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Toward new biosilicones: hydrosilylation of fish oil unsaturated fatty acid esters

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Hydrosilylation of fatty acid methyl esters (FAMEs) were efficiently catalyzed by Speier's and Wilkinson's catalysts in the case of vinylic acid esters, but less efficiently in the case of non-vinylic ones, which gave non-regiospecific additions. In the latter case, initiation by radicals led to regiospecific reactions for oleic esters (C10-silylation). This regiospecificity can be attributed to the higher stability of the C10-silylated adduct and of the corresponding radical intermediate. Only regioselective addition was observed for linoleic esters (C13-silylation $\approx 70\%$, C10 $\approx 20\%$, C9 $\approx 10\%$). Molecular modeling was used to examine the stability of the isomeric products and radicals. The new concept of radical initiation sequence has been successfully applied to FAMEs and then was extended to crude fish oil. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: hydrosilylation; fatty acid esters; fish oil; radical initiation sequence; regiospecific addition; molecular modeling

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1 INTRODUCTION

The aim of this work was to prepare starting materials for the synthesis of new biocompatible silicones from fish oil. These new biopolymers could lead to value-added products from crude fish oil, a by-product in the industrial preparation of fish meal worldwide.

Though the hydrosilylation of olefins has been widely studied,[1–6] only a few studies of fatty acid esters have been reported.[7–17] These interesting studies did not include complete analytical details of the compounds synthesized, and did not examine the regioselectivity of the reactions. Therefore, we decided to complete and extend these studies to fatty acid methyl esters (FAMEs) and crude fish oil.

2 EXPERIMENTAL

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or Carius tubes and dry solvents. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AC 80 (^{1}H, 80 MHz) and AC 200 (^{13}C in the sequence Jmod, 50.3 MHz) spectrometers. Mass and gas chromatography (GC) – mass spectra were measured with a Hewlett Packard HP5989 in electron impact (EI) mode (70 eV) or a Rybermag R10-10 spectrometer operating in EI mode, by chemical desorption (DCi, CH_4) or electrospray techniques. Infrared spectra were recorded with a Perkin Elmer 1600 FT spectrometer. Gel permeation chromatograph (GPC) analyses were done on a Hewlett Packard 5890 ser.II, column SE30. Elemental analyses were done by the Centre de Microanalyses de l'Ecole Nationale Supérieure de Chimie de Toulouse. Molecular modeling was performed with Insight II and Discover 95 modules from Biosym/Molecular Simulations (Force Field esff) System 95.0.9685, (Scranton Road, San Diego, CA, USA).

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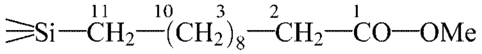
An average molecular unsaturation of 1.52 (local commercial fish oil and subsequent FAME) was calculated from ^{1}H NMR integration of ethylenic signals relative to the methylene group α to carbonyl.

The radical initiation sequence (RIS) was performed with a mixture of radical initiators: AIBN (half-life time $t_{1/2}$: 2 h, 80 °C); Ph—COO—O^{t}Bu ($t_{1/2}$: 1 h, 125 °C); $^{t}Bu_2O_2$ ($t_{1/2}$: 6 h, 130 °C) in a programmed range of temperature from 60 °C to 150–200 °C (24 h).

2.1 Hydrosilylation of undec-10-enoic acid methyl ester

Compounds R_2ClSiH (R = Me, Ph) were reacted with the ester in the presence of Speier's catalyst as described by Saghian and Gertner.[16] RCl_2SiH (R = Me, Ph) and Cl_3SiH were reacted with AIBN in a Carius tube heated to 120 °C. All the adducts obtained were isolated by distillation and identified (except for R = Ph) by GC–Mass Spectrometry (MS) analysis, by NMR data and by comparison with literature data.[16]



$$\geqslant \mathrm{Si}—\overset{11}{\mathrm{CH_2}}—\overset{10}{(\mathrm{CH_2})_8}—\overset{3}{}\overset{2}{\mathrm{CH_2}}—\overset{1}{\mathrm{CO}}—\mathrm{OMe}$$

Formula 1

2.1.1 Trichlorosilylmethylundecanoate (yield: 95%)

B.p.: 110 °C/0.05 mmHg. ^{1}H NMR ($CDCl_3$), δ: 3.64 (s, 3H, OMe); 2.28 (t, $^{3}J = 7.3$ Hz, 2H, H2); 1.1–1.8 (m, 18H, H3 to H11). ^{13}C NMR ($CDCl_3$), δ: 174.35 (C1); 51.47 (OMe); 22.27, 24.33, 24.96, 28.99, 29.14, 29.22, 29.28, 29.37, 31.81, 34.12 (C2 to C11). ^{29}Si NMR ($CDCl_3$), δ: 13.06. IR, ν: 1740 (CO); 1194 (C—O—C). MS (EI), *m/z*: 334 (M^{+}) 12%, 303 (M − OMe) 8%, 199 (M − Cl_3Si) 4%, 74 [$(O{\equiv}C—O—CH_3)^{+}$] 100%. Anal. Found: C, 43.80; H, 7.02; Cl, 31.52. Calc. for ($C_{12}H_{23}Cl_3O_2Si$): C, 43.19; H, 6.95; Cl, 31.87%.

