Castor Oil Hydrogenation by a Catalytic Hydrogen Transfer System Using Limonene as Hydrogen Donor

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ABSTRACT: The hydrogenation of castor oil was investigated using a catalytic transfer hydrogenation system in which palladium on carbon was the catalyst and limonene was the solvent and hydrogen donor. The highest percentage of castor oil modification occurred at 178°C using 1% Pd/C and an oil/limonene ratio of 1:3. The optimized system presented very good reproducibility and 100% conversion of the ricinoleate. GC using a mass spectrometer as detector and ^{1}H NMR spectra of the products indicated that hydrogenation was accompanied by dehydrogenation leading to a mixture of 12-hydroxy and 12-keto stearic derivatives.

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KEY WORDS: CTH, hydrogenation of castor oil, hydrogen donor, hydroxy stearic ester, keto stearic ester, palladium catalyst.

Castor oil is an inedible vegetable oil that is very versatile because of its high ricinoleic acid content (1). This oil is used in the manufacture of plasticizers or is converted into a number of industrially useful products (2). The hydrogenation of carbon–carbon double bonds by heterogeneous catalysts is one of the most important industrial processes for the modification of vegetable oils, and the pressure, temperature, and selectivity of catalytic hydrogenation have been the subject of much research (3–10). However, a major disadvantage of catalytic hydrogenation is the potentially explosive nature of such reactions and the need for special apparatus and reactors able to support high temperatures and pressures.

Catalytic transfer hydrogenation (CTH) is a common procedure in organic chemistry, although there are only a few examples of CTH being used for the hydrogenation of vegetable oils (11–13). The advantage of CTH, compared with classical heterogeneous systems, is its simplicity: It requires only moderate temperatures and pressures, with the hydrogen donor (usually formic acid or alcohols) being used as the solvent and nickel (Ni) or palladium (Pd) as the catalyst. Although nickel is the least expensive, palladium has been preferred because of its higher efficiency and its selectivity with respect to reaction products (14). In some cases, additional solvents have been used to improve solubility and/or to facilitate the diffusion of products through the catalyst. Important CTH reaction condition parameters, such as the nature of the hydrogen donor and temperature conditions, have been reviewed by several authors (15–17).

In this paper we present the results of an investigation of a system for the CTH of castor oil using a citrus industry by-product, limonene, as the hydrogen donor and palladium on carbon (Pd/C) as the metal catalyst.

EXPERIMENTAL PROCEDURES

Chemicals. Refined castor oil was donated by Cleveland Química do Brasil (Gravataí, Brazil). Palladium on carbon (Pd/C, 10% w/w) and boron trifluoride–methanol ($BF_3 \cdot MeOH$, 14% wt/vol) were purchased from Acros Organics (Fairlawn, NJ), and hexane and deuterated chloroform (99.8% pure) were from Merck (Hohenbrunn, Germany). They were used as received. Limonene ([*R*]-4-isopropenyl-1-methyl-1-cyclohexene; [*R*]-*p*-mentha-1,8-diene) was donated by Dierberger Óleos Essenciais (São Paulo, Brazil). All the solvents were analytical reagent grade and used without any pretreatment. The methyl ester standards (all above 99% purity) for GC were palmitic (hexadecanoic acid), stearic (octadecanoic acid), oleic (*cis*-9-octadecenoic acid), and linoleic acids (*cis*-9,*cis*-12-octadecadienoic acid) (Supelco, Bellefonte, PA) and ricinoleic ([*R*]-12-hydroxy-*cis*-9-octadecenoic acid), ricinelaidic ([*R*]-12-hydroxy-9[*E*]-octadecenoic acid) and 12-hydroxyoctadecanoic acid (Aldrich, Milwaukee, WI). The silylation agent *N*,*O*-bis(trimethylsilyl) acetamide was purchased from Pierce Chemical Co. (Rockford, IL).

General CTH procedure. The Pd/C catalyst, castor oil, and limonene were placed in a two-necked round-bottomed flask equipped with a reflux condenser and a thermometer. The mixture was refluxed at 178°C, with vigorous stirring, for 60 min. After refluxing, hexane was added to the flask to facilitate transfer of the suspension to the centrifuge tubes, and the suspension was immediately centrifuged to separate the Pd/C. The hot supernatant was filtered, and the reaction products were dried under vacuum and derivatized for further analysis.

