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Note

A new synthesis of 2-deoxy-β-Kdo, a potent CMP-Kdo synthetase inhibitor

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CMP-Kdo synthetase[1] catalyzes a key step in the biosynthesis of bacterial lipopolysaccharide[2]. Recently, the 2-deoxy derivative of β-Kdo (**7**) was reported to be a potent inhibitor of CMP-Kdo synthetase[3]. Two different syntheses of **7** have been reported[4,5], the first involving hydrogenolysis of the glycosyl chloride of Kdo tetraacetate methyl ester, ant thus requiring Kdo as a starting material[4]. Although Kdo can be prepared in practically useful yield by the Conforth condensation of D-arabinose and oxalacetic acid[1], the preparation is tedious and one of the starting materials, oxalacetic acid, is rather expensive. The second synthesis started with much less expensive D-mannose, but the method gave an α, β mixture of 2-deoxy-Kdo derivatives, together with C-4 epimerized byproducts[5]. In this Note we describe a new, stereospecific synthesis of 2-deoxy-β-Kdo which also starts from D-mannose.

RESULTS AND DISCUSSION

Our synthetic plan was to construct the tetrahydropyran ring of 2-deoxy-β-Kdo by intramolecular C–C bond formation. We selected a 2,3-*O*-isopropylidene-4-*O*-alkoxycarbonylmethyl-D-mannitol derivative having a leaving group at C-1 as the key intermediate, expecting that the 2,3-*O*-isopropylidene group would assist the intramolecular cyclization by forcing the two relevant functional groups into close proximity (they would be *cis* on the five-membered acetal ring).

In order to introduce an ethoxycarbonylmethyl group at O-4, the reaction of 1-*O*-*tert*-butyldimethylsilyl-2,3:5,6-di-*O*-isopropylidene-D-mannitol (**2a**) with ethyl bromoacetate in the presence of sodium hydride in oxolane was first attempted. However, the reaction did not give the expected ether but instead resulted in extensive *O*-desilylation. This result indicated that a base-stable protecting group is necessary at O-1, and the benzyl group was chosen for the purpose. Thus, the primary alcohol function of 1,2:4,5-di-*O*-isopropylidene-D-mannitol[6] (**1**) was selectively benzylated by treatment with benzyl bromide and sodium hydride in Me_2NCHO at 0° to give 1-*O*-benzyl-2,3:5,6-di-*O*-isopropylidene-D-mannitol (**2b**) in 85% yield. Treatment of **2b** with

