Microwave-Assisted $NaHSO_4$-Catalyzed Synthesis of Ricinoleic Glycol Ether Esters

Haifei Zhang[1], Fengfan Zhu[2], Yuan Xu[1], Xiaoxiang Zhang[1], Xinbao Zhu[1,2]

[1]College of Chemical Engineering, Nanjing Forestry University, Nanjing, China, [2]Jiangsu Province Glycol Ether Engineering Technology Research Center, Jiangyin, China

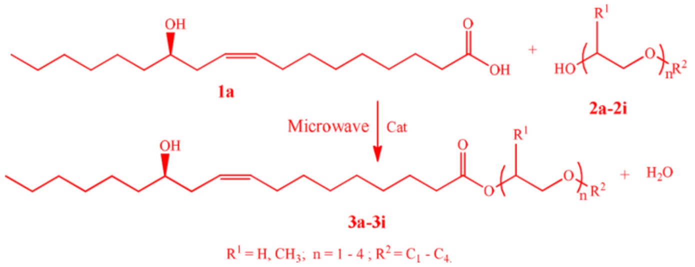
Address correspondence to X. Zhang. E-mail: zhuxinbao@njfu.com.cn

Project supported by the State Forestry Administration 948 project foundation(No. 2015-4-55)
The Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD)

Abstract

The synthesis of several ricinoleic acid glycol ether esters (RAGEE) by high-pressure microwave radiation is described. Ricinoleic acid which is from castor oil reacted fastly with glycol ethers in the presence of $NaHSO_4•H_2O$ and DCM in special microwave reactor. The influences of reaction factors such as catalyst and solvents type, reaction temperature and time were investigated and the optimal reaction conditions were obtained. The activity of catalyst had a higher performance up to the tenth cycle and the excellent values of turnover numbers (TON) and turnover frequency (TOF) were obtained. Compared with the traditional esterification in reflux heating systems., the microwave(MW)-assisted process has many advantages such as shorter reaction time, less side effects, higher yield, which is a great potential for development of green chemistry.

GRAPHICAL ABSTRACT



KEYWORDS: microwave-assisted; ricinoleic acid; glycol ether; esterification; $NaHSO_4$•H_2O.

INTRODUCTION

Plasticizer is one of the most important additives in polymer materials, especially in PVC, which contains more than 60% of the total production of plastics additives[1,2]. Traditional petroleum-based phthalate plasticizer has still the largest production and sale in the current plasticizer industry. However, due to the potential threat to human health and environment, the usage is gradually decreasing in the recent years[3-4]. Since the global environmental regulations become more stringent, people start to pay more attention on the eco-friendly technologies and products. The development of new alternative phthalate plasticizer has become the focus of attention worldwidely.

Transforming castor oil into high value-added energy and new materials is a hot topic nowadays. Castor oil is commonly used in the field of plasticizers by many ways[5,6]. Castor oil is well known as a source of ricinoleic acid, a monounsaturated, 18-carbon fatty acid. Among those fatty acids, ricinoleic acid is unique because it has a hydroxyl group on the 12th carbon which causes ricinoleic acid to be more polar than other fatty acids and presents some peculiar chemical properties, At the meanwhile, the chemical reactivity of the hydroxyl group also allows chemical derivatization in castor oil, but it is impossible for other seed oils. RAGEE is non-toxic and biodegradable and eco-friendly which has excellent cold resistance and high-plasticized efficiency[7–11]. The synthesis of RAGEE has rarely be reported. One common method is obtained by the reaction of castor oil transesterification (Scheme 1). Such methods require long reaction time and also produce byproducts which is difficult to separate from the product[12].

Microwave heating technology is a new green chemistry method that was developed in recent years[13]. Gedye first introduced microwave-heating synthesis into organic synthesis researches[14]. Unlike the synthesis at normal atmospheric pressure, the synthesis of RAGEE microwave radiation requires to heat the reactants to a high pressure in a sealed reactor. This method is easy to operate and eco-friendly which will not destroy the sample structure. Moreover, it can shorten the reaction time and improve the selectivity and product yield[15–19].

In the past few years, our group has studied the synthesis of RAGEE by ionic liquids catalyzed esterification[20], following green and sustainable chemistry principles[21]. As a continuation of our studies, we reported herein the preparation of RAGEE from ricinoleic acid and glycol ethers by microwave radiation method, which is in a faster and more efficient way and can be applied in a wide range of applications [22–24].and the catalyst can be reused for up to 10 runs with a higher performance on its activity. In addition, the TON and TOF values were higher than in reflux heating systems.

RESULTS AND DISCUSSION

Optimization Of Reaction Conditions

Our initial efforts were focused on the preparation of the ricinoleic acid ethylene glycol butyl ether ester (RAEGBEE) **3c** which was derived from ricinoleic acid **1a** and ethylene glycol butyl ether (EGBE) **2c**. We examined the effects of the reaction time and temperature, use of solvent, catalyst on the esterification yields, the results were shown in the Table 1.

