Selective Oxidations of Methyl Ricinoleate: Diastereoselective Epoxidation with Titanium^{IV} Catalysts[1]

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ABSTRACT: Conditions were developed for the selective epoxidation of the double bond of methyl ricinoleate (**1**) with ethylmethyldioxirane (EMDO) to give the homoallylic epoxyalcohol, methyl (*Z*)-9,10-oxido-12-hydroxyoctadecanoate (**2**) in high yields but in poor enantiomeric excess. The diastereomeric ratio for epoxyalcohol **2** was improved modestly when *t*-butylhydroperoxide, coupled with a titanium catalyst and a D-tartrate ligand, was used as oxidizing agent. Reaction of **1** with excess EMDO resulted in the concomitant epoxidation of the double bond and oxidation of the hydroxy group of **1** to give methyl (*Z*)-9,10-oxido-12-oxo-octadecanoate (**4**), along with methyl 8-(5-hexylfuran-2-yl)octanoate (**5**). Alternatively, ketoepoxide **4** was prepared by dioxirane oxidation of methyl 12-oxo-(*Z*)-9-octadecene (**3**) or by treating epoxyalcohol **2** with sodium hypochlorite. The ketoepoxide **4** is acid-labile and rearranges with loss of water to give furan **5** in high yield.
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KEY WORDS: Dioxirane, epoxide, epoxyhydroxy ester, furan, phase-transfer catalyst, *t*-butyl hydroperoxide, titanium.

Ricinoleic acid, (*R*)-12-hydroxy-(*Z*)-9-octadecenoic acid, is the principal fatty acid (FA) of castor oil. Both the oil and the acid have a number of important industrial uses that are based primarily upon the unique presence of the hydroxyl group (1). Utility of these materials is often enhanced by conversion of the unsaturated alcohol structure to other reactive functional groups. Although few other hydroxylated FA are readily available, efforts to exploit novel FA (2–4) and to convert common industrially available FA, such as oleic and linoleic acids, to hydroxylated FA may change this picture (5–8). The chemistry performed on ricinoleic acid and its derivatives therefore can serve as examples of what might be done with new hydroxylated FA. Parenthetically, the chirality of hydroxylated FA has been of less interest to the oleochemicals industries; evidently, chemical configuration plays no demonstrated role in the physical properties sought by these industries as targets for their products. However, the configurational homogeneity resident in such chiral compounds may offer unique properties so they can be sold by oil producers as specialty chemicals.

In this study, we evaluated some oxidations of methyl ricinoleate, **1**, in particular its conversion to the epoxyketone, **4** (Fig. 1). The epoxyalcohol, **2**, has been characterized previously as mentioned below; here, we relate information that suggests the absolute configuration of the diastereomers formed from the epoxidation of methyl ricinoleate. We also describe a preparation of one of the diastereomers in 80% enantiomeric excess (90:10 ratio).

MATERIALS AND METHODS

All solvents, including 2-butanone, were of high-performance liquid chromatography (HPLC) grade or better. Other chemicals were reagent-grade and were purchased from Aldrich Chemical Company (Milwaukee, WI). Methyl ricinoleate was prepared from castor oil as described (6). Gas–liquid chromatography (GLC) was performed with a Chrompack-Packard Model 438A instrument (Avondale, PA) and a split (50:1) capillary column injector. Helium was used as the carrier gas, with a Supelcowax column (0.25 mm × 30 m) (Supelco Inc., Bellefonte, PA) operating at temperatures indicated below. Analytical thin-layer chromatography (TLC) was performed on 0.25-mm silica gel 60 plates (5 × 20 cm), obtained from Analtech (Newark, DE), or on silica gel ultraviolet (UV) plates (2.5 × 10 cm) from Aldrich Chemical Company. HPLC was carried out with a Spectra-Physics SP8800 pump (Mountainview, CA), a Supelcosil LC-Si column (4.6 mm × 25 cm), and a Spectra-Physics SP8480 UV detector, operated as described below. Infrared (IR) spectra were recorded with a Perkin-Elmer 1310 (Norwalk, CT) spectrophotometer with 1% solutions in either CCl_4 or $CHCl_3$. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Gemini 200 (Palo Alto, CA) spectrometer, operating at 200 MHz for proton and at 50 MHz for carbon-13 nuclei. All spectra were recorded in $CDCl_3$ solvent, and chemical shifts are reported as ppm (δ) from tetramethylsilane (TMS). Mass spectra (MS) were obtained with a Hewlett-Packard (Wilmington, DE) Model 5890 Series II gas chromatograph, equipped with a capillary inlet system, a 30 m × 0.25 mm capillary column coated with 0.25 μm 5% cross-linked phenyl methyl silicone (HP-5MS), and an HP Model 5972 mass selective detector set

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to scan from 50 to 600 *m/z* at 1.5 scans per second. The oven temperature was programmed from 80 to 230°C at 10°C per minute at a He carrier gas flow of 1 mL per minute and a split ratio of 50:1. Samples with free hydroxy groups were silylated at room temperature with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSFTA) (Pierce, Rockford, IL).

