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Catalyst-Free Lignin Valorization by Acetoacetylation. Structural Elucidation by Comparison with Model Compounds

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Indulin AT Kraft lignin has been chemically modified without a catalyst by reaction with *t*-butyl acetoacetate. Elucidation and quantification of the modified lignin structure has been facilitated by employing a series of readily prepared model compounds which isolate three of the major hydroxyl containing moieties characteristic of lignin.

Introduction

Lignin, a component of all woody plant material, is an abundant aromatic biopolymer. Notably, it is comprised of polyhydroxylated aromatic units known as monolignols. These phenylpropane monomers (**1**, **2** and **3**) may be enzymatically oxidized (Scheme 1). The radical thus created is capable of crosslinking nearby monolignols, eventually affording lignin[1] (**4**). Lignin's polymerization occurs by a free radical chain reaction which propagates away from the oxidation site. The resulting network has an irregular structure, which gives rise to heterogeneity and a variety of linkages.[1-3] The distribution of chemical linkages depends on the type of plant from which lignin was isolated as well as the isolation technique.[4]

Researchers seeking to valorize lignin have taken two strategic approaches: depolymerization of lignin into small molecular weight commodity chemicals[5-8] and direct functionalization of lignin to afford value-added products.[9, 10] Extensive research into the depolymerization of lignin has utilized model compounds to elucidate the mechanism of depolymerization.[11-18] The majority of these studies have focused on the use of pyrolysis, catalysis or enzymatic degradation to reproducibly process lignin into platform

chemicals. The complex heterogeneous structures encountered in lignin present a significant challenge to direct modification for use in materials science—where reproducible performance is a requisite. This has often forced researchers to focus on subunits of lignin instead of the entire
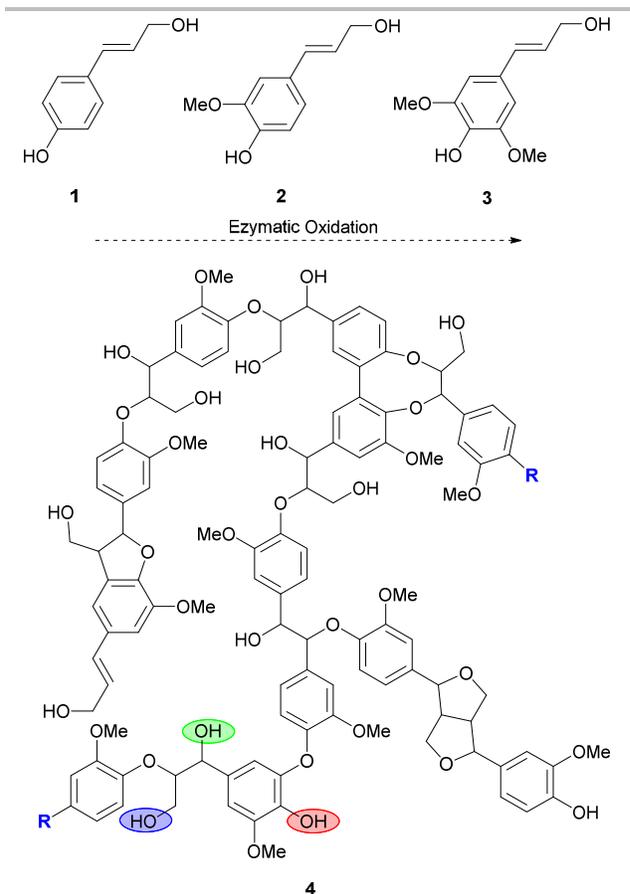
Scheme 1. Monolignols **1** (*p*-coumaryl alcohol), **2** (coniferyl alcohol), **3** (sinapyl alcohol) undergo free radical polymerization upon enzymatic oxidation to form the random structure of lignin **4**. Three predominate hydroxyl environments have been highlighted: primary aliphatic in blue, secondary benzylic in green, and phenolic in red.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See

macromolecule.

Employment of lignin as a polyol has led to its incorporation into a variety of coatings systems.[19-26] Interest in sustainable organic thermoset coatings has engendered a need for alternatives to supplement traditional technologies widely derived from petrochemicals.[27] Natural oils have been employed as a means of increasing the bio-based content in coatings applications;[28-34] however, alternative raw materials offer chemical and mechanical properties that oils cannot.[35] One such source of promise is lignin, which offers a platform for chemical modification with diverse functionalities capable of selective derivatization.

