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Synthesis of (*S*)-ricinoleic acid and its methyl ester with the participation of ionic liquid

Józef Kula *, Radoslaw Bonikowski, Malgorzata Szewczyk, Kornelia Ciolak

Institute of General Food Chemistry, Lodz University of Technology, Lodz 90-924, Poland

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ABSTRACT

(*R*)-Ricinoleic acid methyl ester obtained from commercial castor oil was transformed in a three-step procedure into its *S*-enantiomer in overall 36% yield using ionic liquid (1-butyl-3-methylimidazolium acetate) in the key step process. The developed procedure provides easy access to (*S*)-ricinoleic acid and its methyl ester of over 95% enantiomeric excess. Optical rotations of the newly obtained compounds as well as their chromatographic and spectral characteristics are provided and discussed in the context of enantiopurity both of the substrate material and the final products.

1. Introduction

(*R*)-Ricinoleic acid or (*Z*)-(*R*)-12-hydroxyoctadec-9-enoic acid is a major constituent of castor oil from *Ricinus communis* seeds (Euphorbiaceae family) and comprises up to 87–92% of all fatty acids present in the oil (Broch-Jensen et al., 1997; Pradhan et al., 2012). Methyl (*R*)-ricinoleate is produced by transesterification of castor oil with methanol by chemical or enzymatic catalysis (Knothe et al., 2012; Baron et al., 2014; Goswami et al., 2013). Ricinoleic acid (castor oil) is widely exploited for industrial utilisation (Mutlu and Meier, 2010). This unusual hydroxy fatty acid has an *R*-configured carbon atom and an OH group in homoallylic position, which are the reasons for its multi-directional chemical and biochemical transformations (Behr et al., 2012; Kula et al., 2000; Braga and Belo, 2014). Its *S*-configured enantiomer or (*Z*)-(*S*)-12-hydroxyoctadec-9-enoic acid has not been reported, to the best of our knowledge, to occur in the plant kingdom, although there are several works describing the presence of ricinoleic acid (configuration not reported) in a family other than the large spurge family (Euphorbiaceae) (Parveen and Rauf, 2008; Katagi et al., 2011; Hosamani and Katagi, 2008). It is common knowledge that the biological activity of the chiral compound strongly depends on the configuration of its molecule. Enantiopure hydroxy fatty acids, including the only available (*R*)-ricinoleic acid, are desirable, for instance, to study their impact on the organisation of lipid membranes (Jenske et al., 2008). Taking into consideration the industrial importance of *R*-configured ricinoleic acid, its availability, wide range of application and our experience in the chemical transformation of this acid (Kula et al., 2000, 1996), we decided to attempt access to its *S*-configured enantiomer. In 1982 McGhie et al. (McGhie et al., 1982) tried to make an inversion of the configuration in (*R*)-ricinoleic acid to its optical antipode *via* the Mitsunobu reaction. However, the authors did not provide data on the reaction yield or on the purity of the products obtained. Moreover, the reagents used therein were hazardous and environmentally hostile, and separation of the product from two by-products, hydrazinedicarboxylate and phosphane oxide, is usually problematic (Dembinski, 2004; But and Toy 2006); hence the conclusion that inversion of chiral alcohol *via* the Mitsunobu reaction may not be suitable for large-scale preparations.

There are a number of papers on the SN_2 reaction of secondary alcohol sulfonates (mesylates) with the alkali metal salts of carboxylic acids, however, such a substitution has several drawbacks, especially if it were to be used on a larger scale, which was discussed in a recent work (Shi et al., 2010). The same authors also present an interesting protocol for the inversion of secondary alcohols using the complex of R_3N–RCOOH as a nucleophile providing excellent yields and enantiomer excess for several alcohols. The reaction is carried out in toluene at elevated temperature (60–110 °C), and 2–9 equivalents of the tunable amine-acid complex are necessary. We tried to apply this procedure to transform methyl (*R*)-ricinoleate into its optical antipode. The best result under the conditions tried (TEA–AcOH

* Corresponding author. Tel.: +48 426313418.
E-mail address: jozef.kula@p.lodz.pl (J. Kula).