2.1.2 Methyldichlorosilylmethylundecanoate (yield: 80%)

B.p.: 117 °C/0.05 mmHg. ^{1}H NMR ($CDCl_3$), δ: 3.62 (s, 3H, OMe); 2.27 (t, $^{3}J = 7.3$ Hz, 2H, H2); 1.01–1.67 (m, 16H, H3 to H10); 0.86 (t, $^{3}J = 7$ Hz, 2H, H11); 0.77 (s, 3H, SiMe). ^{13}C NMR ($CDCl_3$), δ: 174.28 (C1); 51.47 (OMe); 21.62, 22.41, 24.95, 29.13, 29.22, 29.35, 29.40, 32.35, 34.09 (C2 to C11), 5.20 (SiMe). ^{29}Si NMR ($CDCl_3$), δ: 32.80. IR, ν: 1728 (CO); 1172 (C—O—C); 1261 (SiMe). MS (EI), *m/z*: 312 (M^{+}) 9%, 281 (M − OMe) 6%, 199 (M − $MeCl_2Si$) 7%, 74 [$(O{\equiv}C—O—CH_3)^{+}$] 100%. Anal. Found: C, 50.27; H, 8.70. Calc. for ($C_{13}H_{26}Cl_2O_2Si$): C, 49.80; H, 8.36%.

2.1.3 Dimethylchlorosilylmethylundecanoate (yield: 92%)

B.p.: 102 °C/0.05 mmHg. ^{1}H NMR ($CDCl_3$), δ: 3.58 (s, 3H, OMe); 2.23 (t, $^{3}J = 7.2$ Hz, 2H, H2); 1.08–1.64 (m, 16H, H3 to H10); 0.75 (t, $^{3}J = 7$ Hz, 2H, H11); 0.33 (s, 6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$), δ: 174.28 (C1); 51.01 (OMe); 22.86, 24.79, 29.11, 29.33, 32.84, 33.81 (C2 to C10), 18.84 (C11), 1.47 (Me_2Si). ^{29}Si NMR ($CDCl_3$), δ: 31.24. IR, ν: 1725 (CO); 1169 (C—O—C); 1259 (SiMe). MS (EI), *m/z*: 292 (M^{+}) 4%, 277 (M − Me) 22%, 261 (M − OMe) 7%, 199 (M − $MeCl_2Si$) 5%, 74 [$(O{\equiv}C—O—CH_3)^{+}$] 100%. Anal. Found: C, 59.19; H, 10.54. Calc. for ($C_{14}H_{29}ClO_2Si$): C, 58.40; H, 9.98%.

2.1.4 Phenyldichlorosilylmethylundecanoate (yield: 65%)

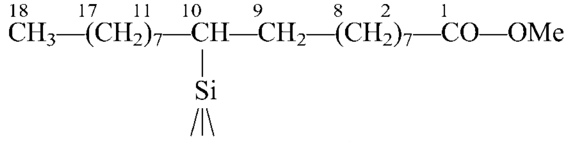
B.p.: 140 °C/0.05 mmHg. ^{1}H NMR ($CDCl_3$), δ: 3.62 (s, 3H, OMe); 2.27 (t, $^{3}J = 6.5$ Hz, 2H, H2); 1.25–1.66 (m, 16H, H3 to H10); 0.86 (t, $^{3}J = 7$ Hz, 2H, H11); 7.10–7.73 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 174.10 (C1); 51.35 (OMe); 22.51, 24.98, 29.08, 29.17, 29.27, 29.39, 29.42, 32.41, 34.07 (C2 to C10), 20.73 (C11), 133.37, 132.75, 131.58, 128.36 (C_6H_5). ^{29}Si NMR ($CDCl_3$), δ: 19.22. IR, ν: 1728 (CO); 1178 (C—O—C); 1430 (SiPh). MS (EI), *m/z*: 374 (M^{+}) 3%, 343 (M − OMe) 10%, 339 (M − Cl) 24%, 199 (M − $PhCl_2Si$) 41%, 74 [$(O{\equiv}C—O—CH_3)^{+}$] 100%. Anal. Found: C, 58.43; H,7.58. Calc. for ($C_{18}H_{28}Cl_2O_2Si$): C, 57.58; H, 7.52%.

2.1.5 Diphenylchlorosilylmethylundecanoate (yield: 92%)

B.p.: 190 °C/0.05 mmHg. ^{1}H NMR ($CDCl_3$), δ: 3.69 (s, 3H, OMe); 2.34 (t, $^{3}J = 7$ Hz, 2H, H2); 1.32–1.46 (m, 18H, H3 to H11); 7.34–7.75 (m, 10H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 174.35 (C1); 51.49 (OMe); 23.04, 25.06, 29.23, 29.32, 29.51, 33.11, 34.19 (C2 to C10), 16.60 (C11), 134.30, 133.97, 130.55, 128.19 (C_6H_5). ^{29}Si NMR ($CDCl_3$), δ: 10.73. IR, ν: 1728 (CO); 1177 (C—O—C); 1428 (SiPh). MS (EI), *m/z*: 416 (M^{+}) 3%, 339 (M − Ph) 19%, 217 [$M - (CH_2)_{10}COOMe$] 100%, 199 (M − Ph_2ClSi) 6%, 74 [$(O{\equiv}C—O—CH_3)^{+}$] 16%. Anal. Found: C, 68.43; H, 7.52; Cl, 8.93. Calc. for ($C_{24}H_{33}ClO_2Si$): C, 69.12; H, 7.98; Cl, 8.50%.

