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Voltammetric determination of condensed tannins with a glassy carbon electrode chemically modified with gold nanoparticles stabilized in carboxymethylcellulose

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ABSTRACT

This paper reports the electroanalytical determination of condensed tannins in extracts of Acacia (*Acacia mearnsii* de wild) using a glassy carbon electrode (GCE) modified with gold nanoparticles (AuNPs) and carboxymethylcellulose (CMC). The AuNPs were synthesized by the reduction of chloroauric acid with sodium borohydride using CMC as a stabilizer. The characterization of the AuNPs was carried out by UV–vis spectroscopy, transmission electron microscopy (TEM) and dynamic light scattering (DLS). The modified surface was characterized by scanning electron microscopy with field emission gun (SEM-FEG), atomic force microscopy (AFM) and profilometry experiments. Electrochemical studies were carried out by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and square-wave voltammetry (SWV). The results show that the nanoparticles obtained are spherical and have an average diameter of 5.3 nm. The modified electrode was prepared by dropping the AuNPs-CMC dispersion onto the surface of the GCE. For the quantification of condensed tannins catechin was used as a model compound. The detection (DL) and quantification (QL) limits for catechin were 0.274 and 0.831 $\mu mol\,L^{-1}$, respectively. The proposed detector was tested by determining the total condensed tannins concentration in real samples using the standard addition method. The curves for the samples exhibited a slope similar to the calibration curve, indicating the absence of interference from the matrix components in the response to condensed tannins. The modified electrode was successfully applied to the analysis of real samples, with results comparable to those obtained using the Folin-Ciocalteu method. Thus, the strategy used in this study creates new opportunities for the sensitive detection of condensed tannins in plant extracts widely used in various industrial segments.

1. Introduction

Tannins are a class of natural polyphenols found in terrestrial plants. The astringent sensation caused by some wines, fruit juices and teas is related in large part to the tannins, due to their precipitation by proline-rich proteins present in saliva. Most of the biological properties of tannins, including the healing action, are related to the capacity to form complexes with metal ions and macromolecules such as proteins present in the skin [1–3]. For this reason, tannins are widely applied in leather tanning, for medical purposes and in the food industry. In natural medicine, widely practiced in China, Japan and India, extracts of tannins are used in cases of diarrhea [4], as diuretics [5,6], to treat stomach pain and duodenal tumors [7] and as an anti-inflammatory and antiseptic [8]. Since tannins are able to precipitate heavy metals and alkaloids (except morphine) they can also be used in cases of intoxication by these substances [9].

According to their chemical structure, tannins are divided mainly into two classes: condensed and hydrolyzable tannins [1,2]. The condensed tannins (determined in this study) are oligomeric and polymeric proanthocyanidins formed by catechin units linked by C—C bonds between C-4 of one unit and C-8 of other unit of catechin [10], as shown in Fig. 1.

Fig. 1.

The multiple hydroxyl groups present in the structure of tannins (hydrolyzable and condensed tannins) lead to the formation of complexes with proteins [11–13], metal ions [14–17], and other macromolecules (e.g., polymers and polysaccharides) [18–20]. In the case of proteins, polymers and polysaccharides, phenolic groups interact via hydrogen bonds or hydrophobic interactions [21,22]. In

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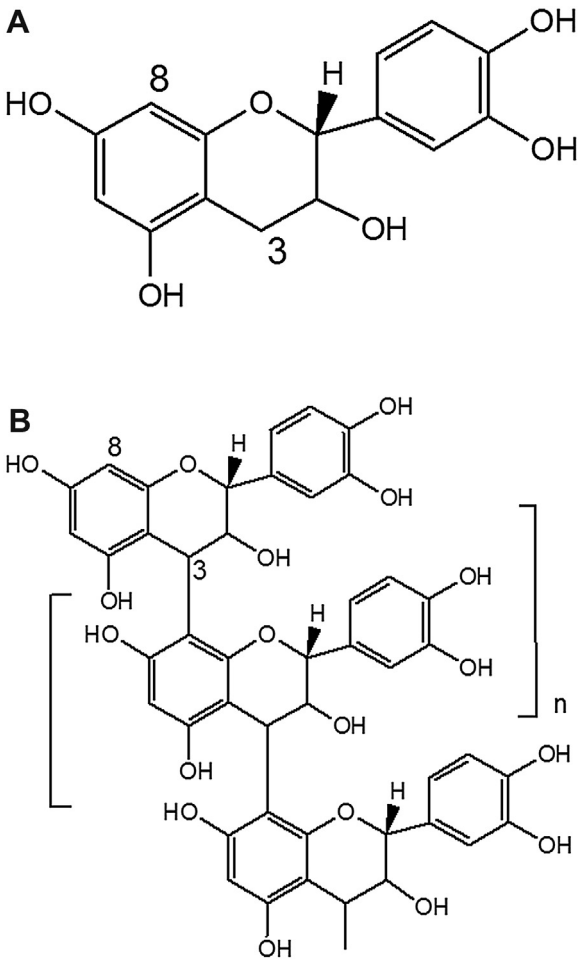

Fig. 1. Chemical structure of (A) catechin and (B) condensed tannin [10].

the case of metal ions, complexation occurs through the deprotonated phenolic groups of the tannins, which generate high electron density centers capable of interacting with ions with a positive charge [16,23]. Several authors have reported the use of tannins in wastewater treatment due to their ability to complex metals [15–17]. In some cases, the use of tannins represents a viable alternative for replacing aluminum or iron salts in the treatment of water and wastewater [17].

