

Electronic Supplementary Informations

GC/MS analyses were carried out on a Shimadzu GCMS-QP2010S equipped with a HP-5B column (30 m, 0.25 mm, 0.25 μ m).

MS/ESI analyses were done on an Agilent 6210 Time-of-Flight LC/MS with a scan rate of 40 s⁻¹.

Synthesis of starting materials

*threo-9,10-dihydroxystearic acid*¹

A mixture of 250 mL tert-BuOH and 105 mL 30% H₂O₂ was placed in a three-necked flask equipped with a stirrer, a thermometer and a reflux condenser. 69.9 g of anhydrous MgSO₄ was added in portions under stirring to this mixture at a temperature of 30 °C. The stirring was continued slurry was filtrated after 4 h, the filtrate was used for the subsequent oxidation. 0.71 g (2.79 mmol) methyltrioxorhenium was dissolved in 210 mL of this oxidation solution and 99.0 g (315.44 mmol) of oleic acid (90%) were added at 40 °C. After complete addition, the reaction mixture was stirred for 48 h at 40 °C. The progress of the reaction was controlled by TLC. Then the spare amount of H₂O₂ was decomposed by Na₂SO₃, tert-BuOH was removed and the residue was diluted with 500 mL n-hexane. The mixture was stored in the refridgerator overnight, the precipitated white solid was filtered off and washed with petroleum ether. Then it was dried and purified by column chromatography (gradient ethyl acetate/hexane 1:1, MeOH).

m.p.: 94 °C; MS-ESI: m/z 315.25 [M-H]⁻; ¹H-NMR (300 MHz, DMSO-d₆): 0.84 (t, *J* = 6.9 Hz, CH₃, 3H), 1.10–1.56 (m, CH₂, 26H), 2.17 (t, *J* = 7.3 Hz, CH₂, 2H), 3.09–3.25 (m, CH, 2H), 4.12 (br s, OH, 2H), 11.94 (br s, COOH, 1H) ppm; ¹³C-NMR (300 MHz, DMSO-d₆): δ = 14.0 (CH₃), 22.1 (CH₂), 24.5 (CH₂), 25.7 (2xCH₂), 28.6 (CH₂), 28.8 (CH₂), 28.9 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 31.4 (CH₂), 32.3 (2xCH₂), 33.7 (CH₂), 73.1 (2xCH), 174.5 (COOH) ppm; C₁₈H₃₆O₄ (316.48): calculated: C 68.31%, H 11.47%; found: C 68.37%, H 11.49%.

*erythro-9,10-dihydroxystearic acid*²

1.0 g (3.54 mmol) oleic acid and 1.0 g (25.0 mmol) NaOH were dissolved in 100 ml of deionized water under slight heating (ca. 40 °C). Then the solution was diluted with 800 mL of cold water (4°C). 80 mL of a 1w% solution of KMnO₄ was added and the mixture was intensely stirred for 5 min. The reaction solution was decolourized with a saturated NaHSO₃ solution and 30 mL of concentrated HCl was added. The precipitated white solid was removed, dried and washed with petroleum ether. Finally, the crude product was purified by column chromatography (ethyl acetate/hexane 1:1).

m.p.: 125-128 °C; ¹H-NMR (300 MHz, DMSO-d₆): 0.85 (t, *J* = 6.9 Hz, CH₃, 3H), 1.09–1.57 (m, CH₂, 26H), 2.16 (t, *J* = 7.3 Hz, CH₂, 2H), 2.92–3.18 (m, CH, 2H) ppm; ¹³C-NMR (300 MHz, DMSO-d₆): δ = 14.0 (CH₃), 22.1 (2xCH₂), 24.6 (CH₂), 25.4 (CH₂), 25.5 (CH₂), 28.6 (CH₂), 28.7 (CH₂), 28.9 (CH₂), 29.1 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 31.3 (CH₂), 32.6 (CH₂), 33.7 (CH₂), 73.8 (2xCH), 174.6 (COOH) ppm; C₁₈H₃₆O₄ (316.48): calculated: C 68.31%, H 11.47%; found: C 68.35%, H 11.23%.

