Journal of Electroanalytical Chemistry 743 (2015) 112–119

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Validated voltammetric method for the determination of antiparkinsonism drug entacapone in bulk, pharmaceutical formulation and human plasma

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ARTICLE INFO

Article history:
Received 31 December 2014
Received in revised form 15 February 2015
Accepted 17 February 2015
Available online 24 February 2015

Keywords:
Entacapone
Carbon paste electrode
Biological fluids

ABSTRACT

Accurate and precise voltammetric method has been developed and validated for quantitative determination of entacapone in bulk, pharmaceutical dosage forms and human plasma at carbon paste electrode in Britton–Robinson buffer of pH range (2–10) in presence of Triton X-100. Several factors such as pH, type of surfactant, scan rate and accumulation time were investigated in order to study the optimum conditions for determination of entacapone. A good linear relationship was obtained within the concentration range from 1.0×10^{-6} to 3.8×10^{-5} mol L^{-1} with mean recovery and relative standard deviation values of 100.26% and 1.72%, respectively. The limits of detection and quantification were found to be 1.13×10^{-7} and 3.76×10^{-7} mol L^{-1}, respectively. The obtained results are in good agreement with those obtained by a reference method. The proposed method is simple, rapid and economic, so it is suitable for routine analysis of entacapone in pure form and dosage forms and for pharmacokinetic studies.

1. Introduction

Entacapone (ENT), (E)-2-cyano-3-(3,4-dihydroxy-5-nitrophenyl)-N,N-diethyl prop-2-enamide (Fig. 1) is a selective, reversible catechol-O-methyl transferase (COMT) inhibitor, used for the treatment of Parkinson's disease [1,2]. It is a member of the class of nitrocatechols. When administered concomitantly with levodopa and a decarboxylase inhibitor (e.g., carbidopa), ENT prevents COMT from metabolizing levodopa into 3-methoxy-4-hydroxy-L-phenylalanine in the periphery, which does not easily cross the blood brain barrier so increased and more sustained plasma levodopa concentrations are reached as compared to the administration of levodopa and a decarboxylase inhibitor, Thus ENT is added to extend the duration and effect of levodopa in the brain, and thus allows levodopa to be given less often and in lower doses [3–5].

Literature survey simply reveals that different analytical techniques have been applied for determination of ENT, including liquid chromatography [6–13], spectrophotometry [14–17], capillary electrophoresis [18] and electrochemical methods which based on the reduction process of ENT at hanging dropping mercury electrode [19,20] and at glassy carbon and platinum electrodes [21].

A surface active agent (surfactant) tends to adsorb at the interface between bulk phases, such as air and water, oil and water or electrode and solution. Surfactants naturally have a very large impact on chemistry of current interest, their behavior in solution involves aggregation or adsorption and organization on the electrode surface and it influences the electrode processes and the rate of electron transfer [22,23]. The role of surfactants to improve the sensitivity and selectivity in electrochemistry is well documented [24–27].

The objective of this investigation is the determination of ENT in bulk powder, tablets and human serum through the electrochemical oxidation of ENT using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) at carbon paste electrode (CPE) based on the enhancement effect of triton X-100.

2. Experimental

2.1. Materials and reagents

All reagents and solvents were of analytical reagent grade and used without further purification.

2.1.1. Pure materials

Entacapone (Batch No. 080603) was kindly supplied by EVA PHARM Co., Cairo, Egypt. Its purity was checked according to the U.S.P. and was found to be 99.80%.

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http://dx.doi.org/10.1016/j.jelechem.2015.02.022
1572-6657/

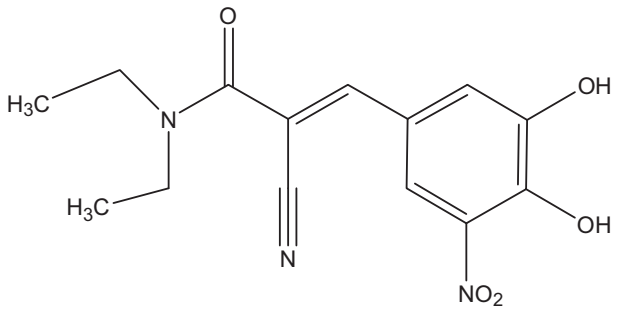

Fig. 1. Chemical structure of ENT.

2.1.2. Market samples

Parkicapone tablets (Batch No. 33021) labeled to contain 200 mg ENT per tablet, produced by Al-Andalus Co., Cairo, Egypt.

2.1.3. Reagents

Britton–Robinson (BR) buffer was prepared by mixing the acid mixture containing 0.04 mol L^{-1} phosphoric acid (Sigma–Aldrich), 0.04 mol L^{-1} acetic acid (Loba Chemie Co., India) and 0.04 mol L^{-1} in boric acid (Sigma–Aldrich). Buffer solutions were adjusted with the appropriate amount of 0.2 mol L^{-1} sodium hydroxide (Winlab, Leicestershire, U.K.) to get the desired pH 2–10.