Methyl (Z)-12-oxo-9-octadecenoate, **3**. To a solution of methyl ricinoleate, **1** (3.13 g, 10.0 mmol) in 30 mL CH_2Cl_2 was added sodium acetate (2.5 g, 30 mmol) and pyridinium chlorochromate (3.24 g, 15 mmol). The mixture was stirred overnight. Ether (150 mL) was added, and the supernatant was poured onto a column of Florisil to filter out inorganics. Ether (2 × 30 mL) was used to rinse the flask and was also added to the column. The combined eluents were freed of solvent by rotary evaporation. The residue was purified by flash chromatography on silica with 7% ethyl acetate-hexane (EA-H, 25-mL fractions). Fractions were monitored by TLC (10% EA-H). Removal of solvent by rotary evaporation from the appropriately combined fractions gave 2.57 g (82.6%) of the ketoalkene, **3** (R_f = 0.55). An analytical sample was obtained by molecular distillation: bath temperature 155–180°C at 0.05 mm of Hg. IR: 3030, 1735, and 1715 cm^{-1}; ^1H NMR, δ: 5.55 (2H, *m*, *H*C=CH), 3.66 (3H, *s*, OCH_3), 3.2 (2H, *bd*, HC=CH–CH_2C=O), 2.41 (2H, *t*, CH_2CH_2C=O), 2.29 (2H, *t*, C$H_2CO_2CH_3$), 2.0 (2H, *m*, CH_2CH_2CH=C), 1.6 (2H, *m*, CH_2CH_2C=O), and 0.86 (3H, *t*, CH_2CH_3) ppm; ^{13}C NMR (diagnostic signals) δ 209.1, 174.2, 133.4, and 121.0 ppm; and MS, *m/z*: 310 (M), 279 (M – OCH_3), and 113 (M – COC_6H_{13}).

*Methyl (*R,Z*)-9,10-oxido-12-hydroxyoctadecanoate,* **2**. This procedure is patterned after that reported by Curci and co-workers (9). Methyl ricinoleate (3.90 g, 12.5 mmol) was dissolved in 25 mL of 2-butanone. Sodium bicarbonate (2.65 g, 3.1 mmol) and tetrabutylammonium bisulfate (0.40 g, 0.1 mmol) were added. To this stirred slurry (maintained in the dark) was added dropwise a solution of Oxone™ (7.7 g, 12.5 mmol) in 50 mL water. Addition time was about 15 min, and stirring was continued for another 45 min. A second equivalent of Oxone™ and sodium bicarbonate was added, and stirring was continued in the dark for 1 h. The reaction mixture was transferred to a separatory funnel, the layers were separated, and the aqueous phase was extracted with ether (25 mL). The combined organic layers were then washed with water (2 × 20 mL) and dried over anhydrous $MgSO_4$. The solvents were removed by rotary evaporation, and the crude product was purified by silica flash chromatography to give the epoxyalcohol **2** as a mobile liquid, 3.70 g (89.4%). GLC analysis (260°C, isothermal) showed that **2** was a mixture of diastereomers with retention times of 19.9 and 20.4 min (ratio of 1:1); IR: 3640, 1740, and 1260 cm^{-1}; ^1H NMR, δ: 3.63 (3H, *s*, CH_3O), 3.09 (1H, m, C*H*–OH), 2.9 (2H, *bm*, epoxy C*H*O), 2.27 (2H, *t*, *J* = 7.8 Hz, CH_2CH_2C=O), 2.0 (O*H*), 1.6 (*m*, CH_2CH_2C=O), 1.2–1.5 (*m*, CH_2), and 0.85 (3H, *t*, CH_3CH_2) ppm; MS, *m/z*: 385 (M − 15), 316 (M – C_6H_{13}), and 187 [M – $(CH_3)_3SiOCHC_6H_{13}$].

Methyl (Z)-9,10-oxido-12-oxooctadecanoate, **4**. Synthesis of **4** from ketoalkene **3** employed ethylmethyldioxirane and 2-butanone in a two-phase oxidation that was conducted exactly as for compound **2**. From 0.62 g (2.0 mmol) of **3** was obtained 0.63 g (100%) of crystalline **4**, mp 32.5–34.5°C (hexane); IR: 1740, 1715, 1260, 1195, and 1170 cm^{-1}; ^1H NMR, δ: 3.66 (3H, *s*, CH_3O), 3.3 (1H, *bm*, C*H*-O), 3.0 (1H, *m*, C*H*–O), 2.62 (2H, *d* of *d*, O–CH–CH_2C=O), 2.46 [2H, *t*, CH_2C(=O)–CH_2], 2.30 (2H, *t*, C$H_2CO_2CH_3$), 1.6 (4H, *m*, CH_2CH_2C=O), 1.2–1.5 (*m*, CH_2), and 0.87 (3H, *t*, CH_3CH_2) ppm; ^{13}C NMR (diagnostic signals), δ: 208.4 and 174.2 ppm; and MS, *m/z*: 326 (M), 295 (M – OCH_3), 241 (M – C_6H_{13}) 213 (M – COC_6H_{13}), and 113 (COC_6H_{13}).

