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From a glycal to a [1,3]dioxolan-4-yl ester

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Abstract—1,2:5,6-di-*O*-Isopropylidene-α-D-glucofuranose can be used as a starting material for the stereoselective synthesis of a novel [1,3]dioxolan-4-yl ester by an acid catalyzed rearrangement reaction of an unusual furanoid glycal.

1. Introduction

The concise synthesis of enantiomerically pure suitably substituted carbocyclic acid [1,3]dioxolan-4-yl esters has gained considerable interest quite recently due to the occurrence of this structural unit in anti-malarial artemisinine derivatives;[1] their use as chiral synthons for the synthesis of nucleoside analogues[2,3] and of biologically active pentaoxacyclopenta[*f*]azulen-9-ones[4] The synthesis of this class of compounds has been accomplished either from dioxolan esters,[5–8] by the reduction of 5-oxo-[1,3]dioxolanes[9] or most recently by Baeyer–Villiger oxidation of 2,3-*O*-alkylidene-1-(cyclo)alkanones.[10–12]

Although a carbohydrate based chiral pool approach for the synthesis of these targets has already been outlined some time ago[13,14] the structure of the obtained compounds remained unclear for many decades[15] and, due to the rather harsh acidic reaction conditions, the yields were usually low with the absolute configuration of many of these compounds remaining uncertain.[13,14,16]

Some improvements could be achieved, however, by the use of mild oxidative transformations using either diacetoxy-phenyl-λ^3-iodane[17] or iodine base oxidations.[18] Interestingly enough, whereas the chemistry of carbohydrate derived 2,6-dioxabicyclo[3.3.0]octanes is well established, there are only a few examples found for the corresponding 2,6-dioxabicyclo[3.3.0] octenes.[19–21]

2. Results and discussion

During the synthesis of novel anti-malarial drugs, we became interested in the straightforward synthesis of the threose derivative **1** in its enantiomerically and diastereomerically pure form. Retrosynthetic analysis revealed a strategy for a chiral pool based approach starting from the well known and commercially available 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **2** whose protection at position HO-C(3) with ethyl chloroformate/pyridine gave 94% of **3**.[22]

Selective partial deprotection was achieved via cleavage of the 5,6-*O*-isopropylidene ring by treating **3** with acetic acid at 80 °C to afford **4**. Compound **4** was mesylated to yield the dimesylate **5** in an almost quantitative yield; treatment of **5** with an aqueous solution of potassium hydroxide in refluxing ethanol finally gave the 3,6-anhydro-sugar **6**.[23]

Treatment of **6** with 1 equiv of potassium *t*-butoxide in dry DMSO[21,24] at 5 °C gave 71% of the hex-5-enofuranose **7**. Reaction of **7** with an excess of this reagent for 30 min at ambient temperature, however, resulted in the formation of 77% of the corresponding hex-4-enofuranose **8**.[25]

Five-membered enol ethers are well known for their high tendency to undergo rearrangement reactions under Pd-catalyzed[26–28] as well as acidic conditions; this methodology has recently been used *inter alia* for the synthesis

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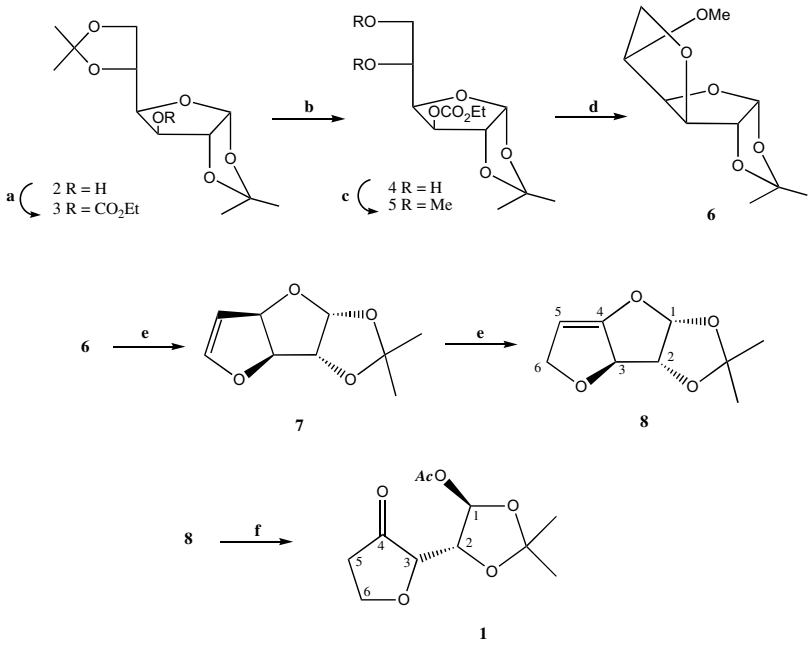


