Hydroxycyclopentanone Derivatives from D-Mannose via Ring Closing Metathesis: An Improved Synthesis of a Key Intermediate of Tricyclo-DNA

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Abstract: A large scale, 10 step synthesis of cyclopentanone **1**, starting from the chiral pool compound D-mannose, is described. The synthesis proceeds via a ring closing metathesis reaction as the key step in an overall yield of 23%. Cyclopentanone **1** is a central intermediate for the synthesis of tricyclo-DNA.

Key words: carbohydrates, metathesis, ring closure, ruthenium, ketones

In an ongoing effort to design, synthesize and evaluate new DNA-analogues for applications as antisense agents in human therapy or diagnosis we recently embarked on a detailed study of tricyclo-DNA (Figure 1).[1] This analogue belongs to the class of conformationally constrained DNA-analogues[2] and shows increased thermal duplex stabilities with complementary natural DNA and, especially, RNA.[1d] Recent very successful biological antisense experiments with tricyclo-DNA[1e] led to a sharply increased demand in the corresponding building blocks for oligonucleotide synthesis.

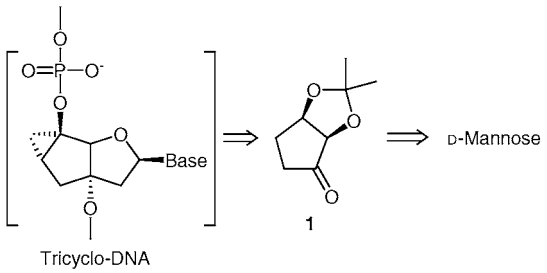
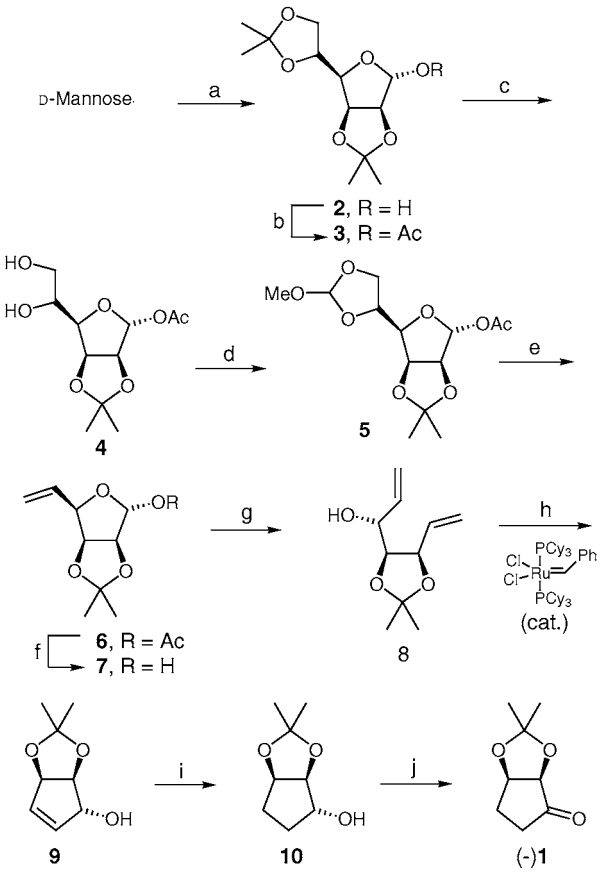


Figure 1 Retrosynthetic correlation of tricyclo-DNA via cyclopentanone **1** to D-mannose

The current synthesis of the corresponding tricyclodeoxynucleosides starts from cyclopentanone and proceeds via racemic **1**.[3] Elaboration into enantiopure intermediates occurs at a later stage via an esterase catalyzed kinetic resolution step.[3b] The inefficiency of this procedure and its limitations in the scale-up prompted us to search for a novel, enantiopure approach that can be performed on a large scale in a practical way.