Experimental conditions. The reaction parameters studied were: concentration of Pd/C catalyst (0.1, 0.25, 0.5, 0.75, 1.0, and 2.0% of Pd/mol double bonds); reaction temperature (160,

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170, and 178°C); castor oil/limonene ratio (1:3 molar ratio); and reaction time (0.5, 1, 2, and 3 h). The reaction of Pd/C and limonene was studied previously (23), and the limonene disproportionation products were characterized. The reaction of Pd/C and castor oil only was performed using the same reaction parameters of temperature, time, and percentage of Pd/C. In all cases, the castor oil was recovered unreacted.

Derivatization. Castor oil and its hydrogenated products were converted to methyl esters by heating with $BF_3 \cdot MeOH$ (18), and the esters were extracted with heptane, dried over anhydrous Na_2SO_4, and silylated using *N*,*O*-bis(trimethylsilyl) acetamide at 25°C for 15 min (19).

GC. The gas chromatograph was a Shimadzu GC model QP5050A (Kyoto, Japan) fitted with a mass spectrometer detector (MSD) operating in the EI ionization mode at 70 eV. The capillary columns used were an HP-1 polydimethyl siloxane fused-silica open tubular column (30 m long × 0.25 mm i.d. × 0.25 μm film thickness); an HP-5 polydimethyl siloxane fused-silica open tubular column with 5% phenyl groups (60 m × 0.25 mm × 0.25 μm); and an HP-20M polyethylene glycol fused-silica open tubular column (25 m × 0.25 mm × 0.10 μm). All columns were purchased from Hewlett-Packard (Folsom, CA). For the HP-1 and HP-5 columns, the initial temperature was 180°C, increasing by 1.3°C min^{-1} to 210°C, followed by a 5°C min^{-1} increase to 250°C, and maintained there for 2 min. The split/splitless injector was set in the split mode (1:50) at 280°C, and the interface was set at 300°C. For the HP-20M column, the initial temperature was 180°C, increasing by 1.3°C min^{-1} to 210°C, and maintained there for 50 min. For all columns, the sample injection volume was 0.2 μL, and helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1}.

NMR analysis. The ^1H NMR spectra were recorded on a model VXR 200 spectrometer (Varian, Palo Alto, CA) operating at 200 MHz at room temperature using $CDCl_3$ as solvent. All chemical shifts quoted are relative to tetramethylsilane using the positive downfield convention. The NMR methodology for iodine determination has been described previously (20–22).

RESULTS AND DISCUSSION

Our preliminary experiments revealed that the order in which the reagents were added played an important role in both the type of reaction products formed and their rate of formation. Castor oil hydrogenation occurred only when the oil was added to the Pd/C catalyst before the limonene; when the oil was added to the catalyst after the limonene, the castor oil was recovered unreacted and only limonene disproportionation products were identified (23). These results suggest that when limonene was added to the catalyst before the castor oil, the active sites of the catalyst became unavailable because they were blocked by the limonene disproportionation reactions, and the double bonds of the castor oil could not reach the sites because of steric hindrance and/or diffusion effects. This was unexpected because recent studies on the hydrogenation of polymeric systems (24,25) have shown that in such systems, CTH proceeds in the same way as classic hydrogenation. Our results suggest the formation of palladium hydride (Pd-H) by hydrogen transfer from the hydrogen donor to the palladium, with the hydride donating hydrogen to the double bond of the castor oil and generating a semihydrogenated intermediate that is converted into the saturated product by transfer of another hydrogen from the hydride. For the reaction to proceed, it is important to promote close contact between the double bond of the castor oil and the Pd/C catalyst before the addition of limonene.

The temperature of the reaction appeared to be an important parameter in the CTH of castor oil using Pd/C as catalyst when limonene was the hydrogen donor (Table 1). The highest percentage of castor oil modification occurred using 1% Pd/C and an oil/limonene ratio of 1:3 at 178°C, the b.p. of limonene (Table 2). After 1 h at 178°C, we found that nearly 100% of the castor oil was converted into principally keto and hydroxy stearic derivatives and that almost 70% of the double bonds were hydrogenated, with the keto derivative being the major product. A reaction temperature of 170°C resulted in different ratios of hydrogenation products. The data in Table 1 show that disproportionation reactions and castor oil hydrogenation were

TABLE 1
Catalytic Transfer Hydrogenation of Castor Oil Using Limonene as the Hydrogen Donor at a Castor Oil/Limonene Ratio of 1:3