Aiming to reduce the reaction time and to improve the yield, we first tested several catalysts (Table 1 Entries 1-5), as well as some different solvents (Table 1 Entries 5-12), the best result was obtained when the reaction was performed in the presence of $NaHSO_4•H_2O$ and DCM. The reason why $NaHSO_4•H_2O$ had such excellent catalytic performance was that it has strong electrolytes and hydrogen ions can be ionized without adding water to forward the reaction. Then, $NaHSO_4•H_2O$ can not only be easily separated after the reaction complete which make post-treatment simple, but also can reduce equipment corrosion. DCM was preferred due to its low boiling point. At 100°C, it form a higher steam pressure than other solvents, which was conducive to carry out the reaction to the positive direction.

Then, the impact of the reaction temperature was examined (Table 1 Entries 13-16). The higher temperature, the better performance. However, when it exceeded 150 °C, the yield decreased. Finally, the effect of reaction time on the yield (Table 1 Entries 15-20) was studied. When the reaction time was longer than 25 min, the yield almost didn’t increased.

Thus, when ricinoleic acid **1a** (10.0 mmol) and EGBE **2c** (12.0 mmol), catalyst (0.01% mol) were simply mixed in the presence of DCM (5.0 ml) at 150 °C under the microwave radiation, the desired RAEGBEE **3c** was obtained in 98% yield after 25 min (Table 1 entry 15).

TON and TOF values which were calculated for all the reactions are given in Table 1, these TON and TOF values which were achieved under MW were higher than those in reflux heating systems.

Substrate Scope

In order to demonstrate the efficiency of our protocol, ricinoleic acid **1a** was treated with other glycol ethers **2a–2i** according to the optimal synthesis method of RAEGBEE **3c** above. the results are summarized in Table 2. We observed that the reaction worked well for a variety of glycol ethers.

As shown in Table 2, in the same type of glycol ether, the longer the chain, the lower the yield. For example, among the ethylene glycol ethers (Table 2 entries 1-7), The ethylene glycol methyl ether **2a** reacted with ricinoleic acid **1a** to afford the Ricinoleic acid ethylene glycol methyl ether ester **3a** in higher yield than ethylene glycol ethyl ether **2b**. Similarly, among the propylene glycol ethers (Table 2 entries 8-9), dipropylene glycol methyl ether **2h** (Table 2 entry 3) than dipropylene glycol elthyl ether **2i**. Ricinoleic acid and glycol ether occurred bimolecular nucleophilic substitution reaction (S_N2). The increasing volume of the alkyl group caused steric hindrance, which lowered the yield.

The ethylene glycol ethers **2a-2g** (Table 2 entries 1-7) gives the respective esters **3a-3g** in slightly superior yield to propylene glycol ethers **2h-2i** (Table 2 entries 8-9) after the same reaction time. These results from the electron correlation effect.

In conclusion, an improved, microwave-assisted technology to prepare RAGEE directly from ricinoleic acid was developed. Ricinoleic acid **1a** (10.0 mmol) and glycol ethers **2a-2i** (12.0 mmol) reacted in the presence of $NaHSO_4•H_2O$ (0.01% mol) and DCM (3.0 ml) at 150 °C under the microwave irritation, after 25 min, the desired product **3a-3i** were obtained in satisfactory yields, which can be valuable to the future scaling-up research for the pilot or industry[27].The minimization of the reaction time and the increase of selectivity and yields are important advantages of this improved procedure. Besides, the obtained esters can be explored as the vegetable oil glycol esters in the synthesis of more complex biomass plasticizers.

Reusability Of Catalyst $Nahso_4•H_2O$

The reusability was investigated on model reaction at optimum reaction conditions and are given in Table 3, $NaHSO_4•H_2O$ can be used economically for several applications since the activity of catalyst has a higher performance after 10 cycles.

Mercury test

As been well known, if the catalytic reaction stops and the catalyst lose activity after mercury is added, it is considered to be a heterogeneous catalyst. Meanwhile, if mercury addition does not affect the catalytic reaction, it is a homogenous catalyst . The mercury test showed that the catalyst had a heterogeneous nature because it lost activity upon the addition of mercury.

EXPERIMENTAL

Instruments and Reagents

Monowave 300 Microwave reactor (Canada Antonpear Company); RE-2000B rotary evaporator (Shanghai Yarong Shenghua Instrument Factory); DF-101S solar collector thermostat heating magnetic stirrer (Zhengzhou Greatwall Scientific Industrial and Trade Co, Ltd.); FTS-135 type Fourier transform infrared spectrometer (BIO-RAD company); PHS-25 pH meter (Shanghai precision scientific instrument Co, Ltd.); Bruker Ascend 400 MHz NMR measurement; Agilent 6540 UHD Q-TOF LC/MS.

All reagents were analytical grade, purchased from Aladdin Co, Ltd.

Mercury Poisoning Test

The model coupling reaction was conducted in the absence of mercury for 25min under microwave heating (yield: 98%). Then 300 molar equivalents of mercury, with relation to the catalyst ($NaHSO_4•H_2O$), were added into the reaction media, and the reaction was allowed to continue for 25min. After the allowed time, the yield of 96% of the expected product was obtained.