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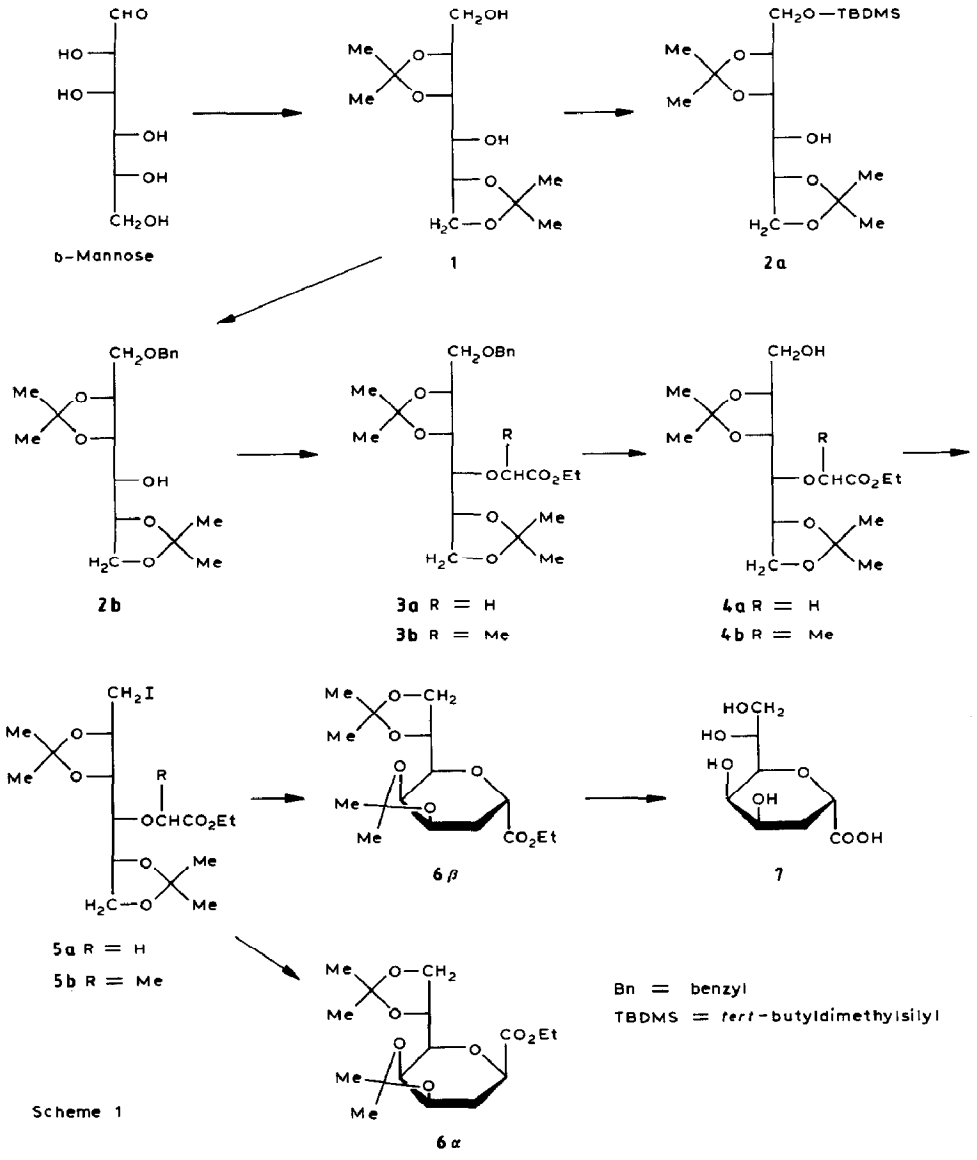
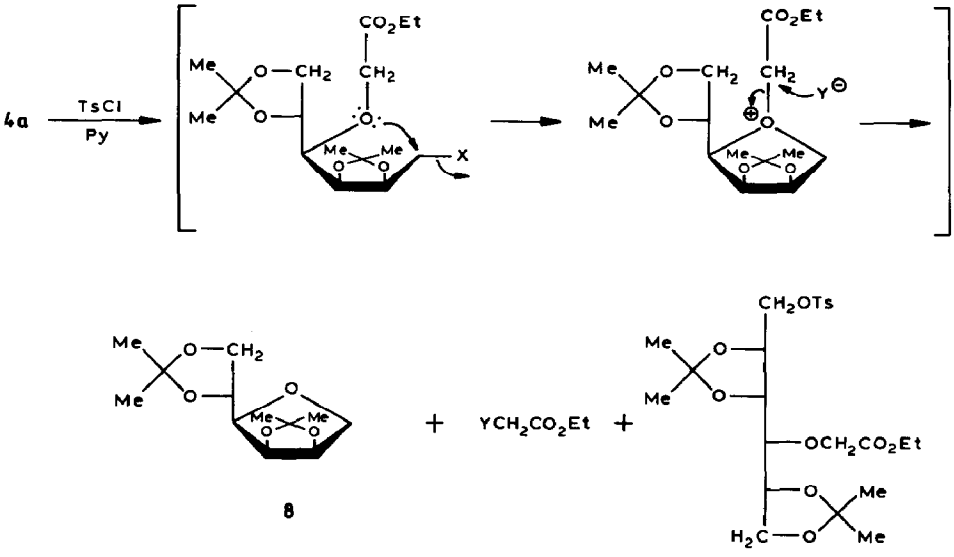


Scheme 1

ethyl bromoacetate in the presence of sodium hydride in oxolane gave the expected 4-*O*-ethoxycarbonylmethylated **3a** in 78% yield. The benzyl group of **3a** was then quantitatively removed by catalytic hydrogenolysis to give 3-*O*-ethoxycarbonylmethyl-1,2:4,5-di-*O*-isopropylidene-D-mannitol (**4a**). The next step was the introduction of a leaving group at the C-1 position. First, the tosylation of **4a** was attempted, with the expectation that the 1-tosylate group would be a good enough leaving group for intramolecular C–C bond formation. Otherwise, the tosyl group could be replaced with a better leaving group, such as iodide. However, treatment of **4a** with tosyl chloride in



