



Voltammetric determination of harmaline in natural food products using boron-doped diamond electrode



L'ubomír Švorc^{a,*}, Kristína Cinková^a, Anchalee Samphao^b, Dalibor M. Stanković^c, Eda Mehmeti^d, Kurt Kalcher^d

^a Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, Bratislava SK-812 37, Slovak Republic

^b Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Ubon Ratchathani University, Ubon Ratchathani 34190, Thailand

^c Department of Analytical Chemistry, Innovation Center of the Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade 11000, Serbia

^d Institute of Chemistry, Department of Analytical Chemistry, Karl-Franzens University, Universitätsplatz 1, Graz A-8010, Austria

ARTICLE INFO

Article history:

Received 14 January 2015

Received in revised form 27 February 2015

Accepted 3 March 2015

Available online 5 March 2015

Keywords:

Harmaline

Boron-doped diamond electrode

Voltammetry

Detection limit

Peganum harmala

Banisteriopsis caapi

ABSTRACT

A novel analytical approach for the sensitive determination of a β -carboline alkaloid, harmaline, was developed using pulse voltammetric techniques with a boron-doped diamond electrode. Cyclic voltammetry showed two irreversible oxidation peaks at about +0.90 and +1.20 V (vs. Ag/AgCl) in Britton–Robinson buffer solution at pH 5. Under optimized experimental conditions, differential pulse and square-wave voltammetry were elaborated for the determination of harmaline in a linear concentration range from 0.2 to 100.7 and from 0.4 to 104.5 $\mu\text{mol L}^{-1}$, respectively, with detection limits of 0.08 and 0.2 $\mu\text{mol L}^{-1}$, respectively. The practical feasibility of the developed method was demonstrated by quantification of harmaline in the extracts of natural food products such as Syrian rue (*Peganum harmala*, also known as *esphant*, *harmal*, *yüzerlik*) seeds, locally used as condiment and medicine in Turkey and the Near and Middle East, and the South American shamanic drink component Ayahuasca liane (*Banisteriopsis caapi*) with results in good agreement with those obtained by high-performance liquid chromatography as a reference method. The proposed sensor represents an effective electrochemical tool and inexpensive alternative for quality control analysis of food products containing harmaline.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

A number of β -carboline alkaloids are naturally distributed in various plants, foodstuffs, insects as well as human tissues and body fluids. Minor contents have also been found in alcoholic beverages, protein-rich foods cooked by heat treatments and mushrooms [1,2]. These compounds have an increasing toxicological significance because of their intense biological activity and adverse effects on human health, being related with Parkinson's disease, alcoholism and cancer [3]. The endogenous formation of some β -carboline alkaloids in mammals and fishes has also been described [4]. Moreover, apart from cigarette smoking, which constitutes a significant source of β -carboline alkaloids, the dietary intake is the most usual way for exposure to these species.

In nature, β -carboline alkaloids usually occur in number of plants, of which the extracts exhibit psychoactive actions. Syrian Rue (*Peganum harmala*) is a perennial herbaceous plant native to

dry parts of North Africa and Middle East traditionally and commonly used for medicinal and psychoactive purposes, because its seeds are known to possess hypothermic and hallucinogenic properties and they are used as a medical remedy, spice or condiment with aphrodisiac, stimulant and sedative effects [5]. Ayahuasca liane (*B. caapi*), a South American jungle woody vine, is popularly known as an ingredient of a sacred and hallucinogenic drink ayahuasca, widely used throughout the Amazon as a medicinal tea for healing and shamanic spiritual exploration. Both plants contain β -carboline alkaloids like harmaline, harmine, harmalol and harmane representing psychoactive compounds and monoamine oxidase A inhibitors [6]. In this way, it is harmful to eat some amine-containing foods (e.g. with tyramine) after ingesting β -carboline alkaloids [7]. In addition, these alkaloids can be also naturally found in foodstuffs due to condensation between indoleamines and aldehydes or α -keto acids [8]. This reaction may occur during food production, processing and storage. In some countries of the Middle East, Syrian Rue seeds are being served as food additives in traditional restaurants for assisting the gastrointestinal tract with digestion. Owing to common use of β -carboline alkaloids for these purposes and eventual abuse, novel and perspective

* Corresponding author.

E-mail address: lubomir.svorc@stuba.sk (L. Švorc).

analytical methods providing simple and sensitive determination of the target analytes are still necessary. Moreover, survey of such alkaloid levels is not meaningful only in food chemistry, but also in controlling people's health and drug management. In this work, our attempt has been solely focused on the detection and quantification of harmaline (HME) as one of the main member of β -carboline alkaloids (structural formula in Scheme 1).

A survey of the literature shows many reports concerning the miscellaneous analytical methods for the quantification of HME and other β -carboline alkaloids in various matrices (plant seeds, plasma, serum, tissues). These techniques particularly include modern separation methods such as capillary electrophoresis [9], high-performance liquid chromatography (HPLC) with electrochemical detection [10,11] and with different types of spectral detection such as UV [12], FTIR [13], NMR [14], chemiluminescence [15], fluorescence [16] and mass spectrometry [17] as well as gas chromatography with a nitrogen-phosphorus detector [18,19] and mass spectrometry [20]. Most of above mentioned methods offer very useful analytical information about HME in terms of identification and quantification, excellent resolution, sensitivity and selectivity, however they require highly sophisticated and expensive instrumentation and often involve long analysis time and time-consuming sample pretreatment processes (derivatization, purification, complex extraction steps). Furthermore, the demands for highly skilled workers often constrain their use in routine analytical practice. In this sense, the development of simple, low-cost and sensitive analytical methods for the detection and quantification of HME and other structurally related alkaloids in the extracts of food additives in terms of the public safety is also still of great interest.

