J Amer Oil Chem Soc (2007) 84:777–784
DOI 10.1007/s11746-007-1089-6

ORIGINAL PAPER

Synthesis of Long Chain Unsaturated-α,ω-Dicarboxylic Acids from Renewable Materials via Olefin Metathesis

Helen L. Ngo · Thomas A. Foglia

Received: 27 February 2007 / Revised: 8 May 2007 / Accepted: 9 May 2007 / Published online: 29 June 2007

Abstract The self-metathesis reaction of soy, rapeseed, tall, and linseed oil fatty acids was investigated for the synthesis of symmetrical long-chain unsaturated-α,ω-dicarboxylic acids. The metathesis reactions were carried out in the presence of a Grubbs catalyst under solvent-free condition at a catalyst loading of 0.01 mol% to fatty acid substrate at 50 °C. Under these conditions, the conversions of starting unsaturated acids to metathesis products were >80% and the isolated yields of unsaturated dicarboxylic acid products were >70% of theoretical. This approach represents an effective and efficient route for the synthesis of these potentially useful dicarboxylic acids since they can serve as important intermediates in the production of several materials such as biodegradable polymers.

Keywords Diacids · Fatty acids · Hydrocarbons · Olefin metathesis · Unsaturated fatty acids

Introduction

Fats and oils are readily available domestic renewable materials that serve as the primary source of long-chain unsaturated fatty acids. The conversion of these long-chain fatty acids to long-chain-α,ω-unsaturated dicarboxylic acids (diacids) therefore is of interest since in addition to being derived from renewable resources, they are biodegradable and environmentally benign materials. Such diacids have potential in the production of biodegradable polyamides, polyesters, and polyurethanes. Presently, α,ω-diacids can be produced industrially by fermentation. For example, α,ω-diacids of C_{11}–C_{18} chain-length are produced in China and unsaturated α,ω-diacids, particularly α,ω-octadecenedioic acid, from vegetable and animal raw materials. Using the latter diacid, nylons, polyamides, polyesters, and polyacrylate esters were synthesized [1]. Although diacids can be successfully produced by fermentation, there are environmental concerns because the aqueous waste products from these processes typically contain bacteria and other waste materials of fermentation, which places significant burden on water treatment systems.

Catalyst-based syntheses are particularly important and account for ~60% of today's chemical products [2, 3]. An important reaction of this type is olefin metathesis, in which an olefin and a transition metal carbene complex react to generate new olefins. Common catalysts used in olefin metathesis are homogeneous ruthenium-based catalysts such as those developed by Grubbs [4, 5]. Grubbs catalysts are typically ruthenium-based alkylidene carbene complexes that are stable to moisture, often show good functional group tolerance and hence work well for functionally substituted alkenes [6].

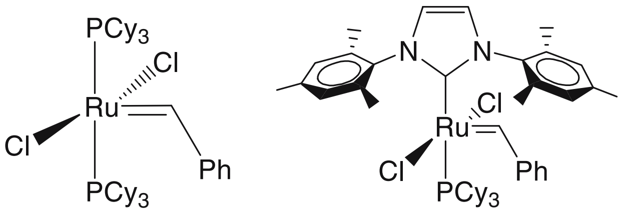
Grubbs type catalysts previously have been used in metathesis reactions of unsaturated fatty acids/esters for the synthesis of α,ω-diacid intermediates. Homogeneous Grubbs catalysts such as $RuCl_2$ (=CH–CH=CPh_2)$(PCy_3)_2$ [1] catalyze the C=C bond self-metathesis of unsaturated fatty acid/esters to give long chain-α,ω-unsaturated

---

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture.

H. L. Ngo (✉) · T. A. Foglia
US Department of Agriculture, Agricultural Research Service,
Eastern Regional Research Center, 600 E. Mermaid Lane,
Wyndmoor, PA 19038, USA
e-mail: helen.ngo@ars.usda.gov

