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Antioxidant and Antiradical Properties of Green Tea Extract Compounds

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Green tea is currently an area of intense scientific research because of its exceptional and effective actions in anticancer therapy. The aim of this research was to determine the antioxidant properties of polyphenols contained in green tea. Examined was the correlation between bioingredients of the product tested and the ability to scavenge free radicals and reduce them by chelating the variable metal ion. A range of innovative research technology combines HPLC with electrochemical (cyclic and differential pulse voltammetry) and spectrophotometric (ABTS, FRAP and DPPH assays) analysis to rate the potential oxidation-reduction components of green tea. Described is the dependence of the chemical structure on antioxidant properties. It was found that a high content of catechins and esters of the gallic-type had a powerful influence on the antiradical properties of the studied tea extract.

Keywords: Green tea; Electrochemical oxidation; UV–VIS; Antioxidant; ABTS, DPPH

1. INTRODUCTION

Currently, intense research on substances with antioxidant properties is being conducted. The mechanism of oxidation reactions is strictly dependent on the chemical structure of the compound. Of interest are derivatives of plants that have high antioxidant activity, such as flavonoids, which are plant based compounds that also act as natural dyes. There are over 6000 known substances in this group [1-6] Due to the different positions of the hydroxyl group in the structure, they can be characterized by specific properties, such as pro-oxidizing and biocides. Publications in recent years mainly concern their antioxidant activity and the mechanism of oxidation and reduction.

The high antiradical activity is derived from hydroxyl groups at specific positions in the structure, such as ortho-hydroxylation on the B-ring and the C2-C3 double bond in the C-ring of the flavonoid. The high content of individual catechins, such as EGCG and EGC, affects the antioxidant potential of tea [7-10].

Flavonoids are mainly analysed in terms of their use for medicinal purposes. They exhibit anti-inflammatory properties; it was confirmed that they can also reduce blood pressure, strengthen the cell walls of blood vessels, and improve the immune system. They have an anti-atherosclerotic effect by inhibition of aggregation lipoproteins (LDL) responsible for transporting the so-called bad cholesterol. Teas are imported from around the world including Vietnam, China, Japan and Thailand. Their origin often determines the values of healing. The impact of growing conditions of green tea affects its contents in terms of polyphenols. Therefore, research on these phytochemicals today is undoubtedly needed [11-14]. Many publications include studies of the antioxidant activity of the total content of polyphenols. Most of the polyphenols of plant origin are characterized by a very low stability. The aim of our study was to analyse the mechanism of an antioxidant mixture of flavonoids derived from green tea extract [15-17].

The presented publication was created for the determination of whether multiple condensed dose levels show higher antioxidant potentials compared to isolated antioxidants. Several substances from the flavonoids group in one mixing may produce a synergistic effect or antagonistic oxidation reactions. Shahidi and Wanasundara [5] have defined polyphenols as the powerful chain breaking antioxidants. [18] presented information about cancer-preventive or anticancer activities of tea. Sadzuka et al. [19] describes the results regarding the use of biochemical modulators in cancer therapy. Additionally, Sochor et al., Belfar et al., Masek et al., [20-23] describe the significant results of research on the positive effect of polyphenols from green tea anti-cancer prevention. This submitted manuscript presents the antioxidant polyphenon in various mixtures of oxidizing electro-oxidation induced currents in the ability to scavenge free radicals and reduce iron ions. To evaluate the activity to deactivate free radicals, spectrophotometric methods relying on the mechanism of hydrogen atom transfer and single electron transfer were used [24-27].

The described methods are a great tool to examine the ability to inhibit the oxidation processes of chemical compounds, for example, preventing lipid peroxidation. The applied research methods do not require special preparation of samples or specialized equipment and are low cost. The great advantage of the methods used is a high sensitivity and a very small amount of material needed for analysis [28-33].

The antioxidant activity of polyphenon 60 has been noted in several studies. The aim of the present work is to characterize the antioxidant and antiradical performance of green tea extract using electrochemical and DPPH, ABTS radical model systems, respectively.