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3:6 equiv., 70 °C, 15 h) allowed us to obtain the inverted product in ca. 25% yield (*R*-**1**–*S*-**1**). However, the optical purity of the sample, which was specially purified by column chromatography (99.6%, GC) was unsatisfactory, showing $[\alpha]_D = -2.40$ (c 8, $CHCl_3$) as compared to the optical rotation of the substrate ester, $[\alpha]_D = 3.03$ (*vide infra*). This may indicate that this homoallylic alcohol is very sensitive to the reaction conditions.

Recently, we turned our attention to the green protocol for the nucleophilic substitution reaction of sulfonate esters by recyclable ionic liquids as published by Yajun Liu (Liu et al., 2012) to develop the transformation of (*R*)-ricinoleic acid into its *S*-enantiomer.

2. Materials and methods

Methyl (*R*)-ricinoleate *R*-**1** was prepared by common transesterificarion of commercial castor oil with methanol in the presence of sodium methoxide to deliver a product (b.p. 173–177 °C/1.5 Torr) of 92% purity (GC). Triethylamine, methanesulfonyl chloride and ion liquid, 1-butyl-3-methylimidazolium acetate (BMIM-OAc), were purchased from Sigma–Aldrich.

Flash chromatography: silica gel for TLC. GC–MS was performed with a Trace GC Ultra chromatograph coupled with a DSQII mass spectrometer (Thermo Scientific) equipped with a Rxi-1ms capillary column (60 m long, 0.25 mm inside diameter, 0.25 mm film thickness), temperature program 50–310 °C at 4 °C/min. Chiral-GC–MS was performed with a Trace GC Ultra chromatograph coupled with an ISQ mass spectrometer (Thermo Scientific) equipped with an RT-BetaDEX-sm capillary column (30 m long, 0.32 mm inside diameter, 0.25 mm film thickness), temperature program 50–140 °C at 4 °C/min (held for 47 min), then to 230 °C at 20 °C/min. ^{1}H NMR (250 MHz) and ^{13}C NMR (62.90 MHz) were recorded using $CDCl_3$ solutions with TMS as internal standard (Bruker DPX-250 Avance). ^{13}C NMR multiplicity was determined using DEPT experiments. Purity of the products was confirmed by both GC and TLC analyses. Optical rotations were measured with an Autopol IV polarimeter (Rudolph Research) and IR spectra were obtained with the FT-IR spectrometer Nicolet 6700 (Thermo Scientific).

2.1. Preparation of (Z)-(R)-12-methanesulfonyloksy-octadec-9-enoic acid methyl ester (mesylate 2)

Methyl (*R*)-ricinoleate (*R*-**1**) (37.5 g, 110 mmol) was dissolved in dichloroethane (230 mL), and triethylamine (24.2 g, 239.9 mmol) was added. The mixture was cooled to −5 °C and methanesulfonyl chloride (20.7 g, 180.2 mmol) was dropped carefully during agitation, maintaining the temperature below +5 °C. Then the reagents were stirred for 3 h at room temperature and acidified with hydrochloric acid (230 mL, 2 M HCl). The organic layer was separated and washed twice with other portions of hydrochloric acid (2 × 100 mL, 2 M) and then three times with water (3 × 60 mL). After the organic solution was dried over anhydrous $MgSO_4$, the solvent was removed by a rotavapor to give a brown product, which was preliminarily purified by passing through a silica gel (20 g) column using hexane/acetone (80:20 v/v) as eluent to furnish crude mesylate **2** (43 g, 91% yield). A sample of the crude material (0.8 g) was purified by flash chromatography on silica gel column using hexane/acetone (90:10) as eluent to afford pure mesylate **2** (0.41 g). $[\alpha]_D = +16.33$ (c 5.0, $CHCl_3$). IR (cm^{-1}, neat): 2927, 2855, 1737, 1172, 905, 725. ^{1}H NMR ($CDCl_3$, δ ppm): 5.51 (m, 1H), 5.38 (m, 1H), 4.67 (qn J = 6.25 Hz, 1H-12), 3.65 (s, 3H-MeO), 2.98 (s, 3H-MeS), 2.44 (m, 2H), 2.29 (dd, J = 7.25 and 7.75 Hz 2H), 2.01 (m, 2H), 1.65 (m, 4H), 1.29 (m, 16H), 0.87 (t, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): 174.28 (s, C1), 133.76 (d, C9), 123.01 (d, C10), 83.59 (d, C12), 51.42 (q, MeO), 38.64 (q, MeS), 34.21 (t), 34.04 (t), 32.50 (t), 31.60 (t), 29.35 (t), 29.05 (t, 22.51 (t), 2 × CH_2), 28.98 (t), 27.38 (t), 25.00 (t), 24.88 (t), 14.00 (q).

