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COMPARISON OF THE β -O-4 BOND CLEAVAGE MECHANISM OF C₆-C₃ AND C₆-C₂ LIGNIN MODEL COMPOUNDS DURING ACIDOLYSIS

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ABSTRACT

The cleavage mechanism of β -O-4 bond was compared between a C₆-C₃ and a C₆-C₂ type lignin model compounds, veratrylglycerol- β -guaiacyl ether (VG), and veratrylglycol- β -guaiacyl ether (V'G), under acidolysis conditions (82% aqueous 1,4-dioxane solution containing HBr or HCl at 85°C). The disappearance rate of V'G was faster than VG. It was confirmed that V'G primarily converts into an enol ether compound, 1-(2-methoxyphenoxy)-2-(3,4-dimethoxyphenyl)ethylene, via the H₂O elimination, and subsequently, the β -O-4 bond cleaves affording guaiacol and a Hibber's ketone, 3,4-dimethoxyphenylacetaldehyde. On the other hand, the mechanism for the VG disappearance was unclear mainly because of the extreme lability of 2-(2-methoxyphenoxy)-3-(3,4-dimethoxyphenyl)prop-2-en-1-ol, another enol ether compound. The proton activity in two acidolysis systems, 0.20 mol/l HBr and 0.25 mol/l HCl, were assumed to be the same based on the observation that the hydrolysis rates of a carbohydrate model compound, methyl α -D-glycopyranoside, were the same in both systems. The disappearance rates of V'G in these systems were almost the same, while VG disappeared faster in the HBr system. These results suggest that the mechanism of the disappearances of VG and V'G is not the same and the counter anions of the acids influence the disappearance rate of VG more significantly than V'G.

BACKGROUND

The mechanism of the β -O-4 bond cleavage during acidolysis of lignin has been discussed in several previously published papers¹⁻⁴⁾. Lundquist and Lundgren have proposed a mechanism for this cleavage (Fig. 1) and suggested that the rate-determining step is the conversion of benzyl cation type intermediate (II) into enol ether type substructure (III) on the basis of two observations¹⁾: (1) a

model compound analogous to III is extremely labile under acidolysis conditions, and (2) an acidolysis of a model compound of III gives reaction products identical to those obtained by the same treatment of a model compound analogous to β -O-4 substructure (I). In acidolyses of a model compound of I, however, the corresponding enol ether compound of type III was not detected at all, so that it has not been proven yet whether or not III certainly forms during acidolysis of I and the rate-determining step is the conversion of II into III, which is the abstraction of the β -proton. It has also been reported that the rate of the β -O-4 bond cleavage is dependent on kind of used acid and the order is: HBr>HCl>H₂SO₄²⁻⁴⁾. It has been suggested that this order is attributed to the different ability of the conjugate bases of the acids to abstract the β -proton from II³⁾. However, this explanation seems to lack the rationality, because it should be more rationale to consider that solvents abstract the β -proton when the pK_a values of the acids and the conjugate acids of solvents are taken into consideration. On the basis of these backgrounds, we have been reexamining the cleavage mechanism of β -O-4 bond during acidolysis of lignin⁵⁾.

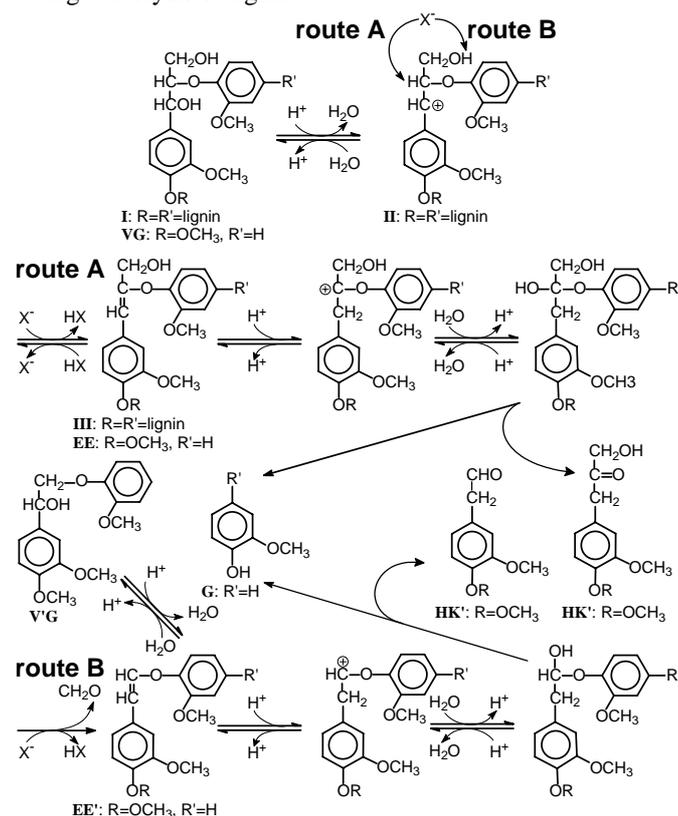


Fig. 1 Suggested mechanism for the β -O-4 bond cleavage during acidolysis of lignin