General Procedure For The Synthesis Of RAGEE

Ricinoleic acid (10.0 mmol) 1a, glycol ethers 2a-2i (12.0 mmol) and DCM (5.0 mL) and $NaHSO_4 \cdot H_2O$ (0.01% mol) were added into a dry 10.0 mL microwave reaction tube, which was put into a microwave reactor. The desired product was afforded after 25 min at 150°C (Scheme 2).

The reaction progress was followed by thin-layer chromatography (TLC) and the crude product was purified on column chromatography of silica gel using ethyl acetate-petroleum ether(1:7) as eluent. All products were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and HRMS and spectrum data of **3a-3i** were listed.

Ricinoleic acid ethylene glycol methyl ether ester (3a), pale yellow liquid, yield 99%. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 5.54-5.52 (m, 1H), 5.39-5.36 (m, 1H), 4.37 (t, J = 7.2 Hz, 2H), 3.69 (t, J = 7.2 Hz, 2H), 3.60 (s, 1H), 3.57 (s, 3H), 3.51-3.44 (m, 1H), 2.32-2.30 (t, J = 7.4 Hz, 2H), 2.28-2.24 (m, 2H), 2.18 (t, J = 7.2 Hz, 2H), 1.72-1.64 (m, 2H), 1.46-1.41 (m, 2H), 1.32-1.28 (m, 16H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 173.9, 132.5, 125.3, 71.4, 70.3, 69.1, 67.7, 65.8, 63.6, 56.4, 36.8, 34.0, 31.9, 29.1, 26.9, 26.7, 25.7, 22.4, 19.1, 14.0, 13.8; (KBr) *v:* 3386, 3009, 2931, 2851, 1744, 1651, 1543, 1454, 1372, 1278, 1251, 1217, 1121, 1109, 1031, 1000, 866, 729, 714, 702, 611 cm^{-1}; (ESI) calcd for $C_{21}H_{40}NaO_4$ $[M+Na]^+$: 379.2824, found: 379.2820.

Ricinoleic acid ethylene glycol ethyl ether ester (2b), pale yellow liquid, yield 98%. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 5.52-5.50 (m, 1H), 5.38-5.36 (m, 1H), 4.55 (t, J = 7.2 Hz, 2H), 3.88 (t, J = 7.2 Hz, 2H), 3.65 (t, J = 7.2 Hz, 2H), 3.60 (s, 1H), 3.42-3.40 (m, 1H), 2.54 (t, *J* =7.4 Hz, 2H), 2.42-2.38 (m, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.80-1.74 (m, 2H), 1.59-1.51 (m, 2H), 1.32-1.28 (t, 16H),1.21 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 173.9, 132.7, 125.2, 70.5, 68.2, 67.6, 60.5, 43.4, 36.7, 35.2, 32.2, 31.7, 31.3, 30.8, 29.0, 27.3 25.7, 23.9, 22.5, 19.3, 14.0, 13.9; FT-IR (KBr) *ν:* 3381, 3008, 2930, 2850, 1744, 1651, 1541, 1455, 1372, 1279, 1252, 1217, 1121, 1106, 1032, 1001, 866, 727, 710, 702, 610 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{42}NaO_4$ $[M+Na]^+$: 393.2981, found: 393.2985.

Ricinoleic acid ethylene glycol butyl ether ester (2c), pale yellow liquid, yield 98%. ^{1}H NMR (400 MHz, CDCl3), δ: 5.54-5.50 (m, 1H), 5.43-5.39 (m, 1H), 4.23 (t, *J* = 7.2 Hz, 2H), 4.13-4.11 (m, 1H), 3.63 (t, *J* = 7.2 Hz, 2H), 3.60 (s, 1H), 3.48 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.27 (m, 2H), 2.05-2.03 (m, 4H), 1.61-1.58 (m, 8H), 1.31-1.25 (t, *J* = 7.2 Hz, 16H), 0.92 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (400 MHz, CDCl3), δ: 173.8, 133.6, 125.1, 70.7, 68.4, 63.6, 61.9, 36.8, 35.4, 34.1, 33.8, 31.4, 29.5, 26.9, 26.7, 25.7, 24.6, 22.3, 19.6, 14.5, 13.9; FT-IR (KBr) ν: 3387, 3004, 2932, 2853, 1745, 1653, 1545, 1465, 1379, 1280, 1251, 1220, 1106, 1045, 1010, 867, 729, 718, 709, 611 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{46}NaO_4$ $[M+Na]^+$: 421.3294, found: 421.3292.

