Identification and Total Synthesis of Novel Fatty Acids from the Siphonarid Limpet *Siphonaria denticulata*

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The novel fatty acids 17-methyl-6(*Z*)-octadecenoic acid and 17-methyl-7(*Z*)-octadecenoic acid were identified for the first time in nature in the mollusk *Siphonaria denticulata* from Queensland, Australia. The principal fatty acids in the limpet were hexadecanoic acid, octadecanoic acid, and (*Z*)-9-octadecenoic acid, while the most interesting series of monounsaturated fatty acids was a family of five nonadecenoic acids with double bonds at either Δ^7, Δ^9, Δ^{11}, Δ^{12}, or Δ^{13}. The novel compounds were characterized using a combination of GC−MS and chemical transformations, such as dimethyl disulfide derivatization. The first total syntheses for the two novel methyl-branched nonadecenoic acids are also described, and these were accomplished in four to five steps and in high yields.

Siphonariid limpets have previously been shown to contain branched-chain polypropionate metabolites of considerable biosynthetic interest.[1] For example, the air-breathing gastropod *Siphonaria diemenensis* contains the diemenensins A and B, compounds that display antimicrobial properties.[2] On the other hand, the pulmonate *Siphonaria denticulata* Quoy and Gaimard biosynthesizes the denticulatins A and B, polypropionate compounds that have attracted considerable attention from both synthetic and bioorganic chemists.[3−5] In addition, *Siphonaria zelandica* produces the siphonarins A and B, which have also been the subject of considerable biosynthetic efforts.[1]

Despite all of these isolation and biosynthetic efforts, the fatty acid composition of *S. denticulata* (class Gastropoda, order Pulmonata, family Siphonariidae) has not been explored. Earlier work with the related *S. diemenensis* revealed the presence of high amounts of 16:0, 18:1*n*−9, and 20:1*n*−9 fatty acids, as well as the non-methylene interrupted fatty acids 20:2($\Delta^{5,11}$ and $\Delta^{5,13}$) and 22:2($\Delta^{7,13}$ and $\Delta^{7,15}$).[6] Unexpectedly, in *S. diemenensis* the fatty acid 18:1*n*−7 was not identified, which translated into a 18:1*n*−9/18:1*n*−7 ratio greater than 10.0.[6] In addition, the isoprenoid fatty acid 4,8,12-trimethyltridecanoic acid was also identified in the limpet. Therefore, on the basis of earlier findings, we examined the fatty acid composition of the pulmonate *S. denticulata* from Queensland, Australia, so as to compare its fatty acid composition with that of other mollusks such as *S. diemenensis*. During this work we uncovered the presence of two novel nonadecenoic acids, namely, the acids 17-methyl-6(*Z*)-octadecenoic acid and 17-methyl-7(*Z*)-octadecenoic acid, which we report herein together with their total synthesis. We also describe the total fatty acid composition of *S. denticulata* at a detection limit of 0.01%.

Results and Discussion

The limpet *S. denticulata* presented a rather complex fatty acid composition of around 59 identifiable fatty acids, as shown in Table 1. These fatty acids were identified on the basis of their GC retention times, mass spectral data, comparison with authentic standards, and dimethyl disulfide derivatization. Fatty acid chain lengths ranged between 14 and 24 carbons, mainly consisting of saturated and monounsaturated fatty acids. Normal-chain saturated fatty acids, such as hexadecanoic acid, were particularly abundant in this pulmonate; they made up 51.4% of the total fatty acid composition. On the other hand, *iso-anteiso* odd-chain fatty acids made up 10% of the fatty acid composition, while monounsaturated fatty acids between C_{16} and C_{22} accounted for almost 30% of the total composition. Among the monounsaturated fatty acids the (*Z*)-9-octadecenoic acid (18:1*n*−9) and the (*Z*)-11-octadecenoic acid (18:1*n*−7) were among the most prominent. In fact, the 18:1*n*−9/18:1*n*−7 ratio was close to 2, in contrast to what was previously reported from other mollusks from the Siphonariidae in Australian waters, such as *Siphonaria diemenensis*, where a ratio of 10 was reported.[6] In fact, for *S. diemenensis* no 18:1*n*−7 fatty acid was reported. Another interesting finding in *S. denticulata* was the identification of the 4,8,12-trimethyltridecanoic acid, a common fatty acid in mollusks, which is most likely arising from a dietary intake of phytol (as chlorophyll).[6] The typical series of non-methylene-interrupted diunsaturated fatty acids with chain lengths between 20 and 22 carbons, characteristic for this type of mollusk, was also found in *S. denticulata*.