		Temperature[b] (°C)			Reaction time[c] (h)				Pd/C concentration[d] (%)					
Methyl ester derivatives[a] (%)	Castor oil	160	170	178	0.5	1	2	3	0.1	0.25	0.5	0.75	1	2
Keto stearate		28	43	48	33	43	47	44	10	11	26	34	46	43
Hydroxy stearate	0	0	11	10	4	12	13	10	0	0	2	2	9	12
Stearate	0.9	2	4	16	5	17	18	20	1	1	2	3	18	17
Oleate (and isomers)	3.5	27	33	20	20	23	20	24	15	18	25	28	21	23
Ricinoleate	88.2	33	7	0	33	0	0	0	63	57	34	20	0	0
Others	5.1	10	3	3	5	5	2	2	11	13	11	13	6	5
Percentage hydrogenation[e]	—	35	62	68	52	74	78	78	6	7	24	36	70	74
Residual hydroxyl groups[e]	—	40	20	12	44	12	13	12	72	65	38	25	9	12

[a] Data obtained from a total ion chromatogram produced using a gas chromatograph fitted with a mass spectrometer detector.
[b] Reaction conditions: 1% Pd/C and 1 h.
[c] Reaction conditions: 1% Pd/C, 178°C.
[d] Reaction conditions: 1 h and 178°C. Concentration of Pd/C based on mol Pd/mol C=C.
[e] Calculated from the ^1H NMR spectrum (20).

TABLE 2
Catalytic Transfer Hydrogenation of Castor Oil Using 1% Pd/C and Limonene as the Hydrogen Donor at a Castor Oil/Limonene Ratio of 1:3 and Different Temperatures

Temperature (°C)	Sample	Hydrogenation (%)	Residual hydroxyl groups (%)
178	1	67	13
	2	66	10
	3	67	16
170	1	72	13
	2	49	39
	3	55	49

already occurring at 160°C and that a high proportion of the products were in the form of the keto derivative, suggesting that partial hydrogenation resulted in double bond migration and other competing reaction mechanisms during Pd-H formation (Fig. 1). It is well documented in palladium chemistry that the carbon–carbon double bond can migrate along the carbon chain (24), and it appears that this happened in our experiments, with the double bond migrating toward the hydroxy group at C12, where dehydrogenation was more likely to proceed (Fig. 1). A recent study by Hayashi *et al.* (17) showed that catalytic hydrogenation of simple olefins with palladium can use benzylic or allylic alcohols as the hydrogen donor and that hydrogen transfer between alcohols and simple olefins can be initiated by dehydrogenation of the alcohols with the olefins serving as efficient hydrogen acceptors, this process being facilitated by palladium.