Scheme 1. (a) EtOCOCl/pyridine; (b) AcOH; (c) $MsCl/NEt_3$; (d) KOH/EtOH; (e) *t*BuOK; (f) AcOH.

of triple helix forming C-glycosides.[29] Similar reactions have also been applied to *exo*-glycals to afford dimerizations of C-glycosides[30–32] but no reactions have been described so far for *exo*-glycals being part of a ring (Scheme 1).

Thus, the smooth reaction of **8** with acetic acid in dichloromethane finally gave the desired target molecule **1** in 72% isolated yield. In order to establish the absolute configuration at C(1) in an unambiguous manner, suitable crystals were grown and subjected to a single crystal X-ray analysis. The results of this analysis are depicted in Figure 1 and clearly demonstrate an (*R*)-configuration for C(1) (Scheme 2).

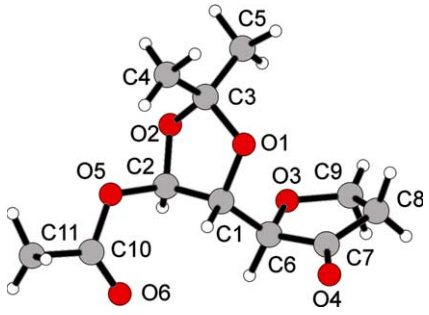
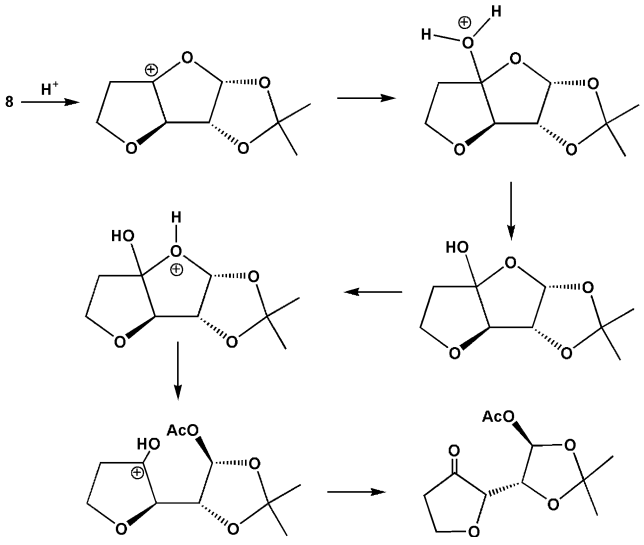


Figure 1. Single crystal X-ray data for **1**. Selected data: $C_{11}H_{16}O_6$, $M_r = 244.24\,g\,mol^{-1}$, orthorhombic, spacegroup: $P2_12_12_1$, $a = 5.456(1)$, $b = 10.166(3)$, $c = 21.810(13)$ Å, Cell volume: 1209.7(9) Å^2, $Z = 4$, $T = 220(2)$ K, $\rho_{calcd} = 1.341\,g\,cm^{-3}$, $\mu = 0.110\,mm^{-1}$, 2θ range = 4.43–47.98°, *hkl*-indices: h: $-6 < h < 7$, k: $-12 < k < 12$, l: $25 < l < 25$, reflections (measured): 6575, reflections (unique): 1899, reflections (unique $[F_o > 4\sigma\{|F_o|\}]$): 1330, $R_{int} = 0.1793$, 219 parameters, R_1/wR_2 (all data): 0.0780/0.1122, R_1/wR_2 ($I > 2\sigma$ (I)): 0.0502/0.0997, Flack-parameter: 0.2826, largest diff. peak/hole: 0.190/−0.225 e Å^{-3}.



