

Xue-Fei ZHOU, Jian-Xin QIN, Shu-Rong WANG

OXIDATION OF A LIGNIN MODEL COMPOUND OF BENZYL-ETHER TYPE LINKAGE IN WATER WITH H_2O_2 UNDER AN OXYGEN ATMOSPHERE CATALYZED BY Co(Salen)

The catalytic properties of Cobalt salen²⁺ complex in the oxidation of a lignin model compound [veratrylglycerol- β -guaiacyl- α,γ -dimethylether, VGD] have been investigated in order to obtain the mechanistic aspects of the reaction between Co(salen) and VGD under an oxygen atmosphere using hydrogen peroxide as an oxidant. VGD was found to undergo structural changes in response to the catalytic reaction as characterised by different analytical techniques (FT-IR, 1H NMR and GC-MS), yielding 2-methoxy phenol and biphenyl. A mechanism for the oxidation of VGD was postulated.

Keywords: catalytic oxidation, veratrylglycerol- β -guaiacyl- α,γ -dimethylether (VGD), Co(salen), FTIR, 1H NMR, GC-MS

Introduction

Salen complexes are known to be an important class of coordination compounds that have been used to catalyse an extremely wide variety of reactions over the past decades since 1933 [Pfeiffer et al. 1933]. Many of these reactions are oxidations of organic substrates, based on the use of terminal oxidants such as molecular oxygen and hydrogen peroxide. Besides being environmentally more benign, the catalytic oxidation of organic compounds with O_2 and H_2O_2 is less wasteful from an economic point of view, and is now an important reaction in both research laboratories and industry [Meyer, Limberg 2007]. Metal salen compounds

Xue-Fei ZHOU, Kunming University of Science and Technology; South China University of Technology, Guangzhou; Nanjing University of Technology; Beijing University of Chemical Technology; Southwest University of Science and Technology, Mianyang, China

e-mail: lgdx602@tom.com

Jian-Xin QIN, Kunming University of Science and Technology, China

Shu-Rong WANG, Zhejiang University, Hangzhou, China.

e-mail: srwang@zju.edu.cn

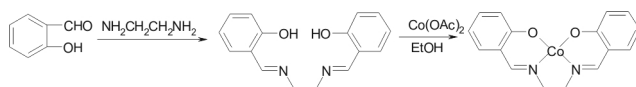
have been investigated as catalysts in several different reactions, for example in epoxidation, epoxide ring opening, carbonyl addition, cycloaddition and the oxidation of sulphides to sulfoxides [Larrow, Jacobsen 2004]. Previous work on Co(salen)-catalyzed O_2 -oxidation of p-substituted phenols to p-benzoquinones has been extended to include substrates that serve as models for lignin phenolic subunits [Salanti et al. 2010]. Lignin is an aromatic, amorphous, heterogeneous polymer that represents the second most abundant natural polymeric material on Earth [Lebo Jr et al. 2001]. It is known that the bulk of lignin in wood consists of nonphenolic aryl-glycerol- β -O-aryl ether units. Other units, such as phenyl-coumaran (β -5), resinol (β - β), and dibenzodioxocins(5-5/ β -O-4, α -O-4) are also present within the lignin macromolecule [Ralph et al. 2000]. Furthermore, lignin is usually covalently linked to carbohydrates forming a refractory lignin-carbohydrate network [Lowoko et al. 2003].

Our laboratory has been investigating the mechanism of Co(salen) catalysed oxidation of lignin using isolated lignins and some model compounds as substrates. In this context, we studied the oxidation of another lignin model compound with special linkage of benzyl-ether type (VGD) as a substrate, using Co(salen) complex as a catalyst to mimic lignin peroxidase. The mechanism of oxidation of such a lignin model compound, using Co complexes as catalysts, is largely unstudied. In the present study, the oxidation of VGD can provide us with information on the reactivity of both the model compound and lignin itself, and assist in the development of new catalysts for environmentally-friendly pulp bleaching processes.

Materials and methods

Synthesis of cobalt salen complex

Ligand for the complex was synthesised using the standard method [Jacobsen 1993]. Cobalt complex was synthesised by refluxing an EtOH solution of the ligand and 2 eq. of $Co(OAc)_2 \cdot 4H_2O$ for 1 h (scheme 1), adding water and filtering out the product.



