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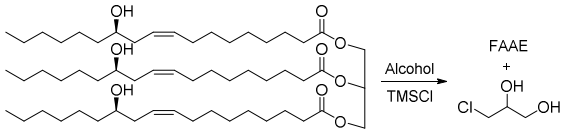

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The reaction between castor oil and various alcohols in the presence of trimethylchlorosilane (TMSCl) as acidic mediator provides two remarkable one pot reactions: transesterification of triglycerides, relevant to BioDiesel production and chlorination of glycerol, with formation of α-monochlorohydrin as predominant product, relevant to the synthesis of epoxide resins. The reaction has been thoroughly investigated to optimize the reaction conditions and separation of the products obtained in good yields. This synthesis represents a highly sustainable production of industrial commodities from available biomass.

1. Introduction

BioDiesel (BD) is a well known commodity, basically consisting in a mixture of fatty acid methyl (FAME) or ethyl (FAEE) esters. There is a lot of literature about BD production methods[1–4] and nowadays the most used process is transesterification of triglycerides (vegetable oil or animal fat) with a basic catalyst, such as sodium methoxide (or ethoxide), but also acid catalysis is used.

In a worldwide scale, BD production deals with economic, political, environmental and ethical issues. In fact, despite BD shows many advantages with respect to fossil fuels, mainly biodegradability and CO_2 compensation, there are some significant drawbacks in BD production, such as the so called "food versus fuel dispute"[3] and the high quantity of glycerol, obtained as co-product of the reaction (about 10% w/w). The latter is mostly a market problem associated to the employment of the oversupply of glycerol coming from the BD production. In this context glycerol could be converted into additives for BD, like glycerol *tert*-butyl ether, or solvents like glycerol carbonates, otherwise it becomes a cheap raw material for the production of fine chemicals (chlorohydrins and epichlorohydrin, acrolein, glyceraldehyde).[4–9]

By the way, the main issue deals with the ethical problem of foodstuff destination. In order to avoid BD production from edible oils (such as soybean, rapeseed and sunflower oil), many efforts have been made to convert feedstock such as non-edible oils (jatropha, karanja or mahua oil), exhausted fried oils, oils from microalgae and waste animal fats into BD.[3,4,10]

Among non-edible oils, castor oil seems to be a good candidate for BD production.[11–17] It is obtained from the seeds of *Ricinus communis* plant. India is the world's largest exporter of castor oil,[18] followed at considerable distance by China, Brazil and Thailand.[19] Nevertheless castor plant is a perennial crop that tolerates variable weather conditions and soil types, so it could be cultivated also in countries where this plant is not autochthonous. Recently Portugal made a preliminary assessment of castor plant for BD production.[16]

Castor oil contains high percentage (up to 90%) of ricinoleic acid [(*R*)-12-hydroxy-cis-9-octadecenoic acid] (see Fig. 1), responsible for castor oil peculiar properties, such as higher hygroscopy, viscosity and alcohol solubility than other oils.[11,15,16] These properties render the use of pure castor BD as fuel unpractical if not in blends with reference diesel.[20]

Castor oil is currently used itself as lubricant, functional fluid and industrial process oil. Castor oil can be also processed to obtain drying oils, surfactants, cosmetics, oil for inks and plasticize coatings. Sebacic acid can be produced from castor oil to synthesize polyamide (i.e. nylon 6,10) partially derived from renewable material. More recently a great focus has

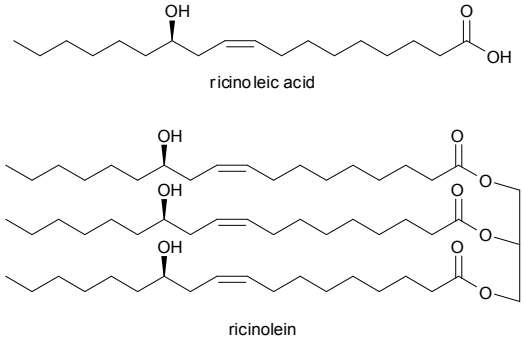

Fig. 1 Ricinolec acid and ricinolein, the prevalent triglyceride in castor oil.

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been made on polyurethanes derived from castor oil, since it is the only commercial available natural polyhydroxylated oil.[18,19]

The interest in BD production from castor oil raised in the last decade. The transesterification reaction (with methanol and ethanol) has been studied both with basic and acid catalysts.[11–17,21–23] For base-catalyzed process, studies concerning yield optimization, have been also performed with statistical approaches, like the surface method.[12,13,22] Encinar and coworkers[14] accomplished the reaction in basic conditions with ultrasonic radiation. The frequency and supplied power dissipation affect the reaction rate, but not the final yield.

Unfortunately, castor oil suffers for a lower conversion with respect to common vegetable oils like cotton[21] or soybean[23] oil when processed in the same basic conditions. On the other hand, the higher solubility of castor oil in alcoholic medium allows the reactions to occur in a monophasic system and kinetic studies revealed comparable reaction rate for acid- and base-catalyzed processes.[11] In general acid-catalyzed reactions are competitive with respect to the basic ones, because they can tolerate the presence of free fatty acids in the starting materials.

