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Paving the Way for the Lignin Hydrogenolysis Mechanism by Deuterium-Incorporated β-O-4 Mimics

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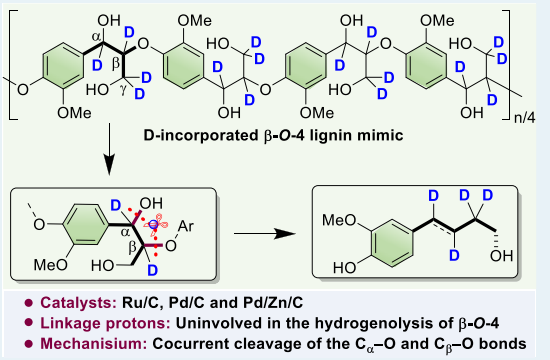
ABSTRACT: Gaining more insight into the lignin hydrogenolysis mechanism is of great importance for developing next-generation catalysts and regulating product distribution because lignin is the only renewable aromatic source leading to aromatic chemicals. However, the inherent complexity of the lignin structure and the multiple pathways in lignin hydrogenolysis make gaining insight into the lignin hydrogenolysis mechanism even more challenging. In this report, a β-O-4 polymer with deuterium incorporated at the α, β, and γ positions which can better model the plant lignin structure was prepared for mechanistic study. The location and retention of deuterium in the monomers resulting from the hydrogenolysis and transfer hydrogenolysis of the deuterated β-O-4 mimics with Ru/C, Pd/C, and Pd/Zn/C in MeOH indicated that the β-O-4 linkage protons did not participate in the cleavage process, which indicated that pathways involving dehydrogenation and/or dehydration reactions are infeasible for these catalysts under these conditions. A concerted process, wherein the C_α−O and C_β−O bonds in β-O-4 structures were cleaved concurrently, was proposed as a potential hydrogenolysis mechanism in the Pd/C and Ru/C systems. Dehydroxylation at the α position was identified as a side reaction in the Pd/C-catalyzed hydrogenolysis of dimer models, from which the same concurrent cleavage mechanism was also inferred. The introduction of a Lewis acid center in Pd/C was conducive to β-O-4 hydrogenolysis, as confirmed by the abatement of the side reaction and the enhanced monomer yield in the polymeric model reactions. The use of deuterium-incorporated β-O-4 mimics paved the way for clearly elucidating the lignin hydrogenolysis mechanism.



KEYWORDS: *lignin, β-O-4 polymer, deuterium, hydrogenolysis, palladium, C−O cleavage*

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INTRODUCTION

Lignin accounts for nearly 25% of plant biomass by weight and is one of few renewable aromatic hydrocarbon sources.[1,2] The upgrading of lignin, which is increasingly noted to be crucial to the economic viability of biorefineries, represents one of the most challenging aspects of the entire utilization of all biomass components.[3] In principle, the depolymerization of lignin leading to valuable aromatic chemicals suitable for downstream processing is an important starting point for lignin valorization.[4−7] For this purpose, various methods, such as reduction,[8−10] oxidative−reductive processes,[11−15] biodegradation,[16−19] and electro-[20,21] and photodriven[22−25] depolymerization, have been developed. Of the possible approaches, catalytic hydrogenolysis of lignin (reductive method), the converse process of lignin biosynthesis, takes advantage of high monomer yields, controllable selectivity, narrow product distribution, and readily purified products.[26−28] A series of heterogeneous metal catalysts based on Ru,[29−33] Pd,[34−38] Ni,[39−47] Cu,[48,49] Mo,[50−54] and Co[55,56] have been utilized for lignin hydrogenolysis and transfer hydrogenolysis.

In protolignin, a β-O-4 alkyl−aryl ether motif featuring a 2° benzylic alcohol (α-OH) and 1° aliphatic alcohol (γ-OH) is the most abundant connection linking the monomeric phenylpropanoid units (Scheme 1).[5,6] Metal catalysts are usually employed to rupture the C_β−O bond in β-O-4 motifs to afford monomeric products during lignin hydrogenolysis. In addition, the catalysts stabilize the formed monomeric products *via* hydrogenation and/or dehydroxylation reactions.[9,30,39,57] A deep understanding of the lignin hydrogenolysis mechanism is therefore of great importance and interest for developing novel catalysts and regulating the product selectivity. However, because of the complexity of the inherent lignin biopolymer structure and the multiple pathways of β-O-4 motif cleavage and the subsequent stabilization processes, it is extremely challenging to clearly elucidate the hydrogenolysis mechanism.[58,59] During the past two decades, several hydrogenolysis and transfer hydrogenolysis pathways

