

Analytical Pyrolysis Pathways of Guaiacyl Glycerol- β -guaiacyl Ether by Py-GC/MS

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A synthetic method for obtaining a lignin model compound of β -O-4 structure, guaiacyl glycerol- β -guaiacyl ether, was researched through five reaction steps from guaiacol. The key step of this synthetic method was the condensation reaction between 4-(α -bromoacetyl)-guaiacol (III) and guaiacol (I). The compounds were characterized by ¹H nuclear magnetic resonance spectroscopy (¹H-NMR) and two-dimensional nuclear magnetic resonance (2D-NMR). Pyrolysis behaviors of guaiacyl glycerol- β -guaiacyl ether were investigated by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The thermal behavior and the evolution profiles of major volatile fragments from the guaiacyl glycerol- β -guaiacyl ether pyrolysis were evaluated. Guaiacol is the major product through C β -O homolysis at low temperatures. C β -O homolysis and C β -O concerted decomposition occurred at moderate temperatures, producing guaiacol, 2-hydroxybenzaldehyde, 2-methoxybenzaldehyde, and various phenolic compounds. At high temperatures, the products obtained from C β -O homolysis and C β -O concerted decomposition experienced secondary thermal cracking, generating a large number of small molecule products, which increased the complexity of the pyrolytic products.

Keywords: Pyrolysis; Lignin model compound; 2D-NMR; Py-GC/MS; TG

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INTRODUCTION

Due to the depletion of fossil reserves and increasingly serious environmental problems, biomass energy has become an attractive sustainable energy because it is abundant, renewable, and environmentally friendly (Bridgewater 2004). Lignin is one of the most abundant components of plant biomass, which accounts for 15 to 30% of lignocellulosic biomass (Zakzeski *et al.* 2012). From a chemical perspective, residual lignin from lignocellulosic biomass is most likely the major renewable source for aromatics, and it offers the only potential direct production pathway for phenolics (Kang *et al.* 2010). Hence, the prospect of converting biomass resources into various forms of fuels and chemicals is very attractive.

A variety of conversion technologies are used for lignin, such as hydrothermal conversion, pyrolysis (Wang *et al.* 2009; Jiang *et al.* 2010a; Jiang *et al.* 2010b), enzymatic degradation (Xia *et al.* 2003), photocatalytic degradation (Lei *et al.* 2013), electrochemical degradation (Tian *et al.* 2010), ionic liquids degradation (Binder *et al.* 2009), and

microwave irradiation oxidation (Ouyang *et al.* 2010). Of these, pyrolysis plays a significant role in lignin conversion to renewable energy. Pyrolysis is the direct thermal decomposition of the organic materials in the absence of oxygen to obtain an array of gas, liquid, and solid products (Bridgewater *et al.* 1999; Mohan *et al.* 2006). Because the structure of the lignin is complicated, pyrolysis is an extremely complex process, with a series of reactions that are influenced by many factors, and it is difficult to understand the intricate reaction pathways (Raveendran *et al.* 1995; Lv *et al.* 2010).

A valuable tool to understand the intricate reaction pathways of lignin conversion is the investigation of model compounds. Due to the highly variable and complex chemical structure of lignin, simple, low-molecular-weight model compounds have been used to study the dissociation of lignin instead of lignin itself (Beste *et al.* 2007; Park *et al.* 2010; Roberts *et al.* 2010). Lignin has many hydroxyl phenyl propane units such as coniferyl alcohols and sinapyl alcohols, which are connected through C–O and C–C linkages. Of these linkages, the β -ether linkage is the most abundant. For example, this type of bond accounts for approximately 46% of the chemical linkages in softwood lignin and 60% in hardwood lignin. These ether bonds are easily broken, making β -ether cleavage the principal reaction in lignin depolymerization (Zakzeski *et al.* 2010). Therefore, the β -ether linkage is notably important in the study of lignin. β -ether has been used as an important model compound for various reactions of lignin, such as pulping, chemical reactivity, and biodegradability, because it does not have unnecessary side chains, and its pyrolysis products are relatively simple (Sarkanen and Ludwig 1971; Tien and Kirk 1983; Ralph and Grabber 1996; Lu and Ralph 1997).

In this study, guaiacyl glycerol- β -guaiacyl ether was synthesized and characterized by $^1\text{H-NMR}$ and 2D-NMR HSQC. The thermal cracking products of the pyrolysis reaction were investigated by gas chromatography/mass spectrometry (GC/MS).

