CELLULOSE CHEMISTRY AND TECHNOLOGY

MOLECULAR AND SPECTROSCOPIC CHARACTERIZATION OF TECHNICAL LIGNIN FROM *TREMA ORIENTALIS* AND *TREWIA NUDIFLORA* OBTAINED FROM FORMIC ACID BIOREFINERY

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Biorefinery has emerged as one of the most prominent topics in recent research, playing a crucial role in establishing a circular bioeconomy. *Trema orientalis* and *Trewia nudiflora*, which are experimentally planted in social forestry in Gazipur district of Bangladesh, are very similar both anatomically and chemically. These two species were fractionated by formic acid (FA) into pulp, hemicelluloses and lignin. In this investigation, the lignin from the FA spent liquor was characterized in terms of molecular weight, and by UV, FTIR, 2D-NMR, ^{31}P NMR spectroscopy to better understand the lignin structure for its reactivity. The weight average molecular weights (Mw) were 10,826 and 8,784, while OCH_3/C_9 units were 1.3 and 1.0 for *T. orientalis* and *T. nudiflora*, respectively. The lignins had almost similar aliphatic OH (1.23 mmole/g vs 1.15 mmole/g) and phenolic OH (2.3 mmole/g and 2.26 mmole/g) contents. As observed from the 2D-NMR, the lignins were constituted of S units, followed by G units, and the S/G ratios were 1.56 and 1.15 for *T. orientalis* and *T. nudiflora*, respectively.

Keywords: hardwood, formic acid treatment, cellulose, resin, furfural

INTRODUCTION

According to current research, the world has an estimated 300 billion tons of available lignin naturally present in plants, making it the second most abundant organic polymer on Earth; this amount is constantly replenished with an annual increase of around 20 billion tons.[1]

Lignin is the most abundant renewable phenolic polymer on Earth, containing phenylpropanoid subunits, accounts approximately 15–35% of the lignocellulosic biomass. Lignin plays a crucial role in plant structure, support, and defense against pests and pathogens. Additionally, it is a promising and renewable polymer with vast potential for biotechnological applications.[2] The chemical composition of lignin, which is generally formed from the oxidative coupling of three monolignols: p-coumaryl (H), coniferyl (G), and sinapyl (S) alcohols, connected by different types of bonds, varies with species, plant family, plant age and climate conditions.

Lignin can be extracted from lignocellulosic materials using a variety of methods, including chemical, physical, physicochemical, and biological treatments. In conventional chemical pulping processes, lignin is removed, and then used in generating energy. However, with the emergence of the circular bioeconomy concept, the value of lignocellulosic biomass has grown significantly, highlighting the potential for more sustainable and resource-efficient practices.

Technical lignin specifically refers to the lignin that is commercially available as a byproduct of the pulping process, which is part of paper manufacturing. Therefore, many delignification processes have been investigated in order to valorize lignin in value-added products.[3–5]

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Due to its higher availability, lower toxicity, and lower cost compared to phenol, lignin presents a potentially attractive alternative for replacing phenol in phenol-formaldehyde resin. Technical lignin was used in activated carbon preparation,[6,7] adhesives, especially lignin–phenol–formaldehyde resins were prepared from technical lignins.[8,9] The phenolated lignin from the potassium hydroxide spent liquor was copolymerized with acrylic acid (AA), and showed inhibition efficiency of steel corrosion.[10]

Trema orientalis and *Trewia nudiflora*, both native, fast-growing species in Bangladesh, were recently planted at a social forestry plantation site in Gazipur district. These two species were fractionated into pulp, lignin and hemicelluloses by formic acid at atmospheric pressure.[11] The isolated lignin needs to be characterized in order to valorize it.

In this work, the physicochemical characterization of two types of industrial (technical) lignins obtained from the formic acid spent liquor of *T. orientalis* and *T. nudiflora* fractionation was carried out. The following analytical techniques were used for characterization: Fourier transform infrared spectroscopy, ultraviolet–visible absorption spectroscopy, 2D NMR, and ^{31}P NMR. Also, the molecular weight of the lignins was determermied.