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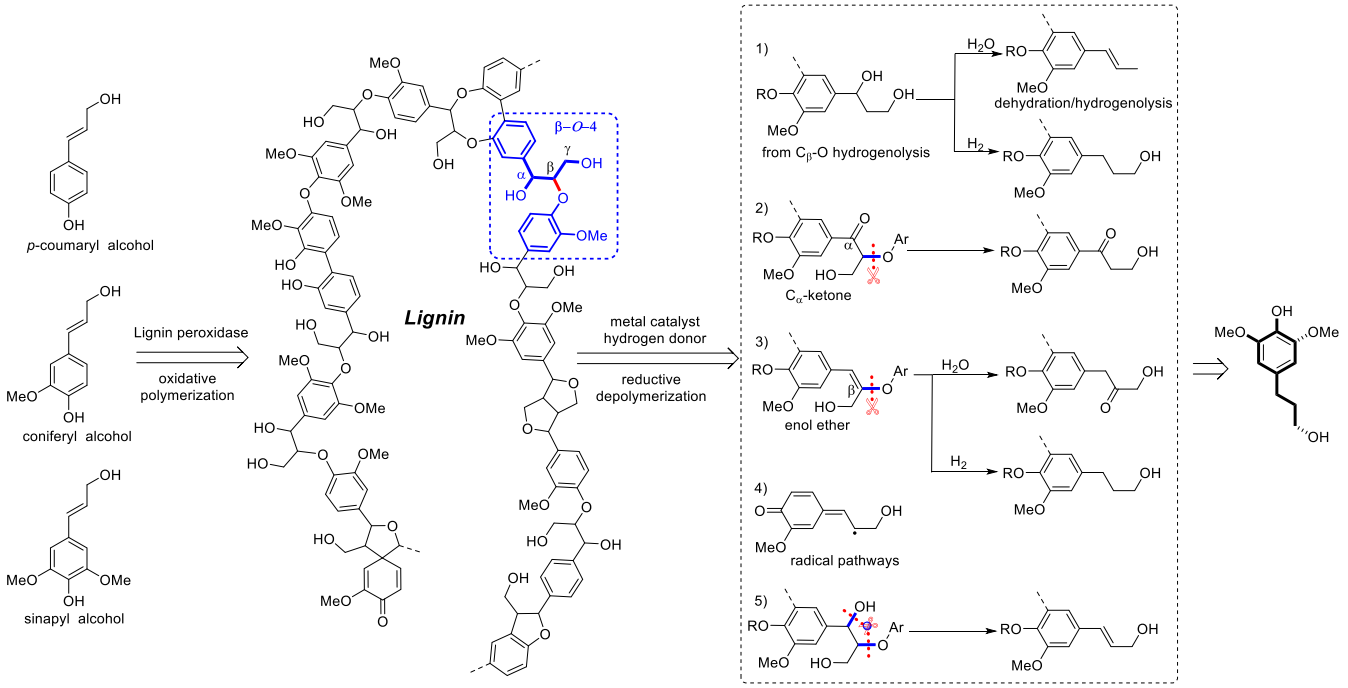
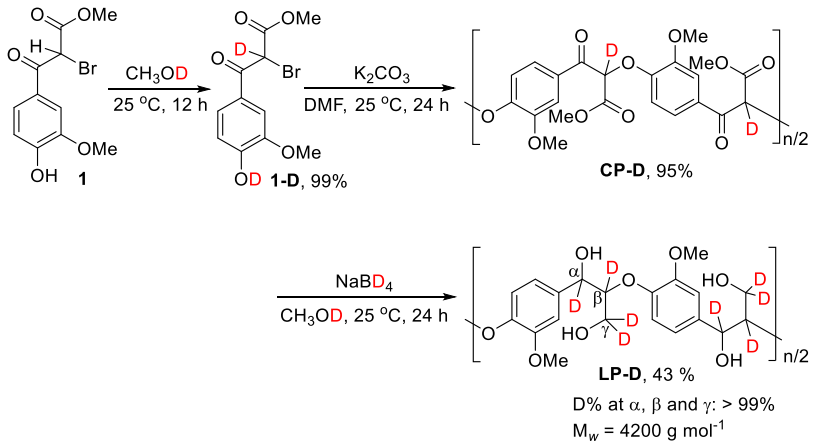
Scheme 1. Reported Pathways for the Hydrogenolysis of β-O-4 Lignin into Monomeric Phenols over Late Transition Metal Catalysts[39,41,48,60−67]



Scheme 2. Synthesis of the Deuterated β-O-4 Lignin Polymer



have been proposed (Scheme 1, see also Figure S1). (1) The direct hydrogenolysis of the C_β−O bond in the β-O-4 motif leads to the formation of propanediol-substituted monophenols, which undergo either sequential dehydration and hydrogenolysis (Ni/C)[39] or the hydrogenolysis of α-OH (Pd/C)[60] to give the final products. (2) A C_α ketone species is initially formed through a dehydrogenation reaction and subsequent C_β−O bond hydrogenolysis, hydrogenation, and dehydration results in monophenols.[48,61,62] (3) An enol ether intermediate is generated *via* a dehydration reaction, and then, the C_β−O bond is cleaved by H_2O (hydrolysis) or H_2 (hydrogenolysis), thus forming the Hibbert ketone or 4-propanol phenols.[63−65] (4) Homolysis of the β-O-4 units, starting from the free phenolic OH group and going through a quinone radical species, was also predicted.[41,66]

Recently, we reported a mechanistic study of the Ru/C-catalyzed hydrogenolysis of lignin using deuterium-incorporated β-O-4 dimers (**GG-D** and **VG-D**).[67] The location and retention of deuteriums offered solid evidence that excluded the possibility of the above pathways in the Ru/C catalytic system. It was proposed that the monolignols are formed primarily through a concerted hydrogenolysis process, in which the C_α−O and C_β−O bonds are simultaneously ruptured (Scheme 1). However, the reaction pathway of dimer model compounds with only one β-O-4 unit might differ from that of actual lignin with polymeric β-O-4 units.[68] For example, the interaction of the catalyst with multiple hydroxy groups on the lignin biopolymer would influence the efficiency of the catalytic reaction, which is difficult to evaluate in dimer model reactions. To link the studies of dimer β-O-4 mimics to actual plant lignin, an artificial lignin polymer composed of the β-O-4 substructure with deuteriums incorporated exclusively at the α, β, and γ positions was prepared in this study. Applying Ru/C, Pd/C, and Pd/Zn/C catalysts to this deuterium-incorporated β-O-4 polymer resulted in explicit evidence for identifying reaction pathways. A comparison of the homology

