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Antioxidant Potential of Hydroxycinnamic Acids in Advanced Oxidation Processes

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The aim of the study was to describe the characteristics of a natural antioxidant derived from the group of the hydroxycinnamic acids (sinapic and ferulic acid). Electrochemical methods and other spectrophotometric assays were studied for the analysis to determine the mechanism of action in the advanced oxidation processes. ABTS and DPPH methods has been allowed to access the potential of natural compounds to scavenge free radicals, but the methods of FRAP and CUPRAC possible to determine the potential for reduction of copper and iron ions. The curve of the differential pulsed and cyclic voltammograms found that ferulic acid is oxidized in one step electrode, and sinapic acid in two stages electrode. Sinapic acid oxidizes easily with superior abilities of antioxioxidant. Based on the survey, it was found that both tested hydroxycinnamic acids have high potential of antioxidants.

Keywords: ferulic acid; synapic acid; electrooxidation; antioxidant; spectrophotometric assay

1. INTRODUCTION

Polyphenols are the most numerous group of secondary metabolites, have high antiallergic, anti-inflammatory, antimicrobial, antiviral, anticarcinogenic and antioxidant activity. Their formation in plants determine mechanisms such as temperature fluctuations, UV radiation, pest attacks and mechanical damage. These include phenolic acids, flavonoids and hydroxycinnamic acids [1-8]. Antioxidant activity of the phenolic acids and their esters depend on the number of hydroxyl groups in the molecule. Additionally, it can be enhanced by the effects of spherical. Cinnamic acid derivatives are effective antioxidants than benzoic acid derivatives due to the fact that the ability of the carboxyl group for receiving the electron has a negative effect on the donor hydroxybenzoate. Phenolic acids are

divided into hydroxy derivatives of benzoic acid or cinnamic acid. Unfortunately, hydrobenzoic acid is present in edible plants in very small amounts. Hydroxycinnamic acids are very widespread in nature through the phenylpropanoid pathway [9-17]. These compounds are most commonly found in the form of derivatives glycosylated or esters with acids: quinic, shikimate, rarely found in free form [18-25]. The most common acids hydroxycinnamic are caffeic acid, occurring among others in the wine, pears, apples, plums, tobacco leaves, potatoes, coffee, spinach, cabbage, lettuce, olive oil, ferulic acid, found in the seeds of barley, wheat, rye and oats acid, *p*-coumaric, the source of which are among other things, apple, black currant and cereals, sinapic acid, found in kale, and citrus juices [26-35]. This work reports the antioxidant activity of selected compounds of plant origin studied by using electrochemistry methods and ABTS, DPPH cation radical decolorization assay. The potential of these natural compounds to reduce iron and copper ions was determined using FRAP and CUPRAC methods based spectrophotometric analysis. Both methods electrochemical and spectrophotometric allow for qualitative assessment and quantitative samples phytochemicals [36-39]. The methods of analysis of antioxidant properties are an excellent complement its capabilities in this type of research. Made analysis are universal help investigate the effect of the molecular structure of natural chemical compounds on its behavior in oxidation reactions.

2. EXPERIMENTAL

2.1. Chemicals

Compounds tested it: ferulic acid ((E)-3-(4-hydroxy-3-methoxy-phenyl)prop-2-enoic acid, $C_{10}H_{10}O_4$) and sinapinic acid (3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoic acid, $C_{11}H_{12}O_5$). All chemicals were used of analytical grade supplied from Fluka (France) and Sigma-Aldrich (Germany). Electrochemical experiments were performed in non-aqueous media. The substrates solutions were prepared by dissolving in 0.1 mol L^{-1} $((C_4H_9)_4NClO_4$ in acetonitrile. 2,2-diphenyl-1-picrylhydrazyl (DPPH), neocuproine ≥98% and TPTZ 2,4,6 –tris(2-pyridyl)-s-triazine for spectrophotometric def of Fe≥99.0% were purchased from Sigma-Aldrich GmbH (Sternheim, Germany). 2,2'-azino-bis-(3-ethylobenzthioazoline-6-sulfonic acid) (ABTS) diammonium salt was purchased from AppliChem (Germany). Trolox®, 97%, 6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid was purchased from Acros Organics (USA). Copper chloride (CUPRAC) standard solution 0.01 mol L^{-1}, hydrochloric acid standard solution 0.04 mol L^{-1} and iron (III) chloride hexahydrate pure (FRAP) p.a. 99.0%, CH_3COONa – CH_3COOH buffer solution pH 3.6, 0.3 mol L^{-1} were purchased from CHEMPUR (Poland). ABTS, DPPH, FRAP and CUPRAC experiments were performed in aqueous media. Ethyl alcohol absolut 99.8% pure p.a. was obtained from POCH (Poland).

