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Polymerisable di- and triesters from Tall Oil Fatty Acids and related compounds†

Marc R. L. Furst, Thomas Seidensticker and David J. Cole-Hamilton*

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Tall Oil Fatty Acids, a low value side product from the paper industry containing mainly oleic and linoleic acids, are used for producing the polyester precursor, dimethyl 1,19-nonadecanedioate by methoxycarbonylation in the presence of [$Pd_2(dba)_3$], 1,2-bis(ditertiarybutylphosphinomethyl)benzene and methanesulfonic acid in methanol. The methoxycarbonylation of methyl linoleate has been used to identify other products formed and approaches to their minimisation have been developed. It has also been used for the production of trimethyl heptadecanetricarboxylates. Finally, conjugated unsaturated esters of different chain length (up to 16 C atoms), some of them available from plant oils, are subjected to methoxycarbonylation to give α,ω-diesters.

Introduction

As petroleum feedstocks dwindle and prices increase, the need for renewable resources for producing the polymers that are ubiquitous in enhancing our lives is becoming more and more obvious. Ideally, from an ecological and economic point of view, the monomers required for such polymers would be derived from non-toxic wastes or side products from plant based feedstocks. We[1,2] and others[3–6] have previously reported the synthesis of a new long carbon chain polyester precursor, dimethyl 1,19-nonadecanedioate and its hydrogenation to 1,19-nonadecanediol.[1,4–6] Mecking and coworkers have shown that these precursors can be copolymerised to aliphatic polyesters with properties very similar to those of polyethylene.[3–5] Our initial synthesis of dimethyl 1,19-nonadecanedioate employed purified methyl oleate as the feedstock[2] but we subsequently showed that unpurified olive, rapeseed and sunflower oils, could provide much cheaper alternatives to purified methyl oleate.[1] Walther *et al.* employed high oleic sunflower oil.[6] All of these oils are used for food, so any process that starts from them would be in competition with food crops, a situation we are keen to avoid.

The Kraft process for the production of pine wood pulp, produces a waste side product known as Tall Oil (2 M tonnes per year), which is rich in Tall Oil Fatty Acids (TOFA, mainly oleic and linoleic acids).[7] TOFA have traditionally been used in inks, rubbers or adhesives.[8] In this paper, we report our studies on the synthesis of dimethyl 1,19-nonadecanedioate using TOFA as the feedstock. Furthermore, suspecting a possible transfer hydrogenation from methanol to the unsaturated dimethyl 1,19-nonadecenedioate (isomers) to form the saturated equivalent,[2] we report our studies on this phenomenon using pure linoleic acid. We also discuss the possible formation of triesters and other products from methoxycarbonylation of TOFA and of linoleic acid. 2-Undecenoic acid, for which the methyl ester is available from metathesis of methyl oleate with dimethyl maleate,[9] undergoes isomerising methoxycarbonylation to the Nylon-12,12 precursor, dimethyl 1,12-dodecanedioate, which we also make from methyl 10-undecenoate, available from cracking castor oil.[10] We show that the double bond can be selectively moved 13 steps along a chain to form dimethyl 1,17-heptadecanedioate from 2-hexadecenoic acid.

Experimental

All reactions were performed using standard Schlenk techniques. All solvents were degassed with nitrogen. Unless otherwise stated, solvents were used as supplied and were not previously dried. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 298 K on a Bruker 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR spectrometer, using the residual solvent peak to reference the spectra to tetramethylsilane at $\delta = 0$ ppm. Elemental analyses were performed by the Elemental Analysis Service of the London Metropolitan University. [$Pd_2(dba)_3$], linoleic acid, dimethyl maleate (Sigma Aldrich), 1,2-bis(ditertiarybutylphosphinomethyl)benzene

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EaStCHEM, School of Chemistry, University of St Andrews, St Andrews, KY16 9ST Scotland, UK. E-mail: djc@st-andrews.ac.uk; Fax: +44 (0) 1334 463 808; Tel: +44 (0) 1334 463 805

† Electronic supplementary information (ESI) available: ^1H-NMR and ^{13}C-NMR spectra of dimethyl 1,19-nonadecanedioate, trimethyl heptadecane-1,*n*,17-trioate, dimethyl 1,12-dodecanedioate, dimethyl 1,17-heptadecanedicarboxylate, trimethyl ethane-1,1,2-trioate, ^1H-NMR of TOFA and linoleic acid, GCMS of crude mixtures obtained from methoxycarbonylation reactions. See DOI: 10.1039/c3gc37071b

(Lucite International), methyl 10-undecenoate, 2-undecenoic acid, 2-hexadecenoic acid (Tokyo Chemical Industry), TOFA (Mistral Lab Chemicals) and methanesulfonic acid (Alfa Aesar) were used as supplied.

