

Catalytic Transfer Hydrogenation of Castor Oil

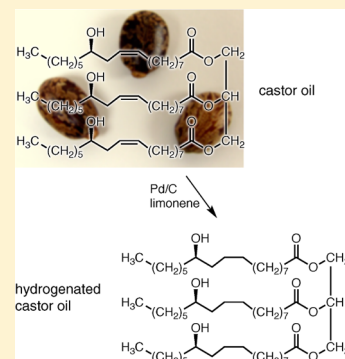
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S Supporting Information

ABSTRACT: The main thickening agent or soap in multipurpose grease, lithium 12-hydroxystearate, is a chemical commodity for the auto industry. This compound is obtained from castor oil via a series of chemical transformations. The first step, hydrogenation of castor oil, has been developed into a laboratory experiment for second-year undergraduate organic chemistry. Students are introduced to catalytic transfer hydrogenation (CTH) as a method to reduce a carbon–carbon double bond in ricinoleic acid, the main fatty acid in castor oil. Students perform a comparative analysis based on calculation of several green metrics: atom economy, E factor, reaction mass efficiency, CO₂ emissions, and costs. The product, hydrogenated castor oil, is characterized by several techniques: ¹H NMR and IR spectroscopy, and melting point.

KEYWORDS: Second-Year Undergraduate, Laboratory Instruction, Organic Chemistry, Hands-On Learning/Manipulatives, Fatty Acids, NMR Spectroscopy, Industrial Chemistry, IR Spectroscopy



General information about grease was recently presented in a review article in this *Journal*.¹ A laboratory experiment where general chemistry students isolated and characterized lithium soaps or thickeners from multipurpose lubricating grease has been described.² After isolating the lithium soaps, students converted them to the corresponding fatty acid methyl esters (FAMES), whereupon they were separated and identified by GC–MS. One fatty acid soap, lithium 12-hydroxystearate, dominated over all others in the different brands of multipurpose lithium grease examined. As it turns out, both the cation and anion of this soap contribute to making a superior multipurpose lubricating grease.¹ Also fascinating was the source of this unique fatty acid soap—castor oil.

Castor oil, similar to other vegetable oils and animal fats, is a triglyceride composed of a mixture of fatty acids. Three key features distinguish castor oil from nearly all other triglycerides. First, it is the only readily available source of ricinoleic acid, (Z)-12-hydroxyoctadeca-9-enoic acid. Second, it contains a very high abundance (~90%) of this one fatty acid. Most triglycerides are not this rich in a single fatty acid. Third, ricinoleic acid contains a hydroxyl group, which is very unusual; rarely do naturally occurring fatty acids contain a hydroxyl group. Besides the hydroxyl group, this eighteen-carbon fatty acid contains one carbon–carbon double bond, making it an unsaturated fatty acid. A complete listing of the fatty acid content of castor oil is provided in Table 1.^{3,4}

The presence of the hydroxyl groups in castor oil accounts for its unusual solubility characteristics in organic solvents compared to other triglycerides. In contrast with most triglycerides, castor oil exhibits very limited solubility in aliphatic hydrocarbon solvents and high solubility in simple alcohols.

Castor oil, obtained from the seed of the castor oil plant, is a vital raw material and was one of the earliest and most versatile contributors to the oleochemical industry.⁵ Today, India produces ~70% of this renewable resource followed by China and Brazil, which together contribute another quarter to the annual production total. A recent review article describes the many industrial applications of castor oil.⁴

Sixty years ago a laboratory experiment published in this *Journal* described the use of castor oil for the preparation of a variety of organic compounds, including heptaldehyde, undecylenic acid, sebacic acid, and azelaic acid.⁶ Starting with one of these four compounds, the authors went on to outline simple procedures to produce nearly twenty additional compounds. One reaction pathway the authors did not describe was the conversion of castor oil to 12-hydroxystearate, its alkali metal salt, or its alkyl ester. Scheme 1 illustrates that the methyl ester of 12-hydroxystearate can be prepared in two steps. One pathway involves transesterification, followed by hydrogenation and a second pathway reverses the order of these two steps. Scheme 1 also illustrates two pathways to the lithium salt of 12-hydroxystearate. The last step in both these approaches involves saponification with lithium hydroxide. The experiment described here focuses on the hydrogenation of castor oil via catalytic transfer hydrogenation (CTH)^{7,8} in the presence of limonene and Pd/C⁹ and is illustrated in Scheme 2.

