig. 4 presents typical scanning kinetic graphs taken at different time intervals during the electrochemical oxidation of PAA at 30 mA cm^{-2}. As can be seen from Fig. 4, two new bands appeared at

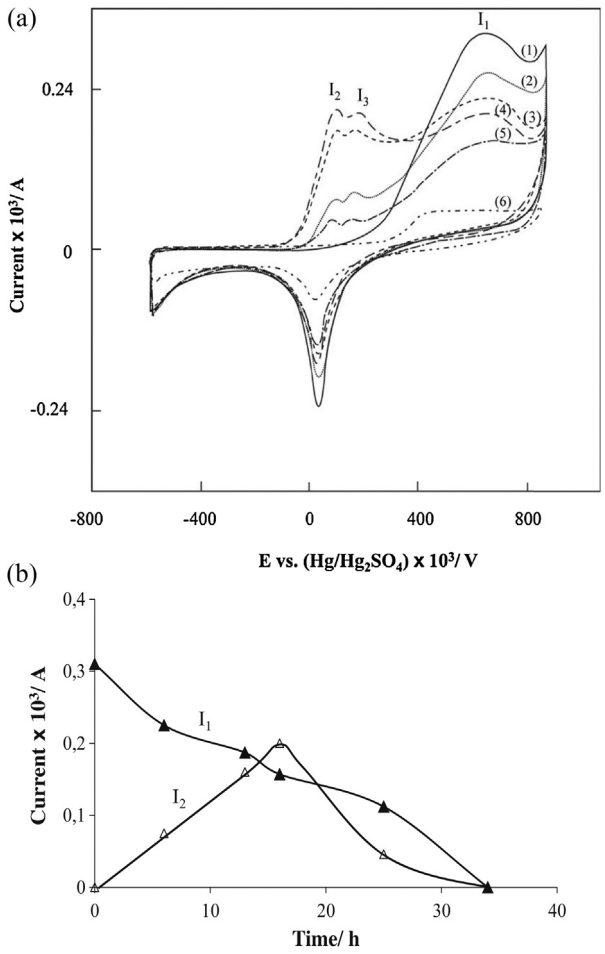

Fig. 3. (a) Cyclic voltamograms of 8 g L^{-1} PAA at Platinum disk in sulfuric acid aqueous solution at potential scan rate of 50 mV s^{-1} as a function of time electrolysis of PAA at PbO_2. j_{app} = 30 mA cm^{-2}, T = 30 °C. Electrolysis time/ h: (1) 0; (2) 6; (3) 13; (4) 16; (5) 25; (6) 34. (b) Variation of current of the peaks (I_1) and (I_2) during anodic oxidation of PAA.

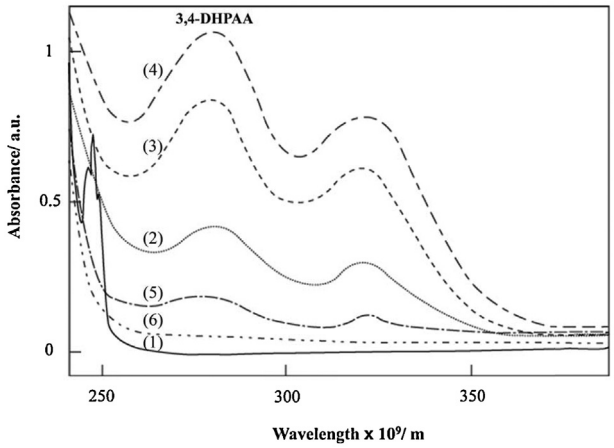

Fig. 4. (a) UV–Visible absorption spectra obtained during the electrolysis of 8 g L^{-1} of PAA solutions in 0.5 mol L^{-1} H_2SO_4 at Ta/PbO_2 anode. Electrolysis time/h: (1) 0; (2) 6; (3) 13; (4) 16; (5) 25; (6) 34.

280 and 321 nm, indicating that intermediate products were formed during the electrochemical oxidation of PAA. The first absorption band which appeared at 280 nm is ascribed to the 3,4-DHPAA by comparison with its authentic absorption spectrum recorded under identical experimental conditions.

After reaching its maximum intensity at 16 hours, the new bands began to decrease until it disappeared, thus demonstrating that the intermediates can be completely electrochemically oxidized.

3.3. Liquid Chromatography–Mass Spectrometry analysis

To elucidate the structures of phenolic compounds present in the electrochemical treatment solution of 3,4-DHPAA, the obtained sample after 16 hours was monitored by liquid chromatography with electrospray mass spectrometry in the negative mode. The structure assignment of phenolic compounds was based on the UV absorbance spectra with a systematic search for molecular ions, using extracted ion mass chromatograms and comparing the MS/MS spectra with those in the literature [32].