Electroanalytical techniques have proved to be excellent alternatives for the determination of structurally and biologically miscellaneous compounds, since they are simple, low-cost and inexpensive and require relatively short analysis times, without the need for derivatization or time-consuming extraction steps [21]. In addition, they provide information about the kinetics and charge transfer mechanism of the electrode reaction [22]. Regarding the electrochemistry of HME, however, there is only one study available on its voltammetric characterization and amperometric determination using HPLC with a carbon nanotube (CNT)-modified electrode as electrochemical detector [10,11] although this molecule is electrooxidisable at several conventional electrodes. In the mentioned study it was found that when using bare glassy carbon (GC) electrodes, the difficulties consisted in electrode surface fouling (passivation of the electrode surface due to irreversible adsorption of products of the electrode reaction) and regeneration when poor electrochemical activity of HME with two small oxidation peaks at about +0.80 and +0.95 V vs. Ag/AgCl was manifested. However, after modifying the electrode surface with CNTs the corresponding peak currents significantly enhanced (6–10 times) due to an increased surface area. The analytical signal

improvement was exploited to achieve high sensitivity in the HPLC–ED determination of HME with a detection limit of $0.09 \mu\text{mol L}^{-1}$ thus allowing its quantification in foodstuffs at low concentration levels. In addition, the antifouling properties of the CNT-modified electrode surface ensured good repeatability of the current response of HME.

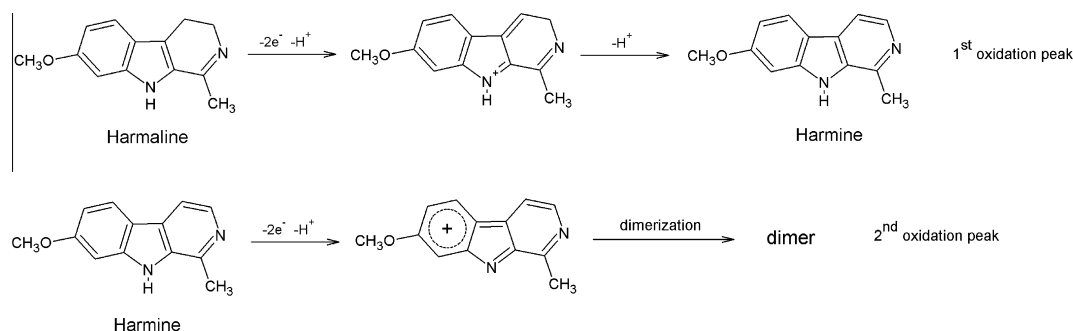
Another approach to effectively overcome the problems with electrode surface fouling by the analyte could involve the application of novel and perspective bare electrode materials. Nowadays, boron-doped diamond (BDD) electrodes offer attractive advantages in electrochemistry such as high stability because of their inertness with respect to the adsorption of chemical species (the presence of sp^3 hybridized of diamond carbon atoms) and the ability to work in a wide usable potential range when compared to the GCE [23–25]. In addition, they provide low and stable background currents (high S/N ratio) and mechanical robustness which is very useful for electroanalytical applications of analytes oxidisable at highly positive potentials [26]. Besides, the physical and chemical nature of BDD electrodes are affected by their surface termination since hydrogen-terminated surfaces are hydrophobic and have high conductivity whereas oxygen-terminated ones are hydrophilic with low conductivity [27]. BDD electrodes represent effective alternatives to conventional carbonaceous electrodes, and our research group extensively used them as versatile electrochemical tool for the sensitive determination of miscellaneous biologically active compounds [28–31]. Recently, several applications of BDD electrode for electrochemical determination of harmful organic compounds in food and beverage samples such as kresoxim-methyl [32] and dimethoform [33] as well as important additives in food industry such as caffeine [31], yohimbine [34], vanillin [35], chlorogenic acid [36] and capsaicin [37] were reported.

In this paper, we demonstrate a novel electrochemical approach for the sensitive determination of HME as simple and low-cost alternative to chromatographic techniques and to previously reported application with CNT-modified electrodes [10,11]. It is important to emphasize that according to literature survey no report dealing with the direct electrochemical determination of HME and other β -carboline alkaloids using a BDD electrode has been published until now. The practical usefulness of the proposed electrochemical methodology is manifested by determining the amount of this alkaloid in the extracts of natural food products such as Syrian Rue seeds and Ayahuasca liane bark.

2. Experimental

2.1. Chemicals

Harmaline (CAS No. 304-21-2, purity $\geq 99\%$, HME) was purchased from Sigma-Aldrich (Austria). Britton–Robinson (BR) buffer solution was prepared in the usual way by mixing of phosphoric



Scheme 1. Proposed oxidation mechanism of HME on BDD electrode.

Download English Version:

<https://daneshyari.com/en/article/218391>

Download Persian Version:

<https://daneshyari.com/article/218391>

[Daneshyari.com](https://daneshyari.com)