2.2. Synthesis of (Z)-(S)-12-acetoxy-octadec-9-enoic acid methyl ester (3)

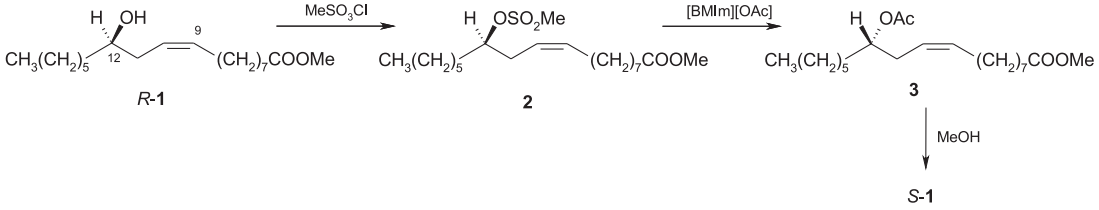
Crude mesylate **2** (42 g, 99 mmol) and 1-butyl-3-methylimidazolium acetate (20.2 g, 102 mmol) were stirred at 40 °C for 48 h. Then water (80 mL) was added and the product was extracted with hexane (3 × 100 mL), washed with water (100 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated to obtain a brown liquid (34 g) which was preliminarily purified by flash chromatography (silica gel, hexane/acetone 90:10) to get rid of the unreacted mesylate (monitored by TLC and ^{1}H NMR) and a little of unsaturated esters. After solvent evaporation, crude diester **3** (26.8 g), 78% pure (GC), was obtained. A sample of the crude material (0.8 g) was purified by flash chromatography on silica gel column using hexane/acetone (95:5) as eluent to afford 97% pure diester **3** (0.38 g). $[\alpha]_D = -21.8$ (c 2.3, $CHCl_3$). IR (cm^{-1}, neat): 2925.8, 2854.9, 1738.1, 1239.5, 1196.6, 1170.8, 1022.7, 724.9. ^{1}H NMR ($CDCl_3$, δ ppm): 5.45 (m, 1H), 5.34 (m, 1H), 4.86 (m, 1H), 3.66 (s, 3H), 2.30 (m, 4H), 2.02 (s, 3H), 1.99 (m, 2H), 1.57 (m, 4H), 1.29 (m, 16H), 0.87 (t, J = 6.5 Hz, 3H). GC–MS (EI, 70 eV), m/z): 294 ($M^+ - 60$), 43 (100%), 262 (5), 207 (5), 150 (8), 124 (9), 96 (20), 81 (24), 67 (40), 55 (37).