Recently we developed a new process for BD production by transesterification of sunflower oil, exhausted oils, and animal fats, in the presence of trimethylchlorosilane (TMSCl) as acid mediator.[24] TMSCl in our process must be used in large amounts, not as a simple catalyst, but its hydrolysis product, the hexamethyldisiloxane (TMSOTMS), is quantitatively recovered and can be converted back into TMSCl by literature simple procedures.[25]

In this context, the present work is focused on the application of the "trimethylchlorosilane method" to the production of BD from castor oil.

2. Experimental

2.1. Materials

All reagents were purchased from Sigma-Aldrich with the exception of castor oil purchased from Herboris Orientis Dacor. Trimethylchlorosilane was distilled before use and purity was checked by ^{1}H-NMR analysis. Methanol, ethanol and *n*-butanol were previously dried with magnesium.[26] All other reactants were used without any further purification.

2.2. Analytical methods

NMR spectra have been recorded with Varian Mercury plus 400 and Varian VXR 200 instruments. ^{13}C-NMR spectroscopy has been used as semi-quantitative method to determine the molar ratio between chlorinated products and residual glycerol, since the CH signals of glycerol, 1-MCH and 1,3-DCH are easily recognizable in the spectra (Fig. 2).[9]

Molar fraction of estolide (χ_E) was estimated via ^{1}H-NMR taking into account the integrals of signals of H-12' and H-9 by the following equation:

$$\chi_E = \frac{E}{\frac{F - E(2r-1)}{r} + E}$$

where E and F are the integrals of signals respectively of H-12' and H-9 and r is the molar percentage of ricinoleic acid in castor oil, which was evaluated via ^{1}HNMR by comparing the integrals of H-12 signal at 3.60 ppm with that of the terminal CH_3 at 0.87 ppm, resulting into 87%. Beside this method could be affected by the presence of oligomers and cyclic forms of estolides, that could change the relation between E and F, there is a quite good agreement between the quantity of estolides calculated by NMR and by GC analyses. So the equation can be used for a qualitative estimation.

GC analyses were performed, according to previous work,[24] on a Shimadzu GC-2010 gas cromatograph equipped with a programmable temperature vaporizing (PTV) injector, a flame ionization detector (FID) and a Zebron ZB-5 HT INFERNO capillary column (5% phenyl- 95% polydimethylsiloxane, 15 m length, 0.32 mm internal diameter, 0.1 µm film thickness). Oven conditions: isotherm at 50 °C (2 min), ramp at 15 °C/min to 180 °C, isotherm at 180 °C (10 min), ramp at 25 °C/min to 380 °C, isotherm at 380 °C (1 min). Gas carrier was helium, with constant flow rate of 1.83 mL/min. PTV conditions: ramp at 200 °C/min from 50 °C to 300 °C and isotherm at 300 °C (10 min). FID temperature set at 385 °C. Quantitative analysis, preparing samples with internal standard, were performed only for BD samples coming from kugelrohr distillation. A sample volume of 1 µL was injected using a split mode, with a split ratio of 10:1. Samples have been prepared mixing 300 µL of a solution of BD (ca. 250 mg in 10 mL of ethyl acetate) with 300 µL of a methyl heptadecanoate solution (ca. 25 mg in 5 mL of ethyl acetate). The purity of BD was detected according to the equation:

$$C = \frac{(\sum A - A_{STD}) * M_{STD}}{A_{STD} * M_{SAMPLE}} * 100$$

where C is the content of methyl esters, expressed as a mass percentage; ΣA and A_{STD} are respectively the total peak area of the methyl esters and the area of methyl heptadecanoate; M_{SAMPLE} and M_{STD} are respectively the mass of sample and the mass of internal standard in the final solution. For all other reaction mixtures, coming from trials performed according to procedures A and B, only semi-quantitative analyses were

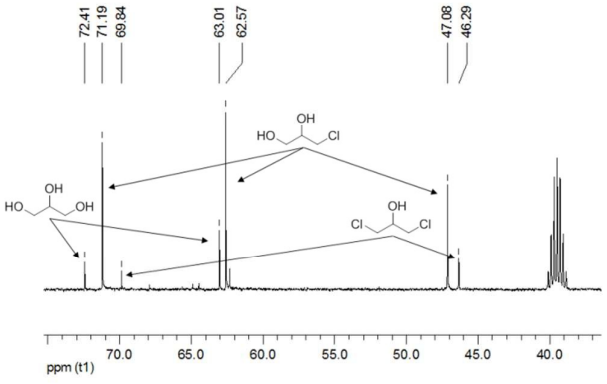


Fig. 2 A typical ^{13}C-NMR spectrum (100 MHz) in DMSO-d_6 of glycerol and chlorohydrins, used for semi-quantitative analysis.

done to determine BD and estolides content, preparing samples without internal standard.

Accurate mass spectra were recorded on a LTQ-Orbitrap high-resolution mass spectrometer (Thermo, San Jose, CA, USA), equipped with a conventional ESI source.

