A Silicon-Mediated Synthesis of 3-Deoxy-D-*manno*-octulosonic Acid (KDO)

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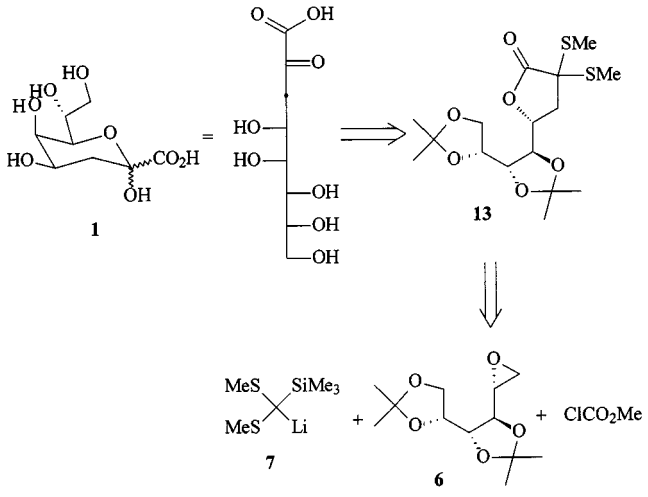
KDO (**1**) is synthesized in five steps, starting from 1,2-anhydro-3,4:5,6-di-*O*-isopropylidene-D-mannitol (**6**). The epoxide **6**, obtained from D-mannitol (**2**), reacts with lithiated silyl dithioacetal **7**, followed by acylation of the alcoholate, to the carbonate **9**. Silicon-induced lactonization affords the lactone **10**, which can be converted into NH_4-KDO by standard deprotection procedures.

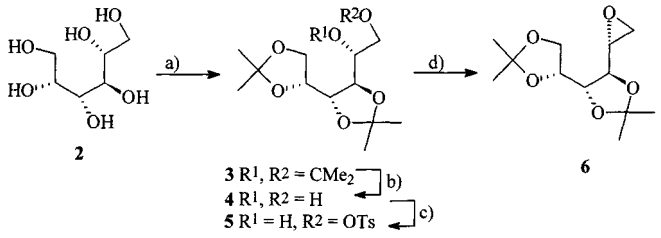
3-Deoxy-D-*manno*-2-octulosonic acid (KDO) (**1**) is an essential component in the outer-cell membrane lipopolysaccharides (LPS) of Gram-negative bacteria[1]. Because of its biological importance, the chemistry of KDO has attracted wide interest and several total syntheses of KDO have been reported. The majority of the syntheses start from D-mannose[2] or D-arabinose[3] derivatives and C_2 or C_3 building blocks, respectively. However, the control of the configuration at C-4 is a major disadvantage of the [5 + 3] strategy. Here, we wish to report the construction of the KDO skeleton following a [6 + 1 + 1] strategy. This synthesis, starting from D-mannitol (**2**), involves an epoxide ring-opening reaction by lithiated silyl dithioacetal **7**, subsequent *O*-acylation with methyl chloroformate and a silicon-induced lactonization as key steps (Figure 1).

Figure 1. Retrosynthetic analysis



Epoxide **6** is available in four conventional steps in 53% overall yield taking advantage of the C_2 symmetry of D-mannitol (**2**). Thus, D-mannitol (**2**) is converted into 1,2:3,4:5,6-tri-O-isopropylidene-D-mannitol (**3**)[4]. Mild acid treatment of **3** with 15% acetic acid in EtOH/H_2O (2:1) allows the selective deprotection of only one of the two stereochemically identical terminal ketal groups in a yield of 25% together with starting compound (73%)[5]. This reaction can be directed to a maximum of deprotected **4** and a minimum of double deprotected product and D-mannitol (**2**). Monotosylation of **4** with tosyl chloride/pyridine to give **5** and subsequent cycloelimination with potassium carbonate[6] afford 1,2-anhydro-3,4:5,6-di-*O*-isopropylidene-D-mannitol (**6**) (Scheme 1).

