Dehydrogenation Polymer (DHP) Condensation Reaction with Glucose

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Dehydrogenation polymer (DHP) was synthesized by free radical coupling dehydrogenation polymerization of the lignin precursor coniferin under the catalysis of various enzymes. DHP has a highly similar connection structure to natural lignin (such as β-O-4, β-β, β-5, *etc.*), so it shows the potential as a new zero formaldehyde release adhesive. In plants, a very stable lignin-carbohydrate complex (LCC) is formed between lignin and cellulose and hemicellulose, which makes plants have excellent mechanical strength. In this paper, the thermal condensation reaction between DHP and D-glucose-$^{13}C_6$ was simulated by hot pressing of wood-based panels, and the DHP-D-glucose-$^{13}C_6$ complex was prepared. The condensation was analyzed by Fourier Transform Infrared (FTIR) and nuclear magnetic response (NMR) characterization. The signals of C_1 and C_6 of glucose in the complex could be clearly observed in the FTIR and NMR spectra, which showed that DHP and D-glucose-$^{13}C_6$ can undergo thermal condensation reaction in the simulated hot-pressing environment. The C_1 on the glucose unit may form a C-C bond with the C_6 on the aromatic ring in DHP. It was found that DHP can function as a formaldehyde-free wood-based panel adhesive, thereby providing new evidence about the mechanism of adhesion within plant fibers.

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Keywords: Dehydrogenation polymer; Glucose; Thermal condensation mechanism; Adhesives

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INTRODUCTION

With standard of living increasing, the demand for building and remodeling supplies is growing ever stronger. Wood is being used more frequently as decorative material for buildings. However, engineered wood-based panels are increasingly being used to ease the pressure on the supply and demand of the material due to the shortage of natural solid wood resources. Wood-based panels are often made from edge debris that is produced during the cutting of wood. These raw materials are subjected to mechanical processing to separate them into distinct unit products, which are then bonded using adhesives to produce composite boards. Among these, urea-formaldehyde resin, phenol-formaldehyde resin, and melamine-formaldehyde resin are the most often used adhesives. However, the produced formaldehyde can be harmful to human health (Gu 2015). Creating formaldehyde-free adhesives is a key task in the continuous production of safe and environmentally friendly wood-based panels.

Lignin is the second largest biomass resource in the plant kingdom after cellulose. In plants, lignin acts as an adhesive that connects cellulose and hemicellulose, giving plants excellent mechanical strength and water resistance (Mili *et al.* 2022). Currently, in the application of lignin as a wood adhesive, it is primarily blended with other chemical adhesives to minimize the release of formaldehyde (Liu *et al.* 2007; Nie *et al.* 2010). For instance, after hydrothermal treatment, corn stover lignin can be used as a modified phenolic resin substitute (Yan *et al.* 2017). In certain circumstances, hydroxymethylated alkali lignin can be co-polymerized with formaldehyde and urea to produce lignin-urea-formaldehyde resin adhesive (Li *et al.* 1996).

After alkaline treatment, heat condensation, and the addition of a small amount of melamine, a timber adhesive with good water resistance was prepared (Li and Yung 1995). However, while these techniques reduce the levels of formaldehyde and phenol in conventional adhesives, they do not fully eliminate the issue of formaldehyde release. (Vázquez *et al.* 1997; Kharazipour *et al.* 1998; Alonso *et al.* 2004; Khan *et al.* 2004; Alonso *et al.* 2005; Khan and Ashraf 2007).

Fortunately, some researchers have proposed the use of biological enzymes to prepare adhesives. In the 1980s, Hüttermann *et al.* (1989) investigated the use of lignosulfonate modified with laccase and peroxidase for adhesive applications. The transverse tensile strength of particleboard produced with this adhesive can reach 0.47 MPa. However, enzymes are limited to altering lignin sulfonates that are dissolved in water. These lignin sulfonates are very soluble and can readily cause particleboard to swell from water absorption.

After that, Yamaguchi *et al*. (1991, 1992, 1994) discovered the use of peroxidase and laccase to treat small molecule phenolic substances to obtain a lignin dehydrogenation polymer (DHP), similar to the natural lignin structure. DHP is coupled with the free phenolic hydroxyl group on the surface of the thermal mechanical pulp (TMP) fiber under the catalysis of the enzyme, which can effectively improve the wet tensile strength of the paper. Coniferin, which occurs naturally in the cambial sap of gymnosperms and angiosperms, is considered to be an important precursor in lignin biosynthesis (Freudenberg and Harkin 1963; Tsuji *et al*. 2005). The authors' research group has prepared DHP with coniferyl under the catalysis of laccase system, thereby producing a compound that is similar to the structure of natural lignin. It has been found that DHP can undergo strong self-condensation reaction in high temperature and acidic environments (Wang 2022). If DHP can form covalent bonds with plant fibers during hot compression, it follows that it has potential to greatly improve the bonding performance of DHP.

