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ScienceDirect
Journal of Molecular Catalysis B: Enzymatic 45 (2007) 21–26
JOURNAL OF MOLECULAR CATALYSIS B: ENZYMATIC
www.elsevier.com/locate/molcatb

Differences in stereo-preference in the oxidative degradation of diastereomers of the lignin model compound 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol with enzymic and non-enzymic oxidants

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Received 24 May 2006; received in revised form 22 October 2006; accepted 1 November 2006
Available online 4 December 2006

Abstract

Mixtures of equal amounts of the *erythro* and the *threo* forms of the β-O-4 lignin model compound 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol were oxidized with different ligninolytic enzymes and non-enzymic oxidants. The oxidants included cerium(IV) ammonium nitrate (CAN), Fenton's reagent, lead(IV) tetraacetate (LTA), laccase, laccase–mediator systems (based on the mediators ABTS, HBT, TEMPO, and VLA), and lignin peroxidase. The stereo-preference of the different oxidants was compared based on analyses of remaining substrate using HPLC and UV-diode array detector or ^{1}H NMR spectroscopy. Fenton's reagent was the only oxidant tested that did not show preferential degradation of either the *erythro* or the *threo* form. CAN, LTA and lignin peroxidase preferentially oxidized the *threo* form. The stereo-preference of the laccase–mediator systems depended on the mediator. Oxidation mediated by HBT, TEMPO or VLA resulted in a preferential degradation of the *threo* form. Laccase/ABTS was the only system tested that showed preferential oxidation of the *erythro* form. The stereo-preference of the oxidants is discussed based on their redox potentials and their classification as outer-sphere and inner-sphere oxidants.

Keywords: Stereo-preference; Oxidation; β-O-4 lignin model compound; Laccase–mediator system; Lignin peroxidase

1. Introduction

Lignins are complex biopolymers consisting of phenylpropane units (reviewed in [1,2]). The arylglycerol-β-aryl ether (β-O-4 ether) substructure is predominant in lignin and occurs both in *erythro* and *threo* configurations. The relative amounts of the *erythro* and the *threo* forms differ in hardwood lignins and softwood lignins. The *erythro* form is predominant in hardwood [3,4], while similar amounts of the *erythro* and *threo* forms are present in softwood [4].

Chemical delignification by alkaline cooking results in a comparatively low *erythro*/*threo* ratio in the arylglycerol β-aryl ether structures remaining in the lignin [5–7]. This implies a preferential degradation of the *erythro* forms. The delignification results are expected since experiments with β-O-4 lignin model compounds have shown that, under alkaline conditions, the diastereomers differ with regard to susceptibility to degradation, the *erythro* forms being degraded more rapidly than the corresponding *threo* forms [8,9].

The effect of oxidation on the *erythro*/*threo* ratio is not well known, but experiments with a β-O-4 compound as model and lignin peroxidase and cerium(IV) ammonium nitrate (CAN) as oxidants demonstrated a preferential degradation of the *threo* form [10]. It remains to be investigated whether there are any differences in stereo-preference between the various types of oxidants commonly considered in biological contexts, such as enzymes, mediators of enzymic oxidation, reactive oxygen species, and biomimetic oxidants.

In this study equal amounts of the *erythro* (**1e**) and *threo* (**1t**) forms of the non-phenolic β-O-4 lignin model compound 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (Fig. 1) were oxidized to elucidate the

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doi:10.1016/j.molcatb.2006.11.001