EXPERIMENTAL

Fractionation

The *T. nudiflora* and *T. orientalis* were fractionated with 90% (v/v) formic acid for 5 h at the boiling temperature in a round joint condenser using a hotplate. After the desired reaction time, the pulp was filtered and washed with 50% formic acid, followed by hot and cold water. The pulp yield was determined gravimetrically. The spent liquor and FA washing liquor were mixed together and kept for further experiment.

Isolation of lignin

The spent liquor was concentrated in a rotary evaporator, then 10 times the volume of water was added into the concentrated liquor and kept for the whole night. The precipitated lignin was separated by centrifugation and dried.

Lignin characterization

The dried lignin was purified by dissolving it in dioxane water (9:1), followed by precipitation in diethyl ether. Acetylation of purified lignin was also done by dissolving it in pyridine and acetic anhydride (1:1). It was kept for 72 h, followed by precipitation in ice cold water, finally, the lignin was vacuum dried for subsequent characterization.

Spectroscopy

UV-VIS: Dioxane and KOH lignin were dissolved in dioxane water and diluted to 40 ppm using the same solvent. The UV reading was taken from 200 to 350 nm using a UV-1800, Shimadzu, Japan.

FT-IR: Fourier transform infrared (FT-IR) spectroscopy was performed using a Perkin Elmer FT-IR spectrometer (Model: Frontier, Perkin Elmer, USA) with a GAAS detector. The spectral range used was 600-4,000 cm^{-1}. For each sample, 32 scans were collected at a spectral resolution of 16 cm^{-1} with an interval of 4 cm^{-1}, then 32 scans were averaged and taken as reflectance percentage (%R). Here, Perkin Elmer Spectrum (Version 10.4.4) software was used for spectral data processing.

NMR analysis

^{31}P NMR: For ^{31}P NMR spectra, each NMR tube (5 mm) was filled with 30 mg of lignin dissolved in 0.5 mL of dimethylformamide (DMF, anhydrous, >99.8%) and 0.5 mL of a pyridine/$CDCl_3$ mixture (1.6/1 v/v) (pyridine >99.5% and $CDCl_3$, 99.8%); 4.3 mg of cholesterol (>99%) added as an internal standard (IS) and 0.5 mg of chromium(III) acetylacetonate (>99.99%) served as a relaxation agent. Just before analysis, 0.1 mL of phosphorylation agent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxophospholane, >95%) was added into the NMR tube.

2D-NMR: For 2D-HSQC spectroscopy experiments, 50 mg of lignin was dissolved in 0.5 mL dimethyl sulfoxide (DMSO)-d6 and then tested on a Bruker AVIII 600 MHz (Bruker, Switzerland) spectrometer at 25 °C. The spectrometer operated ^{1}H and ^{13}C at 400.13 and 100.61 MHz, respectively. The 2D NMR spectra were processed using Topspin 3.0 software. The central DMSO-d6 solvent peak was used as an internal reference (δ^{13}C, 39.5 ppm; δ1H, 2.5 ppm).

RESULTS AND DISCUSSION

Formic acid (FA) fractionation

The fractionation of *T. nudiflora* and *T. orientalis* by formic acid (FA) was discussed in detail in our earlier publication.[11] FA fractionates lignocelluloses efficiently into lignin, hemicelluloses and cellulose. Lignin was recovered from the spent liquor of both *T. orientalis* and *T. nudiflora* through a two-step process. First, formic acid was distilled from the spent liquor. Then, water was added to precipitate lignin, while hemicellulosic sugars remained in the solution. The recovered lignin yield was 16% from *T. orientalis* and 17% from *T. nudiflora*, based on the initial raw material. The hemicelluloses remaining in the water solution were converted to furfural. The furfural yields were 29.12% and 31.93% at 180 °C from the hemicelluloses of *T. nudiflora* and *T. orientalis*, respectively.[11] The concentrated hemicellulosic sugars can also be fermented by *Pitichia stipitis* for ethanol production.[12]