EXPERIMENTAL

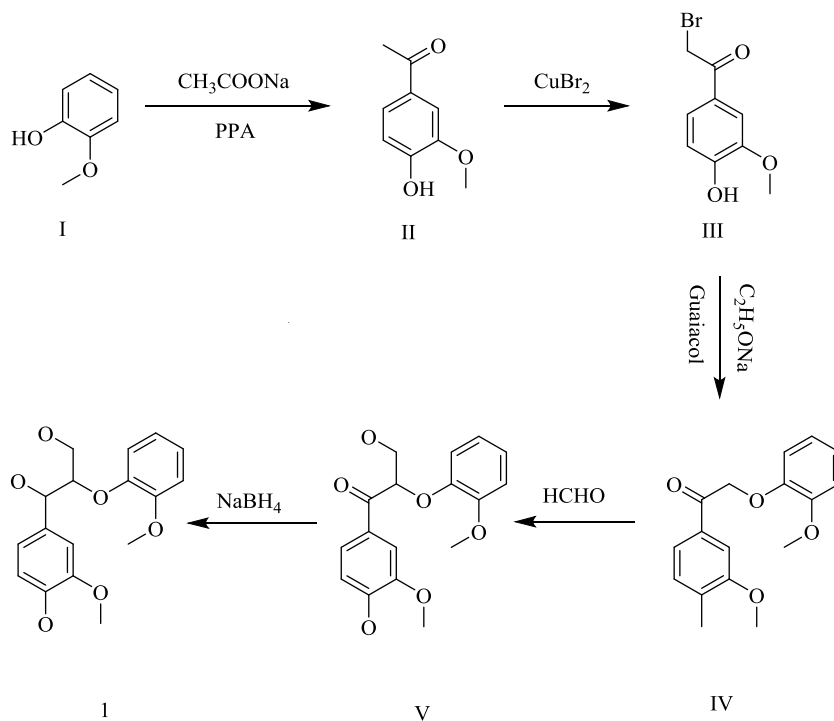
Preparation of Guaiacyl Glycerol- β -guaiacyl Ether

Guaiacol, 85% phosphoric acid, anhydrous phosphorus pentoxide, copper bromide, sodium, sodium borohydride, formaldehyde, N,N-dimethylformamide, petroleum ether, and ethyl acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). A synthetic method for obtaining lignin model compound of β -O-4 structure, guaiacyl glycerol- β -guaiacyl ether (1) was researched through five reaction steps from guaiacol (Fig. 1). The key step of this synthetic method was the condensation reaction between 4-(α -bromoacetyl)-guaiacol (III) and guaiacol (I). The 4-(α -(2-methoxyphenoxy)-acetyl)-guaiacol (IV) was converted to 4-(α -(2-methoxyphenoxy)- β -hydroxypropanoyl)-guaiacol (V) through the condensation reaction with formaldehyde. The compound (V) was then converted to the final compound (1) by the sodium boron hydride reduction. Reactions were monitored by thin layer chromatography (TLC). The compounds were characterized by $^1\text{H NMR}$ and 2D NMR spectroscopy. Detailed information on synthesis and characterization methods were described as follows.

Synthesis of 4-acetyl-guaiacol

136.0 g 85% phosphoric acid and 144.0 g anhydrous phosphorus pentoxide were mixed in a 1L eggplant-shaped bottle and stirred for 1 h at 100 °C in an oil bath to give the poly-phosphoric acid (PPA). PPA was then added to a 500 mL flask with a mixture of

anhydrous sodium acetate (12.0 g) and guaiacol (20.0 g), then stirred for 15 min at 100 °C. The reaction mixture was cooled in an ice-water bath and then extracted with diethyl ether. The diethyl ether layer was dried by anhydrous sodium sulfate and concentrated through a rotary evaporator. The crude product was obtained and recrystallized from ethanol to afford yellowish crystal (10.1 g, 40.5 %). The product was characterized and confirmed by GC-MS.



- I guaiacylglycerol-β-guaiacyl ether
 I gyuiaiacol
 II 4-acetyl-guaiacol
 III 4-(α-bromoacetyl)-guaiacol
 IV 4-(α-(2-methoxyphenoxy)-acetyl)-guaiacol
 V 4-(α-(2-methoxyphenoxy)-β-hydroxypropanoyl)-guaiacol

Fig. 1. Synthetic route of guaiacyl glycerol-β-guaiacyl ether

Synthesis of 4-(α-bromoacetyl)-guaiacol

Copper bromide (4.5 g) was dissolved in 70 mL of ethanol. Then the solution was transferred to a constant funnel and added slowly to a stirred solution of compound II (2.0 g) in ethanol (50 mL). The mixture was stirred for 1.5 h at 70 °C. After being filtered, the filtrate was concentrated, and the reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with dichloromethane, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give crude dark oil. The dark oil was purified by column chromatography to give a slightly yellow solid (compound III, 2.4 g, 80.3%). Analytical results were: ¹HNMR (400MHz, DMSO-d₆) δ10.16 (s, 1H), δ7.56 (dd, *J*=8.4 Hz, *J*=1.6 Hz, 1H), δ7.48 (d, *J*=1.6 Hz, 1H), δ6.88 (d, *J*=8.0 Hz, 1H), δ4.80 (s, 2H), δ3.825 (s, 3H).

Synthesis of 4-(α -(2-methoxyphenoxy)-acetyl)-guaiacol

Sodium (7.0 g) was dissolved in ethanol. Then guaiacol (30.0 g) was added slowly to the solution of sodium ethanol and stirred at 45 °C for 0.5 h. The solution was evaporated in vacuum to give guaiacol sodium as white solid. Then the solution of compound III (5.0 g) in dry DMF was added to a stirred solution of guaiacol sodium. The mixture was stirred for 0.5 h and then poured into ice-water, the solution of 5% hydrochloric acid was added to the mixture until the pH value was 3.0.

The product extracted with dichloromethane and dried over anhydrous sodium sulfate, evaporated in vacuum to give crude pale yellow oil. The pale yellow oil was purified by column chromatography and evaporated under reduced pressure to give slightly yellow oil, drops of ether was added to the slightly yellow oil to give compound IV as slightly yellow solid (4.9 g, 84.1%). ¹HNMR (400 MHz, DMSO-d₆) δ 10.07 (s, 1H), δ 7.58 (dd, J =8.4 Hz, J =2.0 Hz, 1H), δ 7.50 (d, J =1.6 Hz, 1H), δ 6.97 (d, J =7.6 Hz, 1H), δ 6.907-6.866 (m, 4H), δ 5.44 (s, 1H), δ 3.83 (s, 3H), δ 3.77 (s, 3H).