Scheme 2

pyridine at various temperatures gave mainly an unexpected tetrahydrofuran derivative[6] **8**, accompanied by a very small amount of the expected 1-tosylate **9**. These and similar observations reported by Kusumoto *et al.*[6] result from an attack on C-1 by the 4-ether oxygen, driven by a propensity for the formation of a five-membered ring that is induced by the existing five-membered ring comprising C-2, C-3, and the 2,3-*O*-isopropylidene group (scheme 2)[7,8]. Therefore, the direct iodination of C-1 was studied. After examination of various conditions, we found that the treatment of **4a** with iodine, triphenylphosphine, and imidazole[9] in dry dichloromethane gave the expected 1-iodide **5a** in 77% yield, along with a small amount of the tetrahydrofuran byproduct **8**. With the desired key intermediate **5a** in hand, we next focussed on exploring the best conditions for the intramolecular C–C bond formation, and found that treatment of **5a** with 1.1 molar lithium diisopropylamide (LDA) in oxolane at $-75°$ gave the expected 2-deoxy-β-Kdo derivative **6β** stereospecifically in 84% yield. The use of excess LDA (2.2 mol. equiv.) gave a reduced yield of cyclization product, which was now a mixture of **6β** and **6α**.

To investigate the possibility of synthesizing C-2 substituted derivatives[10] of **6β** by intramolecular C–C bond formation, the (1-ethoxycarbonyl)ethyl derivative **5b** was prepared. Thus, the reaction of **2b** with ethyl α-bromopropionate in the presence of sodium hydride gave a mixture of diastereomers, **3b**-I (major) (77%) and **3b**-II (minor) (15%). Although the stereochemistry at C-1′ could not be determined, the major product was converted into **5b** by the same sequence of reactions as described for **5a**. However, treatment of **5b** with LDA under various conditions led only to the recovery of **5b**.

Deprotection of **6β** according to the reported procedure[3] gave the title compound

7. The application of the intramolecular cyclization to the synthesis of other Kdo derivatives and the development of *in vivo*-active 2-deoxy-β-Kdo derivatives[11] are under investigation in our laboratory.

EXPERIMENTAL

General methods. — Melting points were taken with a Yanako Model P hot plate and are uncorrected. ^{1}H-N-m.r. spectra were recorded on a JEOL GX-400 spectrometer at 21–23° in $CDCl_3$, with Me_4Si as internal standard. I.r. spectra were recorded on a Jasco A-202 infrared spectrometer. Specific rotations were measured on a Jasco J-20 polarimeter at 589 nm. Merck silica gel (Art. 7734) was used for column chromatography and Merck silica gel (Art. 5548) for analytical thin layer chromatography.

1-O-tert-*Butyldimethylsilyl*-2,3:5,6-*di*-O-*isopropylidene*-D-*mannitol* (**2a**). — To an ice-cooled mixture of **1** (ref. 6, 160 mg, 0.6 mmol), triethylamine (0.17 mL), and dimethylaminopyridine (5 mg) in Me_2NCHO (15 mL) was added dropwise a solution of *tert*-butyldimethylsilyl chloride (102 mg, 0.67 mmol) in Me_2NCHO (15 mL). The mixture was stirred for 30 min at ice-bath temperature, then water was added and it was extracted with ethyl acetate (10 mL × 3). The extract was washed with satd. NaCl, dried over $MgSO_4$, and concentrated under reduced pressure. The residual syrup was purified by chromatography on a silica gel column with 9:1 benzene – ethyl acetate as eluent to give syrupy **2a** (220 mg, 96%), $[\alpha]_D^{21}$ −18.0° (*c* 0.9, $CHCl_3$); ^{1}H-n.m.r.: δ 0.10 (s, 6 H, $SiCH_3$), 0.91 (s, 9 H, CCH_3), 1.36, 1.38, 1.40, 1.50 (4 s, 12 H, CCH_3), 3.19 (dd, 1 H, $J_{4,OH}$ 3.67, 4-O*H*), 3.67 (m, 1 H, H-4), 3.83 (dd, 1 H, $J_{1a,2}$ 3.7, $J_{1a,1b}$ 11.0 Hz, H-1a), 3.97–4.15 (m, 4 H, H-1b,5,6a,6b), 4.24 (ddd, 1 H, $J_{2,3}$ 7.1, $J_{2,1b}$ 6.7 Hz, H-2), and 4.38 (dd, 1 H, $J_{3,4}$ 1 Hz, H-3).

Anal. Calc. for $C_{18}H_{36}O_6Si$: C, 57.41; H, 9.63. Found: C, 57.30; H, 9.60.