Dimethyl 1,19-nonadecanedioate (4) from TOFA

Method 1: Under air, [Pd$_2$(dba)$_3$] (37 mg, 0.04 mmol, 0.08 mmol Pd) and 1,2-bis(ditertiarybutylphosphinomethyl)-benzene (158 mg, 0.4 mmol, DTBPMB) were introduced into a hastelloy autoclave, sealed and purged with nitrogen. Methanol (10 mL), TOFA (2.5 mL) and methanesulfonic acid (0.05 mL, 0.8 mmol, MSA) were added to the autoclave by cannula. The autoclave was purged three times with CO and the pressure was set to 30 bar. The autoclave was heated to 90 °C for 48 h. It was then cooled to room temperature and degassed. A sample was taken for GC analysis. *Method 2*: An esterification of TOFA (2.5 mL) was carried out over 3 h in dry refluxing methanol (10 mL) in the presence of MSA (0.05 mL) and magnesium sulfate (200 mg) under an atmosphere of dry nitrogen. The solution was cooled and introduced into the degassed autoclave containing [Pd$_2$(dba)$_3$] (37 mg, 0.04 mmol, 0.08 mmol Pd) and DTBPMB (158 mg, 0.4 mmol) by cannula bearing a filter. The autoclave was heated to 90 °C for 10 h, then cooled to room temperature, degassed and a sample was taken for GC analysis. For both Methods 1 and 2, a suspension of Pd/C 5% (170 mg, 0.08 mmol Pd) in methanol (10 mL) was added by cannula. The autoclave was purged three times with H$_2$ and the H$_2$ pressure was set to 30 bar. The temperature was set to 90 °C for 20 h. After cooling, venting and opening, the remaining yellow powder was dissolved by addition of dichloromethane (20 mL) and the yellow solution was filtered through paper. The solvent was removed on a rotary evaporator. Methanol was added and the mixture was warmed until the products dissolved. The mixture was placed in the freezer for 30 min and filtered using a Büchner funnel. The desired product was obtained as a white powder (Method 1: 0.92 g, 32%; Method 2: 1.33 g, 49%). Elemental analysis: found C 70.81, H 11.35%; $C_{21}H_{40}O_4$ requires C 70.74, H 11.31%. ^{1}H NMR (300 MHz; CDCl$_3$): δ = 3.65 (s, 6H, C*H*$_3$O-), 2.28 (t, *J* = 7.5 Hz, 4H, CH$_3$O-COC*H*$_2$-), 1.60 (quintet, *J* = 7.3 Hz, 4H, CH$_3$O-CO-CH$_2$-C*H*$_2$-), 1.23 (s, 26H, C*H*$_2$ chain). ^{13}C NMR (75 MHz; CDCl$_3$): δ = 174.51 (s, *C*O), 51.60 (s, *C*H$_3$O–), 34.28 (s, CH$_3$O-CO-*C*H$_2$-), 29.84–29.32 (s, *C*H$_2$ chain), 25.13 (s, CH$_3$O-CO-CH$_2$-*C*H$_2$-). These data are consistent with those from the literature.[1]

Trimethyl heptadecane-1,*n*,17-tricarboxylate (6) from linoleic acid

Method 1: The carbonylation was carried out as described in Method 1, above but using linoleic acid in place of TOFA, the reaction time being 64 h. After depressurisation of carbon monoxide, dichloromethane was added and the crude mixture was introduced into a round bottom flask. The solvent was removed on a rotary evaporator. The crude product was passed through a silica chromatography column (hexane/ethyl acetate: 92/8). The desired product was obtained as a transparent oil (635 mg, 19%). *Method 2*: In a Schlenk flask containing [Pd$_2$(dba)$_3$] (37 mg, 0.04 mmol, 0.08 mmol Pd), 1,2-bis(ditertiarybutylphosphinomethyl)benzene (158 mg, 0.4 mmol, DTBPMB) and magnesium sulfate (200 mg), dry methanol (10 mL) and TOFA (2.5 mL) were introduced *via* cannula. The solution was stirred under nitrogen for 10 min and introduced in the autoclave by cannula. The autoclave was closed and pressurised with CO (30 bar) and heated to 90 °C with magnetic stirring for 64 h. After cooling and depressurisation of CO, dichloromethane was added and the crude mixture was introduced into a round bottom flask. The solvent was removed on a rotary evaporator. The crude product was passed through a silica chromatography column (hexane/ethyl acetate: 92/8). The desired product was obtained as a transparent oil, 1.38 g, 44%). Elemental analysis: found C 66.52, H 10.07%; $C_{23}H_{42}O_6$ requires C 66.63, H 10.21%. ^{1}H NMR (300 MHz; CDCl$_3$): (mixture of isomers) δ = 3.67 (s, 3H, C*H*$_3$O-(branched)), 3.66 (s, 6H, C*H*$_3$O-), 2.29 (t, *J* = 7.5 Hz, CH$_3$O-CO-C*H*$_2$-), 1.62 (s, CH$_3$ O-CO-CH$_2$-C*H*$_2$-), 1.44 (m), 1.23 (s, C*H*$_2$ chain). ^{13}C NMR (75 MHz; CDCl$_3$): (mixture of isomers) δ = 51.63 (s, *C*H$_3$O-), 45.68–45.53 (s, CH$_3$O-CO-*C*H-(CH$_2$-CH$_2$-)$_2$), 34.29–34.05 (s, CH-(CH$_2$-CH$_2$-)$_2$, 32.70 (s, CH$_3$OCO-*C*H$_2$-), 31.93 (s, CH-(CH$_2$-*C*H$_2$-)$_2$, 29.79–25.13 (*C*H$_2$ chain), 23.01 (s, CH$_3$ O-CO-CH$_2$-*C*H$_2$-).

