Synthesis and Characterization of Biodegradable plastic monomer from Castor oil Using $FeCl_3$ as an Eco-Friendly and Inexpensive Catalyst

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Abstract: **The development of green chemicals from sustainable biomass is a significant advancement in reducing dependence on fossil fuels and minimizing the environmental impact of chemical production. This study presents the efficient synthesis of 1,11-undecanedioic acid from 11-hydroxyundecanoic acid, which was derived from ricinoleic acid, a key fatty acid in castor oil. The synthesis employed a novel oxidation method using ferric chloride ($FeCl_3$) in aqueous sodium hypochlorite to convert ω-hydroxycarboxylic acids into α, ω-dicarboxylic acids an essential step in producing these valuable compounds.**

This method offers a promising alternative to conventional synthesis approaches that often require harsh conditions, high temperatures, or expensive reagents. The use of renewable biomass feedstocks, combined with mild reaction conditions, reduces energy consumption and greenhouse gas emissions while enhancing the sustainability of chemical production. Furthermore, the resulting α, ω-dicarboxylic acids exhibit improved properties, including enhanced biodegradability and biocompatibility, which are crucial for eco-friendly applications.

The study demonstrates that renewable biomass can be a viable, sustainable feedstock for the chemical industry, opening new pathways for producing high-value chemicals with reduced environmental impact. By developing and optimizing green oxidation methods, this approach contributes to the ongoing shift toward sustainable chemical manufacturing. The synthesis of 1,11-undecanedioic acid using environmentally friendly techniques highlights the potential of integrating renewable resources and innovative chemistry to drive the future of green chemical production.

Key words: **Green chemistry, sustainable biomass, renewable feedstock, 1,11-undecane-dioic acid, 11-hydroxyundecanoic acid, ricinoleic acid, castor oil, oxidation methods, ferric chloride, sodium hypochlorite, α,ω-dicarboxylic acids,**

1. INTRODUCTION

Biopolymers are gaining overwhelming interest and recognition worldwide due to health safety and environmental concerns. The development of sustainable chemicals, bioplastics, pharmaceuticals, and cosmetics from renewable biomass sources is an emerging trend aimed at reducing dependence on fossil fuels and petrochemicals. Among these materials, thermoplastic elastomers (TPEs) have gained attention due to their ability to mimic the properties of both plastics and rubber while offering biodegradability.[1] In particular, thermoplastic polyamides exhibit valuable characteristics such as enhanced toughness, strength, thermal stability, and biocompatibility, making them suitable for biomedical applications. Given the environmental concerns associated with petrochemical-derived materials, TPEs present a promising alternative.

Vegetable oils represent one of the most promising classes of renewable resources for the synthesis of sustainable monomers. Medium-chain (C7 to C13) α,ω-dicarboxylic acids and ω-aminocarboxylic acids serve as crucial building blocks in the production of hydraulic fluids, lubricants, pharmaceuticals, plasticizers, and thermoplastic elastomers (TPEs).[2] Abundant oils such as castor oil, soybean, peanut, coconut, and sunflower oils contain long-chain fatty acids, making them valuable precursors for monomers due to their renewability and beneficial properties.[3] These oils can be chemically transformed into biodegradable plastic monomers using eco-friendly methods.[4] Notably, castor oil, which consists of approximately 90% ricinoleic acid, has been extensively utilized for the production of biodegradable plastic monomers (Figure-1, 2).[5]

LITERATURE SURVEY

Various synthetic approaches have been explored to produce these intermediates, including both chemical and biotransformation routes. However, conventional chemical synthesis methods often require harsh reaction conditions, including high temperatures, high pressures, toxic oxidants, and strong acids, making them environmentally and economically unfeasible. For instance, the synthesis of 11-aminoundecanoic acid from ricinoleic acid methyl ester involves the use of hydrobromic acid (HBr) at extreme temperatures of 450–500°C.[6] Although these methods may improve yield, they remain unsustainable.

