Green Organocatalytic Process for Production of Methyl Ricinoleate from Castor Oil

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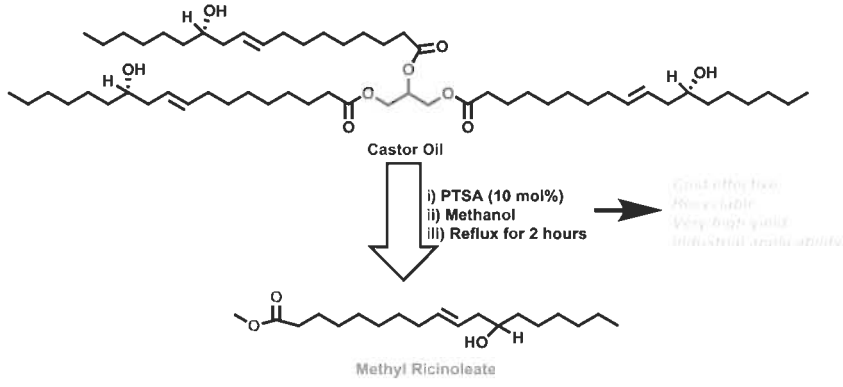
ABSTRACT

Castor oil-a triglyceride of various fatty acids contains 85-95% of Ricinolic acid. Organocatalytic one pot robust and efficient process for large scale production of industrially important Methyl Ricinoleate from castor oil in 50 g scale level has been developed. 10 mol% *Para*-toluene sulfonic acid (PTSA) has been used as the recyclable organocatalyst. This cost effective and green protocol produces 89.63% yield of Methyl Ricinoleate and can be recyclable up to four times without much change in catalytic activity.

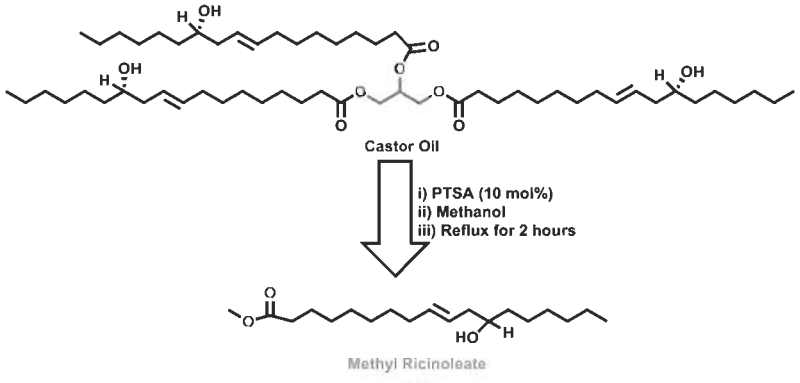


INTRODUCTION

The growing interest on cost effective and handy large scale industrial production of Methyl Ricinoleate (MR) from castor oil serves an area of immense possibilities in the competitive global market due to major demand of the product in oil and cosmetic industries. Castor oil-a triglyceride of various fatty acids (ricinoleic acid constitutes 85-95%) is one of the versatile feedstock of various industrially important chemicals. Besides ricinolic acid, castor oil contains 4.2% linoleic acid, 3% oleic acid, 1% stearic acid, 1% palmitic acid, 0.7% dihydroxy stearic acid, 0.3% eicosanoic acid and 0.2-0.5% other fatty acids.[1-4] Presence of an 18-carbon hydroxylated fatty acid *viz* Ricinolic acid with one double bond makes castor oil as a unappreciated asset for industrial productions of many value added Alkyl Ricinoleates. Methyl Ricinoleate ((*R*)-12-Hydroxy-*cis*-9-octadecenoic acid methyl ester), the transesterification product of castor oil is the privileged chemical of promising worldwide applications such as hydraulic fluid, perfumery chemicals, gear oil, cutting oil, dispersing agent, anti rusting agent, plasticizer etc. because of remarkably lower viscosity, higher cetane number and lower cloud and pour point properties.[1-4] Production of MR from castor oil can be performed by base, acid, ionic liquid and enzyme catalyzed reactions.[1] To date, most of the reported literatures for the industrial production of MR from castor oil involves the alkali or base catalyzed transesterification reactions.[1] Use of homogeneous base catalyst for transesterification of castor oil suffers from serious drawbacks like undesirable side products from saponification reaction which creates serious problem on catalyst/product separation and finally lowers the yield of methyl ester significantly. Ionic liquid and enzyme catalyzed reactions are not commercially viable mainly due to the higher prices as well as the availability. Low reaction rate and lower catalytic activity are also few drawbacks of enzyme catalyst in process development. In this instance solid acid catalyst, mainly Bronsted and homogeneous Lewis acids, offer outstanding advantages on catalyst/product separation, eliminating

