



Mechanism and superoxide scavenging activity of hydroxy substituted tetraphenylporphyrins via coulometric approach



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ABSTRACT

The novel electrochemical approach based on coulometric response of electro-generated superoxide is applied to the radical scavenging activity determination of hydroxy substituted tetraphenylporphyrins. The excellent linearity of the coulometric response of superoxide ion vs. porphyrins concentration for the wide concentration range shows the operational suitability of developed approaches. The most feasible mechanism of antioxidant activity of hydroxy substituted tetraphenylporphyrins is confirmed using analysis of correlations between the electrochemical behavior of porphyrins and their radical scavenging properties.

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1. Introduction

Free radicals (FR) and reactive oxygen species (ROS) are important intermediate products of physiological processes. Their concentration in a healthy cell is maintained at a certain level due to control of ROS formation and decay by enzymes and low molecular weight antioxidants. ROS concentration increase in a cell (oxidative stress) leads to a large number of diseases [1–3] including inflammations, nervous system dysfunctions, diabetes, infarct, senescence, and cancer. Ascorbic acid, tocopherols, natural flavonoids, beta-carotene, etc. are strong natural antioxidants. But despite the fact that they are safer for human health, in some cases, these natural antioxidants do not meet certain requirements as they may be too “mild” or not stable enough, etc. Thus, an urgent problem in modern medicine, pharmacology and food industry is to find new efficient antioxidants both among natural compounds and among synthetic ones [4–7].

Chemical processes with FR and ROS participation in natural conditions are known to be closely connected with the biological function of porphyrins. For example, molecular oxygen transport is facilitated by superoxo- and peroxocomplexes of iron (III) incorporated into the porphyrin platform [8], the catalytic cycle of monooxygenase is provided by the ferments of cytochrome P450 and haem copper [9,10]. A number of studies have shown that porphyrin complexes of transition metals are antioxidants for superoxide anion-radical and are quite promising in their practical application [11,12]. Significant antioxidant

activity is characteristic of heterocyclic compounds of nonporphyrin structure [6,13] and some porphyrin-ligands [14–18]. However, the mechanisms of porphyrin interaction with free radicals and the influence of the porphyrin structure on the antioxidant activity have not been studied well enough yet.

Antioxidant activity is often studied by monitoring the kinetics of the reaction of the compound under study with stable free radicals: 2,2-diphenyl-1-picrylhydrazyl (DPPH) and superoxide (O_2^-), and others. The reaction between the radical and the antioxidant is investigated by UV–VIS spectrophotometry, as a rule [19–23]. The spectrophotometry cannot be used for high concentrations of the reacting substances and for studying antioxidant properties of chromophores with absorption bands in the same region as those of the radical. Such systems can be analyzed by the electrochemical method of radical concentration control. For example, such modified DPPH-test was used to evaluate porphyrins antioxidant properties [24].

The electrochemical method is attractive for antioxidant activity assays using O_2^- because it can be obtained by one-electron electrochemical reduction of the dissolved oxygen in a number of aprotic solvents [25–31] and the electrochemical mechanism is similar to oxygen reduction in animal and vegetable cells. The high radical stability in aprotic solvents enables us to obtain time-stable solutions of superoxide-ion by electrolysis method at controlled potential [32]. The electrochemical oxygen reduction under controlled conditions allows registering the easily-reproduced electrochemical response of the superoxide anion-radical. By comparing different methods of obtaining O_2^- radical in solution, it was proved that it is appropriate to use electrochemical synthesis of superoxide anion-radical to study antioxidant

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properties of different compounds [33]. The value of antioxidant activity can be characterized by IC_{50} parameter (porphyrin concentration required to halve the current of electrochemical reduction of the superoxide anion-radical) or binding constant (K_b) [34–36] determined from the relative change of the $O_2^{\cdot-}$ current electrochemical reduction:

$$\lg \frac{1}{C} = \lg K_b + \lg \left(\frac{I}{I_0 - I} \right), \quad (1)$$

where C is the antioxidant concentration, K_b is the binding constant, I is the $O_2^{\cdot-}$ peak oxidation current density at the given porphyrin concentration, I_0 is the $O_2^{\cdot-}$ maximum peak oxidation current density in a series of experiments with the given porphyrin. These parameters have been successfully applied by us to determining the antioxidant activity of different hydroxyphenylporphyrins and aminophenylporphyrins [15, 17, 37].

However, using the $O_2^{\cdot-}$ oxidation current density as a basic parameter cannot always definitely characterize antioxidant activity as the dependence of the $O_2^{\cdot-}$ peak oxidation current value on the antioxidant concentration is often nonlinear. Only the linear part of such dependences is used to evaluate the antioxidant activity, according to C. Le Bourvellec et al [38]. Calculations of the binding constant [15, 17, 36, 37] by logarithmic coordinates leads to certain data linearization. But it does not solve the problem of antioxidant concentration range selection for antioxidant activity evaluation. The nonlinear dependence of the $O_2^{\cdot-}$ oxidation current on the antioxidant concentration is quite typical due to the antioxidant concentration influence on the antioxidant activity value [39–41], and, probably, due to the antioxidant effect on the oxygen electrochemical reduction [42, 43].

