

Showcasing research on a sustainable Urushi coating material from Professor Masaharu Nakamura's laboratory, Institute for Chemical Research, Kyoto University, Kyoto, Japan.

Synthetic urushiols from biorenewable carbon resources: chemical conversion of enzymatic degradation products of wood lignin to an ancient yet future coating material

A sustainable urushi coating material was developed by combining phenylpropanoids derived from woody lignin with vegetable fats. Artificial Urushiols were synthesized through a five-step chemical transformation using phenylpropanoids available from enzymatic degradation of woody lignin and tri-unsaturated fatty acid as starting materials. Comparing the curing properties of the synthetic urushiol and the structural properties of the polymerized film to those of natural urushiol demonstrated the potential of artificial Urushi as a coating material that bridges the ancient and the future.

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Synthetic urushiols from biorenewable carbon resources: chemical conversion of enzymatic degradation products of wood lignin to an ancient yet future coating material†

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An artificial urushi material was developed by chemical transformations of phenylpropanoids available from enzymatic degradation of woody lignin, demonstrating the potential of renewable biomass in materials science and technology. The succeeding five-step organic synthesis brings about new urushiol analogs, which possess curing and coating properties, such as hardness, comparable to those of the precious natural urushi materials. The present study exemplifies the application of woody biomass to the synthesis of sustainable and high-performance coating materials.

The need for sustainable materials to replace petroleum-derived ones has renewed the interest in a traditional resin used in Asian countries for millennia, *urushi* or Asian lacquer, originating from the sap of *Toxicodendron vernicifluum*.^{1–3} *Urushi* is a natural product, a water-in-oil emulsion composed of urushiol (Fig. 1, 60–80%), water (10–30%), gum (3–6%) and enzymes (2–3%).^{4–8} *Urushi* has long been employed as a coating and adhesive material for both practical and aesthetic purposes, but more recently applications of *urushi* in fields such as biomedical

Sustainability spotlight

Lignin is one of the main components of renewable woody biomass and the most abundant aromatic resource on the earth. Nonetheless, it is burned primarily as an energy source in the pulping industry and therefore finally converted to CO₂. In light of the current green transformation efforts worldwide, the valorization of lignin can be the key step for the development of a sustainable chemical industry fully reliant on a renewable aromatic feedstock. In this work, we demonstrate that lignin could serve as the chemical resource for the synthesis of an *urushi*-like coating material by combinations of enzymatic and chemical transformations. We hope that the present research will contribute to UN SDGs No. 9 (Industry, Innovation, and Infrastructure) and 12 (Responsible Consumption and Production).

and electronics have been proposed and successfully demonstrated.^{9–14} The durability, high stability and aesthetic beauty of *urushi*, combined with its renewable nature, have made *urushi* a good candidate to become a building block for a more sustainable society. Nevertheless, several limitations exist to using natural *urushi* due to its time-consuming and labor-intensive collection and processing steps that require highly skilled labor.

The limited access to this precious raw material has spawned considerable efforts to develop artificial *urushi* coating materials to date.^{12–21} Most of the recent reports focus on the synthesis of urushiol analogs (catechols bearing C15 or C17 unsaturated aliphatic side chains at the 3-position) since the enzymatic oxidative polymerization of this mixture is responsible for the hardness, solvent resistance and durability of this coating. Several urushiol analogs have been synthesized by combining catechol and unsaturated side chain moieties derived from vegetable fats.^{17–21}

Nevertheless, to preserve the sustainability of artificial *urushi*, it is crucial to take advantage of abundant and renewable starting materials for its synthesis. A promising strategy would be to rely on lignocellulosic biomass, particularly lignin, its second principal component, as a renewable chemical feedstock.^{22–24} Lignin is currently underutilized and mostly

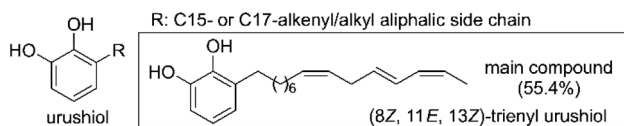


Fig. 1 Molecular structure of natural urushiol.