2.2. Measurement methods

2.2.1. Cyclic and differential pulse voltammetry

All electrochemical experiments were performed by using Autolab potentiostat PGSTAT 30 (Eco Chemie B.V., The Netherlands), equipped with the GPES 4.9 software. A conventional three-

electrode cell was used. The working electrode used in voltammetry experiments was a platinum electrode with geometric surface area of 0.5 cm^2 and platinum wire was used as the counter electrode. A potential of the working electrode was measured vs. ferricinium/ferrocene reference electrode (Fc^+/Fc). Determination of ferulic acid and sinapinic acid and the kinetic parameters of its electrode reactions was performed using cyclic (CV) and differential pulse (DPV) voltammetry. CV were recorded in the potential from 0 to 1.8 or 2.2 V with various scan rates (0.02 to 1 V s^{-1}). Differential pulse voltammograms were recorded in the same potential range with modulation amplitude 25 mV, pulse width 50 ms (scan rate 0.01 V s^{-1}).

Before the measurements, the solutions were purged with argon in order to remove dissolved oxygen. All experiments were carried out at 25±1 °C.

2.2.2. DPPH radical-scavenging activity

The ability to scavenge free radicals was examined using the method DPPH. The ethanol solution of the DPPH (2.0 ml) with a concentration of 40 mg/ml (0.1 mM) was added to 0.5 ml of an alcohol solution (80% ethanol) that contained 0.02 mg/ml antioxidant. Then, 10 minutes after mixing, the absorbance of the solutions was determined by UV-Vis spectra at 516 nm. UV-VIS spectra were recorded with a Thermoscientific Evolution 220 spectrophotometer (2015, USA). As a blank, 70% ethanol was used [40-41]. The capability to scavenge the DPPH radical (AA%) was determined using following equation:

$$\text{Inhibition (A \%)} = [((A_0 - A_1) / A_0) 100] \quad (1)$$

where A_0 was the absorbance of the control and A_1 was the absorbance in the presence of the sample of antioxidant.

2.2.3. ABTS radical-scavenging activity

The ability of hydroxycinnamic acids to scavenge free radicals was evaluated by using ABTS assay. Potassium persulfate (2.45 mM) and ABTS (6 mM) solution were mixed in ethanol, then the mixture was allowed to stand for 16 h. The ABTS /radical solution was diluted with ethanol to an absorbance of 0.70 at 734 nm. UV-VIS spectra were recorded with a Thermoscientific Evolution 220 spectrophotometer, produced in 2015 in the USA. After the diluted ABTS•+ solution (6.0 ml) was added to a 50 µL of each antioxidant solution (6 mg/ml) or Trolox. The inhibition level was calculated using the standard curve of absorbance at 734 nm. Results are presented as Trolox equivalent antioxidant capacity (TEAC), mmol Trolox/100 g antioxidant [42-44].

2.2.4. FRAP assay

The ability to reduce ferric ion (Fe^{3+}-TPTZ complex) under acidic conditions was determined using the method of FRAP.

The analysis involves the study of change in absorbance of blue-colored ferrous form (Fe^{2+}-TPTZ complex) at 595 nm. FRAP reagent was obtained by the addition of 25 mL of acetate buffer (0.3 M, pH 3.6), 2.25 ml of TPTZ solution (10 mM TPTZ in 40 mM HCl) and 2.25 mL of $FeCl_3$ (20

mM) in water solution. Sinapic acid and ferulic acid were dissolved in ethanol. The reaction mixture was held at 37°C for 4 min.

2.2.5. Cupric ions (Cu^{2+}) reducing-CUPRAC assay

$CuCl_2$ was mixed with 0.25 ml (0.01 M), 0.25 ml of an ethanol solution neocuproine ($7.5x10^{-3}$ M) and 0.25 ml of buffer solution CH_3COONH_4 (1 M) in the test tube, followed by addition of various concentrations of samples of antioxidants. Then, the final volume was made up to 2 ml with distilled water and mixed. The pipes were sealed and left at 24°C. Absorbance was measured at 450 nm against a reference sample (water), after waiting for 30 minutes. Increased absorbance of the resulting solution indicates increased reduction capacity of copper ions (Cu^{2+}).

2.2.6. Statistical analysis

Results are presented as the means and the standard deviation of three independent extractions (n=3). Statistical analysis was calculated by using Fischer LSD test (significance level was set at $p< 0.05$).