Synthesis of **4** from the epoxyalcohol **2** was accomplished with NaOCl as follows. The epoxyalcohol **2** (1.00 g, 3.05 mmol) was stirred at room temperature in 6.6 mL of laundry bleach (5.25% NaOCl) that contained 2.1 mL of concentrated acetic acid for 1.5 h. The mixture was chilled in ice, and a cold solution of sodium carbonate (3 g in 10 mL H_2O) was added slowly to neutralize the mixture. The product was obtained by extraction with ether and, after the ethereal extract had been dried with anhydrous $MgSO_4$, the solvent was removed to give crystalline **4** (0.87 g, 87%).

Methyl 8-(5-hexylfuran-2-yl)octanoate, **5**. The ketoepoxide **4** (50 µL) was dissolved in 1 mL tetrahydrofuran with 10 µL of 1.5M $TiCl_4$ in CH_2Cl_2. After 1.5 h at room temperature, a TLC plate showed a single spot (R_f = 0.60) that was characterized as the furan, **5.** A sample was purified by flash chromatography (10% EA-H); IR: 1740 cm^{-1}; ^1H NMR, δ: 5.81 (2H, *s*, furanyl *H*), 3.64 (3H, *s*, OCH_3), 2.53 [4H, *t*, CH_2CH_2C(O)=C], 2.28 (2H, *t*, C$H_2CO_2CH_3$), 1.6 (2H, *m*, CH_2CH_2C=O), 1.2–1.4 (*m*, CH_2), and 0.86 (3H, *t*, CH_2CH_3) ppm; ^{13}C NMR (diagnostic signals) δ: 174.2, 154.7, 154.5, and 104.8 ppm; MS, *m/z* 310 (M), 277 (M – OCH_3), 237, and 165.

Diastereoselective epoxidations of methyl ricinoleate. The following procedure was used to obtain the data listed in Table 1. Freshly ground 3Å molecular sieves (0.25 g) were placed into a nitrogen-purged round-bottom flask. Dry

TABLE 1
Diastereomer Ratios for Methyl (*R,S*)-9,10-Oxido-12-hydroxyoctadecanoate with Different Epoxidizing Agents

Epoxidizing agent	Diastereomeric ratio[a]
m-Chloroperbenzoic acid	60:40
Ethylmethyldioxirane	45:55[b]
t-BuOOH, $Ti^{IV}(OiPr)_4$	75:25
t-BuOOH + $Ti^{IV}(OC[CH_3]_2CH_2CH_2CH_3)$	83:17
t-BuOOH + $Ti^{IV}(OiPr)_4$ + D-diethyl tartrate	86:14[c]
t-BuOOH + $Ti^{IV}(OiPr)_4$ + L-diethyl tartrate	78:22
t-BuOOH + $Ti^{IV}(OiPr)_4$ + D-diisopropyl tartrate	90:10
t-BuOOH + $Ti^{IV}(OiPr)_4$ + D-dicyclohexyl tartrate	87:13

[a]Diastereomeric ratio determined by gas–liquid chromatography (Supelcowax column) or high-performance liquid chromatography of (*S*)-α-methoxytrifluoromethyl phenylacetic acid esters (see the Materials and Methods section).
[b]Data taken from Reference 3.
[c]Reaction at –20°C gave 85:15 ratio. Abbreviation: $Ti^{IV}(OiPr)_4$, titanium isopropoxide.

dichloromethane (10 mL), tartrate ester (0.45 mmol), and titanium isopropoxide catalyst (0.4 mmol) were added sequentially to the flask. The mixture was cooled to –20°C, and the catalyst was aged at this temperature for 0.5 h. Methyl ricinoleate (3.0 mmol) and *t*-butylhydroperoxide (6.0 mmol) were added, and the mixture was allowed to stand at room temperature for 24 h. The mixture was transferred to a separatory funnel, and washed successively with equal volumes of 0.1 M ferrous sulfate (to destroy residual peroxide) and water and dried with anhydrous $MgSO_4$, and the solvent was removed *in vacuo*. The crude epoxyalcohol **2** was purified by silica flash chromatography (20% EA-H) monitoring by TLC (R_f = 0.40, 30% EA-H). GLC analysis of **2** obtained by this method was as described above.

Derivatization of **2** *with chiral reagents.* The epoxyalcohols, **2**, were converted to esters with Mosher's reagent (10), (*S*)-α-methoxytrifluoromethyl-phenylacetic acid (MTPA). The epoxy esters were purified by silica flash chromatography, and 100 µL of **2** was stirred at room temperature in a solution of 0.10 g each of MTPA and dicyclohexylurea in 5 mL CH_2Cl_2 with a trace of dimethylaminopyridine for several hours. The solution was filtered and analyzed directly by HPLC on a silica column with 15% ethyl acetate-hexane as mobile phase at a flow rate of 1 mL/min. The capacity factors for the diastereomers were 1.94 and 2.04 (α = 1.05), respectively. A larger preparation of acylated **2** was made for HPLC separation and isolation of the diastereomeric acylated esters of **2**. Minor differences were noted in the ^{1}H NMR spectra of the diastereomers; the most dramatic is the chemical shift difference for the α-OCH_3 protons. For HPLC peak #1: 3.411 ppm; for HPLC peak #2: 3.424. HPLC peak #2 corresponds to the major diastereomer formed by epoxidation of methyl ricinoleate.