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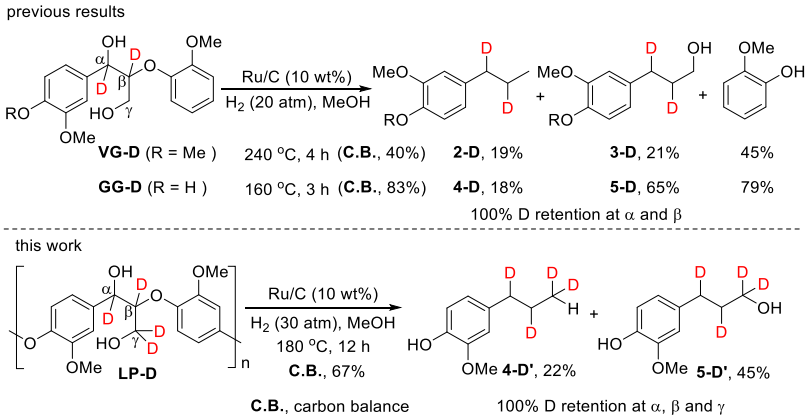
Scheme 3. Hydrogenolysis of Deuterated Lignin Mimics with Ru/C



and dissimilarity of the *β*-O-4 dimers and polymer provided more insight for understanding the lignin hydrogenolysis mechanism.

RESULTS AND DISCUSSION

Preparation of the Deuterated *β*-O-4 Polymer. The preparation of the deuterated lignin polymer (**LP-D**) was based on the synthesis methodology for the *β*-O-4 polymer (Scheme 2).[69,70] Deuteriums were incorporated at the linkages in two stages. Stirring compound **1** in CH_3OD led to the complete H/D exchange of the phenolic OH and methylene proton, thus giving **1-D**. Polymerization of **1-D** in anhydrous DMF with K_2CO_3 resulted in a quantitative yield of a carbonyl polymer (**CP-D**). Upon treatment with $NaBD_4$ in CH_3OD, the carbonyl group at the *α* position and the ester group at the *γ* position of **CP-D** were reduced to benzylic and aliphatic alcohols, respectively. Precipitation with an HCl solution afforded the deuterated lignin polymer (**LP-D**) in 43% yield. In contrast to **CP-D**, in which *β*-D could be readily exchanged by an acidic proton, the incorporated deuteriums in **LP-D** were stable against acidic protons.

The average molecular weight (M_w) of **LP-D** was measured to be 4200 g mol^{-1} by gel permeation chromatography, from which the degree of polymerization (DP_w) was established as 20.5. The degree of polymerization of **LP-D** was higher than that of the nondeuterated synthetic *β*-O-4 polymer (M_w = 3200 g mol^{-1}, DP_w = 15, see Figure S3). In the ^1H NMR spectrum of **LP-D** (DMSO-d_6 with one drop of D_2O), side-chain signals of the nondeuterated *β*-O-4 polymer (**LP**) corresponding to *α*-H (br, 4.76 ppm), *β*-H (br, 4.30 ppm), and *γ*-H (3.52, 3.60 ppm) were not observed (Figure S2). This result indicated perdeuteration of the *β*-O-4 linkages. ^{13}C NMR spectroscopy is a powerful tool for elucidating complicated lignin structures, and most of the signals in lignin have been previously assigned.[69,71] Both the erythro and threo isomers derived from the chiral *α* and *β* carbons were present in **LP-D** and could be identified by comparing its ^{13}C NMR spectrum with those of the phenolic (**GG**) and nonphenolic (**VG**) lignin model dimers.[69] The signals at 59.5, 71.4, and 83.4 ppm were attributed to the *γ*, *α*, and *β* carbons, respectively, of the erythro form; the *α* and *γ* carbon peaks of the threo form were observed at 70.7 and 84.0 ppm, respectively, in an inferior fashion. No clear C−D coupling patterns were observed for the linkage carbons in the ^{13}C NMR spectrum, probably because C−D coupling through more than one bond resulted in multiple patterns.[72] The aromatic carbons were also assigned by comparing the results of the lignin model dimers and polymer. These results clearly suggested that the polymer **LP-D** had *β*-O-4 linkages between guaiacyl monomer units.