Lignin's heterogeneous structure, high degree of crosslinking and intramolecular hydrogen bonding has limited its processability. However, the handling was improved by high temperature treatment with simple oxiranes to extend hydroxyl groups. Notably, such a reaction would selectively target aromatic alcohols (phenols), which often display specialized chemistry apart from aliphatic alcohols. Extending hydroxyls while simultaneously converting all the phenols into aliphatic etherols improved the properties of the lignin by increasing distance between hydrogen bonding sites.[20, 25]

Acetoacetylation[36, 37] of polyols such as cellulose[38] offers complementary chemoselectivity to the reaction with oxiranes. Reduction in hydrogen bonding is also a hallmark of acetoacetylated polyols. Significantly, acetoacetylation has not been reported for lignin.

In the case of lignin, selective modification of aliphatic alcohols over phenols could offer significant benefit to its resins as compared with simple aliphatic polyols due to the adhesive properties of polyphenols.[39] The acetoacetate group adds further value to polyol resins by providing access to crosslinking through a wide variety of mechanisms.[40]

Tert-Butyl acetoacetate (**5**, Scheme 2) has been developed as an efficient reagent to acetoacetylate alcohols in concentrated solution with no catalyst.[36] Acetoacetylation of hydroxy functionalized materials using **5** produces *t*-butanol as a byproduct and can therefore be driven to completion by distillation as dictated by Le Chatelier's principle.[36, 41] Any strategy for preparing value-added products from acetoacetylated lignin would require quantification of the degree to which acetoacetylation has occurred.

This study focused on adding value to Indulin AT Kraft lignin in a catalyst-free fashion by acetoacetylation and interpretation of the resulting modified structure**.** Hydroxyl content of lignin has been determined using various methods.[4, 42] However, because acetoacetate moieties readily tautomerize (Scheme 2) it is difficult to track the amount of lignin-acetoacetylation by methods which rely on hydroxyl-group derivatization followed by quantitative analysis by nuclear magnetic resonance (NMR) spectroscopy. A direct quantification of readily determined proton NMR spectra would offer significant improvement. The utility of such a determination would benefit from verification with well-defined models.

Results and discussion

Functionalization of lignin

Kraft lignin (Indulin AT) was functionalized by reaction with **5** in the absence of a catalyst by simple heating.[43] Compound **5** is a poor solvent for lignin, so 1,4-dioxane was used as a co-solvent due to its ability to interface the reaction components without unduly complicating the ^{1}H NMR spectrum. The reaction flask was placed in an oil bath kept at 130 °C, but the temperature inside the reaction flask was maintained closer to 101 °C due to refluxing 1,4-dioxane. The course of the reaction was followed by different spectroscopic techniques. There was significant difficulty encountered in removing aliquots for NMR analysis during the acetoacetylation of lignin: as the dioxane and *t*-butanol were removed by distillation, the viscosity of the black liquid resin increased. Fortuitously, the modified lignin vitrified upon cooling and could be isolated from the reaction components by isopropanol-trituration.

The functionalization of the lignin was assessed by comparison of FTIR spectra before and after treatment with **5** (Fig. 1). Partial esterification was evident by the identification of two carbonyl stretches at 1741 and 1711 cm^{-1}, which are extremely characteristic of acetoacetate esters.
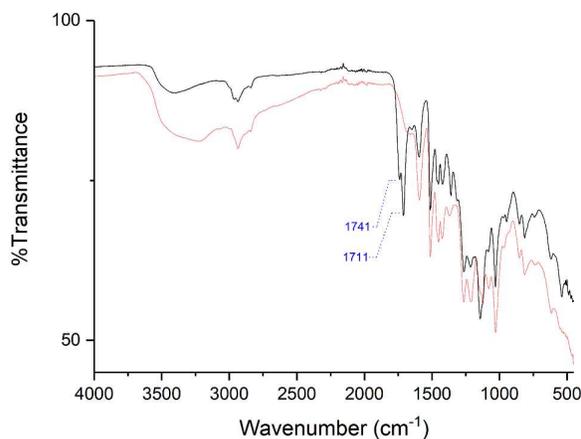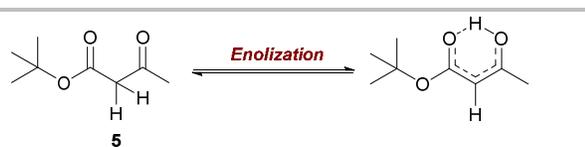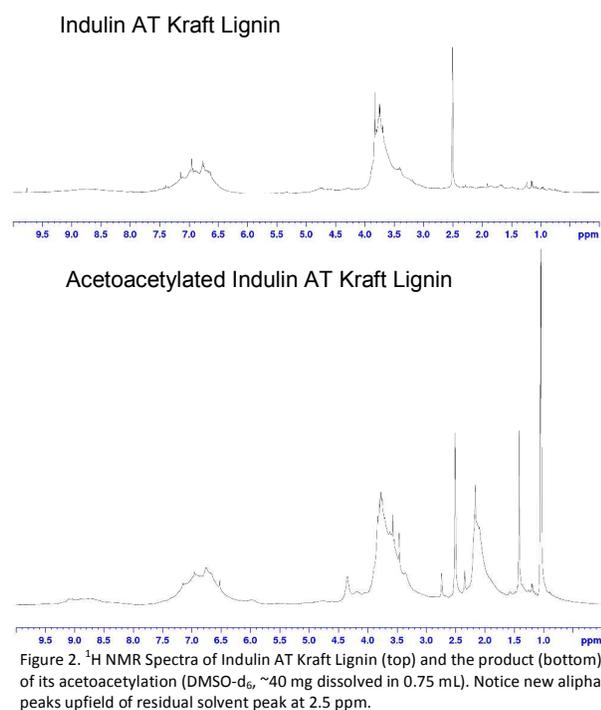