2. EXPERIMENTAL

2.1. Chemicals

Polyphenon 60 (powder: carbon 54.0 - 56.5 %, nitrogen < 3.5 %; total catechin content > 60 %) was used of analytical grade supplied from Sigma-Aldrich. The substrates solutions of electroanalysis

were prepared by dissolving in 0.1 mol L^{-1} ($(C_4H_9)_4NClO_4$ in acetonitrile from Poch (Poland). Concentrations of flavones it was in range on 1×10^{-3} mol L^{-1} to 5.0×10^{-3} mol L^{-1}. Chemicals of chromatography: (+)-Catechin, (-)-epicatechin, (-)-epicatechin gallate and (-)-epigallocatechin gallate were purchased from Sigma (Steinheim, Germany), and (-)-epigallocatechin and procyanidin B1 were purchased from Phytolab (Vestenbergsgreuth, Germany).

2.2. Measurement methods

Phenolic profile of Polyphenon 60.

The phenolic profile was determined using a high-performance liquid chromatography system (Waters, Milford, MA) that consisted of a gradient pump (1525), photodiode array detector (2998), auto-injector (2707), and Breeze 2 system controller equipped with a 250 × 4.6 mm i.d, 5 µm Symmetry C18 column (Waters). The mobile phase was a binary gradient with A, water/formic acid (90:10, v/v), and B, water/acetonitrile/formic acid (40:50:10, v/v/v), with a flow rate of 1 mL min^{-1} [34]. The binary gradient was as follows: 12% B (0 min), 12- 30% B (0-26 min), 30-100% B (26-40 min), 100% B (40-43 min), 12% B (43-48 min), and 12% B (48-50 min). The separated flavanols and gallic acid were detected and measured at 280 nm. The identity of these compounds was based on the congruence of retention times and UV spectra with those of pure authentic standards. Flavonols were detected at 360 nm and were quantified as quercetin 3-*O*-glucoside. The results were calculated as mg of compound in 1 g of Polyphenon 60.

Scavenging of DPPH radicals

The free radical scavenging of polyphenon 60 was evaluated using DPPH. An ethanol solution of DPPH (2.0 mL) at a concentration of 40 mg mL^{-1} (0.1 mM) was appended to 0.5 mL of an ethanol solution (70% ethanol) containing 0.02 mg mL^{-1} of polyphenon 60-DPPH solution, which has a purple colour with a maximum absorbance at a wavelength of 517 nm. During the reaction, the colour of the solution disappears. The progress of the reaction can be spectrophotometrically monitored at a wavelength of 517 nm. As a blank, 70% ethanol was used. The inhibition level (%) of DPPH was calculated by using the following equation:

$$\text{Inhibition (\%)} = [(A_o\text{-}A_1)A_o^{-1}] \times 100 \quad (1)$$

where A_o was the absorbance of the control, and A_1 was the absorbance in the presence of polyphenon 60 [35-37].

Scavenging of ABTS radicals

The free radical scavenging of polyphenon 60 was evaluated using $ABTS^{\bullet+}$ method. The $ABTS^{\bullet+}$ radical was generated by the reaction of a 6 mM ABTS aqueous solution with potassium persulfate (2.45 mM) in the dark at room temperature for 15 h before use. The $ABTS^{\bullet+}$ solution

absorbance was adjusted with ethanol to 0.70 ± 0.02 at 734 nm at room temperature. The diluted $ABTS^{\bullet+}$ solution (4.0 mL) was mixed with a 40 µL aliquot of each investigated solution (2 mg mL^{-1}) or Trolox in ethanol; the absorbance was measured at 734 nm after 2 min at room temperature. Solvent blanks were run in each assay. The inhibition level (%) of absorbance was calculated using the standard curve prepared with Trolox (% inhibition level - µM Trolox). The effect of polyphenon 60 on scavenging $ABTS^{\bullet+}$ is referred to as the Trolox equivalent antioxidant capacity (TEAC) [38, 39, 29].