In addition to the aforementioned fatty acids, a set of unusual nonadecenoic acids was also identified in *S. denticulata* in which the Δ^7, Δ^9, Δ^{11}, Δ^{12}, and Δ^{13} monounsaturations were identified by dimethyl disulfide derivatization. Moreover, two rather unusual methyl-branched nonadecenoic acids with Δ^6 and Δ^7 monounsaturations were also detected. The methyl ester of the Δ^6 isomer presented an equivalent chain-length (ECL) value of 18.37, while the ECL value for the methyl ester of the Δ^7 isomer was 18.33, practically unresolvable peaks in nonpolar capillary gas chromatography. The low fractional chain-length (FCL) values of 0.33−0.37 compared favorably with that of other *iso*-methyl-branched methyl esters, thus supporting a possible *iso*-methyl branching in addition to one unsaturation for both unknown methyl nonadecenoates.

Mass spectrometry was the spectrometric technique of choice used to initially identify structures **1** and **2** because of their low abundance in the mollusk and almost identical

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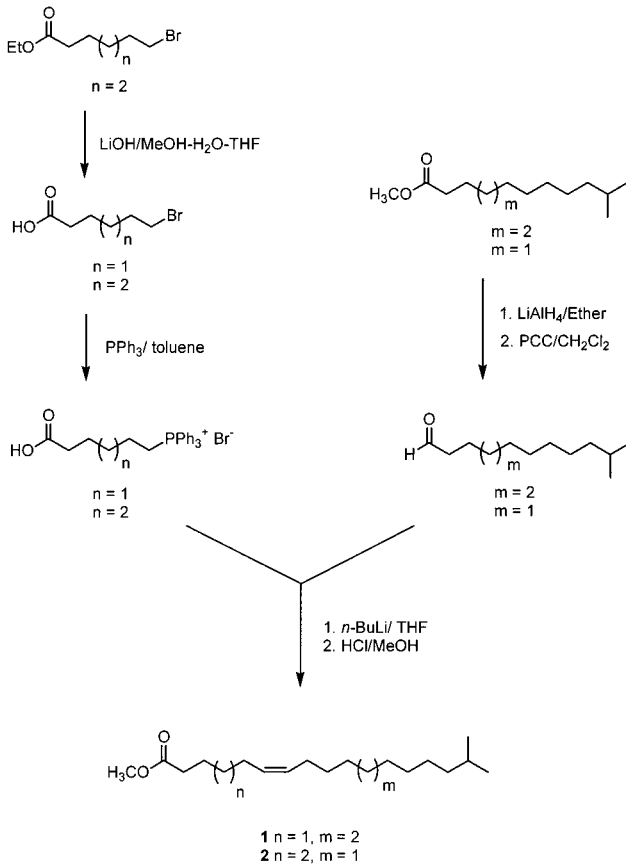
Table 1. Identified Fatty Acids from *S. denticulata*

