J Am Oil Chem Soc (2008) 85:647–653
DOI 10.1007/s11746-008-1235-9

ORIGINAL PAPER

Synthesis and Structural Analysis of Branched-Chain Derivatives of Methyl Oleate

Oliver D. Dailey Jr · Nicolette T. Prevost · Gary D. Strahan

Received: 30 July 2007 / Revised: 12 March 2008 / Accepted: 13 March 2008 / Published online: 6 May 2008

Abstract As part of a project to develop new value-added industrial applications for cottonseed oil (such as biodiesel, fuel additives, and lubricants), studies were conducted on the synthetic conversion of oleic acid to branched-chain fatty acid esters. In these studies, methyl oleate was brominated in the allylic position and subsequently treated with organocuprate reagents to produce novel branched-chain derivatives (methyl, *n*-butyl, phenyl). Original reaction conditions afforded only the branched methyl derivatives as major products. Modification of reaction conditions (lower temperature, less organocuprate reagent) afforded predominantly the desired *n*-butyl and phenyl derivatives and minimized products resulting from attack on the ester functionality. Details of the syntheses, characterization (especially by NMR), and the properties of the products (with emphasis on low-temperature properties) are discussed.

Keywords Allylic bromides · Branched-chain fatty acids · DSC · Low-temperature properties · NMR · Organocuprate reagents