Alternatively, biotransformation processes using microorganisms such as Candida tropicalis have been explored as greener methods for producing these intermediates.[7,8] However, these processes suffer from limitations, including low yields, challenges in the availability of C. tropicalis, which is a known pathogenand reliance on nonane, a petrochemical-derived feedstock.[8] To overcome these challenges, future research should focus on developing more efficient, scalable, and environmentally friendly production methods, such as improved biocatalysis or green chemistry-based synthesis, to facilitate the sustainable production of bioplastics and related materials.

Enzymatic biosynthesis of 1,11-undecanedioic acid (7), 11-hydroxyundecanoic acid(6), and 11-aminoundecanoic acid from renewable biomass has been explored as a sustainable alternative to traditional chemical methods. However, these biosynthetic processes often suffer from low product yields due to the high toxicity of intermediates or final products toward host cells or enzymes. Industrial-scale production of such valuable raw materials requires efficient methods that operate under mild conditions.

To address these limitations, a chemo-enzymatic approach for the synthesis of 11-hydroxyundecanoic acid (6), and 1,11-undecanedioic acid (7), from ricinoleic acid, the major fatty acid component of castor oil, has been recently developed.[8] This method involves a biocatalytic transformation of ricinoleic acid into an ester intermediate via 12-ketooleic acid in a two-step process using recombinant Escherichia coli cells expressing two key enzymes. An alcohol dehydrogenase (ADH) from Micrococcus luteus catalyses the oxidation of the hydroxyl group in ricinoleic acid to form a ketone (Figure-1), which is then further oxidized by Baeyer-Villiger monooxygenase (BVMO) from Pseudomonas putida KT2440, resulting in the formation of an ester intermediate. Subsequent hydrogenation of the olefin functionality of this intermediate using hydrogen gas in the presence of Raney®-Ni, followed by hydrolysis with hydroxide, produces 11-hydroxyundecanoic acid.[8]

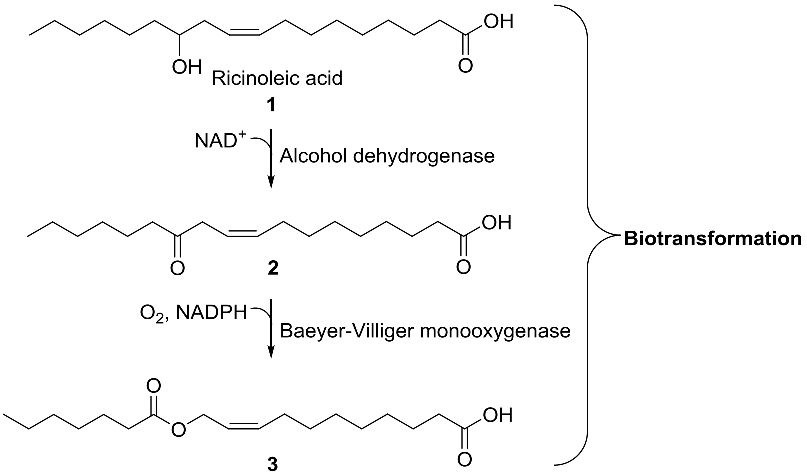
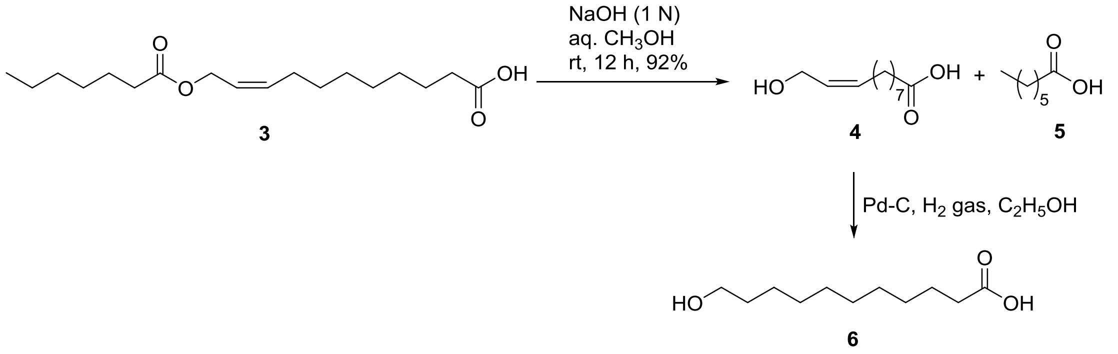


Figure-1. Designed biotransformation pathway of converting ricinoleic acid in *E. coli* cells to ester intermediate (3).