(*S*)-1-(1-Naphthyl)ethyl isocyanate was used to prepare diastereomeric carbamates from **2** by means of the procedure described by us with methyl ricinoleate (11). The products were not separable by HPLC, and the ^{1}H NMR spectra of mixtures of varying composition only indicated that differentiation of the CO_2CH_3 groups was possible (δ = 0.01 ppm). This was of no help in assigning configuration of the epoxide rings.

RESULTS AND DISCUSSION

Oxidation of methyl ricinoleate. Oxidation of the secondary alcohol group of methyl ricinoleate to a ketoalkene, **3** (Fig. 1), has been reported with chromic acid (12,13). We found that pyridinium chlorochromate–sodium acetate was a particularly convenient laboratory reagent for preparing **3**. Yields were higher, and product isolation was easier than previously reported (12).

Epoxidation of the ricinoleate ester is likewise a known reaction and has been accomplished, for example, by microwave irradiation of the ester with *meta*-chloroperbenzoic acid in methylene chloride (14). In our hands, this reagent and the conventional procedure generated two diastereomeric epoxyalcohols in a ratio of 3:2. Earlier, we reported the reactions of dimethyldioxirane (DMDO) and ethylmethyldioxirane (EMDO), generated with Oxone™, with methyl ricinoleate, as well as the ratios of the epoxidized alcohols that were produced by these and other dioxiranes (15). Because the dioxirane reaction procedure is simple and the reagents involved are quite inexpensive, we evaluated this reaction for preparing **2** as well as **4** in several complementary ways, namely, (i) Oxone™ without the added ketone that is normally used to generate a dioxirane, (ii) Oxone™-acetone-chloroform as a two-phase system to generate and use DMDO, (iii) an acetone solution of DMDO prepared as described by Crandall *et al.* (16), and (iv) Oxone™ in varying molar ratios to the homoallylic alcohol with 2-butanone as a cosolvent and source of EMDO in a two-phase reaction.

Alkenes have been epoxidized directly by Oxone™, that is, without the intermediacy of a dioxirane. For example, treatment of cyclooctene with this reagent in aqueous

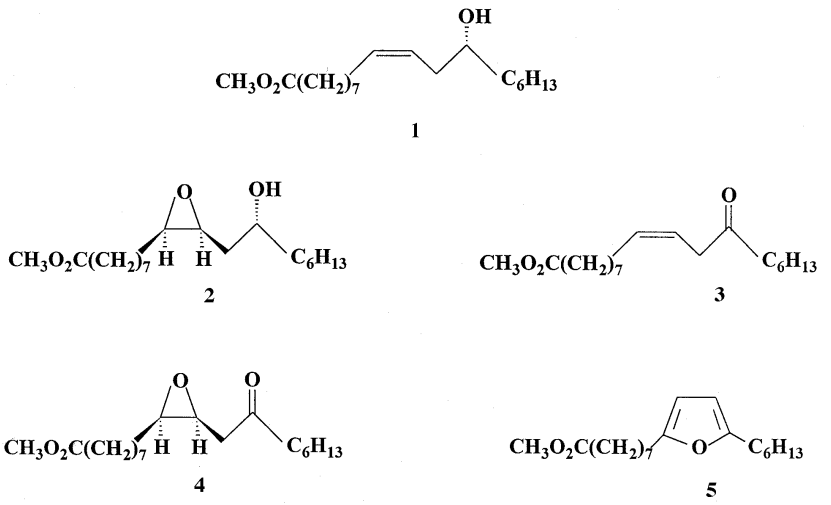


FIG. 1. Structural formulas for methyl ricinoleate (**1**), its oxidation products **2**, **3**, and **4** and furan **5**.

methanol at room temperature for 4 h gave a 94% yield of crude epoxycyclooctane (17). The same conditions applied to methyl ricinoleate gave less than 10% conversion to epoxyalcohol **2**. The two-phase reaction of DMDO in chloroform gave results similar to those for EMDO in 2-butanone as solvent (*vide infra*), but the oxidant was used less efficiently. An acetone solution of DMDO converted the homoallylic alcohol **1** to its epoxide preferentially, but as the amount of DMDO was increased, the epoxyketone **4** and furan **5** became significant products, as determined by GLC. For example, with as much as 14% of the original ester **1** remaining, epoxyalcohol **2** accounted for 28% of the mixture, along with epoxyketone **4** (32%) and furan **5** (28%). Reactions conducted under conditions (iv) above gave a 35% conversion of **1** to epoxyalcohol **2** with one equivalent of Oxone™, and 94% with a 2:1 ratio of oxidant to homoallylic alcohol **1**. Additionally, the product contained about 3% each of **4** and starting material **1**, along with a trace of **5**. An 8:1 ratio of oxidant/substrate succeeded in depleting **1** completely, but the product mixture now was 49% **2**, 33% **4**, and 18% **5**. Judging from the altered ratio of the diastereomers for this last oxidation, it appears that the epoxyalcohols served as precursors for the epoxyketone **4** and ultimately furan **5**.

