A contribution on the elucidation of the electrooxidation mechanism of gentisaldehyde on a glassy carbon electrode

by

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ABSTRACT

The electrochemical behaviour of gentisaldehyde (2,5-dihydroxibenzaldehyde) on a glassy carbon electrode is studied by linear-sweep cyclic voltammetry finding one to three oxidation peaks, depending on both the number of cycles recorded and the pH, and one reduction peak. The oxidation product was the formyl-p-benzoquinone, generated by the oxidation of the biphenolic ring, and not the 2,5-dihydroxybenzoic acid (gentisic acid) that could be formed by oxidation of the aldehyde group. The mechanism proposed at $pH<pK_1$ (8.42) from the analysis of cyclic and convoluted voltammograms involves the loss of an H^+ ion from one hydroxyl group, a first quasi-reversible electron transfer to give a radical, and the release of a proton in a third step (the r.d.s.) followed by the second electron transfer to give the product. At $pK_1<pH<pK_2$, the electroactive species is the anion that losses an ion H^+ to give the dianion, the process being of the CEE type (chemical-electrochemical-electrochemical steps). At $pH>pK_2$ (10.93) the process becomes of the EE type (electrochemical-electrochemical steps), no H^+ ions being involved. Radicals species found justify the antioxidant capacity of gentisaldehyde.

INTRODUCTION

The perception that natural and dietary antioxidants are safer than synthetics has increased the interest on antioxidants of natural origin. Because an antioxidant is a substance that may delay or prevent oxidation of an oxidizable substrate at low concentrations[1], the oxidation mechanism of a given antioxidant can help for understanding its antioxidant activity, as was found for the constituent of sesame oil sesamol[2]: the formation of radicals in the ring cleavage explains in part the ability of sesamol to interact with reactive oxygen species (ROS). In addition, a low oxidation potential is related to a high antioxidant capacity, a good correlation being established between these potentials and the antioxidant capacity measured by the DPPH method[3] (DPPH Radical Scavenging Assay[4] based in the reaction between the antioxidant and the stable radical 2,2-diphenyl-1-picrylhydrazyl, followed by UV-spectroscopic measurements).

Gentisaldehyde (2,5-dihydroxybenzaldehyde) is a natural compound found in olive processing effluents[5] and in *Beta vulgaris* seeds[6] that showed bactericidal activities against some common infectious bacteria[7], can act as sensitizer of antifungal agent[8,9] and, has also antioxidant activity[3,10,11].

The antioxidant capacity of gentisaldehyde was examined by DPPH measurements as well as from the decrease of the anodic wave of H_2O_2 on mercury electrodes by means of differential-pulse voltammetry.[3,10,11] In both cases, the antioxidant capacity is medium-low, similar to that found for sesamol.

The dissociation state of phenolic benzaldehydes and gallic acid derivatives is crucial to understand their chemical and bacteriological activities, which take place in physiological conditions[12]. In a previous work, from the UV-visible spectra of gentisaldehyde, the dissociation constant values pK_1=8.42 and pK_2=10.93 were obtained[13], the higher being in agreement with the previously published value[14]. The antioxidant capacity at two pH values was compared with those of 2,4-dihydroxybenzaldehyde and gallic acid. It was found that the

pH at which the pH of the antioxidant capacity measurements are made is very important, because the hydroxyl groups of the different compounds have different dissociation constants.

Since there are not previously published studies dealing on the redox mechanisms of gentisaldehyde, the aim of this work was to establish its electrochemical oxidation mechanism to help in the understanding of its antioxidant capacity, with special emphasis in the possible quinone formation.

Experimental

All chemicals used were of Merck analytical grade reagents, with the exception of gentisaldehyde and gentisic acid that were from Sigma-Aldrich, and were used without further purification.

As supporting electrolytes, buffer solutions containing 0.1 M in both acetic and phosphoric acids, for *pH*<8, and 0.05 M in both sodium carbonate and phosphoric acid, for *pH*>8, were used. The aqueous solutions were prepared using ultrapure water type I (resistivity 18.2 MΩ.cm at 298 K) obtained from an ultrapure water Millipore system. Ionic strength was adjusted to 0.3 M with NaCl. Stock solutions of gentisaldehyde were stored in the dark at 277 K to avoid decomposition. pH measurements were made prior each experiment with a Metrohm 780 pH-meter, calibrated daily with the corresponding pH standards (Sigma-Aldrich). The pH adjustment was made with solid NaOH.