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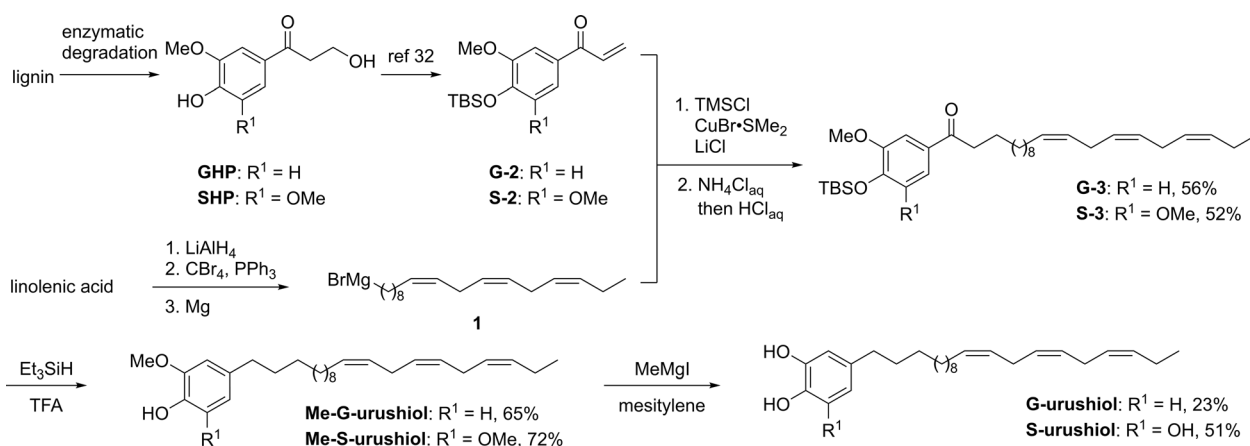
burned as fuel in the paper industry or as waste, despite being the most abundant aromatic carbon resource on the earth. Lignin consists of a randomly polymerized phenylpropanoid backbone cross-linked by a variety of linkages, such as β -O-4, β -5, β - β , 5-5, 4-O-5, and β -1.²⁵ The degradative conversion of lignin to several aromatic compounds has been studied extensively to date by biological and chemical approaches.²⁶⁻²⁹ We previously reported an enzymatic reaction degrading woody lignin efficiently to phenylpropanoid monomers, such as guaiacylhydroxypropanone (GHP) and syringylhydroxypropanone (SHP), by marine microorganisms.^{30,31}

Herein, we report the first synthesis of lignin-derived urushiol analogs by installing vegetable oil-derived polyunsaturated side chains on **G**- and **S**-urushiol through a 5-step chemical transformation. The preparation and characterization of artificial *urushi* films confirmed the similar curing/polymerization properties of lignin-derived urushiol analogs to natural urushiol.

The synthesis of lignin-derived urushiol analogs started by preparing the trienyl side chain and the catechol/pyrogallol moiety and was completed in 5 steps. First, the lignin-derived aromatic monomer guaiacyl- and syringylhydroxypropanone **GHP** and **SHP** were dehydrated and protected by the TBS group according to a previously reported method,³² affording the corresponding TBS-protected enone products **G-2** and **S-2** (Scheme 1). In order to introduce the trienyl side chains, a natural trienyl fatty acid, linolenic acid, was converted to the corresponding Grignard reagent, (9Z,12Z,15Z)-octadeca-9,12,15-trienylmagnesium bromide (**1**) *via* linolenyl bromide (Scheme 1). The 1,4-addition of the Grignard reagent **1** was performed in the presence of chlorotrimethylsilane, copper bromide dimethyl sulfide complex, and lithium chloride, followed by acidic treatment giving the corresponding trienyl side chain-bearing products **G-3** and **S-3** in 56% and 52% yield, respectively. Both the reduction of the ketone group and the deprotection of the TBS group were performed at the same time by the reaction with triethylsilane in trifluoroacetic acid solution to afford the methyl-protected artificial urushiol analogs **Me-G** and **Me-S** in 65% and 72% yield, respectively.