1-O-*Benzyl-2,3:5,6-di*-O-*isopropylidene*-D-*mannitol* (**2b**). — To an ice-cooled solution of **1** (ref. 6, 1 g, 3.8 mmol) in dry Me_2NCHO (100 mL) was added NaH (152 mg, 1.05 mol. equiv.), and the mixture was stirred for 10 min then warmed to room temperature. Benzyl bromide (422 mg, 1.2 mol. equiv.) was added dropwise, and the mixture was stirred for 5 min before water was added to it under cooling in an ice–water bath. The mixture was extracted with ethyl acetate (50 mL × 3), and the extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residual syrup was purified by chromatography on a silica gel column with 9:1 benzene – ethyl acetate as eluent to give syrupy **2a** (1.14 g, 85%), $[\alpha]_D^{21}$ −11.6° (*c* 0.3, $CHCl_3$); ^{1}H-n.m.r.: δ 1.34, 1.37, 1.39, 1.51 (4 s, 12 H, CCH_3), 2.81 (br. d, 1 H, $J_{4,OH}$ 7.1 Hz, 4-O*H*), 3.50 (br. t, 1 H, $J_{4,3}$ and $J_{4,5}$ 6.8 and 1 Hz, H-4), 3.75 (dd, 1 H, $J_{1a,1b}$ 10.5, $J_{1a,2}$ 4.9 Hz, H-1a), 3.83 (dd, 1 H, $J_{1b,2}$ 4.6 Hz, H-1b), 3.96–4.13 (m, 3 H, H-5,6a,6b), 4.36–4.45 (m, 2 H, H-2,3), 4.60 (s, 2 H, OCH_2Ph), and 7.27–7.38 (m, 5 H, Ph-H).

1-O-*Benzyl-4*-O-*ethoxycarbonylmethyl-2,3:5,6-di*-O-*isopropylidene*-D-*mannitol* (**3a**). — A mixture of **2b** (3.6 g, 10.4 mmol) and NaH (480 mg, 1.15 mol. equiv.) in dry oxolane (100 mL) was refluxed for 1 h. To the cooled mixture was added dropwise ethyl bromoacetate (1.8 mL, 1.5 mol. equiv.) at 0°. After the mixture had been stirred at room

temperature for 6 h it was cooled to 0°, EtOH (10 mL) and few drops of acetic acid were successively added, and the whole was concentrated under reduced pressure to give a syrup. The syrup was dissolved in ethyl acetate (50 mL). The ethyl acetate solution was washed successively with satd. $NaHCO_3$, satd. NaCl solution, and water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a syrup. The syrup was purified by chromatography on a silica gel column with 10:1 benzene – ethyl acetate as eluent to give syrupy **3a** (3.49 g, 78%), $[\alpha]_D^{21}$ + 16.8° (*c* 1.3, $CHCl_3$); ^{1}H-n.m.r.: δ 1.27 (t, 3 H, *J* 7.0 Hz, OCH_2CH_3), 1.30, 1.34, 1.49 (3 s, 12 H, CCH_3), 3.63 (dd, 1 H, $J_{1a,1b}$ 9.5, $J_{1a,2}$ 6.2 Hz, H-1a), 3.70 (dd, 1 H, $J_{1b,2}$ 5.1 Hz, H-1b), 3.75 (dd, 1 H, $J_{4,3}$ and $J_{4,5}$ 4.8 and 5.5 Hz, H-4), 4.05–4.09 (m, 2 H, H-6a,6b), 4.11–4.20 (m, 4 H, H-3,5, OCH_2CH_3), 4.23 and 4.38 (ABq,2 H, J_{HCH} 16.5 Hz, OCH_2COOEt), 4.35 (m, 1 H, H-2), 4.54 (ABq, 2 H, J_{HCH} 12.1 Hz, OCH_2Ph), and 7.27–7.53 (m, 5 H, Ph-H).

Anal. Calc. for $C_{20}H_{34}O_8$: C, 63.00; H, 7.82. Found: C, 62.85; H, 7.54.