Hydrogenolysis of LP-D with a Ru/C Catalyst. In lignin hydrogenolysis, phenolic groups would be exposed after the cleavage of internal *β*-O-4 units, which would significantly influence the reactivity. Two dimer models with a complete *β*-O-4 structure, veratrylglycerol-*β*-guaiacyl ether (**VG**) and guaiacyl-glycerol-*β*-guaiacyl ether (**GG**), have often been used to model the internal and phenolic units of lignin, respectively.[39,44,59] Compared with the dimer *β*-O-4 models, the polymeric *β*-O-4 model can better simulate lignin biopolymer as a whole in depolymerization reactions. The deuterium-incorporated polymeric lignin mimic **LP-D** was initially treated with a Ru/C catalyst (10 wt %) in MeOH at 180 °C for 12 h (Scheme 3). The yields of the depolymerized monomers were normalized to the total molar amount of guaiacol units in **LP-D** by comparison with their authorized samples. This reaction gave 4-propyl guaiacol (**4**, 22%) and 4-propanol guaiacol (**5**, 45%) corresponding to 67% of the carbon balance (C.B.) of **LP-D**. These two monomers could be isolated from the reaction mixture by silica gel column chromatography. ^1H NMR and mass analyses indicated that the deuteriums at the *α*, *β*, and *γ* positions in **4** and **5** remained intact after hydrogenolysis (Figure S4). The locations of the deuteriums and the product distribution were in agreement with a previous report that used deuterated dimer models (**VG-D** and **GG-D**, Scheme 3).[67] The consistency between the *β*-O-4 dimers and polymer in the Ru/C catalytic system indicated that they can feasibly emulate the lignin biopolymer. The complete retention of deuterium suggested that the linkage protons in the *β*-O-4 units did not participate in the deconstruction of the linkages and subsequent functionalization, thus ruling out the feasibility of reported pathways involving C_α ketones,[26,48,61] enol ethers,[63−65] or consecutive dehydration/hydrogenolysis in the Ru/C-catalyzed hydrogenolysis process.[39,60] The cleavage of C_α−OH, C_β−Oar, and C_γ−OH (for **4**) should follow a hydrogenolysis pathway rather than undergoing dehydration or dehydrogenation reactions.

Pd/C Catalytic System. The commercially available catalyst Pd/C worked well in the hydrogenolysis of lignin derived from various plants,[36−38] which generally resulted in 4-propanol-substituted phenols from *β*-O-4 units under an H_2 atmosphere.[62,73,74] Abu-Omar and co-workers proposed a mechanism for the Pd/C catalytic system involving the

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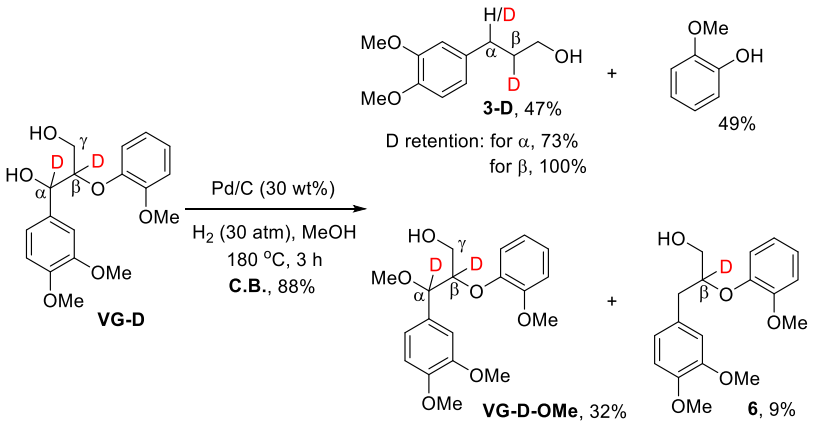
Scheme 4. Depolymerization of VG-D over Pd/C



generation of a propanediol-substituted monophenol *via* C_β–O bond cleavage, followed by the hydrogenolysis of C_α–OH.[60] Marks et al. suggested that enol ethers and the corresponding hydrogenated products (similar to **6** and **7**, *vide infra*, see also Figure S1) act as intermediates in the depolymerization of lignin dimetric models in the presence of Pd/C and a Lewis acid catalyst.[63] Based on a kinetic study, Dumesic and Ralph recently proposed that the deconstruction of *β*-O-4 motifs with and without phenolic end units follows different reaction pathways.[59] To gain more insight into the mechanism of lignin hydrogenolysis, the hydrogenolysis of deuterium-incorporated *β*-O-4 mimics was performed with Pd/C. The nonphenolic dimer **VG-D** was initially treated with 5 wt % of Pd/C in MeOH at 180 °C under H_2 (30 atm), and propanol-substituted veratrole **3** and guaiacol were formed in low yields (12 and 14%, respectively). In addition, two dimeric products, that is, the *α*-methoxylated dimer **VG-OMe** (69%) and *α*-dehydroxylation product **6** (6%), were observed (Figure S5). The **VG-OMe** dimer has been identified as an intermediate of depolymerization in the Ru/C system.[67] Compound **6**, generated *via* the cleavage of the C_α–OH bond with the reservation of C_β–O bond, has been previously reported in the Pd/C-catalyzed hydrogenolysis of **VG**.[59,63] The low yield of **3-D** under this condition made it difficult to isolate for further NMR analysis. The Pd/C dose was then increased to 30 wt %, which led to the formation of **3-D** in 47% yield, **VG-OMe** in 32% yield and **6** in 9% yield, corresponding to an 88% C.B. (Scheme 4). Analysis of the ^{1}H NMR spectrum of isolated **3-D** indicated that 27% of C_α–D was lost, whereas C_β–D remained (Figure S5).