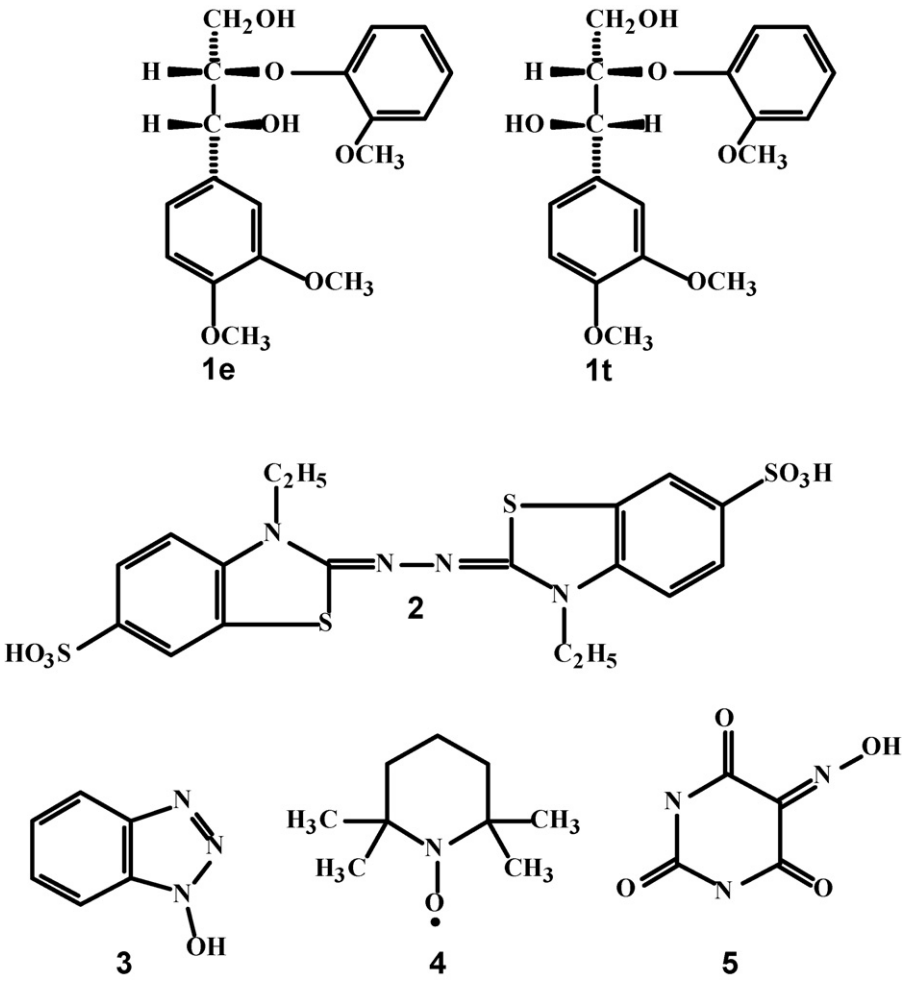

Fig. 1. The *erythro* (**1e**) and *threo* (**1t**) forms of the lignin model compound 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol and the mediators ABTS (**2**), HBT (**3**), TEMPO (**4**), and VLA (**5**).

stereo-preference of different oxidants. Acid-catalyzed equilibration gives a product consisting of nearly equal amounts of **1e** and **1t** suggesting that the diastereomers are equally stable [11]. Crystal structures show that the bulky aryl group and aryloxy group in **1e** are fairly close to each other (the torsion angle between these groups is about 60°) [12], while **1t** adopts an extended conformation in which the aromatic groups are positioned almost as far apart as possible (the torsion angle between the aryl group and the aryloxy group is 176°) [13]. The shape of the substrate molecules may influence the interaction with the oxidants. The experiments included in this investigation cover direct enzymic, mediated enzymic, and non-enzymic oxidation systems. The results reveal both quantitative and qualitative differences in the diastereomer ratio after degradation with the different oxidants.

2. Material and methods

2.1. Chemicals

Reagent grade chemicals were used unless otherwise stated. The *erythro* (**1e**) and *threo* (**1t**) forms of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (Fig. 1) were prepared according to methods described in the literature [14,15].