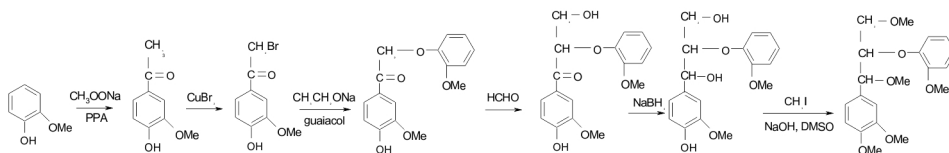
Scheme 1
Schemat 1

The product was washed successively with water and 80% EtOH. Brownish-black powder was then obtained under vacuum drying, yield 96.92 %. Typical characteristic absorption peaks were found with FTIR as follows: C-H stretching vibration ($2869\text{--}2948\text{ cm}^{-1}$), C=N stretching vibration [1635 cm^{-1}], C=C stretching

vibration in aromatic ring (1610, 1577, 1498 cm⁻¹), C-H bending vibration (1373 cm⁻¹), C-O in Ar-O bending vibration (1284 cm⁻¹), C-N stretching vibration (1200, 1149 cm⁻¹), Co-N stretching vibration (568 cm⁻¹), Co-O stretching vibration (470 cm⁻¹).

Synthesis of veratrylglycerol- β -guaiacyl- α,γ -dimethylether (VGD)

Guaiacylglycerol- β -guaiacyl (GG) was basically prepared following the procedure proposed by Hosoya et al. [Hosoya et al. 1980], except for cupric bromide being used instead of Br₂ for the preparation of ω -bromo acetoguaiacone from acetoguaiacone [King, Ostrum 1964; Fukagawa et al. 1992]. GG was methylated fully with methyl iodide in anhydrous methyl sulfoxide (DMSO) in a nitrogen atmosphere according to Hakomori method [Hakomori 1964]. See scheme 2. Typical characteristic absorption.



Scheme 2
Schemat 2

Peaks of VGD were found in FTIR and H-1 NMR spectra as follows (fig. 2, 3): C-H vibration in aromatic ring (3030 cm⁻¹), C-H vibration in CH₃-, CH₂-, CH- (2937 cm⁻¹), C-H vibration in -CH₂- (2841 cm⁻¹), C=C vibration in aromatic ring (1595, 1503, 1456 cm⁻¹), C-H vibration in CH₃- (1369 cm⁻¹), C-O vibration in β -O-4 linkage (1258 cm⁻¹), C-H stretching in aromatic ring (1147 cm⁻¹), C-O-C at α , γ -position (1076 cm⁻¹), C-H stretching in aromatic ring (1031, 951, 815 cm⁻¹); H-Ar (7.03-6.75 ppm), H- β (4.7-4.5 ppm), H- α (4.4-4.3 ppm), 3-OCH₃ and 4-OCH₃ (3.9-3.8 ppm), 3'-OCH₃ (3.8-3.7 ppm), H- γ (3.7-3.6 ppm), α -OCH₃ and γ -OCH₃ (3.6-3.5 ppm).

Oxidation of VGD

30 mg of VGD, 2 mg of catalyst, and 0.48 mg of pyridine were taken in a glass reactor. 0.6 ml of 30% H₂O₂ was added drop by drop. Enough NaOH was added to ensure pH controlled to 12.5 and heated to the reaction temperature in a water bath. The mixture was stirred under oxygen atmosphere. The reaction was carried out for 0.5 h at 90°C. At the end of the reaction, the reaction mixture was cooled to room temperature and then separated with a glass filter to obtain solid and liquid samples. The isolated solid samples were analysed by FTIR (EQUINOX55) and