dicarboxylic acid/esters (C_{18}) with a conversion of ~50%. The process also provides a hydrocarbon coproduct that has potential commercial value [7]. Warwel et al. [8] published a two-step process for the synthesis of long chain dicarboxylate methyl esters using the first generation Grubbs catalyst $RuCl_2(=CHPh)(PPCy_3)_2$ [2] (Fig. 1). The initial reaction was the cross-metathesis of methyl oleate with ethylene in the presence of **2** in toluene to give the terminal unsaturated compound methyl-9-decenoate and 1-decene. The terminal compounds were used in subsequent reactions catalyzed by **2** to give 1,18-dimethyl octadec-9-enedioate and 9-octadecene with an overall yields of 38–40% [8]. Subsequent work by Mol et al. [9] improved the conversions by performing the reaction in one step using the more active Grubbs catalyst $RuCl_2(=CHPh)(H_2IMes)(PCy_3)$ [3] (Fig. 1), which catalyzed the self-metathesis of methyl oleate to 1,18-dimethyl octadec-9-enedioate and 9-octadecene in ~45% conversion. Likewise, olefin metathesis of unsaturated fatty methyl esters derived from soy oil in the presence of **3** gave a 46% conversion of unsaturated methyl esters after 2 h reaction. A detailed kinetic study for this reaction was reported by Holser et al. [10]. Although these works demonstrate the utility of Grubbs type catalysts in olefin metathesis of unsaturated fatty acid methyl esters to useful value-added products, there are drawbacks associated with these metathesis systems. First, the molar conversion of unsaturated fatty acid methyl ester is modest at best (~50%) since typically metathesis reactions are conducted under thermodynamic conditions. Second, these systems typically are carried out in organic solvents, which may be of environmental concern. Recently, we reported the self-metathesis reaction of monounsaturated fatty acids such as oleic acid in high molar conversions under solvent-free conditions in the presence of catalyst **3**. Under the conditions used in that study, the diacid products formed during the reaction are not soluble in the reaction medium and precipitate from the mixture. This phase separation of product increases the conversion of starting acid and yields of diacid product, presumably by driving the reaction towards the diacid product. As a result of this, >80% conversion of oleic acid and a >70% yield of the diacid product (1,18-octadec-9-enedioic acid) was obtained. This solvent-free self-metathesis process also worked well with other types of fatty acids [11]. These interesting results led us to further explore the olefin metathesis process using less expensive feedstocks for the synthesis of unsaturated long-chain dicarboxylic acids. In this paper, we report a highly efficient and practical processes for converting vegetable oil- and animal fat-derived fatty acids into potentially useful and important long chain unsaturated α,ω-dicarboxylic acid mixtures. Such a strategy holds promises for opening new avenues for utilizing domestic oils and fats.



1st generation (**2**) 2nd generation (**3**)

Fig. 1 Structures of the Grubbs catalysts

Materials and Methods

Soybean oil (refined, bleached, deodorized) was a gift from Archer Daniels Midland (ADM, Decatur, IL, USA). Canola oil (rapeseed) was from Archer Daniels Midland Co., ADM (Decatur, IL). Tall oil fatty acid was from Arizona Chemical (Jacksonville, FL). Linseed oil and bis-(2,4,6-trimethylphenyl)-2-(imidazolidinylidene) (dichlorophenylmethylene) (tricyclohexylphosphine) [$RuCl_2$ (=CHPh) (H_2IMes) (PCy_3)] **3**, a second generation Grubbs catalyst, used in this study were from Aldrich Chemical (Milwaukee, WI). All other reagents used were of the highest purity obtainable from commercial suppliers.

The vegetable oils were hydrolyzed to their free fatty acids (FFA) using 1M KOH in ethanol:water (95:5) [12]. The fatty acid distributions in the FFA mixtures are listed in Table 1.

^{1}H and ^{13}C-NMR spectra were collected at RT on a Varian (Palo Alto, CA) Gemini 200 MHz spectrometer. GC was carried out with a Hewlett Packard (Agilent, Wilmington, DE) HP 6890 instrument equipped with an on-column capillary inlet (splitless mode) and an FID detector set at 370 °C. The capillary column used was a Zebron ZB-5 column (30 m × 0.25 mm × 0.25 μm) with N_2 as carrier gas set at 1 mL min^{-1}constant flow. The oven temperature profile was: initial temperature 50 °C; hold for 8 min; ramp at 15 °C min^{-1} to 220 °C; hold for 10 min; ramp at 15 °C min^{-1} to 250 °C; hold for 15 min. GC/MS was carried out with a Hewlett Packard HP 5890 instrument with a capillary inlet (split-split mode) and an HP Model 5972 mass detector set to scan from 40 to 550 *m/z* at of 1.5 scans/s. The capillary column used was a HP DB-5 column (30 m × 0.25 mm × 0.25 μm) with carrier gas (He) set at a linear velocity of 22 cm s^{-1} at 100 °C. The injector and detector transfer line temperatures were set at 250 and 280 °C, respectively. The oven temperature profile was as above for the GC analyses.

Table 1 Percentage composition of fatty acids derived from hydrolysis of fats and oils

Fatty acid/ester (%)	Percentage composition from GC							
	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	Unknown[b]
Soy methyl esters (**4a**)	11	0.3	4.5	21	52	7.4	0.4	3.4
Soy acids (**4b**)	11	0.3	4.5	21	52	7.4	0.4	3.4
Rapeseed acids (**4c**)	3.8	0.2	1.9	57	21	10	0.6	5.5
Tall acids (**4d**)	0.8	0.9	3.4	55	24	0	1.8	14
Linseed acids (**4e**)	5.6	0	3.8	20	18	51	0	1.4

[a] GC was carried out with a Hewlett Packard HP 5890 instrument with a capillary inlet (split-split mode). The capillary column used was a SP™ 2340 column (30 m × 0.25 mm × 0.2 μm) with carrier gas (He) set at a linear velocity of 22 cm s^{-1} at 180 °C. The injector and detector transfer line temperatures were set at 220 and 250 °C, respectively. The oven temperature profile was: initial temperature 180 °C; hold for 10 min; ramp at 2 °C min^{-1} to 190 °C; hold for 10 min