Scheme 1



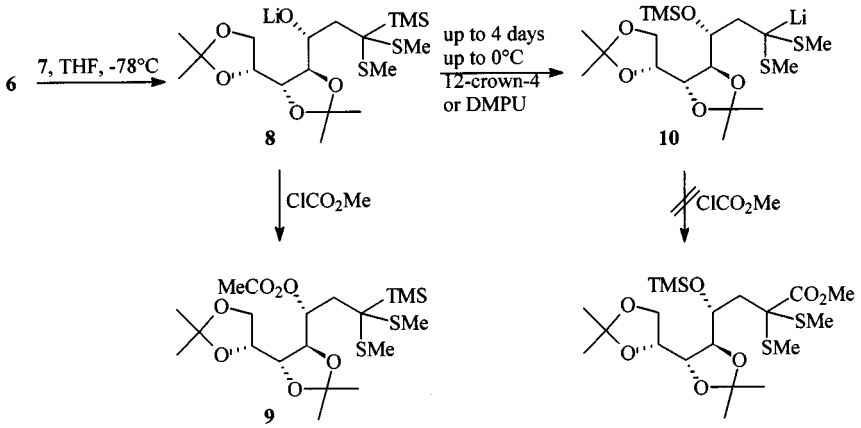
a) acetone, conc. H_2SO_4 (87%); b) 15% acetic acid, EtOH/H_2O (2:1) (92%, based on recovered starting material); c) *p*TsCl, pyridine; d) K_2CO_3, MeOH (66% over 2 steps)

Our original plan was to establish the C_8 framework of KDO in a reaction cascade of epoxide ring opening, Brook 1,4-silyl shift[7] and *C*-acylation by analogy with our cycloalkane synthesis[8] and with the bis(hydroxyalkylation) of anions of type **7**[9]. However, quenching the reaction mixture as formed from epoxide **6** and lithium salt **7** with methyl chloroformate only gave acylation product **9** along with protonated **10** (Scheme 2).

The failure to detect any unreacted epoxide **6** confirms that epoxide ring opening with the bisnucleophilic lithiated silyl dithioacetal **7** takes place quantitatively. However, apparently, the Brook 1,4-rearrangement does not go to completion, but gives an equilibrium mixture of **8** and silyl ether **10**.

  1434–193X/98/1212–2729 $ 17.50+.50/0

Scheme 2

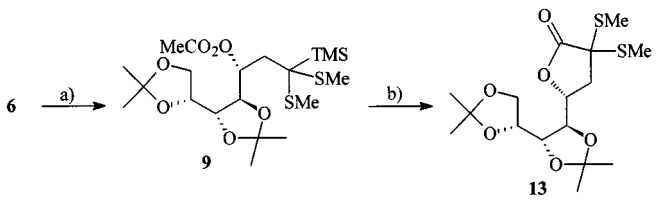


Such an equilibrium may be characteristic of most Brook 1,4-rearrangements, but passed unnoticed where the second electrophile is present in the molecule and in an intramolecular process removes the rearranged silyl ether from the equilibrium driving the reaction cascade to completion. In the present case, change of temperature and solvent, extension of reaction time or addition of a cation-complexing reagent (e.g. 12-crown-4, DMPU) did not lead to more than 57% of **10**, i.e. did not allow quantitative 1,4-migration.

Moreover, methyl chloroformate as electrophile did not quench any present **10**. The difficult acylation of sulfur-stabilized carbanions is a well-known problem[10]. Even a 40fold excess of methyl chloroformate or methyl cyanoformate, a more reactive acylating reagent, did not yield any *C*-acylation product. Only *O*-acylated **9** (9%), obtained from unrearranged lithium alcoholate, could be isolated. So, alternatively the construction of the C_8 skeleton of KDO was pursued in a reaction sequence including epoxide ring opening, subsequent *O*-acylation and silicon-induced lactonization (Scheme 3).

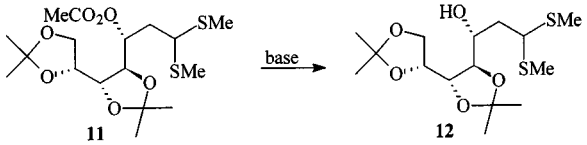
Epoxide ring opening of **6** with lithiated silyl dithioacetal **7** takes place at −78°C within 2 hours. A higher reaction temperature should be avoided as otherwise the silyl migration starts. *O*-Acylation affords carbonate **9**, which can be converted into lactone **13** by silicon-induced lactonization with TBAF at −78°C in 51% yield over 2 steps. Protodesilylated **11** can be isolated as a byproduct (up to 31%) in the silicon-induced lactonization.