2.2. Enzymes and enzyme assays

Laccase and lignin peroxidase were prepared from *Trametes* (*Coriolus* or *Polyporus*) *versicolor*, as previously described [16,17]. The laccase activity was determined spectrophotometrically using a Shimadzu UV-1601PC instrument. The reaction mixture contained 2,2′-azinobis(3-ethylbenzothiazolone-6-sulfonic acid) (ABTS) (0.4 mM solution), acetate buffer (50 mM, pH 5.2), and laccase. The change in absorbance was recorded at 414 nm for 5 min (temperature 21 °C). One unit was defined as the amount of laccase that forms 1 μmol ABTS radical cation ($\varepsilon = 3.6 \times 10^4\ M^{-1}\ cm^{-1}$ [18]) min^{-1}. The lignin peroxidase activity was also determined spectrophotometrically. The reaction was monitored at 310 nm for 5 min (temperature 21 °C). The reaction medium consisted of tartrate buffer (100 mM, pH 3.0), which was 2 mM with respect to veratryl alcohol [(3,4-dimethoxyphenyl)methanol] and 0.2 mM with respect to hydrogen peroxide. One unit was defined as

the amount of enzyme that forms 1 μmol of veratraldehyde ($\varepsilon = 9.3 \times 10^3\ M^{-1}\ cm^{-1}$ [19]) min^{-1}.

2.3. ^1H NMR spectroscopy

^1H NMR spectra were recorded at 400 MHz on a Varian Unity 400 instrument, using deuterochloroform as solvent. The internal reference was $(CH_3)_4$ Si and the temperature was 20 °C. Mixtures of the *erythro* and *threo* forms of **1** were analyzed based on the signal from Hβ [located at δ 4.17 (multiplet) in the *erythro* form spectrum and at δ 4.02 (multiplet) in the *threo* form spectrum].

2.4. High Performance Liquid Chromatography (HPLC)

The separation and quantification of **1e** and **1t** was performed using HPLC. An XTerra Phenyl analytical column (5 μm, 2.1 mm × 150 mm) (Waters, Milford, MA, USA) equipped with an XTerra MS C_{18} (5 μm, 2.1 mm × 10 mm) guard column was used in a VP series HPLC system (Shimadzu, Kyoto, Japan). The autoinjector was set at 4 °C and the injection volume was 20 μl. Detection and quantification was performed using an SPD-M10Avp diode array UV–vis detector (λ 280 nm) and the LCsolution 1.0 software (Shimadzu). The eluent (flow rate: 0.2 ml/min) consisted of a gradient of Milli-Q water (Millipore, Bedford, MA, USA) and acetonitrile, both of which were 2 mM with respect to formic acid. The elution with acetonitrile was conducted as follows: 0–5 min, linear gradient from 5 to 10%; stepped increase to 20%; 5–10 min, isocratic at 20%; 10–20 min, linear gradient from 20 to 23%; 20–35 min, isocratic at 23%; stepped increase to 50%; 35–50 min linear gradient from 50 to 90%; and reconditioning of the column isocratic at 5% for 15 min. For analysis of reactions with TEMPO, a modified elution scheme was used: 0–5 min, linear gradient from 5 to 10%; stepped increase to 15%; 5–15 min, isocratic at 15%; 15–25 min, linear gradient from 15 to 23%; 25–40 min, isocratic at 23%; stepped increase to 50%; 40–55 min, linear gradient from 50 to 90%; and reconditioning of the column isocratic at 5% for 15 min. The samples, which had been flash frozen and stored at −20 °C, were thawed and filtered through 0.45 μm membranes before analysis.

2.5. Oxidation experiments with mixtures of equal amounts of the erythro (*1e*) and threo (*1t*) forms of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol

The oxidations were performed in three stages to produce a sample with each one of the oxidants in which approximately one half of the substrate (composed of equal amounts of the *erythro* and *threo* forms of **1**) had reacted. In Stage 1, the reaction was initiated by addition of the oxidant, and a sample for analysis was taken after 30 min. In Stage 2, a second addition of the oxidant was made, and a sample for analysis was taken after 3.5 h. In Stage 3, a third addition of the oxidant was made, and a sample for analysis was taken after 20 h. The additions of oxidants in Stages 2 and 3 are calculated without consideration of remaining oxidant from previous additions (volume changes due to oxidant additions and sample withdrawals are taken into account). The reaction medium in Stage 1 was always 1 mM with respect to a mixture of equal amounts of the *erythro* (**1e**) and *threo* (**1t**) forms of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (0.5 mM of **1e** and 0.5 mM of **1t**), and 20 mM with respect to acetate buffer (pH 4.0). The reactions were incubated on a shaking platform at 21 °C.