Ricinoleic acid diethylene glycol methyl ether ester (2d), pale yellow liquid, yield 96%. ^{1}H NMR (400 MHz, CDCl3), δ: 5.55-5.52 (m, 1H), 5.38-5.36 (m, 1H), 4.26 (t, *J* = 7.6 Hz, 2H), 3.71-3.68 (m, 2H), 3.65-3.63 (m, 2H), 3.60 (s, 1H), 3.53-3.44 (m, 1H), 3.40 (t, *J* = 7.6 Hz,2H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.29-2.26 (m , 2H), 2.13 (t, *J* = 7.4 Hz, 2H), 1.62-1.55 (m, 2H), 1.48-1.43 (m, 2H), 1.31-1.25 (m, 16 H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$), δ: 173.9, 132.6, 125.3, 74.6, 71.4, 70.2, 69.1, 67.7, 65.8, 63.6, 56.4, 36.8, 34.0, 31.8, 29.1, 26.9, 26.7, 25.7, 22.4, 19.1, 14.1, 13.8; FT-IR (KBr) *v:* 3381, 3008, 2930, 2850, 1744, 1651, 1541, 1455, 1372, 1279, 1252, 1217, 1121, 1106, 1032, 1001, 866, 727, 710, 702, 610 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{42}NaO_4$ $[M+Na]^+$: 393.2981, found: 393.2980.

Ricinoleic acid diethylene glycol butyl ether ester (2e), pale yellow liquid, yield 93%. ^1H NMR (400 MHz, $CDCl_3$), δ: 5.49-5.46 (m, 1H), 5.35-5.32 (m, 1H), 4.17 (t, *J* = 7.2 Hz, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.66-3.44 (m, 6H), 3.60 (s, 1H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.26 (d, 2H), 1.86 (m, 2H), 1.72 (m, 2H), 1.61-1.55 (m, 6H), 1.32-1.28 (t, 16H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ: 173.9, 132.2, 125.3, 71.6, 70.8, 69.6, 67.5, 65.8, 63.7, 56.4, 50.3, 36.9, 34.6, 31.8, 30.7, 29.1, 28.7, 27.2, 26.5, 26.4, 25.7, 22.4, 19.4, 14.3, 13.6; FT-IR (KBr) *v:* 3390, 3012, 2921, 2850, 1746, 1646, 1545, 1460, 1390, 1280, 1246, 1220, 1120, 1105, 1012, 1013, 867, 726, 702, 618 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{48}NaO_4$ $[M+Na]^+$: 435.3450, found: 435.3454.

Ricinoleic acid triethylene glycol methyl ether ester (2f), pale yellow liquid, yield 95%. ^1HNMR (400 MHz, $CDCl_3$), δ: 5.57-5.50 (m, 1H), 5.39-5.37 (m, 1H), 4.21 (t, *J* = 7.2 Hz, 2H), 4.01 (t, *J* = 7.2 Hz, 2H), 3.74 -3.70 (m, 2H), 3.68-3.64 (m, 2H), 3.62-3.58 (m ,4H), 3.55 (s, 1H), 3.51-3.44 (m, 1H), 3.38 (t, *J* = 7.2 Hz, 2H), 3.30 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.28-2.20 (m, 2H), 2.03 (t, *J* = 7.2 Hz, 2H), 1.62-1.54 (m, 2H), 1.48-1.42 (m, 2H), 1.30-1.25 (t, 16H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 173.7, 132.3, 125.2, 71.5, 71.4, 71.0, 70.8, 70.5, 70.3, 69.8, 36.9, 35.4, 34.2, 31.8, 29.6, 29.3, 29.2, 29.1, 29.0, 28.7, 28.6, 27.4, 25.7, 22.6, 14.1; FT-IR (KBr) *ν:* 3381, 3008, 2930, 2850, 1744, 1651, 1541, 1455, 1372, 1279, 1252, 1217, 1121, 1106, 1032, 1001, 866, 727, 710, 702, 610 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{48}NaO_5$ [M+Na]$^+$: 451.3399, found: 451.3398.

Ricinoleic acid triethylene glycol propyl ether ester (2g), pale yellow liquid, yield 93%. ^{1}HNMR (400 MHz, $CDCl_3$), δ*:*5.56 (m, 1H), 5.37 (m, 1H), 4.21 (t, *J* = 7.2 Hz, 2H), 3.67 (t, *J* = 7.2 Hz, 2H), 3.60 (s, 1H), 3.54-3.51 (m, 8H), 3.38 (t, *J* = 7.2 Hz, 2H), 2.75 (t, *J* = 7.2 Hz, 2H), 2.28-2.20 (m, 4H), 2.03 (t, *J* = 7.2 Hz, 2H), 1.62-1.56 (m, 4H), 1.48-1.42 (m, 4H), 1.35-1.25 (m, 16H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100MHz, $CDCl_3$), δ:173.9, 133.3, 125.2, 72.5, 71.9, 71.5, 71.4, 71.0, 71.0, 70.6, 69.2, 63.4, 61.7, 36.9, 35.4, 34.2, 31.8, 31.7, 31.6, 29.6, 29.3, 29.1, 27.4, 25.7, 22.6, 19.3, 14.1, 13.9; FT-IR (KBr) *ν:* 3381, 3008, 2930, 2850, 1744, 1651, 1541, 1455, 1372, 1279, 1252, 1217, 1121, 1106, 1032, 1001, 866, 727, 710, 702, 609 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{54}NaO_5$ [M+Na]$^+$: 493.3869, found: 493.3866.