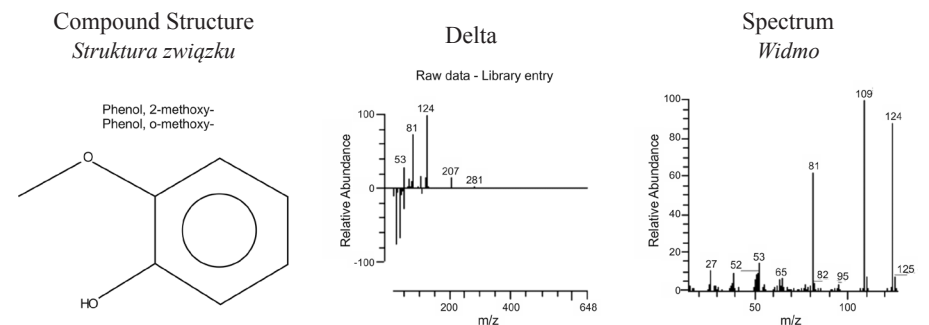
H-1 NMR (BRUKER DRX500). The liquid samples were extracted into dichloromethane. The extract was dried over Na_2SO_4 , filtered and then the solvent was evaporated under reduced pressure. The identity of the products, i.e. 2-methoxy phenol and biphenyl, present in the extract was confirmed by GC-MS (AGILENT TECHNOLOGIES GC-MS HP6890/5973MS). See table 1 and fig. 1.

Table 1. Identity of the products, i.e. 2-methoxy phenol and biphenyl, by GC-MS
Tabela 1. Określenie produktów, tj. 2-metoksy fenolu i bifenylu, za pomocą GC-MS

No. Nr	RT [min]	RSI	SI	Name Nazwa	Molecular formula Wzór cząsteczkowy	Library Biblioteka
1	8.50	919	910	2-Methoxy phenol	$\text{C}_7\text{H}_8\text{O}_2$	Mainlib
2	43.03	773	677	6-Hydroxy-2',3',4'-1,1'- -biphenyl	$\text{C}_{15}\text{H}_{16}\text{O}_4$	Mainlib

With the SI and RSI matching factors, a perfect match results in the value of 1000. As a general guide 900 or greater is an excellent match, 800-900 a good match, and 700-800 a fair match.
 Przy dobrze dobranych czynnikach SI i RSI, doskonale dopasowanie prowadzi do wartości 1000. Ogólnie przyjmuje się, że 900 lub większa wartość oznacza doskonale dopasowanie, 800-900 dobre dopasowanie, a 700-800 dostateczne dopasowanie.

(a)



(b)

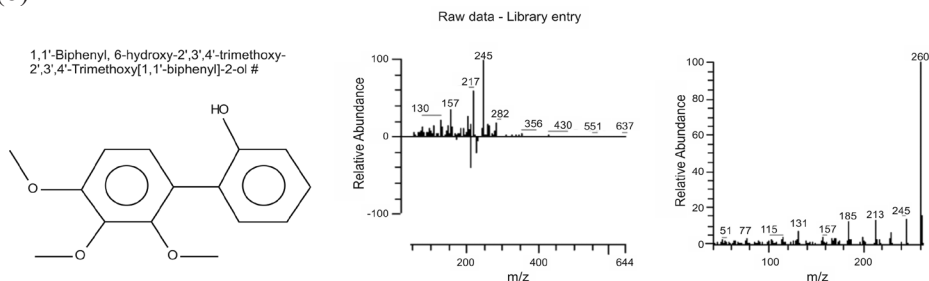


Fig. 1. MS spectra of 2-methoxy phenol (a) and biphenyl (b)

Rys. 1. Widma MS 2-metoksy fenolu (a) i bifenylu (b)

Result and discussion

Oxidative enzymes such as lignin peroxidase (LiP), manganese peroxidase (MnP), and laccase participate in bioconversions of lignin [Boerjan et al. 2003]. The capability of salen-type metal complexes to function as mimics for those enzymes was tested by oxidising VGD with H₂O₂ under oxygen atmosphere catalysed by a prepared Co(salen) complex. The oxidation was carried out at a temperature of 90°C in an alkaline aqueous solution at pH 12.5. The reaction was elucidated with FTIR, H-1 NMR and GC-MS techniques. The structural changes of VGD across the Co(salen) catalytic oxidation were obtained based on the data (tables 2, 3) from FTIR and H-1 NMR spectra (fig. 2, 3). The functional description in FTIR and H-1 NMR spectra was determined following the data from Hu [2003] and Toikka & Brunow [1999], respectively.