2.2 Hydrosilylation of methyloleate

A mixture of methyloleate (1.20 g; 4 mmol) and hydrosilane (6 mmol) with catalytic amounts of AIBN and $^tBu_2O_2$ was heated in a Carius tube from 20 to 150 °C (45 min) then kept for 24 h at 150 °C. Distillation gave the corresponding 10-silylated stearate.



$$\overset{18}{\mathrm{CH_3}}-\overset{17\quad 11}{\mathrm{(CH_2)_7}}-\underset{\substack{|\\ \mathrm{Si}\\ /|\backslash}}{\overset{10}{\mathrm{CH}}}-\overset{9}{\mathrm{CH_2}}-\overset{8\quad 2}{\mathrm{(CH_2)_7}}-\overset{1}{\mathrm{CO}}-\mathrm{OMe}$$

Formula 2

2.2.1 10-Trichlorosilylmethylstearate (yield: 71%)

B.p.: 165 °C/0.05 mmHg. ^1H NMR ($CDCl_3$), δ: 3.64 (s, 3H, OMe); 2.28 (t, $^3J = 7.5$ Hz, 2H, H2); 1.26–1.81 (m, 29H, H3 to H17), 0.86 (t, $^3J = 6.5$ Hz, 3H, H18). ^{13}C NMR ($CDCl_3$), δ: 174.25 (C1); 51.44 (OMe); 33.57 (C10); 22.68, 24.92, 28.08, 29.00, 29.10, 29.17, 29.32, 29.50, 29.56, 29.64, 29.70, 31.88, 34.08 (C2 to C9 and C11 to C17); 14.11 (C18). ^{29}Si NMR ($CDCl_3$), δ: 14.42. IR, ν: 1741 (CO); 1171 (C—O—C). MS (EI), *m/z*: 432 (M^+) 9%, 401 (M – OMe) 6%, 297 ($M - Cl_3Si$) 100%. The classical fragmentation of the carbon skeleton (C18–C10) gave the trichlorosilylated last fragment [($Cl_3Si(CH_2)_9COOMe$, *m/z*: 320], which is characteristic of a C10 silylation. Anal. Found: C, 52.87; H, 8.32; Cl, 24.13. Calc. for ($C_{19}H_{37}Cl_3O_2Si$): C, 53.02; H, 8.60; Cl, 24.42%.

2.2.2 10-Phenyldichlorosilylmethylstearate (yield: 94%)

B.p.: 180 °C/0.05 mmHg. ^1H NMR ($CDCl_3$), δ: 3.65 (s, 3H, OMe); 2.29 (t, $^3J = 7.5$ Hz, 2H, H2); 1.24–1.61 (m, 29H, H3 to H17), 0.88 (t, $^3J = 6$ Hz, 3H, H18); 7.24–7.89 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 174.61 (C1); 51.50 (OMe); 22.75, 24.95, 28.34, 28.56, 29.20, 29.39, 29.53, 29.60, 29.66, 29.74, 30.12, 31.96, 34.10 (C2 to C9 and C11 to C17); 13.94 (C18); 127.90, 128.25, 132.66, 133.95 (C_6H_5). ^{29}Si NMR ($CDCl_3$), δ: 20.00. IR, ν: 1740 (CO); 1197 (C—O—C). MS (EI), *m/z*: 472 (M^+) 5%, 441 (M – OMe) 4%. The elimination of C_6H_5 (*m/z*:394, 24%) followed by fragmentation of the carbon skeleton (C18–C10) occurred principally, leading to the dichlorosilylated last fragment [$Cl_2Si{=}C(CH_2)_9COOMe$ (Y), *m/z*: 281, 14%], which is characteristic of a C10 silylation. The structure of this fragment was verified from its own fragmentation process observed by the mass/mass electrospray technique: 282 (Y – H); 210 ($YH^+ - CH_2COOMe$); 167 ($YH^+ - (CH_2)_4COOMe$); 112 ($YH^+ - CH_2{=}CH(CH_2)_6COOMe$). Anal. Found: C, 62.73; H, 8.81; Cl, 15.25. Calc. for ($C_{25}H_{42}Cl_2O_2Si$): C, 63.40; H, 8.94; Cl, 14.97%.

With the purpose of comparing the regioselectivity of these radical-initiated and Platinum-catalyzed hydrosilylations, we reproduced the Speier-catalyzed hydrosilylation of methyloleate as described by Saghian and Gertner.[16] We observed by mass analyses of the reaction product that the carbon chain fragmentation process led to two different silylated last fragments (*m/z*: 281 and 267 corresponding respectively to the C10 and C9 silylated compounds), thus confirming their hypothesis of two isomeric adducts (C9, C10).

2.2.3 10-Diphenylchlorosilylmethylstearate (yield: 68%)

A mixture of Ph_2ClSiH (0.88 g; 4.04 mmol) and methyloleate (0.61 g; 2.02 mmol) was heated in a Carius tube under RIS conditions (highest temperature: 140 °C, 60 h). Distillation led to an almost pure adduct.

B.p.: 195–200 °C/0.05 mmHg. ^1H NMR ($CDCl_3$), δ: 3.63 (s, 3H, OMe); 2.28 (t, $^3J = 7.5$ Hz, 2H, H2); 1.26–1.73 (m, 29H, H3 to H17), 0.85 (t, $^3J = 7$ Hz, 3H, H18); 7.37–7.68 (m, 10H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 174.40 (C1); 51.50 (OMe); 26.10 (C10), 22.70, 25.0, 27.30, 29.20, 29.41, 29.60, 29.82, 31.90, 32.72, 34.21 (C2 to C9 and C11 to C17); 14.20 (C18); 127.78, 128.01, 134.85, 134.99 (C_6H_5). ^{29}Si NMR ($CDCl_3$), δ: 11.94. IR, ν: 1740 (CO); 1195 (C—O—C). MS (EI), *m/z*: 514 (M^+) 2%, 483 (M – OMe) 3%; 436 ($M - C_6H_6$) 12%, 296 ($M - Ph_2ClSi$) 16%, 217 (Ph_2ClSi) 100%.