[b] Unidentified unsaturated fatty acids that decreases during metathesis

Synthesis of Diacids **7a–7d** (Fig. 2) from Soy Fatty Acids (SFA)

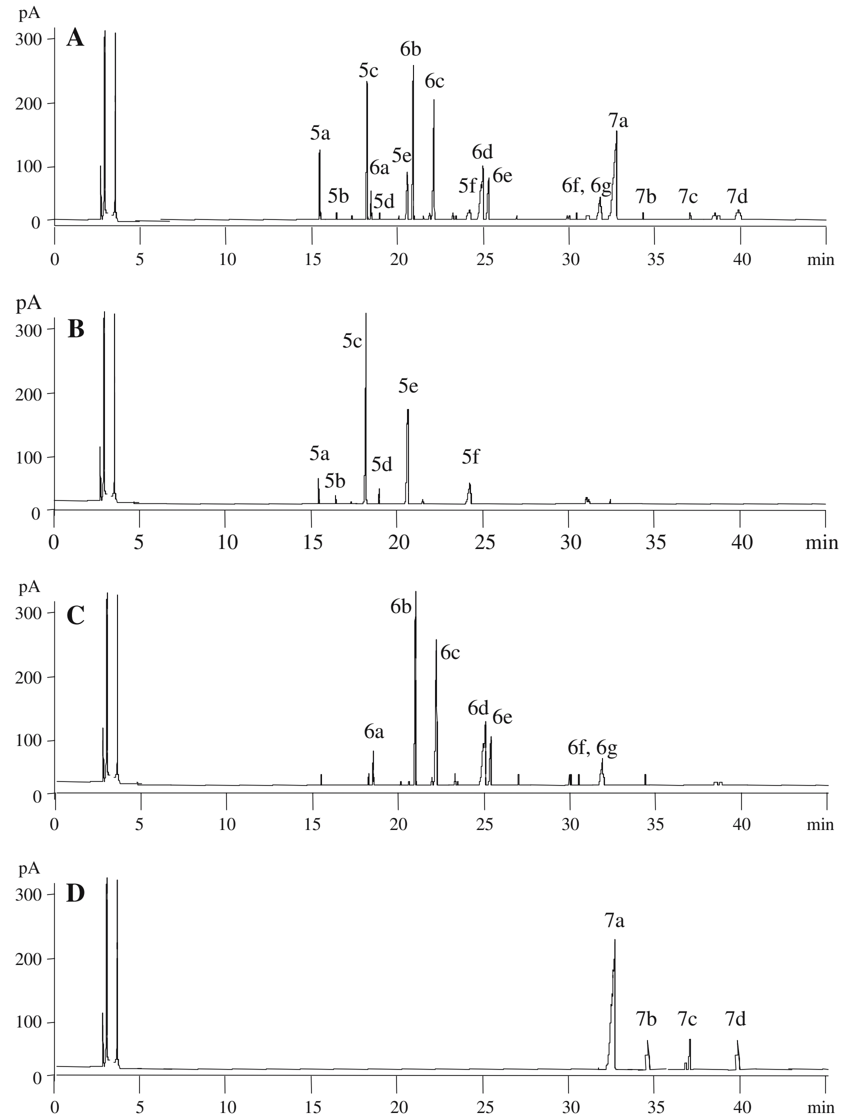
SFA [**4b** (Table 1) 2.5 g, 8.9 mmol] and ruthenium catalyst **3** (7.5 mg, 8.9 μmol) were added to a 25 mL, 2-neck round bottom flask under a nitrogen flow. The reaction mixture was stirred and heated at 53 °C and after ~2 h a precipitate formed. After a total of 8 h reaction, the reaction was quenched with ethyl vinyl ether (~3 mL) and the reaction mixture transferred to a 50 mL 1-neck flask. The solvent was removed under reduced pressure and the dried product residue methylated with methanol (35 mL) containing conc. sulfuric acid (10 drops). The resulting mixture was heated to reflux for 1 h, cooled to room temperature, quenched with 50 mL of saturated Na_2CO_3, extracted with ethyl ether (2 × 75 mL) and the combined ether layers washed with water (3 × 50 mL). The organic layer was dried with $MgSO_4$, filtered, and the solvent removed under reduced pressure. The GC trace of the total methylated product is shown in Fig. 2a. The crude methylated product (1 g) was purified by silica gel chromatography column using hexane:ethyl acetate (95:5 v/v) as eluent to give 52 mg of a hydrocarbon fraction (**5a–5f**, Fig. 2b) as a colorless liquid; 500 mg of mixed unsaturated and saturated fatty methyl esters (**6a–6g**, Fig. 2c); and 427 mg of unsaturated dicarboxylate methyl esters (compounds **7a–7d**, Fig. 2d). GC chromatograms for the isolated fractions are shown in Fig. 2b–d, respectively. The GC/MS spectrum of the methyl esters of **7a**–**7d** showed $[M]^+$ ions at *m*/*z* 340 (**7a**), *m*/*z* 354 (**7b**), *m*/*z* 368 (**7c**), and *m*/*z* 382 (**7d**). The proposed structures corresponding to these molecular $[M]^{+\cdot}$ ions are shown in Fig. 3. The ^{1}H-NMR spectrum of methylated diacids **7a–7d** ($CDCl_3$, 200 MHz) had signals at: δ 5.37 (m, $-CH{=}CH-$, 2H), 3.66 (s, $-CH_2CO_2CH_3$, 6H), 2.3 (t, J = 7.2 and 7.8 Hz, $-CH_2CO_2CH_3$, 4H), 1.97 (m, 4H), 1.61 (m, 5H) 1.29 (s, 15H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 174.2 (s, $-CO_2CH_3$), 130.4 (s, $-CH{=}CH-$), 51.4 (s, $-CH_2CO_2CH_3$), 34.2 (s), 32.6 (s), 29.7 (s), 29.2 (s), 29 (s), 25 (s). GC/MS analysis indicated that the diacids generated were predominately C_{18} fatty acids.

