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Research Article

Chemical modifications of ricinolein in castor oil and methyl ricinoleate for viscosity reduction to facilitate their use as biodiesels

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Illustration of oxidation of castor oil and transesterification of oxidized castor oil to reduce viscosity.

Research Article

Chemical modifications of ricinolein in castor oil and methyl ricinoleate for viscosity reduction to facilitate their use as biodiesels

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Castor beans contain large quantities of oil and can grow in harsh environments. Unlike soybean oil, castor oil cannot be directly used for biodiesel production due to its extremely high viscosity. Here, we report an alternative source of biodiesel which possesses ideal viscosity as soybean oil, and this new biodiesel could be obtained through simple synthetic routes from castor oil. Moreover, the properties of our newly designed ketone-containing triglycerides and its transesterified counterpart as biodiesel were systematically examined in our study, and their structures were characterized by using ¹H NMR and ¹³C NMR.

Keywords: alcohol oxidation / biodiesel / castor oil / transesterification / viscosity reduction

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1 Introduction

Castor is a non-edible oil-bearing plant that can grow in marginal land and even arid regions [1]. The crop yields of castor plants as well as the oil content in castor beans has been known to be relatively high in comparison with other oil-producing plants or seeds [2]. In addition, further studies revealed that the low cost of castor oil and many other well-recognized advantages of castor plant cultivation could make castor oil a promising candidate for future biodiesel production [3, 4]. However, the bottleneck in development of castor oil as biodiesel was known as the extremely high viscosities of ricinolein (triglyceride of ricinoleic acid, one of the major components in castor oil) and methyl ricinoleate (ricinoleic acid methyl ester, a transesterification product of castor oil) where the high viscosity would cause incomplete combustion [4, 5]. In our study, a new chemical approach was firstly designed and developed (Schemes 1 and 2) for the

purpose of reducing high viscosity exhibited by castor oil and its transesterification product methyl ricinoleate.

Unlike triglyceride molecules which are abundantly present in most of plant oils, the predominant triglyceride in castor oil, ricinolein (**I** in Scheme 1), that contains three hydroxyl groups on their hydrocarbon chains bears both proton acceptors and proton donors in its molecular structure. Hence, hydrogen bond could be easily formed between hydroxyl groups among ricinolein molecules, in which case the viscosity of castor oil would exhibit 100 times higher than that of soybean oil [6]. During transesterification reaction between ricinolein and methanol, methyl ricinoleate could be generated. This oil-like product was still five times more viscous than methyl oleate (transesterification product of soybean oil) which is currently used as biodiesel [7]. Herein, we developed a strategy to overcome this problem by allowing ricinolein molecules undergo an alcohol oxidation reaction, followed by a transesterification reaction with methanol. It is our expectation that after oxidation and transesterification reaction, both the viscosities of the oxidized ricinolein and the corresponding methyl ester should be reduced due to the oxidation of hydroxyl groups to carbonyl groups that contains no proton donor for hydrogen bonding. Since the synthetic routes involved was straightforward and would not require advanced instruments or any complicated set-up, the existing production line to make biodiesel could be easily adapted to produce a promising and inexpensive biodiesel derived from castor oil.

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Abbreviations: TLC, thin layer ^{Q4}chromatography; TMS, tetramethyl silane

ricinolein (I)

Scheme 1. Our newly designed structural modification of hydroxyl groups in ricinolein to carbonyl groups.

2 Experimental section

2.1 Materials

Castor oil was purchased from American Health Inc. (Ronkonkoma, USA). Soybean oil was obtained from local supermarket. Dess–Martin periodinane was supplied by Sigma–Aldrich Co. (St Louis, USA). Solvents used in our experiments were analytical grade.