2.2.4 10-Methyldichlorosilylmethylstearate (yield: 78%)

B.p.: 162 °C/0.05 mmHg. ^1H NMR ($CDCl_3$), δ: 3.62 (s, 3H, OMe); 2.29 (t, $^3J = 7.5$ Hz, 2H, H2); 1.25–1.52 (m, 29H, H3 to H17); 0.80 (t, $^3J = 5$ Hz, 3H, H18); 0.72 (s, 3H, MeSi). ^{13}C NMR ($CDCl_3$), δ: 174.19 (C1); 51.36 (OMe); 30.57 (C10); 22.69, 23.40, 24.94, 27.16, 27.20, 28.23, 28.49, 28.94, 29.13, 29.34, 29.55, 29.67, 29.77, 31.92, 32.57, 32.61, 34.05 (C2 to C9 and C11 to C17); 14.10 (C18); 4.85 (MeSi). ^{29}Si NMR ($CDCl_3$), δ: –9.92. IR, ν: 1740 (CO); 1197 (C—O—C). MS (EI), *m/z*: 410 (M^+) 11%, 395 (M – Me) 3%, 379 (M – OMe) 5%, 297 100%. The fragmentation of the carbon

Table 1 Hydrosilylation of undec-10-enoic acid methyl ester

	Hydrosilylation (%)				
	20–130 °C	H_2PtCl_6 (24 h, 20 °C)	H_2PtCl_6 (24 h, 50 °C)	$Rh(Cl)(PPh_3)_3$ (24 h, 120 °C)	AIBN
Me_2ClSiH	75 (48 h)	47	92	87	0 (24 h, 80 °C)
Ph_2ClSiH	2–3 (48 h)	8–10	~100	62	8–10 (24 h, 120 °C)
$MeCl_2SiH$	~100 (48 h)	3–5	~100	72	80 (24 h, 80 °C)
$PhCl_2SiH$	0 (24 h)	0	~100	82	60–65 (24 h, 120 °C)
Cl_3SiH	13 (24 h)	~5	~100	65	95 (72 h, 120 °C)

chain (C18–C10) afforded the dichlorosilylated last fragment [$MeCl_2Si(CH_2)_8COOMe$, *m/z*: 297] 100%, which is characteristic of a C10 silylation. Anal. Found: C, 58.17; H, 9.72; Cl, 16.84. Calc. for ($C_{20}H_{40}Cl_2O_2Si$): C, 58.38; H, 9.80; Cl, 17.23%.

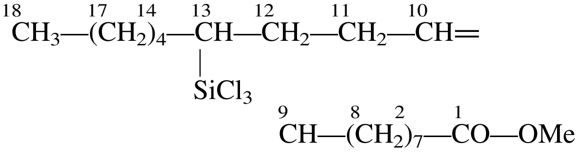
2.3 Hydrosilylation of methyllinoleate

2.3.1 Trichlorosilyl adducts

Under the same experimental conditions used in the case of methyloleate, but with a slightly different heating program (120 °C, 12 h, followed by 180 °C, 12 h); 0.97 g of adduct (57% yield) was isolated by distillation.

B.p.: 160–165 °C/0.05 mmHg. ^{1}H NMR ($CDCl_3$), δ: 3.63 (s, 3H, OMe); 2.28 (t, $^3J = 7.5$ Hz, 2H, H2); 1.99 (td, $^3J = 7.5$ Hz, 4H, H8 or H14 and H11); 1.26–1.81 (m, 20H, H3 to H17 and CHSi), 0.87 (t, $^3J = 6.5$ Hz, 3H, H18). IR, *v*: 1741 (CO); 1171 (C—O—C). MS (EI), *m/z*: 430 (M^+) 2%, 295 ($M - Cl_3Si$) 5%. The characteristic fragmentation of unsaturated FAME leading to a loss of MeOH was also observed: (M – MeOH, *m/z*: 398, 6%). This fragmentation was followed by the classical carbon chain fragmentation (C18–C9). This process gave three silylated fragments that are characteristic of three isomeric hydrosilylated compounds: *m/z*: 327 (C13 silylated); 287 (C10 silylated); 273 (C9 silylated).

2.3.2 C12–C13 hydrosilylation (~70%)

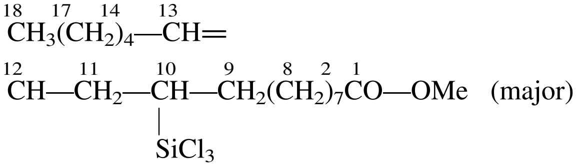


$$\overset{18}{\mathrm{CH_3}}-(\overset{17\ \ 14}{\mathrm{CH_2}})_4-\underset{\mathrm{SiCl_3}}{\overset{13}{\mathrm{CH}}}-\overset{12}{\mathrm{CH_2}}-\overset{11}{\mathrm{CH_2}}-\overset{10}{\mathrm{CH}}=\overset{9}{\mathrm{CH}}-(\overset{8\ \ 2}{\mathrm{CH_2}})_7-\overset{1}{\mathrm{CO}}-\mathrm{OMe}$$

Formula 3

^{13}C NMR ($CDCl_3$), δ: 173.94 (C1); 130.06, 129.90 (C9 and C10); 51.23 (OMe); 22.37 to 33.98 (C2 to C8 and C11, C12, C14 to C17); 27.77 (C13); 14.01 (C18).

