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Synthesis of novel urushiol-like compounds from tung oil using silica-supported phosphotungstic heteropoly acid catalyst

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ABSTRACT

Tung oil, a kind of natural plant oil, has recently received increasing attention due to its high value of research and application. In this study, we report a facile approach to synthesize novel urushiol-like compounds (CAT-ME) starting from tung oil using silica-supported phosphotungstic heteropoly acid (PW/SiO_2) as an effective and recyclable catalyst. To be specific, firstly, eleostearic acid glyceride, the main component of tung oil, is reacted with methanol by *trans*-esterification to obtain methyl eleostearate. And then Friedel-Crafts alkylation reaction of methyl eleostearate with catechol is carried out in the presence of a solid acid catalyst PW/SiO_2. And the CAT-ME productive rate is about 69.3%. Furthermore, the chemical structures of the target compound CAT-ME are characterized by Fourier transform infrared spectroscopy (FTIR), ultraviolet and visible spectrophotometer (UV–vis), proton nuclear magnetic resonance spectra (1H NMR), carbon nuclear magnetic resonance spectra (13C NMR) and mass spectra. The characterization results show the designed alkylation products similar to urushiol have been synthesized successfully. Noting that urushiol (the major component of raw lacquer) can be cured by UV irradiation under air atmosphere without any photoinitiator. Thus, this present study develops a promising approach to guide the further modifications of tung oil and other unsaturated natural oils, which can improve the functional properties and expand the application fields of unsaturated natural plant oils by introducing new UV curing system.

1. Introduction

In recent decades, increasing efforts have been made to synthesize new polymers from green natural resources to replace the application of petroleum-based products (Yang et al., 2015a,b,c; Manh et al., 2011; Liu et al., 2015), due to the depletion of fossil fuels and the desire of environment protection. Especially, plant oil-inspired intermediate and monomer can be applied in coating fields because of their low cost, renewability, and possible biodegradability (Huang et al., 2015; Pillai et al., 2016). As we all known, tung oil, one kind of typical natural seed oils, is mainly comprised of conjugated triene on the triglyceride molecule (eleostearic acid glyceride), and assigned as a conjugated drying oil with high level of unsaturation. Tung oil displays the advantages of quicker drying rate, better water resistance and higher hardness (Yuan et al., 2014; Meiorin et al., 2013) compared to other unconjugated drying oils, such as soybean, cashew nut shell oil and linseed oils. And hence tung oil has received great attention in a wide variety of applications, such as in the fabrication of varnishes, paints and other related materials (Sharma et al., 2011). Tung oil can be directly polymerized by thermal treatment. However, the products obtained from thermal polymerization of tung oil are viscous oils, or viscous and weak toughness films, which demonstrate little utility as coating film materials (Huang et al., 2013). In this regard, modification of tung oil with functional molecules is a promising strategy to address the above problem. One of conventional method for the modification of tung oil is performed by *trans*-esterification with methanol to convert glyceride to methyl ester. In other word, one triglyceride molecule is converted to three methyl ester (namely methyl eleostearate) molecules, which can reduce the viscosity of polymer products (Chen et al., 2012; Mosiewicki et al., 2012; Shang et al., 2012). Furthermore, a process that can effectively convert methyl eleostearate to a useful compound could be very important as an economically sustainable process. In addition, tung oil is also generally modified via Diels-Alder chemistry based on its conjugated double bonds (Cao et al., 2015), and the modified products such as acrylate-modified tung oil, tung oil-rosin adduct and

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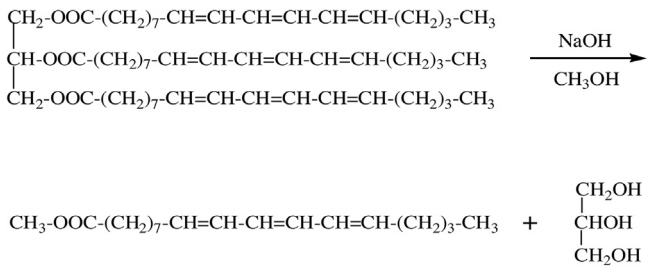

Scheme 1. Synthetic schematic illustration and theoretical structure of methyl eleostearate.

diacrylate-tung oil copolymers (Ge et al., 2015; Wu et al., 2013; Trumbo and Mote, 2001) have the promising application prospect in the coating field. It is worth noting that volatile organic compounds result in the main toxic issues and environmental troubles in the coating application (Thanamongkollit et al., 2012). The development of the modified products of tung oil with the UV-curing properties (UV-curable tung oil derivatives) is a potential strategy to retard the mentioned problem in the coating applications. Therefore, it is highly necessary for modifying tung oil with the UV-curable functional molecules to obtain UV-curable tung oil derivatives for applying in the coating field.

Lacquer urushiol, the major constituent of raw lacquer, is an important component for coating films, and mainly determines the performances and final applications of the coating films (Tang et al., 2015; Ishimura and Yoshida, 2015). The lacquer coating films have been accepted in the industrial production due to their excellent physico-chemical properties including thermo-stability, super-high durability, anticorrosion brilliance and toughness (Xia et al., 2010; Yang et al., 2015a,b,c). Urushiol can be cured by UV irradiation under air atmosphere without any photoinitiator, and is mainly consisted of three-substituted catechol derivatives possessing long chains with n = 15 carbons and 0–3 carbon–carbon double bonds (Tyman et al., 2002). Hence, the alkylation reaction of methyl eleostearate with catechol may be an excellent alternative to develop novel compounds similar to lacquer urushiol, which have the promising application as coating materials.