corrosion, toxicity and environmental problems.[1-5]

Usage of organo acid as catalyst for successful conversion of castor oil to MR in 50 g batch level is the first green process that we reported herewith.10 mol% of *para*-toluene sulfonic acid (PTSA) was used as recyclable cost effective organocatalyst for the synthesis of MR (89.63%) from castor oil in refluxing methanol under oxygenated atmosphere (**Scheme 1**).

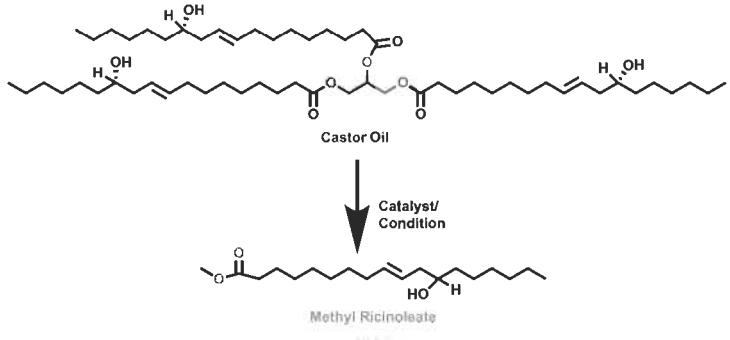


Scheme 1: Synthesis of Methyl Ricinoleate from castor oil using 10 mol% PTSA as organocatalyst.

RESULTS AND DISCUSSION

We initiated our study by choosing different organoacids as catalyst for the synthesis of MR from castor oil using methanol as the solvent. Initially reaction was studied in 1 g batch level. Various organoacids like boronic acid, *para*-toluene sulfonic acid (PTSA), *para*-nitrobenzenesulfonic acid (NBSA) etc were employed in the synthesis of MR (**Entries 1-3, table 1**). Again, 10 mol% of each organoacid catalyst was used in optimization study. After optimization study, it was found that PTSA is the most exclusive catalyst for successful conversion of castor oil to MR (900 mg, 89.63% yield; **entry 2, table 1**). Further study on catalyst loading (especially PTSA) confirms that 10 mol% was the most optimized amount for highest conversion of castor oil to MR (**Entries 2&4, table 1**). Hence the optimized condition (**Entry 2, table 1**) was: castor oil (1 g), PTSA (18.5 mg, 10 mol %), methanol, 65 °C, 2 h, oxygenated atmosphere.

Table 1: Optimization studies on conversion of castor oil to Methyl Ricinoleate[a]



Entry	Catalyst	loading	Solvent	Time/Temp	Yield (%)[b]
1	Boronic acid	10 mol%	MeOH	3h/65 °C	10
2	**PTSA**	**10 mol%**	**MeOH**	**2h/65 °C**	**89.63**
3	NBSA	10 mol%	MeOH	3h/65 °C	45
4	PTSA	5 mol%	MeOH	3h/65 °C	60

[a]Optimized condition: castor oil (1 g), PTSA (18.5 mg, 10 mol%), MeOH, 65 °C, 2 h, oxygenated atmosphere, [b]Yield percentage determined by gas chromatography.