Ricinoleic acid dipropylene glycol methyl ether esters (2h), pale yellow liquid, yield 91%. ^{1}HNMR (400 MHz, CDCl3), δ: 5.52-5.50 (m, 1H), 5.42-5.38 (m, 1H), 4.85 (t, *J* = 7.2 Hz, 2H), 3.93 (t, *J* = 7.2 Hz, 2H), 3.60 (s, 1H), 3.59 (m, 2H), 3.48 (t, *J* = 7.2 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 2.26 (t, *J* = 7.2 Hz, 2H), 2.24-2.20 (m, 2H), 2.03 (t, *J* = 7.2 Hz, 2H), 1.48-1.42 (m, 2H), 1.35-1.25 (m , 22 H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3), δ: 173.9, 133.3, 125.2, 71.3, 71.2, 70.3, 71.0, 69.2, 63.4, 61.7, 36.9, 35.4, 34.2, 31.8, 31.7, 31.6, 29.6, 29.3, 29.1, 27.4, 25.7, 22. 6, 19.3, 14.1, 13.9; FT-IR (KBr) ν:

3389, 3067, 2938, 2850, 1755, 1656, 1547, 1460, 1370, 1280, 1252, 1280, 1144, 1128, 1046, 1022, 867, 710, 611 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{48}NaO_4$ $[M+Na]^+$: 435.3450, found: 435.3453.

Ricinoleic acid dipropylene glycol elthyl ether esters (2i), pale yellow liquid, yield 89%. ^{1}H NMR (400 MHz, CDCl3), δ:5.52 (m, 1H), 5.39 (m, 1H), 3.99 (t, *J* = 7.2 Hz, 2H), 3.61 (t, *J* = 7.2 Hz, 2H), 3.60 (s, 1H), 3.50-3.47(m, 2H), 3.42 (t, *J* = 7.2 Hz, 2H), 3.35-3.32 (m, 2H), 2.33-2.29 (m, 2H), 2.18 (t, *J* = 7.2 Hz, 2H), 2.04-2.02 (m, 2H), 1.35-1.32 (m, 26H), 1.12-1.08, (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ: 178.9, 133.3, 125.2, 71.3, 71.2, 71.0, 71.0, 70.6, 69.0, 65.8, 61.7, 31.8, 31.6, 29.6, 29.3, 29.1, 28.9, 25.7, 24.7, 22.6, 18.3, 17.2, 16.8, 15.0, 14.1, 13.9; FT-IR (KBr) ν: 3389, 3010, 2932, 2855, 1746, 1657, 1546, 1465, 1379, 1280, 1258, 1230, 1127, 1116, 1045, 1024, 869, 738, 719, 711, 616 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{50}NaO_4$ $[M+Na]^+$: 449.3607, found: 449.3609.

ACKNOWLEDGEMENT

The authors would like to thank the State Forestry Administration 948 project foundation for financial support under the Grant No 2015-4-55 and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

REFERENCES

1. Erythropel, H. C.; Maric, M.; Nicell, J. A. Leaching of the plasticizer di(2-ethylhexyl)phthalate (DEHP) from plastic containers and the question of human exposure. *Appl. Microbiol. Biotechnol.* **2014**, *24*, 9967.

2. Rahman, M.; Brazel, C.S. The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. *Prog. Polym. Sci.* **2004**, *12*, 1223.

3. Lithner, D.; Larsson, A.; Dave, G. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. *Scie. Total. Environ.* **2011**, *18*, 3309.

4. Hines, C. J.; Hopf, N.B.; Deddens, J.A. Occupational exposure to diisononyl phthalate (Di NP) in polyvinyl chloride processing operations. *Int. Arch. Occup. Environ. Health.* **2012**, *3*, 317.

5. Perin, G.; lvaro, G. A.; Westphal, E. Transesterification of castor oil assisted by microwave irradiation. *Short communication.* **2008**, *87*, 2838.

6. Manuel, Sánchez-Cantú.; Federico, M.; Reyes-Cruz. Direct synthesis of calcium diglyceroxide from hydrated lime and glycerol and its evaluation in the transesterification reaction. *Fuel.* **2014**, *18*, 126.

7. Wang, B.; Wang, K. Z.; Kong, Y. L. Research Progressof Environment-friendly Plasticizers. *China plastics industry*. **2013**, *5*, 12.

8. Huang, X. F.; Huang, W. B.; Li, X. D.; Li, Z. Studies on the preparation of 10-hydroxy decanonic acid from the caster oil, *You Ji Hua Xue.* **1996**, *2*, 175.

9. Ranu, B. C.; Jana, R.; Dey, S. S. An Efficient and Green Synthesis of 2-Arylbenzothiazoles in an Ionic Liquid [pmIm]Br under Microwave Irradiation, *Chem. Lett.* **2004,** *2*, 274.

10. Black, Brenna. A.; Sun, C. X.; Zhao, Y. Y.; Ganzle, Michael. G.; Curtis, Jonathan, M. Antifungal Lipids Produced by Lactobacilli and Their Structural Identification by Normal Phase LC/Atmospheric Pressure Photoionization–MS/MS. *J. Agric. Food. Chem*, **2013**, *22*, 5338.