Synthesis of 4-(α -(2-methoxyphenoxy)- β -hydroxypropanoyl)-guaiacol

Anhydrous potassium carbonate (2.5 g) and 40 mL formaldehyde were added to a solution of compound IV (3.0 g) in ethanol and stirred for 3 h at 55 °C on an oil bath. Then the mixture was poured into water. Hydrochloric acid (5%) was added to the mixture until the pH value was 3.0. The product was extracted with dichloromethane and dried over anhydrous sodium sulfate followed by removal of solvent under reduced pressure. The resulting residue was purified by column chromatography on silica gel and evaporated under reduced pressure to give slightly yellow oil. Drops of ether were added to the slightly yellow oil to obtain compound V (2.3 g, 70.2%). ¹HNMR (400 MHz, DMSO-d₆) δ 10.10 (s, 1H), δ 7.67 (d, J =8.0 Hz, 1H), δ 7.54 (s, 1H), δ 7.95 (d, J =8.0 Hz, 1H), δ 6.88-6.84 (m, 2H), δ 6.74 (dd, J =16.0 Hz, J =7.6 Hz, 2H), δ 5.58 (t, J =4.8 Hz, 1H), δ 5.15 (t, J =5.6 Hz, 1H), δ 3.94 (d, J =4.4 Hz, 2H), δ 3.87 (s, 3H), δ 3.73 (s, 3H).

Synthesis of guaiacyl glycerol- β -guaiacyl ether

Sodium borohydride (0.3 g) was added in a solution of compound V (1.0 g in 100 mL 0.1 mol/L sodium hydroxide) under nitrogen atmosphere. After stirring for 10 h, 5% hydrochloric acid was added to the mixture until the pH value was 3.0. The product was extracted with dichloromethane, washed with distilled water, and dried over anhydrous sodium sulfate, followed by removal of solvent under reduced pressure. The resulting residue was purified by column chromatography and evaporated in vacuum to give slightly yellow oil. Drops of ether was added to the slightly yellow oil to afford compound VI as white solid (0.6 g, 60.1%); ¹HNMR (400 MHz, DMSO-d₆) δ 8.76 (s, 1H), δ 7.13 (d, J =7.2 Hz, 1H), δ 6.97-6.91 (m, 2H), δ 6.88-6.80 (m, 2H), δ 7.76 (d, J =8.0 Hz, 1H), δ 6.68 (d, J =8.0 Hz, 1H), δ 5.24 (d, J =4.0 Hz, 1H), δ 4.62 (t, J =5.0 Hz, 1H), δ 4.24 (d, J =4.0 Hz, 1H), δ 3.75 (s, 3H), δ 3.71 (s, 3H), δ 3.57 (t, J =5.6 Hz, 1H), δ 3.38 (s, 1H), δ 3.26-3.20 (m, 1H).

¹H-NMR Spectroscopy

The ¹H-NMR spectra were recorded on a 400 MHz Bruker AVANCE III NMR spectrometer (BRUKER, Germany). 10 mg of sample was dissolved in 500 μ L of dimethyl sulphoxide (DMSO-d₆) and stirred to completely dissolved. The chemical shifts were calibrated relative to the signals of DMSO, which was used as an internal standard at 2.49 ppm for the ¹H-NMR spectra. The acquiring time (AQ) was 3.98 s and the relaxation time was 1.0 s.

2D-NMR Spectroscopy

About 80 mg of guaiacyl glycerol- β -guaiacyl ether and 500 μ L of dimethyl sulphoxide (DMSO-*d*₆) were stirred fully to obtain a solution. The solution was then analyzed using a Bruker AVANCE III 400 MHz spectrometer for 12 h, adopting the pulse sequence “hsqcetgpsisp. 2” from Bruker Standard Pulse Library.

Thermogravimetric Analysis (TGA)

In TGA, high purity nitrogen (99.9995%) at a flow rate of 60 mL/min was used as the carrier gas to provide an inert atmosphere and to remove the gases. About 8 mg of samples (particle size < 60 μ m) were pyrolyzed in TGA from room temperature to 900 °C with a heating rate of 20 °C/min.

Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)

The Py-GC/MS system included a JHP-3 model Curie-point pyrolyzer (CDS5200, Oxford, PA, USA) and an Agilent 7890B-5977A GC-MS (Santa Clara, CA, USA). Approximately 0.5 mg of samples were pyrolyzed at a certain temperature for 15 s, and the gas products were purged by high purity helium (99.9995%) into the gas chromatograph *via* a transfer line preheated to 250 °C. The flow rate of the carrier gas was 75 mL/min with a split ratio of 50:1. The injection temperature was 250 °C.

The pyrolysis products were separated in a HP-5MS capillary column (30 m \times 0.25 mm \times 0.25 μ m). The GC oven was kept at 50 °C for 1 min and then heated from 50 °C to 250 °C at heating rate of 10 °C/min. The temperature was then maintained for 2 min. The injector temperature was set at 280 °C in split mode with split ratio of 50:1. The MS detector was operated in electron impact (EI) ionization mode (70 eV) with the ion source temperature and quadrupole temperature set to 230 °C and 150 °C, respectively. The mass range of 45 to 500 *m/z* was scanned. The pyrolysis compounds were identified by comparison of their mass fragments with the NIST mass spectral library (NIST 14).