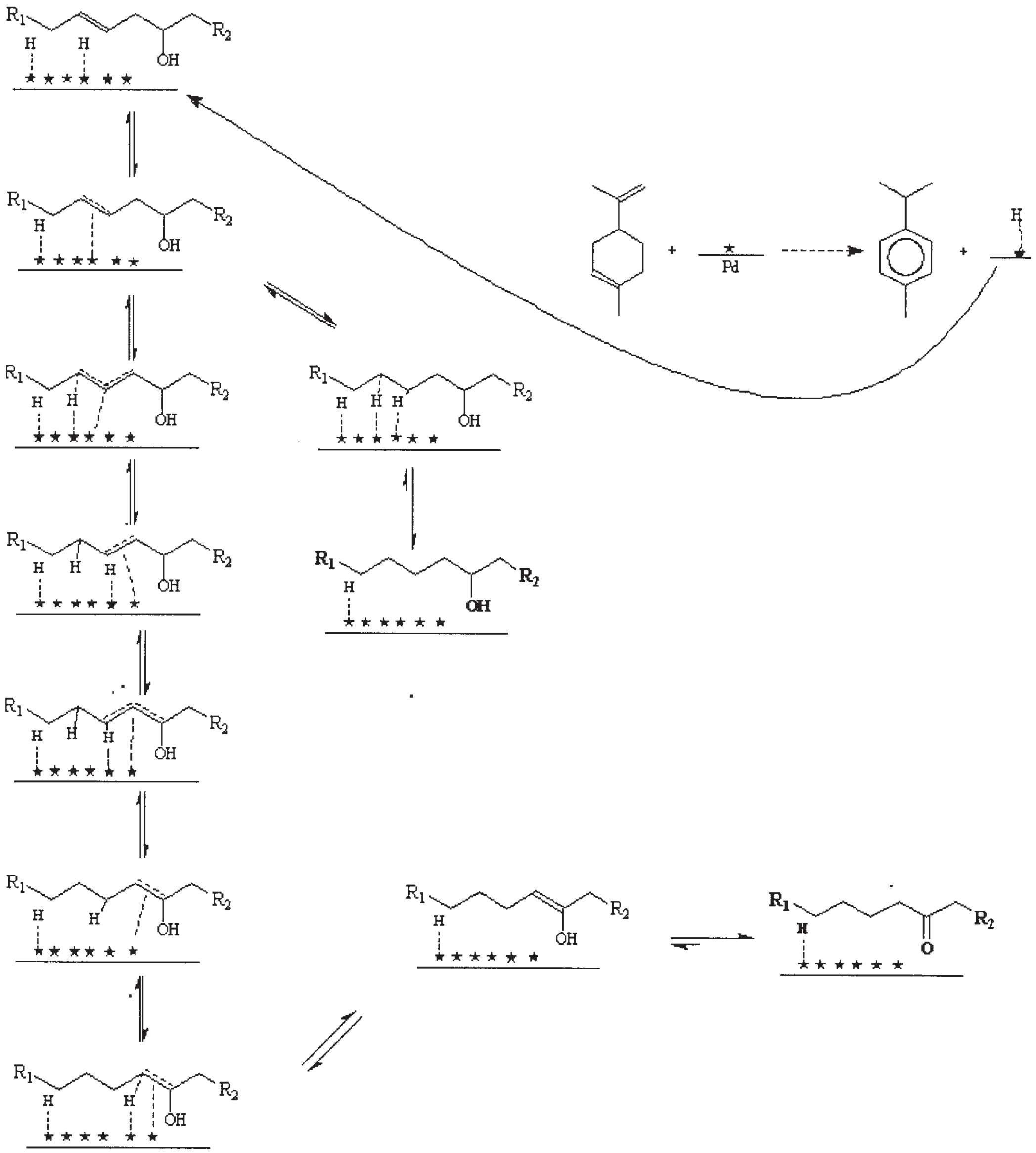

FIG. 1. Proposed mechanism for the hydrogenation and dehydrogenation of castor oil using the catalytic transfer hydrogenation system Pd/C and limonene. R_1 = carbon chain bonded to the TG, and R_2 = terminal carbon chain.

Our reaction time data (Table 1) showed that the total conversion of castor oil was achieved in 1 h and that the type and proportion of the products remained more or less the same even after a reaction time of 3 h.

The Pd/C concentration (Table 1) also played a very important role in the distribution of the reaction products, with a Pd/C concentration of less than 1% resulting in drastically decreased castor oil conversion and the more rapid formation of the keto stearate than the hydroxy stearate.

In our studies we obtained a yield of about 70–80% of hydrogenated castor oil (calculated by ^{1}H NMR—the amount of double bond reacted—and confirmed by GC-MSD), although keto stearate, not hydroxy stearate, was the major reaction product. This selectivity in terms of the type of stearate produced may have been because in palladium-catalyzed systems, migration of the double bond or isomerization of the carbon–carbon double bond can lead to a keto–enol equilibrium that ends by producing the more stable keto form as the final product (26). It is possible that changes in the reaction conditions, including the use of other hydrogen donors, could increase the yield of hydroxy stearate.

Our results show the considerable potential of CTH as an attractive process for the hydrogenation of vegetable oils. Because castor oil contains double bonds and hydroxy groups in the FA chain, its hydrogenation becomes more complex, but under our experimental conditions using Pd/C for CTH, the main products obtained were the keto and hydroxy stearates. With this in mind, we can presume that if CTH were applied to vegetable oils such as soybean oil, which contains mainly unsaturated TG with fewer functional groups, selective systems could seemingly be engineered to produce a range of products. The advantages of CTH systems are that the reactants are processed under mild conditions without the need for the specialized apparatus, molecular hydrogen, and high temperatures and pressures needed in classical catalytic hydrogenation. The data shown in Table 2 suggest that good reproducibility was observed at 178°C; however, because the temperature for this system depends on the disproportionation of limonene, lower temperatures were found to be unreproducible, and higher temperatures (22) did not show an improvement in results.

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