The electrochemical measurements were made on a CHI650A electrochemical workstation from IJCambria. The reference electrode was a Metrohm 6.0733.100 Ag | AgCl | KCl (3 M) and the auxiliary electrode was a platinum rod. Solutions were purged with purified N_2 for at least 30 min to avoid the presence of oxygen that could originate undesired redox reactions on the electrode. The working gentisaldehyde concentration was 1 mM, with the evident exception of

expeiments in which the effect of the concentration was studied. All tests were performed at 298 K.

Electrochemical measurements were made with a glassy carbon working electrode (IJCambria) with 7.5 mm^2 area. The electrode was electrochemically pretreated with five voltammetric cycles between +2 and –2 V in a saturated sodium chloride solution. Then it was polished using first a silicon carbide paper, followed by diamond (0.25 µm) slurry and alumina (0.3 and 0.05 µm) slurries. After each polishing, residual material was removed by sonication of the electrode in an ultrapure water bath for 30 minutes.

The controlled-potential electrolysis was made on a working electrode consisting of a high density graphite rod of 99.995% purity (Aldrich, CAS number 7782-42-5 C) protected with a silicone tube, which allow to use a cylinder with an area of 75.4 mm^2. The electrode was polished with a silicon carbide paper, followed by alumina (0.3 µm) slurry. Residual polishing material was removed from the surface by sonication of the electrode in an ultrapure water bath for 20 minutes after each polishing. The counter electrode was a stainless steel rod. The electrolyses were made with volumes of 5 mL of 1.2-1.5 mM gentisaldehyde and recording the charge along the experiment. To follow the course of the electrolysis, after different amounts of charge were passed, samples of 200 µL were taken, added to 1.5 mL of purified water, and the UV-visible spectrum was recorded. UV measurements were made on a Perkin-Elmer Lambda 750S spectrophotometer with quartz cuvettes Hellma of path-length 1.0 cm.

Results and discussion

Figure 1 shows the cyclic voltammograms obtained for $1 \cdot 10^{-3}$ M gentisaldehyde on GCE. Until three oxidation peaks and one reduction peaks were obtained, depending on the medium pH and the number of cycles recorded. The first voltammetric cycle shows one or two oxidation

peaks, denoted as *Peak 1* and *Peak 2*, the second appearing at more positive potentials than the first. Peak 2 is only observed in basic solutions. The reverse scan of the first cycle shows a reduction peak, denoted as *Peak 3'*, appearing at less positive potentials than Peak 1. In the second voltammetric cycle an additional oxidation peak appears (*Peak 3*) at potentials somewhat positive than Peak 3'; this peak does not appear at pH values below 1.5 and at pH values above 10.

Figure 1

The intensities of Peak 3 depended on the pH in an apparent aleatory manner, as is shown, in part, in figure 1. It was applied a constant potential at a value after Peak 1 and then voltammograms were recorded in the zone of potentials corresponding to the 3-3' system. The results indicate that 3 and 3' peaks do not form a redox pair, as occurred for sesamol[2], but peak 3 is originated by adsorption processes occurring on the electrode surface. This is supported by the fact that the peak intensities of Peak 3 vary linearly with the scan rate, this indicating that the peak is due to a completely heterogeneous process,[15] which produces a layer of gentisaldehyde on the electrode in addition to the oxidation products, as was previously found by Pariente et al.[16]. Therefore, this peak must be originated by the oxidation product obtained at the potentials of Peak 1, which is reduced at the potentials of Peak 3'.

Scheme 1 shows the possible overall oxidation pathways for gentisaldehyde, at least, in a first stage: oxidation of aldehyde group to acid, and the oxidation of the ring. To decide between these two possibilities, several experiences have been made.

Scheme 1

First, it was explored if the oxidation produces the acid by recording voltammograms of gentisaldehyde and gentisic acid, alone and in mixture, as is shown in Fig. 2.

Figure 2

As it can be seen in the figure, the electrochemical oxidation of gentisic acid takes place at lower potentials than gentisaldehyde, this meaning that the –CHO group must be oxidized at higher potentials than the acid. In consequence, the value of the intensity obtained should be much higher than the value corresponding to the acid, approximately in a factor of two if the oxidation of the acid is a two-electron process. As can be seen in the figure, the peaks corresponding to the acid and the aldehyde have similar intensities. In addition, if the acid were the oxidation product of gentisaldehyde, the reduction peak in the reverse scan must correspond to the same process (the reduction of the same product). However, as it can be seen in the figure, this is not true: in the voltammogram of the solution containing both substances, two overlapped reduction peaks appear instead a peak having double intensity. These facts allow one to discard the oxidation of the aldehyde group to an acid group.