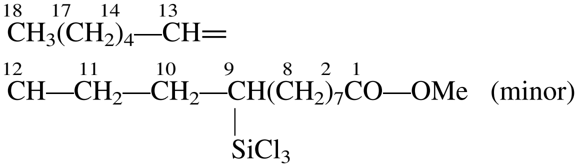
2.3.3 C9–C10 hydrosilylation (~30%)



$$\overset{18}{\mathrm{CH_3}}(\overset{17\ \ 14}{\mathrm{CH_2}})_4-\overset{13}{\mathrm{CH}}=\overset{12}{\mathrm{CH}}-\overset{11}{\mathrm{CH_2}}-\underset{\mathrm{SiCl_3}}{\overset{10}{\mathrm{CH}}}-\overset{9}{\mathrm{CH_2}}(\overset{8\ \ 2}{\mathrm{CH_2}})_7\overset{1}{\mathrm{CO}}-\mathrm{OMe}\quad\text{(major)}$$

Formula 4

^{13}C NMR ($CDCl_3$), δ: 173.94 (C1); 128.00, 128.01 (C12 and C13); 51.23 (OMe); 22.37 to 33.98 (C2 to C9 and C11, C14 to C17); 33.37 (C10); 14.01 (C18).



$$\overset{18}{\mathrm{CH_3}}(\overset{17\ \ 14}{\mathrm{CH_2}})_4-\overset{13}{\mathrm{CH}}=\overset{12}{\mathrm{CH}}-\overset{11}{\mathrm{CH_2}}-\overset{10}{\mathrm{CH_2}}-\underset{\mathrm{SiCl_3}}{\overset{9}{\mathrm{CH}}}(\overset{8\ \ 2}{\mathrm{CH_2}})_7\overset{1}{\mathrm{CO}}-\mathrm{OMe}\quad\text{(minor)}$$

Formula 5

^{13}C NMR ($CDCl_3$), δ: 173.94 (C1); 128.80, 128.70 (C12 and C13); 51.23 (OMe); 22.37 to 33.98 (C2 to C8 and C10, C11, C14 to C17); 33.50 (C9); 14.01 (C18).

2.4 Hydrosilylation of FAMEs from fish oil

A mixture of 2 ml of FAMEs and Cl_3SiH (1.02 g; 7.4 mmol) was heated in a Carius tube under RIS conditions (highest temperature 150 °C). GPC analysis confirmed the hydrosilylation of most of the unsaturated FAMEs. The disappearance of the initial unsaturated ^{1}H NMR signal was about 60%,

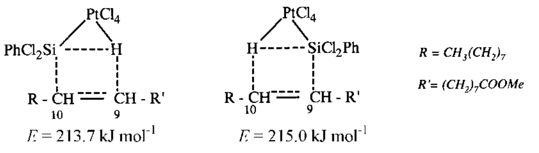


Figure 1 Molecular modeling of platinum-catalyzed reaction intermediates.[18]

corresponding to a yield of about 90% in monohydrosilylation as evidenced by the average unsaturation number (1.52). Cl_3SiCH ^{13}C NMR signals (δ) were about 25 ppm (hydrosilylation of the farthest unsaturated site from the ester function), and about 30 ppm (hydrosilylation of the nearest site to the ester function), confirming hydrosilylation of the corresponding FAME.