As regards compound **1** (t_R, 11.75 min; λmax, 279 nm), it was identified as PAA by the comparison of its absorbance spectrum and retention time with those of an authentic standard. This was confirmed by the MS-MS, which yielded an [M-H]- at m/z 135.

Concerning compound **2** (t_R, 7.97 min; λmax, 270 nm), it was identified as 3-hydroxyphenylacetic acid (Fig. 5) on the basis of co-chromatography with an authentic standard and a mass spectrum with an $[M-H]^-$ at 151 and prominent MS^2 fragments at m/z 151, 133. The ion m/z 133 was obtained by the loss (−18) of a water molecule, providing an anion of $[M–H–H_2O]^-$.

With respect to compound **3**, it was identified as 3,4-DHPAA retained at 5.22 minutes (λ_{max}, 280 nm) (Fig. 5). The MS^1 spectrum exhibited a molecular ion at m/z 167 $[M-H]^-$. The MS^2 spectrum obtained by the fragmentation of the ion m/z 197 presents the following m/z values: 167, 150 and 149. The fragmentation of the Pseudomolecular ion $[M-H]^-$ at m/z 167 yielded a fragment at m/z 149 by the loss of 18 mass units of $[M–H_2O–H]^-$ (Fig. 6). The structure of this compound is confirmed by that of an authentic standard.

As for compound **4** (t_R, 5.62 min; λmax, 325 nm), it was cochromatographed with 3,4-DHPAA (Fig. 5). It also had the same absorbance and mass spectra $[M-H]^-$ at m/z 167 and two major MS^2 fragments at m/z 149 and 137 as 3,4-DHPAA [8], which was previously detected in olive mill wastewater [2]. This compound was identified as 2,5-DHPAA, which is in good agreement with the results obtained by the oxidation mechanism proposed using cyclic voltammetry (Fig. 7). The two isomers can, therefore, be distinguished chromatographically as well as by MS. This is because the predominant MS^2 ion was derived from 2,5-dihydroxyphenyl acetic acid at m/z 137, while the corresponding fragment from 3,4-DHPAA at m/z 149.

3.4. Oxidation mechanism of the PAA

The results presented above suggest that PAA molecules undergo a bi-electronic transfer followed by hydrolysis, producing 3-hydroxyphenylacetic acid (Fig. 7). The latter undergwent a second bi-electronic transfer producing phenoxonium carbocation existing under three mesomeric forms A–C. Taking into account the electronic effects of the oxo and carboxymethyl groups, the radical B was found to be the least stable. Then, the hydrolysis of