FRAP (Ferricion reducing antioxidant power) Fe^{3+} - Fe^{2+}

Various concentrations of polyphenon 60 in ethanol were mixed with sodium phosphate buffer (sodium phosphate buffer; 2.5 mL, 0.2 M, pH 6.6) and potassium ferricyanide (hexacyanoferrate (III) potassium), $K_3[Fe(CN)_6]$ (2.5 mL, 1%). The mixture was incubated for 20 min at 50 °C. Aliquots (2.5 mL) of trichloroacetic acid (10%) were added to the mixture. The upper layer solution (2.5 mL) was mixed with distilled water (2.5 mL) and $FeCl_3$ (0.5 mL, 0.1%), and the absorbance was measured at 700 nm. Increased absorbance of the reaction mixture indicates an increase in reduction capacity [40-41].

FRAP assay

The FRAP assay is based on reduction of the **Fe^{3+}**-TPTZ complex under acidic conditions. In this method, an increase in absorbance of the blue-coloured ferrous form (Fe^{2+}-TPTZ complex) is measured at 595 nm. FRAP reagent was freshly prepared by mixing 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 a water solution. Polyphenon 60 or Trolox was dissolved in ethanol. The reaction mixture was incubated at 37°C. The solution was stirred and incubated for 4 min. Finally, the absorbance of mixture was measured at 595 nm and calcutaded by using the following equation [42, 43]:

$$\Delta A=(A_4 - A_0) \quad (2)$$

A_0-absorbance attempts reagent A_4 - absorbance after 4 minutes of reaction.

Cuprac assay

These assays are based on the reduction of Cu(II) to Cu(I). Approximately 0.25 mL (0.01 M) of $CuCl_2$ was mixed with 0.25 mL of an ethanol solution neokuproiny (7.5×10^{-3} M) and 0.25 mL of buffer solution, CH_3COONH_4 (1 M), in the test tube followed by addition of different concentrations of polyphenon 60 or Trolox. The total sample volume was increased to 2 mL with distilled water and mixed. The tubes were sealed and maintained at room temperature for 30 min. At this time, the absorbance at 450 nm was measured against a reagent blank (water). An increase in absorbance of the reaction mixture indicates an increased capacity of reduction [42].

Electrochemical methods of analysis

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with an Autolab controlled by GPES software, version 4.8 (EcoChemie, The Netherlands). A three-electrode system was used for the measurements. Platinum was used as the working and auxiliary electrodes. The electrode potential was measured against a ferricinium/ferrocene reference electrode (Fc^+/Fc) [44, 45]. Before measurements were taken, the solutions were purged with argon to remove any dissolved oxygen. During measurements, an argon blanket was kept over the solutions. The effect of the scan rate and the substrate concentration on the electrooxidation of polyphenon in a non-aqueous medium was assessed. All of the experiments were performed at room temperature.

S*tatistical analysis*

Calculations were made for the means and standard deviations of three independent extractions (n=3). Statistical analysis was applied for the comparison of the means and then performed using a Fischer LSD test (the significance level was set at $p<0.05$).

3. RESULTS AND DISCUSSION

3.1. HPLC analysis of tea extract

Using the HPLC method, polyphenon 60 was analysed to determine the content of various flavonoids (Figure 1). The content of the identified flavanols of qualitatively and the quantitative in Polyphenon 60 preparation is presented in Table 1.