The main component of plant fiber is cellulose, and its structural unit is glucose. Based on the above analysis, this paper used the lignin precursor coniferin to generate DHP by dehydrogenation polymerization under the catalysis of β-glucosidase and laccase, and then the obtained DHP and D-glucose-$^{13}C_6$ were subjected to thermal condensation reaction in a simulated wood-based panel hot-pressing environment to prepare DHP-D-glucose-$^{13}C_6$ complex. The specific research process is shown in Fig. 1. The structure of the complex was analyzed by FT-IR and NMR techniques, and the possible thermal condensation mechanism between DHP and glucose was explained. The results provide new evidence for DHP as a wood-based panel adhesive, while also elucidating the mechanism underlying development of adhesion within plant fibers.

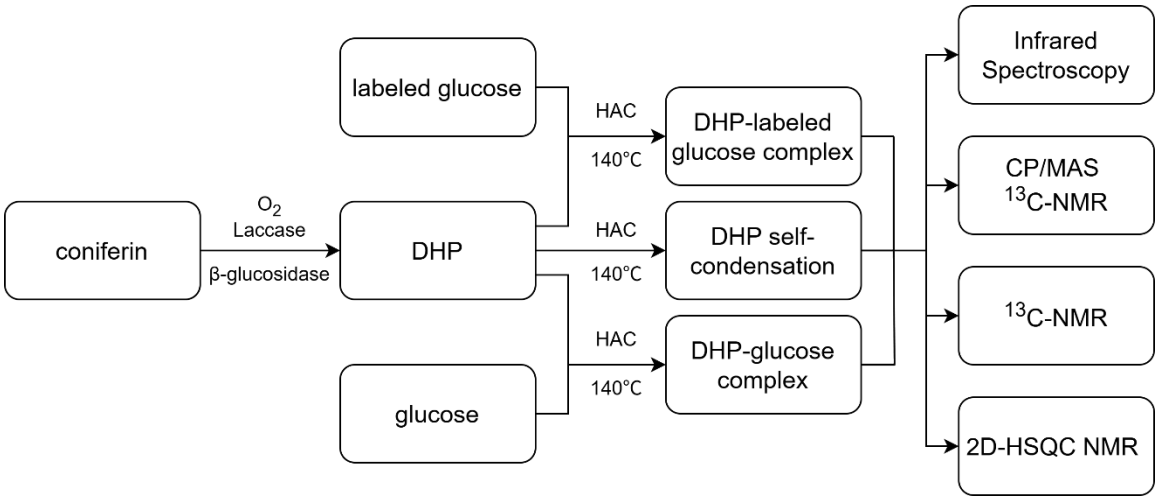

Fig. 1. Flowchart of the research process

EXPERIMENTAL

Materials

Acetic acid, toluene, and dimethyl sulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co. Ltd, all analytically pure. D-glucose was from Shanghai Aladdin Biochemical Science and Technology Co. Ltd. D-glucose-6-^{13}C was purchased from Sigma Aldrich (Shanghai) Trading Co. The coniferin used in this work was self-made in the laboratory. Laccase (E.C.1.10.3.2) was donated by Novozymes A/S (Tianjin, China). β-glucosidase was purchased from Sigma-Aldrich (Shanghai) Trading Co. Ltd.

Preparation of DHP

400 mL HAc-NaAc buffer (pH=4.0) and 4 g coniferin were added to a three-necked flask. After becoming fully dissolved, 715 IU of laccase and 0.16 g of β-glucosidase (specific activity: 6.3 units/mg) were added. The three-necked flask was placed in a constant temperature water bath at 25 °C, and sterile air was continuously pumped into the three-necked flask with an air pump. After 24 hours of reaction, 715 IU of laccase was added and the reaction continued for 48 hours. After the reaction, the crude product was obtained by centrifugal drying. The crude product was completely dissolved with 1,2-dichloroethane/ethanol (2:1, V/V) and centrifuged to remove the insoluble matter. Then, it was evaporated by a rotary evaporator and dried to obtain DHP.

Thermal Condensation of DHP with Glucose

During the hot-pressing process of traditional wood-based panels, the thermal degradation of hemicellulose produces a large amount of acid, which catalyzes the degradation of cellulose into monosaccharides and oligosaccharides (Zeng 2011). In this experiment, acetic acid was used to simulate the acidic environment. First, 1 mL of acetic acid solution (10% by volume) was added to a stainless steel sealed jar. Next, 500 mg of glucose and DHP were added to the sealed jar, and then 2 mL of acetic acid solution was measured and added to the sealed jar. The reaction was carried out in a sealed jar in an oil bath at 140 °C for 25 min. The products were centrifuged several times with the addition of distilled water to remove all residual glucose. The products were washed to be neutral and finally dried to obtain the DHP-glucose complex. The DHP-labeled glucose complex

was prepared by replacing 500 mg of glucose in the above step with a mixture of 450 mg of glucose and 50 mg of labeled glucose, and the rest of the steps were as described above.

