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Laccase-catalyzed bisphenol A oxidation in the presence of 10-propyl sulfonic acid phenoxazine

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ABSTRACT

The kinetics of the *Coriolopsis byrsina* laccase-catalyzed bisphenol A (BisA) oxidation was investigated in the absence and presence of electron-transfer mediator 3-phenoxazin-10-yl-propane-1-sulfonic acid (PPSA) at pH 5.5 and 25°C. It was shown that oxidation rate of the hardly degrading compound BisA increased in the presence of the highly reactive substrate PPSA. The increase of reaction rate depends on PPSA and BisA concentrations as well on their ratio, *e.g.*, at 0.2 mmol/L of BisA and 2 μmol/L of PPSA the rate increased 2 times. The kinetic data were analyzed using a scheme of synergistic laccase-catalyzed BisA oxidation. The calculated constant, characterizing reactivity of PPSA with laccase, is almost 1000 times higher than the constant, characterizing reactivity of BisA with laccase. This means that mediator-assisted BisA oxidation rate can be 1000 times higher in comparison to non-mediator reaction if compounds concentration is equal but very low.

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Introduction

Bisphenol A (BisA) is an important industrial chemical primarily used as an intermediate in the production of polycarbonate plastic and epoxy resins (Sasaki et al., 2005). Residues of these products are found in rivers and wastewater treatment plant effluents (Melcer and Klecka, 2011) as well as in human issues (Vandenberg et al., 2007) and can incite serious risks for the environment and public health (Lee et al., 2014; Erler and Novak, 2010; Benachour and Aris, 2009). BisA has been recognized as an endocrine disrupting chemical. This chemical has the ability to imitate the female estrogen hormones, which disrupt the body's chemical messenger system (Jobling et al., 2003) due to its direct interaction with steroid receptors (Uchida et al., 2001).

Various physical (Zhao et al., 2008), chemical (Govindaraj et al., 2013) and biological (Shin et al., 2007) methods have been used to degrade BisA. The processes using fungi and bacteria have received the largest attention. BisA degrading microorganisms can secrete a series of oxidative enzymes. Some of them, such as laccase (Ji et al., 2009), horseradish peroxidase (Li and Nicell, 2008) and lignin peroxidase (Takamiya et al., 2008) have been shown to catalyze the oxidation of BisA in aqueous solutions. The laccases are the most prospective enzymes for industrial–technical application due to the fact that they don't require any additional oxidizers with exception of dissolved oxygen (Xu, 2005).

Laccase (benzenediol: oxygen oxidoreductase, EC 1.10.3.2) belongs to a group of polyphenol oxidases containing copper atoms in the catalytic center and is usually called multicopper oxidases; enzymes widespread in nature that catalyze the four electron reduction of molecular oxygen to water (Baldrian, 2006). The high stability of laccases in aqueous solutions, the mild reaction conditions used in enzyme-catalyzed reactions and oxidative selectivity for phenolic structures make laccases attractive for biotechnological applications (Xu, 2005). In recent years, the newly isolated *Coriolopsis byrsina* laccase (CbL) catalyzed synthesis of various substituted quinones, two of which were

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powerful redox mediators applicable for bioelectrocatalytic systems based on pyrroquinoline quinone-dependent glucose dehydrogenase (Marcinkevičienė et al., 2013). Moreover, CbL oxidized various substrates including Phenol Red (Marcinkevičienė et al., 2013), which is a weak estrogen mimic (Liu et al., 2013). However, there are no reports on the BisA oxidation by CbL.

The efficiency of laccases-catalyzed substrates oxidation can be increased by using mediators especially for oxidation of hardly degrading compounds (Arboleda et al., 2013; Kurniawati and Nicell, 2007; Fabbrini et al., 2002). Searching for new laccase mediators phenoxazine derivatives, *e.g.*, 2-phenoxazin-10-yl-ethanol, 3-phenoxazin-10-yl-propane-1-sulfonic acid (PPSA), 3-phenoxazin-10-yl-propionic acid and others (Marcinkevičienė et al., 2013; Kulys and Bratkovskaja, 2012) were synthesised. It has been shown that phenoxazine derivatives are high active laccase substrates (Tetianec and Kulys, 2009; Kulys and Tetianec, 2005). They effectively mediated oxidation of aromatic N-hydroxy derivatives (Xu et al., 2000; Kulys et al., 2009).