3. RESULTS AND DISCUSSION

3.1. Electrochemical behaviour of ferulic acid and sinapic acid at Pt electrode

Electrochemical reactivity of ferulic acid and sinapic acid was investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

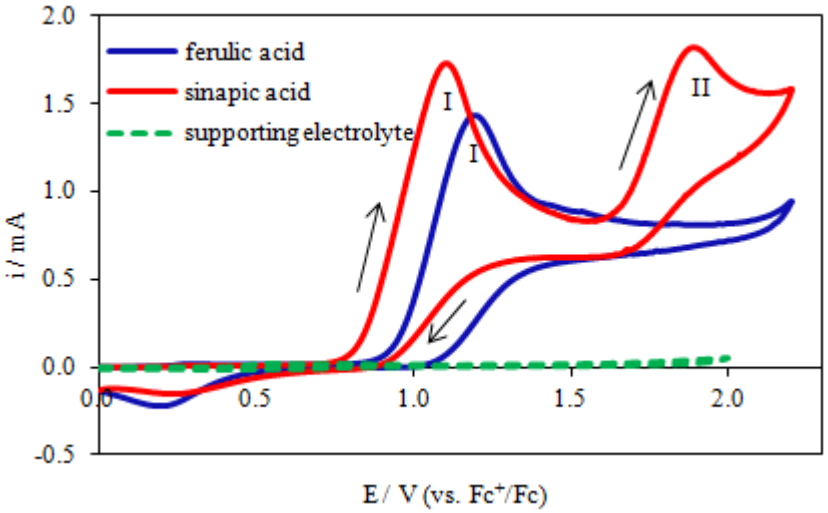

Figure 1. Cyclic voltammogram (CV) oxidation investigated acids in non-aqueous environment; c = 5 x 10^{-3} mol L^{-1} in 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile, v = 0.1 V s^{-1}.

Cyclic voltammetry (CV) and DPV they seem to be a suitable tool in antioxidant assays due to its simplicity, fastness and expempted from pre-treat samples [45, 46]. Sample CV shown in Fig. 1.

Ferulic acid irreversibly oxidized in at least one stage before the electrode potential decomposition of the electrolyte. Peak potential (E_p), the oxidation of ferulic acid is 1.19 V. Sinapinic acid is oxidized more easily than ferulic acid to a lower potential in at least two stages electrode. E_p first oxidation step sinapinic acid is 1.085 V, while the second oxidation step is 1.88 V. DPV electrooxidation of acids tested are shown in Fig. 2. DPV method provides high sensitivity compared with CV. The peak potential (E_p) determined from DPV corresponds to the half-wave potential ($E_{1/2}$) determined from the CV. From the relationship shown in Figure 2 also shows that ferulic acid is oxidized in one step electrode, and sinapinic acid in two stages electrode.

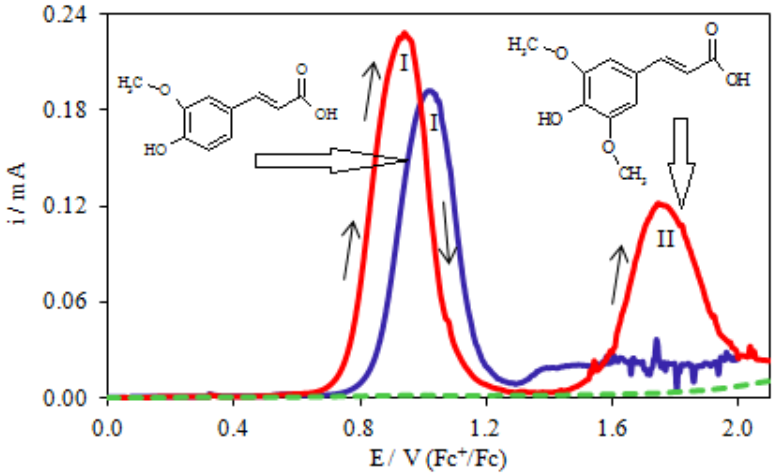

Figure 2. Differential pulse voltammogram (DPV) oxidation of ferulic and sinapinic acids in non-aqueous environment; c = 5 x 10^{-3} mol L^{-1} in 0.1 mol L^{-1} (C_4H_9) $4NClO_4$ in acetonitrile.

Useful information about the mechanism of electrooxidation of the test compound provides a peak current dependence on the speed of the polarization tested reaction. Therefore, the study also included the impact of the speed of the polarization on the current value and potential of electrooxidation of ferulic acid and acid sinapinic. In the cyclic woltamperogramów made for various speeds determined peak potential (E_p), half-peak potential ($E_{p/2}$), half-wave potential ($E_{1/2}$) and peak current (i_p).