To explore the second possibility, the experiments shown in figure 2 (down) were done. The cyclic voltammograms of gentisaldehyde and 1,4-dihydroquinone in the same experimental conditions are very similar, in potentials, intensities and morphology.

The peak intensity in voltammetry cannot be used for comparison because this parameter depends on the mechanism of the redox process as well as on square root of the diffusion coefficient, D. For this reason, convolution voltammetry[17-23] was used for the analysis of the oxidation scans of the voltammograms by computing the integral

$$J = \pi^{-1/2} \int_0^t \frac{I(\nu)}{(t-\nu)^{1/2}} d\nu \qquad (1)$$

where I is the actual current, J is the convoluted current, v is an integration variable, which physical meaning is the time through the convolution is obtained, and t is related to the potential through the scan rate. The limiting values, J_L, obtained are independent of the mechanism of the electrochemical reaction:

$$J_L = nFAD^{1/2}c_0 \qquad (2)$$

where *n* is the number of electrons involved in the process, A is the electrode area, and *D* and c_0 are the diffusion coefficient and the bulk reactant concentration, respectively, all expressed in international units.

The limiting currents of the convoluted voltammograms of gentisaldehyde, 1,4-dihydroquinone and sesamol are very close, this indicating that the number of electrons involved, is the same in all cases.

UV-vis spectra were recorded during electrolyses made at potentials located above Peak 1, as is shown in figure 3. The spectrum obtained at the end of electrolysis is very similar to that obtained for the oxidation product of sesamol[2], and very different of the obtained for both gentisaldehyde and Gentisic Acid. This spectrum shows the characteristic bands of the 1,4-benzoquinone[24], with maximum absorbance values at 360 nm, 290 nm and 260 nm, in this case. The number of electrons taking part in the overall process, was obtained from the plot of charge vs. amount of reactant oxidized, being 2.05.

Figure 3

All these results indicate that the overall oxidation reaction corresponds to the oxidation of gentisaldehyde to give a substituted 1,4-benzoquinone, very probably with semiquinone structures as intermediates[25].

The peak potentials shifted in general towards less positive values as the pH was increased. For Peak 1 this variation was roughly linear with a slope of –59 mV at pH<11; above this pH value the peak potential was constant. The same behaviour was observed for Peak 2, but in this case the slope of the linear segment observed at 8<pH<11 was –63 mV. The pH of the change in slopes is close to the second dissociation pK[13].

Below pH 8, the intensities of Peak 1 and Peak 3' are pH-independent, and decreased at higher pH values. In addition, the intensities of Peak 1 and Peak 2 were very similar, in the pH range at which they appear. It must be noted that the first dissociation pK of gentisaldehyde is 8.4[13].

At a gentisaldehyde concentration of $1 \cdot 10^{-3}$ M, a new peak appears in the reduction scan (Peak 1´) when scan rate was increased; this is shown in Fig. 4. This peak is clearly associated to a heterogeneous process, as can be inferred from the linear dependence of its peak intensity with the scan rate, conversely as occurs for Peaks 1 and 2, which current functions ($I_P/v^{1/2}$) are independent of the scan rate, as expected for mainly diffusion-controlled processes.

Figure 4

For Peak 3', the current function at pH<8 decreases with the scan rate, this indicates that there is a chemical reaction preceding the electron transfers.

The peak potentials were practically independent of the reactant concentration and the peak intensities were proportional to this variable. The peak potentials varied with the scan rate towards more positive values for the oxidation peaks (around 30 mV per decade of scan rate for Peak 1 and 20 mV for Peak 2) and towards less positive values for Peak 3' (around –17 mV per decade of scan rate).

Convolution voltammetry allows the use of diagnostic criteria for the electrochemical processes using logarithmic analyses based on the equation[17-23]:

$$E = E_{1/2} + b \ln[f(I, J)] \qquad (3)$$

where f(I, J), $E_{1/2}$ and b depend on the mechanism of the electrochemical reaction. E, $E_{1/2}$ and b have units of voltage.