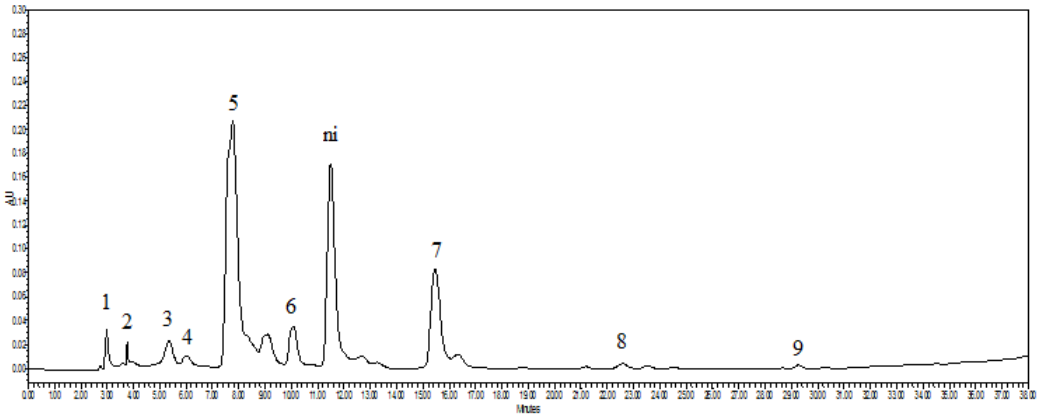

Figure 1. HPLC chromatogram of Polyphenol 60 at 280 nm.

The (-)-epigallocatechin gallate and (-)-epigallocatechin were the most predominant flavan-3-ols in preparation and constituted 37.5% and 36.2% of the total flavanols, respectively. Polyphenon 60 also contains gallic acid and flavonols at concentrations below 8 mg/g.

Table 1. Average concentration of phenolic compounds (mg/g) in Polyphenon 60 preparation.

peak	phenolic compounds	concentration[1]
1	gallic acid	7.18 ± 0.77
2	procyanidin B1	25.75 ± 0.54
3	(-)-epigallocatechin	270.20 ± 17.00
4	(+)-catechin	36.81 ± 2.20
5	(-)-epigallocatechingallate	279.26 ± 14.94
6	(-)-epicatechin	68.60 ± 3.77
7	(-)-epicatechingallate	64.78 ± 3.65
8	flavonols	4.86 ± 0.57

[1] - Mean ± SD, n = 2

3.2. Antioxidant activity of polyphenon 60

To determine the chemical properties of natural antioxidants, several spectrophotometric methods were used. Activity was evaluated for each extract for reducing and chelating iron ions, scavenging of DPPH and ABTS, superoxide free radicals, as well as the decomposition of hydroperoxides, which is one of the main oxidizing agents. The reducing activity of compounds of plant origin is closely linked with the potential to donate hydrogen atoms to free radicals. The reaction mechanism of polyphenols from free radicals can proceed in two ways, one is a hydrogen atom transfer and the second is single electron transfer. The most dangerous forms of oxygen determining the oxidation processes are the oxide radical anion ($O_2^{\bullet-}$), hydrogen peroxide radical ($HO_2^{\bullet}OH^{\bullet}$), hydroxyl radical ($OH^{\bullet}$) as well as singlet oxygen ($^1O_2$), ozone (O_3) and hydrogen peroxide (H_2O_2). Catechins and gallic acid are considered to be two of the most important ingredients that improve human health. Processes of oxidation occur by many mechanisms, therefore it is very important to examine how they react with aggressive polyphenols and forms of oxygen. It is important that they have capacity for reduction and scavenging or deactivation of the unstable forms as hydroperoxides. The results obtained for the antioxidant activity of polyphenon 60 by the ABTS and DPPH methods are shown in Table 2 and Figure 2.

Table 2. Antioxidant activity of polyphenon60 by DPPH and ABTS assays.

Polyphenon	**Inhibition (%)**	
Concentration (μg ml^{-1})	**ABTS**	**DPPH**
10	12.7±1.64	8.0±0.26
28	24.3±0.74	11.1±0.77
45	26.8±0.59	11.6±0.66
62	39.6±2.46	20.7±0.36
79	41.6±2.84	21.6±1.40
110	45.9±2.11	24.4±0.72
247	69.4±2.72	58.2±1.88
363	93.6±2.00	78.3±2.08