Scheme 2. Proposed mechanism for the synthesis of **1**.

The transformation of **1** into anti-malarial compounds is currently underway and will be reported in due course.

3. Experimental

3.1. General

The melting points are uncorrected (*Reichert* hot stage microscope), optical rotations were obtained using a Perkin–Elmer 243B polarimeter (1 cm micro-cell), NMR spectra (internal Me_4Si) were recorded using either a Bruker AM250 or a Varian XL300 instrument (δ given

in ppm, J in Hz), IR spectra (film or KBrpellet) on a Perkin–Elmer 298 instrument, MS spectra were taken either on a MAT311A or a Varian-112S instrument; for elemental analysis a Foss-Heraeus Vario EL instrument was used. TLC was performed on silica gel (Merck 5554, detection by dipping in a solution containing 10% sulfuric acid (400 mL), ammonium molybdate (20 g) and cerium (IV) sulfate (20 mg) followed by heating to 150 °C. All reactions were performed under dry argon.

3.2. Crystal structure determination

The intensity data for the compound was collected on a Stoe-IPDS diffractometer, using graphite-monochromated Mo-K_α radiation. Data was corrected for Lorentz and polarization effects, but not for absorption effects.

The structure was solved by direct methods (SHELXS[33]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97.[34])

All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The absolute structure could not be determined as indicated by the value of the Flack-parameter.

Diamond 2.1e was used for structure representation.[35] Crystallographic data was deposited with the Cambridge Crystallographic Data Centre as supplementary publications (Ref. No. 227083). Copies of this data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-11223/336-033; e-mail: deposit@ccdc.cam.ac.uk

3.3. 3-*O*-Carbethoxy-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 3

To a solution of 1,2;5,6-di-*O*-isopropylidene-α-D-glucofuranose **2** (58.0 g, 199.8 mmol) in abs. dichloromethane containing dry pyridine (50 mL) at −20 °C, a solution of ethyl chloroformate (43 mL, 450 mmol) in dry dichloromethane (100 mL) was added within 1 h. After warming to room temperature, stirring continued for another 2 h after which the reaction mixture was then washed with aq. hydrochloric acid (5%, 20 mL), sat. solution of $NaHCO_3$ (2×10 mL), water (10 mL) and brine (10 mL). The organic phase was dried over Na_2SO_4 and the solvent evaporated. The syrupy residue was dissolved in methanol (250 mL), the solution filtered through activated charcoal and the filtrate then set aside at 0 °C for 12 h to yield crystalline **3** (62.5 g, 94%). Mp 76–78 °C {Lit.[22]: 76–78 °C}; R_F (ethyl acetate/toluene 1:1) 0.51; $[\alpha]_D = -37.9$ (c 1.02, $CHCl_3$) {Lit.[22]: $[\alpha]_D = -38.0$ ($CHCl_3$)}; IR (KBr): ν = 3450s, 2950m, 1740s, 1375m, 1310w, 1260s, 1230w, 1220m, 1160m, 1090m, 1070s, 1020s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 3H, Me), 1.31 (t, J = 7.0 Hz, 3H, Me), 1.32 (s, 3H, Me), 1.41 (s, 3H, Me), 1.51 (s, 3H, Me), 4.01 (dd, J = 4.8, 8.8 Hz, 1H, 6-H_A), 4.07 (dd, J = 5.9, 8.8 Hz, 1H, 6-H_B), 4.19 (dd, J = 2.9, 6.5 Hz, 1H, 4-H), 4.22 (q, J = 7.0 Hz, 2H, CH_2), 4.25 (ddd, J = 4.8, 5.9, 6.5 Hz, 1H, 5-H), 4.57 (d, J = 3.7 Hz, 1H, 2-H), 5.12 (d, J = 2.9 Hz, 1H, 3-H), 5.85 (d, J = 3.7 Hz, 1H, 1-H); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.1 (q, Me), 25.2 (q, Me), 26.1 (q, Me), 26.6 (q, Me), 64.5 (t, CH2), 67.0 (t, 6-C), 72.2 (d, 4-C), 79.2 (d, 3-C), 79.6 (d, 2-C), 83.2 (d, 5-C), 104.9 (d, 1-C), 109.2 (s, C_i), 112.2 (s, C_i), 153.9 (s, C=O); MS (e.i., 70 eV): m/z (%) = 317 (49), 187 (8), 171 (8), 145 (6), 127 (25), 113 (45), 101 (100); MS (c.i., isobutane): m/z = 333 ([M+1]$^+$), 275 ([M-58+1]$^+$); Anal. Calcd for $C_{15}H_{24}O_8$ (332.35): C, 54.21; H, 7.28. Found: C, 54.32; H, 7.15