Finally, refluxing of a mesitylene solution of methylmagnesium iodide resulted in the removal of methyl groups, producing the guaiacyl (**G**)- and syringyl (**S**)-type artificial urushiol analogs **G** and **S**-urushiol in 23% and 51% yield, respectively. It is noteworthy that ¹H and ¹³C NMR revealed that no isomerization of the trienyl side chains had taken place under these reaction conditions.

The synthesized urushiol analogs were applied for the preparation of artificial *urushi* films. The raw *urushi*-like liquids were prepared by mixing the urushiol analogs, protein hydrolysate, and water in the ratio of approximately 70, 7, and 23 wt% in the presence of laccase. The prepared artificial *urushi* liquids were coated on glass substrates and were kept at 30 °C in 80% relative humidity for several days. The lignin-derived S-type urushiol analog **S**-urushiol bearing the C21 trienyl side chain at the 5-position of pyrogallol was instantaneously cured after the addition of laccase, indicating the extremely high reactivity of the electron-rich pyrogallol core toward oxidation (Table 1, entry 1). This curing reaction was slowed down by the addition of terpene oil (Table 1, entry 2), suggesting a possible application of **S**-urushiol for the preparation of rapidly curing coating/adhesive materials. In the case of the lignin-derived G-type urushiol analog **G**-urushiol (Table 1, entry 3), the curing reaction successfully proceeded showing a hardening profile relatively similar to that of natural urushi. In the natural lacquer, the curing mechanism relies on the formation of micelles where the oil phase, or the continuous phase, contains catechols, while the water phase, or the dispersed phase, contains the enzymes. Radicals are first formed by the laccase-catalyzed oxidation of urushiol at the interface layer, and then transferred to the urushiol oil phase, enabling its polymerization. Molecular oxygen can continuously penetrate the aqueous phase to oxidize the reduced laccase, allowing the urushiol polymerization to continue smoothly, mostly leading to the formation of C-C and C-O-C nuclei crosslinks involving nuclei and side chains. Given the high number of polyunsaturations on the catechol side chains, auto-oxidative radical chain reactions proceed as well, enabling the formation of chemical crosslinks between the aliphatic chains.³³ As can be seen from



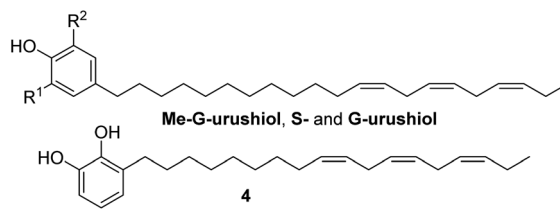
Scheme 1 Synthesis of lignin-derived urushiol analogs.



Table 1 Curing properties of urushiol analogs

Entry	Compound	R ¹	R ²	Days after sample preparation	Martens hardness (N mm ⁻²)
1	S-urushiol	OH	OH	—	Hardened too quick
2	S-urushiol ^a	OH	OH	73	Gradually hardened
3	G-urushiol	H	OH	73	147.4 ± 0.9
4	Me-G-urushiol	H	OMe	73	Not hardened
5	4	—	—	120	140.4 ± 1.5
6	Chinese urushiol	—	—	73	176.7 ± 2.3
7	Cambodian thitsiol	—	—	73	58.5 ± 0.6

^a Terpene oil was added.



