ELECTROANALYTICAL PROFILE OF ANTIOXIDANT NUTRACEUTICALS: IMPLICATIONS FOR PUBLIC HEALTH

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Abstract - The consumption of supplements and nutraceuticals is very prevalent throughout society, being amplified by the growing appeal to healthy lifestyles and the public perception of the relationship between the intake of nutraceutical and supplementary products in the diet with an increase in quality of life. Several nutraceuticals have the antioxidant effect as their main principle in their biological activity of interest. Electroanalytical techniques are extremely applicable to verifying the antioxidant capacity of products. The objective of the work was to evaluate the antioxidant capacity of several nutraceuticals with electroanalysis. During our study, we identified significant variations in the electrochemical profiles of three commercial samples of each of the four nutraceuticals studied. Evidence of significant variations in the electrochemical profiles of nutraceuticals marketed under the same name emphasizes the need for stricter regulations and effective quality control mechanisms in the dietary supplement and nutraceutical sector.

Keywords - Supplements, Vitamins, Regulatory Issues, Functional Foods.

I. INTRODUCTION

The use of nutraceuticals and herbal medicines (phytotherapics) containing antioxidant agents is a highly efficient strategy in combating the oxidative effects associated with free radicals (Carocho et al., 2011). By combating oxidative effects, they mitigate cellular degradation processes (Fiebich et al., 2011). It is undeniable that the efficiency of antioxidants is closely linked to the quality of the phytotherapics and nutraceuticals in use. Harvesting methods, extraction, concentration, cultivation forms, among others, can influence the quality and therapeutic effects (Dhami and Dev, 2015). Regarding detailed information on stability, redox processes, and reversibility of antioxidant compounds, electrochemical methods stand out for determination and characterization (Gil and Couto, 2013).

Therefore, this study aims to evaluate four products of wide and popular consume (Caetano, et al, 2022) through electroanalytical analyses: Turmeric (Curcuma longa), Guarana (Paullinia cupana), Blackberry (Morus nigra), and Green Tea (Camellia sinensis).

II. METHODS

2.1 Samples and Reagents

All electrolytic solutions were diluted in Milli-Q Water (Conductivity ≤ 0.1 μS.cm-1) (Millipore S.S., Molsheim, France). Gallic acid, ethanol, DPPH, and ABTS standards were acquired from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Regarding the products, three different brands of each were purchased in street markets of Goiânia, Goiás, Brazil.

2.2 Sample Preparation

Ten grams of each sample were weighed, with each of the 4 types of nutraceuticals of wide consume, namely, blackberry (Morus nigra) (A), turmeric (Curcuma longa) (B), green tea (Camellia sinensis) (C), and guarana (Paullinia cupana) (D), in which three samples of each numbered from I to III (total of 12 samples) were purchased for this study. They were ground in a mortar and pestle and transferred to a glass tube. Then, 95% pure ethanol was added, forming a 10% w/v extract solution. The extract was centrifuged for 15 minutes (Hitachi® CF16RN Himac centrifuge at 2000 rpm), filtered, and then placed in an ultrasonic bath for 10 minutes.

2.3 Electrochemistry Tests

Differential pulse voltammetry (DPV) and square wave voltammetry (SWV) were performed using a μAutolab III® potentiostat/galvanostat containing a carbon electrode, an Ag/AgCl/KClsat 3 M reference electrode, and a platinum wire, representing the working, reference, and auxiliary electrodes, respectively, integrated with NOVA 2.1 software. Experimental conditions for DPV: pulse amplitude 50 mV, pulse width 0.5 s, and scan rate 10 mV.s-1. Experimental conditions for SWV: pulse amplitude 50 mV with a frequency of 50 Hz, potential step of 2 mV, corresponding to a scan rate of 100 mV.s-1. Data were analyzed and processed using Origin 9.0 software. Experiments were conducted in triplicate (n=3) at 21 ± 1º C, with 0.1 M phosphate buffer pH 7.0.