*9(10)-hydroxy-10(9)-oxostearic acid*³

5.64 g (0.02 mol) oleic acid, placed in a beaker equipped with a pH electrode, a thermometer and a stirrer, was dissolved in a solution of 131.0 g (0.02 mol) KOH (86%) in 60 mL of water. After cooling down the mixture to 10 °C, a solution of 4.20 g (26.60 mmol) KMnO₄ in 200 mL deionized water was added rapidly. The temperature of the reaction solution should not exceed 10–15 °C. The pH value was kept constant at pH 9-9.5 during the addition using a 1.5 N H₂SO₄ solution. The stirring was continued after the completion of addition for 15 min. Then the reaction was stopped and the mixture was decolourized by addition of a saturated NaHSO₃ solution. A pH value of 1-2 was set by a 6N HCl solution. The formed precipitate was filtered off, washed several times with deionized water and dried at 40 °C in a drying oven. The final purification was carried out by column chromatography (ethyl acetate/hexane 1:1).

m.p.: 42-44 °C; MS-ESI: m/z 313.24 [M-H]⁻, ¹H-NMR (300 MHz, CDCl₃): 0.88 (t, *J* = 7.0 Hz, CH₃, 3H), 1.19–1.89 (m, CH₂, 24H), 2.34 (t, *J* = 7.5 Hz, CH₂, 2H), 2.40–2.53 (m, CH₂, 2H), 4.41–4.23 (m, CH, 1H) ppm; ¹³C-NMR (300 MHz, DMSO-d₆): δ = 13.9 (CH₃), 22.1 (2xCH₂), 22.8 (2xCH₂), 24.5 (2xCH₂), 24.7 (CH₂), 28.5 (2xCH₂), 28.6 (2xCH₂), 28.7 (CH₂), 28.8 (CH₂), 28.9 (3xCH₂), 31.3 (CH₂), 33.1 (CH₂), 33.7 (CH₂), 36.9 (CH₂), 76.1 (CH), 174.4 (COOH), 213.8 (C=O) ppm; C₁₈H₃₄O₄ (314.46): calculated: C 68.75%, H 10.90%; found: C 68.65%, H 11.09%.

*9,10-dioxostearic acid*⁴

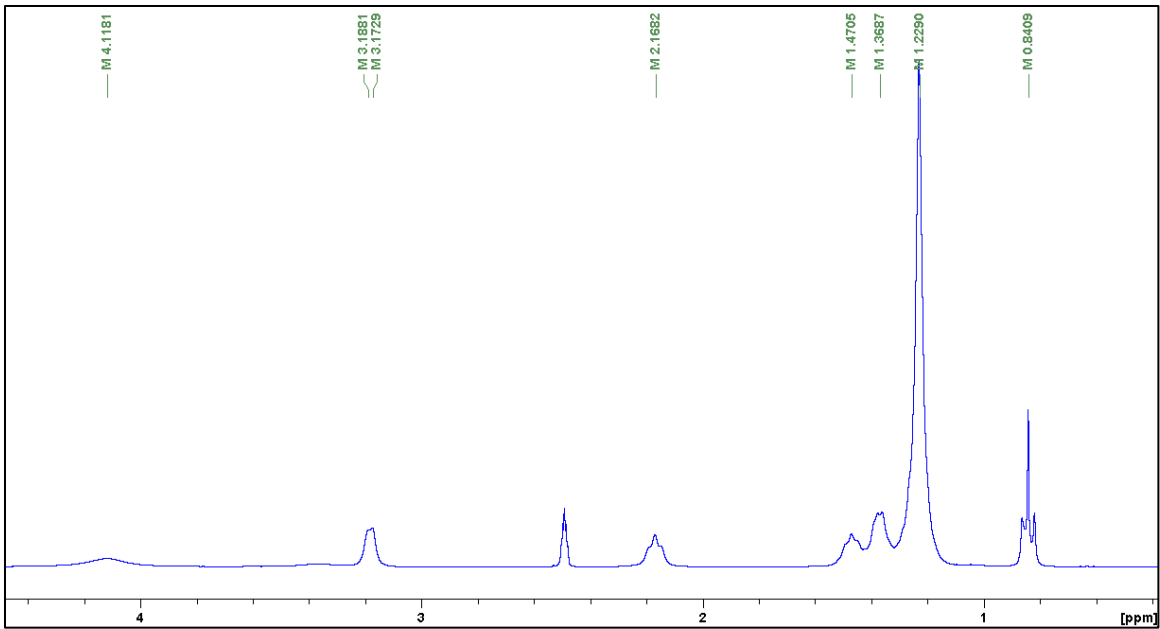
6.4 g (0.02 mol) 9,10-dihydroxystearic acid and 14.4 g (0.08 mol) N-bromosuccinic imide were refluxed in 250 mL ethyl acetate and 200 mL deionized water in an inert atmosphere for 15 min. The the formed bromine was removed by distillation at 80 °C. The volume of the reaction mixture was kept constant during this procedure by continuous addition of ethyl acetate. The organic phase was washed five times with 200 mL each of deionized water and then concentrated on a rotavapour. The residue was dissolved in 100 mL of hot MeOH and the solution was cooled down to 0 °C. The precipitated yellow solid was filtered off and purified by column chromatography (ethyl acetate/hexane 1:1).