Table 2. Structural changes of VGD as determined by FTIR during Co(salen) catalytic oxidation

Tabela 2. Zmiany strukturalne VGD określone za pomocą FTIR podczas katalitycznego utleniania Co(salen)

No. Nr	Functional description <i>Opis funkcjonalny</i>	Wavenumber <i>Numer fali</i>	Signal changes in FTIR spectra <i>Zmiany sygnału w widmach FTIR</i>	
		[cm ⁻¹]	VGD	VGD after reaction <i>VGD po reakcji</i>
1	C-H stretching in aromatic ring <i>rozciąganie się C-H w pierścieniu aromatycznym</i>	3030	m	w
2	C-H vibration in CH ₃ -, CH ₂ -, CH-drgania C-H w CH ₃ -, CH ₂ -, CH-	2937	m	n
3	C-H vibration in -CH ₂ -drgania C-H w -CH ₂ -	2841	m	n
4	C-O vibration in side chain C=O <i>drgania C-O w łańcuchu bocznym C=O</i>	1623	n	m
5	C=C vibration in aromatic ring <i>drgania C=C w pierścieniu aromatycznym</i>	1595, 1503, 1456	s	n
6	C-H vibration <i>drgania C-H</i>	1400	n	s
7	C-H vibration in CH ₃ -drgania C-H w CH ₃ -	1369	m	n

Table 2. Continued
Tabela 2. Ciąg dalszy

8	C-O vibration in β -O-4 linkage <i>drgania C-O w wiązaniu β-O-4</i>	1258	m	n
9	C-H stretching in aromatic ring <i>rozciąganie się C-H w pierścieniu aromatycznym</i>	1147	m	n
10	C-O-C vibration at α , γ -position <i>drgania C-O-C w pozycji α, γ</i>	1076	m	n
11	C-H stretching in aromatic ring <i>rozciąganie się C-H w pierścieniu aromatycznym</i>	1031	s	n
12	C-H stretching in aromatic ring <i>rozciąganie się C-H w pierścieniu aromatycznym</i>	951	m	n
13	C-H stretching in aromatic ring <i>rozciąganie się C-H w pierścieniu aromatycznym</i>	815	w	n
s – strong; m – medium; w – weak; n – nondetectable <i>s – silne; m – średnie; w – słabe; n – niewykrywalne</i>				

Table 3. Structural changes of VGD as determined by H-1 NMR during Co(salen) catalytic oxidation

Tabela 3. Zmiany strukturalne VGD określone za pomocą H-1 NMR podczas katalitycznego utleniania Co(salen)

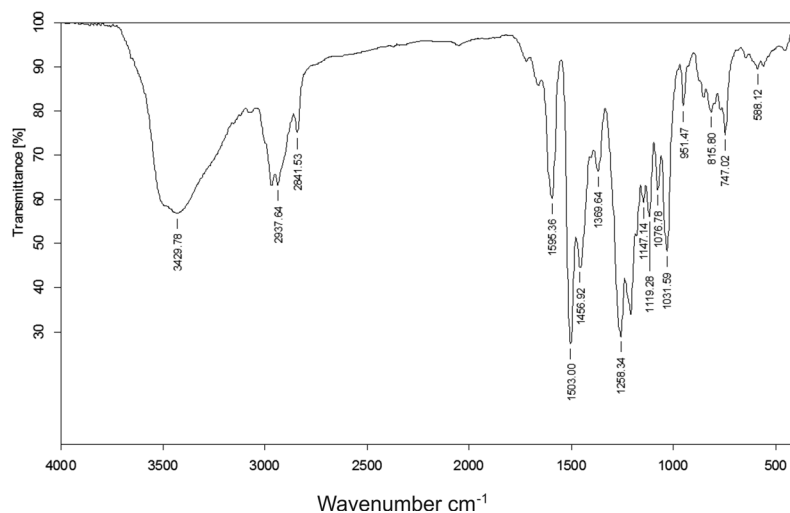
No. <i>Nr</i>	Functional description <i>Opis funkcjonalny</i>	Chemical shift <i>Przesunięcie chemiczne</i>	Signal changes in spectra <i>Zmiany sygnałów w widmach</i>	
		[ppm]	VGD	VGD after reaction <i>VGD po reakcji</i>
1	H-Ar	7.03-6.75	s	m
2	H- β	4.7-4.5	ns	ns
3	H- α	4.4-4.3	ns	ns
4	3-OCH ₃ , 4-OCH ₃	3.9-3.8	s	m
5	3'-OCH ₃	3.8-3.7	s	m