RESULTS AND DISCUSSION

2D- NMR Spectra of Guaiacyl Glycerol- β -guaiacyl Ether

The final product was obtained from guaiacol through five steps, and the yield was 11.5%. The 2D NMR result of the synthesized guaiacyl glycerol- β -guaiacyl ether (1) is presented in Fig. 2.

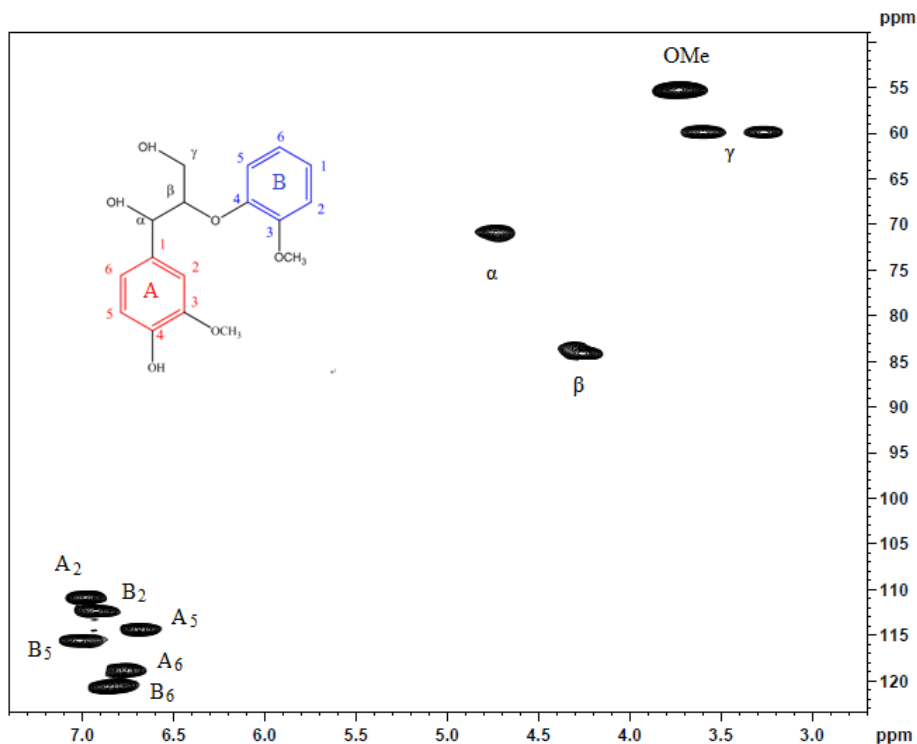


Fig. 2. The 2D-HSQC NMR spectra of guaiacyl glycerol- β -guaiacyl ether (1)

Thermal Analysis

The TG and DTG curves of guaiacyl glycerol- β -guaiacyl ether (1), obtained at a heating rate of 20 °C/min, is plotted in Fig. 3. Guaiacyl glycerol- β -guaiacyl ether (1) was easily decomposed with the weight loss mainly between 221 and 293 °C. The solid residue remaining at 900 °C was 10.83%.

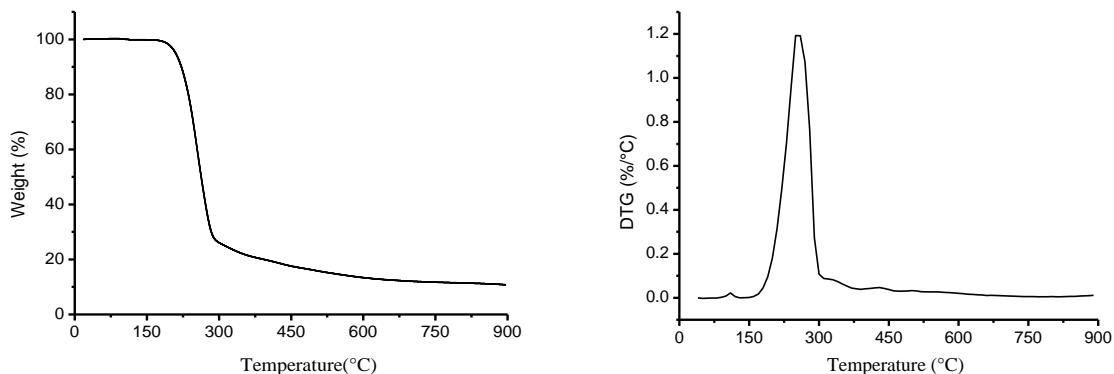


Fig. 3. TG and DTG curves of guaiacyl glycerol- β -guaiacyl ether

Py-GC/MS Analysis

Based on the TG results, the temperatures in the pyrolysis of guaiacyl glycerol- β -guaiacyl ether (1) were programmed at 200, 300, 500, 600, 700, and 800 °C. The main products from fast pyrolysis of guaiacyl glycerol- β -guaiacyl ether (1) are shown in Table 1 and Fig. 4, and the secondary thermal cracking products of the main substances, guaiacol and 2-methoxybenzaldehyde, are shown in Fig. 5 and Fig. 6.