Infrared Spectroscopy

The samples' infrared spectra were obtained using a Fourier transform infrared spectrometer (ThermoFisher Scientific Inc., Waltham, MA, USA). Approximately 2 mg of the sample was mixed with an appropriate amount of potassium bromide, ground, and pressed into a thin slice in a tablet presser. An FTIR spectrometer was used in the wave number range 500 to 4000 cm^{-1} and 32 scans.

CP/MAS ^{13}C-NMR

The solid-state CP/MAS ^{13}C NMR spectra were recorded using an AV-III 400M spectrometer (Bruker Corp., Karlsruhe, Germany). Approximately 90 mg of the sample was weighed into a superconducting NMR spectrometer, and the sample was subjected to ^{13}C continuous scanning with a solid-state probe with the following detection parameters: The observing frequency used was 100.6 MHz and the acquisition time was 0.02 s. The proton 90° pulse time of 3.0 s with a 3.0 s pulse delay, and 3600 scans were accumulated.

^{13}C-NMR

The ^{13}C-NMR spectra were recorded using an AV-III 500M spectrometer (Bruker Corp., Karlsruhe, Germany). The condensation product was subjected to ball milling, and the effective time of ball milling was about 22 h. After ball milling, the sample powder was washed out with toluene, followed by low-temperature centrifugation to remove the toluene and drying to obtain the sample powder. Approximately 100 mg of the sample was weighed, dissolved in 1.2 mL of DMSO-d_6 solution, and pumped into an NMR tube, which was subjected to ^{13}C continuous scanning on a superconducting NMR spectrometer with 9000 scans.

2D-HSQC NMR Test

The 2D-HSQC NMR spectra were recorded using an AV-III 500M spectrometer (Bruker Corp., Karlsruhe, Germany). The 80 mg of ball-milled sample was completely dissolved with 1 mL of DMSO-d6 solution and loaded into an NMR tube, which was placed into a superconducting NMR spectrometer. The 5-mm wideband probe was used for 32 scans with a scanning delay of 1.0 s. Bruker standard pulse sequence: the sample data points of 1H dimension was 2048, and the sample data points of 13C dimension were 256. The spectral width used was 190 ppm in F1 (13C) and 11 ppm in F2 (1H).

RESULTS AND DISCUSSION

Infrared Spectral Analysis

The infrared spectra of DHP self-condensation, DHP-glucose complex, and DHP-labeled glucose complex are shown in Fig. 2. The absorption peaks of aromatic nuclei were observed at 1600, 1510, and 1424 cm^{-1} for DHP-glucose complex and DHP-labeled glucose complex, which indicated that the benzene ring skeleton still existed for DHP-glucose complex and DHP-labeled glucose complex. Compared with the self-condensation of DHP, the intensity of the absorbance peaks of the DHP-glucose complex and DHP-labeled glucose complex at 1078 and 1030 cm^{-1} increased. The absorbance at 1030 cm^{-1} is

relevant to the characteristic absorption peak of sugars. The enhancement of absorbance peak suggested that DHP and glucose may have undergone thermal condensation.

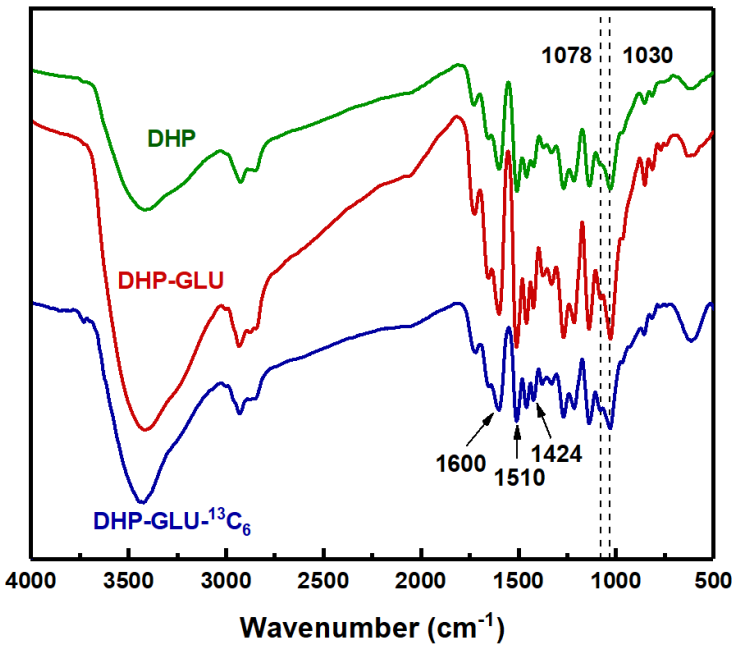

Fig. 2. Infrared spectra of DHP self-condensation, DHP-glucose complexes, and DHP-labeled glucose complexes

CP/MAS ^{13}C-NMR Analysis

The solid-state CP/MAS ^{13}C NMR spectra of DHP self-condensation, DHP-glucose complex, and DHP-band-labeled glucose complex are shown in Fig. 3, and the functional group attributions are shown in Table 1.