fatty acid	abundance (wt %)
tetradecanoic (14:0)	2.2
4,8,12-trimethyltridecanoic (16:0)	2.1
13-methyltetradecanoic (*i*-15:0)	0.2
12-methyltetradecanoic (*ai*-15:0)	0.1
pentadecanoic (15:0)	1.1
14-methylpentadecanoic (*i*−16:0)	0.6
13-methylpentadecanoic (a*i*-16:0)	0.1
(Z)-9-hexadecenoic (16:1)	1.1
(*Z*)-11-hexadecenoic (16:1)	0.1
hexadecanoic (16:0)	26.5
methylhexadecanoic (*br*-17:0)	0.2
methylhexadecanoic (*br*-17:0)	0.2
(6Z)-15-methyl-6-hexadecenoic (*i*-17:1)	0.1
(8Z)-15-methyl-8-hexadecenoic (*i*-17:1)	0.1
(9Z)-15-methyl-9-hexadecenoic (*i*-17:1)	0.1
(10Z)-15-methyl-10-hexadecenoic (*i*-17:1)	0.1
15-methylhexadecanoic (*i*-17:0)	2.0
14-methylhexadecanoic (*ai*-17:0)	5.8
(*Z*)-9-heptadecenoic (17:1)	0.4
(*Z*)-10-heptadecenoic (17:1)	0.1
(*Z*)-11-heptadecenoic (17:1)	0.1
(*Z*)-12-heptadecenoic (17:1)	0.1
heptadecanoic (17:0)	4.4
(9Z,12Z)-9,12-octadecadienoic (18:2)	1.6
(*Z*)-5-octadecenoic (18:1)	0.3
(*Z*)-9-octadecenoic (18:1)	9.5
(*Z*)-11-octadecenoic (18:1)	5.1
(*Z*)-13-octadecenoic (18:1)	0.1
octadecanoic (18:0)	15.7
(*E*)-11-methyl-12-octadecenoic (19:1)	0.4
methyloctadecanoic (*br*-19:0)	0.1
(6Z)-17-methyl-6-octadecenoic (19:1)[a]	0.1
(7Z)-17-methyl-7-octadecenoic (19:1)[a]	0.1
17-methyloctadecanoic (*i*-19:0)	0.5
16-methyloctadecanoic (*ai*-19:0)	0.2
(*Z*)-7-nonadecenoic (19:1)	0.3
(*Z*)-9-nonadecenoic (19:1)	0.2
(*Z*)-11-nonadecenoic (19:1)	0.2
(*Z*)-12-nonadecenoic (19:1)	0.2
(*Z*)-13-nonadecenoic (19:1)	0.1
nonadecanoic (19:0)	0.2
5,8,11,14-eicosatetraenoic (20:4)	0.3
eicosadienoic (20:2)[b]	0.4
eicosadienoic (20:2)[b]	0.2
eicosadienoic (20:2)	1.3
(*Z*)-7-eicosenoic (20:1)	4.7
(*Z*)-11-eicosenoic (20:1)	4.4
(*Z*)-13-eicosenoic (20:1)	2.1
eicosanoic (20:0)	0.9
(*Z*)-7-heneicosenoic (21:1)	0.2
heneicosanoic (21:0)	0.1
docosadienoic (22:2)[c]	1.0
docosadienoic (22:2)[c]	0.6
(*Z*)-7-docosenoic (22:1)	0.3
(*Z*)-9-docosenoic (22:1)	0.1
(*Z*)-13-docosenoic (22:1)	0.1
(*Z*)-15-docosenoic (22:1)	0.1
docosanoic (22:0)	0.3
tetracosanoic (24:0)	0.1

[a] Unprecedented as natural compounds. [b] Most likely $\Delta^{5,11}$ and/or $\Delta^{5,13}$. [c] Most likely $\Delta^{7,13}$ and/or $\Delta^{7,15}$.

GC retention times. Both methyl esters **1** and **2** displayed a molecular ion peak [M^+] at *m*/*z* 310 and typical fragmentations of a monounsaturated methyl ester at *m*/*z* 278 [$M^+ - 32$, loss of methanol], *m*/*z* 255 [$M^+ - 55$], *m*/*z* 236 [$M^+ - 74$, loss of the McLafferty ion], *m*/*z* 194 [$M^+ - 116$], and *m*/*z* 74 [McLafferty rearrangement ion]. However, there were no ions that permitted the unequivocal location of the monounsaturation due to double-bond migration during ionization. For this purpose, dimethyl disulfide (DMDS) adducts were used to "fix" the double bonds and permit their location by mass spectrometry.[7] In fact, it was through the DMDS adducts that it was possible to initially determine the presence of the Δ^6 and Δ^7 isomers in a single GC peak. For example, one of the unknowns yielded methyl 17-methyl-6,7-bis(methylthio)octadecanoate upon reaction with CH_3SSCH_3/I_2. In the mass spectrum of the latter [$M^+ = 404$] the principal cleavage occurred between the carbons that originally constituted the double bonds (C-6 and C-7), yielding two substantial fragment ions (one containing the terminal methyl group of the molecule at *m*/*z* 229 and a second at *m*/*z* 175 containing the ester group). A third prominent peak was observed at *m*/*z* 143 due to the loss of methanol from the *m*/*z* 175 ion. Therefore, one of the unknown methyl nonadecenoates is methyl 17-methyl-6(Z)-octadecenaote (**1**), which to the best of our knowledge has no literature precedence.