11. Lin, Jiann.Tsyh.; Arcinas, Arthur ; Harden, Leslie. A. Identification of Acylglycerols Containing Dihydroxy Fatty Acids in Castor Oil by Mass Spectrometry. *Lipids.* **2009**, *4*, 359.

12. Xu, H.; Zhou, Q.; Wang, J. F. Treatment of Sebacic Acid Industrial Wastewater by Extraction Process Using Castor Oil Acid as Extractant, *Chin. J. Chem. Eng*. **2013**, *9*, 967.

13. (a) Baran, Talat.; Aciksoez, Eda.; Mentes, Ayfer. Highly efficient, quick and green synthesis of biaryls with chitosan supported catalyst using microwave irradiation in the absence of solvent. *Carbohydr Polym*, **2016**, *142,* 189. (b) Baran.; Ayfer, Menteş.; Talat, Baran.; Ayfer, Mente. Highly efficient Suzuki cross-coupling reaction of biomaterial supported catalyst derived from glyoxal and chitosan, *Journal of Organometallic Chemistry*, **2016,** *803,* 30. (c) Talat, Baran.; Tülden, Inanan.; Ayfer, Menteş. Synthesis, characterization, and catalytic activity in Suzuki coupling and catalase-like reactions of new chitosan supported Pd catalyst ,*Carbohydrate Polymers*, **2016,** 145, 20. (d) Talat, Barana.; Idris, Sarginb.; Murat, Kayab.; Ayfer, Menteşa. An environmental catalyst derived from biological waste materials for green synthesis of biaryls via Suzuki coupling reactions, *Journal of Molecular Catalysis A:***2016**, *420,* 216; (e) Talat, Baran.; Ayfer, Mentes. Microwave assisted synthesis of biarlys by C-C coupling reactions with a new chitosan supported Pd(II) catalyst, *Journal of Molecular*

Structure, **2016**, *1122,* 111; (f) Talat, Barana.; Idris, Sarginb.; Murat, Kayab.; Ayfer, Mentes. Green heterogeneous Pd(II) catalyst produced from chitosan-cellulose micro beads for green synthesis of biaryls, *Carbohydrate Polymers,* **2016,** *152,*181; (g) Baran, Idris Sargin.; Ayfer, Menteşa.; Murat, Kaya. Exceptionally high turnover frequencies recorded for a new chitosan-based palladium(II) catalyst, *Applied Catalysis A: General* **2016,** *523,* 12.

14. (a) Gedye , R.;Smith, F.;Westaway , K. The use of microwave ovens for rapid organic synthesis. *Tetrahedron Lett* .**1986**; *3,* 279. (b) Gedye , R.;Smith, F.;Westaway , K . The rapid synthesis of organic compounds in microwave ovens, *Can .J. Chem* **.1988**, *4*, 17.

15. Li, Y.H.; Guo, Y.b.; Tang, T.; Deng, Z. L.; Zhao, K. Q. Gang CuI-catalyzed domino reactions for the synthesis of benzoxazine-fused isoquinolines under microwave irradiation, *Synthetic Commun.* **2016**, *4*,355.

16. Sharifi, Ali.; Ghonouei, Nima.; Abaee, M. Saeed Ethylene glycol, an efficient and recoverable medium for copper-catalyzed N-arylation of diazoles under microwave irradiation, *Synthetic Commun.* **2016**, *3*, 249.

17. Mariappan, Arumugam; Rajaguru, Kandasamy; Muthusubramanian, Shanmugam; Bhuvanesh, Nattamai. Microwave-assisted catalyst-free synthesis of tetrasubstituted pyrroles using dialkyl acetylenedicarboxylates and monophenacylanilines, *Synthetic Commun.* **2016**, *46*, 805.

18. Pei, W.; Dong, Z. G.; Yao, C. P.; Chen, Q. Application of Solid Base Catalysts of Metal Oxide In Organic Synthesis, *Chinese. J. Org.* **2010**, *9*, 1410.

19. Weber, Harald.; Scholten, Frank.; Leinz ,Gerhard. Arzneimittelinformation und Beratung in der Apotheke**,** *Deut Lebensm-Rundsch***.** **2005**, *10*, 425.

20. Zhang, H. F.; Liu, D. M.; Kang, T. T.; Wang, Y.; Zhang, X. X.; Zhu, X. B. Synthesis of Novel Benzothiazolium Ionic Liquids and Research on Their Catalytic Esterification for Ricinoleic Acid, *Chinese. J. Org*. **2016**, *5*, 1104.

21. Lenardao, E. J.;Trecha, D. O.; Ferreira, P. C.; Jacob, R. G.; Perin, G. Green Michael addition of thiols to electron-deficient alkenes using KF alumina and recyclable solvent or solvent-free conditions, *J. Braz. Chem. Soc.* **2009**, *20*, 93.

22. Pelle, Lidstrom.; Jason, Tierney.; Bernard, Wathey. Microwave assisted organic synthesis—a review, *Tetrahedron*, **2001**, *45*, 9225.

23. liver, Kappe. Microwave Reactor for Batchwise Organic Synthesis, *Angew. Chem. Int. Edit.* **2004**, *46*, 6250.