In our earlier communication, the precipitated lignin was also used for phenol-formaldehyde (PF) resins preparation. The shear strength of both lignin-based adhesives, with up to 20% phenol substitution, exhibited comparable values and approached the shear strength of phenol-formaldehyde (PF) resin. While a previous study[8] demonstrated that LFP resin from organic acid rice straw lignin maintained comparable strength to PF resin with up to 50% phenol substitution, this investigation limited phenol substitution to 20%. This limitation likely stems from the lower reactivity of hardwood lignin compared to that of rice straw lignin, particularly in terms of p-hydroxyphenyl units. To increase lignin substitution and enhance reactivity, phenolation can be employed to introduce additional reactive sites.[5] For further valorization and understanding of these hardwood technical lignins, a more thorough characterization is needed.

In lignin chemistry, the empirical formula of lignin gives a primary idea of hydroxyphenyl structural unit, which was discussed in our earlier publication.[11] The technical lignin from *T. nudiflora* and *T. orientalis* was characterized as follows: C = 62.2 and 61.26%; H = 5.9 and 5.8%; O = 31.8 and 32.7%, respectively. The $–OCH_3$ content per C_9 unit was 1.0 for *T. nudiflora* and 1.3 for *T. orientalis*.

Molecular weight

The molecular weight of lignin plays a crucial role in lignin valorization. The weight average molecular weight (Mw), number average molecular weight (Mn), and their corresponding polydispersity indices (Mw/Mn) are presented in Table 1. The Mw of *T. orientalis* was 10826, while it was 8785 for *T. nudiflora*. Both lignins exhibited higher molecular weight (Mw) than the technical lignin from wheat straw.[13] Wörmeyer *et al.*[14] found that the Mw of straw organosolv lignin is higher than that of soda lignin. However, Sun *et al.*[15] found the same order of magnitude for soda and organosolv lignin. Lignin degradation occurred mainly based on the cleavage of ether bonds, which influence the amount of free phenolic OH groups. Therefore, Mw differences are directly related with the free phenolic OH groups. The Mw of milled wood lignin (MWL) from hardwood *T. orientalis* varied from 34,627 to 41,628, while polydispersity decreased with tree age.[3]

Generally, the Mw of softwood lignin is higher than that of hardwood lignin. As for example, the molecular weights of hardwood lignosulfonates were from 5700 g/mol to 12000 g/mol, while the Mw of softwood lignosulfonates was 5000–60000 g/mol.[16] The variation of Mw can be attributed to the lignin isolation process. For example, the Mw for different lignin isolation methods can be ordered as follows: enzymatic mild acidolysis lignin (EMAL) > cellulolytic enzyme lignin (CEL) > MWL.[17] Hardwood ethanol organosolv lignin exhibited slightly higher molecular weights than that of the hardwood lignin extracted by Kraft process.[17] Da Silva *et al.*[18] showed that the alkaline lignin had lower Mw than the acidic organosolv lignin. In other words, the alkaline process resulted in fractions containing lower molecular weights than the acidic process. The depolymerization of high Mw lignin can occur using anthraquinone derivatives, and the Mw decreased from 4020 to 3050 g mol^{-1} and from 1220 to 1000 g mol^{-1} for organosolv bagasse and lignin extracted from bagasse, respectively.[18]

Technical lignin, following extraction from black liquor and purification, generally has an average molecular weight (Mw) ranging from 1000 g/mol to 100000 g/mole, with a polydispersity index (Mw/Mn) between 1.8 and 3.6, depending on the raw material, the pulping process and conditions.[19] As shown in Figure 1, both lignin samples exhibited distinct normalized GPC elution profiles. The polydispersity was very similar (1.44 and 1.46).