As demonstrated in Table 1, the major pyrolytic product produced at low temperatures (200 and 300 °C) was guaiacol. Therefore, the main reaction at low-temperature pyrolysis of guaiacyl glycerol- β -guaiacyl ether (1) was the C β -O homolytic reaction, which agrees well with the findings by Britt *et al.* (2000). In this previous study, the C β -O homolytic reaction was more favorable than C β -O concerted decomposition reaction in the pyrolysis of *o*-CH₃O-PPE (Britt *et al.* 2000). Beste and Buchanan (2009) suggested that the preliminary pyrolysis process mainly involves the homolysis of C β -O and C α -C β bonds. Huang *et al.* (2014) confirmed that the methoxyl group on the phenyl ring adjacent to the ether oxygen of lignin model compound enhances C β -O homolysis but has little effect on C β -O concerted decomposition.

According to the analysis of the products of guaiacyl glycerol- β -guaiacyl ether (1) at 500 °C in Table 1, the main pyrolysis process of compound (1) can be seen in Fig. 4. The compound (1) was split into two fragments; the major pyrolysis products for fragment A were guaiacol (2) and 2-methoxybenzaldehyde (3). Guaiacol was also derived from deep pyrolysis of fragment B. For fragment B, other possible products are 2-methoxy-4-vinylphenol (4), vanillin (5), trans-isoeugenol (6), 2-methoxy-4-propylphenol (7), and 1-(3-hydroxy-4-methoxyphenyl)-ethanone (8). However, the relative content of these compounds was low. Catechol, 2-hydroxybenzaldehyde and 2-methyl-phenol were derived from the pyrolysis of guaiacol (2).

Table 1. Identified Pyrolysis Products of Guaiacyl Glycerol- β -guaiacyl Ether (1) at Various Temperatures ($^{\circ}\text{C}$)

Reaction Time (min)	Compound	Peak Area (%)					
		200	300	500	600	700	800
1.548	cyclopropylacetylene						8.85
2.115	1,4-cyclohexadiene						4.01
2.271	benzene					16.79	43.13
3.542	toluene					12.23	24.95
5.101	ethylbenzene						4.83
5.240	1,3-dimethyl-benzene						2.7
5.615	styrene					8.04	12.56
6.857	benzaldehyde				6.61	10.83	14.06
7.227	phenol				8.89	32.94	51.08
7.469	benzofuran					8.99	19.66
8.272	2-hydroxybenzaldehyde			6.66	27.23	38.62	44.94
8.416	2-methyl-phenol			5.5	19.28	31.46	37.04
8.734	p-cresol					5.46	7.65
9.075	guaiacol	100	100	100	100	100	100
9.317	2-methyl-benzofuran						2.64
9.721	2-ethyl-phenol				8.21	13.78	9.95
10.115	3,4-dimethyl-phenol,					4.81	4.38
10.490	naphthalene					5.07	12.79
10.634	catechol			3.65	14.24	32.24	24.56
10.784	2,3-dihydro-benzofuran					3.78	6.28
11.362	2-methoxybenzaldehyde			14.9	30.32	17.79	16.63
11.523	3-methyl-1,2-benzenediol					3.45	1.75
11.956	2-allylphenol				2.12	4.41	4.68
12.095	2-methyl-naphthalene						3.57
12.326	2-methoxy-4-vinylphenol			2.97	2.44		
12.857	1H-indenol					9.2	3
13.239	biphenyl						3.86
13.481	vanillin			8.42	6.99	10.48	4.71
13.897	2-ethenyl-naphthalene						2.03
14.122	trans-iso Eugenol			2.88			1.23
14.249	2-methoxy-4-propyl-phenol			5.85	2.8	5.29	
14.596	1-(3-hydroxy-4-methoxyphenyl)-ethanone,			6.94	3.41	8.58	
14.867	1-naphthalenol						2.1
15.006	dibenzofuran						8.14
15.809	fluorene						3.69
18.004	phenanthrene						2.11

Note: The maximum peak area was seen as 100%. The peak area percentage of other substance was gained from the ratio of its peak area to the maximum peak area.

At 600 $^{\circ}\text{C}$, the number of pyrolytic products increased. Compared with the product distribution from 300 $^{\circ}\text{C}$, the relative content of 2-hydroxybenzaldehyde and 2-methoxybenzaldehyde increased. Meanwhile, a great number of phenolic compounds including phenol, 2-methyl-phenol, and catechol were found. Analysis of the pyrolytic products showed that these substances were mainly generated through the pyrolysis of guaiacol, 2-methoxybenzaldehyde. This result implied that the $\text{C}_{\beta}\text{-O}$ concerted

decomposition reaction took place in the thermal degradation of compound (1) under medium pyrolysis temperatures, which agrees well with Chen *et al.* (2015), who confirmed that C β -O homolysis and C β -O concerted decomposition occur at moderate temperatures. As the relative content of these products from the concerted decomposition of C β -O is low, C β -O homolysis is still prominent at medium temperature. Kawamoto *et al.* (2008) experimentally confirmed that other reactions occur during the pyrolysis of typical lignin model compounds.