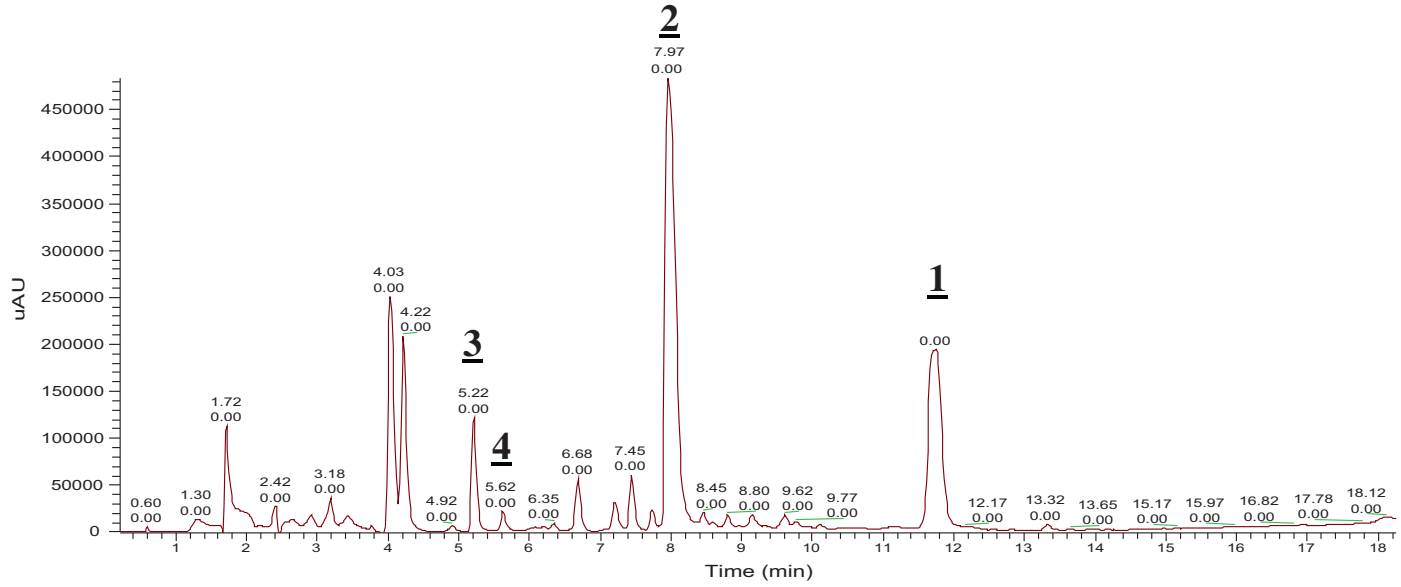

Fig. 5. HPLC chromatogram after 16 hours of PAA anodic oxidation at PbO_2,**1**: PAA; **2**: 3-hydroxyphenylacetic acid; **3**: 3,4-DHPAA; **4**: 2,5-DHPAA.