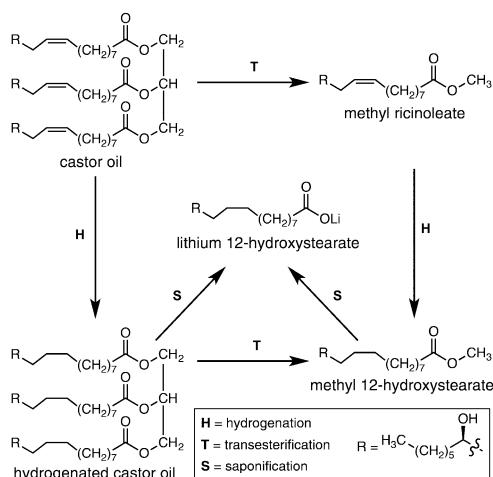
The application of CTH has been illustrated in several experiments published in this *Journal*.^{10–13} The earliest contribution was by Wilen and Kremer and involved the reduction of cinnamic acid to hydrocinnamic acid with Pd/C in tetralin.¹⁰ Reduction of 4-vinylbenzoic acid to 4-ethylbenzoic

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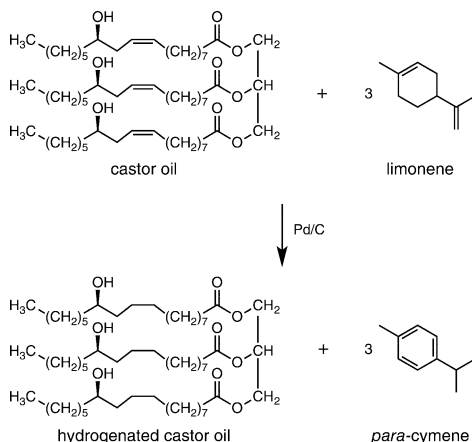
Table 1. Fatty Acid Composition of Castor Oil

Fatty Acid	Structure	Composition (% w/w)	Number of		
			C Atoms	C=C Bonds	OH Groups
Ricinoic		89.5	18	1	1
Linoleic		4.2	18	2	0
Oleic		3.0	18	1	0
Palmitic		1.0	16	0	0
Stearic		1.0	18	0	0
Dihydroxystearic		0.7	18	0	2
Linolenic		0.3	18	3	0
Eicosanoic		0.3	20	0	0

Scheme 1. Castor Oil Conversion to Lithium 12-Hydroxystearate



Scheme 2. Catalytic Transfer Hydrogenation of Castor Oil



acid using either ammonium formate or cyclohexene has been described.¹¹ Ammonium formate has also been employed to reduce nitrobenzene, benzophenone, and fluorenone.¹² A recently published guided-inquiry organic chemistry project involving synthesis and hydrogenation of disubstituted chalcones also utilized CTH and ammonium formate.¹³

Illustration and application of green chemistry principles¹⁴ in organic chemistry laboratory has emerged as an important aspect of experimental design. Although CTH of castor oil applies few of these principles, such as use of renewable resources and alternative sources of energy, the students are given the opportunity to analyze the “greenness” of these applications through a comparative analysis via green metrics, costs, and energy consumption. Additionally, the safety concerns, that is, flammability associated with the traditional heterogeneous hydrogenation of a C=C bond reaction using H₂ and a metal catalyst, are not present in the CTH of castor oil in limonene.

The pedagogic goal in developing this laboratory experiment was to link organic chemistry lecture topics to laboratory practice via the incorporation of a new synthetic methodology applied to a chemical commodity from a green chemistry perspective. The specific objectives were to provide students the opportunity to (1) use CTH, a hydrogenation method not routinely taught in introductory organic chemistry, (2) calculate green metrics and use them in comparative analysis, and (3) use a variety of experimental methods and characterization techniques.

EXPERIMENTAL OVERVIEW

The chemical compounds (list provided in the Supporting Information) were purchased from commercial sources and used without further purification. Students performed the CTH of castor oil with a conventional heat source (reflux at 178 °C for 30 min) and also in a commercial microwave at maximum power level for 20 min during one 4 h laboratory session. The melting point, IR spectrum, and ¹H NMR spectrum (with

CDCl_3 as the solvent) of the hydrogenated castor oil were obtained.

HAZARDS

Limonene is a skin and respiratory irritant. Pd/C may ignite on exposure to air and readily causes ignition of flammable solvents in the presence of air. Castor oil and hydrogenated castor oil should be considered nonhazardous. The byproduct, *para*-cymene, is an eye and skin irritant. Methylene chloride, chloroform, and deuterated chloroform are potential carcinogens, and irritants to eyes, skin, and respiratory tract. Diethyl ether may form explosive peroxides and may cause skin dryness and cracking upon repeated exposure. Methanol is toxic upon inhalation or ingestion. Students should wear gloves when handling these chemicals. Safety goggles should be worn at all times. Chemicals should be disposed of in designated waste containers.

RESULTS AND DISCUSSION

This experiment has been performed in the second-year undergraduate organic chemistry course in eight different sections over two semesters by 162 students. Each pair of students performed the reaction with conventional heating (reflux at 178 °C) and with a commercial microwave. The results were analyzed with respect to yield and purity, and the two methods were compared from a green chemistry perspective. The three experimental phases (reaction, isolation and purification, and characterization) are elaborated upon below.