Scheme 3

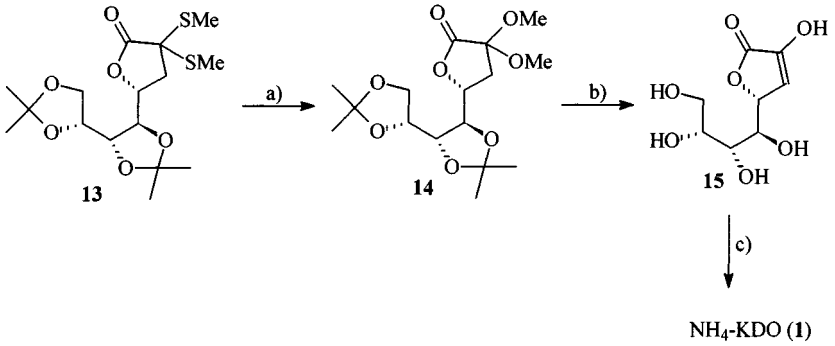


a) 7, -78 °C, 2 hours, then $ClCO_2Me$, -78 °C (74%); b) TBAF, -78 °C (69%)

Scheme 4



Scheme 5



a) [bis(trifluoroacetoxy)iodo]benzene, abs. MeOH (61%); b) 95% CF_3CO_2H (81%); c) 25% NH_3

Exploratory studies have shown that anion generation by desilylation is essential for lactonization. Attemps to obtain the lactone **13** by deprotonation of dithioacetal **11** with different bases yield only the corresponding alcohol **12** (up to 86%, Scheme 4).

Direct conversion of the dithioacetal **13** into the corresponding ketone failed with various methods[10][11]. A two-step process which was required, following the Stork protocol[12], allowed transformation into the dimethyl ketal and subsequently liberation of the carbonyl group with 95% trifluoroacetic acid (Scheme 5).

The known KDO precursor **15**[3a] can be converted into the ammonium salt of KDO (**1**)[13]. So we have achieved a convenient synthesis of KDO (**1**) starting from commercially available D-mannitol. Thus, following a [6 + 1 + 1] strategy for construction of the KDO framework, this synthesis leads to KDO (**1**) in only 9 steps. With respect to yields, availability of reagents and convenience this approach nicely complements related syntheses[2b][2c].

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Experimental Section

General: ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker DPX-200 (200 MHz) instrument using dilute solutions in $CDCl_3$ with TMS as internal standard. Chemical shift values are given in parts per million (ppm). − Infrared spectra were recorded using a Pye-Unicam SP 3−200 or a Bruker Vektor 22 spectrometer as neat film or as KBr pellet. − Elemental analyses were determined in the Institut für Pharmazeutische Chemie, Technische Universität Braunschweig. − The high-resolution mass spectrum was provided by the Hans-Knöll-Institut für Naturstoff-Forschung, Jena. − Column chromatography was carried out using Merck silica gel 6 (70−230 mesh). 1,2:3,4:5,6-Tri-*O*-isopropylidene-D-mannitol (**3**)[4] and bis(methylthio)(trimethylsilyl)methane (**7**)[14] were obtained as described in the literature. − Abbreviations: EE: ethyl acetate; PE: petroleum ether.

3,4:5,6-Di-O-isopropylidene-D-mannitol (**4**): A solution of **3** (4.535 g, 15 mmol) in EtOH/H_2O (2:1, 15 ml/mmol) and 15% acetic acid (5 ml/mmol) was stirred at 60°C for 1 h. The reaction mixture was hydrolysed with dichloromethane/saturated $NaHCO_3$ solution (1:1). The aqueous phase was separated and extracted twice with dichloromethane. The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated. The crude product was purified by column chromatography (PE/EE, 1:1) to give 978 mg (25%) of **4** as a colorless solid (m.p. 36°C) and 3.305 g (73%) recovered starting material **3**. − ^{1}H NMR: δ = 1.37, 1.38, 1.39, 1.47 (each s, 3 H, Me), 2.31 (t, *J* = 6.4 Hz, 1 H, CH_2OH), 3.70−3.82 (m, 5 H), 3.91 (t, *J* = 7.2 Hz, 1 H), 4.01−4.10 (m, 2 H), 4.23 (dd, *J* = 5.6, 8.0 Hz, 1 H). − ^{13}C NMR: δ = 25.0, 26.3, 26.7, 26.8 (Me), 63.8 (C-1), 68.0 (C-6), 72.1, 76.4, 80.7, 80.8 (C-2, C-3, C-4, C-5), 109.6 and 110.3 (Me_2C). − IR: $\tilde{\nu}$ = 3420, 2970, 2920, 2870, 1450, 1370, 1245, 1230, 1205, 1150, 1065, 865, 835, 750 cm^{-1}. − $[\alpha]_D^{20}$ = +5.0 (*c* = 1.0, $CHCl_3$).