We describe here a synthetic access to the key intermediate (–)-**1** starting from the commercially available chiral pool compound D-mannose. The described transformations follow a recent synthesis of intermediate **9** by van Boom and co-workers.[4] We have now optimized and adapted this pathway to >100 gram scale, and extended it to the synthesis (–)-**1**. An alternative, carbohydrate based approach, leading to the unprotected form of triol **9** was recently reported, too.[5]



Scheme 1 Reagents: (a) $Me_2C(OMe)_2$, TsOH, 60 °C, 4 h; (b) Ac_2O, pyridine, r.t.,16 h; (c) 64% aq HOAc, 55 °C, 4 h; (d) $HC(OMe)_3$, reflux, 30 min; (e) Ac_2O, 125 °C, 3 h; (f) MeOH, *t*-BuOK, r.t., 46% from D-mannose; (g) NaH, DMSO, $BrCH_2P(Ph)_3$, 65 °C, 4 h, 60%; (h) 0.05 mol% cat., CH_2Cl_2, r.t., 24 h, 89%; (i) 10% Pd/C, H_2, MeOH, r.t., 16 h, 97%; (j) PCC, CH_2Cl_2, r.t., 16 h, 85%

Diacetal **2** was prepared from D-mannose according to a known procedure.[6] The obtained material after evaporation of the solvents was pure enough to be used directly in the next step. As the protecting group for the anomeric hydroxyl function we preferred the acetate[7] (→ **3**) over the

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previously reported benzoate group[4] due to easier separation of byproducts during distillation. Hydrolysis of the 5,6-isopropylidene group (→ **4**) was effected in aqueous acetic acid (64%) at 55 °C.[8] Compound **4** was obtained by simple evaporation of the solvents and was of sufficient purity to be used in the next step. Subsequent transformation into the methyl orthoformate **5** proceeded smoothly and required no addition of acid as catalyst.[9] Most likely residual HOAc in the starting material was sufficient to catalyze the reaction. We preferred the use of methyl over ethyl orthoformate due to easier removal of the solvents and byproducts upon evaporation. Also in this case, no further purification was necessary. The thermal rearrangement to **6** was effected by treatment of **5** in neat acetic anhydride at 130 °C.[9] The resulting crude **6**, obtained after quenching the reaction with EtOH and removal of the solvents, could be used directly in the following transesterification step to give **7** [10] in pure form after distillation and crystallization. The overall yield over the six steps from D-mannose to **7** amounted to an excellent 46%. The subsequent Wittig reaction utilizing the DMSO anion as the base for ylide production [11] furnished diene **8** in 60% yield after distillation. No traces of products arising from epimerization in the α-position to the anomeric center was observed.

Ring closing metathesis of **8** in dichloromethane proceeded smoothly even on a 100 g scale with 0.05% of the Grubbs' catalyst.[5,12] As the first intermediate in the whole synthesis the resulting cyclopentene **9** had to be purified by column chromatography (catalyst removal) and was obtained in 89% yield. Subsequent hydrogenolysis of **9** (H_2, 10% Pd/C) at atmospheric pressure resulted in the formation of **10** in almost quantitative yield. The subsequent oxidation step to (–)-**1** proved to be somewhat difficult. Given the large scale we refrained from using iodine(V) reagents[13] due to safety reasons (explosive). Catalytic perruthenate oxidation[14] required up to 10 mol% of catalyst and resulted in incomplete conversion of **10**. After screening of a series of transition metal oxidants we finally found PCC to work satisfactorily and to give ketone (–)-**1** in 85% yield. Thus, an overall yield of 23% for (–)-**1** was obtained over the 10 steps of this synthesis. This is a substantial improvement over the previously reported (shorter) synthesis, in which **1** was obtained in only 12% overall yield and as a racemate.