Then, **GG-D**, a more reactive *β*-O-4 dimer bearing a phenolic group,[59] was treated with Pd/C in MeOH under various conditions (Figure 1). At 150 °C under H_2 (30 atm), **GG-D** was fully converted by 5 wt % Pd/C, which was consistent with the results for the nondeuterated version.[36,37,59] 4-Propanol guaiacol **5** was generated as a major depolymerization product (43%) with the same selectivity achieved with plant protolignin (Figure 1a).[74] Dimeric compound **7** (**6** analogue), generated through the hydrogenolysis of C_α–OH, was also observed in 40% yield. The yield of **7**, along with those of **5** and 4-propyl guaiacol **4**, corresponded to 87% of the linkage carbons in **GG-D**. With increasing reaction temperature, the depolymerized products (**5** and guaiacol) increased and dimeric compound **7** decreased (Figure 1b). At 250 °C, only 8% of compound **7** was detected, whereas **5** and guaiacol were formed in 78 and 83% yields, respectively. There existed different opinions on the role of **7** and its analogues in Pd-catalyzed *β*-O-4 hydrogenolysis. Marks et al. proposed that they are intermediates leading to the depolymerized products,[63] whereas Ralph and co-workers very recently described them as nonreactive.[75] Then, compound **7** was independently treated with Pd/C. No depolymerization reaction occurred at 220 or 250 °C (Figure 1c). Therefore, it was concluded that **7** is a side product rather than an intermediate, ruling out the possibility that the hydrogenolysis of *β*-O-4 motifs starts with the C_α–OH bond cleavage in the Pd/C catalytic system. The fact that the formation of **7** was favored by a low reaction temperature implied that it is a kinetically controlled product and should have a relative low energy barrier (Figure 1b). Therefore, it is difficult to cleave the C_β–O bond before cleaving the C_α–OH bond. Because pathways starting with the cleavage of the C_α–OH or C_β–O bond are not compatible with the current *β*-O-4 hydrogenolysis, it was deduced that these two C–O bonds are cleaved instantaneously by the Pd/C catalyst. The same conclusion was previously drawn for the Ru/C catalytic system to account for the simultaneous formation of the C_α=C_β bond and *β*-O-4 cleavage without the participation of *α*-H or *β*-H.[67] From the viewpoint of the cleavage of lignin *β*-O-4 structures, the same conclusion was reached independently for the Pd/C and Ru/C catalysts.

The deuterium retentions of the **GG-D** derivatives were measured based on the analysis of the ^{1}H NMR spectra (Figure 1, see also Figure S6). At relatively low temperatures (150 and 180 °C), both *α*-D and *β*-D were well preserved in **5**, which was consistent with the observation for the Ru/C catalytic system. These results confirmed that *α*-D and *β*-D are not involved in the depolymerization reactions under these conditions. For compound **7**, a partial loss of *α*-D was observed (50 and 15% retentions at 150 and 180 °C, respectively), whereas *β*-D was well-retained. The intactness of *β*-D implied that it is infeasible for **7** to be formed *via* a dehydration reaction (to form an enol ether) followed by a hydrogenation reaction[63] under these conditions. At higher temperatures, the hydrogenolysis of **GG-D** led to the partial loss of *α*-D in **5**, as observed at 220 °C (92% D retention) and 250 °C (37% D retention), but *β*-D was still well-retained. There are two possible explanations for the partial loss of *α*-D. (1) The Pd-catalyzed H/D exchange of **5** or **7** leads to the loss of deuterium or (2) *α*-D participates in the deconstruction of the *β*-O-4 motif at high temperatures and is thus consumed. To probe the feasibility of H/D exchange, **5-D** was treated

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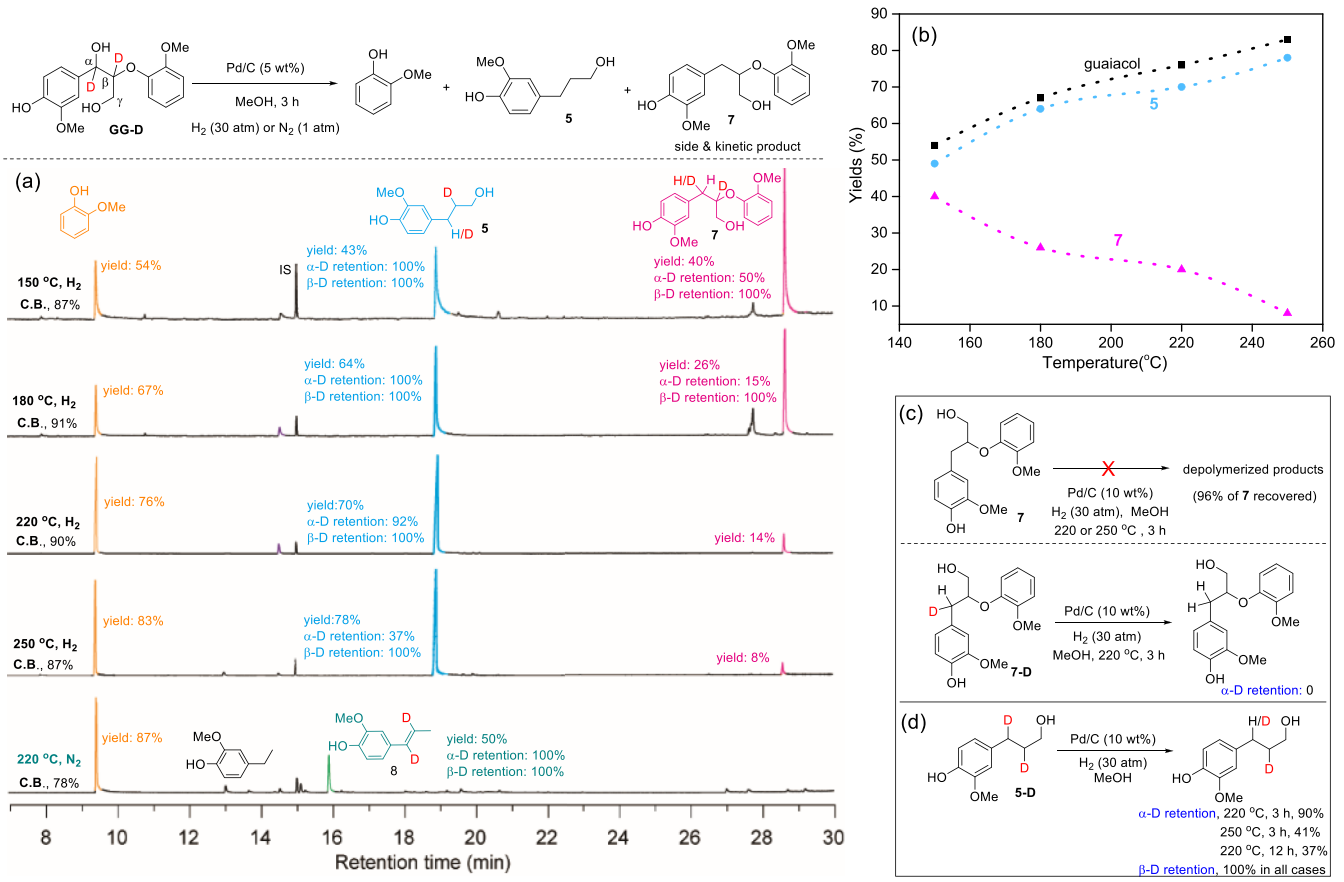