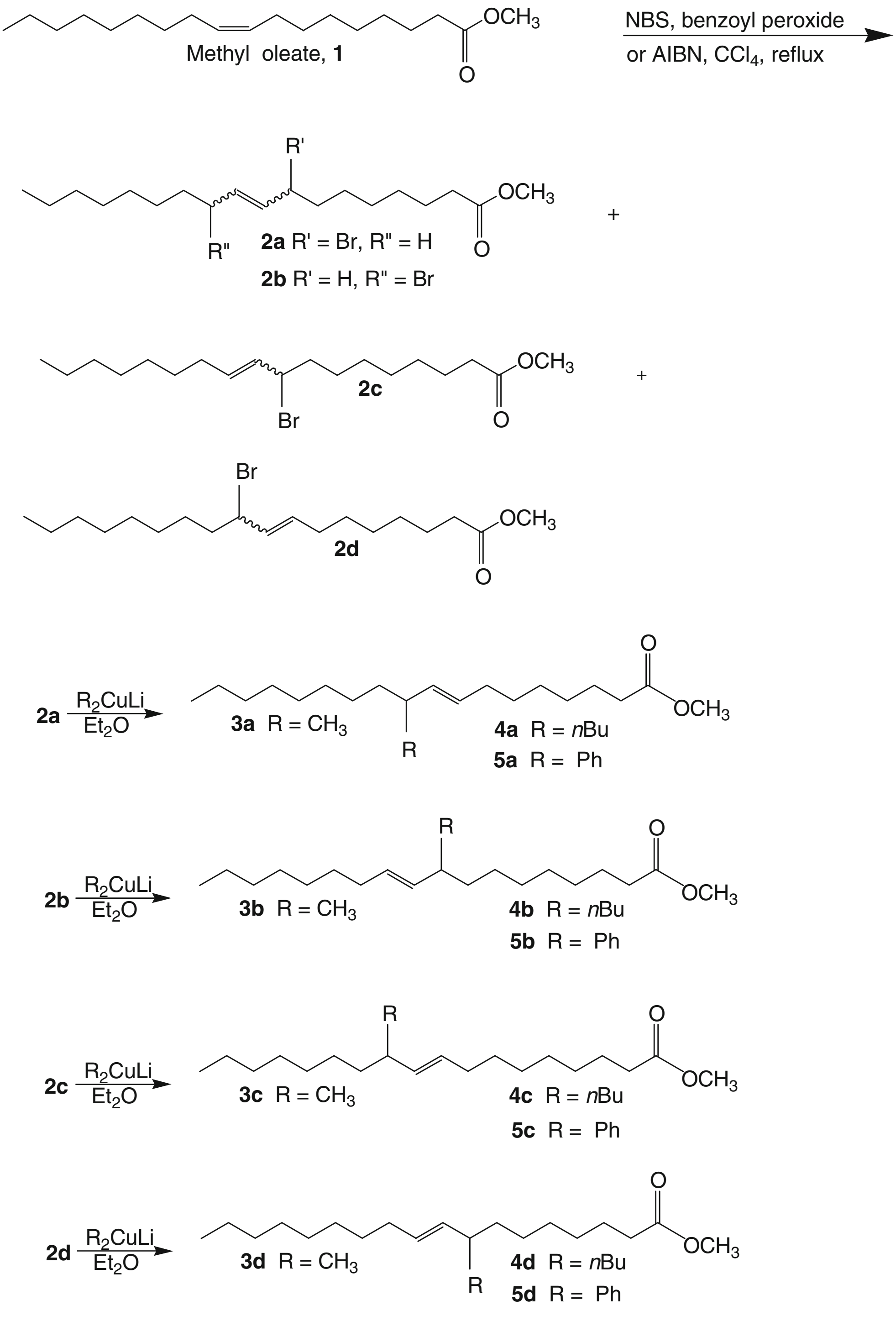
Introduction

The use of vegetable oils as alternative diesel fuels (biodiesel) has been investigated for over a century. In the United States, soybean oil has received the most interest. However, neat vegetable oils pose a problem impairing their widespread use as biodiesel in that they cause engine deposits [1]. In an attempt to overcome this problem, biodiesel is typically obtained by the conversion of vegetable oils or animal fats to simple monoalkyl esters of fatty acids. These products, usually methyl or ethyl esters, can be used as alternative fuels or extenders in diesel engines. However, the relatively poor low-temperature properties (freezing in cold climates) of these biodiesel fuels present an obstacle to their continued development and commercialization [2, 3]. The conversion of vegetable oils and animal fats into esters of branched-chain alcohols, such as isopropyl or 2-butyl, has resulted in improved low-temperature properties, as demonstrated by their reduced crystallization onset temperatures [3–5].

Simple monoalkyl esters or modified oils containing branched-chain fatty acids could have improved or superior low-temperature properties. Oleic acid and linoleic acid are the most abundant fatty acids of many vegetable oils, including cottonseed oil. As part of a project to develop new value-added industrial applications for cottonseed oil (such as biodiesel, fuel additives, and lubricants), studies were conducted on the synthetic conversion of oleic acid to branched-chain fatty acid esters. In these studies, the model compound methyl oleate (**1**) was brominated in the allylic position (Scheme 1) and subsequently treated with cuprate reagents to produce branched-chain derivatives. In previously reported research [6], reaction of the allylic bromides **2** with lithium dimethylcuprate using conditions (fivefold excess of cuprate reagent, quenching of the reaction at 0 °C) described in the literature [7, 8] produced the expected desired products (**3**, Scheme 1).

O. D. Dailey Jr (✉) · N. T. Prevost
USDA, ARS, Southern Regional Research Center,
1100 Robert E. Lee Blvd, New Orleans, LA 70124, USA
e-mail: Oliver.Dailey@ars.usda.gov

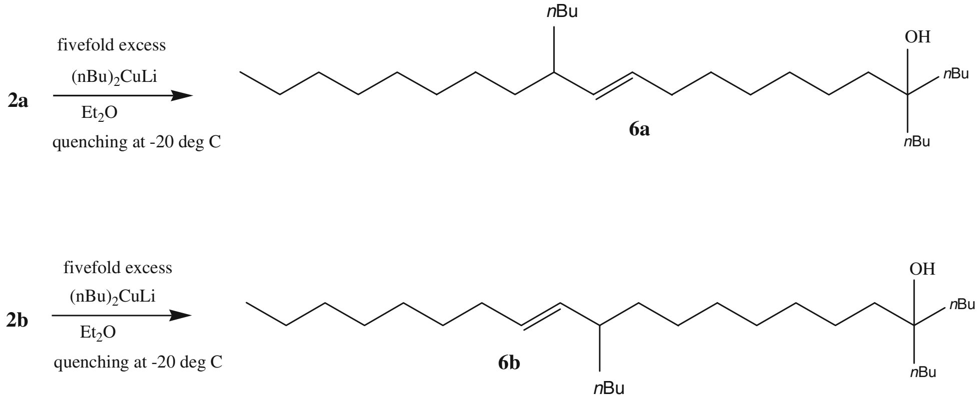
G. D. Strahan
USDA, ARS, Eastern Regional Research Center,
600 E. Mermaid Lane, Wyndmoor, PA 19038, USA



Scheme 1 Synthetic route to branched-chain derivatives of methyl oleate

However, reaction of the allylic bromides with a fivefold excess of lithium di-*n*-butylcuprate and quenching at −20 °C afforded no expected branched chain derivatives but primarily products resulting from attack at the ester functionality (Scheme 2). In this paper, we describe the modification of reaction conditions (less organocuprate reagent, lower temperatures) which provide the desired intact branched-chain derivatives of methyl oleate. Details of the syntheses, characterization, and properties of the products are discussed.