2.3. Methanolysis of diester 3

A mixture of crude diester **3** (26 g, 47 mmol) and anhydrous methanol (100 mL) containing sodium methoxide (0.216 g, 0.004 mmol) was refluxed for 2.5 h, then the methanol was distilled off (60 mL). Water (50 mL) and concentrated hydrochloric acid (4 mL) were added to the residue and the product was extracted with hexane (3 × 25 mL). The combined extracts were washed neutral with water and dried over anhydrous $MgSO_4$ to give, after solvent evaporation, crude hydroxy ester *S*-**1** (22.2 g, purity 77% by GC), which was subjected to silica gel flash chromatography (hexane/acetone 94:6) to get 99.6% pure (GC) hydroxy ester *S*-**1** (12.45 g, 36% total yield based on pure *R*-**1**). $[\alpha]_D = -2.81$ (c 5.0, $CHCl_3$). IR (cm^{-1}, neat): 3422.5, 2925.8, 2854.6, 1740.9, 1197.3, 1172.3, 725.5. ^{1}H NMR ($CDCl_3$, δ ppm): 5.53 (m, 1H), 5.42 (m, 1H), 3.66 (s, 3H), 3.60 (m, 1H), 2.29 (t, J = 7.5 Hz, 2H), 2.20 (t, J = 6.5 Hz, 2H), 2.04 (m, 2H), 1.51 (M, 3H), 1.45 (m, 3H), 1.29 (m, 15H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): 174.24 (s), 133.21 (d), 125.20 (d), 71.42 (d), 51.37 (t), 36.79 (t), 35.30 (t), 34.01 (t), 31.78 (t), 29.51 (t), 29.30 (t), 29.02 (t, 2 × CH_2), 27.31 (t), 25.66 (t), 24.85 (t), 22.56 (t), 14.02 (q). GC–MS (EI, 70 eV), m/z): 294 [$M^+ - 18$ (3)], 55 (100), 198 (24), 124 (48), 98 (45), 96 (53), 84 (58), 82 (43), 74 (73), 69 (50).

2.4. Hydrolysis of hydroxy ester S-1 to (S)-ricinoleic acid

A mixture of hydroxy ester *S*-**1** (2 g), methanol (20 mL) and KOH (2.5 g) dissolved in water (10 mL) was refluxed for 2 h. Then methanol was distilled off (10 mL) and the mixture was acidified with concentrated hydrochloric acid (2.5 mL). The product was extracted with ethyl acetate (3 × 20 mL), washed with water (2 × 15 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated to obtain (*S*)-ricinoleic acid (1.98 g, 100% pure by TLC and ^{1}H NMR). $[\alpha]_D = -3.54$ (c 2.89, $CHCl_3$). IR (cm^{-1}, neat): 3337.3, 2968.7, 2928.1, 2856.8, 1709.3, 1160.5, 1128.0, 950.5, 816.2. ^{1}H NMR ($CDCl_3$, δ ppm): 6.20 (br.m, 1H), 5.52 (m, 1H), 5.40 (m, 1H), 3.62 (qn, J = 6.25 Hz, 1H), 2.33 (t, J = 7.40 Hz, 2H), 2.21 (t, J = 7.0 Hz, 2H), 2.03 (m, 2H), 1.62 (m, 2H), 1.46 – 1.28 (m, 19H), 0.87 (t, J = 6.75 Hz, 3H).). ^{13}C NMR ($CDCl_3$): 179.49 (s), 133.26 (d), 125.14 (d), 71.62 (d), 26.70



Scheme 1. Transformation of methyl (*R*)-ricinoleate into methyl (*S*)-ricinoleate.

(t), 36.22 (t), 34.01 (t), 31.79 (t), 29.47 (t), 29.30 (t), 28.98 (t, 2 × CH_2), 28.91 (t), 27.29 (t), 25.64 (t), 24.63 (t), 22.58 (t), 14.04 (q).

2.5. Methyl (R)-ricinoleate and (R)-ricinoleic acid

For comparison, pure (99.8%, GC) methyl (*R*)-ricinoleate *R*-**1** was isolated from crude (starting) material by flash chromatography (silica gel, hexane/acetone 96:4). $[\alpha]_D$ = +3.03 (c 3.86, $CHCl_3$). Its IR and NMR spectra were in accordance with those reported in (Borsotti et al., 2001; Negelmann et al., 1997). Hydrolysis of the ester in the manner announced above delivered (*R*)-ricinoleic acid: $[\alpha]_D$ = +3.89 (c 3.86, $CHCl_3$), spectra (IR, NMR) which were identical with those recorded for (*S*)-ricinoleic acid.