The direct scans of the voltammograms of Peak 1, below pH 7.5 and at low scan rates, were analyzed using the f(I, J) corresponding to a reversible process[2]. The plots were linear, with

slopes close to 2.303RT/F (c.a. 0.059 V at 298 K). The analyses made with the equation corresponding to irreversible processes were not linear. Nevertheless, as the scan rate was increased, the analyses made with the equation corresponding to irreversible processes become more linear, and those corresponding to reversible processes, more curved. This must be due to a quasi-reversible character of the transfers, taking place at the potentials of Peak 1. This is supported also by the lower intensity of the reduction peak, and by the relatively high separation of the oxidation and reduction peaks.

In more basic media, the analyses of peak 1 were linear with slopes close to 0.059 V, when the function corresponding to EC processes was used[2].

The convoluted limiting current, J_L, of Peak 1 is independent of the scan rate, as is expected for a diffusion-controlled process, this suggesting again that the adsorption of gentisaldehyde on the electrode, if exists, is weak. In addition, J_L values of Peak 1 were proportional to reactant concentration.

On the basis of the above results and conclusions, the following scheme is proposed for the process occurring at the potentials of Peak 1:

$$(OH)_2PhCHO \rightarrow {}^{-}O(OH)PhCHO + H^{+} \quad (4)$$

$${}^{-}O(OH)PhCHO \rightarrow {}^{\bullet}O(OH)PhCHO + e^{-} \quad (5)$$

$${}^{\bullet}O(OH)PhCHO \rightarrow {}^{\bullet}O({}^{-}O)PhCHO + H^{+} \quad (6)$$

$${}^{\bullet}O({}^{-}O)PhCHO \rightarrow \text{quinone-CHO} + e^{-} \quad (7)$$

Where “quinone-CHO” is the product shown in the lower part of scheme 1.

The electron transfer shown in step (5) is reversible or quasi-reversible, being the rate-determining step (r.d.s.), the step (6). This reaction pathway corresponds to a two-electron process, which is first-order with respect to gentisaldehyde concentration and/or order –1 with respect to H^+ ion concentration. From this scheme it follows that the expected dependence of

the peak potential (or the half-wave potential of the convoluted voltammograms) is –2.303RT/F per pH unit (around –0.059 V at 298K).

Above pH 8.4[13] the reaction (4) does not takes place, this implying that the peak potential must be pH-independent, and that the oxidation scan must show one unique peak. However, the peak intensity decreases and the Peak 2 appears, as the pH increases, being both facts associated to the first dissociation reaction. In addition, the pH dependence of the peak potential indicates that it takes place the release of one H^+ ion before or in the r.d.s. Moreover, the convolution analysis of peak 1 is compatible with a reversible or quasi-reversible electron transfer. All these facts are only possible if the electroactive species changes from lower to higher pH values. Since the more abundant species in this pH range is the monoanion, the following reaction scheme is proposed:

$^{-}O(OH)PhCHO \rightarrow {}^{-}O(^{-}O)PhCHO + H^+$ (8)

$^{-}O(^{-}O)PhCHO \rightarrow {}^{\bullet}O(^{-}O)PhCHO + e^-$ (9)

$^{\bullet}O(^{-}O)PhCHO \rightarrow$ quinone-CHO $+ e^-$ (7)

The oxidation of both species, dianion and monoanion, must take place at very close potentials and, for this reason, no discontinuity is observed in the dependence of the peak and half-wave potentials with pH. The process is now of CEE type (chemical-electrochemical-electrochemical steps), that is, two electron transfers occurring at different potentials preceded by a fast chemical step. In this case, steps 8 and 9 correspond to Peak 1 and the step 7, to Peak 2. In very basic media, no H^+ ions are involved in the oxidation and the process is now of EE type (two electron transfers occurring at different potentials) integrated by steps 9 and 7.

One cannot exclude the above presented oxidation patterns could be changed if different kind of electrodes were used, both in cyclic voltammetry and controlled-potential electrolysis, but it is reasonable to think that these oxidation schemes are valid for carbon electrodes in general.

Because the experiments are made in nearly physiological conditions (aqueous media and relatively high ionic strength and especially those made at neutral pH values), radicals and radical anions appearing in the steps 5, 6 and 9 justify the antioxidant capacity of gentisaldehyde in the aspect of radical scavenging, because these radicals can act in SET (electron transfer based) type reactions[26,27], or even in HAT (hydrogen atom transfer based) type reactions by abstracting a hydrogen atom from the oxidizable substrate and interrupting the propagation of radicals[28].