2.2 Alcohol oxidation of ricinolein

A mixture containing 0.77 g of castor oil and 1.58 g of Dess–Martin periodinane was dissolved in 30 mL of dichloromethane and reacted at room temperature under darkness for 40 min until ricinolein was found out to be fully oxidized on TLC plate. There was hardly any ester cleavage observed during the oxidation procedure. The reaction mixture was then quenched by adding 100 mL of deionized water, 0.7 g of sodium bicarbonate and 100 mL of 0.1 N sodium thiosulfate. The turbid solution was vigorously agitated until it became transparent. Upon phase separation, anhydrous sodium sulfate was used to dry the organic layer. The organic solvent was then removed through a rotary evaporator to obtain translucent oil with a yield of 85%.

2.3 Transesterification of ricinolein and methanol

A mixture containing 18 mL of castor oil and 1.5% w/w of sodium hydroxide was dissolved in 180 mL of methanol. The reaction was carried out under ambient temperature (23°C) for 1 h under vigorous stirring as reported by Sousa et al. in 2010 [8]. The remaining catalyst was neutralized by dilute sulfuric acid, after which the solution was transferred into a separatory funnel and allowed to stand for 21 h for phase separation. Once the top layer was extracted, the methanol was then removed via rotary evaporation, and then the product was dried by anhydrous sodium sulfate. The product methyl ricinoleate (**III** in Scheme 3) was confirmed by ^1H NMR and ^{13}C NMR using deuterated dimethyl sulfoxide (DMSO- d_6) as the solvent.

2.4 Transesterification of oxidized ricinolein

As shown in Scheme 4, 3.36 g of castor oil was dissolved firstly in 30 mL of dichloromethane. 7.00 g of Dess–Martin periodinane was then added into the solution. The oxidation reaction was carried out at room temperature under darkness for 40 min until ricinolein had been fully oxidized. The suspension was transferred into a conical flask for vigorous shaking in the presence of 3.11 g of sodium bicarbonate, 500 mL of deionized water and 200 mL of 0.1 N sodium thiosulfate. The turbid solution was shook until it became transparent. After phase separation, anhydrous sodium sulfate was used to dry the organic phase. The solvent was then removed with a rotary evaporator to yield translucent and viscous oil (oxidized ricinolein). One point eight zero grams of the translucent oil was subsequently dissolved in a mixture of dichloromethane and methanol in a round bottomed flask followed by adding 1.5% w/w of sodium hydroxide as catalyst. The reaction was carried out under ambient temperature (23°C) for 1 h with vigorous stirring. The remaining catalyst was neutralized by dilute sulfuric acid. The product was washed with water to remove traces of mono-acylglycerol, di-acylglycerol, triacylglycerol, and glycerol. The solution was then transferred into a separatory funnel for phase separation. The stable middle layer was taken out a microemulsion and the volatile organic contents were evaporated to yield slight orange translucent oil

Scheme 2. Illustration of Dess–Martin periodinane oxidation of ricinolein to 12-keto oleic acid triglyceride.

Scheme 3. Illustration of transesterification of ricinolein and methanol.

Scheme 4. Illustration of Dess–Martin periodinane oxidation and transesterification of oxidized ricinolein to oxidized methyl ricinoleate.

(oxidized methyl ricinoleate). The chemical structure of products was confirmed by ^1H NMR and ^{13}C NMR, respectively.

2.5 Transesterification of soybean oil and methanol

As shown in Scheme 5, 18 mL of soybean oil was dissolved in 240 mL mixture of diethyl ether and methanol (1:3, v/v) followed by adding 1.5% w/w of sodium hydroxide as catalyst. The solution was neutralized by diluted sulfuric acid after 1 h reaction at room temperature (23°C) with stirring, which was subsequently washed with water to remove traces of mono-acylglycerol, di-acylglycerol, triacylglycerol, and glycerol. The mixture was transferred into a separatory funnel and kept for 24 h to allow phase separation. After evaporation of organic solvents, soybean oil methyl esters

2.6 Oxidation of ricinolein under solvent-free conditions

Zero point seven grams of Dess–Martin periodinane was added into 2.6 g of castor oil in a 100 mL of beaker without dichloromethane. The reaction took place at 23°C with vigorous stirring for 40 min. The reaction was subsequently quenched by 77 mL of deionized water, 0.3 g of sodium bicarbonate, and 21 mL of 0.1N sodium thiosulfate, followed by phase separation and desiccation.