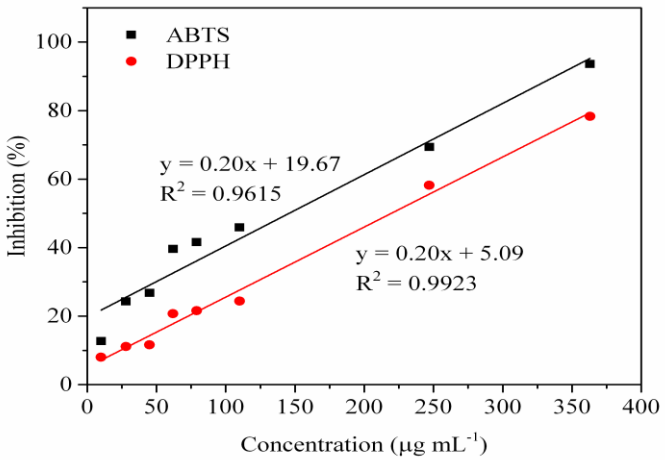

Figure 2. Correlation between total phenolic content and extract (polyphenon60) capacities measured by the ABTS and DPPH assays.

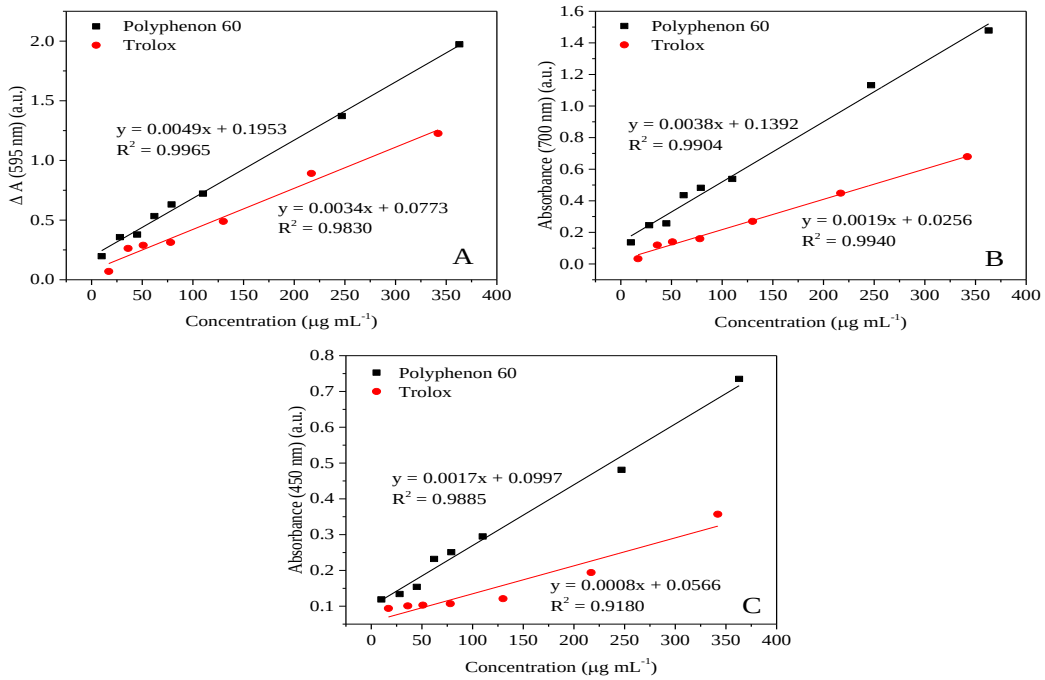

Figure 3. Correlation between total phenolic content and extract (polyphenon 60) capacities measured by the FRAP, CUPRAC assays.

In this paper, the activity of the specified mixture of polyphenols to inactivate various active forms of oxygen is presented. Examined was the affinity of the extract for scavenging as well as the reduction and chelation of metal ions for a variable valence assistive reaction with hydrogen peroxide.