2.6. Ozonolysis of methyl ricinoleates 1

Ozonolysis of crude methyl (*R*)-ricinoleate (3 g) was carried out in a manner reported elsewhere (Kula et al., 2000), but the 98% pure (GC) hydroxy acetal (*R*-**4**) was isolated by flash chromatography (hexane/ethyl acetate 90:10) in 76% yield. $[\alpha]_D$ = −8.95 (c 3, $CHCl_3$). GC–MS (EI, 70 eV), *m*/*z*): 204 (M^+, 0), 173 (2), 119 (5), 97 (3), 87 (26), 75 (100), 59 (54), 58 (17), 55 (11), 43 (12). Its IR and NMR spectra were identical with those published earlier (Kula et al., 2000). Ozonolysis of crude methyl (*S*)-ricinoleate (3 g) in the same manner delivered 98% pure hydroxy acetal *S*-**4**. $[\alpha]_D$ = 8.33 (c 3.4, $CHCl_3$). Its MS data matched the above.

3. Results and discussion

3.1. Inversion of the configuration by ionic liquid

The starting material, methyl (*R*)-ricinoleate (*R*-**1**), was produced by transesterification of commercial castor oil with methanol to deliver methyl ricinoleate of 92% purity (GC). The hydroxy ester was then quantitatively converted to its methanesulfonate (mesylate) **2**, the purity of which was monitored by ^{1}H- and ^{13}C-NMR spectra (Scheme 1).

A proton multiplet at 3.63 ppm (12-H) disappeared to shift to 4.75. Also, in ^{13}C-NMR the signal at 71.41 (12-C) disappeared to become visible at 83.58 ppm. After purification by flash chromatography (FC) on silica gel, the specific optical rotation of the mesylate was +16.3 (c 5, chloroform). Worth noting is the fact that the mesylate is thermally unstable, so that it could not be analysed by GC. Crude mesylate was used for further procedures. In the next step, mesylate **2** was subjected to a configuration inversion reaction with ionic liquid, 1-butyl-3-methylimidazolium acetate (BMIM-OAc) (Liu et al., 2012), to give acetate **3**. The desired product was obtained in moderate to good yields (Table 1) because of the tendency of the mesylate to the unwanted β-elimination.

This step, occurring in an SN_2 fashion, of the *R*-**1** to *S*-**1** transformation is crucial and is worth being discussed herein.

It could be observed (Table 1) that at a higher reaction temperature the competitive side reaction toward double unsaturated esters increased dramatically (Table 1, entry 1). On the other hand, at a lower reaction temperature the yields were better but the reaction time had to be prolonged significantly. The heterogeneity of the reagents seemed to be responsible, to some extent, for the reaction time. We observed that the reaction mixture remained heterogeneous both at 20 °C (room temperature) and at 30 °C, while raising the reaction temperature to 70 °C allowed the reaction mixture to become a clear solution. From the preparative standpoint, precise separation of diester **3** from the unreacted mesylate **2** is very important, otherwise in the next step of the process (alcoholysis), substrate *R*-**1** could be regenerated, thus reducing the enantiomeric ratio. Therefore, the reaction product (Table 1, entry 5), after work up was chromatographically (FC) purified to collect one fraction (free of mesylate) containing double unsaturated esters and diester **3** (78%, GC) and was called crude diester **3**.

For analytical purposes a pure sample (97%, GC) of diester *S*-**3** was isolated by FC (silica gel, hexane/acetone 95:5). Its measured optical rotation was equal to −21.8 (c 2.3, chloroform), while the literature data for *R*-**3** obtained by enzymatic resolution of racemic hydroxyl ester **1** amounts to +23.45 (c 1.06, chloroform) (Nagarajan, 1999).

3.2. Characteristics of (S)-ricinoleic acid and methyl (S)-ricinoleate

Transesterification of crude diester **3** was carried out in methanol in the presence of a catalytic amount of sodium methoxide to give crude *S*-**1**. Pure methyl (*S*)-ricinoleate (>98%, GC) was isolated by flash chromatography and its optical rotation

Table 1
Substitution reaction of mesylate with ionic liquid under various conditions.