The relative reactivity of a secondary alcohol and a disubstituted alkene has been investigated recently (18). Oxidation of unsaturated alcohols favors epoxidation, although alcohol structure and solvent composition can affect product distribution. Epoxidation was the sole reaction observed by these authors for a specific homoallylic alcohol. We briefly explored competitive oxidations of *Z*-5-decene and 2-decanol and observed that the alkene was oxidized at least 20 times faster than the alcohol group. In sharp contrast, the less electrophilic 1-decene reacted at a rate comparable to that of 2-decanol.

The epoxidation of chiral allylic alcohols can give epoxyalcohols with considerable diastereoselectivity when less polar solvents are used (19,20). This has been interpreted in terms of hydrogen bonding of the alcohol to the dioxirane. In all reactions studied, the ketoalkene was not the major product.

Briefly, we found that Oxone™-promoted oxidations of methyl ricinoleate can be employed successfully for preparation of the epoxyalcohol **2** under the conditions (iv) described above. The ketoalkene, **3**, was not observed as a co-product in any of our procedures. Although further oxidation of **2** to the epoxyketone **4** occurs, the process is complicated by epoxide ring opening of **4** to furan **5**. The ability of the hydroxyl group to direct a stereoselective epoxidation of **1** was not useful for obtaining epoxyalcohol **2** in high diastereomeric excess (de).

Because a one-pot transformation from **1** to **4** was not apparent, we examined single-step conversions of **2** to **4**, or of **3** to **4** (Fig. 1). Oxidations of secondary alcohols to ketones abound (21), although many of the procedures introduce electrophiles that might cause the epoxide ring to accept the neighboring hydroxy group as a nucleophile in a competing reaction that opens the ring. Posner's use of trichloroacetaldehyde and activated alumina in a hydride transfer reaction was appealing (22), but unfortunately it requires stringent conditions. The alumina is dried at 400°C for 24 h, and a quartz vessel is employed. Reactions of **2** with nonactivated alumina in pyrex glassware were unsuccessful. However, the epoxyalcohol **2** was converted in high yield to **4** with NaOCl in aqueous acetic acid. Reactions of **2** with pyridinium chlorochromate in dimethyl sulfoxide produced mainly furan **5** and minor amounts of epoxyketone **4**. Additionally, the ketoalkene **3** was epoxidized to **4** with either *meta*-chloroperbenzoic acid or EMDO. The latter reaction was conducted in the manner described above for the epoxidation of **1** (see the Materials and Methods section).

The furan, **5**, that was a byproduct of the DMDO and EMDO oxidations was prepared synthetically from the acid-labile epoxyketone **4**. Earlier accounts describe procedures that involve treatment of **4** with mercuric acetate in acetic acid with microwave heating (14), or with sodium azide and ammonium chloride in aqueous ethanol (23). Brief treatment of **4** with either a catalytic amount of titanium tetrachloride or a trace of perchloric acid in tetrahydrofuran gave furan **5** *via* the dihydrofuran **6** almost exclusively (Fig. 2A). Evidence that **6** is the precursor to **5** was obtained from gas chromatography–mass spectrometry. Direct analysis of **4** gave peaks whose mass spectra corresponded to compounds **5**, **4**, and **6,** in this order. Presumably, compounds **5** and **6** arose from thermal rearrangement of **4**. Prior treatment of ketoepoxide **4** with BSTFA before GLC-MS, however, gave a single peak whose fragmentation pattern matched that predicted for silylated **6** (Fig. 2B). Apparently, the acidity of the BSTFA reagent was sufficient to cause ring-opening of ketoepoxide **4** to **6**, which is silated by this reagent before it dehydrates to furan **5**.

Diastereoselective oxidations of methyl ricinoleate. The diastereoselectivity of epoxidation of chiral allylic alcohols with DMDO has been discussed with other oxidants (20). Oxidation of achiral allylic alcohols with induction of asymmetry by titanium-based chiral catalysts has been developed by K.B. Sharpless (24,25). The mechanisms by which these diastereoselective and steroselective epoxidations are accomplished are such that the competing transition states are better differentiated by the "tighter" arrangements permitted by the location of the alcohol OH as part of an allylic structure. Although the ricinoleic acid structure is homoallylic, we hoped that the configurational purity of **1** (*R*-12-hydroxy), coupled with a chiral catalyst, might allow good π-diastereofacial selectivity. The earlier diastereomeric ratios for epoxyalcohol **2**, obtained by reactions of **1** with *meta*-chloroperbenzoic acid, DMDO, and other dioxiranes, are given in Table 1. A titanium (IV)-catalyzed epoxidation (titanium isopropoxide) with *t*-butyl hydroperoxide as the oxidant led to a 3:1 ratio of diastereomeric epoxyalcohols (Table 1). When the alcohol ligand was replaced with a tertiary alcohol (titanium *t*-amyloxide), the diastereomeric excess (de) rose to 76%. A rationalization for chirality transfer by a titanium catalyst is shown in Figure 3. The side chain, hexyl substituent, prefers the equatorial position to avoid stearic interaction with a group attached to titanium that is oriented axially. We briefly examined Sharpless'