Graphite powder, paraffin oil, acetonitrile, cetyl trimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were supplied from Sigma–Aldrich. Triton X-100 (TX-100) was purchased from Loba Chemie Co., India. Stock solutions of 1.0×10^{-2} mol L^{-1} of CTAB and SDS were prepared by dissolving appropriate amounts in double distilled water. TX-100 surfactant was diluted with double distilled water to get stock solution of 1.0×10^{-2} mol L^{-1}. Methanol HPLC grade (Sigma, Germany).

Fresh human plasma was obtained from blood bank (VACSERA, Cairo, Egypt). Real samples containing ENT were obtained from four healthy volunteers.

2.1.4. Standard solutions

The standard stock solution of ENT (1×10^{-2} mol L^{-1}) was prepared by dissolving an appropriate amount of ENT in methanol. The stock solution was stable when stored in a refrigerator at 4 °C for 1 month.

2.2. Apparatus

All voltammetric measurements were carried out at 25 °C using a computer-driven analytical electrochemical workstation (model AEW2) with electrochemistry software (ECProg3, Sycopel, England) in combination with a three-electrode configured stand (model C-3). The working electrode was a carbon paste electrode (CPE, MF-2010, BAS model), the reference electrode Ag/AgCl/3 mol L^{-1} NaCl (MW-2063, BAS model) and a platinum wire counter electrode (MW-1032, BAS model). A digital pH-meter (Cyber scan 500, EUTECH Instruments, USA) with combined glass electrode was used to carry out the pH measurements.

2.3. Procedures

2.3.1. Preparation of working electrode

Carbon paste electrode was prepared by mixing graphite powder (0.5 g) with paraffin oil (nearly 0.3 mL) in a mortar. The carbon paste was packed into the hole of the electrode body and smoothed on a filter paper until its shiny appearance.

2.3.2. Construction of calibration curve of ENT

Differential pulse voltammetry (DPV) was employed in order to determine ENT in bulk powder. Aliquots of ENT (1.0×10^{-3} mol L^{-1}) were transferred into electrolytic cell containing 5 mL BR buffer of the optimum pH (2.0) and 4.0×10^{-5} mol $L^{-1}$of TX-100 solution. The voltammetric analyses were carried out and differential pulse voltammograms were recorded at CPE. The anodic peak current was plotted versus final concentration of the drug (mol L^{-1}) to get the calibration graph. Alternatively the corresponding regression equations were derived.

2.3.3. Application to pharmaceutical formulations

Ten tablets of Parkicapone were finely powdered, mixed well and weighed. Accurately weighed portion of finely powder needed to get 1.0×10^{-3} mol L^{-1} ENT solution was transferred into a 100 mL volumetric flask containing 60 mL methanol. The flask was sonicated for 25 min and made up to the volume with the same solvent, mixed well and filtered to separate out the insoluble excipients. The filtrate was further diluted with the same solvent for covering the working concentration range. An aliquot of this solution was then analyzed according to the proposed voltammetric procedure based on standard addition method.

2.3.4. Application to human plasma

2.3.4.1. Spiked plasma samples. 1 mL of fresh human plasma was transferred into a 10 mL centrifuge tube containing 2 mL of acetonitrile and spiked with different volumes of standard solution of ENT (1.0×10^{-3} mol L^{-1}), the mixture was centrifuged for 15 min at 5000 rpm in order to eliminate protein residues then the supernatant was taken carefully. 0.5 mL from the supernatant was added to 4.5 mL of BR buffer of the optimum pH in presence of an appropriate amount of TX-100 solution (4.0×10^{-5} mol L^{-1}). The procedure described under construction of calibration curve was followed.

2.3.4.2. Volunteer plasma samples. ENT was determined in plasma real samples using DPV method through standard addition method of ENT standard solution (1.0×10^{-3} mol L^{-1}) to 150 μL of plasma real samples which prepared for analysis as described in the previously in the determination of ENT in spiked human plasma.

3. Results and discussion

3.1. Electrochemical oxidation of ENT

The cyclic voltammetry technique was used to study the reversibility of the oxidation process of ENT. The CV voltammogram of ENT (Fig. 2) displayed only one well anodic peak (anodic peak current (I) = 28.97 μA at 0.641 V), and no cathodic peak in the reverse scan was recorded, which means that the oxidation of ENT is irreversible.

The electrons involved in the reaction can be calculated by the formula of $\omega_{1/2} = 62.4/\alpha n$ [28], where $\omega_{1/2}$ is the peak width at half height, n is the number of electrons transferred, and α is the transfer coefficient of an electron with a value that is often between 0.4 and 0.6. The number of electrons transferred (with $\alpha = 0.5$) was calculated to be $n \approx 2$. The proposed reaction pathway could be represented as shown in Fig. 3.

3.2. Optimization of experimental conditions

3.2.1. Effect of pH

The effect of pH upon the oxidation of ENT was investigated by using cyclic voltammetry (CV) at CPE electrode and scan rate of 100 mV s^{-1}. The cell was filled with 4.5 mL BR buffer, 0.5 mL of