Figure 1. FTIR Spectra (diamond ATR, neat powder): Indulin AT Kraft Lignin (red) and the product of its acetoacetylation (black). Notice appearance of two distinct peaks at 1741 and 1711 cm^{-1}.

Scheme 2. Tautomerization of **5** (tertiary-butyl acetoacetate).

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Figure 2. ^{1}H NMR Spectra of Indulin AT Kraft Lignin (top) and the product (bottom) of its acetoacetylation (DMSO-d$_6$, ~40 mg dissolved in 0.75 mL). Notice new aliphatic peaks upfield of residual solvent peak at 2.5 ppm.

Comparison of ^{1}H NMR spectra (Fig. 2) revealed several distinct changes from the unmodified lignin which have been attributed to acetoacetylation and formation of *t*-butyl ethers. Acetoacetylated Kraft lignin displayed a broadening of the peak at 3.8 ppm, and new peaks appeared at 2.1 ppm, 1.4 ppm and 0.9 ppm. The broadening of the peaks resulted from incorporation of acetoacetate moieties into the irregular macromolecular network. The methylene protons (3.8 ppm) were not resolved from the methoxy resonances.

The broad peak at 2.1 ppm resulted from the terminal methyl group of the acetoacetate and offered an opportunity to determine the molal concentration of acetoacetic esters which had been incorporated into network. These peaks were identified as overlapping methyl groups of acetoacetate moieties (2.1 ppm) in their keto and enol tautomers.

A known amount (~45 mg) of modified lignin was dissolved

in anhydrous deuterated dimethyl sulfoxide by vortex mixing and heating in an NMR tube. The region assigned to acetoacetate methyl groups was integrated and set to 3 H; then a nitromethane standard (~15 mg) was added and reanalyzed. This quantification assumed that the broad peak appearing at 2 ppm in the modified lignin spectrum was solely due to addition of acetoacetate moieties.
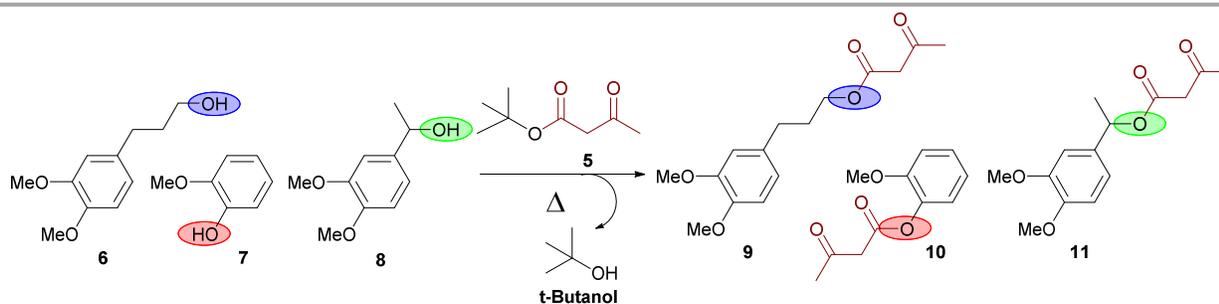
As illustrated in Figs. 2 and S21, there was a minor resonance which developed at ~4.4 ppm during the acetoacetylation which was not pronounced in the unmodified Kraft lignin. While the determination of the degree of lignin functionalization was concerned with the acetoacetyl methyl groups which could be observed at ~2.1 ppm, this quantification method included adding an internal standard (nitromethane) which happened to partially overlap with the new peak at 4.4 ppm. To correct for background resonance at 4.4 ppm, we compared the integration of the region before after addition of the internal standard; see ESI for greater detail.

The modified Kraft lignin (Indulin AT) was determined to contain approximate functionality of 2 mol/kg of acetoacetate ester. Just as in FTIR (Fig. 1), there was no observed diminution of existing peaks (Fig. 2): an indication of the preserved lignin network.

