Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. *83* (12) S364–S365 (2018) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

S–O Acetyl rearrangement in 6-thio-D-glucose derivatives

VELIMIR POPSAVIN[1,2]*, MIRJANA POPSAVIN[1] and DUŠAN MILJKOVIĆ[1]

[1]*University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia and* [2]*Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia*

J. Serb. Chem. Soc. *83* (12) (2018) 1297–1303

CHARACTERISATION DATA FOR THE PREPARED COMPOUNDS

1,2-O-*Isopropylidene-3,6-di*-O-*(*p-*toluenesulphonyl)*-α-*D-glucofuranose* (***2***). Anal. Calcd. for $C_{23}H_{28}O_{10}S_2$: C, 52.27; H, 5.30; S, 12.12 %. Found: C, 52.53; H, 5.16; S, 11.79 %; IR (KBr, cm^{-1}): 3500 (OH); ^{1}H-NMR (250 MHz, $CDCl_3$, δ / ppm): 1.27 & 1.44 (6H, 2×*s*, $(CH_3)_2C$), 2.45 & 2.47 (3H, 2×*s*, 2×C**H**$_3$C$_6$H$_4$SO$_2$), 2.64 (1H, *d*, $J_{5,OH}$ = 5.4 Hz, OH), 3.91–4.10 (3 H, *m*, H-5, H-6a & H-6b), 4.27 (1H, *dd*, $J_{3,4}$ = 2.6 Hz & $J_{4,5}$ = 9.0 Hz, H-4), 4.62 (1H, *d*, $J_{1,2}$ = 3.7 Hz, H-2), 4.92 (1H, *d*, $J_{3,4}$ = 2.5 Hz, H-3), 5.82 (1H, *d*, $J_{1,2}$ = 3.7 Hz, H-1), 7.32–7.84 (8H, *m*, 2×CH$_3$C$_6$**H**$_4$SO$_2$); ^{13}C-NMR (62.9 MHz, $CDCl_3$, δ / ppm): 21.63 (2×**C**H$_3$C$_6$H$_4$SO$_2$), 26.25 & 26.57 ((**C**H$_3$)$_2$C), 66.39 (C-5), 71.82 (C-6), 78.28 (C-4), 81.44 (C-3), 82.86 (C-2), 104.99 (C-1), 112.78 ((CH$_3$)$_2$**C**), 128.02–130.08 (2×CH$_3$**C**$_6$H$_4$SO$_2$); LRMS-EI (*m*/*e*): 513 (M^+−Me).

5-O-*Acetyl-1,2*-O-*isopropylidene-3,6-di*-O-*(*p-*toluenesulphonyl)*-α-*D-gluco-furanose* (***4***). IR (film, cm^{-1}): 1745 (C=O, Ac); ^{1}H-NMR (250 MHz, $CDCl_3$, δ / ppm): 1.25 & 1.45 (6H, 2×*s*, $(CH_3)_2C$), 1.90 (3H, *s*, CH_3C=O), 2.40 (6H, *s*, 2×C**H**$_3$C$_6$H$_4$SO$_2$), 4.05 (1H, *dd*, $J_{6a,6b}$·= 13.0 Hz & $J_{5,6a}$ = 4.0 Hz, H-6a), 4.25––4.50 (2H, *m*, H-4 & H-6b), 4.60 (1H, *d*, $J_{1,2}$ = 5.0 Hz, H-2), 4.75–5.00 (2H, *m*, H-3 & H-5), 5.75 (1H, *d*, $J_{1,2}$ = 5.0 Hz, H-1), 7.25–7.75 (8H, *m*, 2×CH$_3$C$_6$**H**$_4$SO$_2$); ^{13}C-NMR (62.9 MHz, δ / ppm): 20.66 (**C**H$_3$C=O), 21.57 & 21.63 (2×**C**H$_3$C$_6$H$_4$SO$_2$), 26.35 7 & 26.73 ((**C**H$_3$)$_2$C), 67.38 (C-5), 67.80 (C-6), 75.5 (C-4), 80.22 (C-3), 82.95 (C-2), 104.94 (C-1), 113.00 ((CH$_3$)$_2$**C**), 127.98––145.62 (2×CH$_3$**C**$_6$H$_4$SO$_2$), 169.54 (CH$_3$**C**=O); LRMS-EI (*m*/*e*): 570 (M^+).