The self-metathesis of SFA also was carried out as above on a 50 g scale in a 3-neck, 250 mL round bottom flask equipped with a mechanical stirrer. The crude acid product obtained was fractionally distilled at 0.5 mmHg. From 35.5 g of crude acid product the following fractions were obtained: a hydrocarbon fraction (**5a–5d,** ~3 g) as a colorless oil over the temperature range of 110–120 °C; a monocarboxylic acid fraction (**6a–6g,** ~19 g) over the temperature range of 140–210 °C, which solidified to a white solid (m.p. = 36–38 °C); and a light brown solid residue composed primarily of diacids (**7a–7d,** ~14 g**)**. The diacid fraction, which contained <10% mono-fatty acids (by GC), was purified by recrystallization from a mixture of ethyl acetate (~30 mL) and hexane (~100 mL) at 3 °C to give diacids **7a–7d** as a light brown solid [m. p. = 97.5–99.5 °C] in an isolated yield of 12 g (73%). ^{1}H NMR of diacids **7a–7d** (CD_3OD, 200 MHz): δ 5.35 (m, $-CH{=}CH-$, 2H), 2.28 (t, J = 7.2 and 7.6 Hz, $-CH_2CO_2H$, 4H), 1.98 (m, 4H), 1.60 (m, 4H), 1.32 (m, 16H). ^{13}C NMR (CD_3OD, 50 MHz): δ 177.8 (s, CO_2H), 131.7 (s, $CH{=}CH$), 35.1 (s), 33.8 (s), 30.9 (s), 30.4 (s), 30.2 (s), 26.2 (s). GC and GC/MS showed that the diacids were predominantly C_{18} fatty acids.

Synthesis of Diacids (**7a–7d**) from Rapeseed Fatty Acids (RFA)

RFA [(**4c**, (Table 1) 2.5 g, 8.9 mmol] were metathesized with catalyst **3** (7.5 mg, 8.9 μmol) at 53 °C under a nitrogen flow. After ~2 h reaction a significant amount of precipitate was observed in the reaction mixture. After an additional 6 h reaction the acid mixture was isolated and methylated as described above. GC trace of the total methylated product is

Fig. 2 GC chromatograms of total product obtained from the metathesis soy fatty acids (Panel **a**) and after fractionation by column chromatography [Panels **b** hydrocarbon fraction; **c** mono-fatty acid fraction; and **d** diacid fraction]. Peak numbers correspond to structures shown in Fig. 3



shown in Fig. 4b. The crude product (1 g) was purified by silica gel column to give 188 mg of a hydrocarbon mixture (**5a–5f,** Fig. 2), 420 mg of unsaturated fatty methyl esters (**6a–6g,** Fig. 2), and 390 mg of unsaturated dicarboxylate methyl esters (**7a–7d,** Fig. 2). GC/MS of the methyl esters of diacids **7a–7d** gave $[M]^+$ ions at *m/z* 340 (**7a**), *m/z* 354 (**7b**), *m/z* 368 (**7c**), *m/z* 382 (**7d**). ^{1}H NMR of methylated diacids **7a–7d** ($CDCl_3$, 200 MHz): δ 5.37 (m, $-CH{=}CH-$, 2H), 3.66 (s, $-CH_2CO_2CH_3$, 6H), 2.3 (t, J = 7.2 and 7.8 Hz, $-CH_2CO_2CH_3$, 4H), 1.97 (m, 4H), 1.61 (m, 5H) 1.29 (s, 15H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 174.4 (s, $-CO_2CH_3$), 130.5 (s, $-CH{=}CH-$), 51.6 (s, $-CH_2CO_2CH_3$), 34.3 (s), 32.7 (s), 29.7 (s), 29.3 (s), 29.1 (s), 25.1 (s). GC and GC/MS showed that the diacids were predominantly C_{18} chain-length and that **7a** predominated (Fig. 4b).