The rise in viscosity during acetoacetylation may have led to trapping of carbenium intermediates by the active methylene of **5** which would graft the *t*-butyl acetoacetic ester to the macromolecular network and could explain the new peak observed at 1.4 ppm (Fig. 2). The peak appearing at 0.9 ppm (Fig. 2) was attributed to incorporation of *t*-butanol to the lignin network as *t*-butyl ether *via* trapping of benzylic-carbeniums. Another possible mechanism for consideration is Michael addition of *t*-butanol or **5** to a quinone methide intermediate. Such quinone methide intermediates have been proposed in the literature[44] and could arise spontaneously at the elevated temperature employed for this lignin-acetoacetylation.

Acetoacetylation of lignin model compounds

To validate the attribution of the new peaks observed in the ^{1}H NMR spectrum of modified lignin, three representative lignin model compounds were also subjected to acetoacetylation
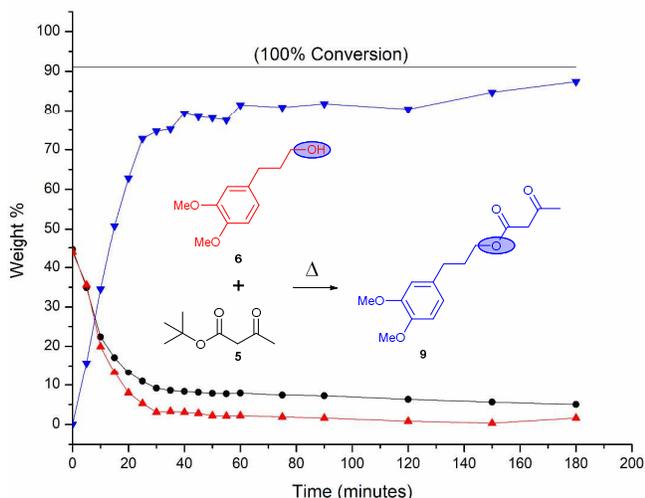

Scheme 3. Substrates **6** (3-(3,4-dimethoxyphenyl)propan-1-ol), **7** (guaiacol) and **8** (1-(3,4-dimethoxyphenyl)ethan-1-ol) reaction with 5 (*tert*-butyl acetoacetate) to afford acetoacetylated **9** (1-acetoacetoxy-3-(3,4-dimethoxyphenyl)propane), **10** (2-acetoacetoxyanisole) and **11** (1-acetoacetoxy-1-(3,4-dimethoxyphenyl)ethane.

Figure 3. Acetoacetylation lignin model compound **6** (red) with **5** (black) to afford **9** (blue).

Figure 4. Acetoacetylation of lignin model compound **7** (guaiacol, red) with **5** (black) to afford **10** (2-acetoacetoxyanisole, blue).

with **5**. Compounds **6**, **7** and **8** were selected as models to isolate each hydroxyl environment while conserving electronics similar to lignin (Scheme 3). It was expected that the aliphatic hydroxyls (**6** and **8**) would be the most susceptible to trans-acetoacetylation but that benzylic esters may be unstable[45, 46] under the reaction conditions. Without the aid of catalyst, acetoacetylation of the phenolic hydroxyl was expected to proceed with comparative lethargy.

Cross sections of the neat reaction mixtures over time for model compounds **9**, **10** and **11** were collected and analyzed by quantitative ^{1}H NMR with nitromethane standard. Extrusion of *t*-butanol was facilitated by nitrogen sparging.

Aliphatic alcohol model compound

The aliphatic alcohol (**6**) was chosen because of its low volatility and its facile preparation from eugenol. Model (**6**) reacted with **5** (Fig. 3) and product (**9**) was formed immediately upon heating of the reaction mixture. The loss of the starting materials (**5** and **6**) corresponded well with the formation of acetoacetate ester (**9**). The reaction rapidly plateaued within the first 25 minutes. The amount of the product never decreased, which indicated the relative stability of this ester linkage even at elevated temperatures.

Detailed inspection of the stacked ^{1}H NMR spectra from the aliquots allowed assignment of resolved resonance signals to the starting materials in the reaction mixture as well as to the products formed as the experiment progressed (Fig. S4). Peak shifts between the methyl and methylene protons of reagent (**5**) were clearly resolved from the methyl and methylene protons of the product (**9**).