A typical experiment with a non-enzymic oxidant, such as cerium(IV) ammonium nitrate (CAN), was conducted as follows: Stage 1 was initiated by mixing 575 μl H_2O, 400 μl 100 mM acetate buffer (pH 4.0), 1000 μl 2 mM **1e/1t** solution, and 25 μl of a 100 mM solution of CAN. At the end of Stage 1, a sample (200 μl) was withdrawn for analysis and an addition of 22.5 μl 100 mM CAN solution was made. At the end of Stage 2, a sample (200 μl) was withdrawn for analysis and an addition of 20 μl 100 mM CAN solution was made. At the end of Stage 3, a final sample was taken for analysis.

A typical experiment with an enzymic oxidant is exemplified by a laccase/ABTS reaction: Stage 1 was initiated by mixing 480 μl H_2O, 400 μl 100 mM acetate buffer (pH 4.0), 1000 μl 2 mM **1e/1t** solution, 100 μl of a 20 mM ABTS solution, and 20 μl of a 50 U/ml laccase solution. At the end of Stage 1, a sample (200 μl) was withdrawn for analysis and an addition of 18 μl of the laccase solution was made. At the end of Stage 2, a sample (200 μl) was withdrawn for analysis and an addition of 16 μl of the laccase solution was made. At the end of Stage 3, a final sample was taken for analysis.

2.5.1. Non-enzymic reactions and controls

CAN

In each stage, CAN was added to a concentration of 1.2 mM. See the experiment described above.

Fenton's reagent

A solution of iron(II) chloride was added in Stage 1 (concentration, 2 mM). Hydrogen peroxide was added to a concentration of 2 mM (Stage 1), 2 mM (Stage 2), and 10 mM (Stage 3).

Hydrogen peroxide control

The conditions were those of the Fenton's reagent experiment but no iron(II) chloride was added.

Lead(IV) tetraacetate (LTA)

In each stage, LTA was added to a concentration of 0.75 mM.

Negative control

No oxidant was added, but **1e/1t** mixture and buffer concentrations were those indicated in the experiment described above.

2.5.2. Enzymic reactions and controls

Laccase control

Laccase was added to a concentration of 0.5 U/ml in each stage.

Laccase–mediator systems

The mediators (Fig. 1) were added in Stage 1 to the following concentrations: 2,2'-azinobis(3-ethylbenzothiazolone-6-sulfonic acid) (ABTS) 1 mM, 1-hydroxybenzotriazole (HBT) 0.5 mM, 2,2,6,6-tetramethylpiperidin-N-oxyl (TEMPO)

1 mM, violuric acid (VLA) 1 mM. See the experiment with ABTS described above. Laccase additions were made in the same way as for the laccase control with the exception of the TEMPO-mediated reaction, in which the laccase concentration was 0.75, 0.13, and 0.10 U/ml in Stage 1, 2 and 3, respectively.
Lignin peroxidase

Lignin peroxidase was added to the concentration 0.35 U/ml in each stage. Hydrogen peroxide was added to a concentration of 0.5 mM (Stage 1), 0.5 mM (Stage 2), and 2 mM (Stage 3).

2.6. Analysis of the reaction mixtures

The peaks of **1e** and **1t** in the HPLC chromatograms (λ 280 nm) of the reaction mixtures were evaluated both with regard to height and area (data shown are based on height). Products were identified using the retention times and spectra of reference compounds analyzed on the same occasion as the samples (the retention times could differ slightly between samples analyzed on various occasions).

For verification of results from HPLC chromatograms in which other peaks were not entirely separated from the peaks of **1**, selected samples were analyzed with ^{1}H NMR and HPLC after extraction of residual **1** with chloroform. The chloroform extract was dried over Na_2SO_4 and the solvent was then evaporated. Prior to the analysis with HPLC, the residue was dissolved in water.