3.4. 3-*O*-Carbethoxy-1,2-*O*-isopropylidene-α-D-glucofuranose 4

A solution of **3** (35 g, 105.31 mmol) in water (15 mL)/acetic acid (70 mL) was stirred at 30 °C for 80 h, then the solvents removed under reduced pressure; toluene (4×50 mL) was added and evaporated and the remaining syrup dissolved in ethyl acetate (200 mL) and filtered through a short path of silica gel. The solvent was removed and the remaining residue recrystallized from dichloromethane/cyclohexane to afford **4** (24.8 g, 78%) as white crystals. Mp 78–79 °C; R_F (ethyl acetate/toluene 5:2) 0.33; $[\alpha]_D = +13.5$ (c 1.2, $CHCl_3$); IR (KBr): ν = 3470s, 3410s, 299ow, 3980w, 2960w, 2920w, 2890w, 1760s, 1470m, 1450w, 1380m, 1310w, 1270s, 1210m, 1160m, 1110w, 1090m, 1070m, 1030m, 1050m cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 3H, Me), 1.29 (t, J = 7.0 Hz, 3H, Me), 1.48 (s, 3H, Me), 3.20 (br s, 2H, exchangeable with D_2O, HO-5, HO-6), 3.51 (ddd, J = 2.9, 4.9, 8.6 Hz, 1H, 5-H), 3.68 (dd, J = 4.9, 10.9 Hz, 1H, 6-H_A), 3.78 (dd, J = 2.9, 10.9 Hz, 1H, 6-H_B), 4.17 (dd, J = 2.6, 8.6 Hz, 1H, 4-H), 4.23 and 4.29 (q×AB, J = 7.2, 11.4 Hz, 2H, CH2), 4.58 (d, J = 3.7 Hz, 1H, 2-H), 5.14 (d, J = 2.6 Hz, 1H, 3-H), 5.87 (d, J = 3.7 Hz, 1H, 1-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (q, Me), 26.1 (q, Me), 26.4 (q, Me), 63.9 (t, CH2), 64.8 (t, 6-C), 68.1 (d, 4-C), 78.9 (d, 3-C), 79.4 (d, 5-C), 82.8 (d, 2-C), 104.7 (d, 1-C), 112.2 (s, C_i), 154.7 (s, C=O); MS (e.i., 70 eV): m/z (%) = 277 (13), 173 (14), 145 (29), 141 (19), 127 (50), 113 (92), 101 (100); MS (c.i., isobutane): m/z = 293 ([M+1]$^+$), 235 ([M−58+1]$^+$); MS (c.i., ammonia): m/z = 310 ([M+NH_3+1]$^+$), 252 ([M−58+NH_3+1]$^+$); Anal. Calcd for $C_{12}H_{20}O_8$ (292.29): C, 49.31; H, 6.90. Found: C, 49.50; H 6.72.