The alkylation reaction of aromatic compounds (named as Friedel-Crafts alkylation reaction) is traditionally catalyzed using mineral acids and Lewis acids. However, the mineral acids and Lewis acids used as the catalysts of Friedel-Crafts alkylation reaction can result in environmental problems, and require relatively complex and time-consuming multistep procedures to achieve product separation and purification. To solve the above problems, solid acids could be used as effective catalysts in alkylation reactions (Cadenas et al., 2014). Recently, solid-supported heteropoly acids (HPAs) used as catalysts have been attracted significant attention, due to their high acidity and favourable redox activities (Kumar et al., 2014). Furthermore, solid-supported HPA catalysts are easily separated from the reaction products and then can be used again. Among various HPAs, Keggin type are broadly studied compounds in different catalytic application fields, because of their relatively high redox activity, excellent thermal stability and high acidic properties. The solid support can make HPAs dispersing over a large surface area, which assists in the increase of their catalytic activity (Yang et al., 2015a,b,c; Ghodke and Chudasama, 2013). Among series of solid supports, SiO_2 is one of the best choices the solid support of HPAs, due to its low interaction with HPAs, high thermal resistance and amphoteric characters (Hafizi et al., 2012).

Methyl eleostearate, the derivative of major component (eleostearic acid glyceride) of tung oil, has conjugated system and meets the requirements for Friedel-Crafts alkylation reaction with aromatic compounds. Herein, the tung oil was *trans*-esterified with methanol to obtain methyl eleostearate. And then urushiol-like compounds (CAT-ME) were synthesized by Friedel-Crafts alkylation reaction of methyl eleostearate and catechol using silica-supported phosphotungstic heteropoly acid (PW/SiO_2) as catalyst. The facile and effective synthesis of urushiol-like compounds starting from tung oil provided an important promising approach to improve the activity of tung oil by introducing a new UV curing system, and would expand the applications of tung oil as coating film materials.

2. Experimental

2.1. Materials

Tung oil was provided by Shandong Jiuxing Chemical Co., Ltd (Jinan, China). Silica was bought from Qingdao Haiyang Chemical Factory. Phosphotungstic acid (PW) was purchased from Tianjian Damao Chemical Reagents Factory. Ether was provided by Tianjian Baishi Chemical Co., Ltd. Phosphoric acid, methanol, petroleum ether, hydrochloric acid (37 wt%) and ethyl acetate were bought from Tianjian Fuyu Fine Chemiacal Co., Ltd. Anhydrous sodium sulfate, anhydrous calcium-chloride, catechol and sodium hydroxide were bought from Tianjian Fuchen Chemical Reagents Factory. Water used in every experiment was distilled water.

2.2. Methods

2.2.1. Synthesis and purification of methyl eleostearate

Tung oil (50 g) was placed into a three-necked flask fitted with a condenser and a magnetic stirrer, and then was heated to 70 °C. Thereafter, sodium hydroxide methanol solution containing 0.5 g sodium hydroxide and 12 g methanol was added into the flask, and the system was magnetically stirred for 1 h at 70 °C. Subsequently, the pH value of the reaction solution was adjusted to 6.5–7.0 by adding phosphoric acid. The reaction solution was transferred into a separatory funnel, and then was separated into two layers. The upper layer (methyl eleostearate layer) was collected and washed with hot water with 2–3 times, and then moderate anhydrous calcium chloride was added to get rid of water. Furthermore, methyl eleostearate was obtained by distilling off the methanol from the resulted solution using a rotating distillation apparatus (Xu et al., 2006; Park et al., 2008; Shang et al., 2010) and then purifying by silver nitrate column chromatography silica gel. The synthetic schematic illustration is described in Scheme 1 (Yuan et al., 2014).

2.2.2. Preparation of silica-supported phosphotungstic heteropoly acid

The silica-supported phosphotungstic heteropoly acid (PW/SiO_2) was effectively prepared by incipient wetness impregnation (Arias et al., 2008; Ha and Li, 2015; He et al., 2012) with weighed amount of PW and silica. Prior to use, silica gel was immersed in concentrated hydrochloric acid (37 wt%) for 14 h at room temperature, and then washed to neutral pH with distilled water. Thereafter, silica gel was dried at room temperature for 3 h and then at 120 °C for 12 h, and next calcined at 350 °C for 3 h. Subsequently, the pretreatment silica gel was soaked in phosphotungstic acid aqueous solution (0.4 g/mL) with the magnetic stirring rate of 100 r/min at room temperature for 24 h. After that, the solid material was collected by filtration and then dried for 3 h at room temperature. After calcination at 180 °C for 3 h, the PW/SiO_2 was obtained and placed in a desiccator for further use.

2.2.3. Synthesis of CAT-ME

The typical procedure for the synthesis of CAT-ME was described as follows. Catechol (1.1 g) and diethyl ether (10 mL) were added into a three-necked flask fitted with a condenser and a magnetic stirrer to form homogeneous solution. Then 2.92 g of methyl