Entry	[BMIM][OAc] Eqv.	Conversion (%)[a]	Yield (%)[b]	Temp. (°C)	Time (h)
1	1	~90	30	90	0.5
2	1	~70	63	70	2
3	1.3	~75	63	70	2
4	1.03	80	65	40	20
5	1.03	90	68	40	48

[a] Monitored by ^{1}H-NMR as decay of the CH_3-S singlet at 2.98.
[b] Yields were determined by TLC and ^{1}H-NMR.

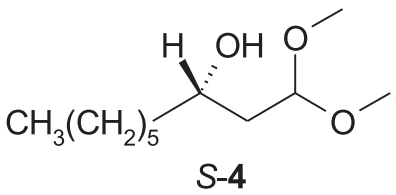


Fig. 1. Ozonolysis product of (*S*)-ricinoleate methyl ester.

amounted to −2.81 (c 5, chloroform), while the reported data for the *R*-enantiomer (measured in chloroform) are higher and some are divergent: +3.4 (Borsotti et al., 2001; Negelmann et al., 1997), +3.33 (Castillo et al., 2008). In this situation, we decided to obtain methyl *R*-ricinoleate of maximum high purity (>99.5%, GC) starting from the castor oil we had at our disposal in order to determine its optical rotation. Rotation measurements were performed three days after product isolation and did not change thereafter. The resulting value, {$[\alpha]_D$ = +3.03 (c 6.56, chloroform)} was, however, much lower than the values given in the literature. Thus, based on the specific optical rotation of the substrate material that we had at our disposal, the inversion of configuration of this homoallylic alcohol *R*-**1** occurred in slightly more than 95% to provide a (*Z*)-(*S*)-12-hydroxy-octadec-9-enoic acid methyl ester (*S*-**1**), independent of the optical purity of the starting material. This result suggests that the nucleophilic substitution of mesylate **2** by BMIM-OAc may also proceed, to some extent, by the SN_1 mechanism.

Hydrolysis of pure methyl esters *R*-**1** and *S*-**1** by conventional method resulted in the formation of corresponding hydroxy acids whose optical rotations measured in chloroform were +3.89 and −3.54, respectively. Although the literature data for optical rotations of *R*-ricinoleic acid are very divergent: −1.05 (c 0.69, $CHCl_3$) (Nagarajan, 1999), +3.9 (c 1.0, $CHCl_3$) (Borsotti et al., 2001), and +3.8 (c 1.1, chloroform) (Negelmann et al., 1997), our results in this respect are consistent with those received for methyl ricinoleates and as referred above.

3.3. Optical purity study by GC and GC–MS

Significant differences in the value of the optical rotations reported for both ricinoleic acid and its methyl ester make it impossible to obtain clear results as far as optical purity of the compounds is concerned. Therefore, we tried to find the chiral GC and HPLC conditions under which the optical resolution of mixed enantiomers **1** could be observed. Unfortunately, all attempts to obtain resolution both for methyl ricinoleates and ricinoleic acid derivatives (trimethylsiloxyricinoleic acid trimethylsilyl ester, trifluoroacetylricinoleic acid methyl ester, perfluoropropionylricinoleic acid methyl ester) failed, thereby frustrating this potential method, likely due to high symmetry of the molecules. However, ozonolysis of methyl (*S*)-ricinoleate (*S*-**1**) and methyl (*R*)-ricinoleate (*R*-**1**) in methanol resulted in the formation of respective hydroxy acetals *S*-**4** and *R*-**4** (Kula et al., 2000) producing, consequently, a volatile molecule of high asymmetry (Fig. 1).

The enantiomers of acetals **4** could be effectively separated on a column with a chiral stationary phase (RT-BetaDEX-sm), and the results are shown in Fig. 1. Their identity was confirmed by GC–MS and NMR analyses (Fig. 2).