3.5. 3-*O*-Carbethoxy-1,2-*O*-isopropylidene-5,6-di-*O*-methanesulfonyl-α-D-glucofuranose 5

To a solution of **4** (23.1 g, 79 mmol) in abs. dichloromethane (500 mL) containing triethylamine (19.7 g, 195 mmol) at 0 °C within 30 min, a solution of methanesulfonylchloride (21.7 g, 190 mmol) in dichloromethane (100 mL) was added. Stirring continued at room temperature for another hour after which the mixture was filtered, the filtrate washed with aq. hydrochloric acid (0.1 M, 2×15 mL), a sat. aq. solution of $NaHCO_3$ (2×10 mL) and brine (20 mL), dried over Na_2SO_4 and the solvents were removed under diminished pressure. The remaining syrup was dissolved in

ethanol (45 mL) and water (50 mL) slowly added. After standing at 5 °C for 24 h, the crystals were collected and recrystallized from ethanol/water to yield **5** (34.1 g, 96%). Mp 105–106 °C; R_F (ethyl acetate/toluene 5:2) 0.53; $[\alpha]_D = -16.6$ (*c* 1.0, $CHCl_3$); IR (KBr): $\nu = 3030$w, 3000w, 2950w, 2920w, 1750s, 1480w, 1380s, 1360s, 1350s, 1305m, 1270s, 1255s, 1125m, 1080s; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.32$ (t, $J = 7.0$ Hz, 3H, Me), 1.37 (s, 3H, Me), 1.51 (s, 3H, Me), 3.08 and 3.11 (each s, each 3H, 2×Me of OMs), 4.23 and 4.28 (q×AB, $J = 7.1$, 10.6 Hz, 2H, CH_2), 4.45 (dd, $J = 4.7$, 11.9 Hz, 1H, 6-H_A), 4.46 (dd, $J = 2.8$, 8.6 Hz, 1H, 4-H), 4.61 (d, $J = 3.5$ Hz, 1H, 2-H), 4.69 (dd, $J = 2.3$, 11.9 Hz, 1H, 6-H_B), 5.11 (ddd, $J = 2.3$, 4.7, 8.6 Hz, 1H, 5-H), 5.25 (d, $J = 2.8$ Hz, 1H, 3-H), 5.92 (d, $J = 3.5$ Hz, 1H, 1-H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.1$ (q, Me), 26.1 (q, Me), 26.7 (q, Me), 37.5 (q, Me of OMs), 38.8 (q, Me of OMs), 64.9 (t, CH_2), 68.3 (t, 6-C), 72.7 (d, 4-C) 75.9 (d, 5-C), 77.7 (d, 3-C) 82.9 (d, 2-C), 104.9 (d, 1-C), 112.9 (s, C_i), 153.7 (s, C=O); MS (e.i., 70 eV): m/z (%) = 433 (61), 345 (77), 277 (28), 247 (37), 231 (20), 205 (100), 127 (30), 109 (30); MS (c.i., isobutane): $m/z = 391$ ($[M-58+1]^+$); Anal. Calcd for $C_{14}H_{24}O_{12}S$ (448.47): C, 37.50; H, 5.39; S, 14.30. Found: C, 37.25; H, 5.52; S, 14.41.

3.6. 3,6-Anhydro-1,2-*O*-isopropylidene-5-*O*-methanesulfonyl-α-D-glucofuranose 6

To a solution of **5** (30.0 g, 67 mmol) in refluxing ethanol (300 mL) an aq. solution of KOH (N, 75 mL) was added and refluxing was continued for another 2 h. The mixture was cooled to room temperature, water (600 mL) then added and the reaction set aside at 5 °C for 3 days. The crystals were collected and recrystallized from ethanol to afford **6** (17.1 g, 91%). Mp 111–112 °C; R_F (ethyl acetate/toluene 5:2) 0.49; $[\alpha]_D = +58.0$ (*c* 1.5, $CHCl_3$); IR (KBr): $\nu = 3050$w, 3020w, 3000w, 2980w, 2960w, 2950w, 2895w, 1390m, 1380m, 1320s, 1270m, 1260m, 1230w, 1210m, 1180s, 1170s, 1120m, 1110m, 1090m, 1070s, 1040s, 1010s cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.33$ (s, 3H, Me), 1.48 (s, 3H, Me), 3.13 (s, 3H, Me of OMs), 3.81 (dd, $J = 7.8$, 8.9 Hz, 1H, 6-H_A), 4.07 (dd, $J = 6.8$, 8.9 Hz, 1H, 6-H_B), 4.55 (d, $J = 3.8$ Hz, 1H, 3-H), 4.62 (d, $J = 3.6$ Hz, 1H, 2-H), 4.96 (dd, $J = 3.8$, 4.2 Hz, 1H, 4-H), 5.04 (ddd, $J = 4.2$, 6.8, 7.8 Hz, 1H, 5-H), 5.97 (d, $J = 3.6$ Hz, 1H, 1-H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 26.7$ (q, Me), 27.3 (q, Me), 38.6 (q, Me of OMs), 68.7 (t, 6-C), 77.1 (d, 4-C), 80.6 (d, 5-C), 84.7 (d, 3-C), 85.1 (d, 2-C), 107.2 (d, 1-C), 112.9 (s, C_i); MS (e.i., 70 eV): m/z (%) = 280 (10), 265 (60), 164 (10), 143 (10), 127 100), 115 (11), 97 (11), 85 (53), 79 (24); MS (c.i., isobutane): $m/z = 281$ ($[M+1]^+$); Anal. Calcd for $C_{10}H_{16}O_7S$ (280.39): C, 42.85; H, 5.75; S, 11.44. Found: C, 42.68; H, 5.84; S, 11.59.