Scheme 2 Synthesis of the tertiary alcohols **6**. Structures of two of the four isomeric products are given



Experimental Procedures

Materials

Methyl oleate (99%), *N*-bromosuccinimide (NBS, 99%), benzoyl peroxide (97%), *n*-butyllithium (2.5 M in hexanes), *t*-butyllithium (1.7 M in pentane), phenyllithium (1.8 M in di-*n*-butyl ether), silica gel (Merck, grade 9385, 230–400 mesh) and diethyl ether (anhydrous, 99%+, ACS reagent) were purchased from Aldrich Chemical Company (Milwaukee, WI, USA). Cuprous iodide (98%) was purchased from Alfa-Aesar (Ward Hill, MA, USA). Calcium hydride (97%+) was purchased from Fluka (Milwaukee, WI, USA). Diethyl ether was distilled from calcium hydride and stored over Type 4A molecular sieves under a nitrogen atmosphere.

Gas Chromatography/Mass Spectroscopy

A 1 μL aliquot of the sample was injected into a split/splitless injector (300 °C) on an Agilent 6890 gas chromatograph (Palo Alto, CA, USA). The initial column pressure was held at 25 psi and a constant flow rate of 1.2 mL/min was maintained through the column using electronic pressure control (EPC). The oven temperature was held at 50 °C for 1 min, and then raised at a rate of 3 °C/min to 80 °C; the rate was changed to 10 °C/min and the oven temperature raised to 340 °C and held for 18 min for a total run time of 55 min. The GC was equipped with a 0.25 mm ID × 30 m capillary column coated with a 0.5 μm film of 5% diphenyl/95% dimethylsiloxane (DB-5MS, J&W Scientific, Folsom, CA, USA). The effluent from the column was analyzed by an Agilent 5973 MSD employing electron ionization and operated in scan mode in the *m*/*z* range 40–550. Initial identification of known compounds was made by comparison with the seventh edition of the Wiley Mass Spectral Library. Percentages of components of crude products based on GC/MS are not meant to be definitive; they are used only as an indication. However, the percentages should be fairly realistic since the compounds analyzed are generally closely related structurally.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a TA Instruments (New Castle, DE, USA) DSC Q100 thermal analytical device. For methyl oleate, the experiment consisted of heating the samples (6 mg) from −100 to +40 °C at a rate of 10 °C/min followed by cooling from +40 to −100 °C at the same rate. The cycle was then repeated, and the thermal transitions recorded. For the methyl (**3**), *n*-butyl (**4**), and phenyl derivatives (**5**) the temperature range was −125 to +30 °C. The second cooling scan was used to find the recrystallization temperature, T_c. The second heating scan was used to find the melting temperature, T_m, and the onset and the midpoint of the glass transition temperature, T_g. The second run is considered more reliable, since the first run results in a more uniform sample.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Solution-state NMR spectra were recorded at 9.4 T on a Varian (Palo Alto, CA, USA) Inova NMR spectrometer, using a 5 mm broadband probe and operating at 25 °C. The ^{1}H (proton) spectra at 400 MHz had a sweep-width of 6,000 Hz, were acquired with a 90° pulse angle and a 2.5 s relaxation delay, and were referenced to internal tetramethylsilane (TMS). The ^{13}C spectra at 100 MHz had a sweep-width of 30,000 Hz for ^{13}C, were acquired with a 45° pulse angle and a 2 s relaxation delay, and were referenced to the $CDCl_3$ peak, 77.05 ppm from TMS. For compounds **4** and **5,** a fully edited distortionless enhancement polarization transfer (DEPT) experiment was run using the standard flip angles of 45°, 90° and 135°, followed by mathematical manipulation to generate the CH, CH_2 and CH_3 spectra. Proton signals for all compounds were assigned by proton spin-decoupling experiments, gradient-enhanced COSY and TOCSY (50 μs mixing time). All homonuclear 2-D experiments used ^{1}H spectral widths of 8,000 Hz, and were acquired with 16 transients, a 2 s relaxation time, and either 400 or 512 indirectly detected points. Gradient-enhanced versions of heteronuclear multiple quantum coherence (HMQC, phase-insensitive) and heteronuclear multiple bond correlation experiments (HMBC) (8 Hz) were performed to assign the ^{13}C signals. These heteronuclear 2-D experiments had ^{1}H spectral widths of 8,000 Hz and ^{13}C spectral widths of 25,000 Hz, and were acquired with 16 directly detected transients, a 2 s relaxation time, and 300–400 indirectly detected points.

Allylic Bromination of Methyl Oleate

A solution of methyl oleate (5.26 g, 17.7 mmol), NBS (3.57 g, 20.1 mmol), and benzoyl peroxide (95.5 mg, 0.41 mmol) in 50 mL of CCl_4 was heated at reflux under nitrogen for 2 h. After cooling, the precipitate was filtered and the solvent removed in vacuo, giving 6.53 g of allylic bromides **2** (Scheme 1). This material, owing to its instability, was used in subsequent reactions without further purification.