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AC-300 spectrometer (TMS as the internal standard; *J* values are given in Hz). LSIMS and EI mass spectral analysis were recorded on a Micromass Autospec Q, matrix: 3-nitrobenzyl alcohol; ESI-MS on VG platform Fisons instruments; ESI-Lock Mass (HRMS) on Applied Biosystem/MDS Sciex Qstar. Optical rotations were measured on a Perkin–Elmer 241 polarimeter (d = 10 cm, *c* in g/100 mL). Mps were obtained on a Büchi 510 mp apparatus and are uncorrected. Flash chromatography (CC) was performed using silica gel with an average particle size of 50 μm. All chemicals were from Acros, Fluka or Aldrich and were reagent grade. Solvents were of technical quality and distilled prior to use.

2,3:5,6-Di-*O*-isopropylidenemannopyranose (2)

To a suspension of D-(+)-mannose (360 g, 2.0 mol) and 2,2-dimethoxypropane (1.08 L, 8.8 mol) was added TsOH monohydrate (1.0 g, 5.26 mmol). After mechanical stirring for 1 h at 50 °C (exothermic reaction), the mixture was heated to reflux (60 °C). Over a period of 4 h, solvent (270 mL) was distilled off. The clear colorless solution was then cooled to r.t., treated with sat. aq K_2CO_3 (2 mL) and stirred for another 20 min. After evaporation of the solvents and drying (high vacuum, 0.2 mbar, 4 h) the crude product **2** (536.8 g), obtained as a crystalline mash, was used immediately without further purification in the next step. Spectral data are from a recrystallized (toluene) sample. Ratio of anomers α:β 100:17 (^{1}H NMR). Only data for the α-anomer are given.

R_f 0.52 (hexane–EtOAc, 1:4); mp 123–124 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28, (s, 3 H), 1.33 (s, 3 H), 1.41 (s, 3 H), 1.42 (s, 3 H), 3.88 (br s, 1 H), 3.99–4.06 (m, 2 H), 4.12 (dd, 1 H, *J* = 6.99, 3.69), 4.31–4.41 (m, 1 H), 4.56 (d, 1 H, *J* = 5.88), 4.76 (dd, 1 H, *J* = 5.88, 3.69).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 24.30, 25.01, 25.69, 26.64, 66.35, 73.18, 79.49, 79.87, 85.38, 100.99, 109.01, 112.46.

MS (LSIMS): *m*/*z* = 261 $[M + H]^+$.

1-*O*-Acetyl-2,3:5,6-di-*O*-isopropylidenemannopyranose (3)

The crude product **2** (536 g, estim. 2.0 mol) was dissolved in anhyd pyridine (330 mL). Ac_2O (378 mL, 4.0 mol) was added at 0 °C under Ar over a period of 30 min. The mixture was stirred for 1 h at 17–22 °C, and then overnight at r.t. The excess of anhydride was quenched with abs. EtOH (180 mL) at 0 °C. After removal of solvents under reduced pressure (60 °C, 6 mbar) crude **9** (630 g) containing traces of HOAc (5.6%, ^{1}H NMR) was obtained as a viscous oil and used without further purification in the next step.

R_f 0.68 (hexane–EtOAc, 1:4).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 3 H), 1.38 (s, 3 H), 1.46 (s, 3 H), 1.48 (s, 3 H), 2.07 (s, 3 H), 3.99–4.13 (m, 3 H), 4.36–4.44 (m, 1 H), 4.70 (d, 1 H, *J* = 5.88), 4.85 (dd, 1 H, *J* = 5.88, 3.69), 6.12 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.03, 24.60, 25. 06, 25.88, 26.95, 66.75, 72.83, 79.23, 82.14, 84.98, 100.72, 109.30, 113.21, 169.39.

MS (LSIMS): *m*/*z* = 303 $[M + H]^+$.

1-*O*-Acetyl-2,3-*O*-isopropylidenemannopyranose (4)

Crude **9** (630 g, estim. 2.0 mol) was dissolved in 64% aq HOAc (3.6 L). The reaction mixture was then heated to 55 °C and acetone (60 mL, 80–190 mbar) was distilled off over a period of 4 h. All solvents were then evaporated under reduced pressure. The crude diol **4** (568.5 g) was obtained as a yellow syrup, which was used directly in the next step.