2.7 NMR characterization

For NMR measurement, 100 μL of the respective oils were dissolved in 450 μL of DMSO- d_6 or CDCl_3 . Tetramethyl silane (TMS) was added as a position standard for the chemical shifts. The ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz on an Avance III 400 NMR spectrometer (Bruker). The numbers of scans done were 8 for ^1H NMR and 100 for ^{13}C NMR.

2.8 Viscosity measurement

Upon oxidation and transesterification reactions, the viscosity of castor oil is expected to fall into the range where it can potentially be used as biodiesel. In order to determine if

Scheme 5. Transesterification of soybean oil and methanol.

there is a significant change in the viscosity, kinematic viscosities of castor oil, oxidized ricinolein, soybean oil, and their corresponding methyl esters were measured at 40°C with Ubbelohde type of viscometers from Thomas Scientific (Cannon Instrument Co.) following standard test ASTM D 445 and ISO 3104. Twenty milliliters of each sample was prepared and added into the storage bulb of the corresponding viscometer, and drawn through the viscometer capillary to the upper bulb by suction. The sample was kept for 1 min to allow small air bubbles to escape, followed by which the sample was released where it would fall vertically between the two marks on the viscometer through the capillary tube. Efflux time of this process was precisely monitored. It is known that the efflux time of liquid, which was taken for a certain volume of such liquid passing through the capillary, is proportional to its viscosity. By using this method, viscosity of all the oils had been measured six times in our studies to obtain an average value. After all, the averaged efflux time was multiplied by viscometer constant of the according viscometer to obtain the final kinematic viscosity.

3 Results and discussion

3.1 Synthesis of oxidized ricinolein from castor oil and comparison of viscosity

Soybean oil is widely used to produce biodiesel through one-step transesterification reaction with methanol [9, 10]. However, castor oil possesses such a high viscosity that limits its utility as precursor for biodiesel [11]. In addition, during our investigation, the viscosity of methyl ricinoleate

(**III**) which was produced by one-step transesterification of castor oil was four times as high as the viscosity of soybean oil methyl esters (see Table S1 in Support Information) and also way above the ideal range of the viscosity for biodiesel [12]. As a result, certain modification should be made to ricinolein, the chief constituent in castor oil, in order to facilitate its use as a new precursor of biodiesel. Here we demonstrated in our studies that oxidation of hydroxyl groups to carbonyl groups on ricinolein was feasible and the product was accordingly characterized by ^1H NMR and ^{13}C NMR. In ^1H NMR spectrum of oxidized ricinolein (**II** in Scheme 2), chemical shifts were at 5.48 ppm (d, $J=5.8$ Hz, 2H, $-\text{CH}=\text{CH}-$), 5.19 ppm (t, $J=4.4$ Hz, 1H, $-\text{CH}_2\text{CHOCO}-$), 4.23 ppm (dd, $J=11.9$ Hz, 2H, $-\text{CHCH}(\text{H})\text{OCO}-$), 4.07 ppm (dd, $J=11.9$ Hz, 2H, $-\text{CHCH}(\text{H})\text{OCO}-$), 3.08 ppm (d, $J=5.8$ Hz, 6H, $=\text{CHCH}_2\text{CO}-$), 2.35 ppm (t, $J=7.4$ Hz, 6H, $-\text{CH}_2\text{COCH}_2\text{CH}_2-$), 2.24 ppm (t, $J=5.4$ Hz, 6H, $-\text{OCOCH}_2-$), 1.95 ppm (d, $J=6.8$ Hz, 6H, $-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-$), 1.20 ppm (m, 42H, $-(\text{CH}_2)_n-$), 0.80 ppm (t, $J=7.0$ Hz, 9H, CH_3-C) (Figure S4). And in ^{13}C NMR spectrum of oxidized ricinolein (**II**), the characteristic signals show at 209.02 ppm ($-\text{CH}_2\text{COCH}_2-$), 173.09 ppm ($-\text{OCO}-$), 133.36 ppm ($=\text{CHCH}_2\text{CO}-$), 121.03 ppm ($-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-$), 68.85 ppm ($-\text{CHOCO}-$), 62.01 ppm ($-\text{CH}_2\text{OCO}-$), 42.27 ppm ($=\text{CHCH}_2\text{CO}-$), 41.57 ppm ($=\text{CHCH}_2\text{COCH}_2-$), 33.91 ppm ($-\text{OCOCH}_2-$), 13.97 ppm (CH_3-C). According to NMR data, we could infer that hydroxyl group of castor oil has been converted to carbonyl group.