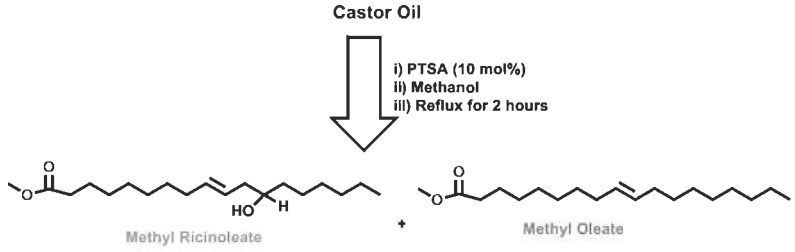
Using this optimized condition we subsequently increased the batch level up to 50 g and 90% (44.76 g) isolated yield of MR was obtained without any difficulty. During our study, we also tried to compare the catalytic activity of the optimized organocatalyst, PTSA with a few available acidic catalysts as shown in **table 2**. A wide variety of acidic catalyst like $AlCl_3.6H_2O$, AcOH, Amberlite, Activated clay–Montmorillonite, Benzoic acid and $[Sn(HPO_4)_2 \cdot H_2O]$ nanodisks[6] (**Entries 2-7, table 2**) have been used during the course of the reaction. From comparison **table 2** it can be concluded that PTSA has the highest activity towards the conversion of castor oil to MR under the mentioned conditions.

Table 2: A comparison of different available acid catalysts in the conversion of castor oil to Methyl Ricinoleate[a]

Entry	Catalyst	loading	Solvent	Time/Temp	Yield (%)[b]
1	**PTSA**	**10 mol%**	**MeOH**	**2h/65 °C**	**89.63**
2	$AlCl_3.6H_2O$	10 mol%	MeOH	3h/65 °C	65
3	AcOH	10 mol%	MeOH	3h/65 °C	35
4	Amberlite resin	10 mol%	MeOH	3h/65 °C	5
5	Activated clay - montmorillonite	10 mol%	MeOH	3h/65 °C	20
6	Benzoic acid	10 mol%	MeOH	3h/65 °C	0
7	$[Sn(HPO_4)_2 \cdot H_2O]$ nanodisks	10 mol%	MeOH	3h/65 °C	25

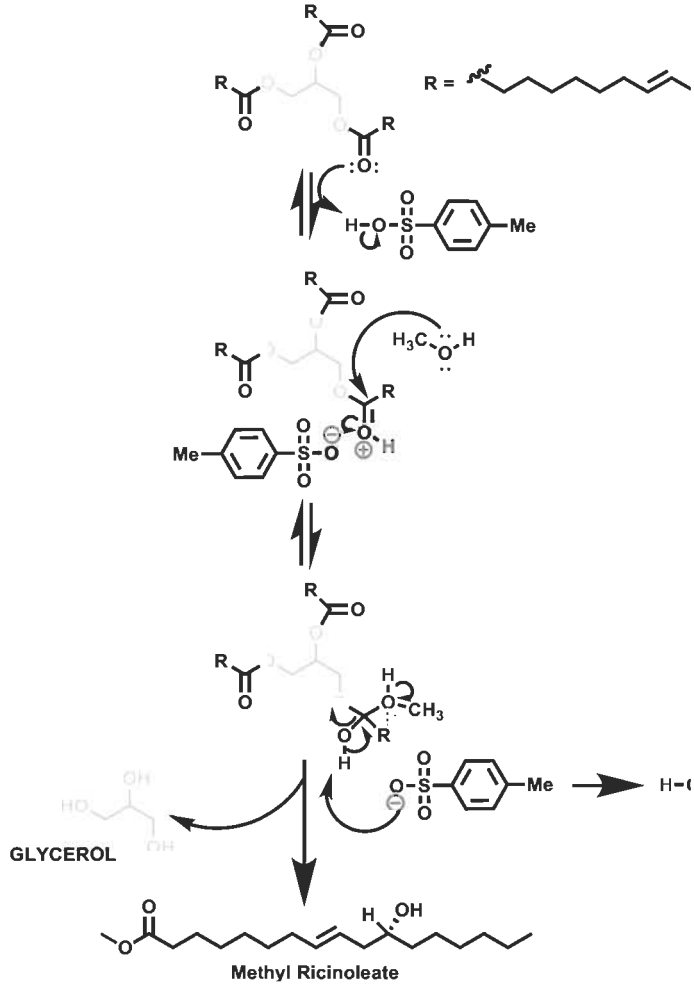
[a]Optimized condition: castor oil (1 g), PTSA (18.5 mg, 10 mol%), MeOH, 65 °C, 2 h, oxygenated atmosphere, [b]Yield percentage determined by gas chromatography