To determine the nature of the electrode reaction that takes place in conditions of diffusion line, or is controlled by adsorption, examine the relationship ip from $v^{1/2}$ and ln i_p of ln v. Fig. 3 shows the dependence of the current peak (i_p) the root of the speed of polarization ($v^{1/2}$).

The relationships shown in Fig. 3 are linear, but do not pass through the origin of a coordinate, suggesting that the test electrooxidation reactions of the tested acids can be controlled by adsorption. In this connection it has been made as ln i_{pa} of ln v and v shown in Fig.4. Dependencies are linear and described by the following equations:

for ferulic acid $\ln i_{pa} = \{0.411\ \ln v(V\ s^{-1})\}$ mA + 1.232 mA, $R^2 = 0.998$ (1)

for sinapic acid (I step) $\ln i_{pa} = \{0.364\ \ln v(V\ s^{-1})\}$ mA + 1.351 mA, $R^2 = 0.996$ (2)

for sinapic acid (II step) $\ln i_{pa} = \{0.374\ \ln v(V\ s^{-1})\}$ mA + 0.769 mA, $R^2 = 0.998$ (3)

The slope of the regression line for the electrooxidation of ferulic acid is 0.411, for the first stage of electrooxidation of sinapic acid is 0.364, while for the second stage is 0.374, which indicates the

nature of the diffusion studied electrode reactions. If the slope is equal or close to 0.5 that means a diffusion-control of the electrode process. Otherwise, if the slope is equal or close to 1.0 than the process is controlled by adsorption [47,48].

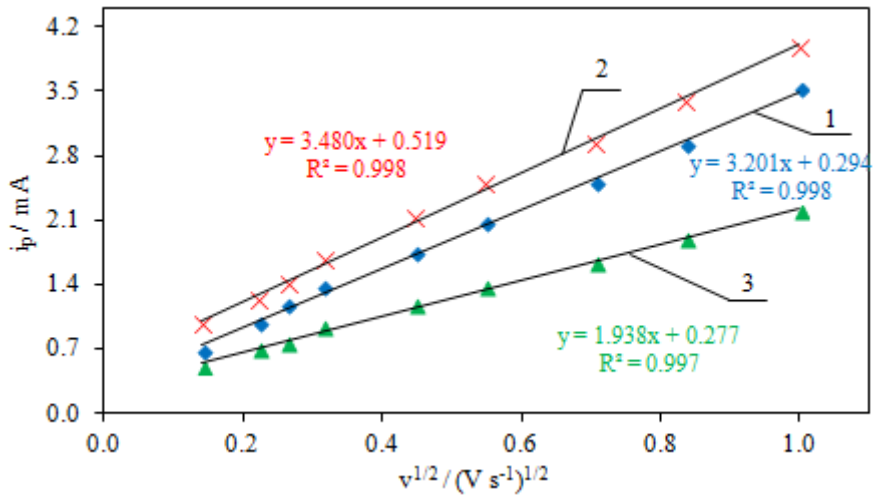

Figure 3. The dependence lnv of the peak current (i_p) of the element of speed polarization electrooxidation ($v^{1/2}$): curve 1 - ferulic acid, curve 2 - sinapic acid (one stage), curve 3 - sinapic acid (second stage).

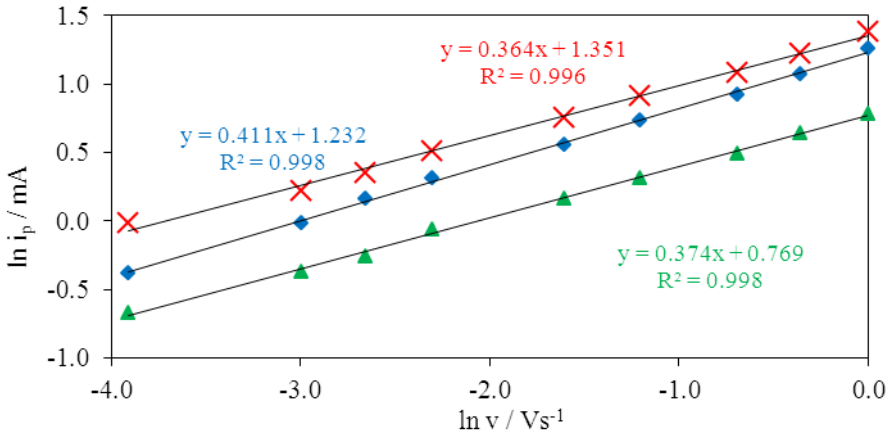

Figure 4. Dependence ln i_p od ln v for the electrooxidation of respondents acids; c = 5 x 10^{-3} mol L^{-1} in 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile.