Conclusions

The voltammograms of gentisaldehyde on GCE showed up three oxidation peaks and one reduction peak, depending on the number of cycles recorded and the pH. The possible oxidation products of this molecule could be either Gentisic Acid, formed by oxidation of the aldehyde group, or formyl-p-benzoquinone, formed by oxidation of the biphenolic ring. From experiments and constant potential electrolysis, made with gentisic acid and 1,4-dihydroquinone, it was concluded that the oxidation product is formyl-p-benzoquinone.

Based on both the electrochemical results and values of the dissociation constants, it was concluded that at $pH<pK_1$ ($pH<8.4$) the mechanism involves a first step corresponding to the loss of an H^+ ion from one of the –OH groups, followed by a first quasi-reversible electron transfer to give a radical, which losses a proton in a third step (r.d.s.). The next step is the second electron transfer to give the substituted 1,4-benzoquinone.

At pH values higher than pK_1 but lower than pK_2 ($8.4<pH<10.9$), the electroactive species is the anion, which losses an ion H^+ to give the dianion that losses an electron in the first electron transfer. The process is now of the CEE type, that is, two electron transfers occurring at different

potentials, preceded by a fast chemical step. At pH>pK_2 (pH>10.9) the process becomes of the EE type, and no H^+ ions are involved in the process.

Radicals species appearing in the electrochemical process justify the antioxidant capacity of gentisaldehyde in the aspect of radical scavenging, because these radicals can act in SET and HAT type reactions.

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Scheme and figure captions

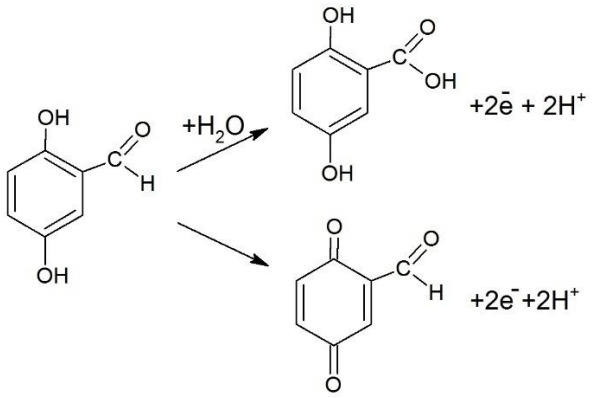
Scheme 1. Possible oxidation products of gentisaldehyde in aqueous media.

Figure 1. Cyclic voltammograms of the two first cycles at different pH values. Gentisaldehyde $1 \cdot 10^{-3}$ mol·L^{-1}, v = 0.1 V·s^{-1}.

Figure 2. Cyclic voltammograms of gentisaldehyde at 0.1 V·s^{-1}. Up: at pH 2.00 and compared with the corresponding carboxylic acid, and with the solution containing both compounds. Down: at pH 1.30 and compared with 1,4-dihydroquinone. All concentrations were $1 \cdot 10^{-3}$ mol·L^{-1}.

Figure 3. Comparison of $2 \cdot 10^{-5}$ mol·L^{-1} gentisaldehyde, the electrolysis product obtained at E = 0.700 V and gentisic acid at pH = 1.52.

Figure 4. First cycle of voltammograms of $1 \cdot 10^{-3}$ mol·L^{-1} gentisaldehyde at different pH values as a function of the scan rate.