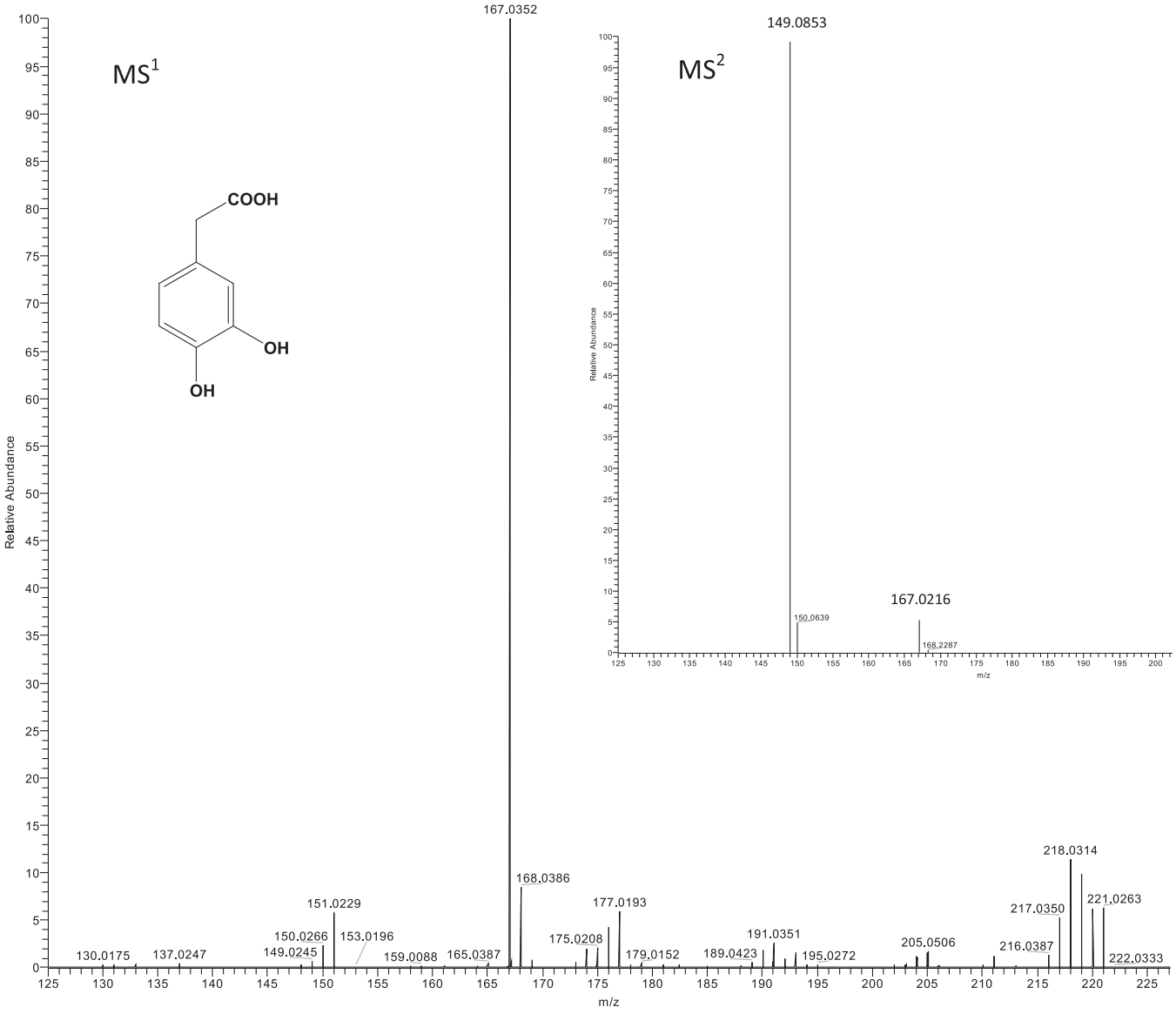

Fig. 6. LC-MS/MS spectrum (MS_1 and MS_2) after 16 hours of PAA anodic oxidation at PbO_2, $j_{app} = 30\,mA\,cm^{-2}$; T = 30 °C.

the carbocation A and C led to the formation of 3,4-DHPAA and 2,5-DHPAA, respectively.

3.5. Antioxidant Activity

The DPPH radical-scavenging activities of PAA solution treated by anodic oxidation at PbO_2 were investigated during the electrolysis of $8\,g\,L^{-1}$ PAA at $30\,mA\,cm^{-2}$ (Fig. 8). The low IC_{50} values designate the potent radical-scavenging effects as low concentrations are adequate to inhibit the DPPH radicals [33,34].

All samples were proven to exhibit antioxidant activity, which shows correlation between the orthodiphenols content and DPPH radical-scavenging activity over all PAA anodic oxidations. The PAA with no hydroxyl groups had $IC_{50} = 57\,mg\,L^{-1}$, which presents limited antioxidant activity. On the other hand, the lower IC_{50} values ($6\,mg\,L^{-1}$), which indicate higher antioxidant potential, were observed for the samples taken at 16 hours of electrolysis. This is probably due to the significant radical inhibition caused by a high concentration of orthodiphenols caused by the presence of 3,4-DHPAA. The antioxidant activity and the level of the orthodiphenols content in the PAA electrolysis solution suggest that the radical scavenging effect in the solution can be attributed to hydroxylated phenolic compounds, particularly the number of hydroxyl substituents in the aromatic ring and the nature of the substituents at the para or ortho position [33]. These compounds react with free radicals formed during autoxidation and generate a new radical that is stabilized by the resonance effect of the aromatic nucleus [35]. It was found that 3,4-DHPAA exhibits antioxidant activity ($IC_{50} = 6\,mg\,L^{-1}$) at a similar level to that of BHT ($IC_{50} = 8.32\,mg\,L^{-1}$).

Cyclic voltammetry has been applied to characterize the reducing ability of natural phenolics [17,36] and good correlations have been observed between redox potentials and antioxidant properties [37,38]. In accordance with the global mechanism proposed for PAA oxidation, the hydroxyl groups are oxidized via two electrons transfer, leading to the generation of a corresponding quinone after the liberation of $2H^+$. These results indicate that the higher number of hydroxyl substituents on the aromatic ring, corresponds to the lower electrochemical potential. Indeed, it was reported that an ortho hydroxyl group at position 3′ appears to be