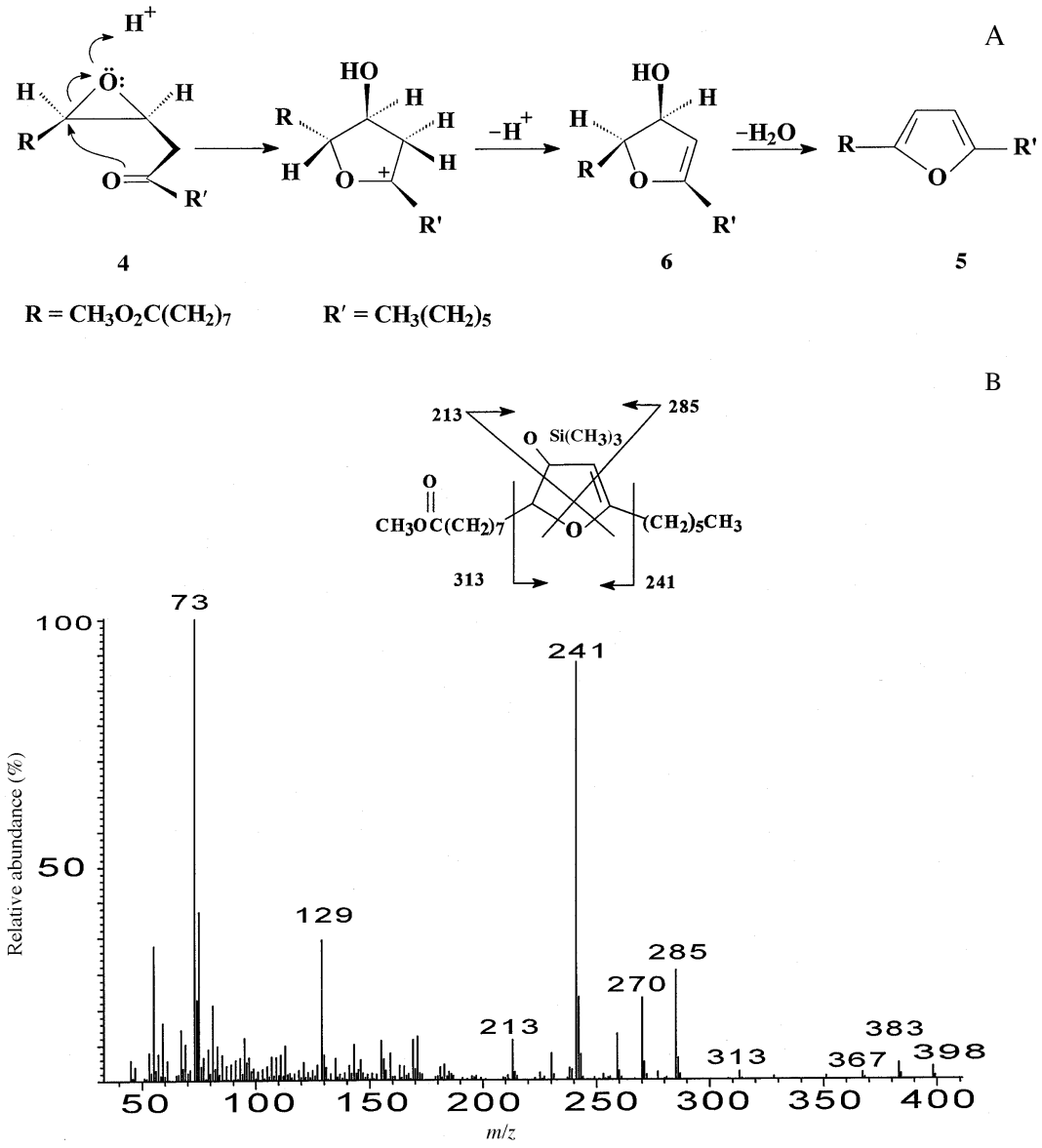
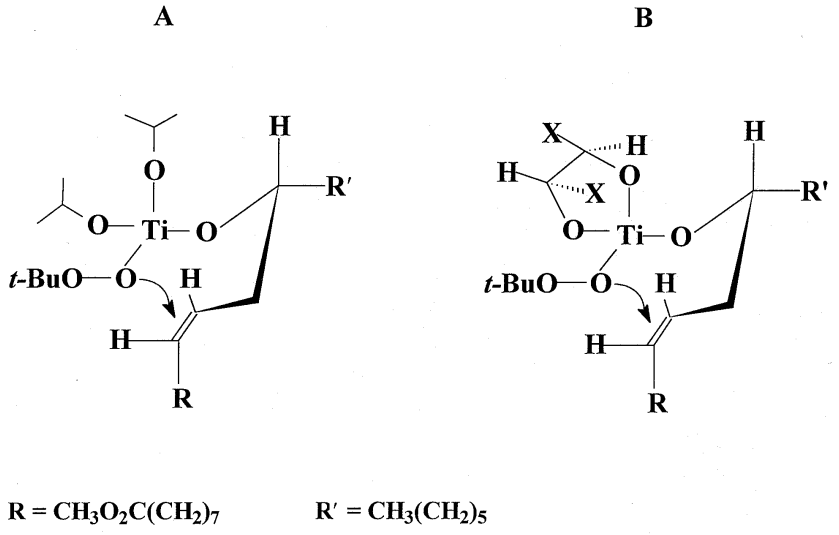