Phenolic hydroxyl model compound

Guaiacol (**7**) was selected to model the phenolic hydroxyls of lignin because of its popular use as a representative structure for lignin phenolic groups.[47] Compared with the aliphatic hydroxyl (**6**), phenolic guaiacol (**7**) was hardly reactive towards
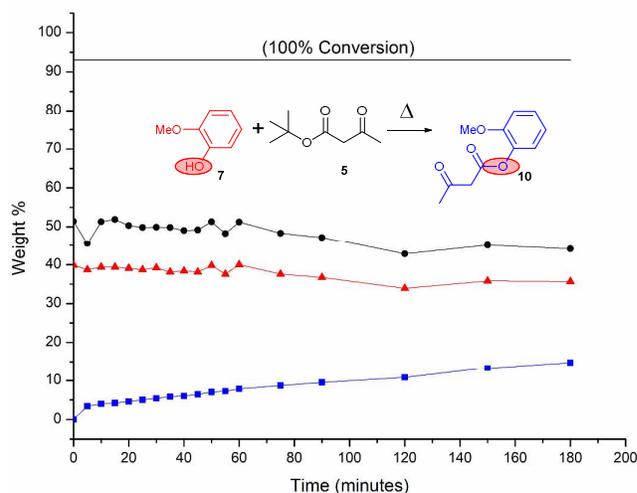
5 (Fig. 4). Starting materials (**5** and **7**) in the reaction mixture steadily decreased over the course of the reaction. The production of 2-acetoacetoxyanisole (**10**) was observed immediately at the onset of heating and steadily increased over the course of the reaction; the amount of **10** never rose much above 15 wt%.

Again, the steady rise in the amount of product closely matched the loss of both starting materials, which indicated the stability of even the phenolic ester. This observation suggested that complete acetoacetylation of lignin may be possible given sufficient reaction time. The NMR spectra for this reaction show a clear peak shift from the methyl (2.20 ppm) and methylene (3.31 ppm) of **5** to the methyl (2.33 ppm) and methylene (3.64 ppm) of **10**. The methoxy group on the benzene ring also showed a clear shift from 3.82 ppm to 3.78 ppm as **10** was formed—an indication that differentiation between phenolic and other acetoacetate esters may prove possible by analysis of the NMR spectra of acetoacetylated lignin.

Secondary benzylic alcohol model compound

Lignin also contains benzylic hydroxyls which have been represented by 1-(3,4-dimethoxyphenyl)ethan-1-ol (**8**). In this case, the analogous electronic environment to that of the larger lignin macromolecule could significantly impact the stability of secondary benzylic hydroxyl moieties upon acetoacetylation. Fig. 5 illustrates the ramifications of acetoacetylating **8**. Qualitatively identical to the reaction of **5** with **6**, in the first 25 minutes of the reaction, a distinct plateau was reached with corresponding depletion of starting materials (**5** and **8**) as **11** was formed.

The behavior of the benzylic acetoacetate product (**11**) drastically diverged from the aliphatic ester **9** as **11** began to noticeably degrade by the 90-minute aliquot. The decomposition of **11** corresponded with detection of vinyl
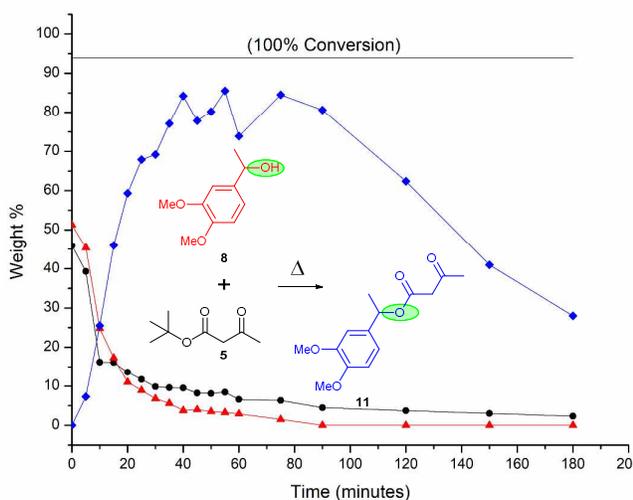
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Figure 5. Acetoacetylation lignin model compound **8** (red) with **5** (black) to afford **11** (blue).

veratrole and secondary decomposition products (Fig. S7), which have been identified as derivatives of spontaneous elimination of acetoacetate anion to afford a secondary carbenium stabilized by the electron-rich veratryl ring.

To further understand how secondary benzylic ester **11** decomposed, the components of the reaction mixture were isolated (Fig. S10) and analyzed (Fig. S11). The presence of vinyl veratrole and its trimer suggested that a limited amount of the veratryl-carbenium can undergo proton abstraction from the α-methyl group in the model compound. Veratryl-carbenium formation most often led to recombination with the nucleophilic acetoacetate enolate followed by subsequent decarboxylation to afford 4-(3,4-dimethoxyphenyl)pentan-2-one. Additional minor products indicated that trapping of the carbenium with **11** could lead to crosslinking of acetoacetylated-lignin corresponding with the loss of secondary acetoacetoxy moieties.