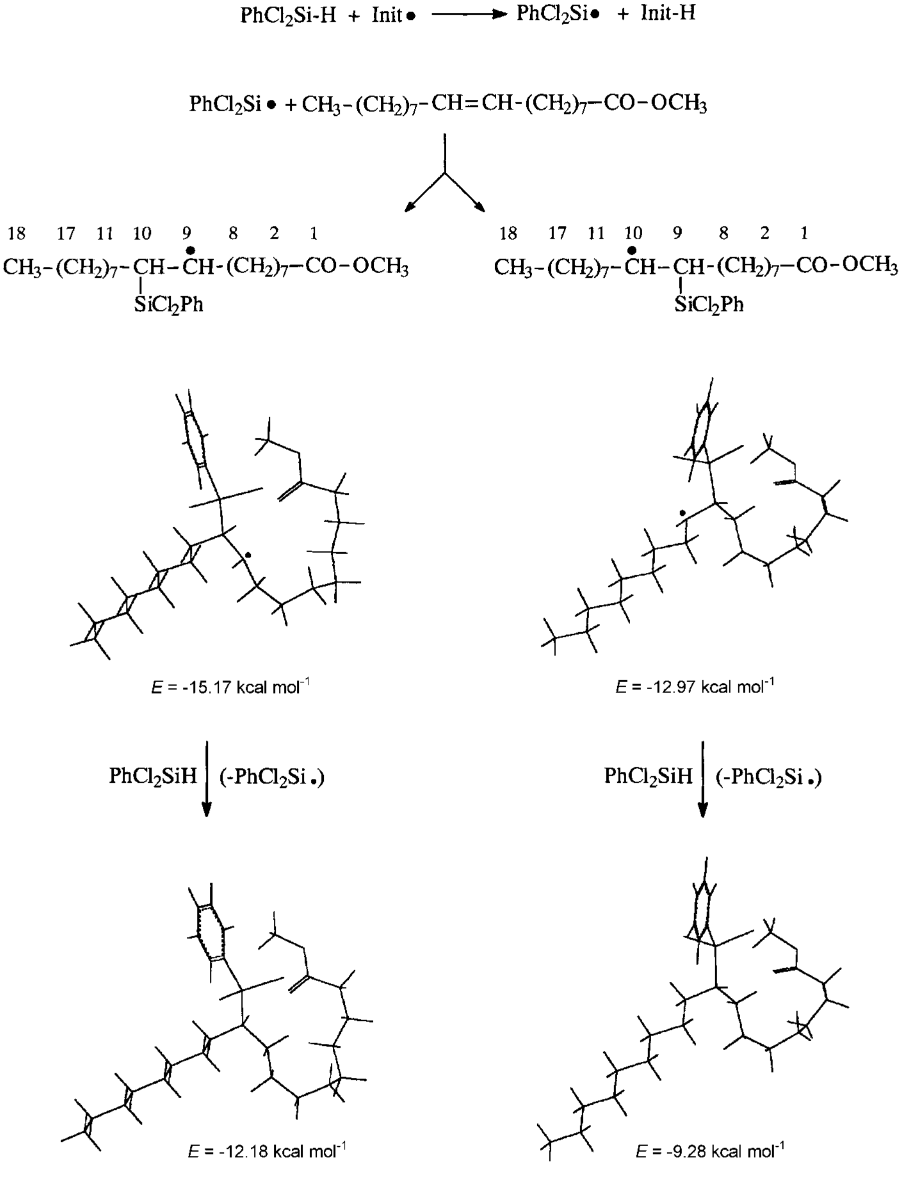


Figure 2 Mechanism and molecular modeling.

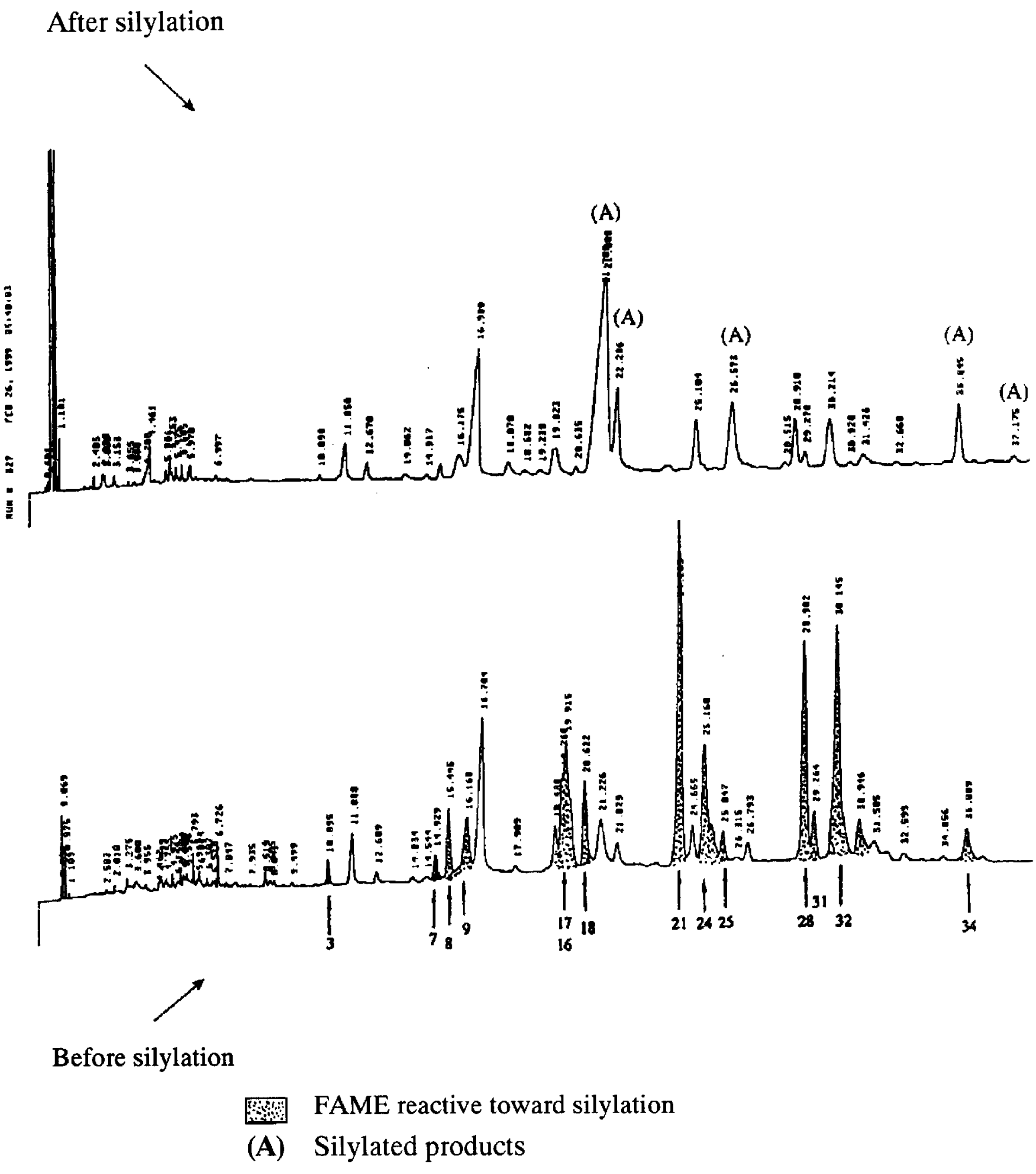


Figure 3 GC analysis of the hydrosilylation of the mixture of FAMEs from fish oil. Unsaturated fatty acids (*carbon number*): 3 (*14*); 7, 8, 9 (*16*); 16, 17, 18 (*18*); 21, 24, 25 (*20*); 28 (*21*); 31, 32 (*22*); 34 (*24*). Others are saturated FAME.