Figure 1. Pd/C-catalyzed hydrogenolysis of **GG-D** and its corresponding derivatives. (a) Product distributions and deuterium retentions. Reaction conditions: **GG-D** (60 mg), Pd/C (3 mg), MeOH (10 mL), 3 h, H_2 (30 atm) or N_2 (1 atm), at the desired reaction temperatures. The yields were determined by gas chromatography (GC), and the retentions of deuterium were measured by analyzing the ^{1}H NMR spectra. (b) Temperature profile of the hydrogenolysis of **GG-D**. (c) Treatment of **7** and **7-D** with Pd/C. (d) Pd/C-catalyzed H/D exchange reaction of **5-D**.

with Pd/C under H_2 and MeOH, and 10 and 59% of α-deuterium were replaced with hydrogen at 220 and 250 °C, respectively (Figures 1d and S7). The similar deuterium retentions obtained by the hydrogenolysis of **GG-D** and the H/D exchange reactions indicated that H/D exchange might cause the loss of α-deuterium after β-O-4 depolymerization. An independent experiment with **7-D1** over Pd/C led to the complete loss of α-deuterium at 220 °C, again confirming the feasibility of the H/D exchange reaction (Figures 1c and S8).

Recently, Galkin and Samec reported the Pd/C-catalyzed transfer hydrogenolysis of lignin samples from birch and pine trees, in which EtOH/H_2O was used as the hydrogen source instead of H_2 and monophenols with a propenyl end group were generated as major products.[37] Because it is difficult for the H/D exchange reaction to occur at a C═C bond, the retention of deuterium at the propenyl group could be used to examine whether α-H participates in the cleavage of the β-O-4 motif. **GG-D** was treated with Pd/C in MeOH under H_2-free conditions, and 4-propenyl guaiacol **8** was obtained as a major product (50% yield) (Figure 1a). A decrease in the C.B. (78%) was noted because of observable recondensation during the H_2-free reaction. The selectivity to **8** was consistent with the transfer hydrogenolysis of plant protolignin samples,[37] in contrast to previous reports that used incomplete β-O-4 models[36,76] or employed formic acid as the hydrogen source for the depolymerization of nonphenolic models,[37] where C_α ketone species were generated as major products in the presence of a Pd/C catalyst. Further ^{1}H NMR and mass spectral analyses of **8** obtained from **GG-D** suggested that α-D and β-D were well-preserved (Figure S9), which clearly showed that the reaction does not involve a dehydrogenation mechanism and C_α ketone species are not intermediates of propenyl phenols.[37] Based on the retained deuteriums, it was concluded that the linkage protons are not involved in the cleavage process, which, together with the formed C═C bond, supported the concurrent cleavage of the C_α–O and C_β–O bonds in the Pd/C-catalyzed transfer hydrogenolysis of the β-O-4 structure under these conditions.

To obtain further insight into lignin hydrogenolysis and transfer hydrogenolysis, the deuterium-incorporated lignin polymer **LP-D** was treated with Pd/C (10 wt %) under various conditions. The monomer yields and deuterium retentions are summarized in Table 1. In an H_2 atmosphere, **LP-D** was depolymerized into 4-propanol guaiacol **5** in 60–72% yields with high selectivity (>95%) (entries 1–3). The characterization of isolated **5** showed that the loss of α-D increased with increasing reaction temperature, which was consistent with the dimer model results. The α-D abundances from **LP-D** depolymerization (32%, at 220 °C for 12 h) were consistent with the H/D exchange reaction of **5-D** (37%, at 220 °C for 12 h, Figures 1d and S10), again confirming that the partial loss of α-D was caused by an H/D exchange reaction. In the absence of H_2, the transfer hydrogenolysis of **LP-D** over Pd/C led to the formation of 4-propenyl guaiacol **8** as the major product (50% yield), and the selectivity was consistent with the dimer model and actual lignin biopolymer

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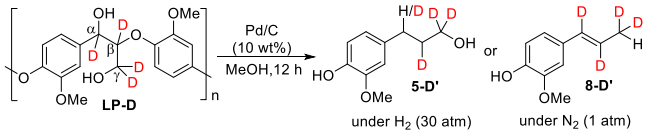
Table 1. Pd/C-Catalyzed Hydrogenolysis of LP-D[a]



			D retention (%)		
entry	conditions	monomer yield (mol %)	α	β	γ
1	H_2, 180 °C	60 (**5-D′**)	76	100	100
2	H_2, 220 °C	68 (**5-D′**)	32	100	100
3	H_2, 250 °C	72 (**5-D′**)	29	100	100
4	N_2, 250 °C	50 (**8-D′**)	100	100	100

[a]Reaction conditions: **LP-D** (60 mg), Pd/C (6 mg), MeOH (10 mL), H_2 (30 atm), 12 h.

results (entry 4). Complete preservation of all deuteriums was observed in **8-D′** (Figure S11), again suggesting that the cleavage of the C_α–O, C_β–O, and C_γ–O bonds does not proceed *via* dehydrogenation and/or dehydration processes.