Chromatographic analysis of the test product indicated the presence of large amounts of epigallocatechin gallate. EGC (epigallocatechin gallate) and GC (gallocatechin gallate) were characterized by the specific structural ortho-trihydroxyl groups in the aromatic B ring. Miller and

Rice-Evans, on the basis of their research, found that the activity of the scavenger is more strictly dependent with the esterification degree of gallates. Antiradical activity is measured spectrophotometrically by the change in absorbance maximum activity at 515 (DPPH) and 734 nm (ABTS). The tested material (polyphenon 60) undoubtedly shows strong antioxidant properties. Green tea extract has a very high activity towards scavenging free radicals, which increases as a function of the concentration of the tested reagents. For the concentration of 363 μg ml^{-1} of the extract, activity of the sweeping radical ABTS is 93.6%, while the activity for the scavenging DPPH is 78.3%. The deactivation of active free radicals in the investigated concentration range of 10 to 363 g mL^{-1} of extract is linear (Figure 3). Lee et. al. introduced in his work a range of antioxidant activity of green tea components by ABTS, DPPH and FRAP methods as follows: EGCg ≥ GCg ≥ ECg > EGC ≥ GC ≥ EC ≥ C [46].

Metal ions with a variable valence, such as iron, have a great impact on the course of the oxidation reaction. Therefore, in the present study we determine the ability of the tested extract to reduce iron and copper ions. In the case of iron, we have used two methods to differentiate the complexes $K_3[Fe(CN)_6]$ and Fe^{3+}-TPTZ, in which the metal is present. The extract polyphenon 60 has a high potential to reduce the iron ions in both assays. Reduction of Fe^{3+}/Fe^{2+} strictly depends on the total content of polyphenolic compounds. The reducing power of the tested product increases linearly, proportional to the concentration of antioxidants. A similar correlation was obtained for the CUPRAC method, which determines the ability of polyphenols to reduce copper ions. Gramza-Michałowska et. al. [47] presented that the antiradical activity and the ability to chelate metal ions and the reduction of variable valence are responsible for the structure of the B ring of polyphenols.

3.3. Cyclic and differential pulse voltammetric behaviours of polyphenon

Cyclic (CV) and differential pulse (DPV) voltammetry were used for testing of polyphenon to the characteristics of antioxidants properties. The half-wave potential ($E_{1/2}$) determined from CV and potential peak determined from DPV are important parameters that provide information about the antioxidant activity of the test compound [48-49]. Examples of CV and DPV electro-oxidation polyphenols in non-aqueous medium are shown in Figure 4. The half-wave potential ($E_{1/2}$) determined from CV should correspond to the peak potential (E_p) designated with DPV. The supporting electrolyte of 0.1 M $(C_4H_9)_4NClO_4$ does not show any peaks in terms of the potential of the test (Figure 4 A, B; curve 3).

Voltammograms in Figure 4 A (curves 1 and 2) show that polyphenol is oxidized irreversibly in at least three stages in the range of electrode potentials lower than the decomposition potential of the electrolyte. The designated CV peak potential (E_p) of the first stage of electro-oxidation of polyphenols is 0.91 V, whereas the half-wave potential ($E_{1/2}$) is 0.83 V. Due to the poorly resolved peaks obtained by the CV for the second and third stages of electro-oxidation determined by E_p, which is suitably 1.12 V and 1.36 V, the designated peak potential (E_p) of the first stage DPV electro-oxidation of polyphenols is 0.83 V and correlates with $E_{1/2}$ designated by CV for the second stage electro-oxidation

at 1.01 V, whereas for the third step is 1.12 V. The scan rate is a parameter that significantly affects the electro-oxidation of the tested compounds and their mechanism.