On the basis of the determined values (E_p, $E_{p/2}$, $E_{1/2}$), the anodic transfer coefficient (βn_β) and heterogeneous rate constant (k_{bh}) were calculated according to the equations presented in papers [49,50]. The results are shown in Table 1. On the basis of calculations it can be concluded that the sinapic acid is oxidized more easily (at a lower potential) and the electron exchange between the electrode and the compound occurs at a higher rate than ferulic acid. K_{bh} of electrooxidation sinapic acids in the first step is 3.52 x 10^{-4} cm s^{-1}, whereas the second stage is oxidized at a slower rate and is 3.21 x 10^{-4} cm s^{-1}.

Table 1. Values of peak potential (E_p), half-wave potential ($E_{1/2}$), anodic transition coefficient (βn_β), and heterogeneous rate constant (k_{bh}) determined for the half-wave potential in the electrooxidation of acids; c = 5 x 10^{-3} mol L^{-1} in 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile, v = 0.01 V s^{-1}.

Compounds	E_p (V)	$E_{p/2}$ (V)	$E_{1/2}$ (V)	βn_β	$D \times 10^6$ ($cm^2\ s^{-1}$)	$k_{bh\ E1/2} \times 10^4$ (cm s^{-1})	E_{HOHO} (eV)
ferulic acid	1.19	1.06	1.13	0.37	6.69	3.43	-8.854
Sinapic acid (I step)	1.10	0.96	1.03	0.29	6.17	3.52	-8.754
sinapic acid (II step)	1.89	1.76	1.83	0.39	6.17	3.21	---

The obtained electrode reaction kinetic parameters ($E_{1/2}$ for electrooxidation of acids) can be correlated with the E_{HOMO} obtained by quantum-chemical calculations. Distribution of loads of electrons in the investigated molecule is uneven and determines the reactivity of each position (Figure 5). Most susceptible to oxidation are the places near hydroxyl groups. The oxidation process corresponds to removal of charge from the HOMO orbitals. In order to obtain the energies of electron removal (ionization potential) considered in the energies of the corresponding Frontier Orbitals affected by oxidation (HOMO). The E_{HOMO} values for all of the studied acids were determined via calculation and correlation to the $E_{1/2}$ of the first electrooxidation step. The more negative the value of energy E_{HOMO}, the harder molecule oxidizes.

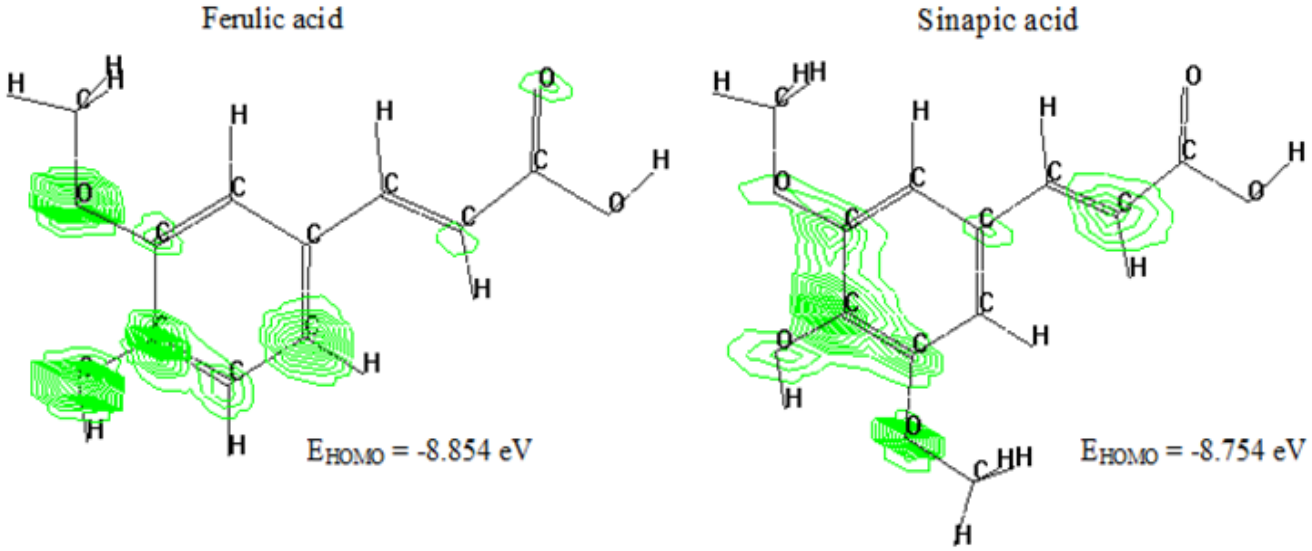

Figure 5. The HOMO frontier molecular orbitals of the compounds.

