# Surface-Active Properties of Lipophilic Antioxidants Tyrosol and Hydroxytyrosol Fatty Acid Esters: a Potential Explanation for the Nonlinear Hypothesis of the Antioxidant Activity in Oil-in-Water Emulsions

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Characterization of new compounds **5**, **6**, **7**, **11** and **15**.

Data for Tyrosol hexanoate (**5**): The pure compound was obtained using vinyl hexanoate as the acylating agent and after column chromatography (hexane: ethyl acetate, 7:1) in 94% yield. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, 2H, *J* = 8.6 Hz, H-2'), 6.79 (d, 2H , *J* = 8.6 Hz, H-3'), 4.26 (t, 2H, *J* = 7.1 Hz, H-1), 2.86 (t, 2H, *J* = 7.1 Hz, H-2), 2.31 (t, 2H, *J* = 7.5 Hz, $CH_2COO$-), 1.61 (m, 2H, $\underline{CH_2}CH_2COO$- ), 1.28 (m, 4H, $CH_2$), 0.88 (t, 3H *J* = 6.9 Hz, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 174.7 (COO-), 154.8 (C-4'), 130.1 (C-2'), 129.5 (C-1'), 115.5 (H-3'), 65.5 (C-1), 34.5 ($CH_2COO$-), 34.3 (C-2), 31.3 ($CH_2$), 24.7 22.4 ($CH_2$), 14.0 ($CH_3$). HRESI-MS: calculated for $C_{14}H_{20}O_3$ : 236.1412, found: 236.1404.

Data for Tyrosol octanoate (**6**): The pure compound was obtained using vinyl octanoate as the acylating agent and after column chromatography (hexane: ethyl acetate, 8:1) in 93% yield. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, 2H, *J* = 8.5 Hz, H-2'), 6.78 (d, 2H, *J* = 8.5 Hz, H-3'), 4.26 (t, 2H, *J* = 7.1 Hz, H-1), 2.86 (t, 2H, *J* = 7.1 Hz, H-2), 2.30 (t, 2H *J* = 7.5 Hz, $CH_2COO$-), 1.60 (m, 2H, $\underline{CH_2}CH_2COO$-), 1.27 (m, 8H, $CH_2$), 0.88 (t, 3H, *J* = 6.7 Hz, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 174.8 (COO-), 154.8 (C-4'), 130.1 (C-2'), 129.6 (C-1'), 115.6 (H-3'), 65.5 (C-1), 34.6 ($CH_2COO$-), 34.4 (C-2), 31.8 ($CH_2$), 29.2 ($CH_2$), 29.0 ($CH_2$), 25.1 ($\underline{CH_2}CH_2COO$-), 22.7 ($CH_2$), 14.2 ($CH_3$). HRESI-MS: calculated for $C_{16}H_{24}O_3$ : 264.1725, found: 264.1704.

Data for Tyrosol decanoate (**7**): The pure compound was obtained using vinyl decanoate as the acylating agent and after column chromatography (hexane: ethyl acetate, 9:1) in 91% yield. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, 2H, *J* = 8.6 Hz, H-2'), 6.79 (d, 2H, *J* = 8.6 Hz, H-3'), 4.26 (t, 2H, *J* = 7.1 Hz, H-1), 2.86 (t, 2H, *J* = 7.1 Hz, H-2), 2.30 (t, 2H, *J* = 7.6 Hz, $CH_2COO$-), 1.61 (m, 2H, $\underline{CH_2}CH_2COO$- ), 1.26 (m, 12H, $CH_2$), 0.89 (t, 3H, *J* = 6.7 Hz, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 174.9 (COO-), 154.8 (C-4'), 130.1 (C-2'), 129.5 (C-1'), 115.6 (H-3'), 65.5 (C-1), 34.6 ($CH_2COO$-), 32.0 ($CH_2$), 29.5 ($CH_2$), 29.4 ($CH_2$), 29.4 ($CH_2$), 29.2 ($CH_2$), 25.1 ($\underline{CH_2}CH_2COO$-), 22.8 ($CH_2$), 14.2 ($CH_3$). HRESI-MS: calculated for $C_{18}H_{28}O_3$ : 292.2038, found: 292.2047.

Data for Hydroxytyrosol hexanoate (**11**): The pure compound was obtained using vinyl hexanoate as the acylating agent and after column chromatography (hexane: ethyl acetate, 3:1) in 94% yield. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, 1H, *J* = 8.0 Hz, H-5'), 6.73 (d, 1H, *J* = 1.8 Hz, H-2'), 6.61 (dd, 1H, *J* = 8.1, 1.8 Hz, H-6'), 4.24 (t, 2H *J* = 7.1 Hz, H-1), 2.80 (t, 2H, *J* = 7.1 Hz, H-2), 2.30 (t, 2H, *J* = 7.5 Hz, $CH_2COO$-), 1.60 (m, 2H, $\underline{CH_2}CH_2COO$-), 1.26 (m, 4H, $CH_2$), 0.87 (t, 3H, *J* = 6.9 Hz, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 175.2 (COO-), 143.9 (C-4'), 142.6 (C-3'), 130.4 (C-1'), 121.3 (C-6'), 116.0 (C-2'), 115.5 (C-5'), 65.4 (C-1),

34.5 ($CH_2COO$-), 34.5 (C-2), 31.3 ($CH_2$), 24.7 ($\underline{CH_2}$CH2COO-), 22.4 ($CH_2$), 14.0 ($CH_3$). HRESI-MS: calculated for $C_{14}H_{20}O_4Na$: 275.1318, found: 275.1311.

Data for Hydroxytyrosol myristate (**15**): The pure compound was obtained using vinyl myristate as the acylating agent and after column chromatography (hexane: ethyl acetate, 3:1) in 96% yield. $^1$H NMR (300 MHz, $CDCl_3$) δ 6.79 (d, 1H, *J* = 8.1 Hz, H-5'), 6.73 (d, 1H, *J* = 1.9 Hz, H-2'), 6.61 (dd, 1H, *J* = 8.1, 1.9 Hz, H-6'), 4.24 (t, 2H *J* = 7.2 Hz, H-1), 2.80 (t, 2H, *J* = 7.2 Hz, H-2), 2.30 (t, 2H, *J* = 7.6 Hz, $CH_2COO$-), 1.59(m, 2H, $\underline{CH_2}CH_2COO$-), 1.25 (m, 18, $CH_2$), 0.88 (t, 3H, *J* = 6.7 Hz, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 175.1 (COO-), 143.9 (C-4'), 142.6 (C-3'), 130.4 (C-1'), 121.3 (C-6'), 116.0 (C-2'), 115.5 (C-5'), 65.4 (C-1), 34.6 ($CH_2COO$-), 34.6 (C-2), 32.1 ($CH_2$), 29.8 ($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$), 29.6 ($CH_2$), 29.5 ($CH_2$), 29.4 ($CH_2$), 29.24 ($CH_2$), 25.1 ($\underline{CH_2}$CH2COO-), 22.82 ($CH_2$), 14.24 ($CH_3$). HRESI-MS: calculated for $C_{22}H_{36}O_4Na$: 387.2511, found: 387.2505.