Table 1. Solid-state CP/MAS ^{13}C NMR Functional Group Attribution of DHP Self-Condensation and DHP-Band-Labeled Glucose Complexes

Peak	Chemical Shift Value (δ)/ppm		Assignment
	DHP self-condensing	DHP-labeled glucose complex	
1	171.28	171.9	O-C=O of acetyl groups in aliphatic esters
2	146.6	147.4	-CH_2OH/C_4(β-5)in cinnamaldehyde, C_3/C_4 in guaiacol
3	131.6	132.5	$C_α$/$C_β$ in cinnamaldehyde, C_1/C_1' in β-5
4	115.67	116.5	C_6 in β-5, C_2/C_5/C_6 in guaiacol
5	86.37	86.19	$C_α$ in β-5, $C_α$ in β-β, $C_β$ in β-O-4
6	74.5	73.53	$C_α$ in β-O-4, $C_γ$ in β-β
7	-	61.6	C_6 in glucose
8	55.51	55.34	-OCH_3
9	20.36	20.22	-CH_3

The signal peaks of the coniferyl alcohol structure, guaiacyl structure, and methoxy structure were obvious. Compared with the spectra of DHP self-condensation and DHP-glucose complex, the intensity of the absorption peak of DHP-labeled glucose complex at 61.6 ppm was obvious, which was inferred to be the C_6 signal peak of labeled glucose, indicating that the occurrence of thermal condensation reaction of DHP with glucose under the high temperature and high-pressure acidic conditions.

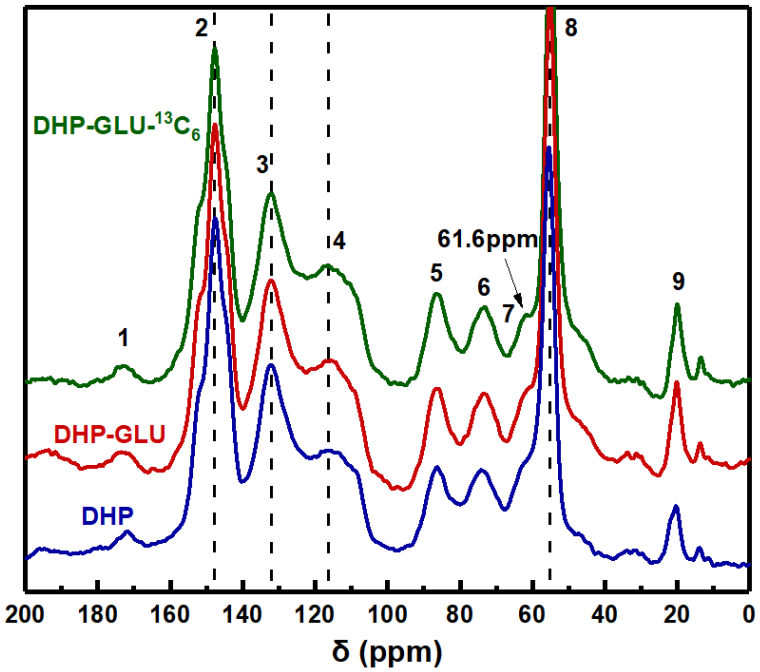

Fig. 3. CP/MAS ^{13}C-NMR spectra of DHP self-condensation, DHP-glucose complex, and DHP-labeled glucose complex

^{13}C-NMR Analysis

The liquid NMR of DHP self-condensation, DHP-glucose complex, and DHP-labeled glucose complex are shown in Fig. 4, and the functional group attributions are shown in Table 2. Compared to DHP self-condensation, the two absorption peaks of DHP-band-labeled glucose complex and DHP-glucose complex were enhanced in the range of 128 to 130 ppm, in which the absorbance peak at 129.5 ppm (No. 10) was from the C_α of the coniferyl alcohol, and that at 128.5 ppm (No. 11) was from the C_β of the coniferyl alcohol. This result indicated that DHP-labeled glucose complex and DHP-glucose complex had higher content of coniferyl alcohol. In addition, both DHP-glucose complex and DHP-labeled glucose complex showed a new absorbance peak at 97.3 ppm (No. 16) compared to DHP self-condensation, which was supposed to be from the glucose C_1 signal.