3. Results and discussion

The results of the non-enzymic and enzymic oxidations of the *erythro* (**1e**) and *threo* (**1t**) forms of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol are summarized in Table 1. The isomer ratio at the beginning of the oxidation experiment was 50:50 (**1e**:**1t**). The laccase control and the hydrogen peroxide control did not exhibit any oxidation of **1**. To obtain comparable results experimental conditions leading to the consumption of one half of the substrate were pursued in the oxidation experiments. The amount of **1** that remained in the reaction mixtures in the experiments reported in Table 1 ranged between 40 and 59% of the initial amount. The measurements were repeated for all oxidants studied. All the experiments carried out with each one of the oxidants (two or more series of experiments and at least four analyses) were consistent with respect to qualitative results (stereo-preference) but quantitative results (*erythro/threo* ratio) were as expected dependent on the extent of consumption of the substrate. Nevertheless, the reported results in Table 1 provide a clear view of the relative stereo-selectivity in the systems examined since the changes in *erythro/threo* ratio in the substrate consumption interval 41–60% was small. The reaction products and their distribution have been addressed in a previous investigation [20].

Table 1
Amounts and ratios of the *erythro* (**1e**) and *threo* (**1t**) forms of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol in oxidation mixtures

	Percentage of initial amount (%)		Isomer ratio[a] (1e:1t)
	1e	**1t**	
Control	100	100	50:50
CAN	62	18	78:22
Fenton's reagent	44	41	51:49
LTA	75	34	69:31
Laccase/ABTS	43	71	37:63
Laccase/HBT	51	38	57:43
Laccase/TEMPO	67	51	58:42
Laccase/VLA	53	44	55:45
Lignin peroxidase	75	35	68:32

[a] The standard deviation was ≤2% (repeated analyses).

In the reaction with CAN, 40% of the *erythro/threo* mixture remained after oxidation (Table 1). CAN oxidized **1t** to a greater extent than **1e**, resulting in a **1e**:**1t** ratio of 78:22 (Table 1). The preferential CAN oxidation of the *threo* form of a different type of β-O-4 model compound, 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propanediol, has been demonstrated [10].

Fenton's reagent oxidized **1e** and **1t** to approximately the same extent resulting in a **1e**:**1t** ratio of 51:49 when 42% of the *erythro/threo* mixture was left (Table 1). Fenton's reagent differed from all the other oxidants (Table 1) in the respect that it did not exhibit any stereo-selectivity. The lack of selectivity may be related to the high redox potential of the reactive oxygen species generated by Fe^{2+}/H_2O_2.

LTA oxidized the *threo* form of **1** preferentially. The **1e**:**1t** ratio was 69:31 when 45% of the *erythro/threo* mixture had been consumed (Table 1). The stereo-preference of LTA resembles that of CAN and lignin peroxidase (Table 1), while the product formation pattern shows clear differences [20]. Pb(IV) differs from Ce(IV) in being recognized as an inner-sphere oxidant, although the possibility that Pb(IV) also can be involved in outer-sphere electron transfer is not excluded [21].

The effect of the non-enzymic oxidants (CAN, Fenton's reagent and LTA) on mixtures of equal amounts of **1e** and **1t** was also studied using non-buffered reaction medium. The results (data not shown) were similar to those obtained with buffered reaction medium.

Stereo-selectivity has also been studied with other oxidants. According to Ohi et al. [22], nitrous acid treatment of a β-ether model resulted in preferential degradation of the *threo* form. Any stereo-preference was not observed in delignification experiments with sodium chlorite as oxidant [6].