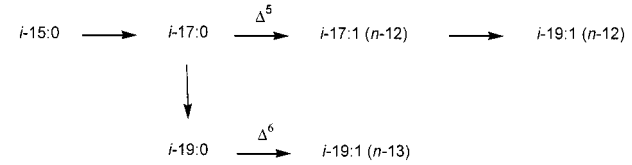
Scheme 1



The second unknown methyl nonadecenoate, upon DMDS derivatization, yielded 17-methyl-7,8-bis(methylthio)octadecanoate. In this case, the DMDS adduct also presented a mass spectrum with a molecular ion peak at *m*/*z* 404 and key fragment ions at *m*/*z* 215 (methyl end) and *m*/*z* 189 (carboxy end), with the latter ion losing methanol to afford a third prominent ion at *m*/*z* 157. Therefore, the mass spectral data indicate that the second methyl nonadecenoate could only be methyl 17-methyl-7(*Z*)-octadecenoate (**2**), which also does not have literature precedence.

Final structural confirmation of **1** and **2**, including the double bond stereochemistry, was achieved by total synthesis (Scheme 1). The synthesis of methyl 17-methyl-6(*Z*)-octadecenoate (**1**) was based on Wittig coupling to generate the Δ^6 double bond and commercially available methyl 11-methyldodecanoate (Sigma) to introduce the *iso* branching. Therefore, the synthesis started with the lithium aluminum hydride reduction of methyl 11-methyldodecanoate to 11-methyl-1-dodecanol. Then, the alcohol was transformed into 11-methyldodecanal, required for the Wittig coupling, upon reaction with pyridinium chlorochromate in dichloro-

Scheme 2



methane, resulting in an almost quantitative yield of the aldehyde. Final Wittig coupling of 11-methyldodecanal with (5-carboxypentyl)triphenylphosphonium bromide (prepared from 6-bromohexanoic acid as described in the Experimental Section) resulted in a 7:2 mixture (as determined by capillary GC of the methyl esters) of 17-methyl-6(*Z*)-octadecenoic acid and 17-methyl-6(*E*)-octadecenoic acid, which together accounted for an 88% isolated yield (86% overall yield from methyl 11-dodecanoate). These acids were then transformed into the corresponding methyl esters by reaction with acidic MeOH. A capillary GC coelution of **1*Z*** (ECL = 18.37) and **1*E*** (ECL = 18.43) with the original methyl esters from *S. denticulata* established the *Z* double bond sterochemistry for **1** and confirmed the structure.

Following a similar strategy methyl 17-methyl-7(*Z*)-octadecenoate (**2**) was synthesized as outlined in Scheme 1. In this case the synthesis started with the lithium aluminum hydride reduction of methyl 10-methylundecanoate to 10-methyl-1-undecanol, which was then transformed into 10-methylundecanal upon reaction with pyridinium chlorochromate in dichloromethane, resulting in an almost quantitative yield of the aldehyde. The Wittig coupling of 10-methylundecanal with (6-carboxyhexyl)-triphenylphosphonium bromide (prepared from ethyl 7-bromoheptanoate after saponification with LiOH and further reaction with triphenylphosphine in toluene) resulted in a 9:1 mixture (88% overall yield from methyl 10-methylundecanoate) of 17-methyl-7(*Z*)-octadecenoic acid and 17-methyl-7(*E*)-octadecenoic acid. The acids were then transformed into the methyl esters (HCl/MeOH) for capillary GC comparisons. In this case capillary GC coelution of **2*Z*** (ECL = 18.33) and **2*E*** (ECL = 18.43) with the methyl esters from *S. denticulata* also confirmed the *Z* double bond stereochemistry for **2** in the original methyl nonadecenoate.