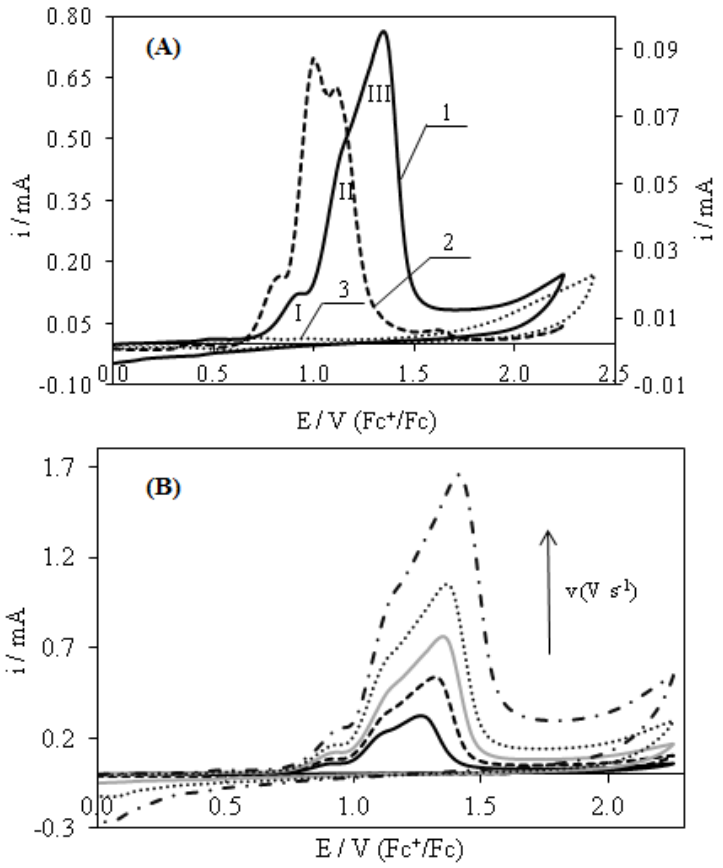

Figure 4. **A)** Voltammograms of polyphenol oxidation at a Pt electrode; c = 1.45 g L^{-1} in 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile; v = 0.1 V s^{-1}. 1: CV, 2: DPV, 3: CV of the supporting electrolyte (0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ in acetonitrile. **B)** CV of polyphenol oxidation at a Pt electrode for various scan rates recorded in the supporting electrolyte (0.1 mol L^{-1} $(C4H_9)_4NClO_4$ in acetonitrile).

Thus, the effect of the scan rate on the anodic peak current of polyphenols was investigated from 0.01 to 1 V s^{-1} using cyclic voltammetry (Figure 4B). For the first stage of the proceeding reaction, electrode oxidation of the polyphenon is designated by the peak potential and peak current, while the second and third stages show only the potential peak. If scan rate increases, the potential shifts slightly towards more positive values, which indicates an irreversibility occurring reaction. Based on the determined value of peak potentials, it can be concluded that the test compound has very good antioxidant properties. Novak et. al also in his research proposes electrochemical analysis as an excellent tool for testing antioxidant properties for green tea extracts [50]. Similarly, Yuan evaluates the performance of TDOM derived from four types of teas using electrochemical methods using similar results [51].

4. CONCLUSIONS

Electrochemical studies (cyclic voltammetry, differential pulse voltammetry) of oxidation of polyphenols give essential information about their antioxidant properties. The low oxidation potential of these compounds makes them excellent as free-radical scavengers. HPLC analysis showed a high content of polyphenols, including epigallocatechin, which may determine the properties of the total extract. Reducing properties are primarily due to the content of catechins and their gallic esters.

polyphenol is oxidized irreversibly in at least three stages in the range of electrode potentials lower than the decomposition potential of the electrolyte. On the basis of the voltammograms it was found that, polyphenol is oxidized irreversibly in at least three stages in the range of electrode potentials lower than the decomposition potential of the electrolyte. Spectrophotometric studies show, that antiradical activity of polyphenon increases as a function of the concentration of this compound.
Strong antioxidant activity of tea extract was confirmed in the presented manuscript. Consumption of green tea by people all over the world is increasing. Detailed knowledge of the properties and the selection of appropriate analytical methods to evaluate its components and their activity is currently the subject of much research. Therefore, appropriate selection correlates with each method of research into the antiradical properties, which is an important aspect. The reducing action of bioactive ingredients of green tea is studied in order to use these properties in anticancer therapy. The inhibition of the oxidation of other components is the most important aspect of medical research. Studies that have been performed expand the base of information on the composition and properties of bioactive components from green tea.

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