The objective of this study was to investigate the synergistic effect of mediators PPSA on BisA oxidation catalyzed by CbL. PPSA is known as the most reactive laccase substrate (Tetianec and Kulys, 2009). The reactivity depends on substrate redox potential which is 0.631 V for PPSA (Tetianec and Kulys, 2009). PPSA redox potential is the smallest compared to redox potentials of other well-known mediators (0.69 V for 2,2-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS), 0.916 V for violuric acid (VLA), 1.08 V for 1-hydroxybenzotriazole (HBT), 1.09 V for N-hydroxyphthalimide (HPI)) (Fabbrini et al., 2002). Among all these well-known mediators studied, ABTS was the most successful at enhancing the laccase-catalyzed oxidation of BisA compared to VLA, HBT, HPI, *etc.* (Kim and Nicell, 2006). ABTS is distinguished from other well-known mediators by good stability of the oxidized form. The radical cations of PPSA have also demonstrated remarkable stability during weeks in water solution (Kulys and Bratkovskaja, 2007). Therefore PPSA was selected due to its good characteristic compared to other well-known mediators. To explain kinetic data a synergistic scheme of substrates action was applied.

1. Materials and methods

1.1. Reagents

BisA (2,2-bis(4-hydroxyphenyl)propane) was received from Merck (Germany). PPSA was synthesized as described by Kulys et al. (2006). The homogeneous CbL was purified as described by Marcinkevičienė et al. (2013). The purified enzyme showed the specific activity 156 U/mg protein. One unit of activity was defined as the amount of enzyme oxidizing 1 μmol of 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) per 1 min at pH 5.5 and 30°C. Protein concentration was measured routinely by the method of Lowry et al. (1951), using bovine serum albumin as the standard. The concentration of CbL in the stock solution was 20 mg/mL.

Sodium acetate was a product of Chempur (Poland). Sample of BisA was weighted and dissolved into 50 mmol/L acetate buffer at pH 5.5. The PPSA and CbL solutions were prepared in deionized water.

1.2. Kinetic measurements

The kinetic measurements were performed at 25 ± 0.1°C in 1-cm thermostated cuvette using a computer-controlled Nicolet evolution 300 spectrophotometer (Thermo Electron Corporation, USA). The increase of absorbance of BisA oxidation products was measured at 276 nm. The kinetic measurements were performed in 50 mmol/L sodium acetate buffer solution at pH 5.5 and 25°C and the reaction mixture contained 0.025–0.3 mmol/L of BisA, 42–212 nmol/L of CbL, and 0–3 μmol/L of PPSA. The reactions started with addition of the enzyme solution.

The increase of absorbance of PPSA oxidation products ($PPSA^{\cdot+}$) was measured at 530 nm (ε_{530} = 16 L/(mmol·cm)) (Tetianec and Kulys, 2009)). The kinetic measurements of

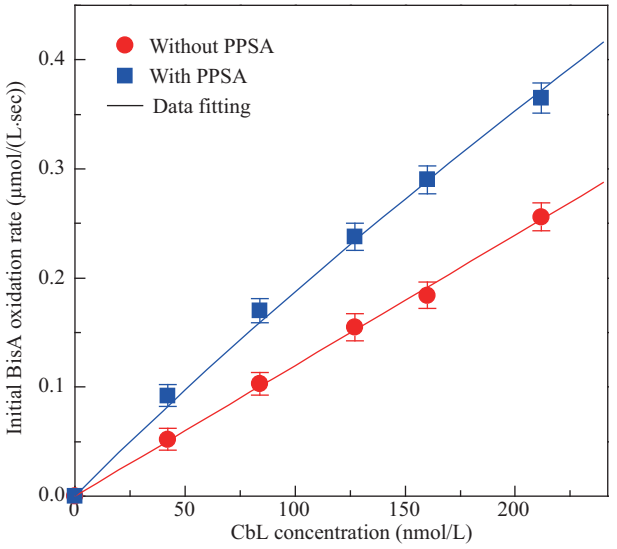

Fig. 1 – Dependence of initial BisA oxidation rates on enzyme concentrations. Conditions: 0.2 mmol/L BisA, 42–212 nmol/L CbL, 2 μmol/L PPSA, 50 mmol/L acetate buffer solution pH 5.5, 25°C. Curves are the result of data fitting with a model Eqs. (5)–(7).