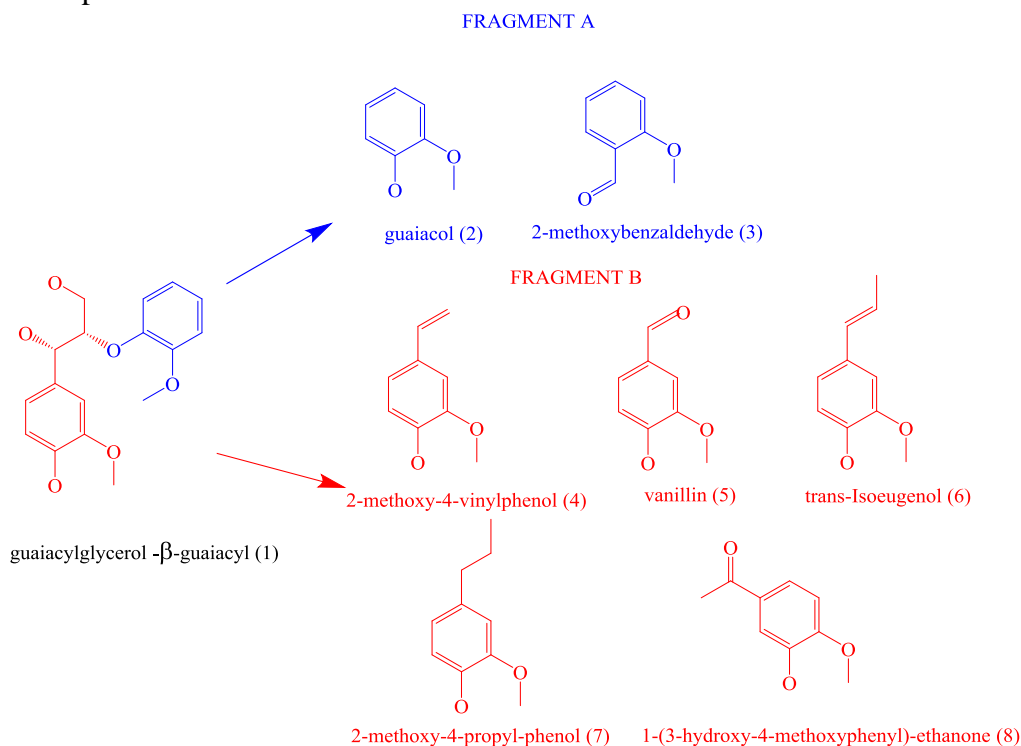


Fig. 4. Fragmentation products derived from guaiacylglycerol- β -guaiacyl (1)