the time-course profile of Martens hardness (Fig. 2), the initial oxidation reaction proceeded very slowly, which is compatible with the slow enzymatic oxidation of the catechol core. After 10 days, the hardness started to increase remarkably, suggesting that the dominant process in the reaction had shifted to the faster auto-oxidation of unsaturated side chains (Fig. S3†).²⁻⁴ Finally, after 73 days, the Martens hardness reached a plateau value of 147.4 ± 0.9 N mm⁻² (Table 1, entry 3), which is comparable to the hardness of the commercially available polyvinyl chloride film (144.6 ± 0.4 N mm⁻², Table S1†), demonstrating a good potential for practical applications. In contrast, the methoxy-protected derivative **Me-G-urushiol** was not cured under the same conditions (Table 1, entry 4), indicating that the catechol moiety is crucial to the initial polymerization step, in line with the current knowledge regarding natural urushiol.¹⁰⁻¹² The urushiol analog **4** bearing the C18 trienyl side chain at the 3-position of catechol³⁴ (for the synthetic protocol see ESI†) was also cured and resulted in a Martens hardness of 140.4 ± 1.5 N mm⁻² after 120 days (Table 1, entry 5). The comparable value of hardness for compounds **4** and **G-urushiol** reveals the negligible contribution of the alkyl chain length and substitution position towards the curing properties of the artificial *urushi* film.

The crosslinking reaction was also investigated using natural urushiol and thitsiol extracted from Chinese raw *urushi* and Cambodian raw *thitsi*, in which the major constituents are catechols bearing the C17 trienyl side chain at the 3-position and catechols bearing the C17 dienyl side chain at the 4-position, respectively.^{5,35,36} The structural difference is clearly represented by their different curing properties, in agreement with previous reports,^{1,35,37-39} resulting in hardness of 176.7 ± 2.3 for Chinese urushiol and 58.5 ± 0.6 N mm⁻² for Cambodian thitsiol (Table 1, entries 6 and 7).^{35,39} The comparable hardness of the artificial *urushi* film from **G-urushiol** to that from Chinese urushiol suggests similar curing properties of lignin-derived

urushiol analogs. Despite the comparable hardness of the artificial *urushi* film from **G-urushiol** to that from Chinese urushiol, the curing reaction proceeds slowly at the initial stage. The similar curing profile was observed with an urushiol analog synthesized from vanillyl alcohol,²⁰ suggesting a slightly different initial reaction step for an artificial *urushi* prepared from synthetically pure urushiol analogs, compared to the one prepared from natural urushiols, which are a mixture of catechols bearing different side chains. The initial slow curing reaction resembles the auto-oxidation profile of vegetable oils,⁴⁰ suggesting that a similar auto-oxidation of trienyl side chains takes place from the initial stage. In addition, the lower value of hardness obtained from Cambodian thitsiol bearing mainly dienyl side chains suggests that the number of unsaturated bonds in the side chain has a much stronger influence on the hardening process compared to the substituent position to the catechol core (Fig. 2).

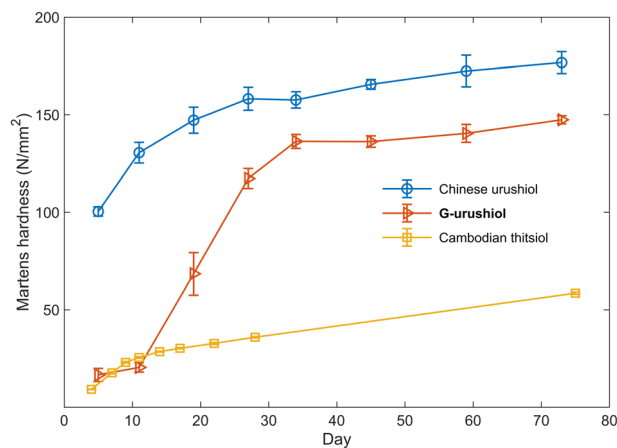


Fig. 2 Time-course curing properties of the film obtained from **G-urushiol** (red line), natural Chinese urushiol (blue line) and natural Cambodian thitsiol (yellow line).