m.p.: 82-84 °C; MS-ESI: m/z 311.23 [M-H]⁻, ¹H-NMR (300 MHz, CDCl₃): 0.87 (t, *J* = 7.0 Hz, CH₃, 3H), 1.16–1.44 (m, CH₂, 16H), 1.48–1.73 (m, CH₂, 6H), 2.34 (t, *J* = 7.7 Hz, CH₂, 2H), 2.72 (t, *J* = 7.3 Hz, CH₂, 4H) ppm; ¹³C-NMR (300 MHz, CDCl₃): δ = 14.1 (CH₃), 22.6 (CH₂), 22.9 (CH₂), 23.0 (CH₂), 24.5 (CH₂), 28.8 (CH₂), 28.9 (2xCH₂), 29.1 (2xCH₂), 29.3 (CH₂), 31.8 (CH₂), 34.0 (CH₂), 36.0 (CH₂), 36.1 (CH₂), 180.0 (COOH), 200.0 (C=O), 200.1 (C=O) ppm; C₁₈H₃₂O₄ (312.44): calculated: C 69.19%, H 10.32%; found: C 69.27%, H 10.33%.

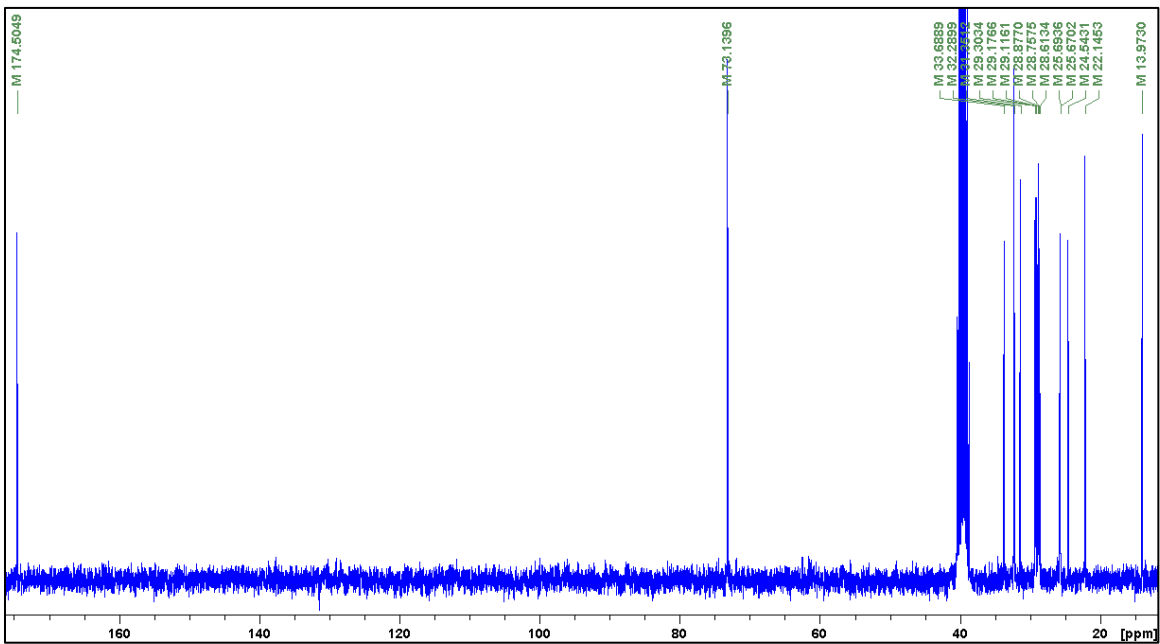
NMR spectra

threo-9,10-dihydroxystearic acid

¹H NMR spectrum

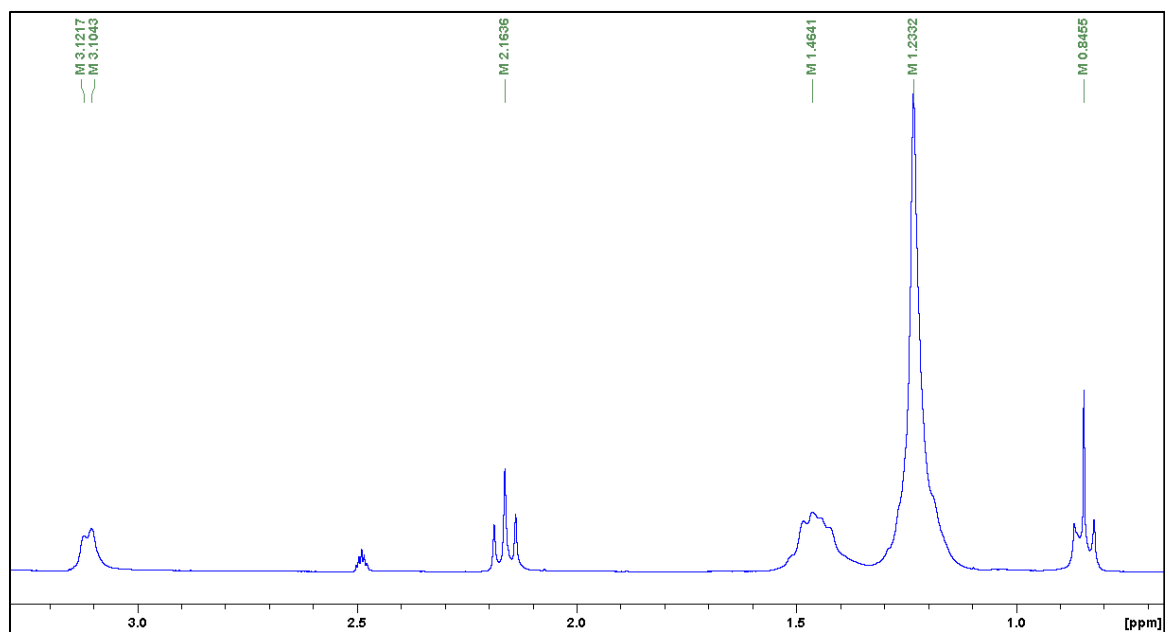


