Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 81 (1) S40–S41 (2016) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

First and efficient synthesis of 4-[((3,4-dihydroxybenzoyl)-oxy)methyl]phenyl *β*-D-glucopyranoside, an antioxidant from *Origanum vulgare*

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J. Serb. Chem. Soc. 81 (1) (2016) 23–28

PHYSICAL, ANALYTIC AND SPECTRAL DATA

4-(Hydroxymethyl)phenyl β-*D-glucopyranoside 2,3,4,6-tetraacetate* (***4***). Yield: 53.2 %; white solid; m.p.: 108–108.7 °C (Lit.: 108.9–109.7 °C[1]); Anal. Calcd. for $C_{21}H_{26}O_{11}$: C, 55.50; H, 5.77 %. Found: C, 55.27, H, 5.49 %; ^{1}H--NMR (400 MHz, $CDCl_3$, δ / ppm): 2.02, 2.04, 2.05, 2.07 (4×3H, 4×*s*, 4×$OCOCH_3$), 3.82–3.87 (1H, *m*, H5), 4.16 (1H, *dd*, *J* = 12.4 and 4.2 Hz, H6a), 4.27 (1H, *dd*, *J* = 12.4 Hz & 5.2 Hz, H6b), 4.66 (2H, *s*, Ar-C**H**$_2$OH), 5.09 (1H, *d*, *J* = 7.2 Hz, H1), 5.14 (1H, *t*, *J* = 9.6 Hz, H4), 5.22–5.31 (2H, *m*, H2 & H5), 6.97 (2H, *d*, *J* = 8.4 Hz, Ar-H), 7.28–7.31 (2H, *m*, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 20.7, 20.8 (4×CO**C**H$_3$), 61.7 (C6), 64.9 (Ar-**C**H$_2$OH), 68.5 (C4), 71.1 (C2), 72.2 (C3), 72.5 (C5), 99.4 (C1), 117.2, 128.4, 136.1, 156.3 (Ar-C), 169.2, 169.4, 170.1, 170.4 (4×**C**OCH$_3$); HRMS(ESI) *m*/*z* calcd. for $C_{21}H_{26}O_{11}Na$ $[M+Na]^+$: 477.1373. Found: 477.1377; specific rotation ($[\alpha]_D^{24}$ / ° (*c* = 1.06 g mL^{-1}, $CHCl_3$)): –12.6.

3,4-Diacetoxybenzoic acid (***6***). Yield: 86.5 %; white crystals; m.p.: 157–158 °C (Lit.:[2] 158–160 °C); Anal. Calcd. for $C_{11}H_{10}O_6$: C, 55.47; H, 4.23 %. Found: C, 55.39, H, 4.18 %; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 2.35 (2×3H, *s*, 2×Ar-$OCOCH_3$), 7.35 (1H, *d*, *J* = 8.8 Hz, Ar-H); 7.97 (1H, *d*, *J* = 2.0 Hz, Ar-H), 8.05 (1H, *dd*, *J* = 8.8 and 2.0 Hz, Ar-H), 11.5 (1H, *s*, COOH); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 20.6, 20.7 (2×OCO**C**H$_3$), 123.7, 125.7, 127.8, 128.8, 142.1, 146.7 (Ar-C), 167.6, 167.9, 170.3 (2×O**C**OCH$_3$ and COOH).

4-[((3,4-Diacetoxybenzoyl)oxy)methyl]phenyl β-*D-glucopyranoside 2,3,4,6--tetraacetate* (***8***). Yield: 95 %; white crystals; m.p.: 59–60 °C; Anal. Calcd. for $C_{32}H_{34}O_{16}$: C, 56.97; H, 5.08 %. Found: C, 56.91; H, 5.03 %; ^{1}H-NMR (400

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MHz, $CDCl_3$, δ / ppm): 2.03, 2.05, 2.07, 2.08 (4×3H, 4×*s*, 4×$OCOCH_3$), 2.32 (2×3H, *s*, 2×Ar-$OCOCH_3$), 3.85 (1H, *ddd*, *J* = 10.0, 5.4 and 2.4 Hz, H5), 4.18 (1H, *dd*, *J* = 12.2 and 2.4 Hz, H6a), 4.27 (1H, *dd*, *J* = 12.2 and 5.4 Hz, H6b), 5.07 (1H, *d*, *J* = 7.3 Hz, H1), 5.17 (1H, *t*, *J* = 9.5 Hz, H4), 5.24–5.35 (2H, *m*, H2 and H3), 5.28 (2H, *s*, Ar-C**H**$_2$O), 7.05 (1H, *d*, *J* = 8.6 Hz, Ar-H), 7.27 (2H, *d*, *J* = = 8.5 Hz, Ar-H), 7.38 (1H, *d*, *J* = 8.6 Hz, Ar-H), 7.86 (1H, *d*, *J* = 1.9 Hz, Ar-H), 7.97 (2H, *dd*, *J* = 8.5 and 1.5 Hz, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 20.5, 20.6 (4-OCO**C**H_3), 20.7, 20.9 (2×Ar-OCO**C**H_3), 61.8 (C6), 66.5 (Ar--CH_2O–), 68.4 (C4), 71.2 (C2), 72.2 (C3), 72.6 (C5), 99.3 (C1), 117.1, 123.2, 125.3, 127.8, 128.1, 128.5, 130.2, 130.5, 142.1, 146.2, 156.7 (Ar-**C**), 164.8, 167.4, 168.1, 169.2, 169.4, 170.1, 170.4 (4×O**C**OCH_3, 2×Ar-O**C**OCH_3, Ar--COOR); specific rotation ($[\alpha]_D^{24}$ / ° (*c* = 0.75 g mL^{-1}, $CHCl_3$)): –13.6.

4-[((3,4-Dihydroxylbenzoyl)oxy)methyl]phenyl β-*D-glucopyranoside* ***(1)***. Yield: 94.8 %; white crystals; m.p.: 205–206 °C; Anal. Calcd. for $C_{20}H_{22}O_{10}$: C, 56.87; H, 5.25 %. Found: C, 56.89; H, 5.23 %; ^{1}H-NMR (400 MHz, CD_3OD, δ / ppm): 3.34–3.51 (4H, *m*, H2, H3, H4, H5), 3.71 (1H, *dd*, *J* = 12.1 and 5.4 Hz, H6a), 3.92 (1H, *dd*, *J* = 12.1 and 2.1 Hz, H6b), 4.94 (1H, *d*, *J* = 7.6Hz, H1), 5.24 (2H, *s*, Ar-CH_2O–), 6.82 (1H, *d*, *J* = 8.1 Hz, Ar-H), 7.13 (2H, *d*, *J* = 8.8 Hz, Ar-H), 7.35 (2H, *d*, *J* = 8.8 Hz, Ar-H), 7.43–7.47 (2H, *m*, Ar-H); ^{13}C-NMR (100 MHz, CD_3OD, δ / ppm): 62.4 (C6), 67.1 (Ar-CH_2O–), 68.4 (C4), 71.2 (C2), 74.7 (C5), 77.8 (C3), 102.1 (C1), 115.6, 117.3, 117.8, 122.5, 123.6, 130.5, 131.6, 146.3, 151.8, 158.7 (Ar-C), 168.2 (Ar-COO–); Specific rotation ($[\alpha]_D^{24}$ / ° (*c* = = 0.45 g mL^{-1}, CH_3OH)): –112.4.

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