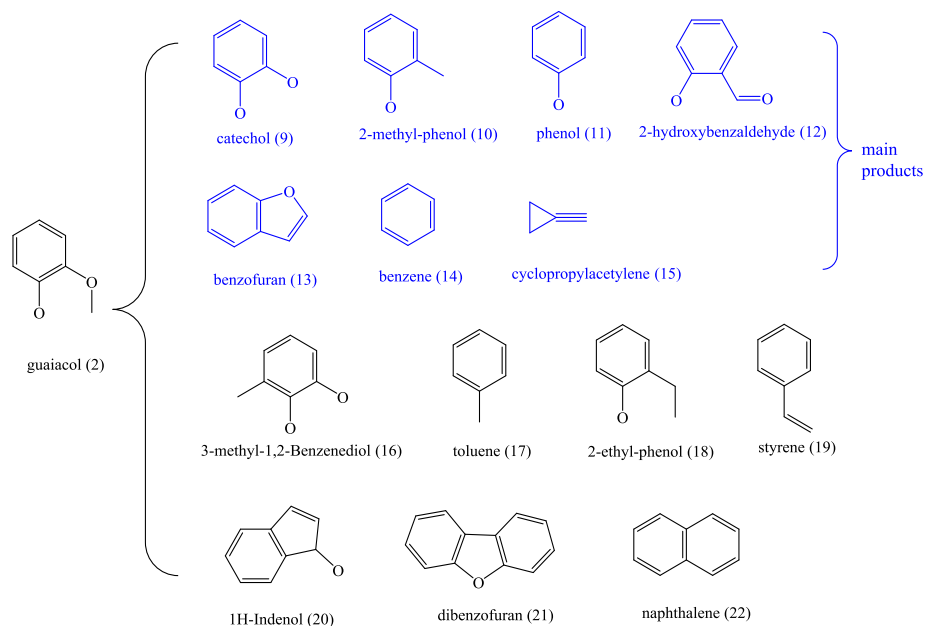


Fig. 5. Fragmentation products derived from guaiacol (2) at 800 °C

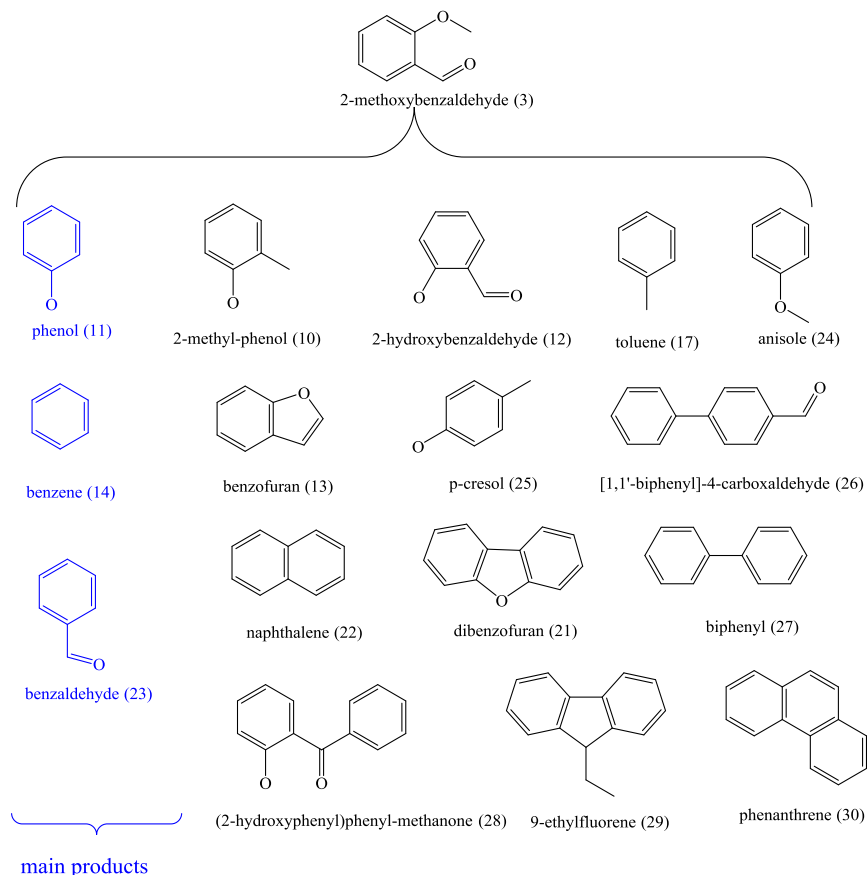


Fig. 6. Fragmentation products derived from 2-methoxybenzaldehyde (3) at 800 °C

At high temperatures (700 and 800 °C), various small molecular substances were formed. According to analysis of the pyrolysis products of guaiacyl glycerol- β -guaiacyl ether (1), guaiacol (2) and 2-methoxybenzaldehyde (3) as shown in Figs. 4, 5 and 6, the products formed from C_{β} -O homolysis and C_{β} -O concerted decomposition undergo dissociation reactions, producing small molecule products (Chen *et al.* 2015). For example catechol, 2-methyl-phenol, and 2-hydroxy-benzaldehyde are mainly produced from guaiacol, whereas benzaldehyde is mainly produced from 2-methoxybenzaldehyde. Benzene, toluene, and phenol are produced from both guaiacol and 2-methoxybenzaldehyde.

CONCLUSIONS

1. A β -O-4 type lignin dimer, namely guaiacyl glycerol- β -guaiacyl ether (1), was synthesized from guaiacol through five reaction steps. The NMR results indicated that it was the title compound.
2. The pyrolysis behaviors of guaiacyl glycerol- β -guaiacyl ether (1) were investigated with the Py-GC/MS technique. The results showed that guaiacol was the major products of C_{β} -O homolysis at low temperatures. C_{β} -O homolysis and C_{β} -O concerted decomposition occurred at moderate temperatures, producing 2-hydroxybenzaldehyde, 2-methoxybenzaldehyde, guaiacol, and phenolic compounds. At high temperatures, the

products were obtained from secondary thermal cracking of the C β -O homolysis and C β -O concerted decomposition products, which generated a large number of small molecule products that increased the complexity of the pyrolytic products.

3. The pyrolysis pathways of guaiacyl glycerol- β -guaiacyl ether deduced here will provide insight for later in-depth study of the pyrolysis mechanism of various lignin. Also the product formation rules with elevated temperature will help to select the appropriate reaction parameters to regulate the lignin pyrolysis products.

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REFERENCES CITED

- Beste, A., Buchanan, A. C., Britt, P. F., Hathorn, B. C., and Harrison, R. J. (2007). "Kinetic analysis of the pyrolysis of phenethyl phenyl ether: Computational prediction of α/β -selectivities," *The Journal of Physical Chemistry A* 111(48), 12118-12126. DOI: 10.1021/jp075861+
- Beste, A., and Buchanan, A. C. (2009). "Computational study of bond dissociation enthalpies for lignin model compounds. Substituent effects in phenethyl phenyl ethers," *The Journal of Organic Chemistry* 74(7), 2837-2841. DOI: 10.1021/jo9001307
- Binder, J. B., Gray, M. J., White, J. F., Zhang, Z. C., and Holladay, J. E. (2009). "Reactions of lignin model compounds in ionic liquids," *Biomass and Bioenergy* 33(9), 1122-1130. DOI: 10.1016/j.biombioe.2009.03.006
- Bridgewater, A. V. (2004). "Biomass fast pyrolysis," *Thermal Science* 8(2), 21-50. DOI: 10.2298/TSCI0402021B
- Bridgewater, A. V., Meier, D., and Radlein, D. (1999). "An overview of fast pyrolysis of biomass," *Organic Geochemistry* 30(12), 1479-1493. DOI: 10.1016/S0146-6380(99)00120-5
- Britt, P. F., Buchanan, A. C., Cooney, M. J., and Martineau, D. R. (2000). "Flash vacuum pyrolysis of methoxy-substituted lignin model compounds," *The Journal of Organic Chemistry* 65(5), 1376-1389. DOI: 10.1021/jo991479k
- Chen, L., Ye, X., Luo, F., Shao, J., Lu, Q., Fang, Y., and Chen, H. (2015). "Pyrolysis mechanism of β O4 type lignin model dimer," *Journal of Analytical and Applied Pyrolysis* 115, 103-111. DOI: 10.1016/j.jaap.2015.07.009
- Huang, J., Liu, C., Wu, D., Tong, H., and Ren, L. (2014). "Density functional theory studies on pyrolysis mechanism of β -O-4 type lignin dimer model compound," *Journal of Analytical and Applied Pyrolysis* 109, 98-108. DOI: 10.1016/j.jaap.2014.07.007
- Jiang, G., Nowakowski, D. J., and Bridgewater, A. V. (2010a). "A systematic study of the kinetics of lignin pyrolysis," *Thermochimica Acta* 498(1), 61-66. DOI: 10.1016/j.tca.2009.10.003