In larger scale reactions, the crude acid product mixtures were purified by vacuum distillation at 0.5 mmHg. From 99.7 g of crude metathesized rapeseed acids the following fractions were obtained: a hydrocarbon fraction (**5a–5d,** ~17 g) over the temperature range of 110–160 °C; a mono-fatty acid fraction, (**6a–6e,** ~44 g) over a temperature range of 170–210 °C; and a solid residue composed primarily of diacids (**7a–7d,** ~41 g). The diacid residue was recrystallized from a mixture of hexane (100 mL) and ethyl acetate (10 mL) at −3 °C to give ~40 g (78% yield) of diacids **7a–7d** as a yellow solid [m.p.= 96.5–98.5 °C]. ^{1}H NMR of acid form of **7a–7d** (CD_3OD, 200 MHz): δ 5.4 (m, $-CH{=}CH-$, 2H), 2.25 (t, J = 7.6 and 7.2 Hz, $-CH_2CO_2H$, 4H), 1.95 (m, 4H), 1.6 (m, 4H), 1.3 (m, 16H). ^{13}C NMR (CD_3OD, 50 MHz): δ 177.9 (s, CO_2H), 131.7 (s, $CH{=}CH$),

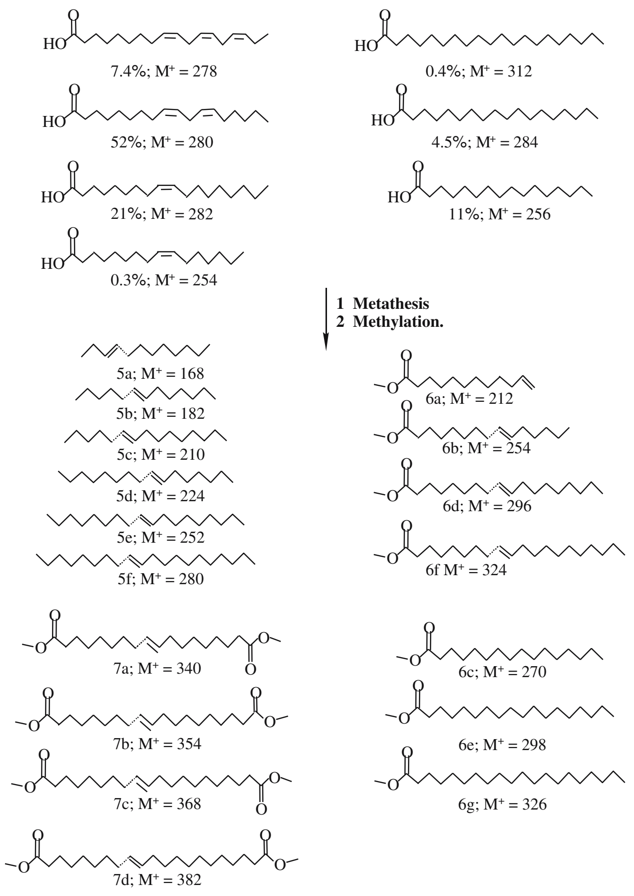


Fig. 3 Products formed during the self-metathesis of soy fatty acids in the presence of 0.01 mol% of ruthenium catalyst **3**

35.1 (s, CH_2CO_2H), 33.7 (s), 30.8 (s), 30.4 (s), 30.2 (s), 26.2 (s).

Synthesis of Diacids (**7a–7d**) from Tall Fatty Acids (TFA)(**4d**)

TFA [**4d**, (Table 1) 2.5 g, 8.9 mmol] and were metathesized with catalyst **3** (7.5 mg, 8.9 μmol) under conditions used for SFA. At the end of the reaction (12 h) only a small amount of diacid precipitate was observed. The crude reaction mixture was isolated and methylated as above. The GC chromatogram for this methyl ester product is shown in Fig. 4c. The crude ester product (1 g) was fractionally separated by silica gel chromatography using hexane:ethyl acetate (95:5 v/v) as the eluant into a hydrocarbon fraction (**5a–5c**, 126 mg); an unsaturated fatty methyl ester fraction (**6a–6g,** 460 mg); and a dimethyl ester fraction (**7a–7d**, 380 mg, 70% yield). The diester fraction (**7a–7d)** was analyzed by GC/MS: $[M]^{+\cdot}$ ions of *m/z* 340 (**7a**); *m/z* 354 (**7b**); *m/z* 368 (**7c**); and *m/z* 382 (**7d**).

Synthesis of Diacids (**7a–7d**) from Linseed Acids **(LFA)**

LFA [**4e** (Table 1), 2.5 g, 8.9 mmol] were metathesized with catalyst **3** (7.5 mg, 8.9 μmol) as described for SFA. Only a small amount of diacid precipitate was observed after ~12 h reaction. The reaction was worked up and methylated as above. The GC chromatogram for this methyl ester product is shown in Fig. 4d. One gram of the crude methylated product was separated into hydrocarbon, mono fatty acid ester, and di-fatty acid ester fractions by silica chromatography. The diester fraction was analyzed by GC/MS and gave $[M]^{+\cdot}$ ions for dimethyl esters of **7a–7d** at: *m/z* 340 (**7a**); *m/z* 354 (**7b**); *m/z* 368 (**7c**); *m/z* 382 (**7d**); with diester **7a** predominating.