Lignin fractionation is very important for the valorization of lignin, particularly in the context of biorefineries and sustainable material production. Fractionation enables selective extraction of high-value lignin compounds, improving the profitability of lignin valorization, compared to treating it as a low-value byproduct. Lignin fractionation transforms a highly variable byproduct into a versatile resource, unlocking its potential for sustainable industries. Without fractionation, lignin's applications remain limited because of its inherent complexity. Low-Mw fractions are more reactive for depolymerization into monomers, while high-MW fractions are suitable for materials requiring strength (*e.g.*, coatings, films). Efficient fractionation minimizes lignin waste by ensuring all fractions are utilized, aligning with circular economy principles.

Table 1
Molecular weight of technical lignin from *T. nudiflora* and *T. orientalis*

Raw material	Mw	Mn	Mw/Mn
T. orientalis	10826	7506	1.44
T. nudiflora	8785	6035	1.46

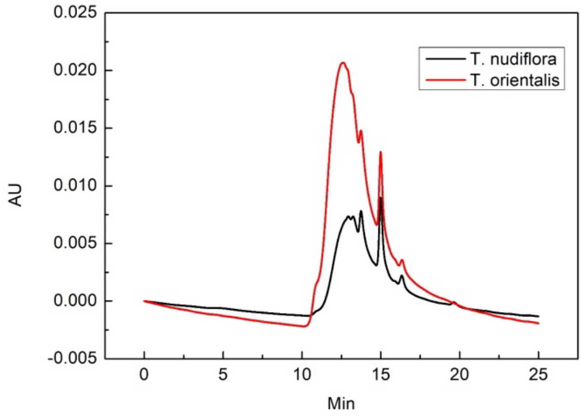

Figure 1: Molecular weight distribution of technical lignins from *T. nudiflora* and *T. orientalis*

The fractionation of softwood kraft lignin using acetone-water, ethanol-water, and PGME-water mixtures has also been documented by Jääskeläinen *et al.*[20] Initially, lignin was dissolved in 80% ethanol, 60% acetone, and PGME solutions. Water was then gradually added to reduce the solvent concentration, causing lignin to precipitate in separate fractions. In all cases, the molecular weight of lignin decreased as the solvent concentration was reduced. The polydispersity index of the fractions initially decreased from 2.5 to 1.4 as the solvent concentration dropped from 80% to 70%, then it remained constant with further reductions in solvent concentration. Lignin was fractionated using γ-valerolactone (GVL) as a green solvent in water mixture.[21] Corn stalk enzymatic hydrolysis lignin was fractionated into three distinct fractions, the lignin was fully dissolved in 60% aqueous GVL first, and then subsequently separated by gradient precipitation using 40%, 30%, and 5% aqueous GVL solutions in sequence. The three fractions presented lower polydispersity than the parent lignin and, furthermore, a gradual decreasing molecular weight due to the different solubility of various molecular weight lignins in aqueous GVL solvent systems.

^{31}P NMR analysis

Nowadays, ^{31}P NMR spectroscopy is considered an important tool for of the quantification of different types of hydroxyl groups, such as aliphatic, and various phenolic hydroxyl groups as well as carboxyl groups in lignin. Both hydroxyl groups define lignin's chemical behavior, making it valuable for sustainable materials, biofuels, and industrial applications. Phenolic groups drive reactivity and stability, while aliphatic groups influence solubility and processability, together enabling lignin's versatility in green chemistry.

The phenolic hydroxyl groups are of crucial importance due to their reactivity, therefore the quantification of these groups in technical lignin is important for its application. Ph-OH groups are highly reactive due to their conjugation with the aromatic ring, making them key sites for chemical modifications (*e.g.*, oxidation, etherification, and grafting).[22] They participate in lignin polymerization (*e.g.*, via radical coupling during lignification). Phenolic groups donate hydrogen atoms to free radicals, making lignin a natural antioxidant for biomaterials and composites.[23] In a study, phenolation was employed to increase the phenolic hydroxyl content of lignin, which significantly enhanced its grafting efficiency in the copolymerization with acrylic acid and in the formation of lignin-based hydrogels with polyvinyl alcohol.[10,24] Aliphatic OH groups (primarily on the propane side-chain of lignin units) contribute to intra- and intermolecular hydrogen bonding, affecting lignin's rigidity and cohesion.[25] The Alp-OH serve as sites for derivatization (*e.g.*, esterification, urethane formation for adhesives and polyurethanes), and increase lignin's affinity for water, influencing its use in hydrogels, dispersants, and emulsifiers.[26] The ^{31}P NMR analysis was performed after the acetylation of the sample material (Fig. 2). Both lignins had almost similar aliphatic OH and phenolic OH contents.