Methyl *n*-oxooctadecanoate (1 and 2) from linoleic acid

Method 1. The carbonylation was carried out as described in Method 1 for TOFA, above but using linoleic acid in place of TOFA. After depressurisation of carbon monoxide, dichloromethane was added and the crude mixture was introduced into a round bottom flask. The solvent was removed on a rotary evaporator. The crude product was passed through a silica chromatography column (hexane/ethyl acetate: 92/8). The desired product was obtained as a white solid (654 mg, 25%, mixture of isomers). This fraction was then passed down a silica chromatography column using hexane/ethyl acetate (90/10) and fractions containing only methyl 17-oxooctadecanoate (**2**) were collected and evaporated to dryness (yield 3%). Elemental analysis: found C 72.90, H 11.60%; $C_{19}H_{36}O_3$ requires C 73.03, H 11.61%. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.66 (s, 3H, C*H*$_3$O-), 2.41 (t, *J* = 7.5 Hz, 2H, CH$_3$-CO-C*H*$_2$-), 2.29 (t, *J* = 7.5, 2H, CH$_3$O-CO-C*H*$_2$-), 2.12 (s, 3H, C*H*$_3$-CO-CH$_2$-), 1.65–1.51 (m, 4H, -CO-CH$_2$-C*H*$_2$-), 1.24 (s, 22H, C*H*$_2$ chain). ^{13}C NMR (75 MHz; CDCl$_3$): δ = 209.53 (s, *C*O (ketone)), 174.48 (s, *C*O (ester)), 51.57 (s, *C*H$_3$O-), 43.97 (s, CH$_3$-CO-*C*H$_2$-), 34.26 (s, CH$_3$O-CO-*C*H$_2$-), 29.98 (s, *C*H$_3$-CO-CH$_2$-), 29.77–29.29 (s, *C*H$_2$ chain), 25.10 (s, CH$_3$O-CO-CH$_2$-*C*H$_2$-), 24.02 (s, CH$_3$O-CO-CH$_2$-*C*H$_2$-). These data are consistent with those in the literature.[11]

Method 2: The reaction was carried out as described in Method 1 for TOFA, above but using methyl linoleate in place of TOFA, and nitrogen (40 bar) instead of carbon monoxide. After depressurisation of nitrogen, dichloromethane was added and the crude mixture was introduced into a round bottom flask. The solvent was removed on a rotary evaporator. The crude product was passed through a silica chromatography column (hexane/ethyl acetate: 92/8). The desired product was obtained as a white solid (1004 mg, 42%, isomers

(**1**) *without* methyl 17-oxooctadecanoate, (**2**). Elemental analysis: found C 73.13, H 11.70%; $C_{19}H_{36}O_3$ requires C 73.03%, H 11.61%. ^{1}H NMR (300 MHz; $CDCl_3$): δ = 3.61 (s, 3H, C*H*$_3$O-), 2.33 (tt, ^3J = 7.5 Hz, ^4J = 2.6 Hz, 4H, C*H*$_2$-CO-C*H*$_2$-), 2.27 (t, *J* = 7.5, 2H, CH$_3$O-CO-C*H*$_2$-), 1.60–1.44 (m, 6H, -CO-CH$_2$-C*H*$_2$-), 1.21 (s, 18H, C*H*$_2$ chain), 0.88–0.80 (m, 3H, -CH$_2$-C*H*$_3$). ^{13}C NMR (75 MHz; $CDCl_3$): δ = 211.54 (s, *C*O (ketone)), 174.24 (s, *C*O (ester)), 51.38 (s, *C*H$_3$O-), 42.79–42.49 (-*C*H$_2$-CO-*C*H$_2$-), 34.07 (CH$_3$O-CO-*C*H$_2$-), 31.82–31.44 (s, CH$_3$-CH$_2$-*C*H$_2$-), 29.66–28.93 (s, *C*H$_2$ chain), 24.94 (s, CH$_3$O-CO-CH$_2$-*C*H$_2$-), 23.85 (s, -*C*H$_2$-CH$_2$-CO-CH$_2$-*C*H$_2$-), 22.64–22.37 (s, CH$_3$-*C*H$_2$-), 14.08–13.86 (s, *C*H$_3$-CH$_2$-). These data are consistent with those in the literature.[11]

Dimethyl 1,12-dodecanedioate from 2-undecenoic acid

Under air, [Pd$_2$(dba)$_3$] (25 mg, 0.027 mmol, 0.054 mmol Pd) and DTBPMB (107 mg, 0.27 mmol) were introduced into a hastelloy autoclave, sealed and purged with nitrogen. Degassed methanol (10 mL), 2-undecenoic acid (1 mL, 5.43 mmol) and methanesulfonic acid (0.07 mL, 1.08 mmol) were added to the autoclave by cannula. The autoclave was purged three times with CO and the pressure was set to 30 bar. The autoclave was heated to 90 °C for 44 h. After cooling, venting and opening, the yellow solution was filtered through paper and the solvent was removed on a rotary evaporator. Methanol was added and the mixture was then stirred at −78 °C for 10 min and filtered using a Büchner funnel. The desired product was obtained as a white powder. Isolated yield (0.6 g, 43%). Elemental analysis: found C 65.15, H 10.19%; $C_{14}H_{26}O_4$ requires C 65.09, H 10.14%. ^{1}H NMR (300 MHz; $CDCl_3$): δ 3.66 (s, 6H, C*H*$_3$O-), 2.29 (t, *J* = 7.5 Hz, 4H, CH$_3$O-CO-C*H*$_2$-), 1.60 (quintet, *J* = 7.3 Hz, 4H, CH$_3$ O-CO-CH$_2$-C*H*$_2$-), 1.26 (broad s, 12H, C*H*$_2$ chain). ^{13}C NMR (75 MHz; $CDCl_3$): δ 51.90 (s, *C*H$_3$O-), 34.53 (s, CH$_3$O-CO-*C*H$_2$-), 29.78–29.55 (s, *C*H$_2$ chain), 25.37 (s, CH$_3$O-CO-CH$_2$-*C*H$_2$-) These data are consistent with the literature.[12]