A similar chemo-enzymatic transformation strategy has been successfully applied to oleic acid, converting it into azelaic acid (1,9-nonanedioic acid) via the ester intermediate 9-(nonanoyloxy)nonanoic acid.[9] In addition to these efforts, further research has focused on developing the most efficient, eco-friendly, and cost-effective oxidation methods for converting ω-hydroxycarboxylic acids into α,ω-dicarboxylic acids, which remain challenging for large-scale synthesis and industrial applications. Additionally, ester intermediates have been modified to yield ω-hydroxycarboxylic acids and ω-aminocarboxylic acids, which serve as valuable building blocks for the production of bioplastics and bioactive compounds. As a part of our research investigation for the development of medium chain α,ω-dicarboxylic acids especially 1,11-undecanedioic acid (7) we have been exploring and optimized of the synthesis of 11-hydroxyundecanoic acid from (Z)-11-(heptanoyloxy)undec-9-enoic acid (3)[unpublished work] (Scheme-1).



Scheme-1. Hydrolysis of (Z)-11-(heptanoyloxy)undec-9-enoic acid (3) and Synthesis of 11-hydroxyundecanoic acid (6).

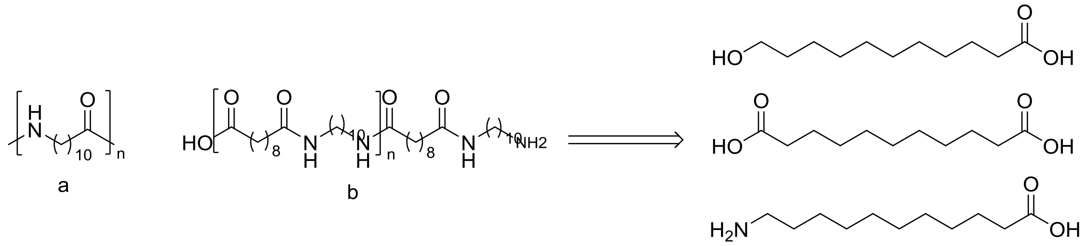


Figure 2. Chemical structure of (a) polyamide 11 (Rilsan) and (b) polyamide 10.10 (Rilsan T)

STATEMENT OF THE PROBLEM

The development of green processes to produce fatty acid derivatives like 1,11-undecanedioic acid from renewable biomasses is highly desirable. This study reports the efficient synthesis of 1,11-undecanedioic acid, from 11-hydroxyundecanoic acid (6), which was derived from ricinoleic acid, a major fatty acid constituent of castor oil. The synthesis of these valuable chemicals was achieved through the development of novel oxidation methods using $FeCl_3$ in aqueous sodium hypochlorite, which will be discussed here. This synthesis route offers a promising alternative to existing method.

HYPOTHESIS

We hypothesize the large-scale synthesis of 1, 11-undecanedioic acid from 11-hydroxy undecanoic using $FeCl_3$ in aqueous sodium hypochlorite under mild conditions which intern generate the powerful ferric oxy hydroxide at low temperatures.

AIMS &OBJECTIVES

To synthesize 1,11-undecane dioic acid from 11-hydroxy undecanoic acid which was derived from ricinoleic acid a major fatty acid constituent of castor oil. To synthesize this important biodegradable plastic monomer through development of novel oxidation method in sodium hypochlorite using eco-friendly and inexpensive catalyst $FeCl_3$ under mild reaction conditions.The main objective of our project is to demonstrate the catalytic efficiency, environmental and economic advantages of $FeCl_3$ as catalyst for oxidation reactions. To characterize the formed monomer through spectroscopic studies.