The aliphatic OH was 1.23 mmole/g and 1.15 mmole/g, while PhOH was 2.3 mmole/g and 2.26 mmole/g for *T. orientalis* and *T. nudiflora*, respectively (Table 2).

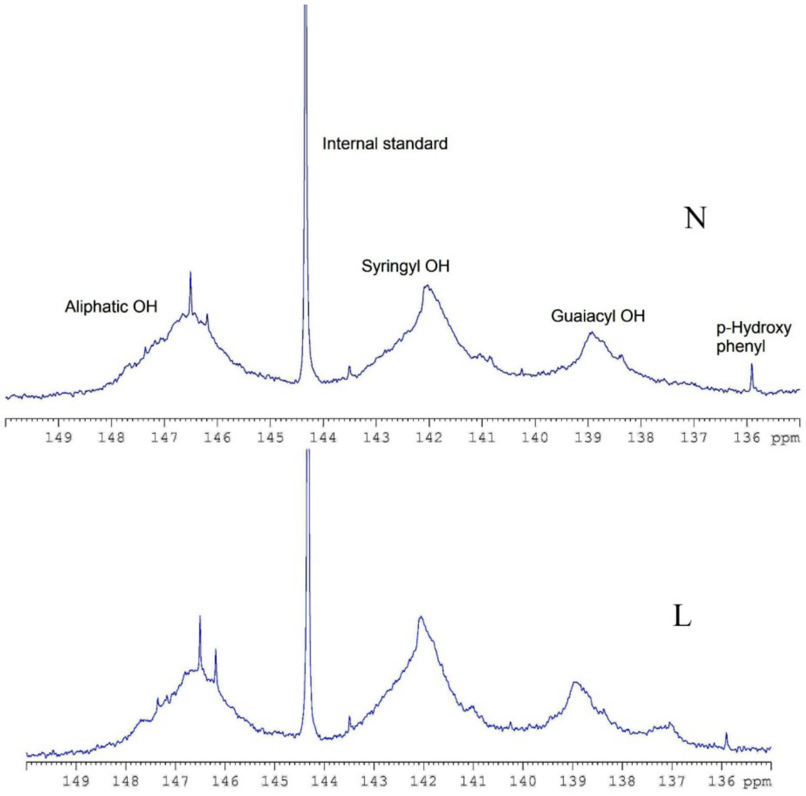

Figure 2: ^{31}P-NMR spectra of technical lignins from *T. nudiflora* (L) and *T. orientalis* (N)

Table 2
^{31}P NMR analysis of technical lignin from *T. nudiflora* and *T. orientalis* (mmol/g lignin)

Technical lignin	Aliphatic -OH, mmol/g	Syringyl -OH, mmol/g	Guaiacyl -OH, mmol/g	p-Hyroxyl phenyl, mmol/g
T. orientalis	1.23	1.61	0.68	0.01
T. nudiflora	1.15	1.60	0.55	0.11

It was noted in an earlier study that the organosolv process generated phenolic-OH-groups, while the soda process reduced aliphatic-OH groups.[27] In this investigation, both organic acid lignins had similar amounts of phenolic -OH- and aliphatic –OH groups. A significant phenolic content in the lignin fractions was very suitable for phenolic substitutions in applications such as phenolic resins. Concerning the amount of phenolic OH-groups, phenolation of lignin was carried out and increased the reactivity of lignin, like in copolymerization, resin preparation *etc*.[10,11,24] Da Silva *et al.*[18] found that the depolymerization of high Mw lignin by AQ led to a decrease in the total phenolic content of lignin and increased the carboxylic acid functional groups, as observed by ^{31}P NMR analysis.