Table 3. Continued

Tabela 3. Ciąg dalszy

6	H- γ	3.7-3.6	ns	ns
7	$\alpha\text{-OCH}_3$, $\gamma\text{-OCH}_3$	3.6-3.5	ns	ns
s – strong; m – medium; ns – not significant <i>s – silne; m – średnie; ns – nieistotne</i>				

(a)



(b)

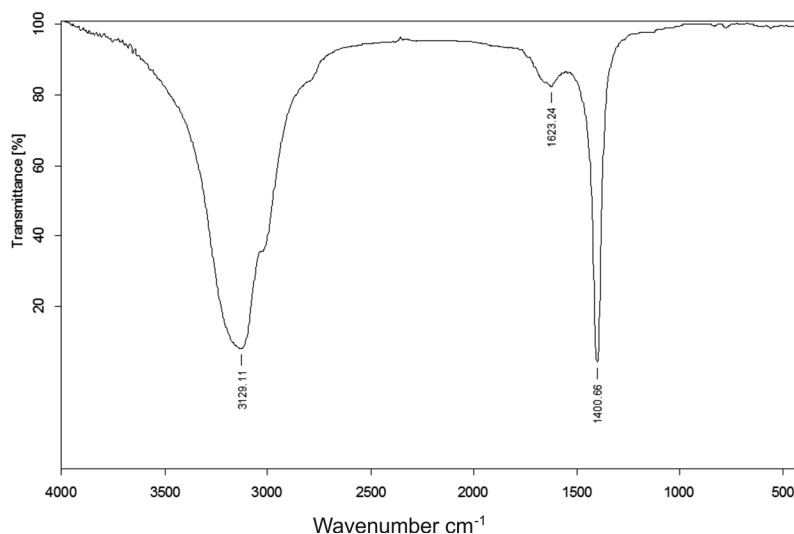


Fig. 2. FTIR spectra of untreated sample (VGD, a) and treated sample (treated VGD, b)
Rys. 2. Widma FTIR próbki niezmienionej (VGD, a) i próbki zmienionej (zmieniony VGD, b)

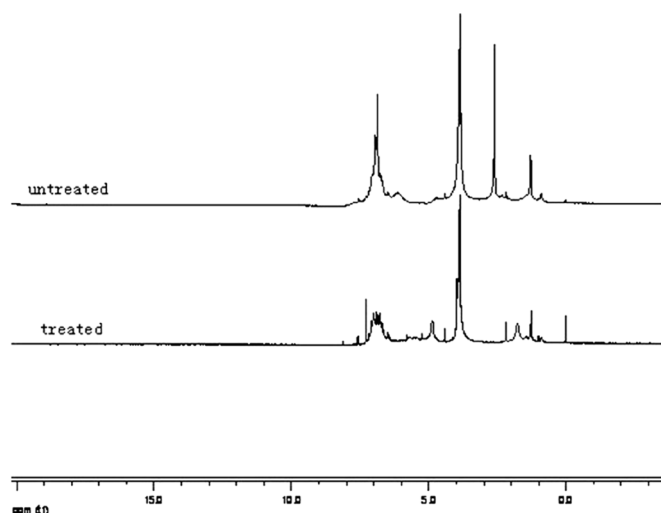


Fig. 3. ^1H NMR spectra of untreated sample (VGD) and treated sample (treated VGD)

Rys. 3. Widma ^1H NMR próbki niezmięnionej (VGD) i próbki zmienionej (zmieniony VGD)

A clear trend is observed according to the signal changes in the FTIR and ^1H NMR spectra in tables 1 and 2. The aromatic ring (3030, 1595, 1503, 1456, 1147, 1031, 951, 815 cm^{-1} , 7.03-6.75 ppm) was seriously degraded; carbonyl ($\text{C}=\text{O}$, 1623 cm^{-1}) occurred in the aromatic side chain due to $\text{Co}(\text{salen})$ catalytic oxidation in the presence of H_2O_2 under oxygen atmosphere. Similarly Kervinen found that veratryl alcohol, a lignin model compound, could be selectively oxidized to veratraldehyde with molecular oxygen in water catalyzed by $\text{Co}(\text{salen})$ [Kervinen 2005].