Comparison of acetoacetylated lignin and model compounds

The findings from the model compounds suggested that the aliphatic and benzylic hydroxyls in Kraft lignin were successfully acetoacetylated; however, it is likely that the benzylic acetoacetate moieties decomposed under the conditions employed. The strong signals at 0.9 ppm in the ^{1}H NMR along with pronounced signals at 25 and 62 ppm in the ^{13}C NMR spectra (Figs. 2—^{1}H NMR and 7—^{13}C NMR) were interpreted as incorporation of *t*-butyl ethers into the lignin network. However, the outcome of the decomposition was very different between the lignin and models. Significantly, there was no evidence of styrene formation or of non-acetoacetate ketones analogous to 4-(3,4-dimethoxyphenyl)pentan-2-one in the acetoacetylated lignin (Figs. 6 and 7). Also, there was no evidence of *t*-butyl ether formation in the models.

The conditions required for complete functionalization of either benzylic or phenolic hydroxyls were determined to be mutually exclusive, which provides an interesting opportunity to create a diverse family of resins by simply selecting the reaction timespan.

It has been noted that temperature inside the reaction flask could have been lower in the lignin acetoacetylation than in the functionalization of the model compounds—due to the evaporative cooling of the cosolvent: dioxane. Another important consideration is the steric hindrance of the lignin arising from condensation and radical coupling reactions during the Kraft pulping process. This could account for the minimal acetoacetate functionalization of the phenolic hydroxyls leading to increased chemoselectivity of this modification. This assertion was supported by a lack of upfield broadening observed for the lignin methoxy peaks between 3 and 4 ppm (Figs. 3 and 6).

The reactivity of each substrate followed the trend of aliphatic hydroxyl (**6**) ≅ secondary benzylic hydroxyl (**8**) >> phenolic hydroxyl (**7**). The composition of each neat reaction mixture was quantified by comparing standardized integration values from periodically collected aliquots to determine mass fractions (molality) of each identified species. This NMR method effectively tracked the formation of products **9**, **10** and **11** as well as additional products derived from the degradation of benzylic acetoacetate esters under the reaction conditions. Remarkably, there was no evidence of non-acetoacetate carbonyl resonances near 208 ppm (as observed in Fig. S63).

Upon completion of each reaction, the mixtures were separated, and the products were characterized by standard synthetic organic techniques. The complete details of these characterizations as well as the preparation of substrates from commercially available materials have been compiled in the
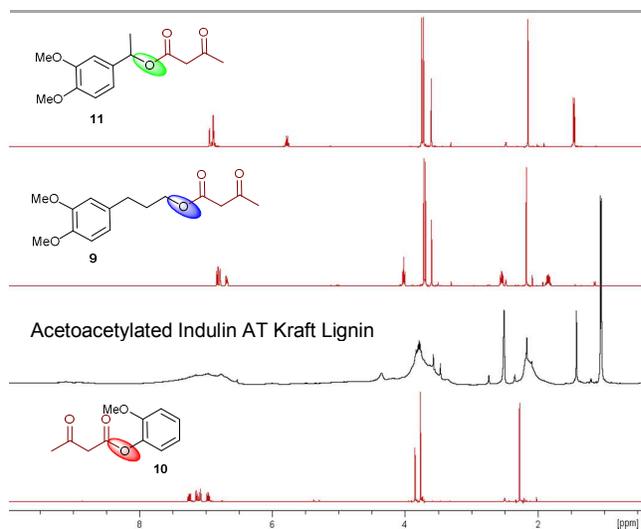