2.4 Electrochemical index determination

The electrochemical index is a parameter used to assess the ability to receive or donate electrons in a redox reaction. Its value comes from the ratio between the anodic peak current (*I*pa) and the anodic peak potential (*E*pa), where the higher the *I*pa (kinetic parameter), the greater the number of electroactive species with a positive potential difference in DPV analysis (Macêdo *et al*., 2017).

$$IE = \left(\frac{I_{pa1}}{E_{pa1}}\right) + \left(\frac{I_{pa2}}{E_{pa2}}\right) + \cdots . + \left(\frac{I_{pan}}{E_{pan}}\right)$$

III. RESULTS AND DISCUSSION

3.1 Electrochemical Characterization

In the assessment of antioxidant capacity and redox profile, the DPV was used for each sample. The DP voltammograms of samples A, B, C and D are presented in Figure 1, in which can be observed one or two anodic peaks in all cases, as follows: blackberry *E*pa1 ca. 0.3 V and *E*pa2 ca. 0.7 V; turmeric *E*pa1 ca. 0.2 V and *E*pa2 ca. 0.5 V; green tea *E*pa1 ca. 0.2 V; guarana *E*pa1 ca. 0.2 V and *E*pa2 ca. 0.6 V.

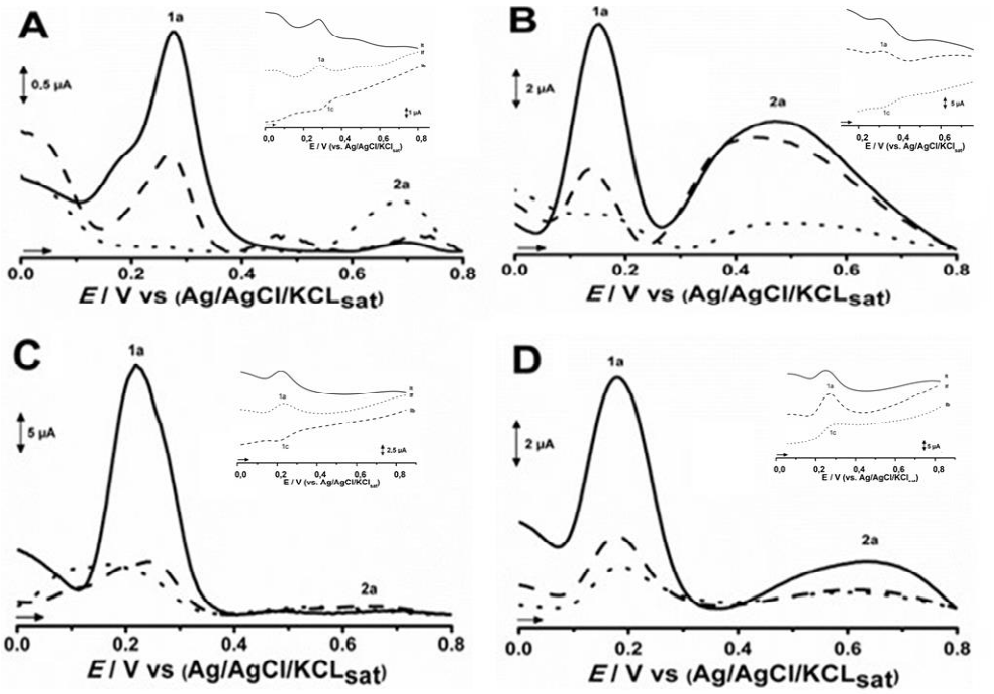


Figure 1. The resulting voltammogram from the tests of differential pulse voltammetry (DPV) of 12 commercial samples, where samples I (—), II (- - -), and III (...) represent samples A, B, C and D. Inset: The related SW voltammograms.

In SWV (Figure 1, inset), the mixtures of the three samples of each nutraceutical were evaluated for oxidative reversibility. All voltammograms showed an oxidation peak at E_{pa} ca. 0.2 V, which indicates a strong reducing capacity. Moreover, the samples A, B and C, exhibited a reversible character with similar values of E_p and I_p for cathodic and anodic peaks. Yet, guarana (*Paullinia cupana)* sample pool D, have exhibited an irreversible character in neutral pH, which is probably related to ascorbic acid (Macedo et al., 2017).