2.5 Hydrosilylation of fish oil

2.5.1 With Cl_3SiH

A mixture of fish oil (0.92 g) and Cl_3SiH (2 g; 14.8 mmol) was heated in a Carius tube under RIS conditions (highest temperature 150 °C). The yield of monohydrosilylation determined by ^1H NMR was about 90%.

^{1}H NMR ($CDCl_3$), δ: 5.30 (m, CH=CH and H—C—O); 4.19 (m, CH_2O); 2.77 [m, $CH_2(C{=}C)_2$], 2.27 (t, $^3J = 7.5$ Hz, CH_2—CO—); 1.95 (m, CH_2—C=C), 1.23–1.75 [s broad, $(CH_2)_n$]; 0.89 (t, $^3J = 7.5$ Hz, CH_3). ^{13}C NMR ($CDCl_3$), δ: 172.6–172.9 (CO); 68.8 (H—C—O); 61.9 (CH_2O); 128.7–130.8 (CH=CH); 22.7 to 34.1 [$(CH_2)_n$]; 23.3, 30.9, 31.3, 33.9 (CHSi); 14.1 (CH_3). IR, v: 1739 (CO, wide); 1147 (C—O—C, strong).

2.5.2 With $MeCl_2SiH$

From $MeCl_2SiH$ (1.1 g; 9.6 mmol) and fish oil (1 g) heated under RIS conditions with a highest temperature of 150 °C, only 20% of monohydrosilylation was observed, whereas at 200 °C the yield of monohydrosilylation was 84%.

^{1}H NMR ($CDCl_3$), δ: 5.34 (m, CH=CH and H—C—O); 4.20 (m, CH_2O); 2.83 [m, $CH_2(C{=}C)_2$], 2.29 (t, $^3J = 7.5$ Hz, CH_2—CO—); 1.96 (m, CH_2—C=C), 1.23–1.52 [s broad, $(CH_2)_n$]; 0.87 (t, $^3J = 7.5$ Hz, CH_3); 0.59 (s broad, CH_3Si). ^{13}C NMR ($CDCl_3$), δ: 172.4–172.9 (CO); 68.9 (H—C—O); 62.1 (CH_2O); 128.1–130.5 (CH=CH); 22.7 to 34.1 [$(CH_2)_n$]; 23.7, 31.5, 34.8 (CHSi); 14.2 (CH_3); 5.70 (MeSi). IR, v: 1739 (CO, wide); 1148 (C—O—C, strong); 1267 (SiMe).

2.5.3 With $PhCl_2SiH$

Following the same procedure described for Cl_3SiH (Section 2.5.1), using fish oil (0.57 g) and $PhCl_2SiH$ (0.95 g; 5.36 mmol), 90% of monohydrosilylated product was obtained.

^{1}H NMR ($CDCl_3$), δ: 5.37 (m, CH=CH and H—C—O); 4.26 (m, CH_2O); 2.85 [m, $CH_2(C{=}C)_2$], 2.33 (t, $^3J = 7.3$ Hz, CH_2—CO—); 1.96 (m, CH_2—C=C), 1.29–1.62 [s broad, $(CH_2)_n$]; 0.90 (t, $^3J = 7.5$ Hz, CH_3); 7.45–7.85 (m, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 173.3–172.5 (CO); 68.9 (H—C—O); 62.2 (CH_2O); 128.3–134.5 (CH=CH and C_6H_5); 22.8 to 34.1 [$(CH_2)_n$]; 23.7–31.5 (CHSi); 14.2 (CH_3). IR, v: 1745 (CO, wide); 1141 (C—O—C, strong); 1429 (SiPh).

3 RESULTS AND DISCUSSION

The addition of a series of silanes to undec-10-enoic acid methyl ester was investigated (Eqn [1] and Table 1). The comparison of these reactions shows a difference in the efficiency of the catalyst used. Hydrosilylation always occurs regiospecifically at the C11 atom.

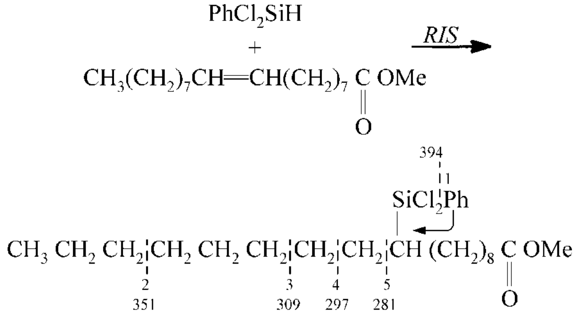
$$\equiv\!Si{-}H + CH_2{=}CH{-}(CH_2)_8COOMe \rightarrow \equiv\!Si(CH_2)_{10}COOMe \quad [1]$$

Although platinum catalysis was effective,[16] Wilkinson's catalyst is a good alternative when Speiers's catalyst causes thermally induced decomposition of silanes. Initiation by radicals was efficient mainly in the case of silanes in which the attractive effect of halogens lowers the hydride character of the reactive hydrogen.