Dimethyl 1,12-dodecanedioate from methyl 11-undecenoate

Under air, [Pd (dba)$_2$] (127 mg, 0.022 mmol) and DTBPMB (439 mg, 1.10 mmol) were introduced into a hastelloy autoclave, sealed and purged with nitrogen. Degassed methanol (20 mL), methyl 11-undecenoate (5 mL, 22.2 mmol) and methanesulfonic acid (0.3 mL, 4.6 mmol) were added to the autoclave by cannula. The autoclave was purged three times with CO and the pressure was set to 30 bar. The autoclave was heated to 90 °C for 20 h. After cooling, venting and opening, the yellow solution was filtered through paper and the solvent removed on a rotary evaporator. Methanol was added and the mixture was then stirred at −78 °C for 10 min and filtered using a Büchner funnel. The desired product was obtained as a white powder. Isolated yield (3.36 g: 58%). Elemental analysis: found C 65.14, H 10.18%; $C_{14}H_{26}O_4$ requires C 65.09, H 10.14%. ^{1}H NMR (300 MHz; $CDCl_3$): δ 3.66 (s, 6H, C*H*$_3$O-), 2.29 (t, *J* = 7.5 Hz, 4H, CH$_3$O-CO-C*H*$_2$-), 1.60 (quintet, *J* = 7.2 Hz, 4H, CH$_3$O-CO-CH$_2$-C*H*$_2$-), 1.26 (broad s, 12H, C*H*$_2$ chain). ^{13}C NMR (75 MHz; $CDCl_3$): δ 51.90 (s, *C*H$_3$O-), 34.53 (s, CH$_3$O-CO-*C*H$_2$-), 29.78–29.55 (s, *C*H$_2$ chain), 25.37 (s, CH$_3$O-CO-CH$_2$-*C*H$_2$-). These data are consistent with these from the literature.[12]

Dimethyl 1,17-heptadecanedioate from 2-hexadecenoic acid

Under air, [Pd$_2$(dba)$_3$] (18 mg, 0.0197 mmol, 0.0394 mmol Pd) and DTBPMB (78 mg, 0.197 mmol) were introduced into a hastelloy autoclave, sealed and purged with nitrogen. Degassed methanol (8 mL), 2-hexadecenoic acid (1.0 g, 3.93 mmol) and methanesulfonic acid (0.05 mL, 0.8 mmol) were added to the autoclave by cannula. The autoclave was purged three times with CO and the pressure was set to 30 bar. The autoclave was heated to 90 °C for 20 h. After cooling, venting and opening, the yellow solution was filtered through paper and the solvent was removed on a rotary evaporator. Methanol was added, the mixture was put in the freezer for 20 min and filtered using a Büchner funnel. The desired product was obtained as a white powder (0.75 g, 58%). Elemental analysis: found C 69.56, H 10.09%; $C_{14}H_{26}O_4$ requires C 69.47, H 11.05%. ^{1}H NMR (300 MHz; $CDCl_3$): δ 3.66 (s, 6H, C*H*$_3$O-), 2.30 (t, *J* = 7.5 Hz, 4H, CH$_3$O-CO-C*H*$_2$-), 1.61 (quintet, *J* = 7.4 Hz, 4H, CH$_3$O-CO-CH$_2$-C*H*$_2$-), 1.24 (broad s, 22H, C*H*$_2$ chain). ^{13}C NMR (75 MHz; $CDCl_3$): δ 174.64 (s, *C*O), 51.73 (s, *C*H$_3$O-), 34.40 (s, CH$_3$O-CO-*C*H$_2$-), 29.92–29.44 (s, *C*H$_2$ chain), 25.24 (s, CH$_3$O-CO-CH$_2$-*C*H$_2$-).

Trimethyl ethane-1,1,2-trioate

Under air, [Pd$_2$(dba)$_3$] (37 mg, 0.04 mmol, 0.08 mmol Pd) and DTBPMB (158 mg, 0.4 mmol) were introduced into a hastelloy autoclave, sealed and purged with nitrogen. Degassed methanol (10 mL), dimethyl maleate (1 mL, 8 mmol) and methanesulfonic acid (0.05 mL, 0.8 mmol) were added to the autoclave by cannula. The autoclave was purged three times with CO and the pressure was set to 30 bar. The autoclave was heated to 90 °C for 24 h. After cooling, venting and opening, the yellow solution was filtered through paper and the solvent removed on a rotary evaporator. The crude mixture was passed through a silica chromatography column (hexane/ethyl acetate: 85/15). The desired product was obtained as a white solid. Isolated yield (1.2 g, 73%). Elemental analysis: found C 47.13, H 5.98%; $C_8H_{12}O_6$ requires C 47.06, H 5.92%. ^{1}H NMR (300 MHz; $CDCl_3$): δ 3.87 (t, *J* = 7.4 Hz, 1H, CH$_3$-OCO-CH$_2$-C*H*-), 3.77 (s, 6H, (C*H*$_3$-O-CO)$_2$CH), 3.71 (s, 3H, C*H*$_3$-O-CO-CH$_2$-), 2.95 (d, *J* = 7.4 Hz, 2H, CH$_3$-O-CO-C*H*$_2$-). ^{13}C NMR (75 MHz; $CDCl_3$): δ 171.39 (s, CH$_3$-O-*C*O-CH$_2$-), 168.90 (s, CH$_3$-O-*C*O-CH-), 53.06 (s, *C*H$_3$-O-CO-CH-), 52.31 (s, *C*H$_3$-O-CO-CH$_2$-), 47.56 (s, *C*H-(CH$_3$-O-CO)$_2$), 33.06 (s, CH$_3$-O-CO-*C*H$_2$-). These data are consistent with those in the literature.[13]

Results and discussion

Composition of the TOFA

The TOFA were analysed using GCMS and ^{1}H NMR techniques. At first sight, the MS spectrum shows a single major peak with the library offering a good match of the MS for linoleic acid (*m*/*z* = 280). However, there was also a peak in the MS at *m*/*z* =

282 possibly arising from oleic acid. The quantitative ratio of oleic : linoleic acids was obtained using a literature method[14] involving ^{1}H NMR analysis. This showed the TOFA to contain 72% of linoleic acid and 28% oleic acid.