1,2-Anhydro-3,4:5,6-di-O-isopropylidene-D-mannitol (**6**): A solution of **4** (4.676 g, 17.83 mmol) in dry pyridine (2 ml/mmol) was cooled to −10°C. 3.4 g of tosyl chloride was added and the reaction mixture was stirred at −10°C for 1 d. Pyridine was evaporated under reduced pressure using toluene as co-solvent. The resulting solid was dissolved in dichloromethane and was washed with saturated $NaHCO_3$ solution, water and brine. After drying ($MgSO_4$), the solvent was evaporated and the obtained crude tosylate was used without further purification. The tosylate was dissolved in methanol (3 ml/mmol) and K_2CO_3 (6.159 g) was added at room temperature. The reaction mixture was stirred at 25°C and the reaction was monitored by TLC. After complete conversion, the mixture was filtered, diluted with dichloromethane, washed with saturated NH_4Cl solution and brine, dried ($MgSO_4$) and concentrated. Column chromatography (PE/EE, 20:1) afforded 2.9 g (67% over two steps) of **6** as a colorless oil. − ^{1}H NMR: δ = 1.29, 1.33, 1.35, 1.36 (each s, 3 H, Me), 2.75 (dd, *J* = 3.8, 5.2 Hz, 1 H, 1-H), 2.77 (dd, *J* = 2.8, 5.2 Hz, 1 H, 1-H), 3.14 (q, *J* = 3.4 Hz, 1 H, 2-H), 3.75 (t, *J* = 7.2 Hz, 1 H), 3.89 (dd, *J* = 4.4, 7.6 Hz, 1 H), 4.00 (dd, *J* = 3.4, 6.8 Hz, 1 H, 3-H), 4.01−4.10 (m, 2H). − ^{13}C NMR: δ = 24.2, 25.6, 25.7 and 26.0 (Me), 43.2 (C-1), 50.9 (C-2), 66.4 (C-6), 75.6, 77.6, 77.7 (C-3, C-4, C-5), 108.7 and 109.0 (Me_2C). − IR: $\tilde{\nu}$ = 2980, 2920, 2870, 1450, 1370, 1250, 1205, 1150, 1060, 985, 905, 840 cm^{-1}. − $C_{12}H_{20}O_5$ (244.2): calcd. C 59.00, H 8.25; found C 58.73, H 8.53. − $[\alpha]_D^{24}$ = +7.8 (*c* = 1.0, $CHCl_3$).