RESEARCH METHODOLOGY

Conventional oxidation methods in organic synthesis are often undesirable due to the large amounts of toxic-metal-containing waste they produce, as well as the necessity of using reagents in excess to ensure reaction completion. While these methods are generally selective and reliable, they pose significant environmental concerns. Industrial oxidation processes frequently employ oxygen or hydrogen peroxide with heterogeneous catalysts, but these conditions can lead to over-oxidation, yielding carbon dioxide and water. Nonetheless, heterogeneous systems remain valuable in the large-scale production of commodity chemicals, where modest selectivity is offset by the low cost of oxidants, typically oxygen gas. However, for fine chemical synthesis involving complex and expensive alcohols, a more selective approach is preferable.

We have developed an effective, practical, and inexpensive method for oxidizing alcohols, aldehydes, and α,β-unsaturated carboxylic acids using readily available iron(III) salts and commercial bleach. The ferric oxide hydroxide formed acts as a selective and high-yielding heterogeneous catalyst,[10]efficiently converting both aliphatic and aromatic substrates to their expected products.Ferric chloride ($FeCl_3$) could form ferric oxyhydroxide in reaction with bleach (sodium hypochlorite, NaOCl) which intern catalyse the oxidation of primary alcohols with an excess amount of commercial bleach to carboxylic acids. Initially we have planned and conducted several experiments with different primary alcohols (Table-1)such as benzyl alcohol. Later the optimised reaction conditions were utilised to get the desire 1,11-un decanoicacid with promising yields.

MATERIALS & METHODS

General Experimental Methods

Chemical reagents were purchased from commercial sources and used without further purification unless noted otherwise. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness), visualization was undertaken with UV light and/or by spraying with a 5% solution of phosphomolybdic acid followed by charring with a heat gun. ^{1}H-NMR spectra were recorded on a Bruker AVANCE III 3000 (300 MHz) FT-NMR spectrometer. Chemical shifts were reported in ppm with tetramethylsilane as an internal standard.

Oxidation of 11-Hydroxyundecanoic Acid (6) to 1,11-Undecanedioic Acid (7) using $FeCl_3$ chloride salt in aqueous sodium hypochlorite

To a stirred solution of $FeCl_3$ (20 mg, 0.12 mmol) in H_2O (1 mL), 11-hydroxyundecanoic acid6 (500 mg, 2.47 mmol) and dichloromethane CH_2Cl_2 (2 mL) were added. Cold aqueous NaOCl (ca. 10%, 15 mL) was added to the reaction mixture over 2 min at 0 °C. The resulting mixture was stirred for 2 h at 0 °C and 2 h at RT. The reaction mixture was then treated with 10% $Na_2S_2O_3$ (10 mL) and stirred for 10 min at RT. Then, it was fully acidified with 1N HCl. The reaction mixture was thoroughly extracted with 10% methanol in CH_2Cl_2 or ethyl acetate (3 X 30 mL). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford 1,11-undecanedioic acid (7) (500 mg, 94%) in an almost pure form as a white solid. If necessary, the final compound could be further purified by recrystallization.^{1}H NMR (300 MHz, DMSO-d_6) δ 2.17 (t, *J* = 6.6 Hz, 4H), 1.49−1.44 (m, 4H), 1.23 (m, 10H).

Similar experiments were conducted with different alcohols (Table-1) with 2.5-5 mol.% of $FeCl_3$ will be discussed in upcoming sections.

RESULTS AND DISCUSSIONS

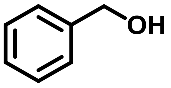
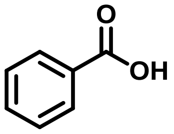
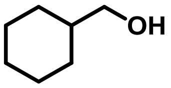
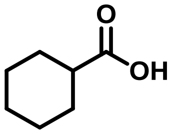
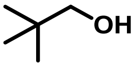
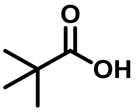
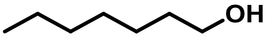
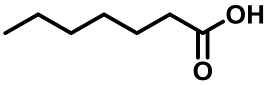
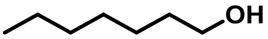
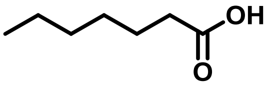
These reactions can often be performed without organic solvents, significantly reducing the environmental impact associated with traditional oxidative transformations, which typically generate substantial organic and toxic metal waste. Initially, benzyl alcohol was dissolved in CH_2Cl_2 and treated with 2.5 mol% ferric chloride in 5 mL of NaOCl solution at 0°C to room temperature for 4 hours. As expected, we successfully isolated the corresponding benzoic acid with an 85% yield. The formation of the product was confirmed through hydrogen nuclear magnetic resonance spectroscopy (^{1}H-NMR) analysis.