- Jiang, G., Nowakowski, D. J., and Bridgwater, A. V. (2010b). "Effect of the temperature on the composition of lignin pyrolysis products," *Energy & Fuels* 24(8), 4470-4475. DOI: 10.1021/ef100363c
- Kang, S., Li, B., Chang, J., and Fan, J. (2010). "Antioxidant abilities comparison of lignins with their hydrothermal liquefaction products," *BioResources* 6(1), 243-252.
- Kawamoto, H., Ryoritani, M., and Saka, S. (2008). "Different pyrolytic cleavage mechanisms of β -ether bond depending on the side-chain structure of lignin dimers," *Journal of Analytical and Applied Pyrolysis* 81(1), 88-94. DOI: 10.1016/j.jaap.2007.09.006
- Lei, J. F., Li, L. B., Shen, X. H., Du, K., Ni, J., Liu, C. J., and Li, W. S. (2013). "Fabrication of ordered ZnO/TiO₂ heterostructures via a templating technique," *Langmuir* 29(45), 13975-13981. DOI: 10.1021/la4027859
- Lu, F., and Ralph, J. (1997). "Derivatization followed by reductive cleavage (DFRC method), a new method for lignin analysis: protocol for analysis of DFRC monomers," *Journal of Agricultural and Food Chemistry* 45(7), 2590-2592. DOI: 10.1021/jf970258h
- Lv, D., Xu, M., Liu, X., Zhan, Z., Li, Z., and Yao, H. (2010). "Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification," *Fuel Processing Technology* 91(8), 903-909. DOI: 10.1016/j.fuproc.2009.09.014
- Mohan, D., Pittman, C. U., and Steele, P. H. (2006). "Pyrolysis of wood/biomass for bio-oil: A critical review," *Energy & Fuels* 20(3), 848-889. DOI: 10.1021/ef0502397
- Ouyang, X., Zaixiong, L., Yonghong, D., Dongjie, Y., and Xueqing, Q. I. U. (2010). "Oxidative degradation of soda lignin assisted by microwave irradiation," *Chinese Journal of Chemical Engineering* 18(4), 695-702. DOI: 10.1016/S1004-9541(10)60277-7
- Park, H. W., Park, S., Park, D. R., Choi, J. H., and Song, I. K. (2010). "Decomposition of phenethyl phenyl ether to aromatics over Cs x H 3.0- x PW 12 O 40 (X= 2.0-3.0) heteropolyacid catalysts," *Catalysis Communications* 12(1), 1-4. DOI: 10.1016/j.catcom.2010.08.002
- Ralph, J., and Grabber, J. H. (1996). "Dimeric β -ether thioacidolysis products resulting from incomplete ether cleavage," *Holzforschung* 50(5), 425-428. DOI: 10.1515/hfsg.1996.50.5.425
- Raveendran, K., Ganesh, A., and Khilar, K. C. (1995). "Influence of mineral matter on biomass pyrolysis characteristics," *Fuel* 74(12), 1812-1822. DOI: 10.1016/0016-2361(95)80013-8
- Roberts, V., Fendt, S., Lemonidou, A. A., Li, X., and Lercher, J. A. (2010). "Influence of alkali carbonates on benzyl phenyl ether cleavage pathways in superheated water," *Applied Catalysis B: Environmental* 95(1), 71-77. DOI: 10.1016/j.apcatb.2009.12.010
- Sarkanen, K. V., and Ludwig, C. H. (1971). *Lignins: Occurrence, Formation, Structure and Reactions*, John Wiley & Sons, Hoboken, NJ, USA.
- Tian, M., Wen, J., MacDonald, D., Asmussen, R. M., and Chen, A. (2010). "A novel approach for lignin modification and degradation," *Electrochemistry Communications* 12(4), 527-530. DOI: 10.1016/j.elecom.2010.01.035
- Tien, M., and Kirk, T. K. (1983). "Lignin-degrading enzyme from the hymenomycete *Phanerochaete chrysosporium* Burds.," *Science* 221(4611), 661-662.
- Wang, S., Wang, K., Liu, Q., Gu, Y., Luo, Z., Cen, K., and Fransson, T. (2009). "Comparison of the pyrolysis behavior of lignins from different tree species," *Biotechnology Advances* 27(5), 562-567. DOI: 10.1016/j.biotechadv.2009.04.010

- Xia, Z., Yoshida, T., and Funaoka, M. (2003). "Enzymatic degradation of highly phenolic lignin-based polymers (lignophenols)," *European Polymer Journal* 39(5), 909-914. DOI: 10.1016/S0014-3057(02)00357-9
- Zakzeski, J., Bruijninx, P. C., Jongerius, A. L., and Weckhuysen, B. M. (2010). "The catalytic valorization of lignin for the production of renewable chemicals," *Chemical Reviews* 110(6), 3552-3599. DOI: 10.1021/cr900354u
- Zakzeski, J., Jongerius, A. L., Bruijninx, P. C., and Weckhuysen, B. M. (2012). "Catalytic lignin valorization process for the production of aromatic chemicals and hydrogen," *ChemSusChem* 5(8), 1602-1609. DOI: 10.1002/cssc.201100699

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