UV spectra of technical lignin

The aromatic nature of lignin results in a strong absorption in the UV region, showing strong bands at 205 and 280 nm. The band near 280 nm is the result of a benzene ring substituted by hydroxyl or methoxyl groups. As shown in Figure 3, the UV spectra of FA spent liquor lignins from both *T. orientalis* and *T. nudiflora* are very similar, and no significant difference was observed within the acquired UV spectra for the two lignin samples. The lignin shows common absorption maxima at around λ = 280 nm due to the aromatic rings/non-conjugated phenolic groups, at around λ = 205 due to $\pi \rightarrow \pi *$ the electronic transition in the aromatic ring in the lignin. As shown in Figure 4, the spectra show two maxima, one at λ = 210-12 nm and another at λ = 286 nm. The extinction coefficients were 12.46 L g^{-1} cm^{-1} for *T. orientalia* lignin and 15.29 L g^{-1} cm^{-1} for *T. nudiflora* lignin, which were close to other reported data.[5,28] It was observed that the absorptivity of the MWL from *T. orientalis* at 280 nm varied from 13.94 to 15.00 L g^{-1}cm^{-1} depending on tree age.[3] Most of the technical lignin showed higher absorptivity due to the condensation reactions during the pulping process.[29] From these results, it can be assumed that the formic acid delignification of hardwood did not condense the lignin structure significantly.

FTIR spectra of technical lignin

Fourier transform infrared (FTIR) spectroscopy revealed highly similar spectral profiles for the technical lignin derived from *T. nudiflora* and *T. orientalis* (Fig. 4).

Hydroxyl groups: a broad band at 3420-3430 cm^{-1} indicated the presence of hydroxyl groups in both phenolic and aliphatic structures.

C-H stretching: the bands between 2938 cm^{-1} and 2838 cm^{-1} were attributed to C-H stretching vibrations in methyl and methylene groups.

Carbonyl/carboxyl region: a strong band at 1717 cm^{-1} and a band around 1610 cm^{-1} corresponded to C=O stretching vibrations. The prominent peak at 1710 cm^{-1}, likely originating from unconjugated ketones and ester groups, supports esterification during formic acid pulping, which is consistent with previous findings.[30]

Aromatic structures: the bands at 1600, 1510, and 1420 cm^{-1}, characteristic of aromatic skeleton vibrations, and a band at 1462 cm^{-1} (C-H deformation combined with aromatic ring vibration) were observed with similar intensities in both lignins.

Aliphatic contributions: a band at 1510 cm^{-1}, attributed to aliphatic positions (including carbohydrates, fatty acids, and aliphatic side chains in lignin), exhibited similar intensity in both samples.

Condensed units: a band at 1330 cm^{-1}, characteristic of condensed syringyl and guaiacyl units,[18] was present in both lignins. This finding aligns with Boeriu *et al.*,[31] who reported a band at 1326 cm^{-1} as a characteristic feature of syringyl and guaiacyl ring condensation in hardwood and non-wood lignins.

Syringyl and guaiacyl units: a strong signal at 1120 cm^{-1} indicated the presence of syringyl rings, while a comparatively weaker band at 1212 cm^{-1} suggested the presence of guaiacyl rings in both lignins.

FTIR results were found consistent with the findings of 2D-NMR analysis discussed below.