2.3. Optimization of the reaction conditions (see Table 1)

For all the reactions the molar weight of castor oil have been considered an average value of 929 g/mol as reported in the literature.[12] All the reactions reported in Table 1 refer to a complete disappearance of starting triglycerides as determined by ^{1}H-NMR.

2.3.1. Procedure A In a typical experiment, under nitrogen atmosphere, castor oil (0.5 g, 0.54 mmol) was placed in a 15 mL screw-cap Pyrex® tube, methanol and TMSCl (purity 94% w/w by ^{1}H-NMR) were added in the reported molar ratios and the mixture was kept at the desired temperature for a variable time (for reaction conditions see Table 1). At the end of the reaction, the mixture was cooled to room temperature. Methanol, TMSOTMS, and excess TMSCl were removed at low pressure.[‡] NMR analyses were performed both in $CDCl_3$ and DMSO-d_6 as solvents, semi-quantitative GC analyses were also carried out to determine the conversion of castor oil into methyl esters.

2.3.2. Procedure B After the first reaction performed according to procedure A, a further amount of methanol was added to obtain the desired ratio with respect to the initial castor oil, as reported in Table 1, and the resulting mixture was allowed to react for a further time at the reported temperature. At the end of the reaction, the mixture was cooled to room temperature, methanol and volatile compounds were evaporated at low pressure, and analyses were performed as reported for procedure A.

2.4. Synthesis of esters of fatty acids from castor oil

2.4.1. Reaction of castor oil with methanol: synthesis of fatty acid methyl esters. Castor oil (2.015 g, 2.17 mmol), methanol (0.39 mL, 9.61 mmol) and TMSCl (0.87 mL, 6.44 mmol) were placed, under nitrogen atmosphere, in a 25 mL screw-cap Pyrex® glass tube. The mixture was allowed to react under continuous stirring at 60 °C. After 8 hours, the reaction was stopped and cooled to room temperature. A further amount of methanol (2.6 mL, 86.5 mmol) was added and the mixture was kept for further 6 hours at 60 °C. At the end of the reaction methanol and the other volatile compounds were removed by evaporation at low pressure obtaining a yellow liquid (2.232 g). Distillation under vacuum (2.7 Pa) in a Kugelrohr apparatus allowed to recover four fractions. The fraction collected at 100 °C (0.095 g) was a 19:1 mixture (^{13}C-NMR analysis) of α-monochlorohydrin (**3**) (yield 37%) and α,γ-dichlorohydrin (**4**) (yield 2%). Between 170 and 240 °C two fractions were collected. The minor one (0.201 g) was a mixture of BD and 1-MCH (**3**), containing about 27% mol/mol (or 49% w/w) of BD (evaluated by ^{1}H-NMR). The major fraction (1.649 g; yield 81%; GC purity 91.0%) consisted of methyl ricinoleate (**2a**)[27] as predominant product; ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 5.54 (m, 1H; H-9), 5.39 (m, 1H; H-10), 3.65 (s, 3H; OCH_3), 3.60 (m, 1H; H-12), 2.29 (t, 2H; H-2), 2.20 (m, 2H; H-11), 2.03 (m, 2H; H-8), 1.60 (m, 2H; H-3), 1.45 (m, 2H; H-13), 1.39-1.21 (m, 16H; CH_2 chain), 0.87 (m, 3H; H-18); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 174.3 (s, C-1), 133.3 (d, C-9), 125.2 (d, C-10), 71.5 (d, C-12), 51.4 (q, OCH_3), 36.8 (t, C-13), 35.3 (t, C-11), 34.05 (t, C-2), 31.8 (t), 29.5 (t), 29.3 (t), 29.1 (t), 29.05 (t), 27.3 (t, C-8), 25.7 (t), 24.9 (t, C-3), 22.6 (t), 14.0 (q, C-18); HRMS (ESI) *m/z* calcd for $C_{19}H_{36}NaO_3$ $[MNa]^+$ 335.2557, found 335.2562.

Table 1 Reactions of castor oil following procedures A and B: reaction conditions and analyses.