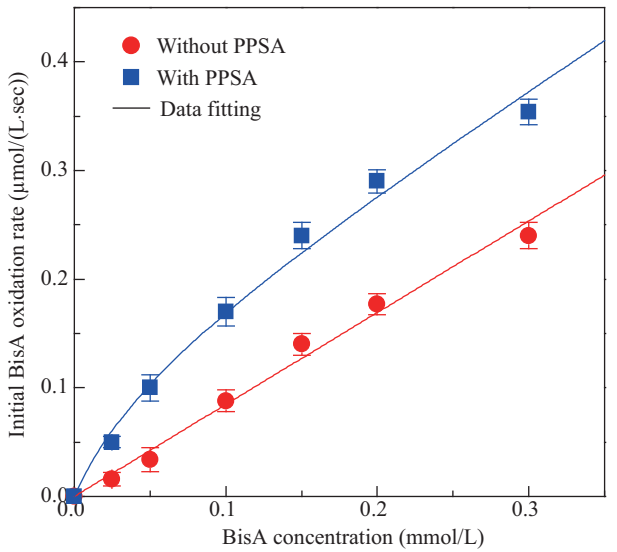

Fig. 2 – Dependence of initial BisA oxidation rates on BisA concentrations. Conditions: 0.025–0.3 mmol/L BisA, 160 nmol/L CbL, 2 μmol/L PPSA, 50 mmol/L acetate buffer solution pH 5.5, 25°C. Curves are the result of data fitting with a model Eqs. (5)–(7).

Table 1 – Kinetic characteristics of laccase-catalyzed oxidation of BisA in the presence of PPSA in 50 mmol/L acetate buffer at pH 5.5 and 25°C.

Determination method	k_1 (L/(mol·sec))	k_2 (L/(mol·sec))	k_3 (L/(mol·sec))	k_4 (L/(mol·sec))
Experimental data	2×10^6	$4.3 \times 10^6 \pm 0.3 \times 10^6$	$5.2 \times 10^3 \pm 0.6 \times 10^3$	–
Mathematical modeling	2×10^6	$3.9 \times 10^6 \pm 0.2 \times 10^6$	$5.8 \times 10^3 \pm 0.3 \times 10^3$	$>1.6 \times 10^3$

Note: The value of k_1 was taken from literature (Palmer et al., 2001).

PPSA oxidation were performed in 50 mmol/L sodium acetate buffer solution at pH 5.5 and 25°C and the reaction mixture contained 2–45 μmol/L of PPSA and 4 nmol/L of CbL.

1.3. Calculations

The absorbance increase that appears due to BisA oxidation products is received by removing the initial absorbance of BisA from the total absorbance. In order to receive the BisA product concentration the absorbance increase was normalized by differential extinction coefficient. Differential extinction coefficient was received from a distinct experiment, when low concentration of BisA was oxidized by a high enzyme concentration. When absorbance increase achieves saturation and extra enzyme addition does not influence any change all BisA turns into oxidation products. Differential extinction coefficient is obtained by dividing the value of saturated absorbance increase by BisA concentration. The initial reaction rate (V) was calculated as a slope of the oxidation products concentration change during 50 sec. The absorbance during this period changed almost linearly. The programs OriginPro and Mathcad 2001 Professional were employed for data processing.

2. Results and discussion

2.1. Effect of mediator PPSA on bisphenol A oxidation

The initial rate of 0.2 mmol/L of BisA oxidation linearly increased in the range 0.05–0.26 μmol/(L·sec) if enzyme concentration increased from 40 to 200 nmol/L. When 2 μmol/L PPSA was added to the reaction mixture, the initial rate of BisA oxidation increased from 0.09 to 0.37 μmol/(L·sec) (Fig. 1). At low CbL concentrations (42–84 nmol/L) the initial reaction rate increased approximately 2 times compared to the initial reaction rate with no PPSA added. On increase in CbL concentration (127–212 nmol/L) the initial rate of oxidation with PPSA added increased almost 1.5 fold compared to the initial reaction rate with no PPSA added.

The initial rate of BisA oxidation (0.02–0.24 μmol/(L·sec)) was linearly dependant on BisA concentration which varied from 0.025 to 0.3 mmol/L. In the presence of 2 μmol/L PPSA, the initial rate of substrate oxidation changed in the range 0.05–0.35 μmol/(L·sec) (Fig. 2). The data indicated that the presence of 2 μmol/L PPSA in the reaction mixture results in 2–3 fold increase in the initial reaction rate at relatively low BisA concentrations (0.025–0.2 mmol/L) compared to the initial reaction rate with no PPSA added. On 0.3 mmol/L BisA concentration the initial rates of oxidation differ 1.5 fold, when comparing oxidation with and without PPSA added.