The methoxycarbonylation of linoleic acid

In order to identify the products from and hence to optimise the methoxycarbonylation of TOFA (see later) as well as to address the question of whether or not transfer hydrogenation of dimethyl 1,19-nonadecenedioate esters (**3**) to dimethyl 1,19-nonadecanedioate (**4**) occurs, the methoxycarbonylation of pure linoleic acid was carried out in methanol at 30 bar and 90 °C over 48 h using a catalyst prepared *in situ* from [$Pd_2(dba)_3$] (dba = dibenzylideneacetone), 1,2-bis(ditertiary-butylphosphinomethyl)benzene (DTBPMB) and methanesulphonic acid (MSA). GC analysis of the crude product showed several components (Fig. 1). Compound **3** was readily identified as the expected dimethyl nonadecenedioate, existing as a mixture of esters with the double bond at different positions in the chain. It is clear that there is little, if any of the saturated diester, dimethyl nonadecanedioate (**4**), which has a retention time slightly longer than that of the unsaturated diesters and is observed in the methoxycarbonylation products of TOFA (Fig. 2).

In our original paper[2] we suggested that dimethyl 1,19-nonadecanedioate could be produced from methyl linoleate or linolenate by methoxycarbonylation followed by transfer hydrogenation from methanol. Our subsequent work on natural oils[1] as well as work on methyl linoleate by Mecking and co-workers[5] suggested that this transfer hydrogenation does not occur to any large extent in the presence of CO. These new results confirm that significant transfer hydrogenation does not occur under methoxycarbonylation conditions.

In order to identify the other products formed during the methoxycarbonylation of linoleic acid, they were separated by column chromatography and fully characterised (see Experimental and ESI†). Compounds **1** and **2** are known[11] C18 keto esters, with **2** being methyl 17-oxooctadecanoate and **1** being a mixture of isomers of methyl *n*-oxooctadecanoate with the keto group at different positions along the chain. Compound **5** has not been fully identified but appears to be a mixture of methyl methoxyoctadecanoates. Finally, compound **6** was isolated (19% yield, 44% if the reaction was carried out in the presence of $MgSO_4$) and fully characterised as a mixture of trimethyl 1,*n*,17-heptadecanetricarboxylates, where *n* indicates that the extra carbomethoxy group is at any position along the chain. These triesters are discussed in more detail later on, but arise from methoxycarbonylation of the double bonds in the various isomers of dimethyl 1,19-nonadecenedioates.

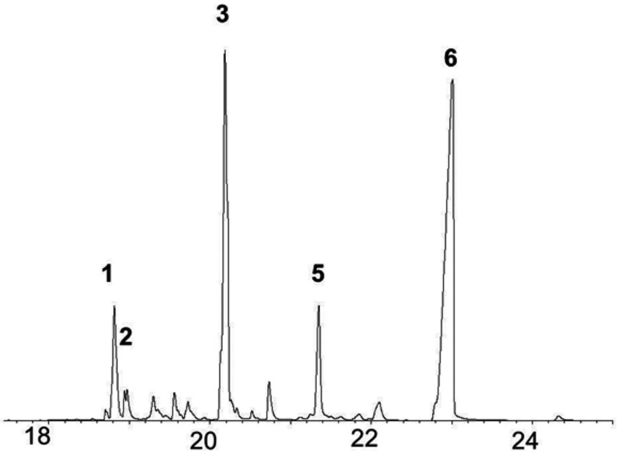


Fig. 1 GCFID trace of the crude mixture from the methoxycarbonylation of linoleic acid. The numbered peaks arise from compounds shown in Scheme 1.

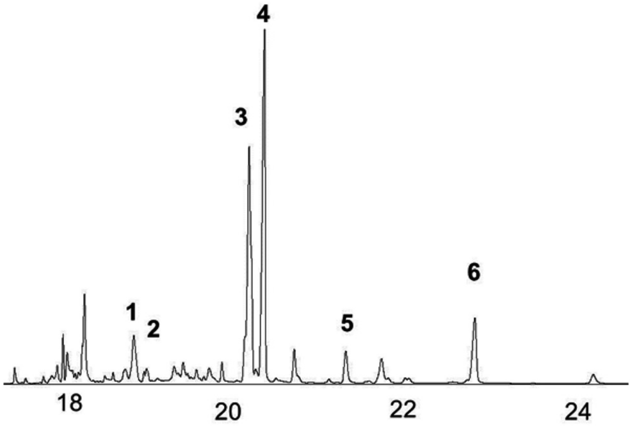


Fig. 2 GC/FID of the crude mixture from the methoxycarbonylation of TOFA.