In this study, we focused on the difference in the mechanism of the β -O-4 bond cleavage between a C₆-C₃ type lignin model compound, 2-(3,4-dimethoxyphenoxy)-1-(2-methoxyphenyl)propane-1,3-diol (veratrylglycerol- β -

guaiacyl ether, **VG**), and a C₆-C₂ type model compound, 1-(3,4-dimethoxyphenoxy)-2-(2-methoxyphenyl)ethanol (veratrylglycol- β -guaiacyl ether, **V'G**). The effect of counter anion of used acid was also discussed taking the proton activity into consideration.

EXPERIMENTAL

The model compounds, **VG** and **V'G**, were synthesized, and one of them was acidolyzed in an 82% aqueous 1,4-dioxane solution containing HBr or HCl for 6 h at 85°C. At several prescribed times, the concentrations of the starting compound and 2-methoxyphenol (guaiacol, **G**) were mainly quantified by GC or HPLC.

A carbohydrate model compound, methyl α -D-glucopyranside (**MGP**), was acidolyzed under exactly the same conditions with those for the lignin model compounds. The concentration of **MGP** was quantified by GC after converting it into the acetyl derivative. The model compounds used as a starting compound and identified reaction products are shown in Fig. 1.

RESULTS AND DISCUSSION

Mechanism of the **V'G** disappearance

The disappearance of **V'G** followed the pseudo-first-order rate law, and the observed rate constant was 0.00854 in the 0.2 mol/l HBr system. An enol ether compound, 1-(2-methoxyphenoxy)-2-(3,4-dimethoxyphenyl)ethylene (**EE'**), which is produced by the H₂O elimination, **G**, and a Hibber's ketone, 3,4-dimethoxyphenylacetaldehyde (**HK'**), formed. The total yield of **V'G**, **EE'**, and **G** was always 100% at any reaction time. The yields of **G** and **HK'** were almost the same at any reaction time. When **EE'** was acidolyzed in the same system, the disappearance followed the pseudo-first-order rate law, and the observed rate constant was 0.00825. In this case, no **V'G** was detected at all. On the basis of these results and the mathematical calculations, it was confirmed that **V'G** primarily converts into **EE'**, and successively, the β -O-4 bond is cleaved⁵. There is no route in which the β -O-4 bond directly cleaves without the formation of **EE'**.

Difference in the mechanism between **VG** and **V'G**

The disappearance of **VG** fairly followed the pseudo-first-order rate law, and the observed rate constant was 0.00192 in the 0.2 mol/l HBr system. **G** and 1-hydroxy-3-(3,4-dimethoxyphenyl)propan-2-one (**HK**), another Hibber's ketone compound, were detected, and the total yield of **VG** and **G** was always 100% at any reaction time. The detection of **HK** was not quantitative. An enol ether compound, 2-(2-methoxyphenoxy)-3-(3,4-dimethoxyphenyl)prop-2-en-1-ol (**EE**), which is produced by the H₂O elimination, was not detected at all, probably because of its extreme lability. In the 0.2 mol/l HCl

system, the behavior of **VG** was similar to that in the 0.2 mol/l HBr system, but the disappearance rate was slower (rate constant 0.00072), which is accordance with the result of the previously published paper⁴.

As a possible reason for the slower disappearance in the HCl system, it can be considered that the activities of proton in these two organic solvent systems are different even though the molar concentration of the acids is the same. It is required to prepare a HBr and a HCl systems in which the activities of proton are the same with each other.

To measure the proton activity, **MGP** was chosen as a standard compound. The hydrolysis of **MGP** is known to be a reaction following the specific acid catalysis in aqueous systems⁶. It was assumed that the proton activity could be determined by the hydrolysis rate of **MGP**. When the concentration of HBr and HCl was 0.20 and 0.25 mol/l, respectively, the hydrolysis rate was the same in these systems.

When **VG** was acidolyzed in the 0.20 mol/l HBr and 0.25 mol/l HCl systems, the observed rate constants for the disappearance were 0.00192 and 0.00107, respectively. The disappearance was clearly faster in the HBr system. On the other hand, the disappearance rates of **V'G** were almost the same in these systems. These results suggest that the mechanism of the β -O-4 bond cleavage of **VG** is different from **V'G** and the counter anions of the acids influence the disappearance rate of **VG** more significantly than **V'G**.

CONCLUSIONS

V'G primarily converts into **EE'**, and subsequently, the β -O-4 bond cleaves under the acidolysis conditions. On the other hand, the mechanism of the **VG** disappearance is not clear. However, it is suggested that the mechanism of the **VG** disappearance is different from **V'G** and the counter anions of the acids influence the **VG** disappearance rate more significantly than **V'G**.

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