Reaction of Allylic Bromides with Lithium Dialkylcuprate Reagents

General Procedure

A twofold excess of lithium di-*n*-butylcuprate, lithium di-*t*-butyllithium or lithium diphenylcuprate was prepared at −40 to −50 °C, the allylic bromides were added at −78 °C, and the reaction mixture was stirred for 2–3 h. The reaction was quenched at −78 °C by the dropwise addition of methanol, with the temperature maintained at −50 °C or below during the addition. The reaction mixture was allowed to warm to room temperature overnight. The precipitate was removed by filtration and the filtrate containing the organic product was dissolved in ethyl ether (50 mL). The ether solution was washed with saturated ammonium chloride solution (pH 8) (2 × 50 mL). Combined aqueous layers were extracted with ether (50 mL); combined ether layers were washed with deionized water (100 mL) and brine (100 mL) and dried over $MgSO_4$. Solvent was removed in vacuo and the product was dried to a constant weight at ca. 1 torr.

Preparation of *n*-Butyl Derivatives **4**

Lithium di-*n*-butylcuprate was prepared in situ by the addition of 10.8 mL (27.0 mmol) of *n*-butyllithium (2.5 M in hexanes) to 2.63 g (13.8 mmol) of cuprous iodide stirred in 50 mL of dry ether for 0.5 h under nitrogen at −40 °C. The resulting black solution was stirred at −40 °C for 20 min and cooled to −78 °C over 30 min. To the solution was added 2.91 g (ca. 7.74 mmol) of allylic bromides (**2**) in 30 mL of ether. The solution was stirred at −78 °C for 2 h and then the reaction was quenched with 10 mL of methanol added dropwise. Following work-up, 2.84 g of crude product was isolated as a colorless liquid (theoretical yield: 2.73 g).

Flash chromatography (first column: silica gel, 2% ethyl acetate/petroleum ether eluant; second column: silica gel, 1% ethyl ether/petroleum ether) [9] provided the analytical sample (16.0% yield): MS (EI): *m*/*z* (%) = 352 (53), 321 (45), 310 (23), 295 (36), 263 (39), 211 (43), 210 (51), 153 (57), 152 (48). 151 (57), 143 (55), 139 (54), 125 (72), 111 (76), 97 (88), 83 (91), 69 (95), 55 (100), 41 (91); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3, side-chain CH_3), 0.88 (t, 3, terminal CH_3), 1.60 (m, 2, $\mathbf{CH_2}$–$CH_2CO_2CH_3$), 1.62 (m, C$\mathbf{H_2}$–CH–*n*Bu), 1.83 (m, 1, CH_2CH=CHC$\mathbf{H}$–*n*Bu), 1.96 (q, 2, $\mathbf{CH_2}$CH=CHCH–*n*Bu), 2.31 (t, 2, C$\mathbf{H_2}$$CO_2CH_3$), 1.0–1.4 (m, 24, remaining 12 CH_2), 3.66 (s, 3, OC$\mathbf{H_3}$), 5.08 (m, 1, CH_2CH=C***H***CH–*n*Bu), and 5.28 (m, 1, CH_2C**H**=CHCH–*n*Bu); ^{13}C NMR ($CDCl_3$) δ, 14.16 (terminal **C**H_3 and branch-chain **C**H_3), 22.72, 22.86, 25.01 (**C**H_2–$CH_2CO_2CH_3$), 27.13, 27.25, 27.32, 28.72, 28.92, 29.04, 29.09, 29.14, 29.22, 29.31, 29.40, 29.58, 29.61, 29.69, 29.77, 29.84, 31.96, 32.52, 32.58, 32.62, 34.15 (**C**$H_2CO_2CH_3$), [35.33, 35.54, 35.59, 35.61] (**C**H_2–CH–*n*Bu), 42.81 (CH_2CH=CH**C**H–*n*Bu), 51.44 (O**C**H_3), [129.78, 129.89, 130.09, 130.14] (CH_2**C**H=CHCH–*n*Bu), [135.02, 135.08, 135.25, 135.33] (CH_2CH=**C**HCH–*n*Bu), [174.34, 174.36] (**C**=O).