24. He, P.; Haswell, S. J.; Fletcher, P. D. I. Microwave-assisted Suzuki reactions in a continuous flow capillary reactor, *Applied Catalysis A. Genera.* **2004**, *1*,111.

25. Xu, R.; Xie, H.; Huang, L. Curing Kinetics of Dehydrated Castor-oil Polyamide-epoxy Resin System, *Chemistry and Industry of Forest Products*. **2009**, *2*, 59.

26. Lin, Jiann.Tsyh.; Arcinas, Arthur.; Harden, Leslie. R.; Fagerquist, Clifton.K. Regiospecific Analysis of Diricinoleoylacylglycerols in Castor (Ricinus communis L.) Oil by Electrospray Ionization−Mass Spectrometry. *J. Agric. Food Chem.* **2006**, *10*, 3498.

Table 1. Optimization reaction conditions of ricinoleic acid and EGBE[a]

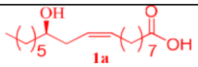
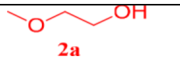
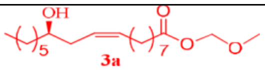
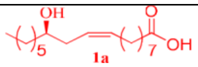
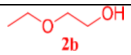
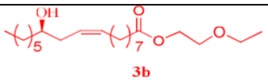
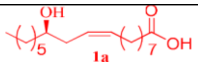
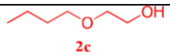
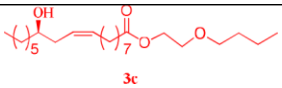
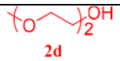
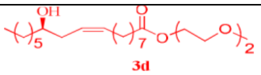
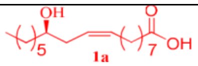
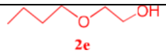
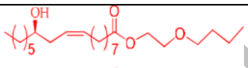
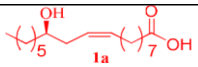
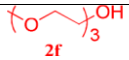
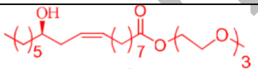
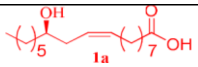
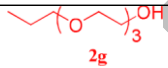
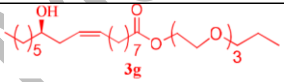
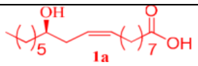
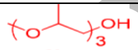
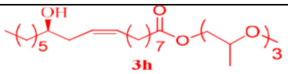
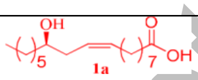
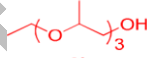
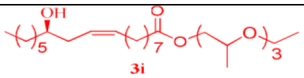
Entry	Catalyst	Solvent	Time/min	Temp/°C	Yield/%[b]	TON	TOF
1	TsOH	DCM	25	100	91	9100	21840
2	HCl	DCM	25	100	85	8500	20400
3	H_2SO_4	DCM	25	100	90	9000	21600
4	$SnCl_2•2H_2O$	DCM	25	100	80	8000	19200
5	$NaHSO_4•H_2O$	DCM	25	100	93	9300	22320
6	$NaHSO_4•H_2O$	acetonitrile	25	100	80	8000	19200
7	$NaHSO_4•H_2O$	dichloroethane	25	100	89	8900	21360
8	$NaHSO_4•H_2O$	toluene	25	100	87	8700	20880
9	$NaHSO_4•H_2O$	hexane	25	100	91	9100	21840
10	$NaHSO_4•H_2O$	tetrahydrofuran	25	100	79	7900	18960

11	$NaHSO_4$•H_2O	chlorobenzene	25	100	85	8500	20400
12	$NaHSO_4$•H_2O	DMSO	25	100	81	8100	19440
13	$NaHSO_4$•H_2O	DCM	25	75	79	7900	18960
14	$NaHSO_4$•H_2O	DCM	25	125	95	9500	22800
15	$NaHSO_4$•H_2O	DCM	25	150	98	9800	23520
16	$NaHSO_4$•H_2O	DCM	25	160	97	9700	23280
17	$NaHSO_4$•H_2O	DCM	15	150	87	8700	34800
18	$NaHSO_4$•H_2O	DCM	20	150	89	8900	26700
19	$NaHSO_4$•H_2O	DCM	30	150	98	9800	19600
20	$NaHSO_4$•H_2O	DCM	35	150	97	9700	16629
21[c]	$NaHSO_4$•H_2O	toluene	300	110	90	9000	1800

[a] Reaction conditions: ricinoleic acid (10.0 mmol), EGBE (12.0 mmol), catalyst (0.01% mol), solvent (5.0 mL), under MW, [b] Yield: the esterification yields.

[c] Reaction conditions: ricinoleic acid (10.0 mmol), EGBE (12.0 mmol), catalyst (0.02% mol), solvent (5.0 mL), in reflux heating systems.