Results and Discussion

Long-chain oils such as soy, rapeseed, tall, and linseed, which contain a high proportion of C_{18} chain-length unsaturated fatty acids, were subjected to olefin metathesis using Grubbs' catalyst **3**. The oils were first hydrolyzed under basic condition to their corresponding free fatty acids. The compositions of the fatty acid mixtures obtained from the oils after hydrolysis are listed in Table 1. Hydrolysis of soy oil gave a mixture of fatty acids (**4b**, Table 1) with the following composition: (21%) oleic acid with one double bond; (52%) linoleic acid with two double bonds; and (7.4%) linolenic acid with three double bonds (Table 1, entry 2). The unsaturated fatty acids derived from rapeseed, tall, and linseed oils also are listed in Table 1 and their fatty acid distributions correspond to those reported previously [12]. In contrast to previous studies, the metathesis reactions in this study were carried out in the presence of catalyst **3** under solvent-free conditions. Extensive self- and cross-metathesis of the unsaturated FFA mixtures afforded two additional product classes, namely unsaturated hydrocarbons and unsaturated dicarboxylic acids in high molar conversions. When SFA (**4b**, Table 1) were metathesized using a 0.1 mol% catalyst loading, at a reaction temperature between 50 and 53 °C, newly formed diacid products started to precipitate from the reaction milieu in ~2 h. After a total reaction time of 8 h, the reaction was terminated, the crude product isolated, and the acid products converted to methyl esters. As shown in Fig. 2a, the ester product obtained was a complex mixture since the oleic, linoleic, and linolenic acids in the SFA mixture undergo both self- and cross-metathesis type reactions. GC analysis of this product, however, indicated an 88% conversion of the starting unsaturated fatty acids to metathesis products. Conversions were determined by measuring the difference in the sum of unsaturated fatty

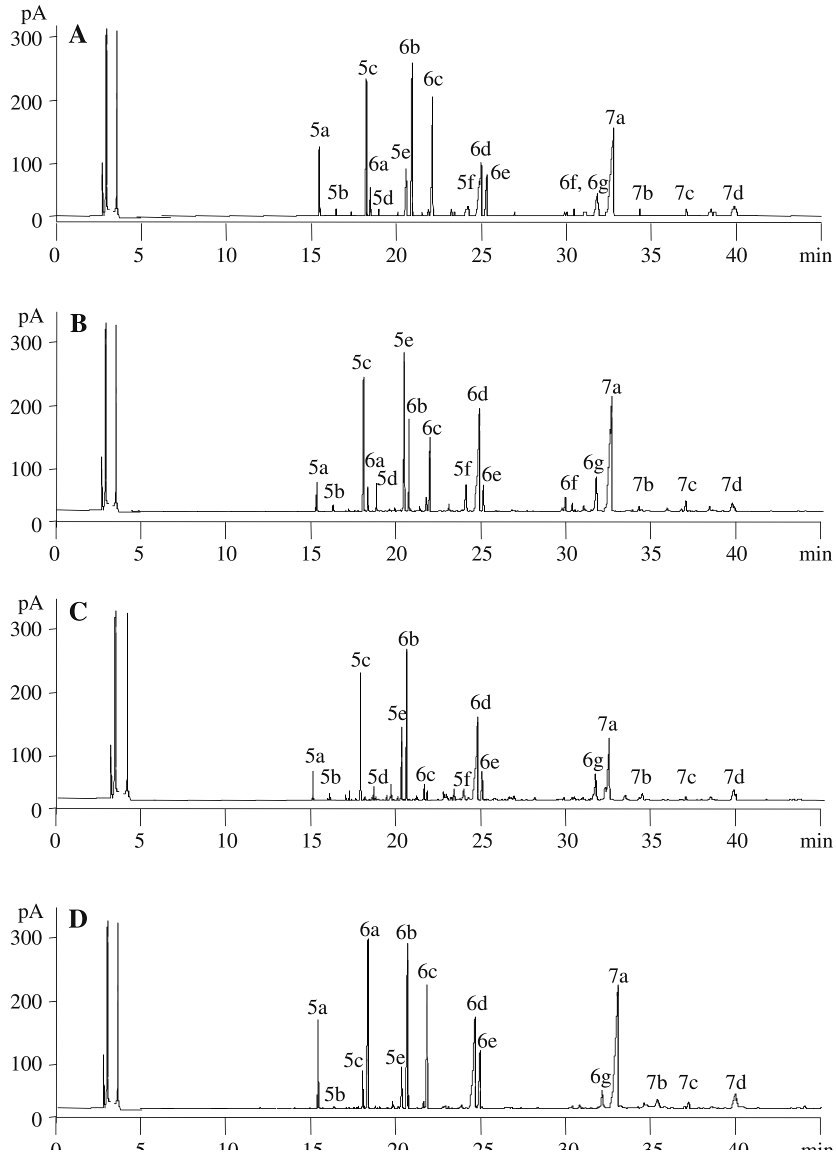


Fig. 4 GC traces of total products obtained from the metathesis of soy (**a**), rapeseed (**b**), tall (**c**), and linseed (**d**) fatty acids