Preparation of Phenyl Derivatives **5**

A similar procedure was followed for the reaction of the allylic bromides (1.54 g, 4.10 mmol) with a twofold excess of lithium diphenylcuprate, affording 1.86 g of crude product as a pale yellow liquid. Correcting for the presence of biphenyl, GC/MS analysis indicated that the crude product consisted of 64.1% **5**. Flash chromatography (first column: silica gel, 3% ethyl acetate/hexanes eluant; second column: silica gel, 3% ethyl ether/hexanes) afforded the analytical sample (26.2% yield): MS (EI): *m*/*z* (%) = 372 (46), 341 (21), 273 (21), 259 (41), 241 (25), 229 (59), 227 (44), 215 (39), 209 (42), 145 (34), 143 (44), 131 (71), 130 (47), 129 (71), 128 (47), 117 (100), 115 (60), 91(89), 69 (37), 55 (52), 43 (52), 41 (55); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3, CH_3), 1.60 (m, 2, $\mathbf{CH_2}$–$CH_2CO_2CH_3$), 1.64 (m, 2, $\mathbf{CH_2}$CHPh), 1.98 (q, 2, $\mathbf{CH_2}$CH=CHCHPh), 2.27 (t, 2, $\mathbf{CH_2}$$CO_2CH_3$), 1.0–1.4 (m, 18, remaining 9 CH_2), 3.16 (m, 1, CH_2CH=CHC**H**Ph), 3.65 (s, 3, OC$\mathbf{H_3}$), 5.42 (m, 1, CH_2C**H**=CHCHPh), 5.52 (m, 1, CH_2CH=C**H**CHPh), 7.15

(m, *p* aromatic H), 7.16 (m, 2, *o* aromatic H) and 7.26 (m, 2, *m* aromatic H); ^{13}C NMR (CDCl$_3$) δ, 14.34 (**C**H$_3$), 22.91, 25.17 (**C**H$_2$–CH$_2$CO$_2$CH$_3$), 27.66, 27.77, 27.85, 28.96, 29.20, 29.31, 29.36, 29.39, 29.44, 29.55, 29.64, 29.68, 29.74, 29.79, 29.83, 32.12, [32.70, 32.76, 32.81] (**C**H$_2$CH=CHCHPh), 34.33 (**C**H$_2$CO$_2$CH$_3$), 36.38 (**C**H$_2$CHPh) 49.12 (CH$_2$CH=CH**C**HPh), 51.66 (O**C**H$_3$), 126.05 (*p* aromatic C) 127.72 (*o* aromatic C), 128.54 (*m* aromatic C), [130.13, 130.25, 130.45, 130.48] (CH$_2$**C**H=CHCHPh), [134.14, 134.20, 134.37, 134.47] (CH$_2$CH=**C**HCHPh), [145.88, 145.94, 145.98] (quaternary phenyl C), 174.54 (**C**=O).

Reaction of the allylic bromides (1.560 g, 4.16 mmol) with a twofold excess of lithium di-*t*-butylcuprate provided 1.222 g of product. However, GC/MS analysis showed a complex mixture with no evidence of desired product.

Results and Discussion

The conversion of oleic acid and methyl oleate to saturated branched-chain derivatives has been reported [10]. In this paper we report the conversion of methyl oleate to branched-chain derivatives in which the double bond is retained. The free-radical allylic bromination of methyl oleate [11] gives four different isomeric products (Scheme 1). Only two of the four structures were given in our initial report [6]. Reaction of the allylic bromides **2** with selected lithium dialkylcuprate reagents yields the branched-chain derivatives **3**–**5** (Scheme 1). The four isomeric allylic bromides give rise to four distinct products (confirmed by ^{13}C NMR spectral analysis) correspondingly designated **a** through **d**. The proposed structural assignments of the products are based upon nucleophilic attack at the γ-carbon via the S$_N$2′ mechanism [12]. Finally, the assignment of the *trans* configuration to the products is based on the findings of proton spin-decoupling experiments.

Lithium dialkylcuprates were selected for the introduction of branch chains since these reagents are reported to be unreactive toward esters under the conditions employed. The ester *n*-C$_4$H$_9$CO$_2$CH$_3$ was recovered (>85%) when treated with three equivalents of lithium dimethylcuprate at 18 °C or three equivalents of lithium di-*n*-butylcuprate at −10 °C [13]. In previously reported research [6], reaction of the allylic bromides **2** with lithium dimethylcuprate using conditions (fivefold excess of cuprate reagent, quenching of reaction at 0 °C) described in the literature [7, 8] produced the expected desired products **3**. However, the tertiary alcohols **6** (Scheme 2) were the major products obtained in the reaction of **2** with lithium di-*n*-butylcuprate, and the expected products **4** (Scheme 1) were not observed.