We propose a coulometric antioxidant assay that allows obtaining practically any linear dependence of the electrochemical response of superoxide anion-radical in a rather wide concentration range of porphyrins displaying antioxidant activity [44]. This work describes approbation of this test on a number of hydroxy-substituted tetraphenylporphyrins. The most feasible mechanism of antioxidant activity of hydroxy substituted tetraphenylporphyrins is confirmed by analyzing correlations between the electrochemical behavior of porphyrins and their radical scavenging properties.

2. Experimental

2.1. Solvents and solutions

Dimethylsulfoxide (DMSO ≥ 99.5 , ALDRICH) was purified by zone melting and then stored over molecular sieves in a dry box before use. Tetrabutylammonium perchlorate (TBAP ≥ 98.0 , ALDRICH) was purified by recrystallization from ethanol. Concentrated solutions of porphyrins containing 0.02 M TBAP as the supporting electrolyte were prepared by the gravimetric method using the electronic analytical balance «Sartorius» ME215S (the mass determination error did not exceed 3%). The solutions of smaller concentrations were prepared by the method of serial dilution.

2.2. Porphyrins

Porphyrins (Fig. 1) were synthesized by the two-step method [45–48]. The chromatographically purified (aluminum oxide, Brockmann Activity III) products were characterized by thin-layer chromatography (silufol plates), UV–VIS spectrometry (Varian Cary 50 spectrometer) and 1H NMR spectrometry (Bruker AVANCE-500 spectrometer) methods. The location and intensity of the absorption bands of the porphyrin solutions under study are in good agreement with the literature data and do not change in electrolyte presence, which indicates the absence of interaction between the ions of the supporting electrolyte and porphyrin molecules.

2.3. Electrochemical procedure

Potentiostat PI-50PRO3 (Elins, Russia) was used for electrochemical measurements. The experiments were carried out in three-electrode temperature-controlled (25 ± 0.5 °C) electrochemical cell in freshly prepared solutions. The saturated calomel electrode (SCE) inserted into the electrochemical cell through the Luggin capillary was used as the reference electrode. The Pt spiral wire with a geometric surface area about 5 cm² was used as auxiliary electrode. As the working electrode, we used a polishing Pt strip (working surface equaled 1.2 cm²) rigidly fixed in the fluoroplastic lid. Before every measurement, the active surface of the working electrode was mechanically mirror-polished,

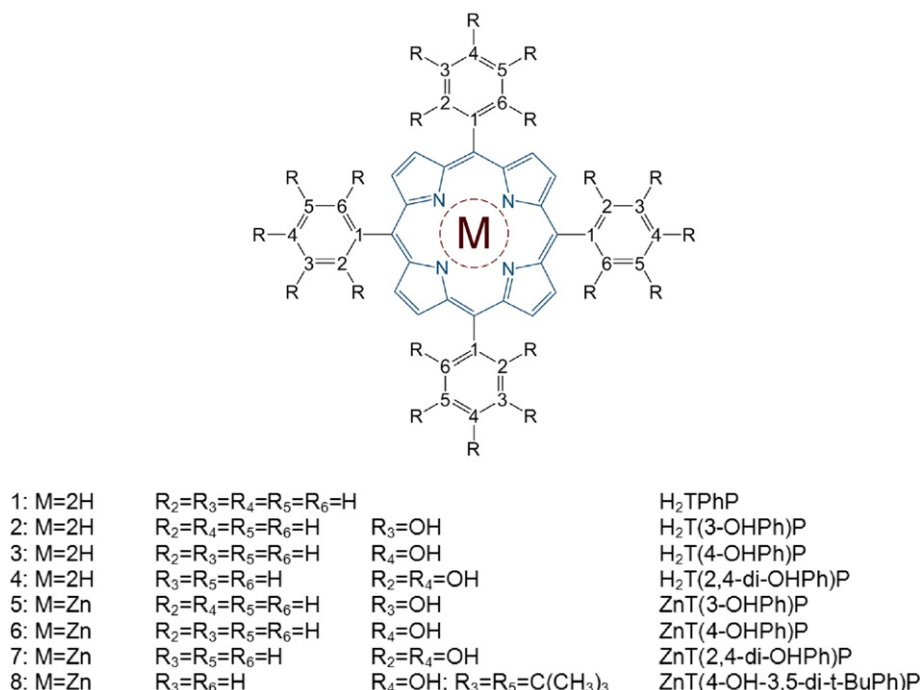


Fig. 1. Structural formulas of the porphyrins used in the present work.

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