In order to analyze the curing reaction of lignin-derived urushiol analog **G-urushiol** and natural urushiol extracted from Chinese *urushi* the prepared *urushi* films (after 73 days of curing) were characterized by FT-IR spectra (Fig. 3). Both the artificial and the natural *urushi* films appear translucent (Fig. 3, inset), but the artificial film presents a paler color (yellow) compared to the natural film (red/brown). From the IR spectra, we can notice that artificial *urushi* and natural *urushi* films differ mainly in the regions corresponding to the two vibrational bands at 1139 and 1504 cm^{-1} ; these two peaks are clearly observed in the artificial *urushi* film but not in the cured film from Chinese urushiol. These vibrations are assigned to the out-of-plane bending and aromatic stretching vibrations of 4-substituted catechol²¹ based on the DFT calculation (Fig. S1†). When comparing the liquid and cured films, we can notice that the aromatic vibrational band at 1608 cm^{-1} of **G-urushiol** was broadened after the polymerization, in a similar way to the 1593 and 1628 cm^{-1} bands in natural urushiol, in agreement with a previous report.⁴¹ An additional significant spectral change from liquid to cured film was observed for both natural and artificial *urushi* with the appearance of two peaks centered at 1635 and 1714 cm^{-1} . These two strong and broad peaks originate from the formation of quinone and the oxidation of side chains.²¹ Furthermore, the disappearance of the olefinic C–H vibration at 3011 cm^{-1} suggests the complete oxidation of the unsaturated side chains by autooxidation. These IR spectra demonstrate that the lignin-derived urushiol analog **G-urushiol** and natural urushiol undergo similar enzymatic polymerization reactions.

In summary, artificial *urushi* materials were developed by utilizing lignin-derived phenylpropanoids as aromatic nuclei. Vegetable oil-derived polyunsaturated side chains were

installed on lignin-derived aromatic compounds **GHP** and **SHP** to afford the lignin-derived urushiol analogs. Artificial *urushi* films were successfully prepared by mixing the lignin-derived urushiol analogs with protein hydrolysate and water in the presence of laccase enzyme. Time-course analysis of Martens hardness shows a stepwise oxidation reaction in the curing process, similar to natural *urushi*. The natural *urushi*-like properties were also confirmed by FT-IR analysis, suggesting remarkably similar molecular transformations during the curing process. The sufficiently high hardness of the lignin-derived artificial *urushi* film paves the way for future applications as an environmentally benign and sustainable coating material.

Author contributions

This work was carried out in collaboration between all authors. Authors H. M. and J. J. performed the synthetic experiments. Authors M. I. and Y. T. analyzed the curing properties and FT-IR of urushiol films. Authors K. I., Y. O., and M. N. designed and supervised the study. K. I., Y. O., Y. T., F. P., and M. N. prepared the manuscript. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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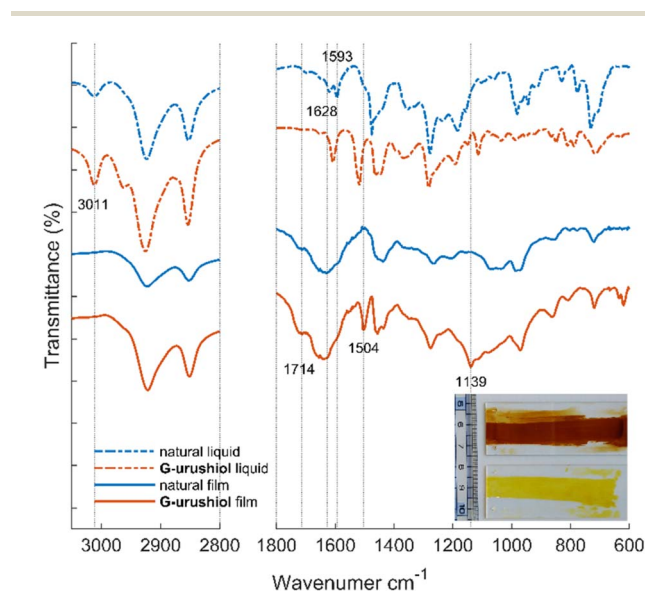


Fig. 3 IR spectra of the liquid state (dotted line) and cured film (solid line) obtained from natural Chinese urushiol (blue line) and **G-urushiol** (orange line). All spectra have been shifted and normalized for clarity. Inset: photo of natural Chinese *urushi* film (top, red film) and artificial (**G-urushiol**) *urushi* film (bottom, yellow film) deposited on glass.



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