Reaction conditions were modified (lower temperature, less organocuprate reagent) in order to obtain the desired branched-chain *n*-butyl derivatives **4.** The allylic bromides **2** were added to a solution containing a twofold excess of lithium di-*n*-butylcuprate at −78 °C, and the reaction was quenched at −78 °C. GC/MS analysis of the isolated liquid showed that the major products (63.2%) had M+ of 352, corresponding to the expected products **4**. The most abundant secondary products (10.4%) were the tertiary alcohols **6**. Flash chromatography afforded fractions containing 95.0% **4** (GC/MS analysis) as a colorless liquid. Under the same low-temperature conditions, reaction of lithium diphenylcuprate with the allylic bromides afforded a product consisting of 64.1% **5** (Scheme 1) based on GC/MS analysis. A second component with M$^+$ 372 (2.0%) was also observed, as well as M$^+$ 296 (3.8 % unreacted methyl oleate) and M$^+$ 294 (5.9%, dienes). Flash chromatography afforded fractions containing 75.6% **5** as a colorless liquid. The remaining material exhibited M$^+$ 294 (16.1%) and M$^+$ 372 (8.3%).

The proton NMR spectrum of phenyl derivatives **5** is shown in Fig. 1 and is consistent with the structure as shown. Peak assignments are given for structure **5a**; analogous assignments would be made for **5b**, **5c**, and **5d**, taking into account the configuration about the double bond. Since the structures of the four isomers are so closely related, the proton NMR spectra are expected to be indistinguishable. Peak assignments were accomplished by proton spin-decoupling experiments and the 2-D experiments, using the proton NMR spectrum of methyl oleate [14] as a guide. The signals associated with the olefinic protons were very complex. However, analysis of a series of spin-decoupling experiments did allow for a definitive assignment of configuration about the double bond. The signal centered at 5.52 ppm (–CH$_2$CH=C**H**CHPh–) was determined to be a doublet of doublets with coupling constants of 15.2 Hz and

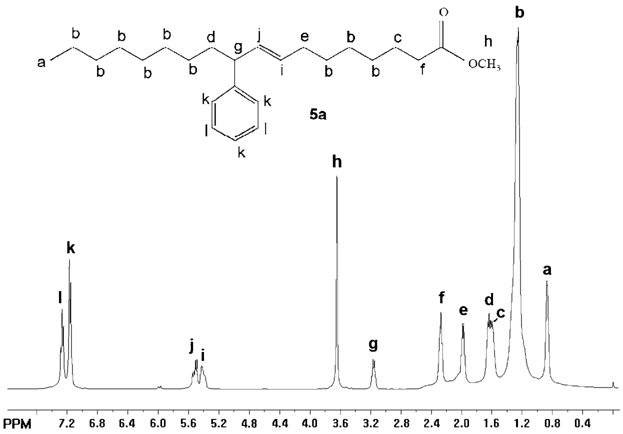


Fig. 1 Proton NMR spectrum of phenyl derivatives **5**. Assignments of *peaks* to the corresponding protons are made in the structural diagram of isomer **5a**

approximately 7.5 Hz. Analysis of the signal centered at 5.42 ppm (–CH$_2$**CH**=CHCHPh–) yielded coupling constants of 15.2 Hz and approximately 6.9 Hz. The signal centered at 1.98 ppm (–**CH$_2$**CH=CHCHPh–) appears to be a quartet but actually consists of two overlapping triplets or a triplet of doublets, with $J = 6.9$ Hz. The signal centered at 3.16 ppm (–CH$_2$CH=CHC**H**Ph–) also appears to be a quartet but actually consists of two overlapping triplets, with $J = 7.5$ Hz. These splitting patterns are consistent with the isomeric structures **5a–d**, in which 15.2 Hz corresponds to the coupling of the olefinic protons, and 7.5 and 6.9 Hz are the couplings of each olefinic proton and adjacent alkyl proton**.** The coupling constant of 15.2 Hz for the olefinic protons is definitive for the *trans* conformation.

Coupling constant analysis of the olefinic region of the ^{1}H spectrum of the *n*-butyl derivatives **4** also yielded *J* values that indicated the *trans* conformation. Upon the analysis of spin-decoupling experiments, the signal centered at 5.28 ppm (–CH$_2$**CH=**CHCH–*n*Bu–) was determined to be four overlapping triplets (triplet of two doublets) and the signal centered at 5.08 ppm (–CH$_2$CH=C**H**CH–*n*Bu–) was determined to be a doublet of two doublets. The coupling constant between the two olefinic protons was 15.1 Hz, specifying a *trans* geometry. The signal centered at 1.96 ppm (–**CH$_2$**CH=CHCH–*n*Bu–) appears to be a quartet but actually consists of two overlapping triplets or a triplet of doublets, with $J = 6.8$ Hz. The signal centered at 1.83 ppm (–CH$_2$CH=CHC**H**–*n*Bu–) was too complex for resolution but the coupling constant with the adjacent olefinic proton was determined to be approximately 8.4 Hz.