Entry (Procedure)	Step	MeOH[a]	TMSCl[a]	Temp	time	χ_E[b]	Glycerol[c]	1-MCH[c]	1,3-DCH[c]	Esters[d]	Glycerides[d]	Estolides[d]
1 (A)	1	5.0	3.0	rt	8h	6%	25%	75%	0%	87%	4%	8%
2 (A)	1	4.9	3.0	60 °C	8h	19%	0%	85%	15%	76%	2%	22%
3 (A)	1	10.0	3.0	60 °C	8h	12%	19%	81%	0%	81%	5%	14%
4 (A)	1	22.4	3.0	60 °C	8h	6%	52%	48%	0%	85%	3%	13%
5 (A)	1	45.3	3.0	60 °C	8h	3%	83%	17%	0%	96%	>1%	3%
6 (A)	1	44.8	3.0	100 °C	8h	3%	74%	26%	0%			
7 (A)[e]	1	45.0	3.0	60 °C	8h	3%	83%	17%	0%			
8 (B)	1	4.7	2.2	60 °C	8h	19%	7%	82%	11%	76%	3%	21%
	2	45.0	2.2	60 °C	+3h	11%	2%	88%	11%	89%	1%	10%
9 (B)	1	4.5	3.0	60 °C	5h	15%	0%	82%	18%	77%	9%	14%
	2	47.4	3.0	60 °C	+3h	5%	0%	81%	19%	92%	1%	7%
10 (B)	1	4.5	3.0	60 °C	8h	22%	0%	83%	17%	80%	1%	19%
	2	45.3	3.0	60 °C	+6h	7%	0%	75%	25%	93%	>1%	6%
11 (B)	1	4.4	5.0	60 °C	5h	15%	0%	73%	27%	75%	7%	17%
	2	45.2	5.0	60 °C	+3h	3%	0%	58%	42%	94%	1%	5%
12 (B)	1	4.5	5.0	100 °C	5h	26%	0%	76%	24%	70%	3%	26%
	2	45.0	5.0	100 °C	+3h	15%	0%	63%	37%	81%	2%	17%

[a] Molar ratio with respect to starting castor oil; [b] χ_E molar fraction of estolides evaluated by ^{1}H-NMR; [c] Relative percentages obtained via ^{13}C NMR analyses based on the CH signals of 1-MCH, 1,3-DCH, and eventually glycerol; [d] Relative percentages determined by GC analyses based on the chromatographic peaks of the 'ester fraction'. The data were used only for semi-quantitative purpose, because the determination of estolides was not in complete accordance with the gravimetric data obtained by distillation; [e] 10% mol/mol of acetic acid has been added to the mixture.

The distillation residue (0.229 g; yield 12%) was a brownish liquid, containing **5a** as the main product; ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 5.51 (m, 1H; H-9), 5.47-5.33 (m, 2H; H-9' H-10), 5.29 (m, 1H; H-10'), 4.85 (m, 1H; H-12'), 3.63 (s, 3H; OCH_3), 3.58 (m, 1H; H-12), 2.30-2.21 (m, 6H; H-2 H-2' H-11'), 2.20 (m, 2H; H-11), 2.05-1.93 (m, 4H; H-8 H-8'), 1.63-1.53 (m, 4H; H-3 H-3'), 1.49 (m, 2H; H-13'), 1.43 (m, 2H; H-13), 1.37-1.17 (m, 32H; CH_2 chain), 0.84 (m, 6H; H-18 H-18'); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 174.3 (s, C-1'), 173.5 (s, C-1), 133.3 (d, C-9), 132.5 (d, C-9'), 125.2 (d, C-10), 124.3 (d, C-10'), 73.7 (d, C-12'), 71.5 (d, C-12), 51.4 (q, OCH_3), 36.85 (t, C-13), 35.4 (t, C-11), 34.7 (t, C-11'), 34.1 (t, C-2'), 33.6 (t, C-13'), 32.0 (t, C-2), 31.8 (t), 31.7 (t), 29.6 (t), 29.5 (t), 29.3 (t), 29.2 (t), 29.15 (t), 29.1 (t), 27.4 27.3 (t, C-8 C-8'), 25.7 (t), 25.3 (t), 25.1 24.9 (t, C-3 C-3'), 22.6 (t), 22.55 (t), 14.1 14.0 (q, C-18 C-18').