R_f 0.31 (hexane–EtOAc, 1:4).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 3 H), 1.48 (s, 3 H), 2.06 (s, 3 H), 3.71 (dd, 1 H, *J* = 11.76, 5.52), 3.87 (dd, *J* = 11.76, 5.52, 1 H), 3.98–4.11 (m, 2 H), 4.70 (d, *J* = 5.88, 1 H), 4.88–4.95 (m, 1 H), 6.15 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.95, 24.63, 25.84, 63.87, 69.71, 79.57, 81.07, 84.63, 100.56, 113.15, 169.58.

MS-ESI: *m*/*z* = 285 $[M + Na]^+$.

1-*O*-Acetyl-5,6-*O*-methoxymethylene-2,3-*O*-isopropylidene-mannopyranose (5)

The crude diol **4** (568.5 g, estim. 2.0 mol), containing traces of AcOH, was refluxed in $HC(OMe)_3$ (1.094 L, 10.0 mol). After 30 min the solution was cooled to r.t. and the solvent removed under reduced pressure (45–50 °C, 6 mbar). The crude orthoester **5** (634 g, α:β 86:13) was obtained as a viscous syrup and was used without

further purification in the next step. Analytical data are from a recrystallized (MeOH) sample.

R_f 0.64 (hexane–EtOAc, 1:4); mp 99–100 °C.

^{1}H NMR (300 MHz, C_6H_6, only signals of α-anomer): δ = 1.12 (s, 3 H), 1.37 (s, 3 H), 1.53 (s, 3 H), 3.11 (s, 3 H), 3.96–4.05 (m, 1 H), 4.12–4.21 (m, 1 H), 4.31–4.42 (m, 2 H), 4.52–4.63 (m, 2 H), 5.75 (s, 1 H), 6.45 (s, 1 H).

^{13}C NMR (75 MHz, C_6H_6): δ = 20.40, 24.57, 25.99, 51.23, 66.85, 73.15, 79.79, 83.19, 85.50, 101.20, 112.97, 116.64, 168.53.

MS (LSIMS): *m*/*z* = 327 $[M + Na]^+$.

HRMS-ESI: *m*/*z* calcd for $C_{13}H_{20}O_8Na$ $[M + Na]^+$: 327.1055; found: 327.1042.

1-*O*-Acetyl-5,6-dideoxy-2,3-*O*-isopropylidene-α-D-lyxo-5-hexenofuranose (6)

The crude orthoester **5** (634 g, estim. 2.0 mol) was dissolved in Ac_2O (1.512 kg, 14.81 mol), and the resulting reaction mixture was carefully heated under stirring. At 125 °C, vigorous gas evolution started. Heating was continued and solvents (80 mL) were distilled off at the temperature range of 127–130 °C. After 3 h the reaction was cooled to r.t. The excess Ac_2O was quenched with abs EtOH (900 mL) at 0 °C. After the exothermic reaction had stopped, stirring was continued for 30 min and the solvent evaporated under reduced pressure (50 °C, 6 mbar). Crude **6** (474 g) was obtained as a brown oil which was used without further purification in the next step.

R_f 0.44 (hexane–EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3 H), 1.48 (s, 3 H), 2.07 (s, 3H), 4.70–4.77 (m, 2 H), 5.39 (dd, *J* = 17.31, 10.28), 5.95 (ddd, 1 H, *J* = 17.31, 10.28, 7.32), 6.17 (s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.92, 24.86, 25.95, 81.02, 83.17, 85.14, 100.46, 113.00, 119.47, 131.42, 169.30.

HRMS-ESI: *m*/*z* calcd for $C_{11}H_{16}O_5Na$ $[M + Na]^+$: 251.0895; found: 251.0895.