2-Deoxy-4,5:6,7-di-O-isopropylidene-3-O-methoxycarbonyl-1-trimethylsilyl-D-manno-heptose Dimethyl Thioacetal (**9**): To a solution of protonated **7** (1.3 equiv.) in dry THF (4 ml/mmol) 1.1 equiv. of *n*BuLi (1.6 M in hexane) was added at −78°C. The solution was stirred at 0°C for 2 h and cooled again to −78°C. 250 mg (1.023 mmol) of **6** in dry THF (4.1 ml) was added dropwise, the reaction mixture allowed to warm to −70°C and stirred until complete epoxide ring opening had been achieved (monitored by TLC). Subsequently, the reaction mixture was added to a stirred solution of methyl chloroformate (40 equiv.), dissolved in the same volume of dry THF, via a cannula at −78°C. The mixture was allowed to warm to room temperature within 12 h and then hydrolysed with diethyl ether/saturated NH_4Cl solution (1:1). The aqueous phase was extracted twice with diethyl ether, the combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Column chromatography (PE/EE, 40:1) afforded 363 mg (74%) of **9** as a colorless oil. − ^{1}H NMR: δ = 0.25 (s, 9 H, $SiMe_3$), 1.38 (s, 6 H, Me), 1.41, 1.44 (each s, 3 H, Me), 2.08, 2.10 (each s, 3 H, SMe), 2.22 (dd, *J* = 8.4, 15.9 Hz, 1 H, 2-H), 2.30 (dd, *J* = 1.4, 15.9 Hz, 1 H, 2-H), 3.80 (s, 3 H, OMe), 3.93 (dd, *J* = 6.4, 8.4 Hz, 1 H, 7-H), 3.98 (dd, *J* = 6.4, 8.4 Hz, 1 H, 7-H), 4.08 (dt, *J* = 8.0, 6.4 Hz, 1 H, 6-H), 4.12 (dd, *J* = 4.4, 6.2 Hz, 1 H, 4-H), 4.17 (dd, *J* = 6.2, 8.0 Hz, 1 H, 5-H), 5.28 (ddd, *J* = 1.4, 4.4, 8.4 Hz, 1 H, 3-H). − ^{13}C NMR: δ = −1.0 ($SiMe_3$), 11.2, 12.2 (SMe), 25.4, 26.4, 26.8, 27.2 (Me), 37.5 (C-2), 45.1 (C-1), 54.7 (OMe), 67.8 (C-7), 75.1, 77.1, 78.5, 82.2 (C-6, C-5, C-4, C-3), 109.9 (Me_2C), 155.1 (OCO_2Me). − IR: $\tilde{\nu}$ = 2980, 2950, 2910, 1750, 1435, 1370, 1270, 1205, 1150, 1060, 1000, 935, 870, 840, 775 cm^{-1}. − $C_{20}H_{38}O_7S_2Si$ (482.6): calcd. C 49.76, H 7.93, S 13.28; found C 49.49, H 8.14, S 13.08. − $[\alpha]_D^{23}$ = +21.6 (*c* = 1.0, $CHCl_3$).

2-Deoxy-4,5:6,7-di-O-isopropylidene-3-trimethylsilyloxy-D-manno-heptose Dimethyl Thioacetal (**10**): Typical procedure: To a solution of **7** (1.3 equiv.) in dry THF (4 ml/mmol) at −78°C a solution of **6** in dry THF (4 ml/mmol) was added dropwise. Eventually, a cation-complexing reagent (1 equiv.) was added. The mixture was allowed to warm to −40 to −30°C and stirred for 3−4 d at this temperature. Acylation, aqueous workup and purification took place as described above. − ^{1}H NMR: δ = 0.00 (s, 9 H, $SiMe_3$), 1.17, 1.18, 1.22, 1.25 (each s, 3 H, Me), 1.67 (ddd, *J* = 3.0, 10.4, 14.4 Hz, 1 H, 2-H), 1.89, 1.93 (each s, 3 H, SMe), 1.92 (ddd, *J* = 4.2, 9.2, 14.4 Hz, 1 H, 2-H), 3.55 (t, *J* = 7.2 Hz, 1 H, 5-H), 3.62 (dd, *J* = 4.2, 10.4 Hz, 1 H, 1-H), 3.74 (dd, *J* = 5.8, 8.0 Hz, 1 H,

7-H), 3.80 (dd, J = 3.0, 7.0 Hz, 1 H, 4-H), 3.88 (dt, J = 7.4, 6.0 Hz, 1 H, 6-H), 3.96 (dd, J = 6.0, 8.0 Hz, 1 H, 7-H), 4.07 (dt, J = 9.2, 3.0 Hz, 1 H, 3-H). − ^{13}C NMR: δ = 0.5 ($SiMe_3$), 11.7, 13.0 (SMe), 25.2, 26.6, 27.0, 27.1 (Me), 37.2 (C-2), 50.7 (C-1), 67.5 (C-7), 70.1, 77.3, 78.0, 83.9 (C-6, C-5, C-4, C-3), 109.6, 109.8 (Me_2C). − IR: ṽ = 2970, 2940, 2910, 1425, 1370, 1240, 1205, 1145, 1125, 1065, 960, 910, 835 cm^{-1}. − $C_{20}H_{38}O_7S_2Si$ (482.6): calcd. C 50.91, H 8.55, S 15.10; found C 50.52, H 8.45, S 15.40. − $[\alpha]_D^{23}$ = +19.7 (c = 1.6, $CHCl_3$).