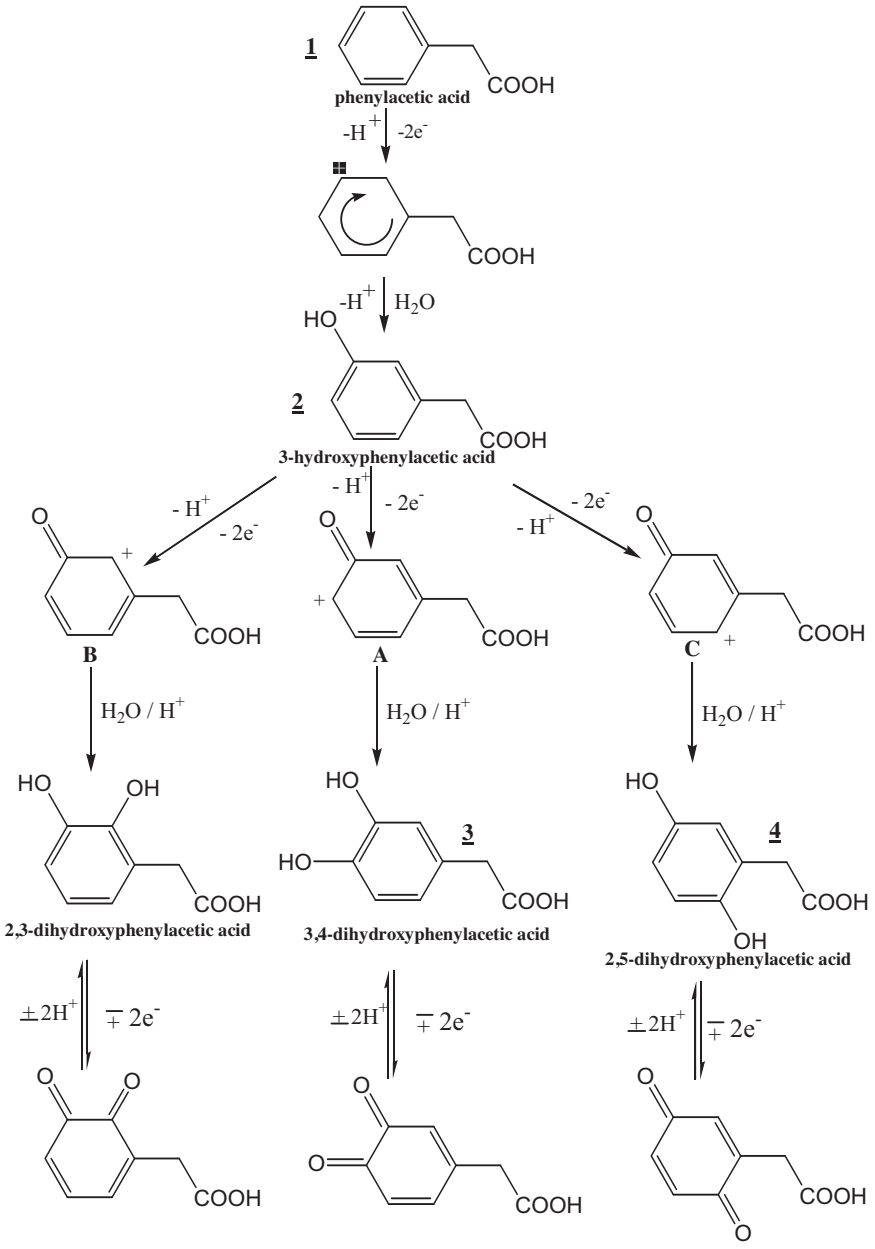

Fig. 7. Oxidation pathways of PAA in aqueous sulfuric acid medium at treated Platinum.

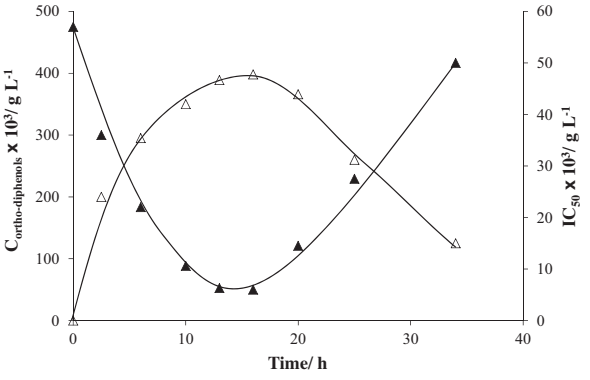

Fig. 8. Free radical scavenging activity and ortho-diphenols tests during anodic oxidation of PAA at PbO_2. j_{app} = 30 mA cm^{-2}; T = 30 °C.

desirable to obtain an anti-oxidative response [33]. Therefore, the 3,4-DHPAA which is easily oxidized (E_{pa2} = 100 mV) than 2,5-dihyroxyphenylacetic acid (E_{pa3} = 185 mV), has a higher antioxidant activity.

Consequently, according to our previous work [24], this study confirmed again that the application of electrochemical methods using anode material with a high over-potential for oxygen evolution and a low cost, is a novel easy clean and solvent free route for conversion of toxic compound into product with important biological activities.

4. Conclusion

The results obtained in this study have revealed that the electrochemical oxidation using PbO_2 anode is a rapid, simple and efficient tool for the conversion of PAA into high-added-value products such as 3,4-DHPAA. Using LC/MS analysis, it was possible to determine the structure of majors phenolic intermediates (3,4-

DHPAA and 2,5-DHPAA) produced during the electrochemical treatment of PAA.

It has reported that oxidation potential measured by cyclic votammetry was closely related to the compounds structures. The phenolic structure also influences antioxidant activity. Besides, the ortho-diphenol compound (3,4-DHPAA) has lower anodic peak potential and higher antioxidant ability than para-diphenol compound (2,5-DHPAA).

Finally, the electrochemical conversion of PAA could be used as a tool to produce a high added value compound, such as 3,4-DHPAA, which could make significant contributions to the health benefits associated with the consumption of various food ingredients.

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