Next, we prepared a series of primary and secondary alcohols based on the above experiment. We further optimized the reaction by increasing the catalyst loading to 5 mol% with hydroxyl hexane (entry 5), which resulted in an 82% yield. Additionally, we tested the same reaction under solvent-free conditions, obtaining a promising isolated yield of 69% (entry 5). Under standard reaction conditions, primary alcohols were smoothly oxidized to the corresponding carboxylic acids following acidic workup. The isolated yields for these reactions ranged from 72% to 89%, with high initial purities, indicating minimal by-product formation (Table 1). Since these alcohols are liquid and/or water-soluble, similar outcomes were anticipated in the absence of organic solvents. Indeed, solvent-free conditions resulted in comparable yields and gas chromatography (GC) purities, demonstrating that these substrates can be efficiently oxidized without the need for organic solvents. Building on these experiments, we focused on the synthesis of 1,11-undecanedioic acid monomer. Initially, 11-hydroxyundecanoic acid was oxidized under optimized conditions with $FeCl_3$ (2.5 mol %) and NaOCl solution in H_2O/CH_2Cl_2, yielding the diacid product in 82% yield. Increasing the $FeCl_3$

concentration to 5 mol% under similar reaction conditions resulted in a 94% isolated yield of a fairly pure product. This result is excellent compared to previously reported methods.

These oxidations were carried out using cost-effective reagents such as household bleach (NaOCl) in an aqueous medium, with or without an organic solvent, offering an attractive green strategy with enhanced efficiency and practicality. Oxidation reactions conducted in small volumes of other organic solvents, such as acetonitrile, also performed well. Interestingly, compound 6 was efficiently oxidized in water alone to produce the diacid product (8) in very good yield (entry 4, Table 2).

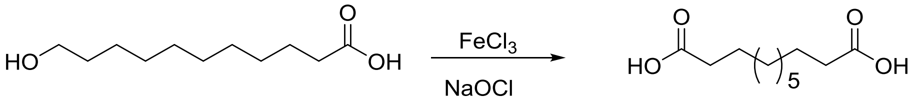
Table 1. Oxidation of Primary Alcohols under Standard Reaction Conditions.

entry	Substrate	Product	Isolated yield
1			85
2			89
3			85
4			72
5[b]			69/82[c]

[a]Standard reaction conditions: 2.5 mol. % of $FeCl_3$, 0.82 mmol alcohol, 1 mL of CH_2Cl_2, 5 mL of ~5% aq. NaOCl, 2 h at 0 °C, then 2 h at 20 °C.[b] Organic solvent-free conditions: same, except no CH_2Cl_2.[c] The isolated products were at least 97% pure and same reaction condition expect 5 mol. % of $FeCl_3$.

We further utilized the above-optimized method for the synthesis of 1,11-undecanedioic acid monomer from ω-hydroxy carboxylic acids, as described in the previous section. Additionally, we conducted a small set of yield optimization studies, as outlined in Table 2. Among the oxidation reactions of ω-hydroxy carboxylic acids developed so far, we believe this method represents one of the most eco-friendly, cost-effective, and practical approaches for the large-scale synthesis of 1,11-undecane-dioic acid under mild conditions at room temperature.