The quantification of condensed tannins is a difficult task because of the structural complexity of these molecules [24]. Therefore, several studies have been carried out to investigate the use of a simpler model compound to represent the structure of tannins. In this study, catechin ((2*R*,3*S*)-2-(3,4-dihydroxyphenyl)-3,4-dihydro-2H-chromene-3,5,7-triol, Fig. 1A) is a flavonoid found in many plants and food products. Its antioxidant activity provides protection against diseases directly or partially related to the accumulation of free radicals in the human body [25]. Several analytical methods have been used to quantify tannins in vegetable extracts. Chromatographic and spectrophotometric techniques are the most commonly applied for this purpose [26]. These methods generally include the oxidative depolymerization of molecules, reactions with an aromatic aldehyde and oxidation-reduction reactions. Other methods involve precipitation reactions, enzyme inhibition and gravimetric analysis [24]. However, some methods are not sensitive enough or do not have the necessary selectivity for accurate quantification [27]. In relation to the spectrophotometric methods, the Folin-Ciocalteu method [28] has been widely applied in the determination of tannins in different matrices. However, this method is based on a redox reaction and other reducing agents present in the sample may cause interference, so the method has poor selectivity [27]. Moreover, solid particles present in the sample can also induce inaccurate results. Hence, sample preparation steps are commonly performed prior to analysis. Protein precipitation [29,30] and chromatography [31,32] have also been described in the literature for the determination of tannins. However, these methods require expensive and sophisticated instruments and their use is therefore limited [27]. Other analytical methods less frequently employed are atomic absorption spectrometry (AAS), chemiluminescence and fluorometry [27]. Electrochemical methods for the quantification of phenolic compounds (e.g., catechin) have also been frequently reported in the literature and offer some advantages compared to other procedures, such as a fast response time, low detection and quantification limits, easy sample preparation and low cost [33–35]. Electrochemical techniques employing electrodes modified with different species have been used, aimed at improving the sensitivity by lowering the detection and quantification limits and increasing the selectivity of the proposed sensors [36–39]. Accordingly, various sensors and biosensors have been developed and employed for the quantitation of catechin in different samples, as in the studies published by Yao and collaborators [40] in which a glassy carbon electrode was modified with carboxylic group-functionalized single-walled carbon nanotubes for the electrochemical determination of catechin. Under optimized conditions, the modified electrode showed a wide linear response for catechin in the concentration range of 0.039 to 40.84 μmol L^{-1}, with a detection limit of 0.013 μmol L^{-1}. In 2008, Fernandes and collaborators [35] developed a biomimetic sensor based on a novel copper (II) complex for the determination of catechin. The calibration curve was linear from 4.95 to 32.7 μmol L^{-1} with a detection limit of 0.28 μmol L^{-1}. The sensor was successfully applied for the determination of catechin in green tea samples, with recovery percentages ranging from 93.8 to 106.9%. The electrochemical properties of catechin were investigated by Yang and co-workers using a single-walled carbon nanotube (SWNT)-cetyltrimethylammonium bromide (CTAB) modified glassy carbon electrode (GCE) [41]. Three peaks were observed for catechin in the potential range of −0.4 to 1.0 V in PBS (pH 7.0): a couple of peaks indicating a reversible oxidation-reduction reaction and a single peak indicating an irreversible oxidation reaction. The reduction peak current increased linearly with the catechin concentration in the range of 0.32–2.38 nmol L^{-1}. The detection limit was 0.11 nmol L^{-1}. However, the electrochemical quantification of tannins has not been reported. Electrochemical studies on tannins with more complex chemical structures are still limited to their application as a corrosion inhibitor, as in the work carried by Tan and Mourya [42,43] or as modifiers of electrodes [44].

In recent years, gold nanoparticles (AuNP) [45] and gold nanorods [46] have attracted considerable interest due to their particular attributes, such as high conductivity, catalytic properties, low toxicity, biocompatibility and easy preparation, enabling its widespread use to build chemically modified electrodes for simultaneous determination of isoproterenol and uric acid [47] and carbofuran [48]. Despite of this, the use of gold nanoparticles stabilized in carboxymethylcellulose as electrode modifier has not yet been reported in the literature.

Within this context, the aim of this study was to develop a simple, inexpensive but competitive detector based on a glassy carbon electrode (GCE) modified with gold nanoparticles stabilized in carboxymethylcellulose (AuNP-CMC) to quantify condensed tannins in plant extracts commercialized for leather tanning. Catechin was used as the model compound in order to gain a better understanding of the electrochemical processes at the proposed detector.