It is noteworthy to mention that while E_p values are related to thermodynamic force to perform a redox reaction, the *I*p values express the kinetic and global amount of electroactive species undergoing an electrochemical reaction at the corresponding potential (Lino, *et al*, 2014). Therefore, the antioxidant activity can be properly achieved by means of Electrochemical Index (Table 1).

	EI Samples (µA/V)			Anodic peaks		Marker Antioxidant (E_{pa}/V)	Reference
Nutraceutical	I	II	III	E_{pa1}(V)	E_{pa2}(V)		
A	11,62	5,95	1,04	0,3	0,7	Morina (0.2)	Ziyatdinova et al., 2014
B	93,11	44,27	13,87	0,2	0,5	Curcumina (0.2; 0.41)	Cheraghi et al., 2016
C	605,12	194,96	112,04	0,2		Gallic Acid (0.2)	Leite et al., 2016
D	609,7	192,91	111,11	0,2	0,6	Ascorbic Acid (0.6)	Menezes Peixoto et al., 2017

Table 1. Calculated EI values table, oxidation potential *E*pa and literature found antioxidant markers.

IV. DISCUSSION

In blackberry (A), the oxidation peak at Epa1 ca. 0.3 V is related to the presence of morin or similar flavonoid compounds (Ziyatdinova et al., 2014). The peak at Epa2 *ca*. 0.7 V is related to electroactive species containing monophenol or resorcinol like moieties (Cata et al., 2016).
Turmeric (B) presented two peaks at *E*pa1 *ca*. 0.2 V and Epa2 *ca*. 0.5 V, with the respective oxidative peaks belonging to flavonoids and curcumin (Cheraghi et al., 2016; Ziyatdinova et al., 2012).
Green tea (C) showed only one oxidative peak at *E*pa1 *ca*. 0.2 V, which may be related to the presence of gallic acid or a similar compound (Leite et al., 2018). The analysis of guarana (D) presented two oxidative peaks at Epa1 *ca*. 0.2 V and Epa2 *ca*. 0.6 V, that are very similar to those found in samples of Turmeric and Blackberry, thus being possible to infer that they possess similar compounds.

Studies have shown that these nutraceuticals exhibit anti-inflammatory and antimicrobial activities due to the presence of antioxidant compounds such as curcumin, gallic acid, and flavonoids (Cheraghi et al., 2016; Ziyatdinova et al., 2012).

Due to significant differences in the results of the voltammetric analysis samples, an argument could be made to indicate that there may be adulteration or inconsistencies in the quality control of the products.
In SWV analyses, the presence of polyphenolic compounds was observed, revealing the reversibility of *E*pa1 < 0.3 V redox processes in A, B and C samples, which is consistent with catechol like moieties of the related major compounds. In turn, the sample D, the irreversible profile of *E*pa1 indicates the presence of ascorbic acid, one of the main compounds of guarana.

Finally, it was observed that sample I (solid line) presented the best EI values for all type of nutraceuticals (A, B, C and D), indicating higher antioxidant power and therefore quality (Table 1). In contrast, the sample III (dotted line) of samples A and B exhibited an anomalous profile, when compared with samples I and II, suggesting possible adulteration (Figure 1).

V. CONCLUSION

This study underscores the importance of an integrated approach in public health that includes consumer education on the rational use of nutraceuticals, strengthening regulation and market oversight of these products, and promoting ongoing research to ensure their safety and efficacy. In the context, the use of electroanalytical methods to evaluate the quality of nutraceuticals of antioxidant appeal combine simplicity to lower cost.