Scheme 1

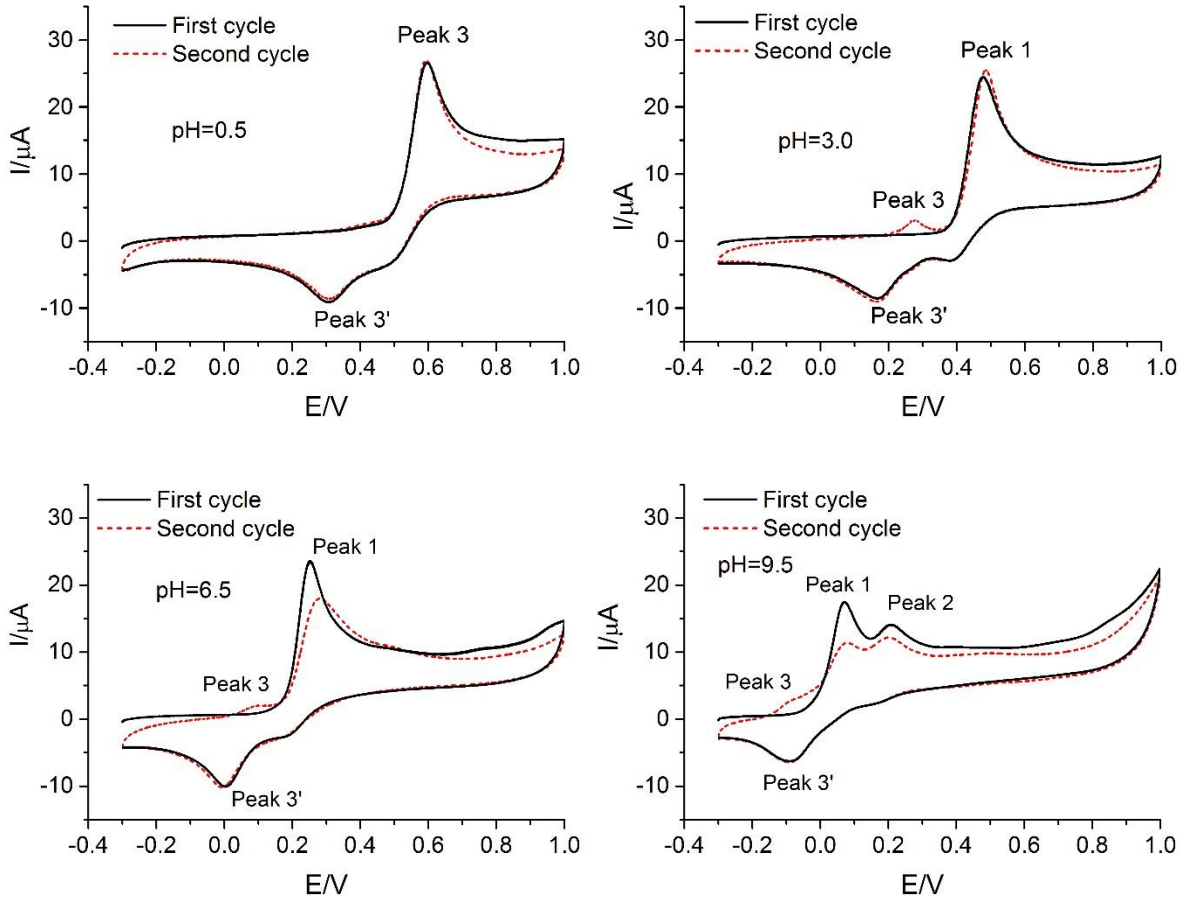

First cycle
Second cycle
pH=0.5
Peak 3
Peak 3'
I/μA
E/V
pH=3.0
Peak 1
Peak 3
Peak 3'
pH=6.5
Peak 1
Peak 3
Peak 3'
pH=9.5
Peak 1
Peak 2
Peak 3
Peak 3'