Analysis of the ^{13}C NMR chemical shifts of the olefinic carbons of the methyl derivatives **3** and alcohols **6** using alkene shift parameters [15] had previously led to the conclusion that these compounds were probably in the *cis* conformation [6]. Similar analyses for compounds **4** and **5** would lead to similar conclusions. However, these analyses of small changes in chemical shifts are based on empirical generalizations and are therefore inconclusive. Instead, the coupling constants conclusively indicate that the configuration about the double bond of the branched-chain derivatives is exclusively *trans*.

The ^{13}C resonance analysis (DEPT, HMQC and HMBC) for **4** and **5** allowed for the specific assignments made in the "Experimental Procedures" section. All of the remaining carbons in the range 20–33 ppm are CH$_2$ and cannot be unambiguously assigned due to spectral overlap. The DEPT spectrum analysis confirmed the assignments of all primary, tertiary, and quaternary non-aromatic carbon atoms.

As was the case with the methyl derivatives **3** and tertiary alcohols **6**, there are two sets of four distinct peaks in the olefinic region of the ^{13}C NMR spectra of compounds **4** and **5**, providing concrete evidence of the presence of the four isomers of each of the branched-chain derivatives. Assuming that similar carbons have similar relaxation rates, there are roughly equal amounts of each of the four isomers.

Table 1 DSC properties of branched-chain derivatives of methyl oleate

Compound(s)	R	T_c (°C)	T_m (°C)	T_g (°C)
Methyl oleate **1**	H	−45.8, −47.2	−19.5	
3	CH$_3$	−41.8, −79.0	−72.1	
4	*n*-Bu	−85.4, −89.4	−81.6	
5	Ph			−92.8

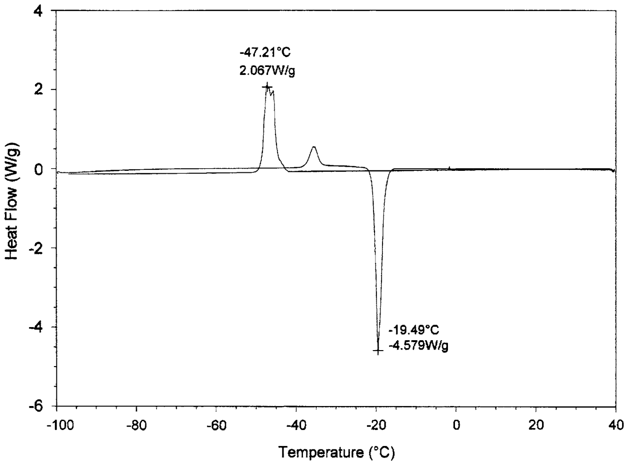


Fig. 2 DSC thermogram of methyl oleate. The *lower* scan is the heating curve. The *upper* scan is the cooling curve

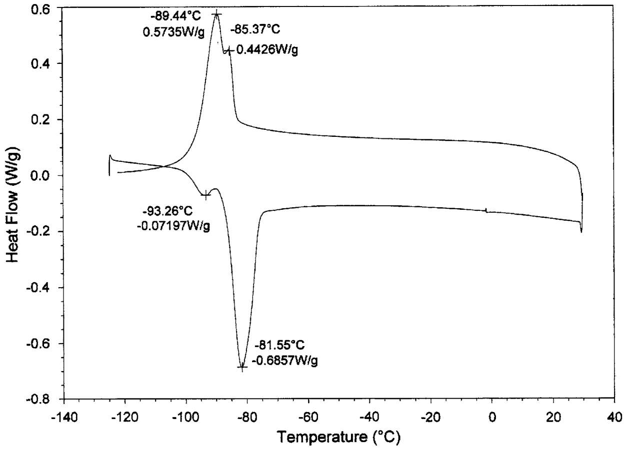


Fig. 3 DSC thermogram of *n*-butyl derivatives **4**. The *lower* scan is the heating curve. The *upper* scan is the cooling curve

The results of DSC studies of branched-chain derivatives **3**, **4**, and **5** are summarized in Table 1. The DSC thermograms of methyl oleate and methyl derivatives **3** have been reported previously [6] but are included for comparison of all branched-chain derivatives on the same basis. Since a different newer instrument was used in these