5,6-Dideoxy-2,3-*O*-isopropylidene-α-D-lyxo-5-hexenofuranose (7)

Crude **6** (474 g, estim. 2.0 mol) was dissolved in MeOH (1.0 L), and *t*-BuOK (85 g, 0.76 mol) was added slowly at 0 °C. After stirring at r.t. until TLC showed complete conversion, the solvents were reduced in vacuo and the residue poured on ice and neutralized with aq HCl (2 M). The aq phase was extracted with EtOAc–hexane (1:1; 1 × 500 mL, 2 × 150 mL), the combined organic phases were washed with sat. aq $NaHCO_3$ (100 mL) and brine (100 mL). After treatment with charcoal and drying ($MgSO_4$), the solvent was removed and crude **7** (379.9 g) was obtained as a yellow oil. Distillation followed by crystallization from hexane (–20 °C) gave analytically pure **7**.

Yield: 171.3 g [46% from D-(+)-mannose **1** (6 steps)]; R_f 0.25 (hexane–EtOAc, 3:1); bp 69–74 °C, (0.04 mbar); mp 57–58 °C; $[\alpha]_D^{25}$ –33.6 (*c* 1.2, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (s, 3 H), 1.54 (s, 3 H), 2.84 (br s, 1 H), 4.54–4.75 (m, 3 H), 5.32–5.44 (m, 3 H), 5.99 (ddd, 1 H, *J* = 17.64, 10.29, 7.35).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.78, 25.97, 81.38, 81.43, 85.72, 96.64, 100.94, 112.57, 119.24, 132.06.

MS (LSIMS): *m*/*z* = 187 $[M + H]^+$.

(1*R*,4′*S*,5′*R*)-1-(2′,2′-Dimethyl-5′-vinyl[1′,3′]dioxol-4′-yl)prop-2-en-1-ol (8)

To a suspension of NaH (55–65%, 61.4 g, 1.53 mol) in anhyd THF (3.9 L) was added at 0 °C (mechanical stirring) anhyd DMSO (194 mL, 2.73 mol) within 15 min. After 30 min at r.t., $BrCH_2P(Ph)_3$ (644 g, 1.8 mol) was added at once, followed by a solution of **7** (171 g, 0.91 mol) in anhyd THF (150 mL) at 0 °C after 2 h. The reaction mixture was carefully warmed to r.t. and gradually (gas evolution) warmed up to 65 °C. After 4 h at reflux, the mixture was cooled to r.t., diluted with hexane (1.0 L), filtered over Celite and washed with hexane (4 × 500 mL). The solvents were evaporated, the residue triturated in H_2O (700 mL) and extracted with *t*-BuOMe (3 × 500 mL). The combined organic phases were washed with H_2O (5 × 100 mL), sat aq $NaHCO_3$ (100 mL), brine (100 mL) and dried. After evaporation, the residue was purified by distillation to give **8**.

Yield: 88.5 g (60%); colorless oil; R_f 0.42 (hexane–EtOAc, 7:3); bp 58–68 °C, 0.05 mbar; $[\alpha]_D^{25}$ –17.1 (*c* 0.77, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40 (s, 3 H), 1.54 (s, 3 H), 1.78–2.42 (br s, 1 H), 4.05–4.17 (m, 2 H), 4.61 (t, 1 H, *J* = 6.98), 5.21–5.47 (m, 4 H), 5.79–6.10 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.94, 27.33, 70.49, 78.86, 80.58, 108.70, 116.97, 119.29, 133.88, 136.61.

MS (LSIMS): *m*/*z* = 185 $[M + H]^+$.

HRMS-ESI: *m*/*z* calcd for $C_{10}H_{16}O_3Na$ $[M + Na]^+$: 207.0997; found: 207.1000.

