合成漆および混合漆（アジア漆）サンプルの開発と特性評価：新しい持続可能な機能性材料に向けて

ピンチェラ　フランチェスカ*

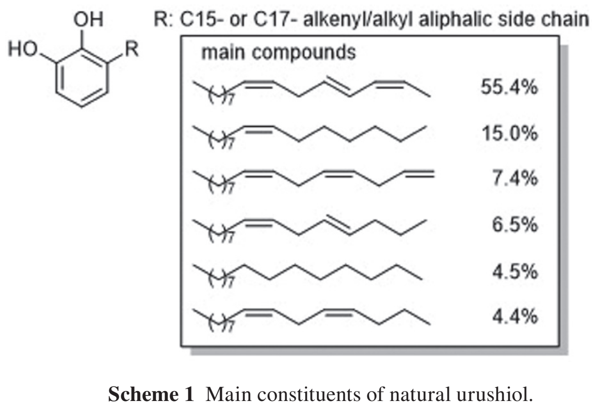
Development and Characterization of Synthetic and Blended Urushi (Asian lacquer) Samples: Towards New Sustainable Functional Materials

Francesca PINCELLA*

Urushi, sometimes referred to as the first plastic, has long been used as a natural material to provide durable and aesthetically pleasing glossy films. The synthesis of the most abundant compound in natural urushiol, (8*Z*, 11*E*, 13*Z*)-trienyl pentadecylcatechol, is envisioned via iron catalyzed coupling reaction involving an iron-catalyzed aryl-alkyl coupling, an alkenyl-alkenyl coupling reaction and an alkenyl-propargyl coupling reaction. The optimization of the reaction conditions is currently in progress to access the natural product in large scale. Additionally, urushiol analogs are being synthesized to aide in the optimization of the urushi film properties.

1. Introduction

The need for sustainable materials to replace petroleum-derived ones has renewed the interest in a traditional resin that has long been used in Asian countries, urushi or Asian lacquer. Urushi is a complex natural product, a water-in-oil emulsion composed of urushiol (60–80%, see Scheme 1), water (10–30%), gum (3–6%), and enzymes (2–3%). The durability, high stability, and aesthetic beauty of urushi, combined with its renewable nature, have made urushi an excellent candidate to become a building block for a future society. Nevertheless, several limitations exist to the use and extraction of this product (expensive, time-consuming, requiring highly skilled labor to collect the raw sap and process it). Moreover, the complex nature of this cross-linked and heterogeneous material and the fact that urushi formulations often include mixtures of several other components have also hindered a systematic and in-depth characterization of this material and its applications. So far, several reports have attempted to develop synthetic alternatives to natural urushi, notable examples being cardanol-based artificial urushi [1] and analogs with the alkyl chain connected at the 4 position of catechol with different linkages [2]. Currently only two reports of total synthesis of trienyl urushiol exist, but the first one requires 16-steps and has a 0.2% overall yield [3], while the second one only focused on the stereoselective construction of the skipped trienyl side chain by utilizing the cobalt-catalyzed isomerization of 1,3-diene to (2*Z*, 4*E*)-diene [4].



Scheme 1 Main constituents of natural urushiol.

2. Results and discussion

The total synthesis of the main component of urushiol (see Scheme 1, first compound from the top), (8*Z*, 11*E*, 13*Z*)-trienyl pentadecylcatechol, is envisioned proceeding via iron-catalyzed reactions according to Scheme 2. (8*Z*, 11*E*, 13*Z*)-trienyl pentadecylcatechol can be synthesized via an iron-catalyzed aryl–alkyl cross-coupling reaction of protected catechol with the alkyl halide bearing the original pentadecatrienyl configuration.

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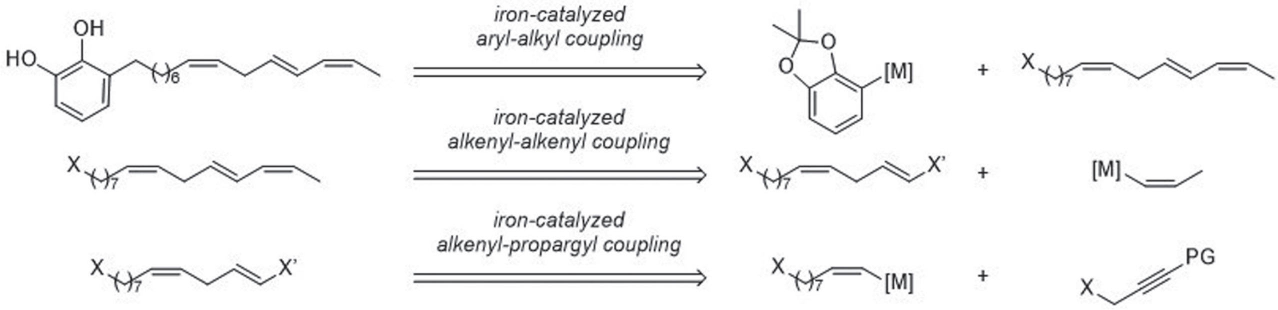
* 豊田理研スカラー
京都大学化学研究所



Scheme 2 Retrosynthetic approach to the synthesis of the most abundant component of natural urushiol.

The necessary triene framework of the side chain is to be stereospecifically constructed via an alkenyl–alkenyl cross-coupling reaction of a (*Z*)-propenyl metal reagent with a vinyl electrophile, which is obtained from the hydrohalogenation of 1,4-enyne. The 1,4-enyne can be synthesized through an iron-catalyzed alkenyl–propargyl cross-coupling reaction of (*Z*)-vinyl metal reagent with propargyl electrophile. Currently, the efforts towards the total synthesis of the target main component of natural urushiol, (8*Z*, 11*E*, 13*Z*)-trienyl pentadecylcatechol, are still ongoing, with the development of new methods for the stereocontrolled synthesis of the intermediates.

The researcher has also been working on the improved synthesis of simple urushiol analogs using renewable resources as feedstock, as a continuation of the recently published achievement on urushiol analog synthesis from biomass and naturally derived fatty acids [5]. The current focus has now shifted to the large-scale iron-catalyzed synthesis of 3-substituted urushiol analogs. The simple synthetic method allows us to easily access many urushiol analogs with different degrees of unsaturation and different aromatic units and to investigate the properties of different artificial urushi films in a systematic manner. Currently several analogs are being synthesized and they are characterized before and after polymerization under different conditions. These efforts are aimed at the rational synthesis of artificial urushi with optimal performance, and at the development of a reference library of model urushi compounds and films to aide in the interpretation of complex mass spectra from natural urushi samples [6].

3. Conclusions

In conclusion, the total synthesis of the natural product (8*Z*, 11*E*, 13*Z*)-trienyl pentadecylcatechol is proceeding via iron-catalyzed coupling reactions, with the main challenges being the development and optimization of stereocontrolled methods for the large-scale synthesis of intermediate compounds. Parallelly to the effort to obtain the main component of natural urushiol, urushiol analogs are being synthesized to study the polymerization mechanism and hardened film properties in a systematic way, with careful control of composition and polymerization conditions.

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