1-O-Benzyl-4-O-(1-ethoxycarbonylethyl)-2,3:5,6-di-O-isopropylidene-D-mannitol (**3b**). — Compound **3b** was prepared essentially as described for **3a**, using ethyl α-bromopropionate instead of ethyl bromoacetate as the alkylating agent. The two diastereomers had R_F 0.62 (**3b-I**, major) and 0.72 (**3b-II**, minor) on t.l.c. in 3:1 benzene – ethyl acetate. They were purified by chromatography on a silica gel column with 10:1 benzene – ethyl acetate as eluent. The yield of **3b-I**, syrup, was 2.91 g, (77%), $[\alpha]_D^{21}$ − 10.1° (*c* 0.3, $CHCl_3$); ^{1}H-n.m.r.: δ 1.24 (t, 3 H, *J* 7.3 Hz, OCH_2CH_3), 1.28, 1.31, 1.37, 1.44 (4 s, 12 H, CCH_3), 1.40 [d, 3 H, *J* 7.0 Hz, $OCH(COOEt)CH_3$], 3.70 (dd, 1 H, $J_{1a,2}$ 6.6, $J_{1a,1b}$ 9.9 Hz, H-1a), 3.81 (dd, 1 H, $J_{1b,2}$ 4.8 Hz, H-1b), 3.90 (dd, 1 H, $J_{4,5}$ 4.0, $J_{4,3}$ 6.2 Hz, H-4), 3.95 (dd, 1 H, $J_{6a,5}$ 7.3, $J_{6a,6b}$ 8.4 Hz, H-6a), 4.04 (dd, 1 H, $J_{6b,5}$ 7.0 Hz, H-6b),4.05 (ddd, 1 H, H-2) 4.13–4.21 (m, 3 H, H-5, OCH_2CH_3), 4.41 [q, 1 H, $OCH(COOEt)CH_3$], 4.57 and 4.61 (ABq, 2 H, J_{HCH} 12.1 Hz, OCH_2Ph), and 7.27–7.52 (m, 5 H, Ph-H).

Anal. Calc. for $C_{24}H_{36}O_8$: C, 63.70; H, 8.02. Found: C, 63.50; H, 8.12.

Diastereomer **3b-II** was a syrup, 0.72 g (15%), $[\alpha]_D^{21}$ + 76.0° (*c* 0.3, $CHCl_3$), ^{1}H-n.m.r.: δ 1.26 (t, 3 H, *J* 7.0 Hz, OCH_2CH_3), 1.24, 1.28, 1.36, 1.49 (4 s, 12 H, CCH_3), 1.36 [d, 3 H, J 6.6 Hz, $OCH(CH_3)COOEt$], 3.51 (dd, 1 H, $J_{1a,2}$ 6.6, $J_{1a,1b}$ 9.9 Hz, H-1a), 3.63 (dd, 1 H, $J_{1b,2}$ 3.7 Hz, H-1b), 3.64 (dd, 1 H, $J_{4,5}$ 6.2, $J_{4,3}$ 8.8 Hz, H-4), 4.00 (q, 1 H, $J_{5,6a}$ = $J_{5,6b}$ 6.6 Hz, H-5), 4.05 (t, 1 H, $J_{6a,6b}$ 7.7 Hz, H-6a), 4.08–4.22 (m, 4 H, H-3,6b, OCH_2CH_3), 4.32 (ddd, 1 H, $J_{2,3}$ 5.9 Hz, H-2), 4.53 [q, 1 H, J 6.6 Hz, $OCH(COOEt)CH_3$], 4.55 (s, 2 H, OCH_2Ph), and 7.27–7.52 (m, 5 H, Ph-H).

Anal. Calc. for $C_{24}H_{36}O_8$: C, 63.70; H, 8.02. Found: 63.62; H, 7.86.

3-O-Ethoxycarbonylmethyl-1,2:4,5-di-O-isopropylidene-D-mannitol (**4a**). — A mixture of **3a** (700 mg, 1.6 mmol) and Pd(OH) (15 mg) in MeOH (20 mL) was shaken under an H_2 atmosphere for 1 h at room temperature. After the catalyst was removed by filtration, the filtrate was concentrated to give a syrup. The syrup was purified by chromatography on a silica gel column with 1:1 benzene – ethyl acetate as eluent to give **4a** (539 mg, 97%) as a syrup, $[\alpha]_D^{21}$ + 56.6° (*c* 0.7, $CHCl_3$); ^{1}H-n.m.r.: δ 1.29 (t, 3 H, *J* 7.2 Hz, OCH_2CH_3), 1.34, 1.36, 1.43, 1.50 (4 s, 12 H, CCH_3), 2.53 (br. s, 1 H, O*H*), 3.67 (br. dd, 1 H, $J_{6a,5}$ 6.2, $J_{6a,6b}$ 11.4 Hz, H-6a), 3.78–3.84 (m, 2 H, H-3,6b), 4.08–4.27 (m, 7 H, H-1a,1b,2,4,5, OCH_2CH_3), 4.36 and 4.42 (ABq, 2 H, J_{HCH} 16.5 Hz, OCH_2COOEt).