Table 2. Functional Group Attribution of DHP Self-Condensation and DHP-bearing Labeled Glucose Complexes

Peak	Chemical Shift Value(δ)/ppm		Assignment
	DHP self-condensing	DHP-labeled glucose complex	
1	194.1	194.6	γ-CHO in cinnamaldehyde
2	172.1	172.4	C_γ in ferulic acid
3	169.5	169.9	-COO- in ferulic acid ester
4	150.6	150.1	C_3/C_4 in guaiacol
5	147.5	148.1	C_3/C_5 in guaiacol, etherified
6	145.9	145.6	C_4/C_4' in 5-5', etherified
7	143.6	143.9	C_4 in 5-5
8	132.2	132.8	C_1 in β-O-4 guaiacol, non-etherified
9	131.3	131.3	C_1/C_1' in β-5
10	129.3	129.5	C_α in cinnamaldehyde
11	128.7	128.5	C_β in cinnamaldehyde
12	119.5	119.6	C_6 in guaiacol
13	118.7	118.1	C_5 in guaiacol
14	115.3	115.5	C_5 in guaiacol
15	110.4	110.9	C_2 in guaiacol
16	—	97.3	C_1 in glucose
17	87.1	87.5	C_α in β-5
18	85	85.7	C_α in β-β，C_β in β-O-4
19	83.8	84.3	C_β in β-O-4
20	76.9	77.3	C_α in β-O-4
21	71	71.2	C_γ in β-β
22	62.9	63.2	C_γ in β-5
23	—	61.6	C_6 in glucose
24	60.1	60.6	C_γ in β-O-4
25	55.6	56	-OCH_3
26	53.7	53.5	C_β in β-5
27	39.4	40	DMSO
28	21	21.4	-CH_3

The DHP-labeled glucose complex showed a new absorbance peak at 61.6 ppm (No. 23) with obvious intensity compared with DHP self-condensation, DHP-glucose complex, which was the labeling signal from glucose C_6. Combined with the previous solid-state NMR analyses, it can be shown that DHP underwent a thermal condensation reaction with glucose at high temperature and high pressure under acidic conditions.

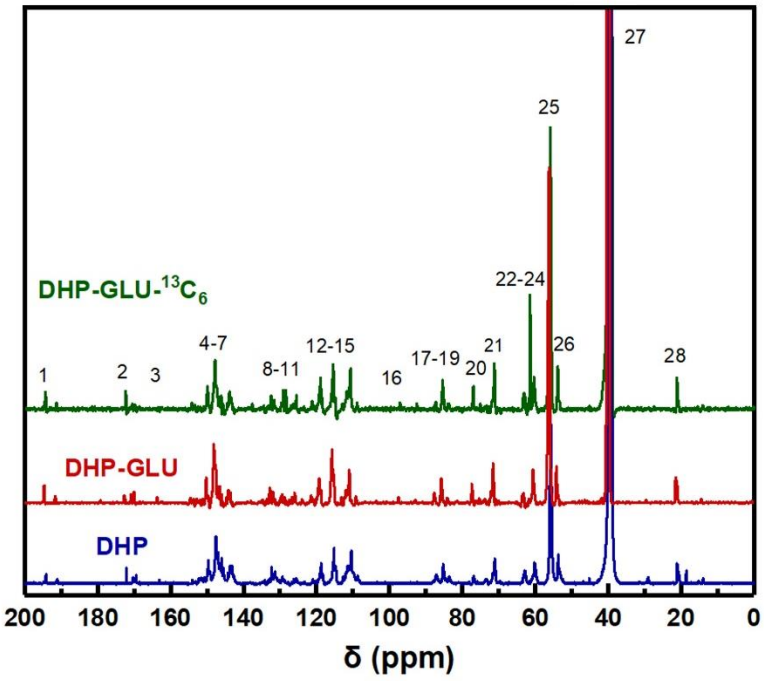

Fig. 4. ^{13}C-NMR spectra of DHP self-condensation, DHP-glucose complexes, and DHP labeled glucose complexes

2D-HSQC NMR Analysis

The 2D-HSQC NMR spectra of DHP-glucose complexes in the side chain region (δC/δH 50-100/2.4-6.1) and aromatic ring region (δC/δH 95-135/5.4-7.9) are shown in Figs. 5 and 6, and the functional groups of the main signals in the 2D-HSQC NMR spectra were attributed as shown in Table 3 (Wen *et al.* 2013). In the 2D-HSQC NMR spectra, the main basic linkages of the side chain and aromatic ring regions are shown in Fig. 7. In the side chain region of the NMR pattern (Fig. 5), the β-O-4 structure (A), the β-β structure (B), and the β-5 structure (C) had correlated signals at the α-position, β-position, and γ-position, and also, the pattern contained the C-H signals in the methoxy group, the C_γ-H_γ signals in the terminal group of coniferyl alcohol, and the C_1 signals of glucose. The correlation signal of the guaiacyl-type (G) unit can be observed in the aromatic ring region of the NMR pattern (Fig. 6). This result suggested that the thermal condensation reaction between DHP and glucose occurred under high temperature and high pressure acidic environment.