acids in the initial and final products by GC (Table 2). Similar conversions were obtained in larger scale reactions that were separated into a hydrocarbon, mono-ester, and diester fractions by silica gel column chromatography as shown in Fig. 2b–d, respectively. A similar separation was made in larger scale reactions by fractional distillation of the crude acid product that gave an 88% isolated yield of diacid product (Table 2). Theoretical diacid yields are based on the initial amount of unsaturated fatty acid that could be converted to unsaturated diacid. The isolated hydrocarbon and mono- and di-ester or acid fractions were subsequently characterized by GC/MS and ^{1}H and ^{13}C-NMR spectroscopy. Figure 3 shows the starting fatty methyl esters in SFA and the methylated metathesis products that were identified. The saturated fatty acids hexadecanoic (**6c**), octadecanoic (**6e**), and eicosanoic (**6g**), which are saturated fatty acids, do not undergo metathesis and remain in the product mixture. Dodecene (**5a**), pentadecene (**5c**), pentadecenoic (**6b**), and 1,18-octadecenedioic (**7a)** were the major metathesis products identified (Fig. 3). Tridecene (**5b**), dodecenoic (**6a**), hexadecene (**5d**), eicodecene (**5f**), and 1,19-nonadecenedioic (**7b**), 1,20-eicosecenedioic (**7c**), and 1,21-heneicosendioic (**7d**) acid were present as minor products and these compounds are thought to result from secondary metathesis reactions of the initially formed alkenes and unsaturated acids (Fig. 3). Octadecenoic (**6d**) and eicosenoic (**6f**) acid, present in the starting SFA, also were minor components of the reaction product. It should be noted that all of the unsaturated mono- and diacids products contain were predominately *trans* isomers as is the case for metathetic reactions and the results are confirmed by infrared (IR) data [6]. The yield of

Table 2 Olefin metathesis of unsaturated fatty acids with second generation Grubbs catalyst

Entry	Fatty acid/ester	Percentage fatty acid composition from gas chromatography			Wt. % diacids[l]
		C16:0+C18:0+C20:0[i]	C18:1+C18:2+C18:3 + unknown[j]	Conv.[k] (%)	
1	Soy acids (**4b**)[a]	16	84	–	–
2	Soy acids (**4b**)[b,c]	16	10	88	88
3	Soy acids (**4b**)[b,e]	17	9.9	88	88, 73[m]
4	Soy acids (**4b**)[b,f]	16	12	86	75
5	Soy methyl esters (**4a**)[a]	16	84	–	–
6	Soy methyl esters (**4a**)[b,f]	16	41	51	50
7	Soy methyl esters (**4a**)[b,c]	16	9.6	89	60
8	Rapeseed acids (**4c**)[a]	6.3	94	–	–
9	Rapeseed acids (**4c**)[b,c]	6.9	19	80	72
10	Rapeseed acids (**4c**)[b,f]	6.9	41	56	48
11	Tall acids (**4d**)[a]	6.0	94	–	–
12	Tall acids (**4d**)[b,d]	6.0	17	82	70
13	Tall acids (**4d**)[b,g,h]	6.0	53	43	–
14	Linseed acids (**4e**)[a]	9.9	90	–	–
15	Linseed acids (**4e**)[b,d]	9.9	13	86	79

[a] Composition of fatty acids before reaction

[b] Composition of fatty acids after reaction

[c] Reaction was run with 0.1 mol% catalyst **3** loading at 53 °C for 8 h

[d] Reaction was run with 0.1 mol% catalyst **3** loading at 53 °C for 20 h

[e] Reaction was run with 0.1 mol% catalyst **3** loading at 53 °C for 3 days

[f] Reaction was run with 0.01 mol% catalyst **3** loading at 50 °C for 20 h

[g] Reaction was run with 0.01 mol% catalyst **3** loading at 50 °C for 3 days

[h] Did not observe any precipitation

[i] Composition of SFA summed

[j] Composition of UFA + unknown summed. Unknown was added to the total because the unknown peaks disappeared after reaction

[k] % conversion $= [\sum \mathrm{UFA}_{\mathrm{initial}} - \sum \mathrm{UFA}_{\mathrm{final}} / \sum \mathrm{UFA}_{\mathrm{initial}}]$

[l] Isolated yields of diacid mixtures after methylation and purification by silica gel chromatography column using hexane:ethyl acetate (95:5 v/v) as eluent. Wt% = [(isolated yield/theoretical yield) × 100]

[m] Isolated yields of diacid mixtures by vacuum distillation at high temperatures

diacid products did not improve beyond 8 h reaction nor did the conversion of SFA and change in product distribution occur with longer reaction times or conditions (Table 2, entries 1–3). The metathesis reactions also worked well at 0.01 mol% catalyst loading giving an 86% conversion of starting fatty acids to products and a 75% isolated yield of diacids (Table 2, entry 4).