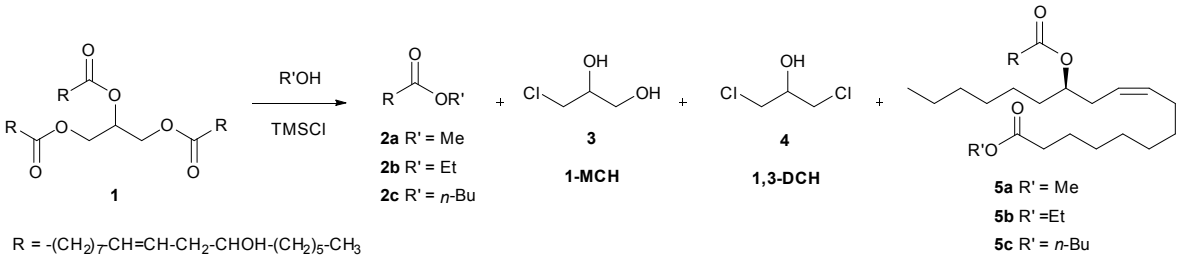
2.4.2. Reaction of castor oil with ethanol: synthesis of fatty acid ethyl esters. Operating as above, castor oil (2.023 g, 2.18 mmol), ethanol (0.58 mL, 10.2 mmol) and TMSCl (0.88 mL, 6.52 mmol) were allowed to react under continuous stirring at 60 °C. After 8 hours, ethanol (5.25 mL, 92.1 mmol) was added and the mixture was kept for further 6 hours at 60 °C. Evaporation of volatiles compounds left a dark yellow liquid (2.388 g) tha was subjected to Kugelrohr distillation under vacuum (2.7 Pa) affording three fractions. The fraction collected until 150 °C (0.206 g) was a 85:15 mixture (^{13}C-NMR analysis) of α-monochlorohydrin (yield 73%) and α,γ-dichlorohydrin (yield 11%). The major fraction was collected between 170 and 240 °C (1.698 g; yield 80%; GC purity 91.3%) was mainly constituted of ethyl ricinoleate (**2b**) ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 5.53 (m, 1H; H-9), 5.39 (m, 1H; H-10), 4.10 (q, 2H; OCH_2), 3.59 (m, 1H; H-12), 2.26 (t, 2H; H-2), 2.19 (m, 2H; H-11), 2.02 (m, 2H; H-8), 1.59 (m, 2H; H-3), 1.44 (m, 2H; H-13), 1.36-1.20 (m, 18H; CH_2 chain + CH_3), 0.86 (m, 3H; H-18); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 173.8 (s, C-1), 133.2 (d, C-9), 125.2 (d, C-10), 71.5 (d, C-12), 60.1 (t, OCH_2), 36.8 (t, C-13), 35.3 (t, C-11), 34.3 (t, C-2), 31.8 (t), 29.5 (t), 29.3 (t), 29.1 (t), 29.0 (t), 27.3 (t, C-8), 25.7 (t), 24.9 (t, C-3), 22.5 (t), 14.2 (q, CH_3), 14.0 (q, C-18); HRMS (ESI) *m/z* calcd for $C_{20}H_{39}O_3$ $[MH]^+$ 327.2894, found 327.2898. The distillation residue (0.426 g; yield 19%) was a brownish liquid, mainly containing **5b** ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 5.55 (m, 1H; H-9), 5.50-5.36 (m, 2H; H-9' H-10), 5.31 (m, 1H; H-10'), 4.88 (m, 1H; H-12'), 4.12 (q, 2H; OCH_2), 3.60 (m, 1H; H-12), 2.31-2.23 (m, 6H; H-2 H-2' H-11'), 2.20 (m, 2H; H-11), 2.09-1.96 (m, 4H; H-8 H-8'), 1.65-1.56 (m, 4H; H-3 H-3'), 1.52 (m, 2H; H-13'), 1.45 (m, 2H; H-13), 1.37-1.20 (m, 35H; CH_2 chain + CH_3), 0.88 (m, 6H; H-18 H-18'); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 173.8 (s, C-1'), 173.5 (s, C-1), 133.3 (d, C-9), 132.5 (d, C-9'), 125.2 (d, C-10), 124.3 (d, C-10'), 73.6 (d, C-12'), 71.5 (d, C-12), 60.1 (t, OCH_2), 36.8 (t, C-13), 35.4 (t, C-11), 34.6 (t, C-11'), 34.4 (t, C-2'), 33.6 (t, C-13'), 32.0 (t, C-2), 31.8 (t), 31.7 (t), 29.6 (t), 29.5 (t), 29.3 (t), 29.2 (t), 29.15 (t), 29.1 (t), 27.4 27.3 (t, C-8 C-8'), 25.7 (t), 25.3 (t), 25.1 24.9 (t, C-3 C-3'), 22.6 (t), 22.55 (t), 14.2 (q, CH_3), 14.1 14.0 (q, C-18 C-18').