Figure 1

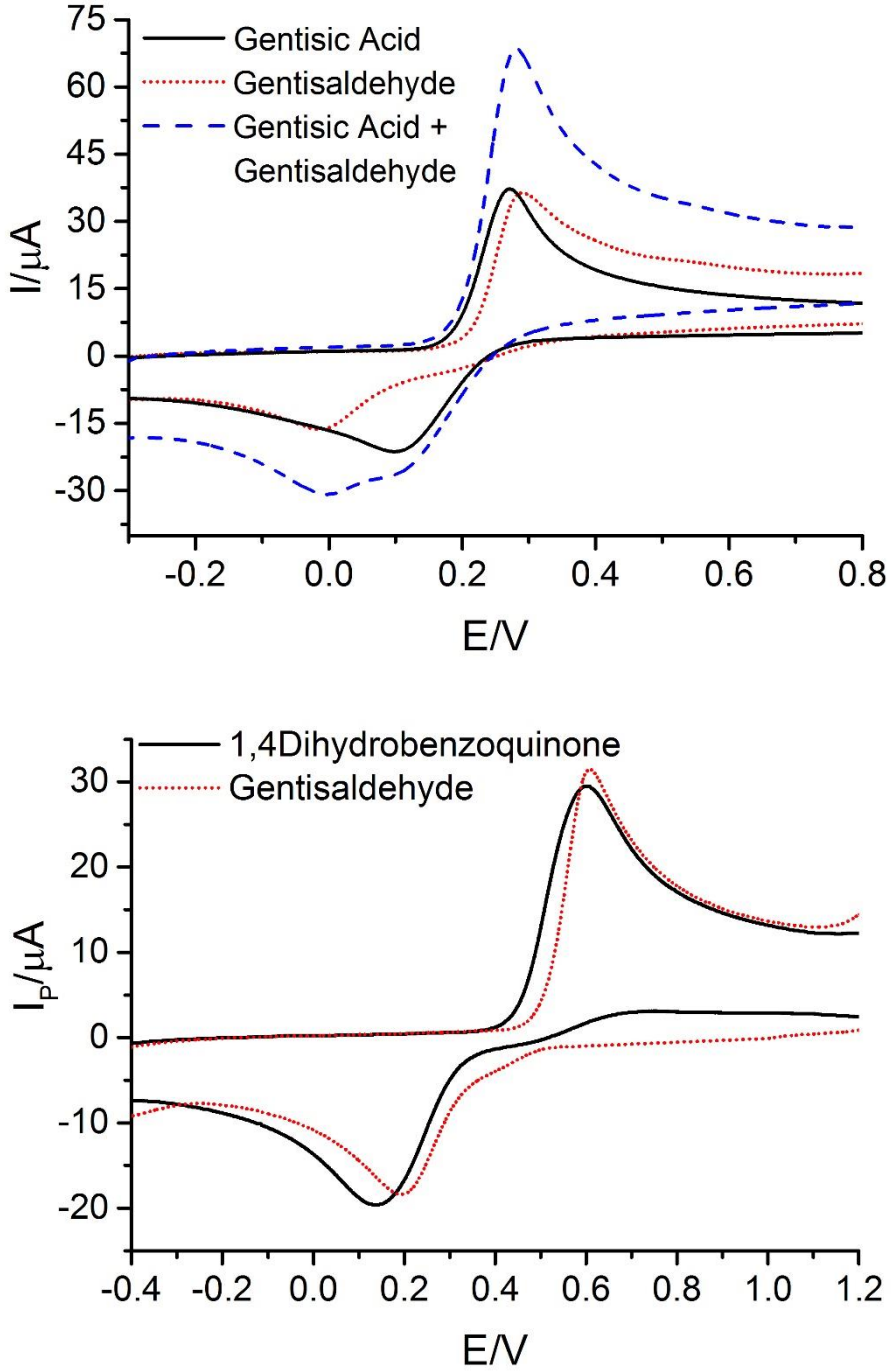

Gentisic Acid
Gentisaldehyde
Gentisic Acid +
Gentisaldehyde
I/µA
E/V
1,4Dihydrobenzoquinone
Gentisaldehyde
I_p/µA
E/V

Figure 2

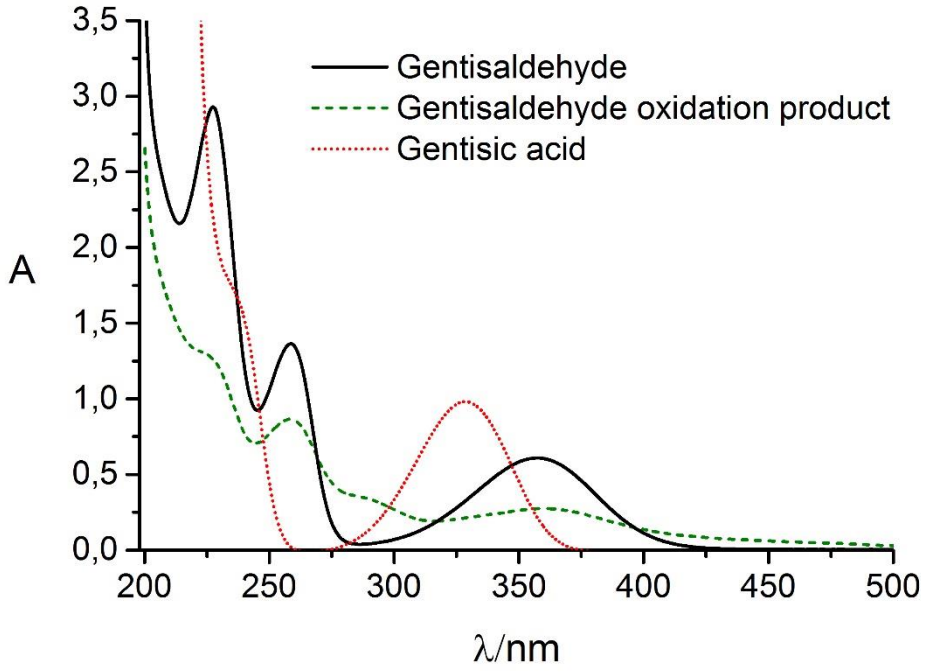

3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
A
200
250
300
350
400
450
500
λ/nm
Gentisaldehyde
Gentisaldehyde oxidation product
Gentisic acid