We also carried out control experiments using soy methyl esters under similar reaction conditions. When ester mixture **4a** was treated with 0.01 mol% catalyst **3**, an equilibrium distribution of products (51% molar conversion) and a diester fraction was obtained in an isolated yield of 50% (Table 2, entries 5, 6). In general, a decrease in both SFA conversion and yield of diester fraction was obtained in the metathesis of fatty acid methyl esters compared to the acid mixtures. This is a result of the greater miscibility of the metathesis products in ester reactions compared to the free acid reactions. A higher catalyst loading (0.1 mol%) of **3** gave an 89% conversion of starting esters but only a 60% isolated yield of diesters (**7a–7d**) (Table 2, entry 7). Again, the soy acids give higher yields because of the lower solubility of diacids in the soy acid mixtures. As olefin metathesis of SFA proceeds, the long-chain diacids precipitate out of the solution and the equilibrium is shifted to the diacid products. Thus, it is worth noting that it is critical to run the metathesis reactions in the temperature range of 50–53 °C. If the temperature is below 50 °C the reaction mixture solidifies, which results in a lower conversion of starting fatty acids. In contrast, if the temperature is above 53 °C the reaction mixture remains liquid and lower yields of diacids are obtained since they undergo further cross metathesis. With the reaction conditions used in this work, the precipitation of the diacid mixtures increases both the conversion of starting unsaturated fatty acids and yields of the diacid products.

Fatty acid mixtures derived from rapeseed, tall, and linseed oils also were prepared using the solvent-free olefin metathesis conditions reported herein. Relatively high conversions and isolated yields of diacid mixtures were obtained when the molar ratio of fatty acids to catalyst **3** was 1000:1 (Table 2, entries 8-15). This suggests that the ratio of oleic, linoleic, and linolenic has little affect on either the conversion or yield of diacid product obtained in this study. The product distribution obtained for these acid mixtures varied but in general was similar to the product mixture obtained with the soy fatty acids (Fig. 4). When the molar ratio of fatty acids to catalyst **3** was 10,000:1, these acid mixtures did not metathesize as well as the soy acid mixture in that the conversion of starting acids and diacid yields dropped significantly. Of the fatty acid mixtures examined in this study (Table 2), the soy fatty acid mixture gave the best results for olefin metathesis of unsaturated fatty acids to diacid products even at low catalyst loadings. For example, in the presence of 0.005 mol% catalyst, the metathesis of soy acids at 75 °C for 20 h gave a 63% conversion and an isolated yield (50%) of diacids. This metathetic reaction was performed at 75 °C because the diacid products were not observed at the typical temperature range 50–53 °C (Table 2, entry 4).

Overall the process reported represents an efficient route to the synthesis of long chain symmetrically unsaturated-α,ω-dicarboxylic acids. This solvent-free metathesis process worked well with unsaturated mixture of fatty acids derived from a variety of oils. High conversions to products were obtained for the fatty acids from soy, rapeseed, tall, and linseed oils when the reactions were performed under solvent-free conditions and high yields of diacid products were obtained from these processes. The availability of these diacids could be of significance since they can serve as monomers in the synthesis of biodegradable linear long-chain polyesters and polyamides.

Acknowledgments We thank Mr. Kerby Jones for experimental help with the GC studies and Dr. Gary Strahan for the NMR studies.

References

1. Kroha K (2004) Industrial biotechnology provides opportunities for commercial production of new long-chain dibasic acids. Inform 15:568–571
2. Ngo HL, Lin W (2005) Hybrid organic-inorganic solids for heterogeneous asymmetric catalysis. Top Catal 34:85–92
3. Parshall GW, Ittel SD (1992) Homogeneous catalysis. Wiley, New York
4. Trnka TM, Grubbs RH (2001) The development of L_2X_2Ru:CHR olefin metathesis catalysts: an organometallic success story. Acc Chem Res 34:18–29
5. Grubbs RH, Johnson LK, Nguyen ST (1994) Ruthenium and osmium metal carbene complexes for olefin metathesis polymerization. US Patent 5,342,909
6. Grubbs RH (2003) Handbook of metathesis. Wiley-Vch, Verlag GmbH KGaA, Weinheim
7. Grubbs RH, Nguyen ST (1998) Polymer depolymerization using ruthenium and osmium carbine complexes. US Patent 5,728,917
8. Warwel S, Demes C, Steinke GJ (2001) Polyesters by lipase–catalyzed polycondensation of unsaturated and epoxidized long-chain α,ω-dicarboxylic acid methyl esters with diols. J Polym Sci A: Polym Chem 39:1601–1609
9. Dinger MB, Mol JC (2002) High turnover numbers with ruthenium-based metathesis catalysts. Adv Synth Catal 344:671–677
10. Holser RA, Doll KM, Erhan SZ (2006) Metathesis of methyl soyate with ruthenium catalysts. Fuel 85:393–395
11. Ngo HL, Jones K, Foglia TA (2006) Metathesis of unsaturated fatty acids: synthesis of long chain unsaturated α,ω-dicarboxylic acids. J Am Oil Chem Soc 83:629–634
12. Christie WW (1982) Lipid analysis: isolation, separation, identification, and structural analysis of lipids. Pergamon, New York