2.4.3. Reaction of castor oil with n-butanol: synthesis of fatty acid *n*-butyl esters. Following the same procedure, castor oil (2.002 g, 2.16 mmol), *n*-butanol (0.88 mL, 9.60 mmol) and TMSCl (0.87 mL, 6.44 mmol) were allowed to react under continuous stirring at 60 °C. After 8 hours, *n*-butanol (8.0 mL, 87.2 mmol) was added and the mixture was kept for further 6 hours at 60 °C. Evaporation at low pressure of the volatile compounds gave a dark yellow liquid (2.489 g). Kugelrohr distillation under vacuum (1.3 Pa) afforded three fractions. The fraction collected until 150 °C (0.158 g) was a 19:1 mixture (^{13}C-NMR analysis) of 1-MCH (yield 63%) and 1,3-DCH (yield 3%). The major fraction was collected between 200 and 240 °C (1.8670 g; yield 82%; GC purity 96.1%) and mainly consisted of *n*-butyl ricinoleate (**2c**). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 5.53 (m, 1H; H-9), 5.39 (m, 1H; H-10), 4.05 (t, 2H; OCH_2), 3.59 (m, 1H; H-12), 2.27 (t, 2H; H-2), 2.19 (m, 2H; H-11), 2.03 (m, 2H; H-8), 1.65-1.54 (m, 4H; H-3 OCH_2CH_2), 1.44 (m, 2H; H-13), 1.36 (m, 2H; CH_2CH_3), 1.36-1.20 (m, 16H; CH_2 chain), 0.91 (t, 3H; CH_3), 0.86 (m, 3H; H-18); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 173.9 (s, C-1), 133.2 (d, C-9), 125.2 (d, C-10), 71.4 (d, C-12), 64.0 (t, OCH_2), 36.8 (t, C-13), 35.3 (t, C-11), 34.3 (t, C-2), 31.8 (t), 30.7 (t, OCH_2CH_2), 29.5 (t), 29.3 (t), 29.1 (t), 29.0 (t), 27.3 (t, C-8), 25.7 (t), 24.9 (t, C-3), 22.6 (t), 19.1 (t, CH_2CH_3), 14.0 (q, C-18), 13.6 (q, CH_3); HRMS (ESI) *m/z* calcd for $C_{22}H_{43}O_3$ $[MH]^+$ 355.3207, found 355.3210. The distillation residue (0.400 g; yield 20%) was a brownish liquid mainly containing compound **5c** ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) 5.54 (m, 1H; H-9), 5.50-5.35 (m, 2H; H-9' H-10), 5.31 (m, 1H; H-10'), 4.87 (m, 1H; H-12'), 4.06 (t, 2H; OCH_2), 3.60 (m, 1H; H-12), 2.31-2.22 (m, 6H; H-2 H-2' H-11'), 2.20 (m, 2H; H-11), 2.08-1.96 (m, 4H; H-8 H-8'), 1.65-1.55 (m, 6H; H-3 H-3' OCH_2CH_2), 1.52 (m, 2H; H-13'), 1.46 (m, 2H; H-13), 1.42-1.20 (m, 34H; CH_2 chain + CH_2CH_3), 0.92 (t, 3H; CH_3), 0.86 (m, 6H; H-18 H-18'); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 173.9 (s, C-1'), 173.5 (s, C-1), 133.3 (d, C-9), 132.5 (d, C-9'), 125.2 (d, C-10), 124.3 (d, C-10'), 73.6 (d, C-12'), 71.5 (d, C-12), 64.1 (t, OCH_2), 36.8 (t, C-13), 35.3 (t, C-11), 34.6 (t, C-11'), 34.4 (t, C-2'), 33.6 (t, C-13'), 32.0 (t, C-2), 31.8 (t), 31.7 (t), 30.7 (t, OCH_2CH_2), 29.6 (t), 29.5 (t), 29.3 (t), 29.15 (t), 29.1 (t), 29.05 (t), 27.4 27.3 (t, C-8 C-8'), 25.7 (t), 25.3 (t), 25.1 25.0 (t, C-3 C-3'), 22.6 (t), 22.5 (t), 19.1 (t, CH_2CH_3), 14.05 14.0 ppm (q, C-18 C-18') 13.7 (q, CH_3).

3. Results and discussion

The reaction of castor oil with MeOH and a stoichiometric amount of TMSCl at room temperature provides the complete disappearance of triglycerides after 8 hours leading to an emulsion containing glycerol, methyl ricinoleate (**2a**), α-monochlorohydrin (1-MCH) (**3**), and minor amounts of side products (Table 1, entry 1). On the other hand performing the reaction at 60 °C for 8 hours, a homogeneous solution was obtained. NMR and GC analyses showed the complete disappearance of glycerol and the formation of methyl ricinoleate (**2a**) and 1-MCH (**3**) as predominant products, together with minor amount of α,γ-dichlorohydrin (1,3-DCH) (**4**) and methyl ricinoleate estolide (**5a**) (Scheme 1, Table 1, entry 2).

These results, appear different from those observed in the reaction with sunflower oil, in particular for the complete conversion of glycerol. In fact, with sunflower oil, a



Scheme 1 Reaction of castor oil with alcohols using TMSCl as acid mediator, considering ricinolein as the main triglyceride.

two-phase system consisting of BD and a 1:1 mixture of glycerol and α-monochlorohydrin was obtained.[24] The different behavior of castor oil can be associated to its peculiar properties with respect to other vegetable oils, as previously stated.[11,15,16] Now, the higher solubility of the ricinoleic moieties in alcoholic medium allows the transesterification reaction in homogeneous phase. This situation is also responsible for the complete conversion of glycerol into α-monochlorohydrin (1-MCH) and α,γ-dichlorohydrin (1,3-DCH) (Table 1, entry 2) favoring the reaction with TMSCl as chlorinating agent, as confirmed by ^{13}C-NMR analysis of the reaction mixture. In fact, the ^{13}C-NMR technique allowed a semi-quantitative analysis affording the relative percentages of compounds by comparison of the integrals related to the CH signals of glycerol and chlorohydrins. An example is reported in Fig. 2.