The kinematic viscosity of oxidized ricinolein (**II**) was greatly reduced (by 92% in contrast with castor oil) and it was verified to be almost as low as that of grape seed oil and

soybean oil (see Table 1) [13]. Therefore, it is our anticipation that oxidized ricinolein could serve as an alternative promising biodiesel precursor, similar to soybean oil which has been widely used for long period of time.

3.2 Comparison between viscosity of oxidized methyl ricinoleate and existing biofuel

Structures of methyl esters from oxidized ricinolein were first characterized by ^1H NMR and ^{13}C NMR, respectively. The peaks of oxidized methyl ricinoleate (**IV** in Scheme 4) in proton NMR are at $\delta = 5.49$ ppm (d, $J = 6.8$ Hz, 2H, $-\text{CH}=\text{CH}-$), 3.60 ppm (s, 3H, $-\text{COOCH}_3$), 3.09 ppm (d, $J = 5.9$ Hz, 2H, $=\text{CHCH}_2\text{CO}-$), 2.36 ppm (t, $J = 7.4$ Hz, 2H, $-\text{COCH}_2\text{CH}_2-$), 2.24 ppm (t, $J = 7.5$ Hz, 2H, $-\text{OCOCH}_2-$), 1.96 ppm (q, $J = 6.9$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-$), 1.24 ppm (m, 14H, $-(\text{CH}_2)_n-$), 0.81 ppm (t, $J = 6.9$ Hz, 3H, CH_3-C). The chemical shift values in carbon NMR spectrum of oxidized methyl ricinoleate (**IV**) are 209.06 ppm ($-\text{CH}_2\text{COCH}_2-$), 174.13 ppm ($-\text{OCO}-$), 133.41 ppm ($=\text{CHCH}_2\text{CO}-$), 121.00 ppm ($-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}-$), 51.33 ppm ($\text{CH}_3\text{OCO}-$), 42.27 ppm ($=\text{CHCH}_2\text{CO}-$), 41.57 ppm ($=\text{CHCH}_2\text{COCH}_2-$), 33.97 ppm ($-\text{OCOCH}_2-$), 13.95 ppm (CH_3-C).

Since the viscosity of oxidized ricinolein (**II**) was similar to the chief constituent in soybean oil, it is our expectation that oxidized castor oil would also be a source of biodiesel. Biodiesel is known to be produced by transesterification of soybean oil and methanol [9, 10]. The same transesterification reaction was carried out in our study to the oxidized ricinolein (**II**) for the purpose of determining whether oxidized methyl ricinoleate (**IV**) would have the same desired properties when it used as biodiesel. Our results showed that the viscosity of oxidized methyl ricinoleate was on the same level of some existing biofuels (Table 2 and [Supporting Information](#)) and within the ideal viscosity range of biodiesel, as well [12].

3.3 Correlation between viscosity of partially oxidized ricinolein and degree of oxidation

After oxidation, viscosity of oxidized ricinolein (**II**) was reduced considerably in comparison to castor oil. In some

Table 1. Kinematic viscosities of grape seed oil, soybean oil, castor oil, and our newly synthesized oxidized ricinolein at 40°C

Name of oils	Kinematic Viscosity (mm^2/s)
Grape seed oil	52.8 ^a
Soybean oil	36.1
Castor oil	560.3
Oxidized ricinolein	40.8

^aKinematic viscosity of grape seed oil at 25°C [13].