FIG. 2. (A) Proposed acid-catalyzed rearrangement pathway for ketoepoxide **4** to furan **5** through intermediate **6**. (B) Mass spectrum for silylated dihydrofuran intermediate **6**.

methodologies of enhancing the diastereoselectivity of epoxidation. L-Diethyl tartrate as ligand did not significantly alter the enantiomeric ratio of **2**, but the D-ester increased de to 72%. D-Diisopropyl tartrate as a ligand gave 80% de (9:1 ratio). Replacement of the isopropoxy groups on titanium by a chelate formed from a D-, as opposed to an L-tartrate ester ligand, might be expected to enhance stereo selection according to this picture. Figure 3 also suggests that the oxygen is delivered preferentially to that face, leading to the 9*S*,10*R* configuration for epoxyalcohol **2**.

In summary, the oxidation of methyl ricinoleate **1** can be conveniently conducted to produce selective oxidation of the alkene or the alcohol structures to epoxyalcohol **2** or ketoalkene **3**, respectively, as well as the concomitant oxidation of both functional groups to ketoepoxide **4**. Oxo and epoxy ricinoleic acid derivatives, such as those represented by structures **2**, **3**, and **4** in this paper, are of interest because of their potential in several industrial applications. For example, materials similar in structure to those obtained in this study have applications as nondrying polymer coatings, polyol surfactants, drying oils, and as emulsifiers and emollients in personal care products (4). Oxone™ is an inexpensive source of EMDO, which is becoming yet more useful as more convenient procedures for preparing it become available (26,27) and as alternate procedures for *in-situ* generation and use of other dioxiranes are reported (28,29). The ability of the 12-OH group of **1** to direct EMDO epoxidation in our trials was modest, but one can obtain a 9:1 ratio of diastereomeric epoxyalcohols by using *t*-butylhydroperoxide and a titanium catalyst coupled with D-diisopropyl tartrate ligand.



$R = CH_3O_2C(CH_2)_7$ $R' = CH_3(CH_2)_5$

FIG. 3. Selective diastereomeric epoxidation of methyl ricinoleate with *t*-butylhydroperoxide catalyzed by chiral titanium^{IV} complexes.