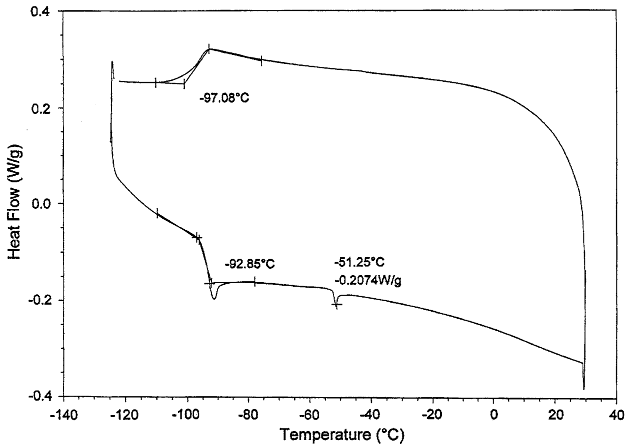


Fig. 4 DSC thermogram of phenyl derivatives **5**. The *lower* scan is the heating curve. The *upper* scan is the cooling curve

studies, somewhat different thermograms were obtained. A commercial sample of methyl oleate was used for comparison purposes (Fig. 2). In the DSC thermogram of **3**, there were two T_c maxima (−41.8 and −79.0 °C). The latter was of the greatest magnitude and was substantially lower than the T_c of methyl oleate. The T_m was observed at −72.1 °C. The DSC thermogram of the branched-chain *n*-butyl products **4** is shown in Fig. 3. It exhibits pronounced T_c maxima at −85.4 and −89.4 °C and $T_m = -81.6$ °C. The DSC thermogram of the branched-chain phenyl derivatives **5** (Fig. 4) is best described by the low glass transition temperature of −92.8 °C.

The significantly lower recrystallization temperature of branched-chain derivatives (**3** and **4**) of methyl oleate provides evidence that simple monoalkyl esters of branched-chain fatty acids could have improved or superior low-temperature properties and may prove useful as additives to biodiesel for use at low temperatures.

Acknowledgments Thanks to Steven Lloyd (SRRC) for conducting the GC/MS studies. Mention of a trademark, proprietary product, or vendor does not constitute a guarantee or warranty of the product by the US Department of Agriculture and does not imply its approval to the exclusion of other products or vendors that may also be suitable.

References

1. Knothe G, Dunn RO, Bagby MO (1997) Biodiesel: the use of vegetable oils and their derivatives as alternative diesel fuels. In: Fuels and chemicals from biomass (ACS Symp Ser 666). American Chemical Society, Washington, DC, pp 172–208
2. Dunn RO (1999) Thermal analysis of alternative diesel fuels from vegetable oils. J Am Oil Chem Soc 76:109–115
3. Lee I, Johnson LA, Hammond EG (1995) Use of branched-chain esters to reduce the crystallization temperature of biodiesel. Ibid 72:1155–1160
4. Foglia TA, Nelson LA, Dunn RO, Marmer WN (1997) Low-temperature properties of alkyl esters of tallow and grease. Ibid 74:951–955
5. Wu W-H, Foglia TA, Marmer WN, Dunn RO, Goering CE, Briggs TE (1998) Low-temperature property and engine performance evaluation of ethyl and isopropyl esters of tallow and grease. Ibid 75:1173–1178
6. Dailey OD Jr, Prevost N (2007) Conversion of methyl oleate to branched-chain derivatives. Ibid 84:565–571
7. Corey EJ, Posner GH (1967) Selective formation of carbon–carbon bonds between unlike groups using organocopper reagents. J Am Chem Soc 89:3911–3912
8. Corey EJ, Posner GH (1968) Carbon–carbon bond formation by selective coupling of *n*-alkylcopper reagents with organic halides. Ibid 90:5615–5616
9. Still WC, Kahn M, Mitra A (1978) Rapid chromatographic techniques for preparative separation with moderate resolution. J Org Chem 43:2923–2925
10. Biermann U, Metzger JO (2004) Alkylation of alkenes: ethylaluminum–sesquichloride-mediated hydro-alkyl additions with alkylchoroformates and di-*tert*-butylpyrocarbonate. J Am Chem Soc 126:10319–10330
11. Ucciani E, Naudet M (1963) Sur l’halogenation en position allylique des chaines grasses monoinsatutees. V. Isomerie de place et de position des chaines mono- et dihalogenees. Bull Soc Chim Fr 28–32
12. Anderson RJ, Henrick CA, Siddall JB (1970) Stereoselective synthesis of olefins. Reactions of dialkylcopper–lithium reagents with allylic acetates. J Am Chem Soc 92:735–737
13. Posner GH, Whitten CE, McFarland PE (1972) Organocopper chemistry. Halo-, cyano-, and carbonyl-substituted ketones from the corresponding acyl chlorides and organocopper reagents. Ibid 94:5106–5108
14. The Lipid Library (2003) ^{1}H-NMR spectroscopy of fatty acids with non-conjugated double bonds. http://www.lipidlibrary.co.uk/nmr/1NMRdbs/index.htm. Accessed July 2003
15. Dorman DE, Jautelat M, Roberts JD (1971) Carbon-13 nuclear magnetic resonance spectroscopy. Quantitative correlations of the carbon chemical shifts of acyclic alkenes. J Org Chem 36:2757–2766