Anal. Calc. for $C_{16}H_{28}O_8$: C, 55.16; H, 8.10. Found: C, 55.12; H, 7.89.

Catalytic hydrogenolysis of **3b-I**. — The catalytic hydrogenolysis of **3b-I** by a procedure similar to that just described gave 3-*O*-(1-ethoxycarbonylethyl)-1,2:4,5-di-*O*-isopropylidene-D-mannitol (**4b**) in 97% yield, syrup, $[\alpha]_D^{21}$ +10.9° (*c* 0.4, $CHCl_3$); ^{1}H-n.m.r.: δ 1.28 (t, 3 H, *J* 7.0 Hz, OCH_2CH_3), 1.32, 1.45 (2 s, 12 H, CCH_3), 1.38 [d, 3 H, *J* 7.0 Hz, OCH(COOEt)CH_3], 2.85 (br. s, 1 H, O*H*), 3.72 (br. dd, 3 H, $J_{6a,5}$ 5.9, $J_{6a,6b}$ 11.4 Hz, H-6a), 3.94 (br. dd, 3 H, $J_{6b,5}$ 5.9 Hz, H-6b), 3.97 (dd, 1 H, $J_{1a,2}$ 7.0, $J_{1a,1b}$ 8.4 Hz, H-1a), 4.01 (dd, 1 H, $J_{3,2}$ 4.4, $J_{3,4}$ 5.9 Hz, H-3), 4.12 (dd, 1 H, $J_{1b,2}$ 7.0, Hz, H-1b), 4.15 (t, 1 H, $J_{4,5}$ 6.2 Hz, H-4), 4.26 (ddd, 1 H, H-5), and 4.50 [q, 1 H, OC*H*(CH_3)COOEt].

Anal. Calc. for $C_{17}H_{30}O_8$: C, 56.34; H, 8.34. Found: C, 56.25; H, 8.14.

1-Deoxy-4-O-ethoxycarbonylmethyl-1-iodo-2,3:5,6-di-O-isopropylidene-D-mannitol (**5a**). — A mixture of **4a** (150 mg, 0.43 mmol), imidazole (220 mg, 2.5 mol. equiv.), triphenylphosphine (136 mg, 1.2 mol. equiv.), and iodine (220 mg, 2.0 mol. equiv.) in dry dichloromethane (5 mL) was stirred overnight at 0°, then additional triphenylphosphine (34 mg) was added. The mixture was stirred another 2 h at 0° before the reaction was stopped by the addition of 10% aq. $Na_2S_2O_3$ (5 mL). The mixture was extracted with dichloromethane (10 mL) and the organic layer was washed with satd. aq. NaCl solution and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residual syrup was purified by chromatography on a silica gel column with 10:1 benzene – ethyl acetate as eluent to give **5a** (145 mg, 77%), $[\alpha]_D^{21}$ +57.0° (*c* 1.4, $CHCl_3$); ^{1}H-n.m.r.: δ 1.29 (t, 3 H, *J* 7.2 Hz, OCH_2CH_3), 1.33, 1.36, 1.44, 1.51 (4 s, 12 H, CCH_3), 2.23 (dd, 1 H, $J_{1a,2}$ 9.5, $J_{1a,1b}$ 9.9 Hz, H-1a), 3.61 (dd, 1 H, $J_{1b,2}$ 4.4 Hz, H-1b), 3.80 (dd, 1 H, $J_{4,3}$ and $J_{4,5}$ 7.0 and 5.9 Hz, H-4), 4.07 (m, 6 H, H-3,5,6a,6b, OCH_2CH_3), 4.35 and 4.43 (ABq, 2 H, J_{HCH} 16.5 Hz, OCH_2COOEt), and 4.41 (ddd, $J_{2,3}$ 5.5 Hz, H-2).

Anal. Calc. for $C_{16}H_{27}IO_7$: C, 41.95; H, 5.94: Found: C, 41.84; H, 5.78.

