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Functionalization and molecular structure control of lignin degradation products by neighboring group participation

M. Masaki[1)], K. Watanabe[1)], T. Watanabe[2)], M. Funaoka[3)] and K. Mikame*[1)]
[1)] Faculty of Agriculture, Niigata University 8050, Ikarashi 2-no-cho, Nishi-Ku, Niigata, 950-2181, Japan
[2)] Research Institute for Sustainable Humanospher, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan [3)] LIPS (Lignophenol & Systems), 2-9-7, Minaminanamatsu-cho, Amagasaki, Hyogo, 660-0053
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Corresponding author*: mikame@agr.niigata-u.ac.jp

Abstract

This study demonstrated that the molecular weight regulation of lignin polymer by degradation to enhance its functionality. The unique feature of this study is the use of Neighboring Group Participation (NGP) to control the molecular weight. We obtained various types of phenolated lignin (lignophenol: LP) using the phase separation system. The LP was depolymerized under alkaline conditions, and their molecular weights were controlled intentionally based on the substituent pattern of the phenolic derivatives grafted. In addition, the degradants were found to have a much higher long-wavelength UV absorption property than the original LP. Degradation products of various sizes obtained by molecular weight control can contribute to a variety of physiological activities: antioxidant activity, protein absorption, and enzyme inhibition activity.

1. Introduction

Lignin is a phenolic polymer compound contained in the plant cell wall. Adding of value is required for effective utilization of lignin. Polyphenol compounds, such as flavonoids, stilbene, have attracted attention because of their various physiologic activity. However, lignin has little physiologic activity despite the similarity to these structures. One of the reasons for this is that the phenolic hydroxyl groups decrease during the biosynthesis process.

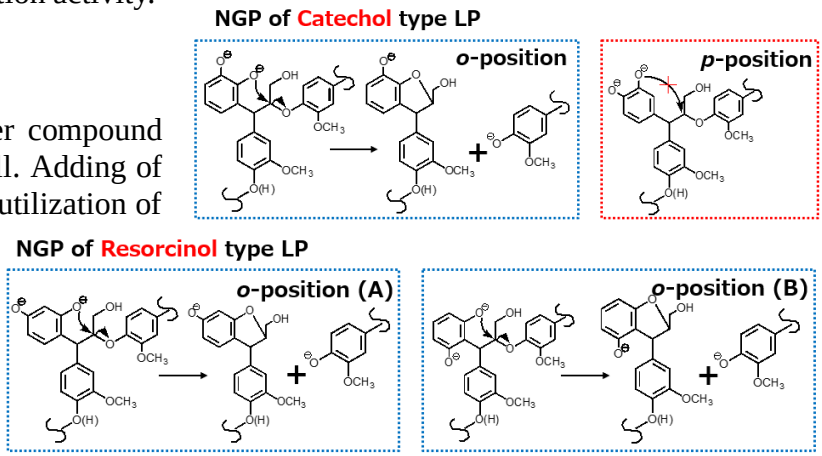

Fig. 1 Degradation of catechol and resorcinol-type LP by NGP

We have prepared a catechol-type LP, which was designed based on the structure of high physiologically active polyphenols; it has achieved high antioxidant activity through alkaline cupric oxidative degradation[1)], but it showed low anti-tyrosinase activity. Therefore, controlling to lower molecular weight than catechol-type LP seems effective to improve the functionality. LP causes NGP under alkaline conditions only when the phenol derivative is bound at the *o*-position to the lignin benzyl position (Fig. 1). Since catechol binds to lignin at both the *o*- and *p*-positions, catechol-type lignophenol remains in relatively high molecular weight. By contrast, resorcinol is introduced only at the *o*-position; the degradant become low molecular weight. Therefore, the combination of these two phenol derivatives may contribute to the intentional molecular weight control and high functionality of LP, keeping the amount of phenolic hydroxyl group.

2. Experiment

2.1. *Preparation of LP from birch*

The operation was performed according to phase separation system[1-2]. *p*-Cresol, Catechol, and Resorcinol were used as phenol derivatives, and sulfuric acid and phosphoric acid mixture were used as acid catalysts.

2.2. *Alkaline degradation of LP*

LP was allowed to react with 1.0N NaOH at 170℃ for 30 min[1-2].

3. Results and discussion

The molecular weight could be intentionally controlled by mixing two types of polyhydric phenols (Table 1). Molecular weights around 1000-2000 were expected to contribute to the adsorption of proteins and metals due to the π-π stacking interactions. The graft of each phenolic derivative in LP degradants were confirmed by LC-MS analysis. It was also confirmed that the resorcinol-type LP degradant absorbed a longer wavelength UV than the catechol-type (Fig. 2). Though it was assumed that the quinone structure was formed under alkaline conditions, no peaks could be considered as conjugated carbonyl in the FT-IR measurement results. C-C bonds from the condensation of aromatic rings were inferred.

From these results, we achieved intentional control of the molecular weight, keeping the hydroxyl group amount by introducing polyhydric phenol, and a long-conjugated structure of LP.

Table 1 Molecular weights of LP and their degradants

Birch Lignophenol	*Mw* (oliginal)	*Mw* (degradants)
Catechol type	6600	**4200**
Catechol:Resrcinol=2:1 type	5700	**2500**
Catechol:Resrcinol=1:1 type	6100	**2100**
Catechol:Resrcinol=1:3 type	5800	**1900**
Resorcinol type	6400	**1700**
p-Cresol type	8400	1200

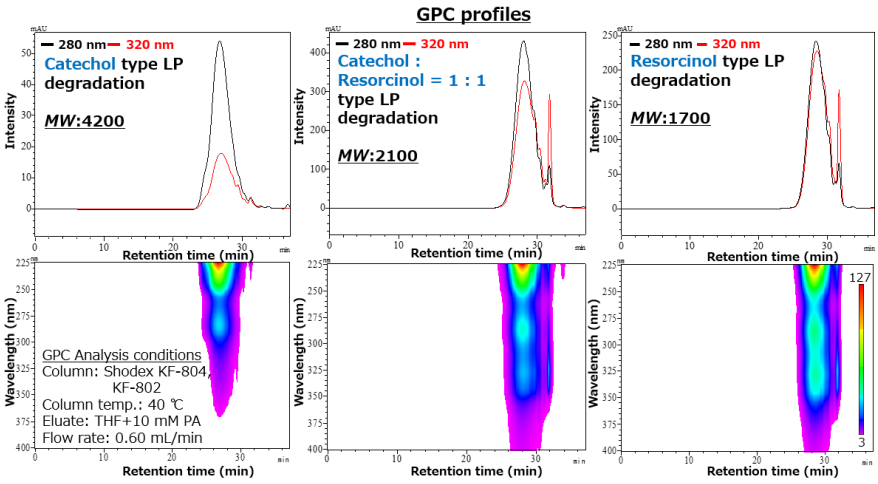

Fig. 2 Effect of NGP on LP degradants: catechol, resorcinol, and their mixture-type

4. Conclusions

In this study, we showed that the molecular weight of LP degradants can be intentionally controlled by using NGP. They were also characterized by the maintenance of high hydroxyl content and high UV-absorbing ability. Therefore, it was speculated that lignin can be used as a high value-added material to design structures that express various biological activities.

Reference

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2) M. Funaoka, *Polymer International*, **47**, 277-290 (1998).