In the absence of PPSA, the dependence of initial oxidation rate on substrate concentration was linear. Apparent bimolecular constant k_3 was calculated from the ratio of the slope of a linear dependence on laccase concentration and was equal to $5.2 \times 10^3 \pm 0.6 \times 10^3$ L/(mol·sec) (Table 1).

A plot of the initial rate of BisA oxidation *versus* PPSA concentration is presented in Fig. 3. The initial rate of BisA oxidation linearly increased from 0.18 μmol/(L·sec) in the absence of PPSA, to 0.32 μmol/(L·sec) in the presence of 3 μmol/L PPSA.

The oxidation of various PPSA concentrations exhibited saturation kinetics (data not shown). The apparent bimolecular rate constant k_2 was calculated according to $k_2 = V_{max} / (K_m \cdot [CbL])$ using the estimated parameters $V_{max} = 0.12 \pm 0.01$ μmol/(L·sec) and $K_m = 6.91 \pm 0.01$ μmol/L and it was $4.3 \times 10^6 \pm 0.3 \times 10^6$ L/(mol·sec) (Table 1).

2.2. Model of laccase-catalyzed bisphenol A oxidation with mediatory effect

The following equations (Bratkovskaja et al., 2006) were proposed to explain laccase-catalyzed oxidation of BisA and PPSA mediator effect on this process:

$$E_{red} + O_2 + 4H^+ \xrightarrow{k_1} NI + 2H_2O \quad (1)$$

$$NI + PPSA \xrightarrow{k_2} E_{red} + PPSA^{\cdot+} + 4H^+ \quad (2)$$

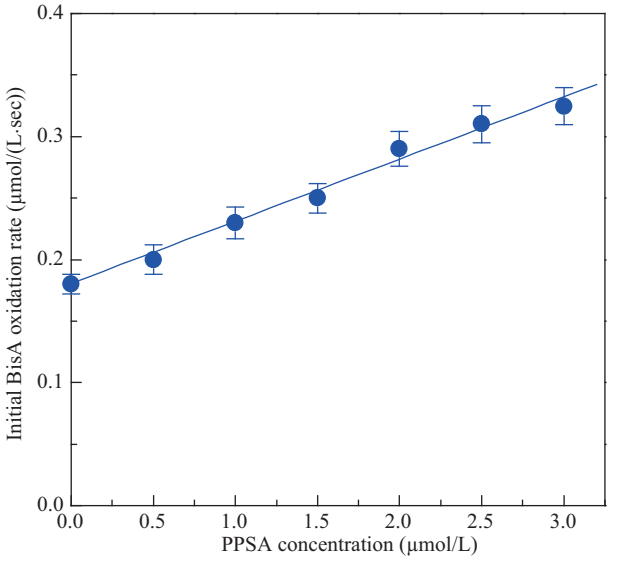

Fig. 3 – Dependence of initial BisA oxidation rates on PPSA concentrations. Conditions: 0.2 mmol/L BisA, 160 nmol/L CbL, 0–3 μmol/L PPSA, 50 mmol/L acetate buffer solution pH 5.5, 25°C. Curve is the result of data fitting with a model Eqs. (5)–(7).

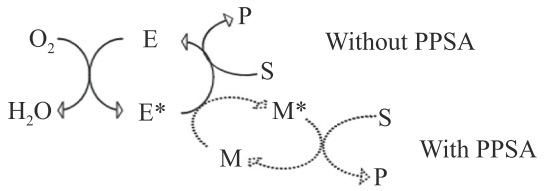

Fig. 4 – Scheme of synergistic biocatalytic substrate BisA oxidation without mediator PPSA and with PPSA. E: native laccase; E*: oxidized laccase; S: substrate; P: products; O_2: dioxygen; H_2O: water; M: mediator; M*: oxidized mediator (Kurniawati and Nicell, 2007).

$$NI + BisA \xrightarrow{k_3} E_{red} + BisA_{ox} \quad (3)$$

$$PPSA^{\cdot+} + BisA \xrightarrow{k_4} PPSA + BisA_{ox} \quad (4)$$

where, E_{red} and NI are reduced form of laccase and native intermediate of laccase; PPSA and $PPSA^{\cdot+}$ correspond to reduced and oxidized PPSA; BisA and $BisA_{ox}$ correspond to reduced and oxidized substrate (BisA), respectively. The rate constants k_1, k_2, k_3 and k_4 correspond to Reactions (1)–(4). According to Reactions (1)–(4), one-electron oxidation of BisA occurs simultaneously with four-electron reduction of molecular oxygen. When PPSA is involved into the enzymatic process, transport of an electron from mediator to enzyme is accompanied by electron transfer from a BisA molecule to the oxidized mediator; this results in regeneration of the mediator Reactions (3)–(4). According to this scheme the initial BisA oxidation reaction rate is (Bratkovskaja et al., 2006):