Since castor oil contains Oleic acid and other fatty acids in minor amounts like stearic acid, palmitic acid, dihydroxy stearic acid, eicosanoic acid etc. Henceforth, along with methyl ester of ricinolic acid, there is the possibility of generation of methyl ester of the above mentioned acids in transesterification of castor oil. In this context, we observed 6.82% yield of Methyl Oleate (MO) along with 89.63% yield of MR using this green catalytic system (**Scheme 3**).

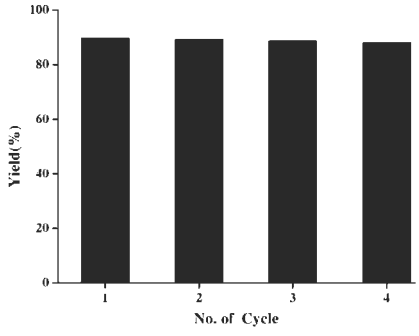


Scheme 3: Synthesis of Methyl Ricinoleate along with Methyl Oleate from castor oil using PTSA.

PTSA catalyzed transesterification mechanism of castor oil has been discussed in **scheme 4**. Through this converted to MR by the same mechanism during the course of the reaction at a time. Transesterification of three ester groups of ricinolic acid of castor oil (1 equivalent) resulted 3 equivalents MR and 1 equivalent glycerol. Generated glycerol reaction mechanism we showed the PTSA catalyzed transesterification of one ester group of ricinolic acid to MR in methanol solvent. The other two ester groups also with PTSA can be recyclable further for transesterification of castor oil. The recyclability of the catalyst (**Scheme 5**) was performed up to 4 times without any significant loss of the yield percentage.



Scheme 4: Transesterification mechanism of castor oil to generate Methyl Ricinoleate using PTSA as organo catalyst.



Scheme 5: Recyclability study of the organocatalyst in the production of MR from castor oil.

EXPERIMENTAL SECTION

Castor oil was obtained from local grocery shop (Dabur, 99%). Methanol (99.8%), *Para* toluene sulfonic acid (PTSA) and all other organocatalysts were purchased from Sigma Aldrich, USA and were used without any further purification. All NMR (^{1}H, ^{13}C) spectra were recorded on a Bruker Avance DPX 500 MHz spectrometer. Chemical shifts were reported on the δ scale (ppm) downfield from TMS (δ = 0.0 ppm) using the residual solvent signal at δ = 7.26 ppm (^{1}H) or δ = 77 ppm (^{13}C) as an internal standard. Spectrum 100 FTIR-Spectrometer (resolution: 4 cm^{-1}) was used for recording IR data. Product was purified by column chromatography using silica gel (60-120 mesh) and ethyl acetate/petroleum ether.

Experimental procedure for the synthesis of MR from castor oil.

Synthesis of MR from castor oil was studied in 50 g scale level. 50 g refined castor oil and 550 mg PTSA (10 mol %) were added in 250 mL round bottom flask containing 100 mL distilled methanol. The reaction mixture was stirred for 3 hours at 65 °C under open atmosphere. After completion of the reaction (monitored by TLC) the solvent was distilled off under reduced pressure. The light brown solution was treated with 100 mL petroleum ether (40-60 °C), stirred for 15 minutes and finally kept overnight so that clear partition of the two liquid layers took place. The petroleum ether layer (upper layer) was separated through separating funnel and then distilled off the solvent to get mixture of MR and MO. Separation and purification of the products were carried out by column chromatography and finally got 44.76 g MR (yield: 89.63%) and 6.82% yield of MO. The bi-product glycerol with PTSA was reused for the second batch again in 50 g level.

CONCLUSION

In summary, we have developed a green process for the large scale industrial production of value added product Methyl Ricinoleate from castor oil in 89.63% yield. This organocatalytic one pot process is highly efficient, cost effective and environmentally benign. The organocatalyst can be recyclable up to four times without much change in catalytic activity.

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