On the basis of these results some unprecedented biosynthetic pathways for *iso* odd-chain fatty acids in nature can be postulated (Scheme 2). Our new *iso*-$C_{19:1}$ fatty acids could have very well originated from *i*-15:0. For example, chain elongation of *i*-15:0 to *i*-17:0 and desaturation at C-5 is a likely pathway for the known *i*-17:1Δ^5, a reported fatty acid.[8] A subsequent two-carbon elongation of *i*-17:1Δ^5 can then result in the novel *i*-19:1Δ^7. The other new acid, *i*-19:1Δ^6, could very well have originated from a four-carbon elongation of *i*-15:0 to *i*-19:0 followed by Δ^6 desaturation to *i*-19:1Δ^6.

Experimental Section

General Experimental Procedures. Fatty acid methyl esters were analyzed by GC−MS at 70 eV using a Hewlett-Packard 5972A MS ChemStation equipped with a 30 m × 0.25 mm special performance capillary column (HP-5MS) of polymethylsiloxane cross-linked with 5% phenyl methylpolysiloxane. The temperature program was as follows: 130 °C for 1 min, then increased at a rate of 3 °C/min to 270 °C, and maintained for 30 min at 270 °C.

Mollusk Collection. Specimens (40 g) of *S. denticulata* Quoy and Gaimard (class Gastropoda, order Pulmonata, family Siphonariidae) were collected from the rock platform at Caloundra, SE Queensland, in May 1999, placed onto ice for transport back to Brisbane, and stored at −18 °C until needed. A voucher of the animals (Voucher No. sd-1) is held at the Department of Chemistry, the University of Queensland.

Isolation and Identification of Fatty Acids. Approximately 150 animals were shelled and extracted with 3 × 200 mL of CH_2Cl_2/MeOH (1:1). The extract was filtered through Celite, concentrated in vacuo, and then partitioned between EtOAc (3 × 100 mL) and water (50 mL) to give a crude extract (0.73 g) after concentration. An aliquot (30 mg) of crude extract was dissolved in methanolic HCl (1.5 M; 7 mL) and refluxed for 2 h. The soluble products were concentrated, then resuspended in toluene (0.5 mL) and passed through a pipet column (Celite, 0.25 g Celite) eluting with 3 mL of toluene. A second purification step involved silica column chromatography using hexane (10 mL) as eluant, giving the fatty acid methyl ester extract (2.9 mg).

11-Methyl-1-dodecanol. To a stirred solution of lithium aluminum hydride in ethyl ether (10 mL) at 0 °C was added dropwise methyl 11-methyldodecanoate (0.050 g, 0.22 mmol) in ether (1 mL). The resulting gray mixture was stirred for 2 h and then quenched carefully with a saturated aqueous ammonium chloride solution. The product was extracted with diethyl ether, and the organic layer was dried over $MgSO_4$. The solvent was filtered and concentrated in vacuo, affording 0.042 g (98% yield) of 11-methyl-1-dodecanol with spectral data identical to that reported in the literature.[9]

11-Methyldodecanal. To a stirred solution of pyridinium chlorochromate (0.16 g, 0.75 mmol) in 15 mL of CH_2Cl_2 was added dropwise 11-methyl-1-dodecanol (0.043 g, 0.21 mmol) in 1 mL of CH_2Cl_2 at room temperature. After 24 h the reaction mixture was filtered through Florisil and washed with diethyl ether (50 mL). Evaporation of the solvent afforded 11-methyldodecanal in a 100% GC yield with spectral data identical to that reported in the literature.[10]

(5-Carboxypentyl)triphenylphosphonium Bromide. Into a 50 mL round-bottomed flask were placed 6-bromohexanoic acid (5.0 g, 23.9 mmol) and triphenylphosphine (6.3 g, 23.9 mmol) in 20 mL of toluene. The mixture was refluxed for 24 h, after which it was cooled to room temperature and the toluene was removed in vacuo. The product was washed several times with diethyl ether, affording (5-carboxypentyl)-triphenylphosphonium bromide (2.2 g, 98% yield) as a white solid with spectral data identical to that reported in the literature.[11]