In a spectroscopic study of the hydrosilylated undecanoic acid methyl ester synthesized previously by Saghian and Gertner,[16] the ^{13}C NMR analysis confirmed the silylation of C11. Mass spectra (EI) of all the adducts showed the molecular ion and the two fragmentation pathways characteristic of saturated FAMEs,[18] i.e. loss of the methoxy group and fragmentation of the carbon chain that begins by the expulsion of the silyl group (α-cleavage).

In the case of methyloleate the hydrosilylation occurred less efficiently with the platinum catalyst, leading, through a non-regiospecific mode, to a mixture of 9,10 silylated adducts.[16] Molecular modeling (see Section 2) of the two isomeric reaction intermediates according to the published structure[19] showed that they have almost the same stability (Fig. 1), accounting for the low regioselectivity.

On the other hand, with initiation by radicals the hydrosilylation of methyloleate occurred in high yield and was regiospecific. Only the C10 silylated adduct was formed, as is evident from the GC–MS analysis (Eqn [2]).



Successive fragmentations: [2]

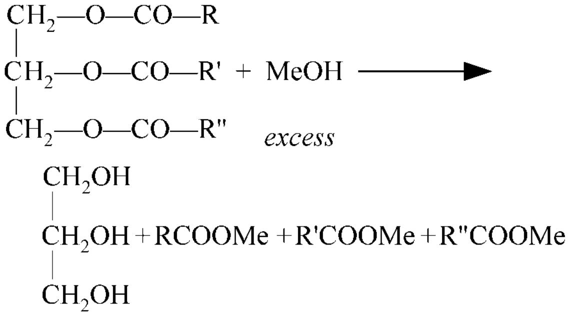
In the case of the phenyldichlorosilylated methylstearate, the molecular ion ($M^{+\cdot} = 472$), after an initial loss of C_6H_6, fragmentation (*1*), underwent the expected classical fragmentations (*2, 3, 4, 5*) (Eqn. [2]) of the hydrocarbon chain.[18] This process ended with the last typical dichlorosilylated ion fragment ($M^{+\cdot} = 281$) belonging to the C10-silylated compound. The structure of this silylated ion was confirmed by the mass/mass electrospray technique (see Section 2).

In the context of the radical mechanism (Fig. 2), the regiospecificity comes from the difference in the stability of the two possible isomeric radical intermediates. Their molecular modeling shows that the C10-silylated one is notably the most stable ($\Delta E = 2.2\,\mathrm{kcal\ mol^{-1}}$). This value is similar to the difference between tertiary, secondary and primary carbon-centered radicals, however, which induce high regioselective radical addition to olefins.[20–22] Molecular modeling also showed that the C10-silylated adduct is the most stable one (Fig. 2). The difference in the stability of the two isomeric adducts could be the result of an intramolecular complexation of the ester function on the silicon, and the longer the carbon chain the easier is the complexation.

Under the same conditions, methyllinoleate treated with trichlorosilane led to a mixture of hydrosilylated products resulting from two competitive regio-addition reactions. The major one resulted from addition at the C12=C13 bond (~70%) with a complete regiosilylation at the C13 atom. The minor and less regioselective one (~30%) was the result of the C9=C10 addition (Si—C10 ≈ 20%; Si—C9 ≈ 10%).

Identification of each isomer was achieved by ^{1}H and ^{13}C NMR using the methyloleate as a reference (see Section 2).

These results define the required experimental conditions that are necessary to obtain direct hydrosilylation of natural fatty acid esters from fish oil. A mixture of FAMEs was extracted from fish oil, using a transalkoxylation reaction (Eqn. [3]).[18]



$$\begin{array}{l} \mathrm{CH_2{-}O{-}CO{-}R} \\ | \\ \mathrm{CH_2{-}O{-}CO{-}R'} + \mathrm{MeOH} \longrightarrow \\ | \\ \mathrm{CH_2{-}O{-}CO{-}R''} \quad \textit{excess} \\ \quad \mathrm{CH_2OH} \\ \quad | \\ \quad \mathrm{CH_2OH + RCOOMe + R'COOMe + R''COOMe} \\ \quad | \\ \quad \mathrm{CH_2OH} \end{array}$$

R,R',R'' = saturated or unsaturated chains [3]

The FAMEs obtained were identified by GC–MS, and by comparison with literature data[23] and then reacted with trichlorosilane using the RIS. This technique allowed each unsaturated FAME to be hydrosilylated under the best conditions. About 60% of the ethylenic functions have been hydrosilylated, as evident from the ^{1}H NMR spectra. This result corresponds to a high yield in monohydrosilylation (~90%) of unsaturated FAMEs, since several FAMEs are polyunsaturated (the average number of molecular unsaturation is about 1.5). This result was confirmed by GC analysis of the reaction mixture, which showed that the FAMEs belonging to unsaturated C16, C18 and C20 fatty acids completely disappeared, and that more than 80% of the others were transformed (Fig. 3).

Hydrosilylation was also obvious in ^{13}C NMR Jmod. spectra from the signal of the carbon α to silicon. The lower-field signal belongs to the hydrosilylation of the ethylenic function, which is the less distant from the ester function. Under the same RIS conditions, monohydrosilylation of crude dried fish oil also gave high yields (Cl_3SiH 90%, $PhCl_2SiH$ 90%, $MeCl_2SiH$ 85%). ^{1}H and ^{13}C NMR analyses showed the characteristic signals of the glyceryl skeleton and the characteristic δ^{13}CSi.

These last results open the way to direct synthesis of materials for new organometallic biosilicones from crude fish oil and represent a fundamental work study that may give rise to industrial applications.

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