(5R)-3,3-Bis(methylthio)-5-(1,2:3,4-di-O-isopropylidene-D-arabino-butyl)tetrahydrofuran-2-one (**13**): A solution of **9** (410 mg, 0.848 mmol) in dry THF (4 ml/mmol) was cooled to −78°C and 1.5 equiv. of TBAF in dry THF (4 ml/mmol) was added dropwise. The reaction mixture was stirred for about 12 h and was allowed to warm to room temp. The mixture was hydrolysed with diethyl ether/saturated NH_4Cl solution (1:1), the aqueous phase was extracted twice with diethyl ether, the combined organic layers were dried and the solvent was evaporated. Column chromatography (PE/EE, 20:1) afforded 222 mg (69%) of **13** as a colorless oil. − ^{1}H NMR: δ = 1.34, 1.39 (each s, 3 H, Me), 1.41 (s, 6 H, Me), 2.16, 2.23 (each s, 3 H, SMe), 2.27 (dd, J = 6.0, 13.6 Hz, 1 H, 4-H), 2.81 (dd, J = 10.0, 13.6 Hz, 1 H, 4-H), 3.60 (t, J = 7.2 Hz, 1 H, butyl-2-H), 3.83−4.12 (m, 3 H), 4.22 (dd, J = 3.6, 7.2 Hz, butyl-1-H), 4.79 (ddd, J = 3.6, 6.0, 10.0 Hz, 5-H). − ^{13}C NMR: δ = 12.6 and 13.2 (SMe), 25.1, 26.7, 27.0, 27.2 (Me), 38.5 (C-4), 57.7 (C-3), 67.4 (butyl-C-4), 76.5, 76.6, 77.9, 79.3 [butyl-(C-3, C-2, C-1), C-5], 109.9, 110.7 (Me_2C), 170.6 (C-2). − IR: ṽ = 2990, 2930, 2880, 1770, 1460, 1440, 1385, 1375, 1335, 1260, 1240, 1215, 1180, 1120, 1070, 980, 945, 880, 845, 755, 735, 705 cm^{-1}. − $C_{16}H_{26}O_6S_2$ (378.4): calcd. C 50.78, H 6.93, S 16.94; found C 51.12, H 7.03, S 16.61. − $[\alpha]_D^{24}$ = +32.9 (c = 0.7, $CHCl_3$).

2-Deoxy-4,5:6,7-di-O-isopropylidene-3-O-methoxycarbonyl-D-manno-heptose Dimethyl Thioacetal (**11**): ^{1}H NMR: δ = 1.36 (s, 6 H, Me) 1.39, 1.42 (each s, 3 H, Me), 2.08, 2.12 (each s, 3 H, SMe), 2.12−2.24 (m, 2 H, 2-H), 3.80 (s, 3 H, OMe), 3.73−4.19 (m, 6 H), 5.30 (dt, J = 4.0, 9.0 Hz, 1 H, 3-H). − ^{13}C NMR: δ = 12.0, 12.7 (SMe), 25.2, 26.5, 26.9, 27.3 (Me), 34.9 (C-2), 50.5 (C-1), 54.9 (OMe), 67.7 (C-7), 75.4, 77.0, 78.6 (C-4, C-5, C-6), 81.0 (C-3), 109.9, 110.2 (CMe_2), 155.4 (OCO_2Me). − IR: ṽ = 2986, 2958, 2920, 1751, 1442, 1381, 1372, 1269, 1214, 1156, 1073, 946, 848, 790 cm^{-1}. − $C_{17}H_{30}O_7S_2$ (410.5): calcd. C 49.74, H 7.37, S 15.62; found C 49.18, H 7.31, S 14.17; $[\alpha]_D^{22.5}$ = +26.4 (c = 0.6, $CHCl_3$).