Figure 3

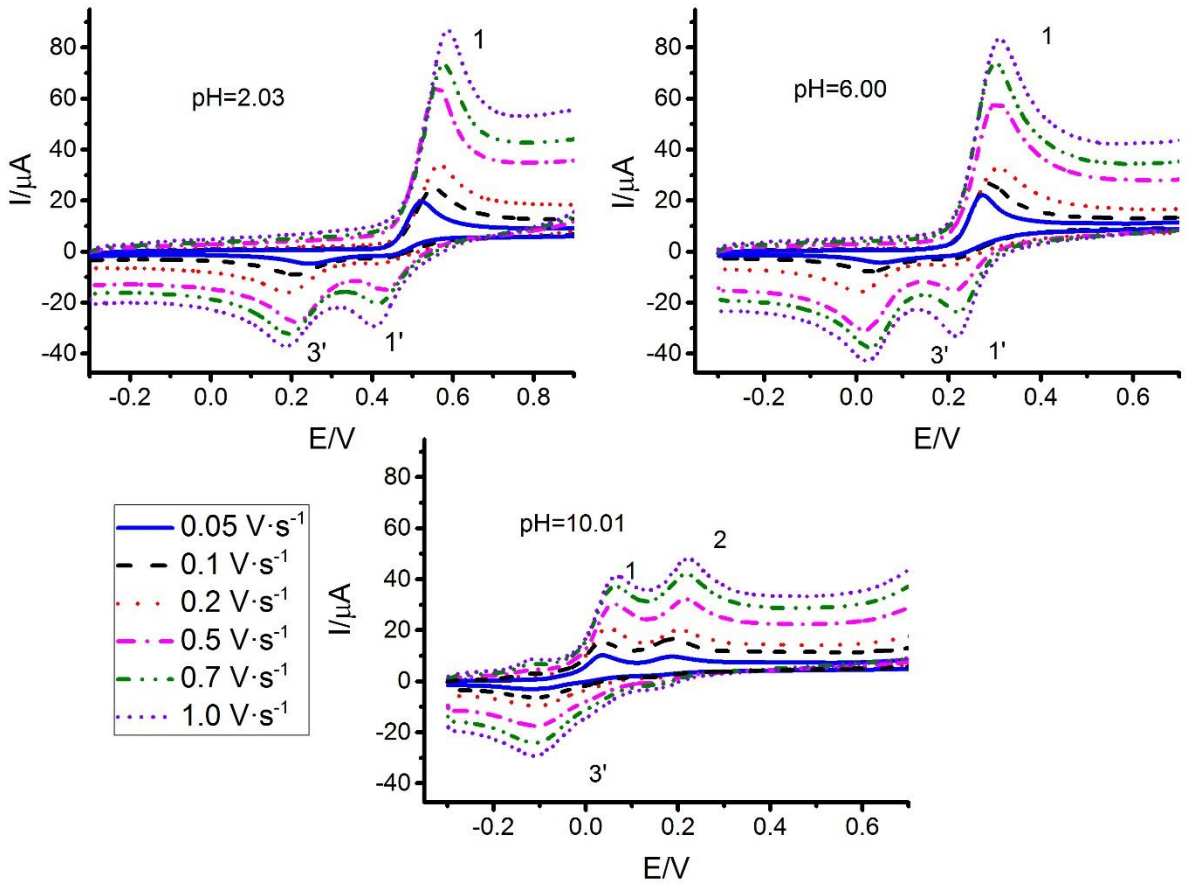

pH=2.03
pH=6.00
pH=10.01
I/μA
E/V
1
1'
2
3'
0.05 V·s-1
0.1 V·s-1
0.2 V·s-1
0.5 V·s-1
0.7 V·s-1
1.0 V·s-1

Figure 4

Research Highlights:

- The oxidation of gentisaldehyde on GCE gives formyl-p-benzoquinone.

- At pH <pK_1 the mechanism is CECE but at pH>pK_2 the process becomes of the EE type.

- Radicals species generated justify the antioxidant capacity of gentisaldehyde.