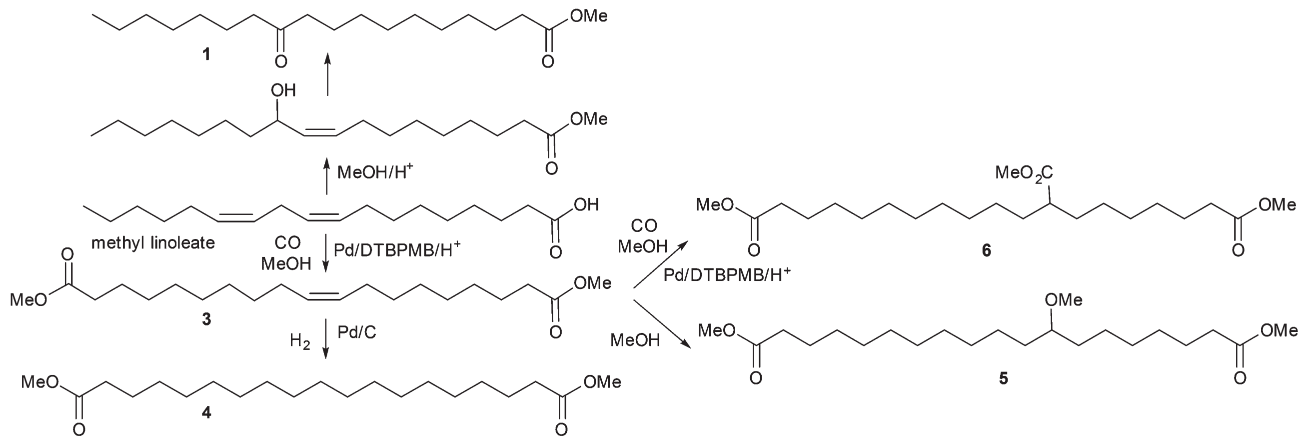
We surmised that compounds **1** and **2** might arise from addition of water to linoleic acid or methyl linoleate followed by isomerisation of the enol to the ketone. Possible isomerisation of the double bonds into conjugation catalysed by the Pd complex might enhance this reaction. **1** and **2** do not appear previously to have been synthesised by hydration of linoleic acid or its methyl ester, but they have been formed by bacterial oxidation of oleic acid in an aqueous environment.[15] Under the same conditions,[15–19] or using metal catalysts[20] linoleic acid gives unsaturated keto esters, which can dehydrate to give conjugated dienoic acid esters.[16,17,19]

Drying the reagents did not reduce the amount of products **1** and **2**, but water is formed from esterification of linoleic acid by methanol and this water might then add across the methyl linoleate. To test this, a reaction was carried out under identical conditions to those used for the methoxycarbonylation of methyl linoleate, but under N_2 in place of CO. Compounds **1** and **2** were the major products confirming that this reaction is independent of the methoxycarbonylation. Interestingly, in this reaction, some methyl oleate was formed, suggesting that transfer hydrogenation is possible in the absence of CO.

The origin of the various products is shown in Scheme 1.

Methoxycarbonylation of TOFA

The methoxycarbonylation of TOFA using the same catalytic system as was used for linoleic acid, leads to a variety of different products (see GC in Fig. 2). Most of the major



Scheme 1 Products formed from the methoxycarbonylation of linoleic acid or TOFA. The positions of the double bond in **3** and the mid-chain substituents in **1**, **5** and **6** are variable. **2**, methyl 17-oxooctadecanoate, contains the terminal methyl ketone. The identification of **5** is tentative.

Table 1 Products from the methoxycarbonylation/hydrogenation of TOFA[a]

	1	2	3	4	5	6
M	5	2	28	26	3	10
M/H	10	4	4	49	6	12
E/M[b]	2	1	26	33	1	13
E/M/H[c]	4	2	3	55	2	13

[a] GC conversion/% (uncalibrated area of all products M = methoxycarbonylation, H = hydrogenation, E = esterification with methanol in the presence of $MgSO_4$); [b] methyl oleate 11%; [c] methyl stearate, 10%.

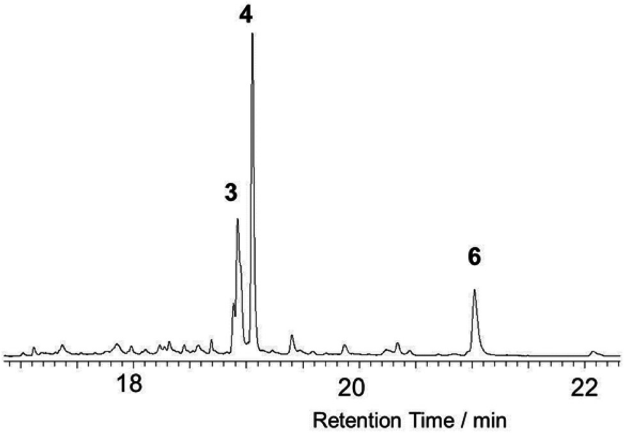


Fig. 3 GCFID trace of the crude mixture from the methoxycarbonylation of TOFA following esterification with methanol in the presence of $MgSO_4$. Note that the GC conditions and retention times are slightly different from those in Fig. 1 and 2. The identities of the shown compounds have been confirmed by GCMS.

products are the same as those produced from linoleic acid, except that dimethyl 1,19-nonadecanedioate (**4**) from methoxycarbonylation of methyl oleate is a significant component. Hydrogenation of this mixture using Pd/C led to the desired 1,19-nonadecanedioate in very good purity and 32% isolated yield (Table 1).

When the methoxycarbonylation was carried out using syngas in place of pure CO, it led to a similar ratio between saturated and monounsaturated diesters proving the reaction does not need high purity CO, but works with lower (and less expensive) CO grades. This reaction also shows that the palladium catalyst does not promote hydrogenation.

Knowing that compounds **1** and **2** are formed from a reaction between methyl linoleate and water produced during the initial esterification of linoleic acid by methanol and that the proportion of compound **6** increases with increased reaction time, we attempted to increase the yield of the desired **4** from TOFA. TOFA was stirred for 3 h in methanol containing the amount of MSA required for the subsequent methoxycarbonylation reaction and $MgSO_4$. GC analysis showed that complete conversion of the acids to methyl oleate and methyl linoleate occurred. After filtration, this solution was used for methoxycarbonylation under the standard conditions, but for 10 h in an attempt to reduce the amount of triester, **6**, formed. GC analysis showed mainly compounds **3** and **4** with some **6** (Fig. 3). Hydrogenation of this solution (Fig. 4) gave, in addition to methyl stearate and **6**, predominantly the desired **4**, which was isolated in 49% yield.