¹³C NMR spectrum

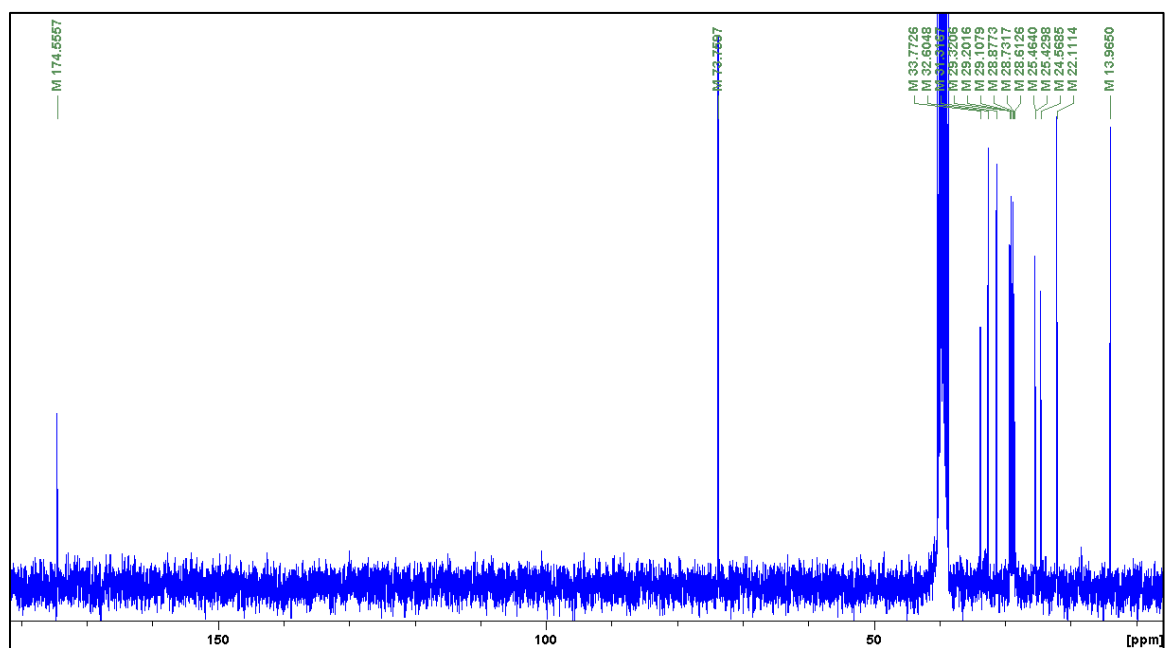


erythro-9,10-dihydroxystearic acid

^1H NMR spectrum

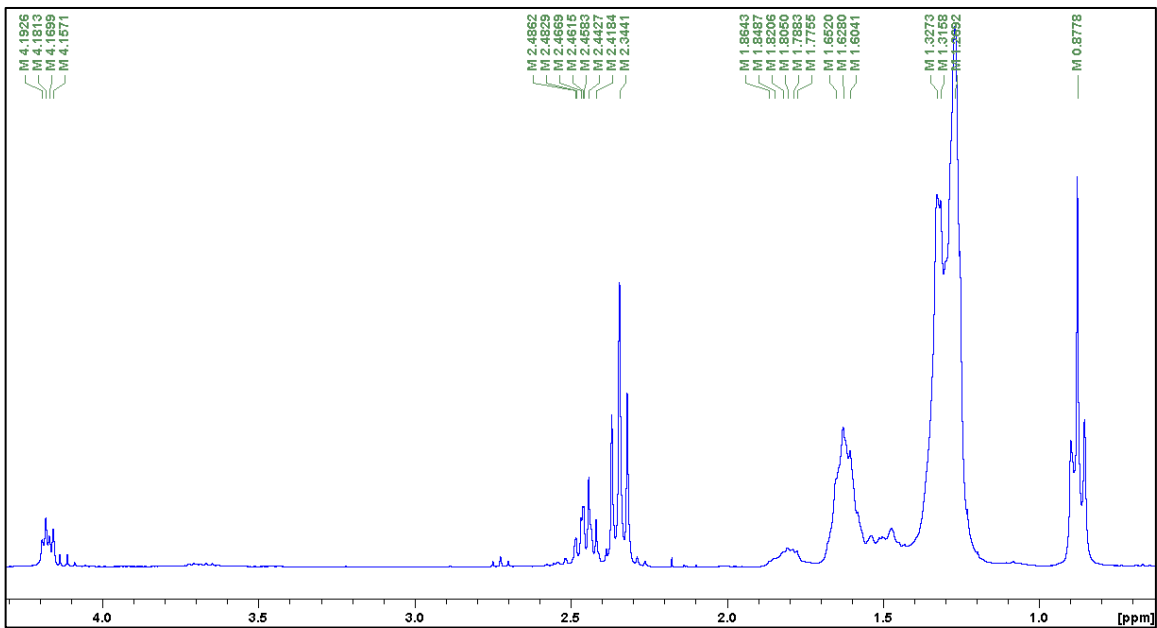


^{13}C NMR spectrum

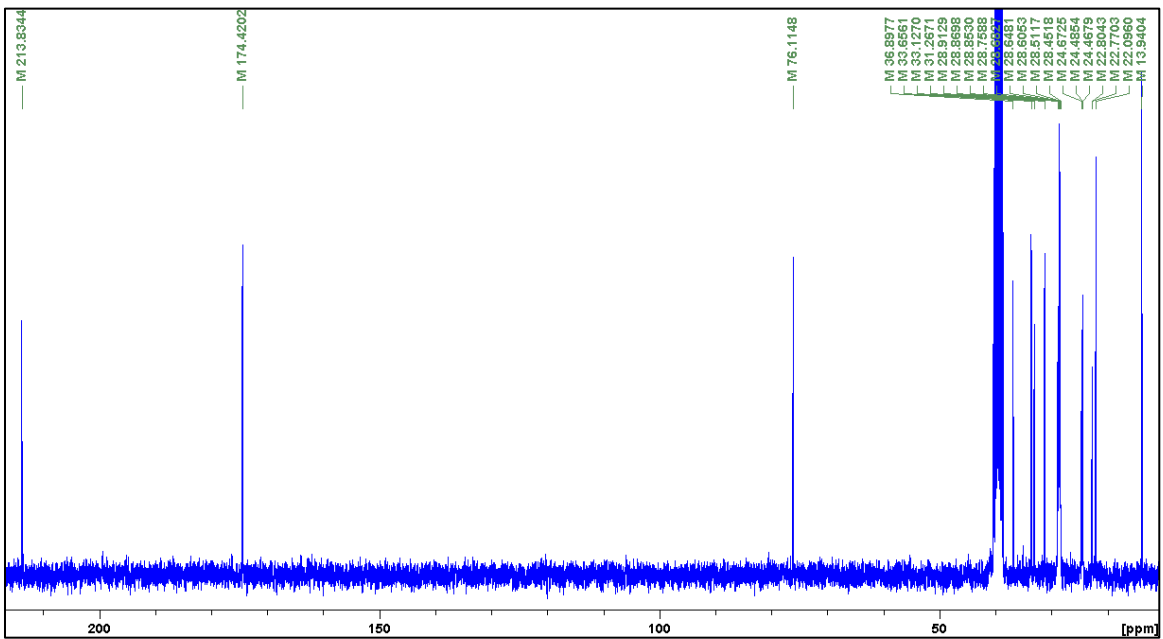


9(10)-hydroxy-10(9)-oxostearic acid

¹H NMR spectrum

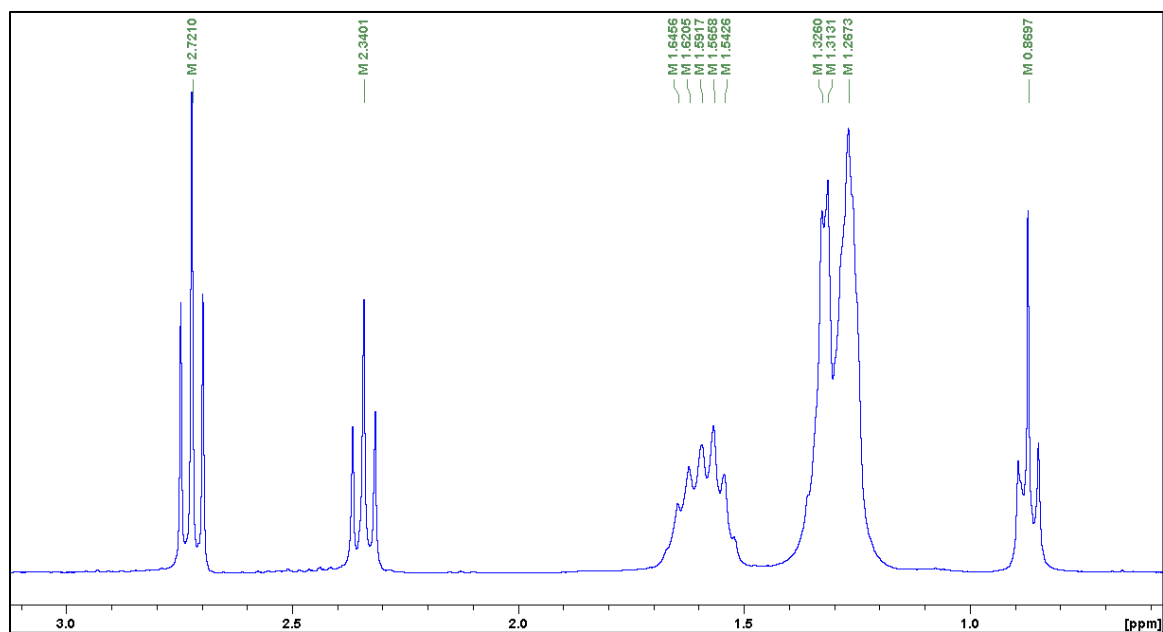


¹³C NMR spectrum