3.7. 3,6-Anhydro-5-deoxy-1,2-*O*-isopropylidene-α-D-xylo-hex-5-enofuranose 7

To a solution of **6** (3.5 g, 9.77 mmol) in dry DMSO (10 mL) at 5 °C, potassium *tert*-butoxide (1.2 g, 10 mmol) was added in several portions under argon. Stirring was continued at room temperature for another 5 min, after which diethylether (250 ml) was added and the reaction mixture washed with cold water (2×20 mL). The organic layer was dried over Na_2SO_4, the solvents evaporated and the residue subjected to chromatography (silica gel, toluene/ethyl acetate 3:1) to afford **7** (1.3 g, 71%). Mp 29–31 °C; R_F (toluene/ethyl acetate 3:1) 0.53; $[\alpha]_D = +9.5$ (*c* 3.4, $CHCl_3$); IR (KBr): $\nu = 3447$s, 2999m, 1752m, 1636s, 1458s, 1376s, 1262s, 1064s, 1050s cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.35$ (s, 3H, Me), 1.50 (s, 3H, Me), 4.71 (d, $J = 3.9$ Hz, 1H, 2-H), 4.86 (d, $J = 5.9$ Hz, 1H, 3-H), 5.20 (t, $J = 2.7$ Hz, 1H, 5-H), 5.39 (dd, $J = 2.7$, 5.9 Hz, 1H, 4-H), 5.84 (d, $J = 3.9$ Hz, 1H, 1-H), 6.46 (d, $J = 2.7$ Hz, 1H, 6-H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 27.2$ (q, Me), 27.9 (q, Me), 85.0 (d, 4-C), 85.1 (d, 3-C), 87.7 (d, 2-C), 102.6 (d, 5-C), 105.6 (d, 1-C), 113.0 (s, C_i), 150.5 (d, 6-C); MS (e.i., 70 eV): m/z (%) = 184 (4), 169 (9), 167 (9), 126 (8), 100 (14), 97 (17), 86 (9), 71 (11), 59 (11), 55 (100); MS (c.i., isobutane): $m/z = 185$ ($[M+1]^+$); Anal. Calcd for $C_9H_{12}O_4$ (184.19): C, 58.69; H, 6.57. Found: C, 58.61; H, 6.63.