2-Deoxy-3-hydroxy-4,5:6,7-di-O-isopropylidene-D-manno-heptose Dimethyl Thioacetal (**12**): Typical procedure: To a solution of **11** in dry THF (4 ml/mmol) at −78°C 1 equiv. base was added, the mixture allowed to warm to room temperature and stirred for about 12 h. The mixture was hydrolysed with diethyl ether/saturated NH_4Cl solution (1:1). The aqueous phase was extracted twice with diethyl ether, the combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Column chromatography (PE/EE, 5:1) afforded **12** as a colorless oil. − ^{1}H NMR: δ = 1.27, 1.28, 1.29, 1.37 (each s, 3 H, Me), 1.85 (ddd, J = 4.2, 9.8, 14.2 Hz, 1 H, 2-H), 2.00, 2.06 (each s, 3 H, SMe), 2.01−2.07 (m, 1 H, 2-H), 3.62−3.70 (m, 2 H), 3.86−4.02 (m, 5 H), 4.11 (dd, J = 6.0, 8.4 Hz, 1H). − ^{13}C NMR: δ = 11.6, 13.2 (SMe), 25.1, 26.4, 26.8, 26.9 (Me), 38.6 (C-2), 50.6 (C-1), 68.0 (C-7), 69.8, 76.4, 80.9, 83.2 (C-6, C-5, C-4, C-3), 109.4, 110.2 (Me_2C). − IR: ṽ = 3440, 2970, 2900, 2870, 1750, 1680, 1425, 1370, 1240, 1205, 1150, 1060, 970, 870, 840 cm^{-1}. − $C_{15}H_{28}O_5S_2$ (352.4): calcd. C 51.11, H 8.01, S 18.19; found C 50.42, H 8.04, S 17.03. − $[\alpha]_D^{23.5}$ = +18.1 (c = 0.5, $CHCl_3$).

(5R)-5-(1,2:3,4-Di-O-isopropylidene-D-arabino-butyl)-tetrahydro-3,3-dimethoxyfuran-2-one (**14**): To a solution of **13** (61 mg, 0.161 mmol) in dry MeOH (4 ml/mmol) was added 3 equiv. [bis(trifluoroacetoxy)-iodo]benzene in small portions at room temperature and the solution was stirred until complete conversion of the dimethyl ketal (nearly 2 h). The aqueous workup was carried out as described in the literature[12]. Flash chromatography (PE/EE, 10:1) afforded 34 mg (61%) **14** as a colorless oil. − ^{1}H NMR: δ = 1.26, 1.30, 1.31, 1.33 (each s, 3 H, Me), 2.22 (dd, J = 6.2, 12.8 Hz, 1 H, 4-H), 2.37 (dd, J = 8.8, 12.8 Hz, 1 H, 4-H), 3.26 (s, 6 H, OMe), 3.64 (t, J = 7.2 Hz, 1 H, butyl-2-H), 3.84−4.08 (m, 3 H), 4.14 (dd, J = 4.0, 7.0 Hz, 1 H, butyl-1-H), 4.61 (ddd, J = 4.0, 6.2, 9.0 Hz, 1 H, 5-H). − ^{13}C NMR: δ = 25.1, 26.6, 27.0, 27.2 (Me), 33.7 (C-4), 50.9, 51.0 (OMe), 67.3 (butyl-C-4), 75.9, 76.6, 78.0, 79.4 [butyl-(C-3, C-2, C-1), C-5], 99.6 (C-3), 109.9, 110.6 (Me_2C), 168.9 (C-2). − IR: ṽ = 2988, 2940, 2842, 1794, 1457, 1378, 1213, 1067, 988, 847, 758 cm^{-1}. − HRMS: calcd. 331.1393 [M − 15], found 331.1395 [M − 15]. − $[\alpha]_D^{25}$ = +10.7 (c = 0.9, $CHCl_3$).

3-Deoxy-D-manno-oct-2-enosono-1,4-lactone (**15**): 33 mg (0.095 mmol) of **14** was dissolved in 95% trifluoroacetic acid (20 ml/mmol) and stirred until complete conversion. The workup wass in accord with the procedure described in the literature[3a]. Flash chromatography ($CHCl_3$/EtOH, 3:1) afforded 17 mg (81%) of **15** as a colorless solid (m.p. 190−192°C, ref.[13]: 192−194°C). − ^{1}H NMR ([D$_6$]DMSO): δ = 3.36−3.66 (m, 6 H, 4-H, 5-H, 6-H, 7-H, 8-H), 4.42, 4.55, 4.60, 4.84 (each s, 1 H, OH), 4.88 (d, J = 6.4 Hz, 1 H, 3-H), 6.31 (s, 1 H, OH). − ^{13}C NMR ([D$_6$]DMSO): δ = 63.7 (C-8), 70.3, 70.7, 71.2 (C-5, C-6, C-7), 78.4 (C-4), 118.9 (C-3), 143.0 (C-2), 169.3 (C-1). − $[\alpha]_D^{23.5}$ = +31.7 (c = 0.3, H_2O) [ref.[13]: $[\alpha]_D^{24}$ = +31.8 (c = 1.4, H_2O)].

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