1-Deoxy-4-O-(1-ethoxycarbonylethyl)-1-iodo-2,3:5,6-di-O-isopropylidene-D-mannitol (**5b**). — Compound **5b** was prepared from **3b-I** in 86% yield by a procedure similar to that described for **5a**, syrup, $[\alpha]_D^{21}$ +12.2° (*c* 1.1, $CHCl_3$); ^{1}H-n.m.r.: δ 1.28 (t, 3 H, *J* 7.1 Hz, OCH_2CH_3), 1.32, 1.48 (2 s, 12 H, CCH_3), 1.36 [d, 3 H, *J* 7.0 Hz, OCH(COOEt)CH_3], 3.30 (t, 1 H, $J_{1a,2} = J_{1a,1b}$ 9.5 Hz, H-1a), 3.81 (dd, 1 H, $J_{1b,2}$ 4.4 Hz, H-1b), 3.88–4.00 (m, 2 H, H-4,6a), 4.09–4.24 (m, 5 H, H-3,5,6b, OCH_2CH_3), 4.41 (ddd, 1 H, H-2), and 4.45 [q, 1 H, OC*H*(CH_3)COOEt].

Ethyl 2,6-anhydro-3-deoxy-4,5:7,8-di-O-isopropylidene-D-glycero-D-talo-octonate (**6β**) *and ethyl 2,6-anhydro-3-deoxy-4,5:7,8-di-O-isopropylidene-D-glycero-D-galacto-octonate* (**6α**). — To a stirred solution of **5a** (580 mg, 1.27 mmol) in oxolane (10 mL) was added under N_2 lithium diisopropylamide in oxolane (3.1 mL, 0.5M) at −75°. The solution was stirred for 2 h at that temperature before addition of satd. aq. NH_4Cl (15 mL). The mixture was extracted with ethyl acetate (20 mL) and the organic layer was washed with satd. aq. NaCl and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residual syrup was purified by chromatography on a silica gel column with 10:1 benzene and ethyl acetate as eluent to give semisolid **6β** [271 mg, 84% based on **5a** consumed; 114 mg (23%) of **5a** was recovered], $[\alpha]_D^{21}$ −42.5° (*c* 1.2, $CHCl_3$), lit.[5] −43.8°; ^{1}H-n.m.r.: δ 1.24 (t, 3 H, *J* 7.1 Hz, OCH_2CH_3),

1.37, 1.39, 1.42, 1.49 (4 s, 12 H, CCH_3), 1.86 (ddd, 1 H, $J_{3ax,4}$ 2.2, $J_{3ax,2}$ 11.2, $J_{3ax,3eq}$ 14.0 Hz, H-3*ax*), 2.31 (ddd, 1 H, $J_{3eq,4}$ 3.2, $J_{3eq,2}$ 5.9 Hz, H-3*eq*), 3.51 (dd, 1 H, $J_{6,5}$ 1.5, $J_{6,7}$ 8.3 Hz, H-6), 4.08–4.25 (m, 5 H, H-7,8a,8b, OCH_2CH$_3$), 4.35 (dd, 1 H, $J_{5,4}$ 7.8 Hz, H-5), 4.50 (dd, 1 H, H-2), and 4.59 (ddd, 1 H, H-4).

Anal. Calc. for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.12; H, 7.64.

The use of excess LDA (2.2 mol. equiv.) gave **6β** (42%) and solid **6α** (11%), $[\alpha]_D^{21}$ + 27.8° (*c* 0.9, $CHCl_3$), lit[5] + 28.9°; ^{1}H-n.m.r.: δ 1.28 (t, 3 H, *J* 7.3 Hz, OCH$_2$CH_3), 1.36, 1.38, 1.44, 1.49 (4 s, 12 H, CCH_3), 1.98 (ddd, 1 H, $J_{3ax,4}$ 8.1, $J_{3ax,2}$ 8.8, $J_{3ax,3eq}$ 13.9 Hz, H-3*ax*), 2.18 (ddd, 1 H, $J_{3eq,4}$ 5.6, $J_{3eq,2}$ 4.2 Hz, H-3*eq*), 3.54 (dd, 1 H, $J_{6,5}$ 2.0, $J_{6,7}$ 8.1 Hz, H-6), 4.31 (dd, 1 H, H-2), 4.11–4.27 (m, 5 H, OCH_2CH$_3$, H-5,8a,8b), and 4.34–4.47 (m, 2 H, H-4, 7).

Anal. Calc. for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 57.28; H, 8.06.

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