$$V = [BisA]\left(k_3[NI] + k_4\left[PPSA^{\cdot+}\right]\right) \quad (5)$$

where, [BisA], [NI] and $[PPSA^{\cdot+}]$ are initial concentrations of BisA, native intermediate of laccase and oxidized PPSA, respectively; where steady-state $PPSA^{\cdot+}$ and NI concentrations are:

$$\left[PPSA^{\cdot+}\right] = \frac{k_2[NI][PPSA]_t}{k_2[NI] + k_4[BisA]} \quad (6)$$

$$[NI] = 2[E]_t k_1[O_2]k_4[BisA]\left(\frac{1}{k_4[BisA]k_1[O_2] - k_2[E]_t k_1[O_2] + k_4[BisA]^2 k_3 + \frac{1}{+k_4[BisA]k_2[PPSA]_t + \sqrt{(k_2)^2[E]_t^2(k_1)^2[O_2]^2 + 2k_2[E]_t(k_1)^2[O_2]^2 k_4[BisA] + \frac{1}{\sqrt{+2k_2[E]_t k_1[O_2]k_4[BisA]^2 k_3 - 2(k_2)^2[E]_t k_1[O_2]k_4[BisA][PPSA]_t + k_4[BisA]^2(k_1)^2[O_2]^2 + \frac{1}{\sqrt{+2(k_4)^2[BisA]^3(k_1)^2[O_2]^2 k_3 + 2(k_4)^2[BisA]^2 k_1[O_2]k_2[PPSA]_t + \frac{1}{\sqrt{+(k_4)^2[BisA]^4(k_3)^2 + 2(k_4)^2[BisA]^3 k_3 k_2[PPSA]_t + [BisA]^2[PPSA]_t{}^2(k_4)^2(k_2)^2}}}}}}}\right) \quad (7)$$

where, $[E]_t$ and $[PPSA]_t$ correspond to the total enzyme CbL and mediator PPSA concentrations, respectively. The derived Eqs. (5)–(7) were used for fitting the experimentally obtained initial rate dependences. The experimental results obtained in the absence of PPSA were fitted with $[PPSA]_t = 0$. Additionally, the rate constant of reduced laccase interaction with oxygen Reaction (1) was taken as $k_1 = 2 \times 10^6$ L/(mol·sec) at 25°C (Palmer et al., 2001). It is also assumed that the concentration of dissolved oxygen is constant and is equal to 2.53×10^{-4} mol/L (Koppenol and Butler, 1985). Kinetic constants obtained by mathematical modeling using Reactions (1)–(4) and by solving Eqs. (5)–(7) are close in value to those obtained experimentally (Table 1). This demonstrates that the considered process properly corresponds to the suggested scheme Reactions (1)–(4).

As it can be seen from Table 1, k_2 and k_3 values, obtained both from modeling and experimental data, are equal within the calculation error. Approximated constant k_4 shows the smallest value, at which chemical reaction can limit the process. The calculated value of k_2 constant characterizes the reactivity of PPSA with laccase, which is almost 1000 times higher than bimolecular constant k_3, characterizing reactivity of BisA with laccase. The high PPSA reactivity determines the proportional increase of mediator process rate.

Good fit of calculated constants supports the synergistic mechanism of CbL-catalyzed BisA-PPSA oxidation. Such oxidation process is schematically represented by the following well-known scheme (Fig. 4).

3. Conclusions

The kinetics of laccase-catalyzed oxidation of BisA in the presence of PPSA functioning as a redox-active mediator was analyzed. Addition of PPSA mediator increases the laccase catalyzed initial oxidation rate of BisA up to 3 times. The suggested kinetic scheme of synergistic oxidation of low active BisA in the presence of PPSA and a mathematical model of this process were experimentally proved. It was shown that depending on the experimental conditions (the ratio of enzyme, substrate, and mediator concentrations), the process can proceed under steady-state conditions. The calculated constant, characterizing reactivity of PPSA with laccase, is almost 1000 times higher than bimolecular constant, characterizing reactivity of BisA with laccase. The results are of interest for further search for enzyme-mediator systems, which not only enlarge the spectrum of enzyme-oxidized substrates but also increase degradation efficiency of slowly oxidized phenol compounds.

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