Methyl 17-Methyl-6(*Z*)-octadecenoate. To 20 mL of a THF stirred solution of previously dried (5-carboxypentyl)-triphenylphosphonium bromide (0.66 g, 0.33 mmol) was added dropwise *n*-BuLi (2.5 M, 2.2 mmol) at 0 °C. The resulting mixture was stirred for 30 min at room temperature. Then, 11-methyldodecanal (0.025 g, 0.13 mmol) in 1 mL of THF was slowly added. After 2 h, the mixture was poured into ice and the solution was acidified with 1 M HCl. The acidic solution was extracted with diethyl ether (2 × 20 mL), and the organic layer was washed with H_2O (2 × 10 mL), dried over $MgSO_4$, and filtered. After rotoevaporation of the solvent the acid was obtained as a yellow oil (0.034 g) for an 88% yield of a 7:2 *Z*/*E* mixture, which were characterized as the methyl esters after refluxing the acids in 1 M HCl (MeOH) for 4 h. The spectral data for the *Z* isomer follows: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.34 (2H, m, H-6, H-7), 3.66 (3H, s, $-OCH_3$), 2.30 (2H, t, J = 7.6 Hz, H-2), 2.01 (4H, m, H-5, H-8), 1.65 (2H, m, H-3), 1.53 (1H, m, H-17), 1.35−1.25 (16H, m, $-CH_2$), 1.15 (2H, m, H-16), 0.86 (6H, d, J = 6.6 Hz, H-18, Me-17); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 174.3 (s, C-1), 130.5 (d, C-7), 129.0 (d, C-6), 51.5 (q, $-OCH_3$), 39.0 (t, C-16), 34.0 (t, C-2), 29.9 (t), 29.7 (t), 29.6 (t), 29.5 (t), 29.3 (t), 29.2 (t), 27.9 (d, C-17), 27.4 (t), 27.2 (t), 26.9 (t), 26.8 (t), 24.6 (t), 22.6 (q, C-18, Me-19); ECL = 18.37, GC−MS (70 eV) *m*/*z* 310 $[M]^+$ (3), 279 (8), 278 (18), 260 (1), 255 (6), 249 (2), 236 (10), 221 (1), 208 (1), 194 (10), 180 (4), 166 (3), 152 (6), 141 (8), 138 (6), 137 (8), 128 (5), 123 (17), 111 (19), 110 (23), 101 (8), 97 (45), 96 (54), 95 (34), 87 (38), 84 (63), 81 (49), 79 (18), 74 (78), 69 (53), 67 (51), 57 (44), 55 (100); HREIMS *m*/*z* 310.2880 (calcd for $C_{20}H_{38}O_2$, 310.2872).

Methyl 17-methyl-6,7-bis(methylthio)octadecanoate: GC−MS (70 eV) *m*/*z* 404 $[M]^+$ (11), 355 (1), 325 (1), 309 (1),

277 (2), 230 (14), 229 (85), 213 (3), 193 (1), 187 (1), 175 (59), 174 (25), 157 (1), 144 (8), 143 (100), 127 (25), 126 (7), 121 (3), 115 (12), 111 (6), 101 (6), 97 (18), 95 (22), 87 (19), 85 (22), 83 (25), 81 (27), 79 (13), 74 (13), 69 (38), 67 (52), 61 (57), 59 (15), 57 (26), 55 (61).

7-Bromoheptanoic Acid. Into a 50 mL round-bottomed flask was placed LiOH (1 g, 4.8 mmol) in 30 mL of MeOH/H_2O/THF (1:1:3) together with ethyl 7-bromoheptanoate (10.95 g, 46.2 mmol). The reaction mixture was refluxed for 4 h, and then it was cooled to room temperature and neutralized to pH 7. The organic solvents were removed under vacuum, and the remaining water solution was acidified to pH 2. The product was extracted with dichloromethane (2 × 15 mL), and the organic layer was dried over $MgSO_4$. Dichloromethane was removed under vacuum, affording 6.4 g of the known 7-bromoheptanoic acid for a 66% yield.[12,13]

10-Methyl-1-undecanol. To a stirred solution of lithium aluminum hydride in ethyl ether (10 mL) at 0 °C was added dropwise methyl 10-methylundecanoate (0.050 g, 0.23 mmol) in ether (1 mL). The resulting gray mixture was stirred for 2.5 h and then carefully quenched with a saturated aqueous ammonium chloride solution. The product was extracted with diethyl ether, and the organic layer was dried over $MgSO_4$. The solvent was filtered and concentrated in vacuo, affording 0.043 g (100% yield) of 10-methyl-1-undecanol, whose spectral data were identical to that previously reported.[14]