Table 2. Synthesis of 11-undecanedioic acid



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7

entry	Solvent Mixture	Catalyst	Temp/Time	Yield(%)
1	H_2O/DCM	$FeCl_3$ (2.5 mol%), NaOCl (15 mL)	0 °C/2 h → rt/2 h	82
2	H_2O/DCM	$FeCl_3$ (5 mol%), NaOCl (15mL)	0 °C/2 h → rt/2 h	94

3	H_2O /ACN	$FeCl_3$(5 mol%), NaOCl (15mL)	0 °C/2 h → rt/2 h	94
4	H_2O	$FeCl_3$(5 mol%), NaOCl (15 mL)	0 °C/2 h → rt/2 h	85

The ^1H NMR data for 1,11-undecanedioic acid in DMSO-d_6 at 300 MHz(Figure-2) is explained as:

- δ 2.17 (t, J = 6.6 Hz, 4H) → This corresponds to the methylene (-CH_2-) groups adjacent to the carboxyl (-COOH) groups at both ends of the molecule. The deshielding effect of the electron-withdrawing carboxyl groups shifts these protons downfield.

- δ 1.49−1.44 (m, 4H) → These are the methylene (-CH_2-) protons next to the terminal -CH_2COOH groups. They are slightly more shielded than the ones directly adjacent to -COOH.

- δ 1.23 (m, 10H) → These correspond to the internal methylene (-CH_2-) groups in the alkyl chain. They experience similar electronic environments, leading to a broad multiplet in this region.

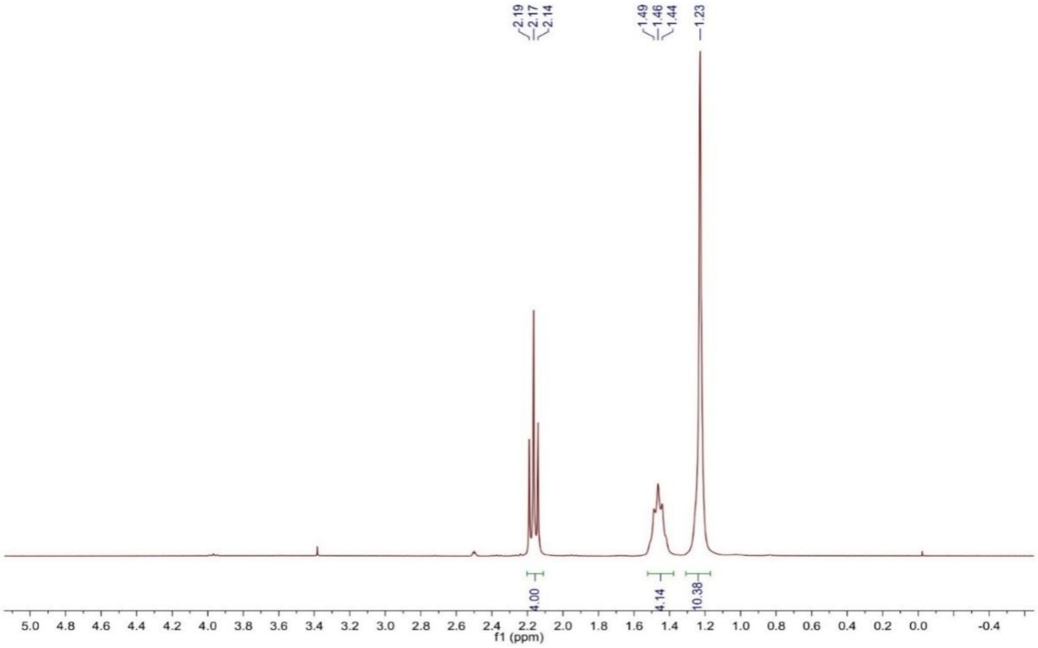

Figure-3:^1H-NMR spectra of 1,11-undecanedioic acid in DMSO-d_6

CONCLUSION

In our project we could develop the novel oxidation method using sodium hypochlorite and ferric chloride catalyst for the synthesis of 1,11-undecanedioic acid which is an important biodegradable plastic monomer from 11-hydroxyundecanoic acid prepared from ricinoleic acid a major fatty acid of castor oil.We also highlighted the potential of renewable biomass as a sustainable feedstock for the chemical industry. Our moto is to go green,eco-friendly and use of renewable resources.Future research will focus on extending this catalytic oxidation to other medium chain fatty acids and their derivatives.

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