On the basis of the determined values of $E_{1/2}$, and the calculated energy E_{HOMO} (Table 1) it can be concluded that the sinapic acid is oxidized more easily than ferulic acid. It can be clearly describe, that sinapic acid is characterized by improved antioxidant properties.

3.2. Evaluation of the antioxidant capacity of the cinnamic derivatives by using ABTS, DPPH, FRAP and CUPRAC spectrophotometric assays.

Antioxidant activity of selected compounds determined by ABTS and DPPH is depicted in Fig. 3 and 4. The activity of inhibiting increases linearly in the method ABTS (table 2, figure 5) both ferulic acid as for sinapic acid. Ferulic being stronger acid has the potential to scavenge the ABTS radicals, wherein the concentration of 30 μg ml^{-1}recorded AA equal to 52.6 ± 0.47 and in the same method at the same concentration sinapic acid AA has activity at a lower level of about 13.2%. The reverse trend was observed for DPPH method, namely ferulic acid has a lower potential for DPPH radical scavenging by several percent (Figure 6).

Table 2. Free radical scavenging ability of the ferulic and sinapic acid by the DPPH and ABTS assays.

Concentration (μg ml^{-1})	**Inhibition (%)**			
	Ferulic acid		Sinapic acid	
	ABTS	DPPH	ABTS	DPPH
5	10.8±0.29	1.7±0.18	8.4±0.46	3.6±0.25
10	19.7±1.25	3.3±0.22	14.7±0.20	9.4±0.19
15	25.6±1.32	5.4±0.17	20.2±0.55	10.5±0.07
20	33.8±0.91	7.5±0.68	25.0±0.22	12.8±0.09
25	38.9±0.65	7.7±0.68	30.1±0.66	15.2±0.48
30	52.6±0.47	11.6±0.01	39.4±0.44	17.3±0.10

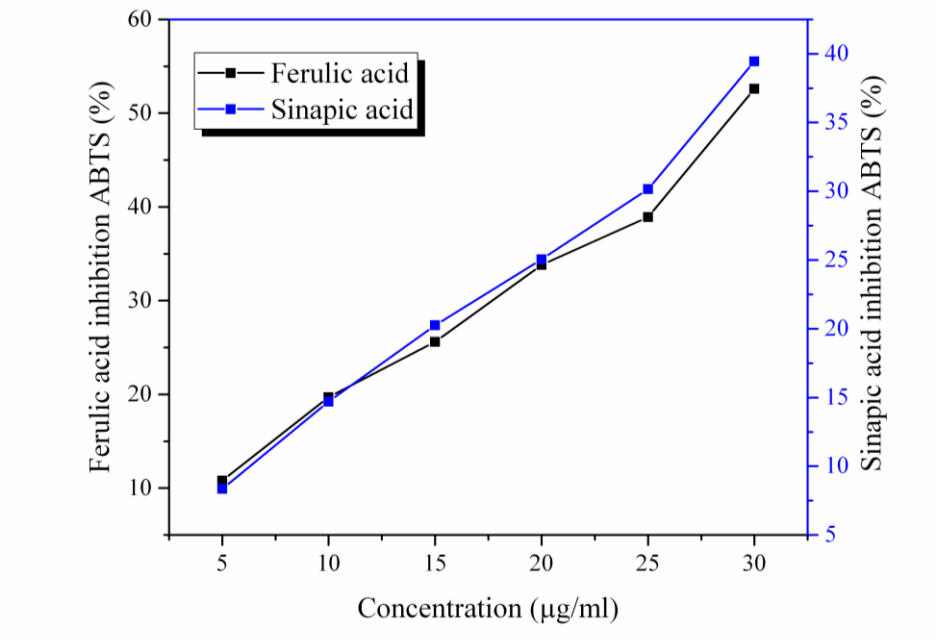

Figure 6. Activity of 2,20-azino-bis-(3-ethylbenzothiazoline-6 sulphonic acid of scavenging capacities of the ferulic and sinapic acid.

The antioxidant power of phenolic compounds of natural origin as well as hydroxycynaminic acids is known to be highly associated with the structure, primarily to electron delocalization in the aromatic molecules. Phenoxyl radical formed is stabilized by the resonance effect of the aromatic ring and hydrogen bonding.