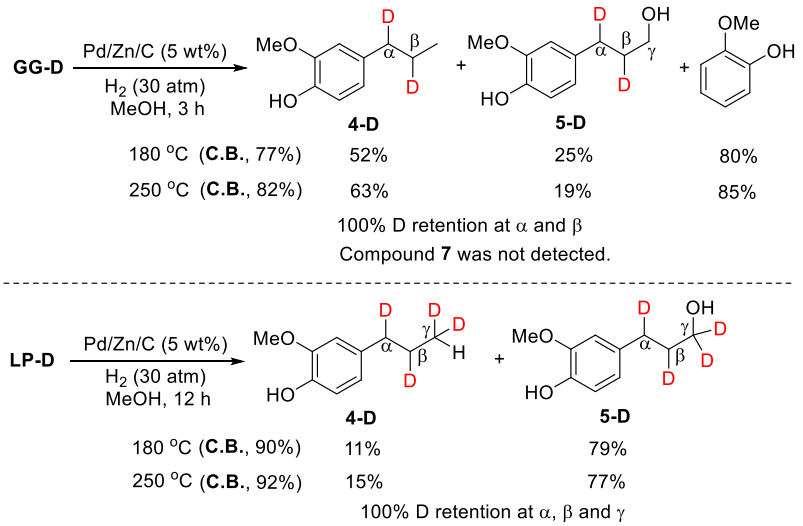
Pd/Zn/C Catalytic System. Recent results have indicated that the binding of the OH groups in lignin to the catalyst plays an essential role in its depolymerization.[35,75] Compared to C_γ–OH, C_α–OH may play a more critical role in the cleavage of the C_β–O bond. For instance, lignin dimers without C_α–OH (such as phenethoxybenzene) were difficult to depolymerize,[77,78] whereas the C_β–O bond cleavage also occurred for dimer models without C_γ–OH.[44,62] We hypothesized that introducing a Lewis acid center with an affinity for oxygen atoms[79] into Pd/C may be beneficial to lignin hydrogenolysis. To verify this assumption, Pd/Zn/C, which was used for lignin hydrogenolysis by Abu-Omar and co-workers,[35,60] was chosen for further study. This catalyst was prepared by mixing Pd/C with $ZnCl_2$ (Pd/Zn molar ratio = 1:2) at 150 °C in MeOH under H_2 and subsequently drying the mixture under vacuum.[60] Transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy characterizations indicated that Pd(0) nanoparticles were distributed on the carbon, and no Pd–Zn alloy species were formed (Figure S13), which was consistent with previous conclusions.[60]

After treating **GG-D** with Pd/Zn/C in MeOH at 180 °C under H_2 (30 atm) for 3 h, monomeric phenols, including 4-propyl guaiacol (**4**, 52%), 4-propanol guaiacol (**5**, 25%), and guaiacol (80%), were obtained (Scheme 5). Increasing the reaction temperature to 250 °C led to a slight increase in the depolymerized products. These results were consistent with previous reports in terms of the activity and selectivity.[60] Unlike Pd/C, side product **7** was no longer detected in the Pd/Zn/C-catalyzed hydrogenolysis of **GG-D**. The characterization of compounds **4** and **5** implied that α-D and β-D remained intact during the Pd/Zn/C-catalyzed depolymerization reaction (Figure S14), again confirming that α-H(D) and β-H(D) dissociated during the deconstruction of the β-O-4 motif and the subsequent functionalization. Obviously, the H/D exchange reaction no longer occurred at the α position in **4** and **5** in the presence of the Pd/Zn/C catalyst.

In the case of the catalytic hydrogenolysis of **LP-D**, the Pd/Zn/C catalyst produced monomeric phenols in 90% yield at 180 °C and 92% yield at 250 °C, and these yields were higher than those obtained over the Pd/C catalyst under the same conditions (60 and 72%, respectively, see Table 1). The deuterium content of **5** was determined by ^{1}H NMR and mass spectral analyses. No loss of deuterium was detected, which was consistent with the **GG-D** reactions (Figure S15). The NMR characterization of **4** was difficult to achieve because of its low yield, and the mass analysis suggested that all the deuteriums were well-retained by **4** compared with the standard sample. Therefore, the experimental results showed that α-H(D), β-H(D), and γ-H(D) do not participate in the cleavage of lignin during Pd/Zn/C-catalyzed hydrogenolysis.