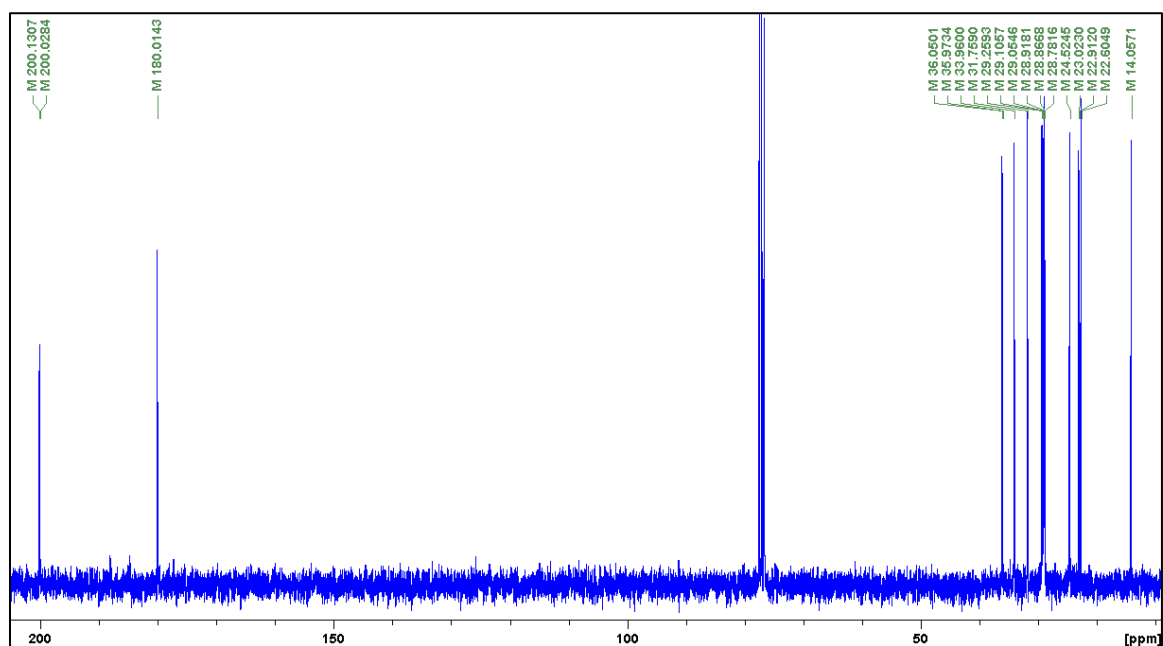


9,10-dioxostearic acid

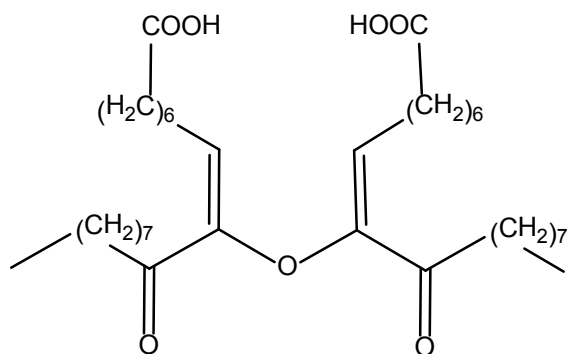
^1H NMR spectrum



^{13}C NMR spectrum



Suspected by-product in the oxidative cleavage of HK and DK



Chemical Formula: $\text{C}_{36}\text{H}_{62}\text{O}_7$

Exact Mass: 606.45 g/mol

MS-ESI: m/z 605.44 $[\text{M}-\text{H}]^-$

¹ W. A. Herrmann, R. W. Fischer, D. W. Marz, *Angew. Chem.*, 1991, **103**, 1706–1709.

² A. Lapworth, E. N. Mottram, *J. Chem. Soc.*, 1925, 1628–1631.

³ J. E. Coleman, C. Ricciuti, D. Swern, *J. Org. Chem.*, 1956, **78**, 5342–5345.

⁴ W. A. Cramp, F. J. Julietti, J. F. McGhie, B. L. Rao, W. A. Ross, *J. Chem. Soc.*, 1960, 4257–4263.