5-O-*Acetyl-6*-S-*acetyl-1,2*-O-*isopropylidene-3*-O-*(*p-*toluenesulphonyl)-6-*-thio-α-D-glucofuranose* (***5***). Anal. Calcd. for $C_{20}H_{26}O_9S_2$: C, 50.63; H, 5.48; S, 14.50 %. Found: C, 50.78; H, 5.39; S, 14.26 %; IR (KBr, cm^{-1}): 1745 (C=O, Ac), 1700 (C=O, SAc); ^{1}H-NMR (250 MHz, $CDCl_3$, δ / ppm): 1.31 & 1.51 (6H

* Corresponding author. E-mail: velimir.popsavin@dh.uns.ac.rs

2×*s*, $(CH_3)_2C$), 1.91 (3H, *s*, CH_3CO_2), 2.23 (3H, *s*, CH_3CS), 2.46 (3H, *s*, $C\mathbf{H}_3C_6H_4SO_2$), 2.98 (1H, *dd*, $J_{6a,6b}$ = 14.5 Hz & $J_{5,6a}$ = 4.3 Hz, H-6a), 3.61 (1H, *dd*, $J_{6b,6a}$ = 14.5 Hz & $J_{5,6b}$ = 3.5 Hz, H-6b), 4.36 (1 H, *dd*, $J_{4,5}$ = 9.5 Hz & $J_{3,4}$ = 2.8 Hz, H-4), 4.71 (1H, *d*, $J_{1,2}$ = 3.6 Hz, H-2), 4.96 (1H, *d*, $J_{3,4}$ = 2.8 Hz, H-3), 5.08 (1H, *ddd*, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 4.3 Hz & $J_{5,6b}$ = 3.5 Hz, H-5), 5.84 (1H, *d*, $J_{1,2}$ =3.6 Hz, H-1), 7.35–7.81 (4H, *m*, $CH_3C_6\mathbf{H}_4SO_2$); LRMS-EI (*m*/*e*): 474 (M^+).

5-O-*Acetyl-1,2*-O-*isopropylidene-3*-O-*(p-toluenesulphonyl)*-α-*D*-*gluco-furanose* (***6***). Anal. Calcd. for $C_{18}H_{24}O_9S$: C, 51.91; H, 5.81; S, 7.70 %. Found: C, 52.12; H, 5.61; S, 7.41 %; IR (film, cm^{-1}): 3500 (OH), 1745 (C=O, Ac); ^{1}H-NMR (250 MHz, $CDCl_3$, δ / ppm): 1.11 & 1.32 (6H, 2×*s*, $(CH_3)_2C$), 1.92 (3H, *s*, CH_3CO_2), 2.32 (3H, *s*, $C\mathbf{H}_3C_6H_4SO_2$), 2.55 (1H, *bs*, OH), 3.80–4.35 (4H, *m*, H-4, H-5, H-6a & H-6b), 4.40 (1H, *d*, $J_{1,2}$ = 5.0 Hz, H-2), 4.82 (1H, *d*, $J_{3,4}$ = 3.5 Hz, H-3), 5.71 (1H, *d*, $J_{1,2}$ = 5.0 Hz, H-1), 7.15–7.75 (4H, *m*, $CH_3C_6\mathbf{H}_4SO_2$); LRMS-EI (*m*/*e*): 401 (M^+−Me).

5-O-*Acetyl-1,2*-O-*isopropylidene-6-thio-3*-O-*(*p-*toluenesulphonyl)*-α-*D*-*glucofuranose* (***8***). Anal. Calcd. for $C_{18}H_{24}O_8S_2$: C, 50.00; H, 5.55; S, 14.81 %. Found: C, 50.22; H, 5.35; S, 14.59 %; IR (KBr, cm^{-1}): 2590 (SH), 1740 (C=O, Ac); ^{1}H-NMR (250 MHz, $CDCl_3$, δ / ppm): 1.27 & 1.50 (3H, 2×*s*, $(CH_3)_2C$), 1.15–1.40 (1H, *m*, SH), 1.99 (3H, *s*, CH_3CO_2), 2.45 (3H, *s*, $C\mathbf{H}_3C_6H_4SO_2$), 2.55–3.25 (2H, *m*, H-6a & H-6b), 4.55–4.70 (2H, *m*, H-2 & H-4), 4.90–5.12 (2H, *m*, H-3 & H-5), 5.85 (1H, *d*, $J_{1.2}$ = 3.5 Hz, H-1), 7.30–7.85 (4H, *m*, $CH_3C_6\mathbf{H}_4SO_2$); ^{13}C-NMR (62.9 MHz, $CDCl_3$, δ / ppm): 20.77 ($\mathbf{C}H_3CO_2$), 21.61 ($\mathbf{C}H_3C_6H_4SO_2$), 26.02 (C-6), 26.41 & 26.75 (($\mathbf{C}H_3)_2C$), 68.85 (C-5), 77.26 (C-4), 80.36 (C-3), 83.07 (C-2), 104.80 (C-1), 112.81 ($(CH_3)_2\mathbf{C}$), 128.05–145.43 ($CH_3\mathbf{C}_6H_4SO_2$), 169.41 ($CH_3\mathbf{C}$=O); LRMS-EI (*m*/*e*): 432 (M^+), 47 $(CH_2{=}SH)^+$.