The normal β-O-4 polymer **LP** was used as the substrate and treated with Pd/C and Pd/Zn/C at 180 °C for 12 h, respectively. Similar to **LP-D**, Pd/Zn/C (82%) was superior to Pd/C (58%) in terms of the monomer yields. The resulting oily products from **LP** were measured by two-dimensional HSQC NMR spectroscopy (Figure 2). In both cases, cross-signals derived from β-O-4 units (**A**) completely disappeared. The correlation signals resonated at δ_C/δ_H = 36.1/2.81 (α), 80.2/4.29 (β), and 61.3/3.45 (γ) ppm were assigned as de-α-OH species (**7** analogues) based on the NMR spectrum of compound **7** (Figure S12). These signals could be observed in the Pd/C-catalyzed hydrogenolysis reaction, whereas they were

Scheme 5. Hydrogenolysis of D-Incorporated β-O-4 Mimics with Pd/Zn/C



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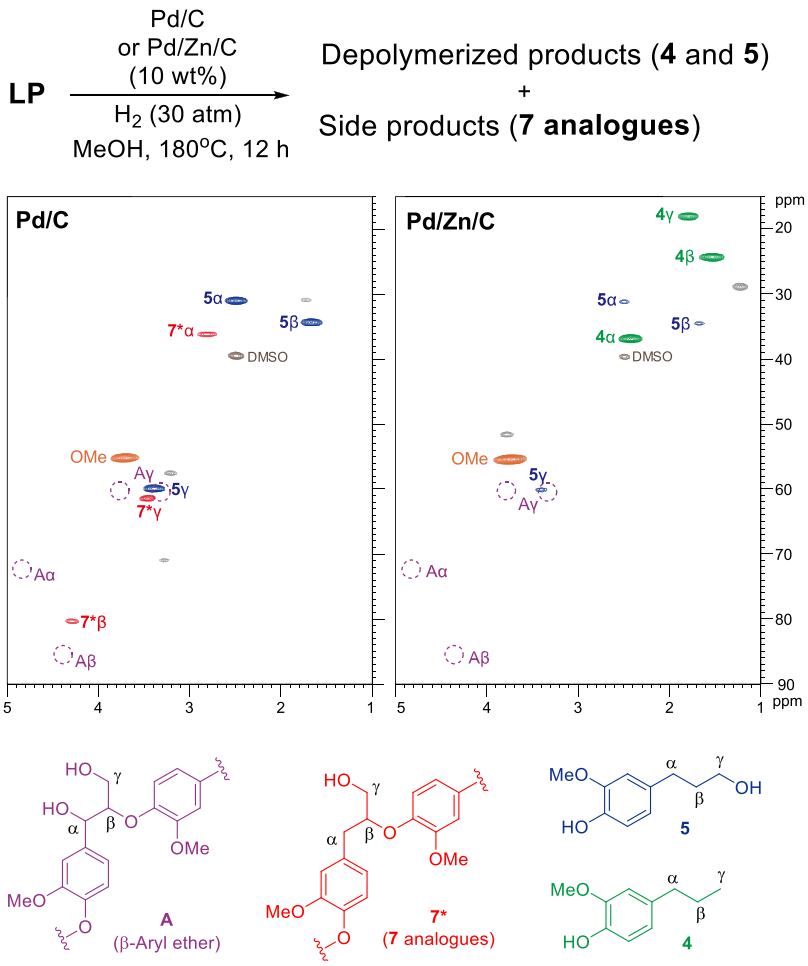

Figure 2. HSQC NMR spectra of the oily products from the hydrogenolysis **LP** with Pd/C and Pd/Zn/C.

absent in the Pd/Zn/C-catalyzed reaction, being in line with the observation in dimeric **GG-D** reactions. An independent treatment of **7** with Pd/Zn/C at 250 °C did not give any monomeric phenols, suggesting that the absence of **7** and its analogues during β-O-4 hydrogenolysis may be caused by being suppressed rather than being consumed. We proposed that the binding of Zn^{2+} to hydroxy groups either on the catalyst surface or in the solution[60] might facilitate the cleavage of the C_β−O bond, preventing the cleavage of only C_α−OH. The abatement of the side reactions and the increase in monomeric products in polymeric model reactions suggested that the Pd/Zn/C catalyst is better able to catalyze the hydrogenolysis of lignin because of the oxygen atom affinity of the Lewis acid zinc center.

CONCLUSIONS

In summary, an artificial lignin polymer with a perdeuterated β-O-4 substructure, which is a better model for the actual plant lignin structure, was synthesized and characterized. Using this deuterated polymer and complementary dimer models, the mechanism of lignin hydrogenolysis and transfer hydrogenolysis over Ru/C, Pd/C, and Pd/Zn/C catalysts was systematically studied. The location of deuterium after the catalytic reactions demonstrated that the linkage protons do not participate in the cleavage of the β-O-4 substructure and subsequent functionalization reactions, thus negating the hypothesized routes including consecutive C−O cleavage, C_α ketones, and enol ethers for these catalytic systems. Using different points of view, a pathway involving the concurrent cleavage of the C_α−O and C_β−O bonds was proposed for the hydrogenolysis of β-O-4 over the Pd/C catalyst. The sole α-dehydroxylation reaction, which always occurred for the dimer models in the presence of Pd/C, was identified as a side reaction. The introduction of Zn ions into Pd/C was conducive to β-O-4 hydrogenolysis, and this hypothesis was confirmed by using a Pd/Zn/C catalyst that suppressed the side reactions and resulted in an improved monomer yield in the polymeric model reactions. Because lowering the catalyst cost is one of the challenges for lignin depolymerization, these results provided useful information for designing new heterogeneous catalysts by reducing the amount of reducing precious metals together with introducing cheap metals. Overall, these deuterium-incorporated β-O-4 mimics paved a definitive path for lignin hydrogenolysis mechanistic studies, providing useful information for designing novel catalytic systems and controlling the selectivity of lignin depolymerization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c02339.

Details of experimental procedures, GC chromatograms, and mass and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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