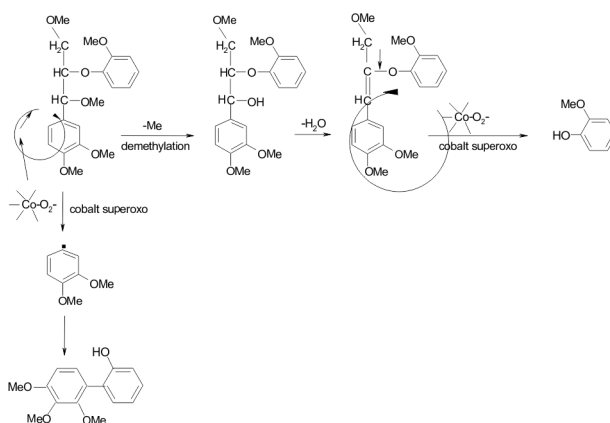


Fig. 4. Postulated mechanism for transformation of VGD catalyzed by $\text{Co}(\text{salen})$

Rys. 4. Postulowany mechanizm transformacji VGD katalizowanego $\text{Co}(\text{salen})$

Demethylation was observed during the catalytic oxidation based on the signals at 1369, 1076 cm⁻¹ (FTIR), 3.9-3.8, 3.8-3.7 ppm (H-1 NMR). The cleavage of β -O-4 linkage (1258 cm⁻¹) gave 2-methoxy phenol, and C-C coupled biphenyl, a compound arising from radical coupling, was obtained as well, as detected by GC-MS analysis (table 1, fig. 1), which commonly involves the hydrogen atom abstraction by the cobalt superoxo complex [Mayer 1998; Mayer et al. 2006]. The mechanism postulated is given in fig. 4.

Conclusions

VGD, a lignin model compound with benzyl-ether type linkage, was found to undergo obvious changes in structure during the catalytic reaction by Co(salen) with hydrogen peroxide under oxygen atmosphere. The reaction of aromatic ring-opening, demethylation and β -O-4 cleavage was observed, yielding 2-methoxy phenol and biphenyl.

Acknowledgements

The authors are grateful for the financial support of the National Natural Science Foundation of China (No. 21166011, 20766002), the Scientific Research Foundation of the Department of Education of Yunnan Province (No. 2010J059), the Open Project of the State Key Laboratory of Clean Energy Utilization of Zhejiang University (No. ZJUCEU2010004), the Open Project of the State Key Laboratory of Pulp and Paper Engineering of South China University of Technology (No. 201033), the Open Project of the State Key Laboratory of Materials-Oriented Chemical Engineering of Nanjing University of Technology (No. KL10-12), the Open Project of the State Key Laboratory of Chemical Resource Engineering of Beijing University of Chemical Technology (No. CRE-2011-C-305), the Open Project of the Key Laboratory of Solid Waste Treatment and Resource Recycling of the Ministry of Education of Southwest University of Science and Technology (No. 11zxgk07), and the Analysis and Testing Foundation of Kunming University of Science and Technology.

References

- Boerjan W., Ralph J., Baucher M.** [2003]: Lignin bios. *Ann. Rev. Plant Biol.* 54: 519-549
- Fukagawa N., Meshitsuka G., Ishizu A.** [1992]: 2D NMR study of residual lignin in beech Kraft pulp combined with selective cleavage with pivaloyl iodide. *J. Wood Chem. Technol.* 12 [4]: 425-445
- Hakomori S.** [1964]: A rapid permethylation of glycolipid and polysaccharide catalyzed by methylsulfinyl carbanion in dimethyl sulfoxide. *J. Biochem.* [55]: 205-208
- Hosoya S., Kanazawa K., Kaneko H., Nakano J.** [1980]: Synthesis of gaiacylglycerol- β -gaiuacyl ether (in Japanese). *Mokuzai. Gakkaishi* 26: 118-121