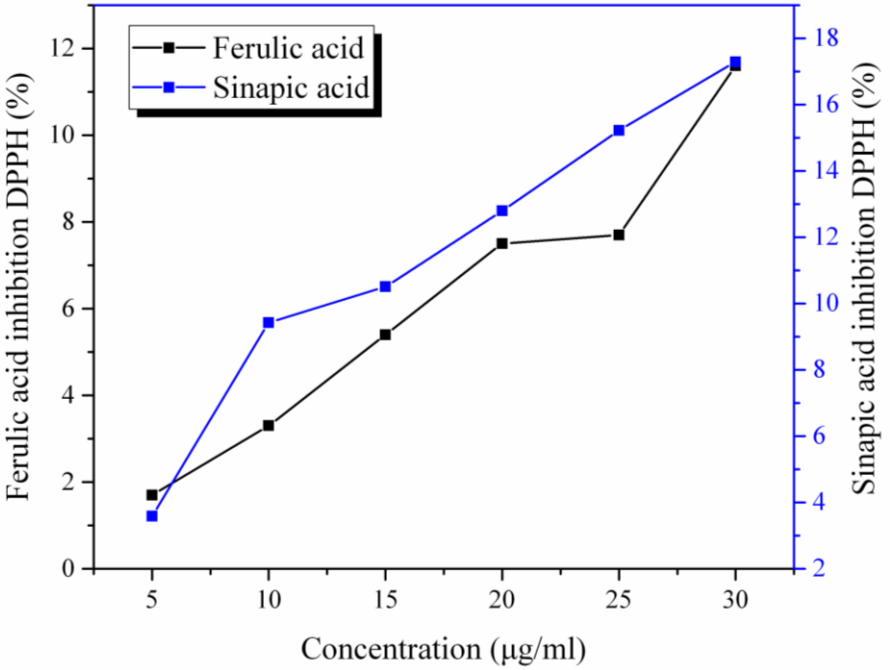

Figure 7. Activity of 2,2-diphenyl-1 picrylhydrazyl scavenging capacities of the ferulic and sinapic acid.

Table 3. Total antioxidant (FRAP) activity of the ferulic and sinapic.

Concentration (µg ml^{-1})	**FRAP (ΔA*100%)**	
	Ferulic acid	Sinapic acid
5	5.5	5.7
10	12.5	11.4
15	12.6	14.7
20	18.2	20.4
25	19.9	24.4
30	21.1	28.2

The strength of natural antioxidant compounds may be due to the different properties associated with the mechanism of action in the redox reaction. Tested antioxidants the same as those of other phytochemicals have a strong influence on the reaction of generation of radical, which is catalyzed by transition metal ions. Among other things, the reduction of metal ions with a variable valence, such as iron is evidently activity affecting the inhibition of the oxidation processes. Much more active reduction of iron ions shows sinapic acid, the biggest jump of activity for the reduction of this acid was observed when changing concentrations of 5 to 10 µg ml^{-1}. Then, the linear trend seen in the direction of increasing the antioxidant function of concentration. In the case of the curve changes

ferulic acid reducing power of iron ions it is linear while the antioxidant at a concentration of 20 to 25 10 μg ml^{-1}.capacity reduction is almost the same. Undeniably a greater duty to the activity for the reduction of iron ions according to the method FRAP shows sinapic acid (Figure 8, Table 3).