Figure 6. ^{1}H NMR (DMSO-d[6]) of acetoacetylated lignin and model compounds: **11** (1-acetoacetoxy-1-(3,4-dimethoxyphenyl)ethane), **9** (1-acetoacetoxy-3-(3,4-dimethoxyphenyl)propane) and **10** (2-acetoacetoxyanisole).
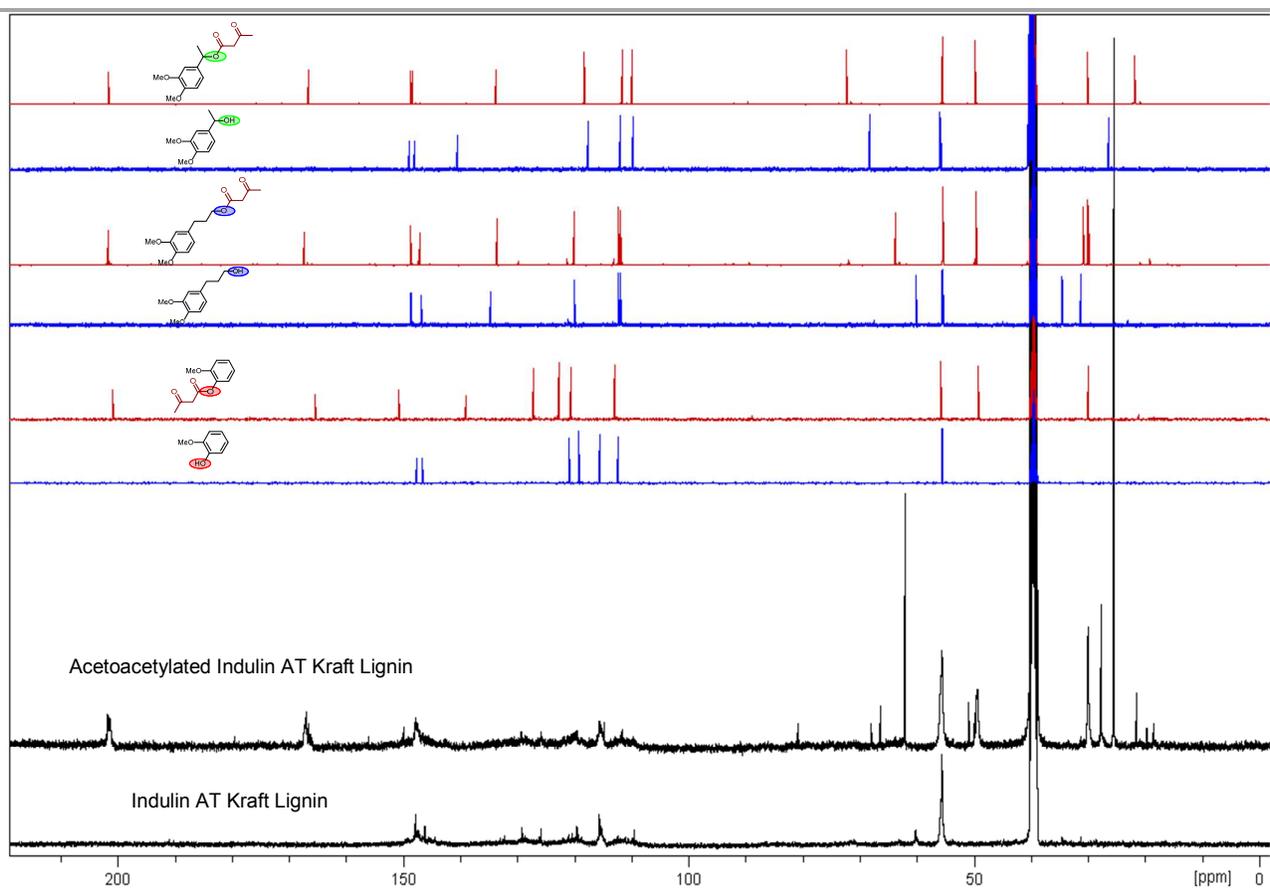
Figure 7. ^{13}C NMR spectra from top to bottom: model compounds both acetoacetylated (**11**, **9** and **10** in red) and unmodified (**8**, **6** and **7** in blue), acetoacetylated lignin (black), unmodified lignin (black)

electronic supporting information.

Benchtop stability of model compounds

The lignin-acetoacetylation reaction was aged open in a well-ventilated fume hood for 6 weeks prior to isolation to assess the stability of the crude resin. The vitreous black residue was triturated with isopropyl alcohol. Except for the disappearance of the peak attributed to dioxane, there was little change in the spectrum of the isolated and crude acetoacetylated lignin. A fine tan solid was isolated by suction filtration and vacuum drying.

The 60-minute reaction mixture aliquots for **9** and **11** along with the 180-minute aliquot from the phenolic ester **10** were saved and reexamined after storage on the bench-top with no special protection from light. Spectra (^{1}H NMR) were compared across all three reaction mixtures to check the stability of each ester (Fig. 8).

Acetoacetate **9** underwent no significant change after 6 weeks while esters **10** and **11** had each developed new resonance peaks corresponding to vinyl protons. At 2.1 ppm a new peak had formed in both esters **10** and **11** and has been assigned to tautomer equilibration as evinced by a shift in concentration when the pure samples were examined in the more polar solvent, DMSO-d_6. The greater change in 2-

acetoacetoxyanisole (**10**) likely occurred due to the stabilizing influence of extending conjugation from the aromatic π-system to an additional three atoms afforded by the acetoacetic enol.