Students observed that at the end of the heating time, a white precipitate formed. The product is insoluble in limonene, which served as both the solvent and hydrogen source compound in the reduction. The most challenging step of the workup was the separation of the catalyst from the reaction mixture, which involved solvation of the hydrogenated castor oil in methylene chloride followed by centrifugation and filtration. To maximize the yield of product, this process was repeated several times.

This experiment was also used to expose students to NMR spectroscopy as a structure elucidation technique. Prior to the experiment, students were given a copy of the ^1H NMR spectrum of castor oil and interpreted the spectrum with the assistance of an instructor. This prelaboratory discussion of castor oil enabled students to identify the region of interest when they compared the ^1H NMR spectrum of castor oil to that of hydrogenated castor oil. Specifically, students recognized that the peaks of interest, vinylic protons in the region 5–6 ppm, should disappear upon hydrogenation of castor oil. Figure 1 shows the ^1H NMR spectra of castor oil and hydrogenated castor oil, the latter taken by a student. The small residual peak, around 5.2 ppm, corresponds to the methine of the glycerol moiety as evidenced by its disappearance upon transesterification of either castor oil or hydrogenated castor oil. Several students attributed the peak to unreacted material; the assignment was clarified through group discussions.

Students obtained a melting point, ^1H NMR spectrum, and an IR spectrum of their product and commented on the success of their experiment based on these data. For departments in which access to an NMR spectrometer is not possible or is limited, IR spectroscopy can be used as an alternative. Two changes were noted in the IR spectra of hydrogenated castor oil compared to castor oil. The first was disappearance of a weak signal at 1650 cm^{-1} that was attributed to the $\text{C}=\text{C}$ bond. The

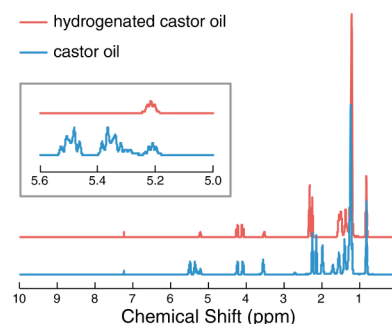


Figure 1. ^1H NMR spectra of castor oil and hydrogenated castor oil in CDCl_3 at 400 MHz.

second was absence of a hydroxyl stretch that was previously reported¹⁵ as the result of increased symmetry and length of the hydrocarbon backbone that weakens the ability of the hydrogenated castor oil to participate in intermolecular hydrogen bonding. IR spectra of both castor oil and hydrogenated castor oil are included in the Supporting Information. The same pattern was observed upon hydrogenation of methyl ricinoleate, which was performed as a control experiment.

The yields reported by students were similar for the two experimental setups, conventional heating and microwave irradiation. Yields and melting points ranged from 61–91% and 67.0–84.1 °C, respectively (individual results are provided in the Supporting Information). Although all student pairs were able to perform both reactions within one laboratory session, judicious use of the microwave oven was required. This lab could be further streamlined by implementing one or more of the following options: (1) several commercial microwave ovens could be used, (2) students could proceed with the workup of the conventional reaction while they were waiting for their turn to use the microwave oven, (3) students could perform the reactions during one laboratory session and continue with the workup and characterization of their product during a subsequent laboratory session, or (4) an experimental reflux model setup could be presented to the class at the beginning of the laboratory session.

In addition to reporting on the yield and characteristics of the product, students performed a comparative analysis for CTH and the industrial method¹⁶ on the basis of the following criteria: (1) green chemistry metrics (atom economy, E factor, and reaction mass efficiency), (2) energy consumption, (3) CO_2 emissions,¹⁷ and (4) costs associated with starting materials. This analysis is provided in the Supporting Information. Although the majority of students acknowledged that, with respect to yield and purity, the CTH methods were very similar and superior to the industrial method, the latter has lower costs and generates significantly less waste. With respect to the two methods of heating, students pointed to the ease of use of the microwave, but, at the same time, acknowledged its lack of advantage in terms of energy efficiency for this reaction.

SUMMARY

In this experiment, an important reaction, hydrogenation of a $\text{C}=\text{C}$ double bond, was performed on a substrate that is both a renewable resource and a commodity for the chemical and auto industries. Students were introduced to (1) catalytic transfer hydrogenation, (2) NMR and IR spectroscopy as characterization techniques, and (3) application of green chemistry

metrics. The success of the experiment in achieving these goals was assessed by instructor examination of the students' analysis of their NMR and IR spectra and their comparison of yields for the synthetic approaches. Although this laboratory experiment is not greener than the industrial version, it is nonetheless a valuable learning experience. It offers students an opportunity to compare alternative routes for the preparation of hydrogenated castor oil from the perspective of yield and purity, costs, green metrics, and energy consumption.

■ ASSOCIATED CONTENT

📄 Supporting Information

Instructor notes, a student handout, list of required reagents with CAS numbers, student data. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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