Table 2. Kinematic viscosity of existing [O6](#)biofuel and oxidized methyl ricinoleate measured at 40°C

Name of biofuels	Kinematic viscosity (mm^2/s)
Existing biofuel (methyl esters transesterified from soybean oil)	4.1
Oxidized methyl ricinoleate	3.9

cases, researchers would expect to synthesize biofuel with a controllable range of viscosity, which could be achieved by manipulation of viscosity of partially oxidized ricinolein that acts as precursor of biofuel. The viscosity of oxidized ricinolein is related to degree of oxidation. Here, to further explore the correlation between viscosity of castor oil and its degree of oxidation, the amount of oxidant, Dess–Martin periodinane, added into the reaction system was precisely controlled. The degree of oxidation was obtained from integrated ^1H NMR spectrum of castor oil under oxidation. It was shown in our results that higher degree of oxidation to castor oil will cause a decrease in its viscosity. Thus, as shown in Table 3 and Fig. 1, viscosity of the mixture of ricinolein (**I**) and oxidized ricinolein (**II**) is inversely related to the degree of oxidation.

3.4 Investigation of castor oil oxidation under solvent-free conditions

Our previous oxidation reaction of castor oil was carried out in the presence of dichloromethane solvent following the procedures stated in recent studies [14]. As an extension of our previous work, the feasibility of solvent-free oxidation, a more economical and environmental friendly condition, was thus investigated in our following studies. The degree of oxidation from castor oil to the ketone-containing triacylglycerides could be obtained by corresponding ^1H NMR spectrum. Compared with the reaction taken place in dichloromethane, 42% of oxidized ricinolein (**II**) was produced under solvent-free condition (see Figure S1 for details). It is our belief that the incompleteness of reaction was due to insufficient interaction between the ricinolein in liquid phase and the oxidizing agent in solid phase.

Table 3. Correlation between viscosity of partially oxidized ricinolein and its degree of oxidation measured at 40°C

Proportion of oxidized ricinolein in the mixture of ricinolein and oxidized ricinolein (%)	Kinematic viscosity (mm^2/s)
0	560.3
20	381.2
40	265.5
60	161.3
80	97.5
100	40.8

Figure 1. Correlation between viscosity of partially oxidized ricinolein and the proportion of oxidized castor oil.

3.5 Effect of reaction order on the viscosity and yield of oxidized methyl ricinoleate

Oxidized methyl ricinoleate (**IV**) was generated through oxidation of castor oil followed by transesterification with methanol. Here, an alternative experimental procedure was conducted to identify whether the viscosity could be influenced by altering the reaction order in which transesterification was conducted before oxidation. Castor oil was firstly transesterified with excess methanol using sodium hydroxide as catalyst. The transesterified product was then characterized by using ^1H NMR and ^{13}C NMR as shown in Figs. S2 and S3. Oxidation reaction was subsequently performed in the presence of Dess–Martin periodinane. The chemical structure was further analyzed by ^1H NMR and ^{13}C NMR, and the yield of oxidized product was confirmed to be the same as the product obtained from the previous procedures. In addition, kinematic viscosity and density were found to be similar as well and thus we could infer that the order in which the two reactions are carried out does not affect the production of biodiesel.

4 Conclusions

In conclusion, a novel ketone-containing triglyceride has been designed and accordingly synthesized in our current study. This newly designed triglyceride which was oxidized from castor oil was proved to possess promising properties as an alternative biofuel precursor. Economical and efficient synthetic routes have been subsequently examined and

developed during our investigations. Furthermore, the chemical structures as well as the physical properties of our new biofuels have been well characterized. Compared to soybean oil that has already been utilized as a source to produce biodiesel, our newly designed 12-keto oleic acid triglyceride possesses reasonable viscosity, which is one of the limiting factors as to why castor oil by itself was not an ideal biodiesel candidate. In addition, our findings demonstrate that the viscosities of 12-keto oleic acid methyl ester and methyl esters produced from soybean oil are similar, which show its potential as an ideal biodiesel. Above all, we report here our novel design and development of a ketone-containing triglyceride which could have promising applications in bioenergy-related issue in the near future.

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