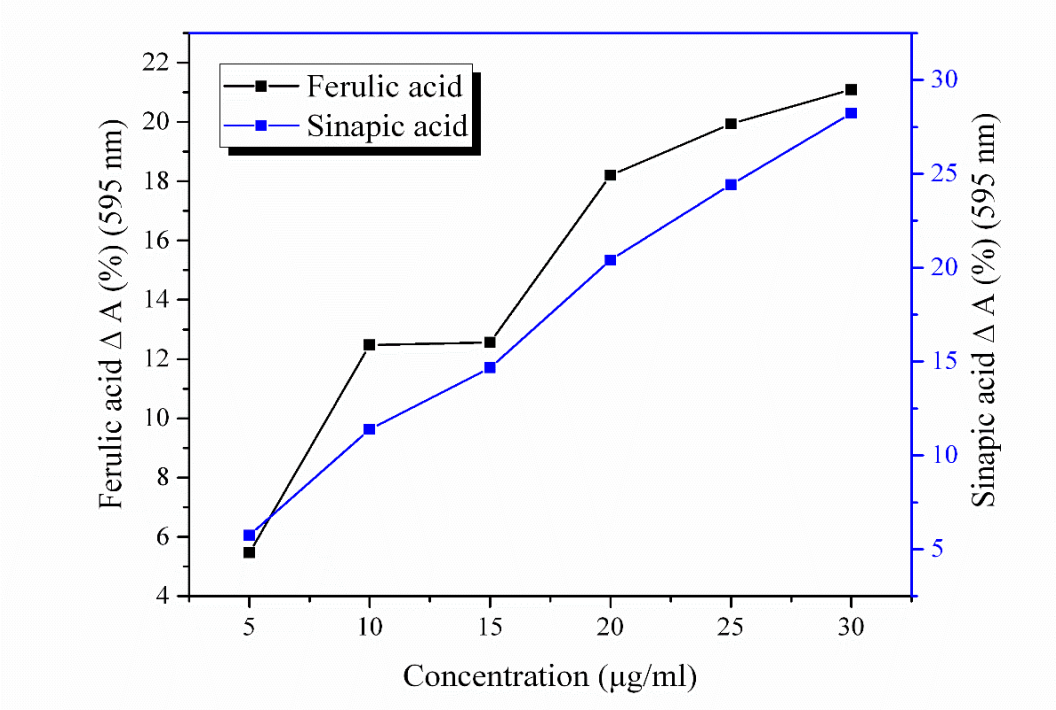

Figure 8. Ferric reducing antioxidant power capacities of the ferulic and sinapic acid.

CUPRAC assay is used for the analysis for determining the ability of phytochemicals for the reduction of copper ions and has been classified as one of the electron transfer-based methods. Thoroughly tested ability to reduce complex neocuproine cupric (Cu (II) -NC), which shows maximum light absorption at 450 nm. On the basis of the data calculated by the method CUPRAC activity for the reduction of copper ions (Cu(II)/Cu(I)) are both ferulic acid and sinapic acid is high. Slightly more active reduction in the present case, however, has a sinapic acid (Figure 9, Table 4).

Table 4. Antioxidant capacities of the ferulic and sinapic acids as measured by CUPRAC method.

Concentration (μg ml^{-1})	**CUPRAC (ΔA)**	
	Ferulic acid	Sinapic acid
5	0.28	0.29
15	0.66	0.82
10	0.65	0.53
20	0.97	1.11
25	1.11	1.38
30	1.14	1.47

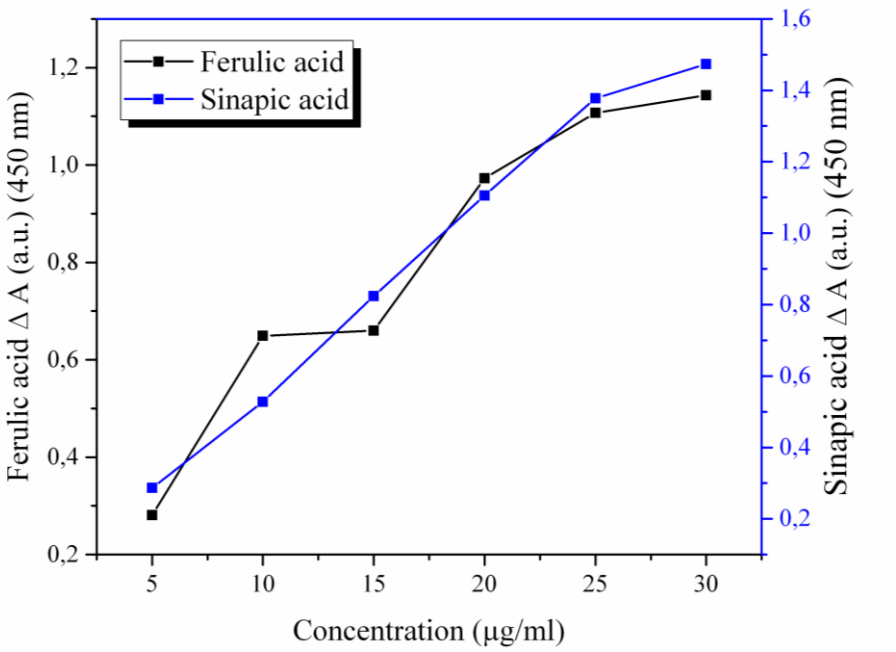

Figure 9. Cupric reducing antioxidant capacity of the ferulic and sinapic as measured by CUPRAC method.

4. CONCLUSIONS

Behavior of ferulic acid and sinapinic acid on a platinum electrode were tested using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in a non-aqueous medium. Electrooxidation was investigated acid diffusion controlled, all the stages are irreversible. Sinapic acid oxidizes in at least two stages electrode, and ferulic acid in at least one stage electrode. Based on the determined and calculated kinetic parameters with CV and quantum-chemical it may be stated that sinapic acid has better antioxidant than ferulic acid.

Undoubtedly, on the basis of the analyzes can be confirmed very high antioxidant activity both as sinapic acid and ferulic acid. Tested phytochemicals inhibits the oxidation of both rollers scavengers and have a high reduction potential relative to the iron or copper ions that are responsible for catalyzing oxidation.

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