In summary, it was observed in the infrared spectrum that the DHP-glucose complex and the DHP-labeled glucose complex had a signal enhancement at 1030 cm^{-1} that was attributable to sugars. In the solid-state NMR spectrum, the C_6 signal peak of D-glucose-6-^{13}C in the DHP-labeled glucose complex was clearly observed. The signal peaks of C_1 and C_6 of glucose in DHP-glucose complex and DHP-labeled glucose complex were observed in one-dimensional liquid NMR, and the signal peak of C_6 in DHP-labeled glucose complex was obviously abnormal, which further demonstrated that glucose can be thermally condensed with DHP.

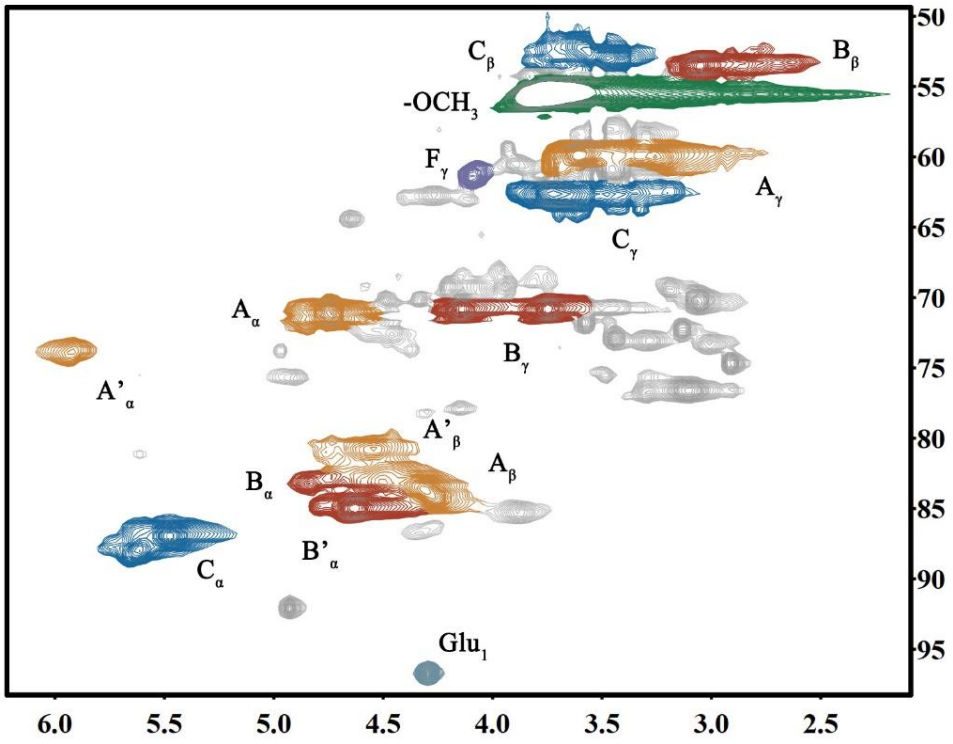

Fig. 5. 2D-HSQC NMR spectrum of DHP-glucose complex (side chain region)