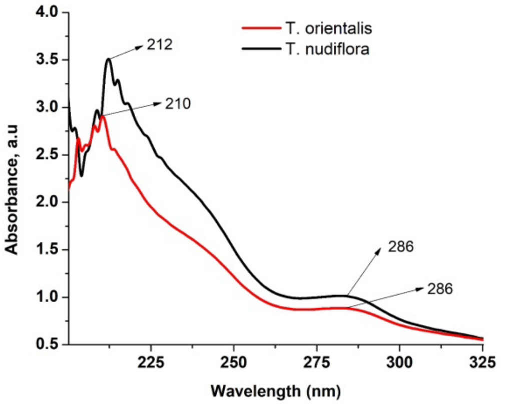

Figure 3: UV spectra of technical lignins from *T. nudiflora* and *T. orientalis*

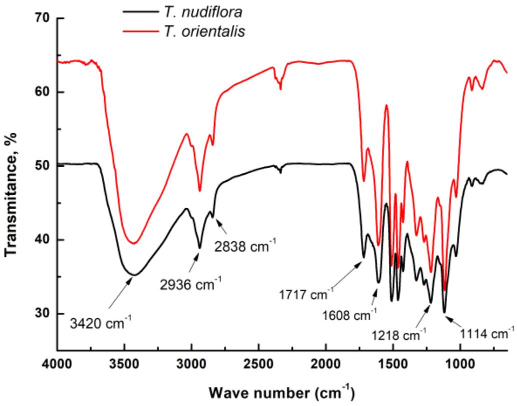

Figure 4: FTIR spectra of FA lignins from *T. orientalis* and *T. nudiflora*

2D NMR analysis

Figures 5–6 present the most informative region of the HSQC spectra of formic acid spent liquor lignin from *T. orientalis* and *T. nudiflora*. The HSQC spectra show the aromatic ^{1}H–^{13}C correlations (δ_H/δ_C 5.5–7.5/100–135 ppm region) and the aliphatic ^{1}H–^{13}C correlations (δ_H/δ_C 2.5–6.5/50–90 ppm region) informing on lignin aromatic units and side-chain inter-unit linkages, respectively.

Both lignins showed a strong signal of S units for the $C_{2,6}$-$H_{2,6}$ correlations at δC/δH 104/6.7, and G-units for C_2-H_2 at δC/δH 110.9/6.99, for C_5-H_5 at δC/δH 114.9/6.72 and 6.94, and for C_6-H_6 at δC/δH 118.7/6.77. In S units, only C_2 and C_6 are protonated, resulting in a unique and large $H_{2,6}$–$C_{2,6}$ correlation (δ_H/δ_C 6.67/104.0 ppm) signal. Both lignins had clear signals for the $C_{2,6}/H_{2,6}$ correlations of Cα-oxidized S-lignin units (S′) at δC/δH 106.2/7.30 and 106.4/7.18. The signal for the $C_{2,6}/H_{2,6}$ correlations of H-lignin units at δC/δH 127.7/7.20 was absent, which are abundantly present in non-wood lignin.[32,33]

As can be seen from Table 3, the both technical lignins were constituted of S units, followed by G units. The S units were 61% and 54% for *T. orientalis* and *T. nudiflora*, respectively. The S/G ratios were 1.56 and 1.15 for *T. orientalis* and *T. nudiflora*, respectively. This trend is very consistent with the methoxyl per C_9 unit.[11] Higher S/G ratios are mainly associated with increased concentrations of β-O-4 linkages because S-units, with their two methoxyl groups, are limited in the types of bonds they can form. Additionally, β-O-4 bonds are more readily degraded during pulping.[34]

Both lignins showed strong signals corresponding to methoxyls (δC/δH 55.6/3.73) and β-O-4′ aryl ether linkages. *T. orientalis* lignin showed intense signals for β–β′ resinols in this region of the spectrum, with their Cβ/Hβ and the double-Cγ/Hγ correlations at δC/δH 53.4/3.05, and 70.9/3.81 and 4.18, respectively.