The stereo-preference of the laccase–mediator systems depended on the mediator used (Table 1). With ABTS, the **1e**:**1t** ratio was 37:63 when 57% of the *erythro/threo* mixture remained (Table 1). The preference of laccase/ABTS for **1e** oxidation was confirmed by extraction of remaining substrate with chloroform and analysis of the extract with ^{1}H NMR and HPLC (Fig. 2). This is the only case studied (Table 1) in which the *erythro* form was preferentially oxidized. This result differs from that reported in another study, in which no stereo-preference was observed [23]. The other mediators (HBT, TEMPO and VLA) resulted in a preferential oxidation of the *threo* form of **1** (Table 1, Fig. 2). In reaction mixtures where 44–59% of the substrate remained, the **1e**:**1t** ratio ranged from 55:45 (VLA) to 58:42 (TEMPO) (Table 1). The preference for *threo* form oxidation was less

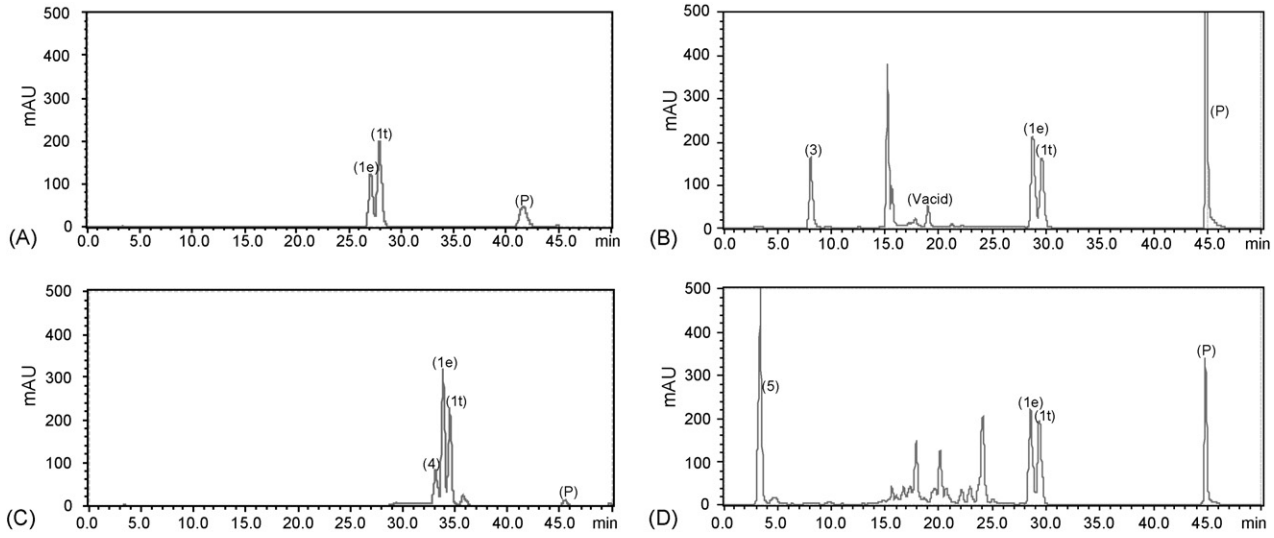

Fig. 2. HPLC chromatograms of reaction mixtures (λ 280 nm) from oxidation experiments with the *erythro* (**1e**) and *threo* (**1t**) forms of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol: (A) laccase/ABTS (Stage 3) (chloroform extract), (B) laccase/HBT (Stage 2), (C) laccase/TEMPO (Stage 1), (D) laccase/VLA (Stage 2). Peaks due to **1e**, **1t** and the products 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone (P) and veratric acid (Vacid) are indicated.

pronounced in the laccase oxidations mediated by HBT, TEMPO or VLA than that observed with CAN or LTA (Table 1).

Lignin peroxidase oxidized **1t** to a greater extent than **1e** resulting in a **1e**:**1t** ratio of 68:32 when 45% of the *erythro/threo* mixture had been consumed (Table 1). Preferential degradation of the *threo* form of the β-O-4 model 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propanediol with lignin peroxidase from *T. versicolor* has been reported [10]. Tokimatsu et al. [24] oxidized a lignin model compound related to **1** with lignin peroxidase from *Phanerochaete chrysosporium*. The results point to a preferential oxidation of the *threo* form.

In addition to direct oxidation of the *erythro/threo* mixture of **1** with lignin peroxidase, the lignin peroxidase experiment was also performed with veratryl alcohol present as mediator. The presence of veratryl alcohol did not influence the *threo* preference.

