

Supporting Information

A Short and Efficient Synthesis of Crocetin-dimethylester and Crocetinindial

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General experimental methods (S2), characterization data for compounds **1**, **2**, and **5** (S3),

characterization data for compounds **7**, and **8** (S4).

All ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, using deuterated chloroform (CDCl_3) as solvent; chemical shifts are in ppm downfield from a tetramethylsilane internal standard. IR spectra were measured with a IFTIR spectrometer, and the most intense or representative bands are reported (in cm^{-1}). Mass spectra were determined at an ionizing voltage of 70 eV, using a fused silica capillary GC columns: HP-1 (25 m length x 0.2 mm i.d. x 0.33 μm phase thickness) or HP-5 (25 m length x 0.32 mm i.d. x 0.52 μm phase thickness). The column temperature was 100 $^\circ\text{C}$ (3 min) ramped to 220 $^\circ\text{C}$ at 20 $^\circ\text{C min}^{-1}$. The mass spectra of compound **1** were performed by electrospray ionization (ESI), using a LC/MS spectrometer. Solutions were infused into the Z-spray source at 10 $\mu\text{l.min}^{-1}$ (0.5 mg.mL^{-1}) and the protonated parent ion was observed at 357. TLC was performed on plates precoated with silica gel 60 F₂₅₄ (0.25 mm thick) and column chromatographies were performed with silica gel 60 (70-230 mesh). Except where specified, all reagents were purchased from commercial sources and were used without further purification. Melting points are uncorrected.

Dimethyl (2E,4E,6E,8E,10E,12E,14E)-2,6,11,15-tetramethylhexadeca-2,4,6,8,10,12,14-heptaene-1,16-dioate (1): brick-red solid (mp = 215-218°C, literature:^{6a} 222°C): IR (KBr) ν_{\max} 1715, 1618, 1430, 1285, and 1170 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (dd, $J_1 = 1.3$ Hz, $J_2 = 10.6$ Hz, 2H), 6.72 (m, 2H), 6.63 (d, $J = 15.0$ Hz, 2H), 6.55 (dd, $J_1 = 10.3$ Hz, $J_2 = 15.0$ Hz, 2H), 6.36 (dd, $J_1 = 1.3$ Hz, $J_2 = 8.1$ Hz, 2H), 3.77 (s, 6H), 2.01 (d, $J = 1.3$ Hz, 6H), and 1.99 (d, $J = 1.3$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.9 (C=O), 143.7 (CH), 138.8 (CH), 136.7 (C), 135.3 (CH), 131.3 (CH), 126.4 (C), 123.8 (CH), 51.8 (OCH_3), 12.8 (CH_3), and 12.7 (CH_3); MS m/z quasi ion $[\text{M} + \text{H}]^+$ in 357.

(2E,4E,6E,8E,10E,12E,14E)-2,6,11,15-Tetramethylhexadeca-2,4,6,8,10,12,14-heptaene-1,16-dial (2): red solid (mp = 198-200°C, literature:^{6d} 190-191°C): IR (KBr) ν_{\max} 1671, 1611, 1573, 1378, and 1010 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 9.47 (s, 2H), 6.94 (m, 2H), 6.77 (dd, $J_1 = 3.0$ Hz, $J_2 = 7.8$ Hz, 2H), 6.73 (m, 4H), 6.46 (m, 2H), 2.04 (br s, 6H), and 1.91 (d, $J = 1.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.9(C=O), 149.2 (CH), 145.8 (CH), 137.7 (C), 137.4 (C), 137.1 (CH), 132.3 (CH), 124.0 (CH), 13.2 (CH_3), and 10.0 (CH_3); MS m/z (relative intensity) 296 (M^+ , 28.09), 128 (27.25), 91 (97.37), 53 (37.90), and 18 (100.00).

(2E)-1,1,4,4-Tetramethoxybut-2-ene (5): colorless oil: IR (film) ν_{\max} 2917, 1696, 1446, 1353, 1115, and 1060 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.4 (m, 2H), 4.7 (br s, 2H), and 3.1 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.5 (=CH), 101.6 (CH), and 53.8 (OCH_3); MS m/z (relative intensity) 145 ($\text{M}^+ - 31$, 8.78), 101 (6.80), 75 (100.00), and 31 (7.14).

Dimethyl (2E,4E,6E)-2,7-dimethylocta-2,4,6-triene-1,8-dioate (7): white solid (mp = 142-144°C, literature:¹⁵ 139-140°C) IR (KBr) ν_{\max} 1709, 1620, 1438, 1294, 1238, 1162, 1111, and 755 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.2 (ddq, $J_1 = J_2 = J_3 = 1.3$ Hz, $J_4 = 3.0$ Hz, $J_5 = 8.0$ Hz, 2H), 6.7 (m, 2H), 3.7 (s, 6H), and 1.9 (d, $J = 1.3$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.8 (C=O), 137.4 (CH), 134.0 (CH), 130.3 (C), 52.4 (OCH_3), and 13.3 (CH_3); MS m/z (relative intensity) 224 (M^+ , 5.49), 149 (4.04), 105 (12.52), 59 (11.78), and 28 (100.00).

(2E,4E,6E)-2,6-Dimethylocta-2,4,6-triene-1,8-diol (8): white solid (mp = 92-95°C, literature:¹⁸ 94-96°C): IR (KBr) ν_{\max} 3480, 1610, 1430, and 1257 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.45 (m, 2H), 6.16 (ddq, $J_1 = J_2 = J_3 = 1.6$ Hz, $J_4 = 2.5$ Hz, $J_5 = 7.7$ Hz, 2H), 4.10 (br s, 4H), 1.81 (d, $J = 1.6$ Hz, 6H), and 1.64 (br s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.4 (C), 128.3 (CH), 125.2 (CH), 68.5 (CH_2), and 14.2 (CH_3); MS m/z (relative intensity) 84 ($\text{M}^+ - 84$, 1.01), 43 (11.66), 32 (32.43), 28 (100.00), 18 (4.90), and 14 (19.21).