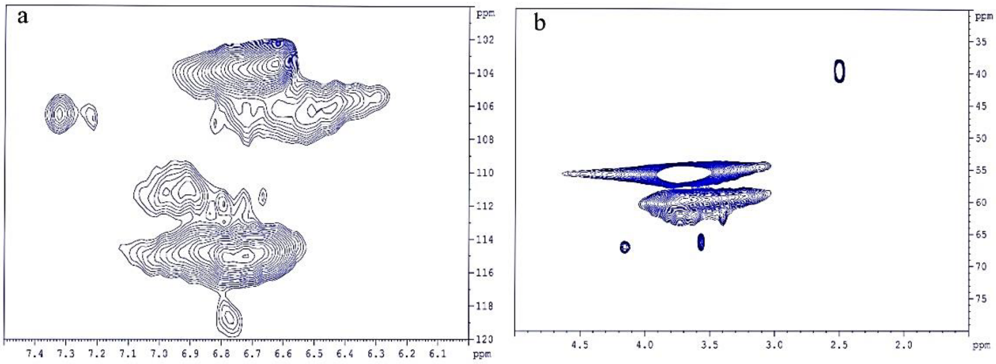

Figure 5: 2D NMR of technical lignin from *T. nudiflora*

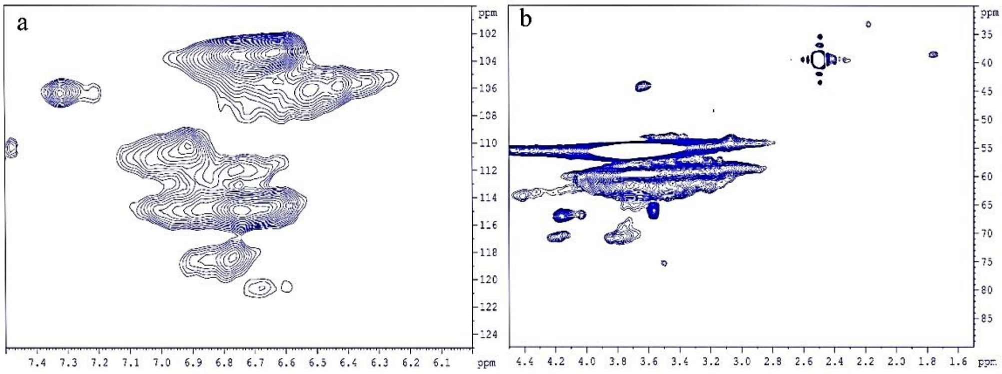

Figure 6: 2D NMR of technical lignin from *T. orientalis*

Table 3
Amounts of G and S units in technical lignins

Technical lignin	Guaiacyl unit (%)	Syringyl unit (%)	S/G
T. orientalis	39	61	1.56
T. nudiflora	46	54	1.15

CONCLUSION

The formic acid lignins extracted from *T. orientalis* and *T. nudiflora* exhibit highly similar structural characteristics, with only minor differences observed in their molecular weights and subunit compositions. The lignin from *T. orientalis* had a slightly higher molecular weight (Mw = 10,826), compared to that of *T. nudiflora*

(Mw = 8,785). Both lignins demonstrated nearly identical aliphatic OH (1.23 mmole/g for *T. orientalis* and 1.15 mmole/g for *T. nudiflora*) and phenolic OH (2.30 mmole/g for *T. orientalis* and 2.26 mmole/g for *T. nudiflora*) contents, indicating comparable hydroxyl group distributions. UV spectra and FTIR analysis further confirmed the structural similarity, with both lignins displaying a characteristic FTIR band at 1330 cm^{-1}, indicative of condensed syringyl (S) and guaiacyl (G) units. Notably, *T. orientalis* lignin exhibited more intense signals for β–β′ resinols, as evidenced by Cβ/Hβ and double-Cγ/Hγ correlations at δC/δH 53.4/3.05, 70.9/3.81, and 4.18, respectively. Both lignins were predominantly composed of S units, with *T. orientalis* having a higher S unit content (61%) compared to *T. nudiflora* (54%), resulting in S/G ratios of 1.56 and 1.15, respectively. Overall, these findings highlight the structural consistency between the two lignins, with minor variations in molecular weight and subunit composition, suggesting their potential for similar applications in lignin-based materials or processes.

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