Moreover, the ^{1}H-NMR analysis of the reaction mixture revealed signals neither attributable to BD nor to chlorohydrins or glycerol esters (i.e. mono-, di- and triglycerides), that, on the basis of literature data, were assigned to ricinoleic estolides.[28–36]

Estolides are a class of esters obtained from hydroxylated fatty acids and organic acid (generally a fatty acid). In particular ricinoleic acid gives estolides in which the OH group at C-12 position is esterified by another fatty acid. Otherwise estolides can be also synthesized from unsaturated fatty acid, like oleic acid, via oxidative process (i.e. with perchloric acid).[29] Estolides, like vegetable oils, are successfully used as lubricants and functional fluids in place of mineral oil, because of their better viscosity, lower toxicity and higher biodegradability. Moreover they have a lower pour point and higher resistance to thermal oxidation than vegetable oils, that could be proficient for the use as fuels.[29,30,34] Since ricinoleic acid is a non-toxic and natural hydroxylated fatty acid, estolides obtained from it are used also in the alimentary field as viscosity controllers for chocolate or as emulsifier for margarine.[36]

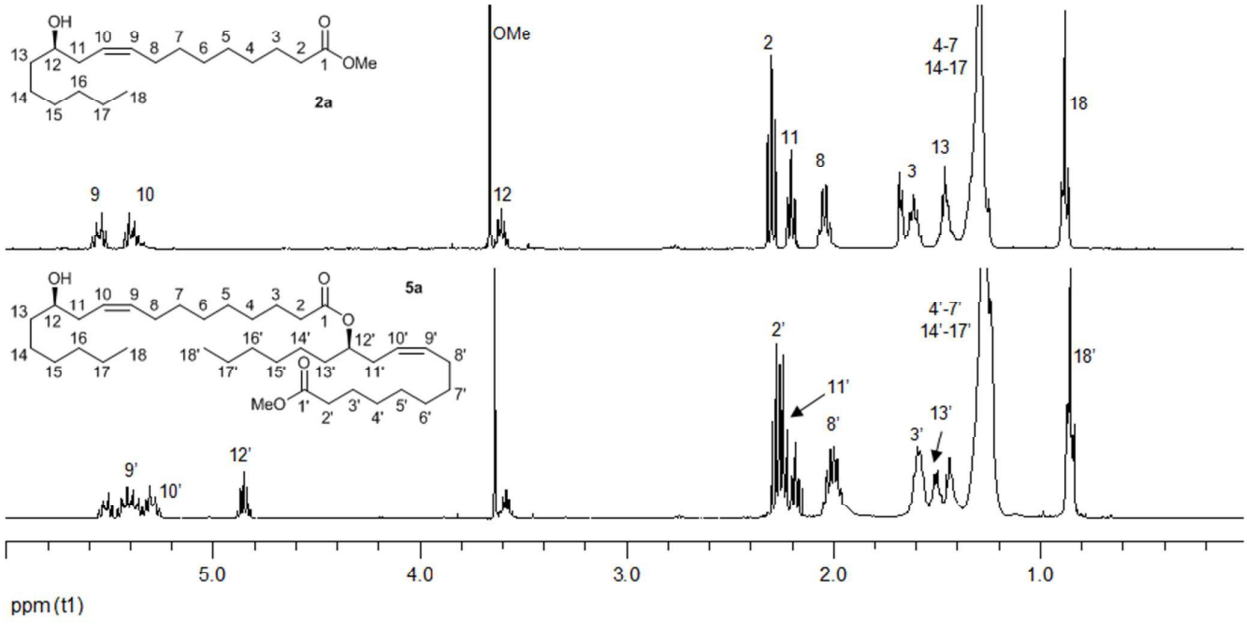


Fig. 3 ^{1}H-NMR spectra (400 MHz) in $CDCl_3$ of methyl ricinoleate (top) and of the ricinoleate estolide of methyl ricinoleate (bottom) with signal attribution, according to literature.[28]

However to provide the best selectivity of the process the present study was focused on the search of the best reaction conditions to convert castor oil into BD and chlorohydrins avoiding or at least limiting the estolides formation. Then, in the transesterification reaction with methanol, the first problem was to evaluate the amount of estolides with respect to FAME. This evaluation was achieved via ^{1}H-NMR analyses of the reaction crudes, by comparison with the data of samples obtained by distillation (see experimental). In Fig. 3 the upper ^{1}H-NMR spectrum refers to the fraction of FAME, with methyl ricinoleate (**2a**) as predominant component, while the second one is the spectrum of the distillation residue, in which the main product was the methyl ricinoleate estolide (**5a**). The detection of **5a** in a reaction mixture is mainly ascertained by the presence of signals that are shifted with respect to those of **2a**. In particular H-12' shifts from 3.60 to 4.85 ppm, H-9' from 5.54 to 5.43 ppm, H-10' from 5.39 to 5.29 ppm, H-11' from 2.20 to 2.27 ppm and H-13' from 1.45 to 1.49 ppm.

Thereby, with some approximation, it is possible to estimate the molar fraction of estolides (χ_E) by ^{1}H-NMR analysis (see experimental). These data were also confirmed by semi-quantitative GC analyses (see Table 1).