(1*R*,3*S*,4*R*)-2,2-Dimethyl-4,6a-dihydro-3a*H*-cyclopenta[1,3]dioxol-4-ol (9)

To a solution of **8** (88.0 g, 0.478 mol) in anhyd CH_2Cl_2 (4.8 L) was added under Ar benzylidenebis(tricyclohexylphosphine)dichlororuthenium (1.97 g, 2.39 mmol). The dark red solution was stirred for 24 h at r.t. The solvent was evaporated and the residue purified by CC (800 g SiO_2; gradient of 50–80% *t*-BuOMe in hexane). To remove residual catalyst components, the product was dissolved in *t*-BuOMe (300 mL), treated with charcoal, filtered over a short pad of SiO_2 and the solvent evaporated to give **9**.

Yield: 63.9 g (89%); colorless oil; R_f 0.19 (hexane–EtOAc, 7:3); $[\alpha]_D^{25}$ –118.1.0 (*c* 0.95, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 3 H), 1.40 (s, 3 H), 1.81 (d, 1 H, *J* = 6.24), 4.52 (d, 1 H, *J* = 5.52), 4.80 (d, 1 H, *J* = 5.52), 5.29 (d, 1 H, *J* = 5.52), 5.91 (m, 1 H), 6.03 (d, 1 H, *J* = 5.52).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.55, 27.13, 80.53, 84.15, 85.74, 111.55, 134.67, 135.00.

HRMS-ESI: *m*/*z* calcd for $C_8H_{12}O_3Na$ $[M + Na]^+$: 179.0684; found: 179.0678.

(1*R*,3*S*,4*R*)-2,2-Dimethyltetrahydrocyclopenta[1,3]dioxol-4-ol (10)

A solution of **9** (63.0 g, 0.403 mol) in anhyd MeOH (300 mL) was charged with Pd/C (10%; 1.26 g) at 0 °C and hydrogenated (H_2) at atmospheric pressure overnight at r.t. The reaction mixture was filtered through a pad of SiO_2 and washed with MeOH. After evaporation of the solvent, **10** was obtained.

Yield: 62.0 g (97%); white solid; R_f 0.34 (hexane–EtOAc, 3:1); mp 65 °C, $[\alpha]_D^{25}$ –9.0 (*c* 0.8, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 3 H), 1.41 (s, 3 H), 1.61–1.65 (m, 1 H), 1.83–2.00 (m, 3 H), 4.18 (d, 1 H, *J* = 3.66), 4.36 (dd, 1 H, *J* = 5.52, 1.47), 4.76 (t, 1 H, *J* = 4.79).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.69, 25.99, 29.88, 30.47, 76.12, 80.26, 86.40, 109.71.

MS (EI): *m*/*z* = 143 $[M + CH_3]^+$.

HRMS-ESI: *m*/*z* calcd for $C_8H_{14}O_3Na$ $[M + Na]^+$: 181.0840; found: 181.0836.

(1*R*,3*S*)-2,2-Dimethyltetrahydrocyclopenta[1,3]dioxol-4-one (1)
To a solution of **10** (56 g, 0.354 mol) in anhyd CH_2Cl_2 (500 mL) was added pyridinium chlorochromate (130.0 g, 0.60 mol) in one portion at 0 °C. After stirring overnight at r.t., the dark reaction mixture was filtered through a pad of SiO_2 (200 g) and the filtrate treated with charcoal to give an almost colorless solution. Evaporation of the solvent afforded **1**.

Yield: 47.0 g (85.0%); white fluffy crystals; R_f 0.17 (hexane–EtOAc, 4:1); mp 46–47 °C; $[\alpha]_D^{25}$ –55.8 (*c* 1.07, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 3 H), 1.43 (s, 3 H), 1.98–2.11 (m, 1 H), 2.21–2.32 (m, 2 H), 2.53–2.66 (m, 1 H), 4.18 (d, 1 H, *J* = 4.80), 4.82 (t, 1 H, *J* = 4.59).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.38, 24.82, 26.71, 32.98, 77.31, 78.94, 112.03, 170.97, 214.86.

MS (EI): *m*/*z* = 156 $[M + H]^+$.

HRMS-EI: *m*/*z* calcd for $C_8H_{12}O_3$ $[M]^+$: 156.07864; found: 156.07860.

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