

SUPPLEMENTARY DATA (Domergue et al.,)

Synthesis of (7Z)-Hexadec-7-enoic acid

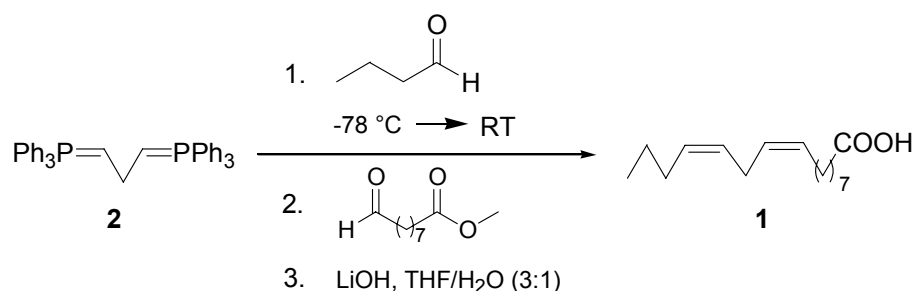
(6-methoxycarbonyl-hexyl)-triphenyl-phosphonium bromide (3 g, 6.2 mmol) in dry THF (50 ml) were cooled to -78°C . A solution of potassium bis(trimethylsilyl)amide (6.8 mmol, 13.6 ml of a 0.5 M solution in toluene) was added over a period of 10 min. The cooling bath was removed and the orange solution was allowed to warm to room temperature (RT). After stirring for an additional 30 min at RT the solution was re-cooled to -78°C and nonanal (0.85 g, 6 mmol) was added slowly. The reaction mixture was allowed to reach RT over a period of 2 hours and then hydrolyzed by addition of 1 N HCl (30 ml). After extraction with ether, drying over sodium sulfate and flash chromatography on silica gel using a binary solvent mixture of light petroleum:ether (9:1, v/v) for elution afforded (7Z)-hexadec-7-enoic acid methyl ester. 0.65 g (40 %). Treatment of the methyl ester (400 mg) with 3 eq. LiOH in 12 ml THF:water (3:1, v/v) afforded the free fatty acid. 340 mg (90 %).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ = 0.88 (t, $J=6.9$ Hz, 3H), 1.21-1.40 (m, 16H), 1.64 (m, 2H), 2.02 (m, 4H), 2.35 (t, $J=7.5$ Hz, 2H), 5.27-5.41 (m, 2H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ = 14.25 (CH_3), 22.83 (CH_2), 24.72 (CH_2), 27.11 (CH_2), 27.38 (CH_2), 28.84 (CH_2), 29.46 (CH_2), 29.47 (CH_2), 29.49 (CH_2), 29.67 (CH_2), 29.90 (CH_2), 32.05 (CH_2), 34.20 (CH_2), 129.53 (CH), 130.42 (CH), 180.40 (CO).

Other spectroscopic data are in agreement with a previous report [methyl ester, Tewari N, Rohatgi A, Bhushan KH, Subramanian GBV (1995) Preparation of 7,8,16-Trihydroxy-Hexadecanoic Acid from Aleuritic Acid and a Synthesis of E/Z-7-Hexadecen-1,16-Olides and Hexalure. Indian Journal of Chemistry Section B-Organic Chemistry Including Medicinal Chemistry 34: 851-855]

Synthesis of (9Z,12Z)-Hexadeca-9,12-dienoic acid



To a cold (-78°C) suspension of propane-1,3-bis(triphenylphosphonium) bromide (0.76 g, 1 mmol) in dry THF (20 ml) was slowly added a solution of potassium bis(trimethylsilyl)amide (1.1 mmol, 2.2 ml of a 0.5 M solution in toluene). To complete deprotonation, the reaction mixture was allowed to come to RT. Stirring was continued for 30 min, the solution re-cooled to -78°C, and butanal (72 mg, 1.0 mmol) in dry THF (2 ml) was slowly added to the dark red solution. Following addition, the reaction mixture was allowed to reach RT and stirring was continued for 15 min. After re-cooling to -78°C the second carbonyl compound, 9-oxononanoic acid methyl ester (0.20 g, 1.1 mmol) was added slowly. The reaction mixture was warmed to RT over 2 hours and hydrolyzed by the addition of 1 N HCl (10 ml). Extraction with ether, drying over sodium sulfate and flash chromatography on silica gel using a binary solvent mixture of light petroleum:ether (9:1, v/v) for elution yielded pure (9Z,12Z)-hexadeca-9,12-dienoic acid methyl ester. 110 mg (42 %). Treatment of the methyl ester (30 mg) with 3 eq. LiOH in 2.4 ml THF:water (3:1, v/v) afforded the free fatty acid. 25 mg (88 %).

¹H NMR (CDCl₃, 400 MHz): δ = 0.91 (t, *J*=7.4 Hz, 3H), 1.26-1.36 (m, 8H), 1.37 (sext, *J*= 7.4 Hz, 2H), 1.64 (quint, *J*=7.5 Hz, 2H), 2.04 (m, 4H), 2.35 (t, *J*=7.5 Hz, 2H), 2.77 (t, *J*=6.0 Hz, 2H), 5.29-5.43 (m, 4H).

¹³C NMR (CDCl₃, 100 MHz): δ = 13.95 (CH₃), 22.95 (CH₂), 24.84(CH₂), 25.80 (CH₂), 27.33 (CH₂), 29.18 (CH₂), 29.22 (CH₂), 29.29 (CH₂), 29.45 (CH₂), 29.73 (CH₂), 33.86 (CH₂), 128.23 (CH), 128.28 (CH), 130.11 (CH), 130.19 (CH), 178.30 (CO).

IR (neat): ν = 3010, 2928, 2856, 1708, 1462, 1413, 1377, 1285, 935, 723 cm⁻¹.

MS (70 eV) m/z (%): 252 (41, M⁺•), 123 (10), 109 (24), 95 (40), 81 (72), 67 (100), 55 (47).

HR-MS (EI) m/z: 252.2090 M⁺•; calcd. for C₁₆H₂₈O₂ 252.2089.