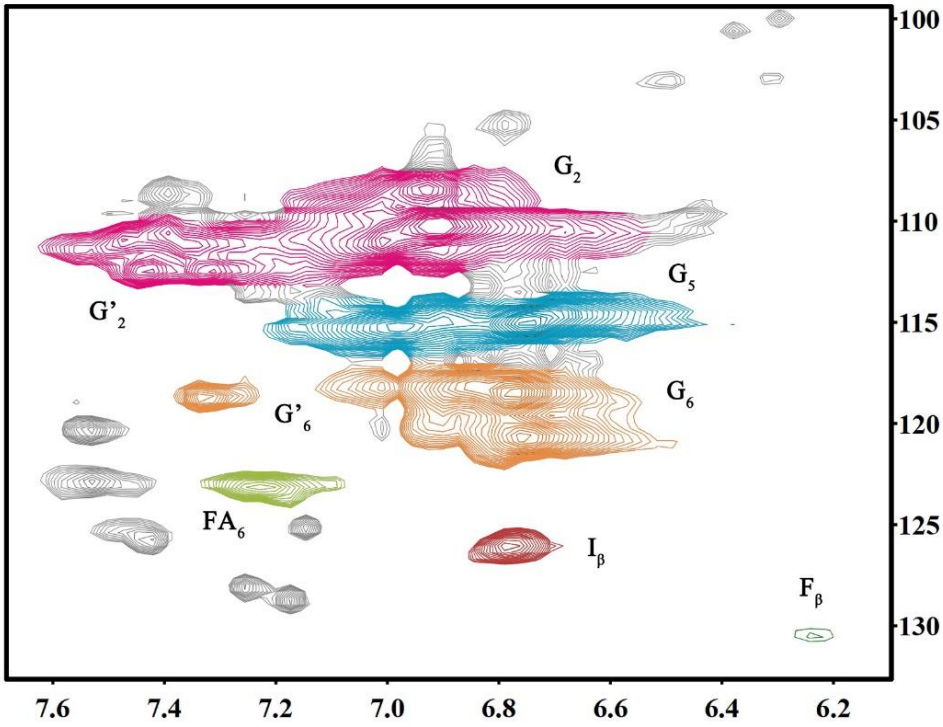

Fig. 6. 2D-HSQC NMR spectrum of DHP-glucose complex (aromatic ring region)

Table 3. 2D-HSQC NMR Functional Group Attribution of DHP-Glucose Complexes

Label	δ_C/δ_H (ppm)	Assignments
C_β	52.97/3.48	C_β-H_β in phenylcoumaran (C)
B_β	53.48/3.06	C_β-H_β in β-β (resinol) (B)
OCH_3	55.43/3.79	C-H in methoxyls
A_γ	59.77/3.61	C_γ-H_γ in in β-O-4 substructures (A)
F_γ	61.32/4.10	C_γ-H_γ in cinnamyl alcohol end-groups (F)
C_γ	62.64/3.72	C_γ-H_γ in phenylcoumaran (C)
B_γ	70.73/3.76	C_γ-H_γ in β-β resinol (B)
	70.75/4.15	
A_α	71.10/4.74	C_α-H_α in β-O-4 at the γ-OH (A)
A'_α	73.74/5.92	C_α-H_α in β-O-4 linked to G (A')
A'_β	80.74/4.52	C_β-H_β in β-O-4 linked to G (A')
	83.11/4.50	
A_β	83.71/4.30	C_β-H_β in β-O-4 at the γ-OH (A)
B_α	84.93/4.63	C_α-H_α in β-β resinol (B)
B'_α	83.01/4.85	C_α-H_α in β-β (B', tetrahydrofuran)
C_α	86.85/5.49	C_α-H_α in phenylcoumaran (C)
Glu_1	96.70/4.30	C_1 in glucose
G_2	108.38/6.93	C_2-H_2 in guaiacol units (G)
	110.18/6.91	
G'_2	110.52/7.38	C_2-H_2 in guaiacol units with oxidized α-position (G')
	112.35/7.32	
G_5	114.91/6.75	C_5-H_5 in guaiacol units (G)
	115.17/6.98	
G_6	118.38/6.79	C_6-H_6 in guaiacol units (G)
	120.63/6.76	
G'_6	118.64/7.33	C_6-H_6 in guaiacol units with oxidized α-position (G')
I_β	125.97/6.79	C_β-H_β in cinnamyl aldehyde end-groups (I)
F_β	130.44/6.25	C_β-H_β in cinnamyl aldehyde end-groups (F)
FA_6	123.14/7.23	C_6-H_6 in ferulic acid ester

In the side chain region of the 2D-HSQC NMR spectrum, it was also found that there was a glucose C_1 signal in the DHP-glucose complex. It can be determined that DHP and glucose underwent a thermal condensation reaction in an acidic environment at high temperature and high pressure. Glucose removed a hydroxyl group under acid catalysis to form a carbocation intermediate, which was connected to the carbon ion on the benzene ring in DHP through a C-C bond to form a DHP-glucose complex. The condensation process is shown in Fig. 8 (Yasuda and Murase 1995).