REFERENCES

1. Vignolo, R., and F. Naughton, Castor: A New Sense of Direction, *INFORM 2*:692–699 (1991).
2. Haumann, B.F., Work Continues on New Oils for Industrial Use, *Ibid. 2*:678–690 (1991).
3. Carlson, K.D., and S.P. Chang, Chemical Epoxidation of a Natural Unsaturated Epoxy Seed Oil from *Vernonia galamensis* and a Look at Oil Markets, *J. Am. Oil Chem. Soc. 62*:934–939 (1985).
4. Derksen, J.T.P., F.P. Cuperus, and P. Kolster, Paints and Coatings from Renewable Resources, *Ind. Crops Prod. 3*:225–236 (1995).
5. Rushing, J.F., G.R. Riser, M.E. Snook, and W.E. Scott, Epoxidation of Alkyl Esters of 12,13-Epoxyoleic Acids and Evaluation of the Diepoxides as Plasticizers for Poly(vinyl chloride), *J. Am. Oil Chem. Soc. 45*:760–763 (1968).
6. Watanabe, S., T. Fujita, and M. Sakamoto, Epoxides of Unsaturated Fatty Acids as Anti-Rust Derivatives in Water-Based Cutting Fluids, *Ibid. 65*:1311–1312 (1988).
7. Klaas, M.R.G., and S. Warwel, Chemoenzymatic Epoxidation of Unsaturated Fatty Acid Esters and Plant Oils, *Ibid. 73*:1453–1457 (1996).
8. Yadav, G.D., and D.V. Satoskar, Kinetics of Epoxidation of Alkyl Esters of Undecylenic Acid. Comparison of Traditional Routes vs. Ishii-Venturello Chemistry, *Ibid. 74*:397–407 (1997).
9. Curci, R.M., M. Fiorentino, and L. Troisi, Epoxidation of Alkenes by Dioxirane Intermediates Generated in the Reaction of Potassium Caroate with Ketones, *J. Org. Chem. 45*:4758–4768 (1980).
10. Dale, J.A., D.L. Dull, and H.S. Mosher, α-Methoxy-α-trifluoromethyl-phenylacetic Acid, a Versatile Reagent for the Determination of Enantiomeric Composition of Alcohols and Amines, *Ibid. 34*:2543–2549 (1969).
11. Sonnet, P.E., R.L. Dudley, S. Osman, P.E. Pfeffer, and D. Schwarz, Configuration Analysis of Unsaturated Hydroxy Fatty Acids, *J. Chromatogr. 586*:255–258 (1991).
12. Lie Ken Jie, M.S.F., and Y.F. Zheng, A Convenient Route to a Linear C_{18} Carboxylic Acid Derivative Containing a Thiophene Ring in the Chain *via* a 9,10-Epithio-12-oxo Intermediate, *Synthesis 23*:467–468 (1988).
13. Maletz, R., H.J. Schafer, and R. Quermann, Conversion of Unsaturated Fatty Acids: Nucleophilic Additions to Methyl (*E*)-12-Oxo-10-octadecenoate, *Fett-Lipid 98*:370–379 (1996).
14. Lie Ken Jie, M.S.F., and Y.-K. Cheung, The Use of a Microwave Oven in the Chemical Transformation of Long Chain Fatty Acid Esters, *Lipids 23*:367–369 (1988).
15. Sonnet, P.E., M.E. Lankin, and G.P. McNeill, Reactions of Dioxiranes with Selected Oleochemicals, *J. Am. Oil Chem. Soc. 72*:199–204 (1995).
16. Crandall, J.K., D.J. Batal, D.P. Sebesta, and F. Lin, 1,4-Dioxaspiro[2.2] Pentanes. Synthesis, Spectroscopic Properties and Reactions with Nucleophiles, *J. Org. Chem. 56*:1153–1166 (1991).
17. Bloch, R., J. Abecassis, and D. Hassan, Epoxidation of Alkenes with Potassium Hydrogen Persulfate, *Ibid. 50*:1544–1552 (1985).
18. Murray, R.W., M. Singh, B.L. Williams, and H.M. Moncrief, Diastereoselectivity in the Epoxidation of Substituted Cyclohexenes by Dimethyldioxirane, *Ibid. 61*:1830–1841 (1996).
19. Adam, W., and A.K. Smerz, Solvent Effects in the Dimethyldioxirane Oxidation of Allylic Alcohols: Evidence for Hydrogen Bonding in the Dipolar Transition State of Oxygen Transfer, *Tetrahedron 51*:13039–13046 (1995).
20. Adam, W., and A.K. Smerz, Solvent Effects in the Regio- and Diastereoselective Epoxidations of Acyclic Allylic Alcohols by Dimethyldioxirane: Hydrogen Bonding as Evidence for a Dipolar Transition State, *J. Org. Chem. 61*:3506–3510 (1996).
21. Carey, F.A., and R.J. Sundberg, *Advanced Organic Chemistry, B,* 3rd edn., Plenum Press, New York, 1993, pp. 615–624.
22. Posner, G.H., R.B. Perfetti, and R.W. Runquist, Organic Reactions at Alumina Surfaces. V. Highly Selective Alcohol and Diol Oxidation Reactions on Alumina, *Tetrahedron Lett. 39*: 3499–3502 (1976).
23. Lie Ken Jie, M.S.F., and K. Syed-Rahmatullah, Chemical and Enzymatic Preparation of Acylglycerols Containing C_{18} Furanoid Fatty Acids, *Lipids 30*:79–84 (1995).
24. Finn, M.G., and K.B. Sharpless, Asymmetric Epoxidations, Chapter 8, in *Asymmetric Synthesis*, edited by J.D. Morrison, Academic Press, New York, 1985, Vol. 5, pp. 247–281.
25. Gao, Y., R.M. Hanson, J.M. Klunder, Y.K. Soo, H. Masamune, and K.B. Sharpless, Catalytic Asymmetric Epoxidation and Kinetic Resolution: Modified Procedures Including *in situ* Derivatization, *J. Am. Chem. Soc. 109*:5765–5779 (1987).
26. Adam, W., J. Bialas, and L. Hadjiarapoglou, A Convenient

Preparation of Acetone Solutions of Dimethyldioxirane, *Chem. Ber. 124*:2377–2381 (1991).
27. Ferrer, M., M. Gilbert, F. Sanchez-Baeza, and A. Messeguer, Easy Availability of More Concentrated and Versatile Dimethyldioxirane Solutions, *Tetrahedron Lett. 37*:3585–3589 (1996).
28. Yang, D., M.-K. Wong, and Y.-C. Yip, Epoxidations of Olefins Using Methyl(trifluoromethyl)dioxirane Generated *in situ*, *J. Org. Chem. 60*:3887–3889 (1995).
29. Yang, D., Y.-C. Yip, M.-W. Tang, M.-K. Wong, J.-H. Zheng, and K.-K. Cheung, A C_2 Symmetric Chiral Ketone for Catalytic Asymmetric Epoxidation of Unfunctionalized Olefins, *J. Am. Chem. Soc. 118*:491–494 (1996).

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