REFERENCES

[1] Caetano, M.P., Nielson, S.E. de O., Macedo, I.Y.L. de, Batista, E.A., Barbosa, D.B.M., Brito, A. de S., Silva, G.R.A., Gil, E. de S., 2022. Comercialização, dispensação e prescrição de Nutracêuticos antioxidantes por farmacêuticos. Brazilian J. Heal. Rev. 5, 18045–18059. https://doi.org/10.34119/bjhrv5n5-019

[2] Carocho, M., Morales, P., Ferreira, I.C.F.R., 2018. Antioxidants: Reviewing the chemistry, food applications, legislation and role as preservatives. Trends Food Sci. Technol. 71, 107–120. https://doi.org/10.1016/j.tifs.2017.11.008

[3] CĂta, A., ŞtefĂnuţ, M.N., Pop, R., TĂnasie, C., MoşoarcĂ, C., Zamfir, A.D., 2016. Evaluation of antioxidant activities of some small fruits containing anthocyanins using electrochemical and chemical methods. Croat. Chem. Acta 89, 37–48. https://doi.org/10.5562/cca2656

[4] Cheraghi, S., Taher, M.A., Karimi-Maleh, H., 2016. Fabrication of Fast and Sensitive Nanostructure Voltammetric Sensor for Determination of Curcumin in the Presence of Vitamin B9 in Food Samples. Electroanalysis 28, 2590–2597. https://doi.org/10.1002/elan.201600252

[5] de Macêdo, I.Y.L., Garcia, L.F., Oliveira Neto, J.R., de Siqueira Leite, K.C., Ferreira, V.S., Ghedini, P.C., de Souza Gil, E., 2017. Electroanalytical tools for antioxidant evaluation of red fruits dry extracts. Food Chem. 217, 326–331. https://doi.org/10.1016/j.foodchem.2016.08.082

[6] Dhami, N., Dev, A., 2015. Phytochemical variation : How to resolve the quality controversies of herbal medicinal products ? Perspect. Med. 5, 118–127. https://doi.org/10.1016/j.hermed.2015.04.002

[7] Fiebich, B.L., Knörle, R., Appel, K., Kammler, T., Weiss, G., 2011. Pharmacological studies in an herbal drug combination of St. John's Wort (Hypericum perforatum) and passion flower (Passiflora incarnata): In vitro and in vivo evidence of synergy between Hypericum and Passiflora in antidepressant pharmacological models. Fitoterapia 82, 474–480. https://doi.org/10.1016/j.fitote.2010.12.006

[8] Gil, E.S., Couto, R.O., 2013. Flavonoid electrochemistry: A review on the electroanalytical applications. Brazilian J. Pharmacogn. 23, 542–558. https://doi.org/10.1590/S0102-695X2013005000031

[9] Leite, K.C. de S., Garcia, L.F., Lobón, G.S., Thomaz, D.V., Moreno, E.K.G., Carvalho, M.F. de, Rocha, M.L., Santos, W.T.P. dos, Gil, E. de S., 2018. Antioxidant activity evaluation of dried herbal extracts: an electroanalytical approach. Rev. Bras. Farmacogn. 28, 325–332. https://doi.org/10.1016/j.bjp.2018.04.004

[10] Lino, F.M.A., de Sá, L.Z., Torres, I.M.S., Rocha, M.L., Dinis, T.C.P. Dinis, Ghedini, P.C., Somerset V.S., Gil, E.S., Voltammetric and spectrometric determination of antioxidant capacity of selected wines, Electrochim. Acta, 128, 25-31, 2014. https://doi.org/10.1016/j.electacta.2013.08.109

[11] Menezes Peixoto, C.R. de, Fraga, S., Rosa Justim, J. da, Silva Gomes, M., Gonçalves Carvalho, D., Jarenkow, J.A., Fernandes de Moura, N., 2017. Voltammetric determination of total antioxidant capacity of Bunchosia glandulifera tree extracts. J. Electroanal. Chem. 799, 519–524. https://doi.org/10.1016/j.jelechem.2017.07.003

[12] Ziyatdinova, G., Ziganshina, E., Budnikov, H., 2014. Electrooxidation of morin on glassy carbon electrode modified by carboxylated single-walled carbon nanotubes and surfactants. Electrochim. Acta 145, 209–216. https://doi.org/10.1016/j.electacta.2014.08.062

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