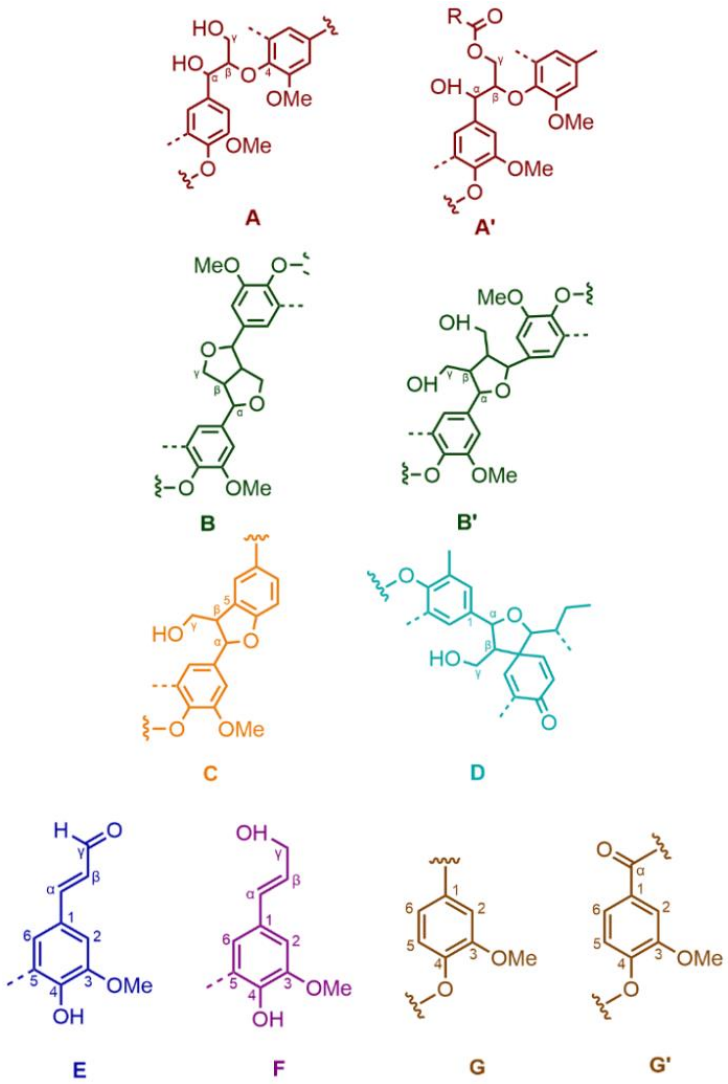

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Fig. 7. The main basic linkage structures and structural units of the side chain and aromatic ring regions of DHP in 2D spectra. A: β-O-4 ether-bonded structure (γ-position hydroxyl); A': β-O-4 ether-bonded structure (γ-position is acetyl); B: resinoid alcohol structure, consisting of β-β linked to α-O-γ'; B': tetrahydrofuran structure, β-β linked; C: phenyl coumarin structure, β-5 and a-O-4 linkage; D: spirocyclic dienone structure, β-1, and α-O-α' linkage; E: cinnamaldehyde unit; F: cinnamyl alcohol unit; G: guaiacol structure; G': oxidized guaiacol structure

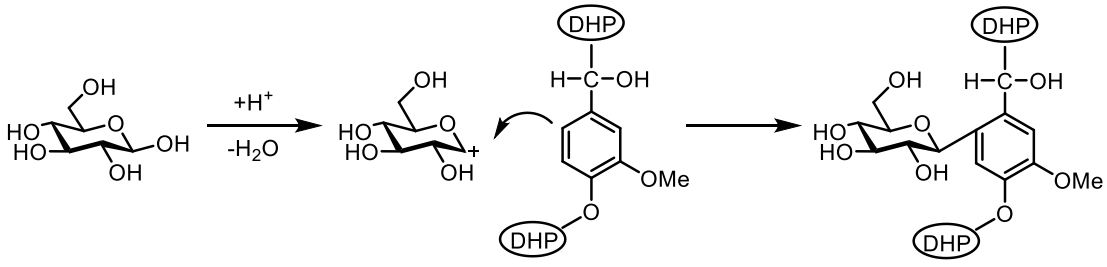

Fig. 8. Thermal condensation reaction process of DHP and glucose

CONCLUSIONS

1. In this work, the coniferin was used as lignin precursor, and dehydrogenation polymer (DHP) was synthesized by dehydrogenation polymerization under the catalysis of β-D-glucosidase and laccase. Then DHP was reacted with D-glucose and D-glucose-$^{13}C_6$ at 140 °C for 25 min under the catalysis of acetic acid to prepare DHP-glucose complex and DHP-D-glucose-$^{13}C_6$ complex.
2. Through the analysis of infrared spectra and nuclear magnetic spectra, the results showed that the signal absorbance peaks of glucose appeared in both DHP-glucose complex and DHP-D-glucose-$^{13}C_6$ complex, and the signal intensity of glucose C_6 in DHP-D-glucose-$^{13}C_6$ complex was stronger. These results showed that DHP can undergo thermal condensation reaction with glucose under simulated hot-pressing environment, forming a lignin carbohydrate complex (LCC)-like connection bond. In addition, the possible mechanism of thermal condensation between DHP and glucose was that the C_1 on the glucose unit forms a C-C bond with the C_6 on the aromatic ring.
3. By studying the condensation mechanism of DHP and glucose, this work has provided a new theoretical basis for the application of DHP in the field of wood-based panel adhesives. In the future development process, by optimizing the preparation process and conducting industrial tests, DHP can be expected to achieve commercial application in the wood-based panel industry and promote the industry to develop in the direction of environmental protection and high performance.

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