Identification of triesters, 6

Compound **6** gave an MS trace with a parent ion of $m/z = 415$. This molecular mass corresponds to that of a triester, trimethyl heptadecane-1,*n*,17-tricarboxylate (HDTC, where *n* designates any position within the hydrocarbon chain) (Scheme 1), which could be formed from methoxycarbonylation of dimethyl 1,19-nonadecenedioate. Apart from reactions of styrene[21,22] and vinyl acetate,[23,24] which give predominantly branched products, all other studies using Pd/DTBPMB/MSA for methoxycarbonylation have shown very high selectivity to carbonylation at the terminus of carbon chains[1–6,21,25] even if the double bond is buried deep in the chain (methyl oleate, methyl erucate)[1–6] or conjugated to an ester function[2,21] (see below and second carbonylation of alkynes[21]). However, all of the substrates we have examined have the possibility of

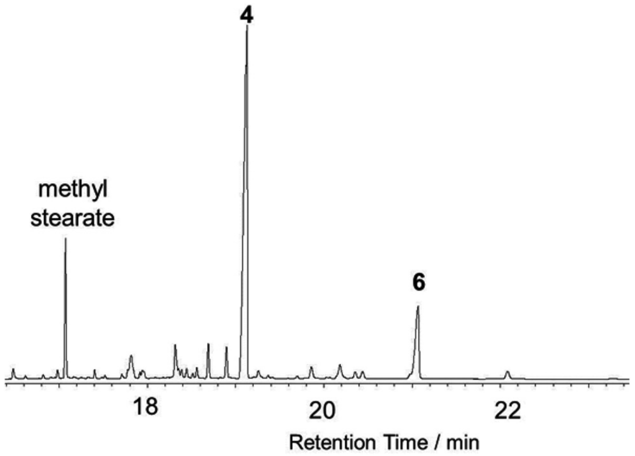


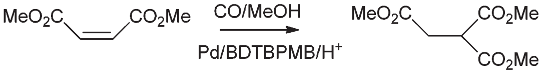
Fig. 4 GCFID trace of the crude mixture from the sequential esterification with methanol in the presence of $MgSO_4$, methoxycarbonylation and hydrogenation of TOFA. Note that the GC conditions and retention times are slightly different from those in Fig. 1 and 2. The identities of the shown compounds have been confirmed by GCMS.

Table 2 Main fragments obtained on GCMS of compound **6** and proposed assignments

m/z	Fragment
415	$[M]^+$
383	$[M - OMe]^+$
355	$[M - CO_2Me]^+$

isomerisation of the C=C to the C terminus where it can be trapped by methoxycarbonylation. The one exception to this generalisation is the carbonylation of internal alkynes, where the first carbonylation occurs at one end of the triple bond[21] because triple bond isomerisation does not occur. In the case of dimethyl 1,19-nonadecenedioate, the double bond cannot migrate to the end of the chain because both ends are already esterified, so there is the possibility of adding a third ester group wherever the double bond is in the chain.

A triester could explain the different fragments seen in the mass spectrum (Table 2), so we isolated the proposed HDTC (compound **6**) in a microanalytically pure form from the crude mixture (GCFID shown in Fig. 1), obtained from the methoxycarbonylation of linoleic acid, by column chromatography and analysed it by ^1H and ^{13}C NMR techniques. In the DEPT ^{13}CNMR spectrum, there are at least three resonances near δ 46 ppm, which are upside down compared with the signals from methylene groups. These resonances correlate with ^1H NMR resonances near δ 2.3 ppm, slightly upfield from the resonance arising from the methylene groups next to the terminal $-CO_2Me$ functions (δ 2.32 ppm). These resonances are exactly where the resonances from the CH attached to a mid-chain $-CO_2Me$ would be expected to appear. The fact that there are at least 3 C signals near δ 46 ppm suggest that at least 3 different isomers are present. Given that the methoxycarbonylation catalyst is also a good double bond isomerisation catalyst, it seems likely that the dimethyl 1,19-nonadecenedioate will exist as various isomers with double bonds in different positions along the chain and that methoxycarbonylation will then place the third ester group in a variety of positions along the chain. In support of this, there is also more than one methoxy resonance near δ 3.7 ppm. All of the NMR, MS and analytical data are consistent with the formation of trimethyl heptadecanetricarboxylates, with the third methoxycarbonylation occurring at a variety of places along the chain. The triester which has two geminal carboxylate groups at one end (malonate) would be expected to show NMR resonances near δ 3.3 ppm (^1H) and δ 50 ppm (^{13}C) for the methylene group. Although the ^1H NMR spectrum of the isolated triester does have very weak peaks in the region near δ 3.3 ppm, they appear to be singlets and do not correlate with appropriate ^{13}C resonances. This suggests that very little of the triester containing a geminal diester is formed, as expected, since the amount of α,β-unsaturated diester has been measured as only 3–5%. These triesters may be important as cross linkers in polymerisation reactions using naturally derived monomers.



Scheme 2 Synthesis of trimethyl ethane-1,1,2-trioate from methoxycarbonylation of dimethyl maleate.

Further to confirm the suggestion that Pd/BDTBPMB/MSA could catalyse the methoxycarbonylation of a trapped internal double bond, we carried out the methoxycarbonylation of dimethyl maleate. The reaction led efficiently to trimethyl ethane-1,1,2-trioate (Scheme 2), together with some dimethyl fumarate, formed by *Z*–*E* isomerism of dimethyl maleate.