10-Methylundecanal. To a stirred solution of pyridinium chlorochromate (0.14 g, 0.64 mmol) in 15 mL of dichloromethane was added dropwise 10-methylundecanol (0.040 g, 0.22 mmol) in 1 mL of dichloromethane at room temperature. After 24 h the reaction mixture was filtered through Florisil and washed with diethyl ether (50 mL). Evaporation of the solvent afforded 0.040 g of the previously reported 10-methylundecanal for a 100% GC yield.[15]

(6-Carboxyhexyl)triphenylphosphonium Bromide. Into a 50 mL round-bottomed flask were placed 7-bromoheptanoic acid (1.0 g, 4.8 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) in 20 mL of toluene. The mixture was refluxed for 24 h, after which it was cooled to room temperature and the toluene was removed in vacuo. The product was washed several times with diethyl ether, affording (6-carboxyhexyl)triphenylphosphonium bromide (1.9 g, 86% yield) as a white solid.

Methyl 17-Methyl-7(*Z*)-octadecenoate. To 20 mL of a THF/DMSO (2:1) stirred solution of previously dried (6-carboxyhexyl)triphenylphosphonium bromide (0.05 g, 0.11 mmol) was added dropwise *n*-BuLi (2.5 M, 3.4 mmol) at 0 °C. The resulting mixture was stirred for 30 min at room temperature. Then, 10-methylundecanal (0.020 g, 0.11 mmol) in 1 mL of THF was added dropwise. After 2 h, the mixture was poured into ice and the solution was acidified with 1 M HCl. The acidic solution was extracted with diethyl ether (2 × 20 mL), and the organic layer was washed with H_2O (2 × 20 mL), dried over $MgSO_4$, and filtered. After rotoevaporation of the solvent 0.030 g of a yellow oil (88% yield) was obtained as a 9:1 *Z*/*E* mixture, which were characterized as the methyl esters after refluxing the acids in 1 M HCl (MeOH) for 4 h. The spectral data for the *Z* isomer follows: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.34 (2H, m, H-7, H-8), 3.66 (3H, s, $-OCH_3$), 2.30 (2H, t, J = 7.6 Hz, H-2), 2.01 (4H, m, H-6, H-9), 1.65 (2H, m, H-3), 1.53 (1H, m, H-17), 1.35−1.25 (16H, m, $-CH_2$), 1.15 (2H, m, H-16), 0.86 (6H, d, J = 6.6 Hz, H-18, Me-17); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 174.3 (s, C-1), 130.2 (d, C-8), 129.5 (d, C-7), 51.4 (q, $-OCH_3$), 39.0 (t, C-16), 34.0 (t, C-2), 29.9 (t), 29.74 (t), 29.68 (t), 29.5 (t), 29.35 (t), 29.32 (t), 28.8 (t), 27.4 (t), 27.2 (t), 27.0 (t), 27.9 (d, C-17), 24.8 (t), 22.6 (q, C-18, Me-19); ECL = 18.33, GC−MS (70 eV) *m*/*z* 310 $[M]^+$ (3), 279 (7), 278 (14), 260 (1), 255 (5), 249 (1), 236 (7), 221 (1), 208 (1), 194 (4), 180 (2), 166 (2), 152 (4), 141 (6), 138 (5), 137 (7), 128 (3), 123 (12), 111 (15), 110 (15), 101 (6), 97 (33), 96 (35), 95 (27), 87 (33), 84 (41), 81 (32), 79 (12), 74 (56), 69 (58), 67 (44), 57 (43), 55 (100); HREIMS *m*/*z* 310.2869 (calcd for $C_{20}H_{38}O_2$, 310.2872).

Methyl 17-methyl-7,8-bis(methylthio)octadecanoate: GC−MS (70 eV) *m*/*z* 404 $[M]^+$ (11), 216 (10), 215 (79), 207 (16), 190 (8), 189 (62), 158 (10), 157 (93), 140 (30), 121 (3), 115 (4), 111 (9), 101 (3), 97 (24), 95 (26), 87 (27), 85 (12), 83 (32), 81 (72), 79 (19), 74 (22), 69 (56), 67 (49), 61 (84), 59 (23), 57 (35), 55 (100).

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