It seems that there is no reason why during the ozonolysis process, partial racemisation of the substrate hydroxy esters **1** could take place, and that is why the outcomes based on enantiomer composition of the acetals can be transferred onto the optical purity of the starting methyl ricinoleates. Thus, enantiomer excess (*ee*) of the title methyl (*S*)-ricinoleate is 95.6% and this is in good agreement with the value obtained by polarimetric measurements (*vide supra*). The same refers to the (*S*)-ricinoleic acid reported in this paper. Although ricinoleic acid isolated from castor oil is generally considered to be optically pure, according to the best of our knowledge no work has been published confirming this notion by the chromatographic method. This is very likely to be the first report indirectly showing high *ee* (99.2%) of (*R*)-ricinoleic acid, which is a popular natural compound. In the light of the above the first use of newly obtained (*S*)-ricinoleic acid was to aid in determining the enantiomeric composition of the major constituent of commercial castor oil.

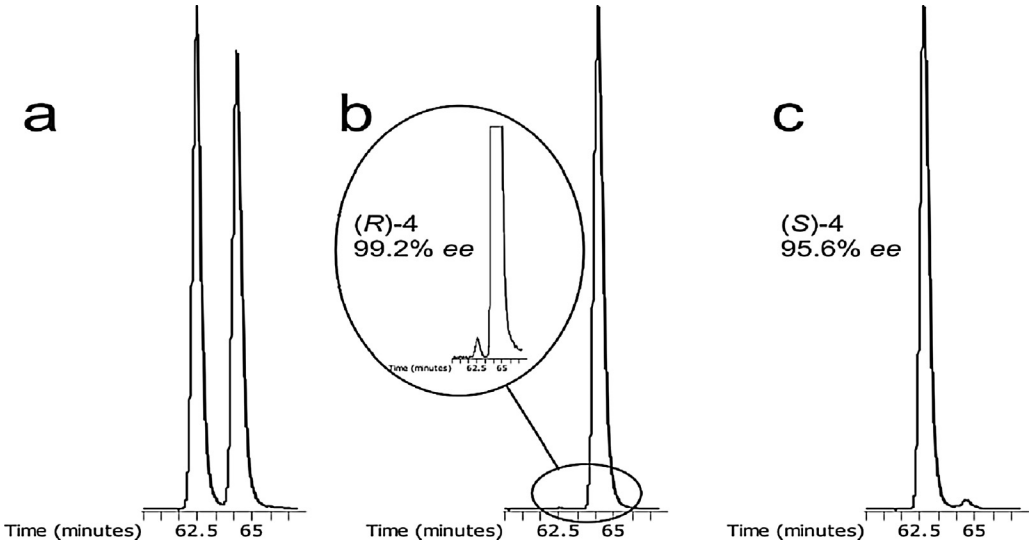


Fig. 2. Chromatograms (chiral-GC) of hydroxy acetals **4** showing, indirectly, the optical purity of (*R*)- and (*S*)-ricinoleic acids and their methyl esters: (a) mixture of enantiomers *R*-**4** and *S*-**4**; (b) hydroxy acetal *R*-**4** obtained by ozonolysis of methyl (*R*)-ricinoleate; (c) hydroxy acetal *S*-**4** obtained by ozonolysis of methyl (*S*)-ricinoleate.

4. Conclusions

In summary, the simple and effective procedure for the transformation of (*R*)-ricinoleic acid into its antipode of high optical purity has been developed. The reaction protocol uses, in the key step of the process, an ionic liquid as a reagent that may be regenerated and reused several times (Liu et al., 2012). The developed protocol provides easy access to (*S*)-ricinoleic acid and its methyl ester with a 36% total yield based on pure methyl (*R*)-ricinoleate, which is available from commercial castor oil. The enantiomeric purity of the product is 95.6% *ee*, which was shown by chiral GC analysis. This analytical procedure was also successfully used to determine the enantiopurity of ricinoleic acid and its methyl ester available from commercial castor oil; it turned out to be 99.2% *ee*.

Conflict of interest

The authors declare that there are no conflicts of interest.

Transparency document

The Transparency document associated with this article can be found in the online version.

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