3.8. 3,6-Anhydro-5-deoxy-1,2-*O*-isopropylidene-α-D-erythro-hex-4-enofuranose 8

A solution of **7** (0.9 g, 4.9 mmol) in dry DMSO containing potassium *tert*-butoxide (0.2 g, 1.8 mmol) was stirred for 30 min at 25 °C; work up as described for **7** gave **8** (0.7 g, 77%) as a white solid. Mp 77–88 °C; R_F (toluene/ethyl acetate 3:1) 0.51; $[\alpha]_D = +68$ (*c* 1, $CHCl_3$); IR (KBr): $\nu = 3446$s, 2932s, 1759s, 1636m, 1463m, 1376m, 1261s, 1165s, 1072s cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.47$ (s, 3H, Me), 1.54 (d, $J = 0.9$ Hz, 3H, Me), 4.56 (ddd, $J = 2.7$, 3.6, 11.2 Hz, 1H, 6-H_A), 4.68 (d, $J = 5.2$ Hz, 1H, 2-H), 4.77 (ddd, $J = 1.4$, 4.9 Hz, 1H, 6-H_B), 5.01 (ddd, $J = 3.3$, 3.6, 4.9 Hz, 1H, 3-H), 5.97 (dd, $J = 0.9$, 5.2 Hz, 1H, 1-H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 27.9$ (q, Me), 28.4 (q, Me), 77.4 (t, 6-C), 82.8 (d, 3-C), 87.8 (d, 2-C), 97.9 (d, 5-C), 111.7 (d, 1-C), 115.8 (s, C_i), 156.0 (s, 4-C); MS (e.i., 70 eV): m/z (%) = 184 (10), 167 (16), 149 (29), 127 (26), 115 (26), 97 (30), 87 (50), 85 (80), 73 (39), 57 (100); MS (c.i., isobutane): $m/z = 185$ ($[M+1]^+$); Anal. Calcd for $C_9H_{12}O_4$ (184.19): C, 58.69; H, 6.57; C, 58.62; H, 6.61.

3.9. (*4R*,*5R*) 2,2-Dimethyl-5-[(2*R*)-3-oxotetrahydro-2-furanyl]-1,3-dioxolan-4-yl acetate [(1*R*)-1-*O*-acetyl-3,6-anhydro-5-deoxy-1,2-*O*-isopropylidene-L-threose] 1

A solution of **8** (0.8 g, 4.3 mmol) in abs. dichloromethane (25 mL) containing glacial acetic acid (0.4 g, 6.64 mmol) was stirred for 2 h at room temperature. The solvents were removed under diminished pressure and the residue subjected to chromatography (silica gel, toluene/ethyl acetate 15:1) to afford **1** (0.76 g, 72%); an analytical sample was obtained by recrystallization from hexane. Mp 80–82 °C; R_F = (toluene/ethyl acetate 15:1) 0.16; $[\alpha]_D = +159.8$ (*c* 1.1, $CHCl_3$); IR (KBr): $\nu = 3440$w, 2995m, 2945m, 1765s, 1740s, 1460w, 1390s, 1370s, 1240s, 1215s, 1170s, 1130s, 1075s, 1040s, 1015s cm^{-1}; ^{1}H

NMR (400 MHz, $CDCl_3$): $\delta = 1.45$ (s, 3H, Me), 1.48 (s, 3H, Me), 2.07 (s, 3H, CH-OAc), 2.48 (ddd, $J = 7.6$, 7.8, 8.0 Hz, 1H, 5-H_A), 2.53 (ddd, $J = 6.1$, 7.2, 7.6 Hz, 1H, 5-H_B), 4.02 (d, $J = 2.6$ Hz, 1H, 3-H), 4.20 (ddd, $J = 7.6$, 7.8, 8.9 Hz, 1H, 6-H_A), 4.37 (ddd, $J = 6.7$, 6.9, 7.8 Hz, 1H, 6-H_B), 4.44 (t, $J = 2.6$ Hz, 1H, 2-H), 6.28 (d, $J = 2.7$ Hz, 1H, 1-H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 21.3$ (q, Me of OAc), 26.5 (q, Me), 26.9 (q, Me), 37.2 (t, 5-C), 66.1 (t, 6-C), 76.7 (d, 3-C), 82.5 (d, 2-C), 96.9 (d, 1-C), 113.3 (s, C_i), 170.1 (s, CO of Ac), 212.9 (s, 4-C); MS (e.i., 70 eV): m/z (%) = 229 (21), 187 (24), 159 (31), 145 (15), 127 (29), 101 (51), 86 (100), 71 (14), 59 (47), 55 (45); MS (c.i. isobutane): $m/z = 245$ ($[M+1]^+$); Anal. Calcd for $C_{16}H_{16}O_6$ (244.25): C, 54.09; H, 6.60. Found: C, 54.31; H, 6.72.

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