Table 2. Synthesis of RAGEE from ricinoleic acids **1a** and glycol ethers **2a-2i**[a]

Entries	Ricinoleic acid	glycol ethers	Product	Yield [b]
2a	 **1a**	 **2a**	 **3a**	99%
2b	 **1a**	 **2b**	 **3b**	98%
2c	 **1a**	 **2c**	 **3c**	98%
2d	 **1a**	 **2d**	 **3d**	96%
2e	 **1a**	 **2e**	 **3e**	93%
2f	 **1a**	 **2f**	 **3f**	95%
2g	 **1a**	 **2g**	 **3g**	93%
2h	 **1a**	 **2h**	 **3h**	91%
2i	 **1a**	 **2i**	 **3i**	89%

[a] Reaction conditions: ricinoleic acid (10 mmol), glycol ether (12mmol), catalyst (0.01%mol), solvent (5.0mL), 150°C, 25min, under MW; [b] Yield: the esterification yield.

Table 3. Reusability of catalyst $NaHSO_4{\bullet}H_2O$

The number of cycle	Yield (%)	TON
1st	98	9800
2nd	97	9700
3rd	97	9700
4th	96	9600
5th	95	9500
6th	95	9500
7th	94	9400
8th	93	9300
9th	92	9200
10th	92	9200

Reaction conditions: ricinoleic acid (10.0 mmol), EGBE (12.0 mmol), catalyst (0.01% mol), solvent (5.0 mL), 150 °C, 25.0 min, under MW; [b]Yield: the esterification yield.

Table 4 Optimization of reaction conditions of ricinoleic acid and binary alcohol ether

Entry	Catalyst	solvent	Time/min	Temp/℃	Yield/%[b]
1	TsOH	dichloromethane	25	100	91
2	HCl	dichloromethane	25	100	85
3	H_2SO_4	dichloromethane	25	100	90
4	$SnCl_2$•$2H_2O$	dichloromethane	25	100	80
5	$NaHSO_4$•H_2O	dichloromethane	25	100	93
6	$NaHSO_4$•H_2O	acetonitrile	25	100	80
7	$NaHSO_4$•H_2O	dihloroethane	25	100	89
8	$NaHSO_4$•H_2O	toluene	25	100	87
9	$NaHSO_4$•H_2O	hexane	25	100	91
10	$NaHSO_4$•H_2O	tetrahydrofuran	25	100	79
11	$NaHSO_4$•H_2O	chlorobenzene	25	100	85
12	$NaHSO_4$•H_2O	DMSO	25	100	81
13	$NaHSO_4$•H_2O	dichloromethane	25	75	79
14	$NaHSO_4$•H_2O	dichloromethane	25	125	95
15	$NaHSO_4$•H_2O	dichloromethane	25	150	98
16	$NaHSO_4$•H_2O	dichloromethane	25	160	97
17	$NaHSO_4$•H_2O	dichloromethane	15	100	87
18	$NaHSO_4$•H_2O	dichloromethane	20	100	89
19	$NaHSO_4$•H_2O	dichloromethane	30	100	98
20	$NaHSO_4$•H_2O	dichloromethane	35	100	97

[a] ricinoleic acid (10 mmol) and glycol ether (12 mmol) and sodium bisulfate monohydrate (30 mg), dichloromethane (3ml) 150W 25 min.

[b] the esterification rate.

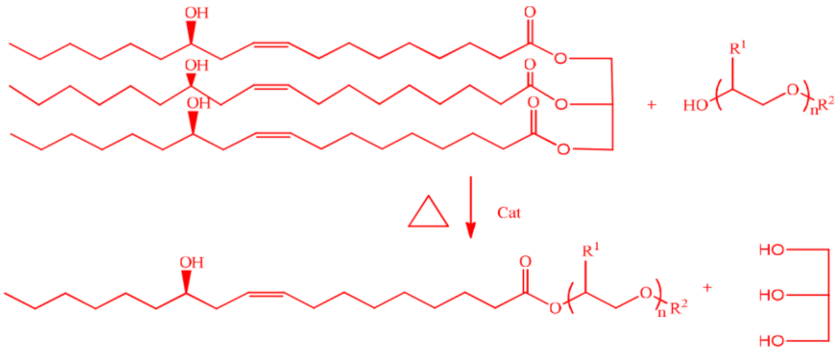
Table 5 Synthesis of Castor oil Derivatives[a]

Product	R^2	Yield
2a	$CH_3OCH_2CH_2$	99%
2b	$CH_3CH_2OCH_2CH_2$	98%
2c	$CH_3(CH_2)_3OCH_2CH_2$	98%
2d	$CH_3\ (OCH_2CH_2)_2$	96%
2e	$CH_3(CH_2)_3(OCH_2CH_2)_2$	93%
2f	$CH_3(OCH_2CH_2)_3$	95%
2g	$CH_3(CH_2)_2(OCH_2CH_2)_3$	93%
2h	$CH_3[OCH\ (CH_3)CH_2]_2$	91%
2j	$CH_3CH_2[OCH(CH_3)CH_2]_2$	89%

[a] ricinoleic acid (10 mmol) and glycol ether (12 mmol) and add sodium bisulfate monohydrate (30 mg), dichloromethane (3 ml) 150 W 25min.

[b] the esterification rate.

Scheme 1.



$R^1 = H, CH_3$; n = 1- 4 ; $R^2 = C_1 - C_4$

Scheme 2.