Compound **5** was not clearly identified. At first sight, the ^1H NMR spectrum suggests the presence of a diester bearing an extra functional group on the carbon chain. Indeed, the spectrum shows a resonance at δ 3.30 ppm correlated with a ^{13}C resonance at δ 56.5 ppm (DEPT CH_3), probably from a methyl ether. The MeO*CH* group could then give the correlated resonances at δ 81 ppm (^{13}C NMR, DEPT CH) and δ 3.10 ppm (quintet, ^1H NMR), Methyl ester groups are also present (^1H NMR, δ 3.73 ppm correlating with ^{13}C NMR, δ 52.5 ppm). The highest mass peak in the mass spectrum is at 354, which could be consistent with loss of methanol from dimethyl *n*-methoxynonadecane-1,19-dioate $M_r = 386$. Such a product could be formed by addition of methanol to dimethyl 1,19-nonadecenedioate. The difficulty in isolating a pure sample of this product from all the other various side-products present in the mixture did not allowed an unequivocal identification.

Shorter chain diesters from natural resources

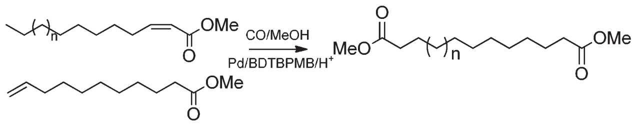
The diesters described in this paper and our previous carbonylation work on methyl oleate[2] or natural oils[1] all contain 19 carbon atoms, with the advantage that all the C atoms of the oleate end up in the product. However, there is considerable interest in diesters of different chain lengths, also derived from natural resources. It is well established that dimethyl

Table 3 Methoxycarbonylation of 2-undecenoic and 2 hexadecenoic acids, conversion and selectivity

Substrate	Methyl 10-undecenoate	2-Undecenoic acid	2-Hexadecenoic acid
Conv/% (GC FID)[a]	83	84	79
Sel. linear di.	89	92	90
Sel. ω-2 br. di.	6	4.3	3.5
Sel. ω-3 br. di.	1.5	1	1
Other br. di.	3.5	2.6	5.5
Isolated yield	58	43	58

[a] Uncalibrated, based on areas; Sel = selectivity, br = branched, di = diester.

1,18-octadecanoate can be formed by self-metathesis of methyl oleate[9,26–28] followed by hydrogenation, but in this case, half the C atoms end up in a long chain hydrocarbon. In order to improve the atom efficiency for obtaining shorter chain diesters from methyl oleate and related compounds, we have proposed and demonstrated[9] the metathesis of methyl oleate with dimethyl maleate to produce dimethyl 1,11-undec-2-enedioate, a C_{11} diester and methyl 2-undecenoate, an α,β-unsaturated monoester. These products can also be formed by cross metathesis of methyl oleate with methylacrylate.[29] In order to make the C_{12} diester, we attempted the methoxycarbonylation of 2-undecenoic acid, which requires the double bond to move 8 bonds into the least thermodynamically favoured position before being trapped there by methoxycarbonylation. Previously the maximum distance for isomerisation that has been observed in this isomerising methoxycarbonylation chemistry was 8 bonds (for methyl oleate[1–6] or methyl erucate[4,5]) if the double bond was not conjugated or 7 bonds where the double bond was conjugated to an ester (second carbonylation of 1-octyne to give dimethyl 1,10-decanedioate).[21] Gratifyingly the reaction worked well and produced dimethyl 1,12-dodecanedioate with high selectivity (Table 3). The same product, which is an important component of Nylon-12,12, was also prepared by the methoxycarbonylation of methyl 10-undecenoate, which is available from cracking castor oil,[10] although shorter reaction times could be used in this case. This reaction has previously been demonstrated using other catalysts.[30] To test the isomerising ability of the catalyst still further, 2-hexadecenoic acid, which requires the double bond to move 13 places out of conjugation to make the α,ω-diester, was successfully methoxycarbonylated to dimethyl 1,17-heptadecanedioate in high selectivity (Table 3). These reactions are summarised in Scheme 3.



Scheme 3 Methoxycarbonylation of unsaturated C_{11} (n = 1) and C_{16} (n = 6) esters.

Conclusion

Tall Oil Fatty Acids, which constitute a waste from paper manufacture and contain mainly oleic and linoleic acids, have been methoxycarbonylated to a mixture of dimethyl 1,19-nonadecanedioate and dimethyl 1,19-nonadecenedioate (mixture of isomers). Some of the latter is converted into a mixture of isomers of trimethyl 1,n,17-heptadecanetricarboxylate, which may be interesting as cross-linkers in polyesters prepared from plant based diesters. Other products include keto esters derived from addition of water (generated in the initial esterification of the acids by methanol) to isomerised methyl linoleate. In addition to helping with the identification of the products obtained from TOFA, the methoxycarbonylation of linoleic acid shows that esters containing two double bonds give unsaturated diesters and triesters as major products with no transfer hydrogenation to give saturated diesters. By pre-esterifying the TOFA and following the methoxycarbonylation with hydrogenation, dimethyl 1,19-nonadecanedioate, which is potentially an important polyester precursor can be obtained in 49% yield. Undecenoic acids or esters with the double bond conjugated to the carbonyl group (available from metathesis of methyl oleate with dimethyl maleate)[9] or in the terminal position (available from castor oil) can both be methoxycarbonylated to dimethyl 1,12-dodecanedioate, a component of Nylon-12,12, whilst the conjugated double bond in 2-hexadecenoic acid can be moved 13 bonds along the chain to the least thermodynamically favoured terminal position before methoxycarbonylation to furnish dimethyl 1,17-heptadecanedioate.

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