The redox potentials of the oxidants differ considerably. Hydroxyl radicals arising from Fenton's reagent have very high redox potential (2.8 V [25,26]). CAN, LTA and lignin peroxidase are expected to have high redox potentials (Ce^{4+}/Ce^{3+} and Pb^{4+}/Pb^{2+} have standard redox potentials of 1.76 V and 1.69 V, respectively [27], and lignin peroxidase is known to oxidize substrates with a redox potential of over 1.36 V [28]). Laccase from *T. versicolor* has a relatively high redox potential in comparison to many other laccases [29] and is therefore a suitable oxidant in combination with various mediators. The redox potentials of the laccase–mediator systems are around 1 V (HBT, 1.08 V [30]; VLA, 0.916 V [30]; ABTS, 1.1 V ($ABTS^{\bullet+}/ABTS^{2+}$) [30]; TEMPO, 0.722 V versus Ag/AgCl [31] corresponding to approximately 0.92 V versus NHE). The dication $ABTS^{2+}$ has been implied to be responsible for the oxidation of non-phenolic lignin substructures, while the cation radical $ABTS^{\bullet+}$ oxidizes phenolic substructures [32]. With regard to the *N*-hydroxy compounds and their derivatives, oxidations of HBT and VLA to the corresponding nitroxyl radicals and oxidation of TEMPO to the corresponding oxoammonium ion are considered in this context (cf. review by Sheldon and Arends [33]).

Nakatsubo et al. studied degradation of enantiomers of a different type of lignin model compound, 1,2-bis(3-methoxy-4-ethoxyphenyl)propane-1,3-diol, in cultures of *P. chrysosporium* by analysis of optical activity [34], but did not analyze the effect on the ratio of the diastereomers. Zitzelsberger et al. [35] report that no stereospecific degradation of diastereomers of veratrylglycerol-β-2,4-dichlorophenyl ether occurs in cultures of *P. chrysosporium* or *Corynebacterium equi*. A lowering of the original *threo/erythro* ratio occurred initially but the authors considered that this was a consequence of high substrate/enzyme ratio. Crestini et al. [36] studied biodegradation of milled straw lignin by the white-rot fungus *Lentinula edodes* and reported that the results possibly implied a decrease in the *erythro/threo* ratio of the arylglycerol-β-aryl ether structures.

The differences in product profiles on oxidation of **1e** by non-enzymic oxidants, lignin peroxidase and laccase/ABTS have been reported previously [20]. Results from oxidation experiments with β-ether models using CAN as oxidant exhibit striking similarities to those obtained with lignin peroxidase as oxidant, both with regard to the product profiles and the preferential degradation of the *threo* forms ([10,20], this work). CAN is a known outer-sphere oxidant [21]. The similarities between CAN and lignin peroxidase as concerns oxidation properties suggest that lignin peroxidase also acts as an outer-sphere oxidant. The laccase/ABTS system differs from the other oxidants in the respect that it causes a preferential oxidation of **1e** (Table 1). In the previous study [20] it was found that laccase/ABTS oxidation of **1e** resulted in a nearly quantitative conversion to 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone. CAN or lignin peroxidase oxidation led to a rather diverse product pattern [20]. A possible explanation of the particular oxidation properties of the laccase/ABTS system may be that it

acts as an inner-sphere oxidant (cf. [20]). The laccase/HBT, laccase/TEMPO and laccase/VLA systems exhibit a preferential oxidation of **1t** but the stereo-preference is not very pronounced (Table 1). 1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)-1-propanone is a significant constituent in the oxidation mixtures obtained. This is in accordance with results reported by Barreca et al., who studied product formation from **1** in laccase-catalyzed oxidations mediated by HBT and VLA [37].

The differences in stereo-preference reflect the different properties of the oxidants. The results are relevant with regard to the understanding of the initial phase of biological lignin degradation and the identification of specific oxidants involved in the reactions.

Acknowledgements

This work was supported by grants form the Swedish Research Council and the Carl Trygger Foundation.

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