With the aim to optimize the BD and chloroydrins production, the castor oil transesterification was repeated under different reaction conditions. Initially a direct procedure (see Procedure A in the experimental section) was applied simply by mixing all the reagents and heating at the desired temperature for 8 hours. By increasing the alcohol to castor oil ratio the formation of estolides was reduced (Table 1, entries 2-5). Nevertheless the high dilution of the oil dramatically affected the chlorination process, leading to minor amount of 1-MCH together with unreacted glycerol. Even rising the reaction temperature or adding a small amount of acetic acid, that was found to be an excellent catalyst for the glycerol chlorination with TMSCl,[9] the yields of chlorohydrins were not improved (Table 1, entries 6 and 7). For these reasons, a different procedure (see Procedure B in experimental section) was tested, performing the reaction in two steps: a first one, achieved with a minor amount of alcohol (methanol to oil ratio about 4.5) to favour glycerol chlorination and a second one, involving a significant methanol addition (final methanol to oil ratio about 45), to convert estolides into FAME. Different trials were made varying TMSCl to castor oil ratio, reaction times and temperatures (Table 1, entries 8-12).

The optimal conditions for the first step involved a 3:1 TMSCl/castor oil ratio and heating at 60 °C for 8 hours (Table 1, entry 10). In fact a lower TMSCl/castor oil ratio was not able to convert completely glycerol (Table 1, entry 8), while a higher ratio just increased the percentage of 1,3-DCH with respect to 1-MCH, reducing the selectivity of chlorination, either operating at 60 or 100 °C (Table 1, entries 11 and 12).

Concerning reaction time, 8 hours turned out to be necessary for the first step. For lower reaction times (Table 1, entry 9), GC analyses revealed the presence of peaks likely associated to products of partial transesterification, such as mono- and diglycerides, simply reported in Table 1 under the generic term of glycerides. Comparing GC chromatograms and

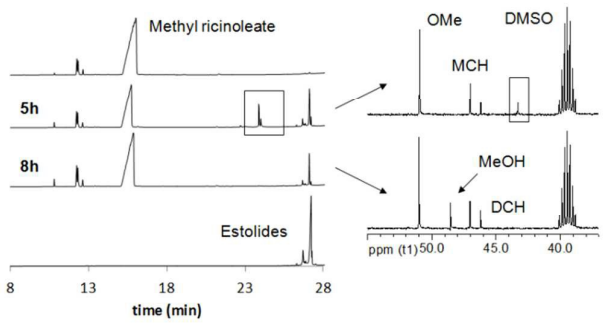


Fig. 4 ^{13}C-NMR spectra (100 MHz) in DMSO-d_6 (right) of two sample coming from trial 9 respectively after 5 and 8 hours of reaction. On the left chromatograms of both samples compared with distilled methyl esters and estolides (obtained as residue of distillation).

Table 2 Molar yields of the products isolated from the reaction between castor oil and different alcohols.

	FAAE[a]	1-MCH	1,3-DCH	Estolides
Methanol	81%	37%	2%	12%
Ethanol	80%	73%	11%	19%
n-Butanol	82%	63%	3%	20%

[a] FAAE Free Acid Alkyl Esters.

^{13}C-NMR spectra (Fig. 4) of the reaction mixtures deriving from the first and second step of trial 9, the new peaks (in the frames) were likely associated to esters of fatty acids with 1,3-DCH. Nevertheless any further analyses were avoided, since these compounds disappeared increasing reaction times and/or methanol to oil ratios.

The optimized reaction conditions (Table 1, entry 10) were applied to the transesterification of castor oil with different alcohols. All the reactions were performed at 60 °C in two steps (8 + 6 hours, see experimental section) and involved in the second one a further addition of the alcohol. After removal of the volatiles compounds, yellow-brownish liquids were obtained. Simple Kugelrohr distillation at reduced pressure allowed to recover α-monochlorohydrin (**3**), BD and estolides (See Experimental Section). The results obtained for the transesterification of castor oil with respectively methanol, ethanol and *n*-butanol are summarized in Table 2.

4. Conclusions

In conclusion, a facile process for producing chlorohydrins and fatty acid alkyl esters from castor oil has been disclosed. Thanks to the presence of an hydroxyl group, ricinoleic acid provides to castor oil a high solubility in alcohols that allows transesterification reactionss in homogeneous phase. In this particular conditions, an acid mediator like TMSCl, which was already found to be a good chlorinating agent for glycerol, drives the reaction towards BD and chlorohydrins. The sustainability of the process in relation to the use of large amounts of TMSCl (that, should be stressed here, behaves as a transesterification mediator and a chlorinating agent at the same time) is warranted by the complete recovery of

hexamethyldisiloxane (TMSOTMS), the hydrolysis product of the mediator, which can be converted back into TMSCl by literature simple procedures.[25]

Moreover, by controlling the alcohol to oil ratio it's possible to achieve a good selectivity for α-monochlorohydrin (**3**) formation with respect to α,γ-dichlorohydrin (**4**) as well as to limit the amount of estolides.

The present method does not allow an efficient production of estolides from castor oil. However, some preliminary results show the possibility to enhance the estolides yields by treatment of methyl ricinoleate with TMSCl and a little amount of acetic acid at 60 °C for 24 hours. Further studies on this line are ongoing in our laboratories.

Notes and references

‡ The mixture of MeOH, TMSOTMS, and TMSCl can be quantitatively recovered and recycled for the transesterification of oils after restoring the appropriate molar ratio of MeOH and TMSCl (see Ref. 24)

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