The protons appearing at 5.05 ppm and 5.60 ppm indicated formation of vinyl veratrole. However, this degradation
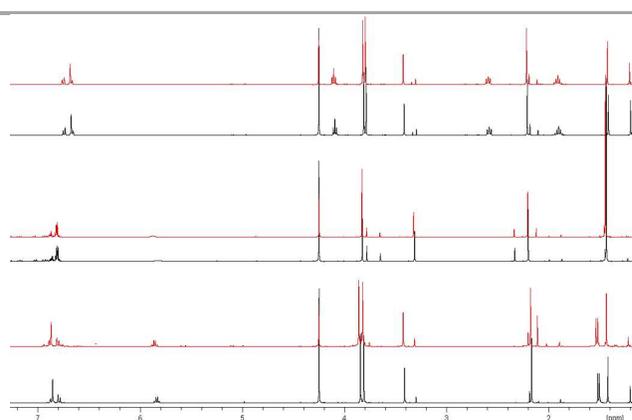

Figure 8 ^{1}H NMR spectra: Synthesized acetoacetate esters (**9**, **10** and **11** from top to bottom) on day 1 (black) and 6 weeks later (red). Stability of these synthesized esters was used to simulate stability of an acetoacetylated Kraft lignin.

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product was not observed in the NMR spectra and HRMS collected from an isolated sample stored in a cool dark place during the same six weeks. In addition, **11** showed traces of two new peaks at 5.05 and 5.60 ppm. This suggested that ester **11** was relatively unstable in the reaction medium, even at room temperature, and formed similar decomposition products independent of temperature.

From these results it can be concluded that all the hydroxyl environments in lignin are susceptible to acetoacetylation by reaction with **5** at 130 °C on a time span measured in minutes. The duration of the functionalization step greatly affected which type of esters would be present in the final resin. Aliphatic esters were formed quickly; however, benzylic esters were not stable at high temperatures and may also be unstable upon prolonged storage on the benchtop. Formation of the phenolic ester was possible; however, it occurred much slower than the formation of the aliphatic esters, and so complete functionalization of all phenolic residues would require sacrificing all the benzylic esters.

Conclusions

Kraft lignin (Indulin AT) was acetoacetylated in a chemoselective fashion by an uncatalyzed reaction with *t*-butyl acetoacetate. The amount of acetoacetate functionalization was determined to be 2 mol/kg resulting from a modest 3 h reaction time and mild workup. Model compounds were used to determine which hydroxyl environments in lignin were functionalized and to validate a quantification protocol which considered new resonances in the ^{1}H NMR spectrum to be solely attributable to incorporation of acetoacetate moieties. While there was some difficulty encountered in adapting established acetoacetylation protocols, a satisfactory method for directly acetoacetylating lignin with little purification and minimal cosolvent was established which allowed for isolation of modified material in powder form.

Interpretation of model compounds under the conditions of acetoacetylation suggested that primary and benzylic hydroxyls reacted very rapidly. However, prolonged heating resulted in benzylic acetoacetate decomposition. Phenolic hydroxyls were acetoacetylated at a much slower rate than aliphatic hydroxyls. The neat reaction conditions employed during the study of liquid-model compounds suggests that any solubilized lignin could be directly acetoacetylated by this protocol. Currently we are investigating benign cosolvents such as *t*-butanol during valorization of lignin. Findings from this study and the techniques described herein are currently being employed to inform the formulation of bio-based organic thermoset coatings derived from Kraft lignin.

Conflicts of interest

There are no conflicts to declare.

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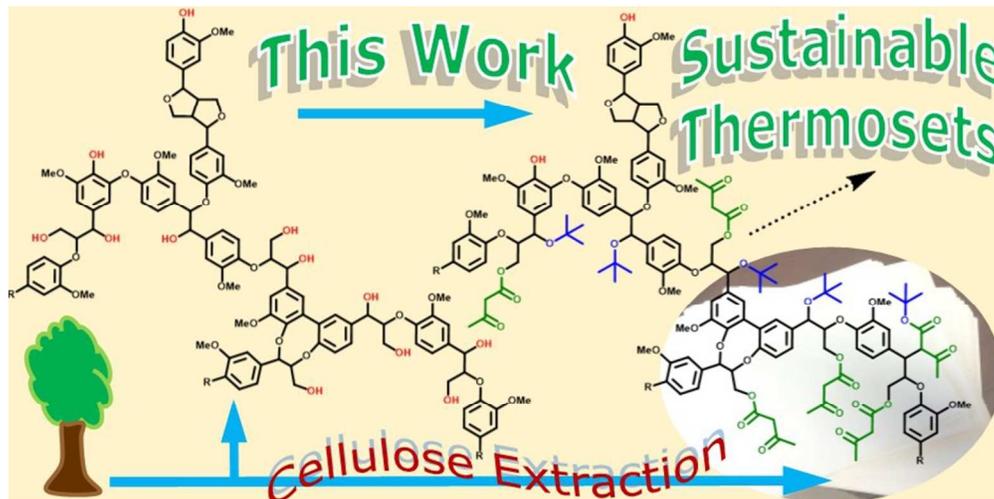Eric M. Serum: 0000-0002-5395-7792
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