- Hu Z. J.** [2003]: Degradation of lignin-carbohydrate complexes catalyzed by GIF biomimetic system (in Chinese). South China University of Technology, Guangzhou
- Jacobsen E. N.** [1993]: Catalytic Asymmetric Synthesis. VHC, New York
- King L. C., Ostrum G. K.** [1964]: Selective bromination with copper (II) bromide. *J. Org. Chem.* 29: 3459-3461
- Kervinen K.** [2005]: Studies on veratryl alcohol oxidation catalyzed by Co(salen) type complexes and molecular oxygen in aqueous solution. University of Helsinki
- Larrow J. F., Jacobsen E. N.** [2004]: Asymmetric processes catalyzed by chiral (salen) metal complexes. *Topics Organomet. Chem.* 6: 123-152
- Lebo Jr S. E., Gargulak J. D., McNally T. J.** [2001]. Lignin. In: *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley and Sons, Hoboken
- Lowoko M., Henriksson G., Gellerstedt G.** [2003]: New method for the quantitative preparation of lignin-carbohydrate complex from unbleached softwood kraft pulp: Lignin-poly-saccharides networks I. *Holzforschung* 57: 69-74
- Mayer J. M.** [1998]: Hydrogen atom abstraction by metal-oxo complexes: Understanding the analogy with organic radical reactions. *Acc. Chem. Res.* 31: 441-450
- Mayer J. M., Mader E. A., Roth J. P., Bryant J. R., Matsuo T., Dehestani A., Bales, B. C. Watson E. J., Osako T., Valliant-Saunders K., Lam W. H., Hrovat D. A., Borden W. T., Davidson E. R.** [2006]: Stoichiometric oxidations of σ -bonds: Radical and possible non-radical pathways. *J. Mol. Catal. A: Chem.* 251 [1-2]: 24-33
- Meyer F., Limberg C.** [2007]: *Organometallic Oxidation Catalysis*. Springer-Verlag, Berlin, Heidelberg
- Pfeiffer P., Breith E., Lübke E., Tsumaki T.** [1933]: Tricyclic ortho-condensed partial valence rings. *Justus Liebig's Annalen der Chemie* 503: 84-130
- Ralph J., Marita J., Ralph S., Hatfield R., Lu F., Ede R., Peng J., Quideau S., Helm R., Grabber J., Kim H., Jimenez-Monteon G., Zhang Y., Jung H., Landucci L., Mackay J., Sederoff R., Chapple C., Boudet A.** [2000]: Solution-state NMR of lignins. In: *Advances in Lignocellulosic Characterization*. Argyropoulos D., Rials T., Eds.; TAPPI Press, Atlanta
- Salanti A., Orlandi M., Tolppa E.-L., Zoia L.** [2010]: Oxidation of isoeugenol by salen complexes with bulky substituents. *Int. J. Mol. Sci.* 11: 912-926
- Toikka M., Brunow G.** [1999]: Lignin-carbohydrate model compounds. Reactivity of methyl 3-O-(α -L-arabinofuranosyl)- β -D-xylopyranoside and methyl β -D-xylopyranoside towards a β -O-4-quinone methide. *J. Chem. Soc., Perkin Trans. L.*: 1877-1883

UTLENIANIE MODELOWEGO ZWIĄZKU LIGNINY Z TYPEM WIAZANIA BENZYLOWO-ETEROWEGO W WODZIE Z H_2O_2 W ATMOSFERZE TLENU KATALIZOWANE Co(Salen)

Streszczenie

Zbadano katalityczne właściwości kompleksu Co(Salen) w utlenianiu modelowego związku ligniny (veratrylglycerol- β -guaiacyl- α,γ -dimetyleter, VGD) w celu określenia mechanicznych aspektów reakcji pomiędzy Co(salen) i VGD w atmosferze tlenu przy zastosowaniu nadtlenu wodoru jako utleniacza. Zaobserwowano, że w VGD zaszły zmiany strukturalne w odpowiedzi na reakcję katalityczną, co przedstawiono za pomocą różnych technik analitycznych (FTIR, ^1H NMR oraz GC-MS). W efekcie otrzymano 2-metoksy fenol i bifenyl.

Słowa kluczowe: utlenianie katalityczne, veratrylglycerol- β -guaiacyl- α,γ -dimetyleter (VGD), Co(salen), FTIR, ^1H NMR, GC-MS