49. A New Total Synthesis of D-*threo*-L-*talo*-Octose[1])

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Dedicated to Prof. Dr. *Horst Prinzbach* on the occasion of his 60th birthday

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A new approach to the total, asymmetric synthesis of D-*threo*-L-*talo*-octose ((−)-**1**) and its derivatives is presented. It is based on the chemoselective *Wittig-Horner* monoolefination of a 5-deoxy-D-*ribo*-hexodialdose derivative **4** obtained by selective reduction of (−)-5-deoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hexofuranurono-6,1-lactone ((−)-**3**). Allylic bromination of the resulting methyl (*E*)-oct-6-enofuranuronate (+)-**5** followed by intramolecular nucleophilic displacement of the so-obtained bromides gave a 13.3:1 mixture of (−)-methyl (*E*)-1,4-anhydro-6,7-dideoxy-2,3-*O*-isopropylidene-β-L-*talo*-oct-6-enopyranuronate ((−)-**8**) and methyl (*E*)-1,4-anhydro-6,7-dideoxy-2,3-*O*-isopropylidene-α-D-*allo*-oct-6-enopyranuronate (**9**). The double hydroxylation of the enoate (−)-**8** followed *Kishi*'s rule and gave the corresponding D-*threo*-β-L-*talo*-octopyranuronate derivative (−)-**11** with a good diastereoselectivity. Reduction of ester (−)-**11** and deprotection led to pure (−)-**1**.

Introduction. – Enantiomerically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives ('naked sugars' [1]) have been shown to be valuable synthetic intermediates for the preparations of a large variety of natural products and compounds of biological interest. We have now extended their chemistry to the asymmetric total synthesis of higher-carbon sugars and analogues and wish to present here a new and efficient synthesis of D-*threo*-L-*talo*-octose ((−)-**1**)[3]).

One of the earlier methods for the synthesis of higher-carbon sugars is the *Kiliani-Fischer* cyanohydrin reaction which is used to extend the aldose chain by one C-atom at the reducing end [12]. A similar iterative but more stereoselective homologation method employing 2-(trimethylsilyl)thiazole as formyl-anion equivalent has been proposed recently by *Dondoni* and coworkers [13]. Other approaches for the C_1 chain extension of aldoses rely on the addition of nitromethane [14] and of S-[15] or Si-stabilized [16] methide anions [17]. The number of methods has been augmented by procedures that permit extension of the sugar chain by two or more C-atoms; they include the *Wittig-*

[1]) Enantiomerically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives ('naked sugar' [1]) as synthetic intermediates, Part XV; Part XIV, see [2]; Part XIII, see [3].

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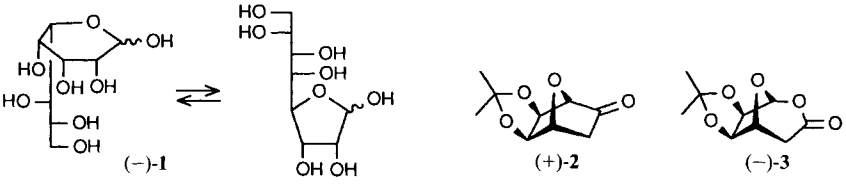
[3]) Monosaccharides with eight consecutive C-atoms have stirred a great interest in recent years [4]. A few octoses have been found in plants [5], an octitol has been observed recently in human eye lenses [6]. Lincosamine, an amine octose, is a component of the antibiotic lincomycins [7], and ezoaminuroic acid is the octose nucleoside portion of ezomycins that are antifungal antibiotics [8]. The octosyl acids are bicyclic C_8 sugars which are *N*-glycosidically linked to pyrimidine bases [9]; some derivatives are powerful phosphodiesterase inhibitors [10]. Another octose, KDO (= 3-deoxy-D-*manno*-2-octulosonic acid), is an important connecting link in the membrane structures of *Gram*-negative bacteria [11].

Horner olefination of sugar-derived aldehydes [18], followed by hydroxylation of the newly created double bond [19] (a similar approach will be used in this work), the *Reformatsky* reaction [20], the *Ivanov* reaction [21], the *Darzens* reaction [22], the *Henry* reaction with nitroethanol and other nitroalkane derivatives [23], the *Knoevenagel-Doeber* condensation [24], and other nucleophilic additions involving various organometallic reagents [25]. Other methods involving radical C–C bond formation [26], cycloadditions of sugar-derived aldehydes to dienes [27], cross-aldolisations [28], and related condensation reaction [29] have been proposed recently.

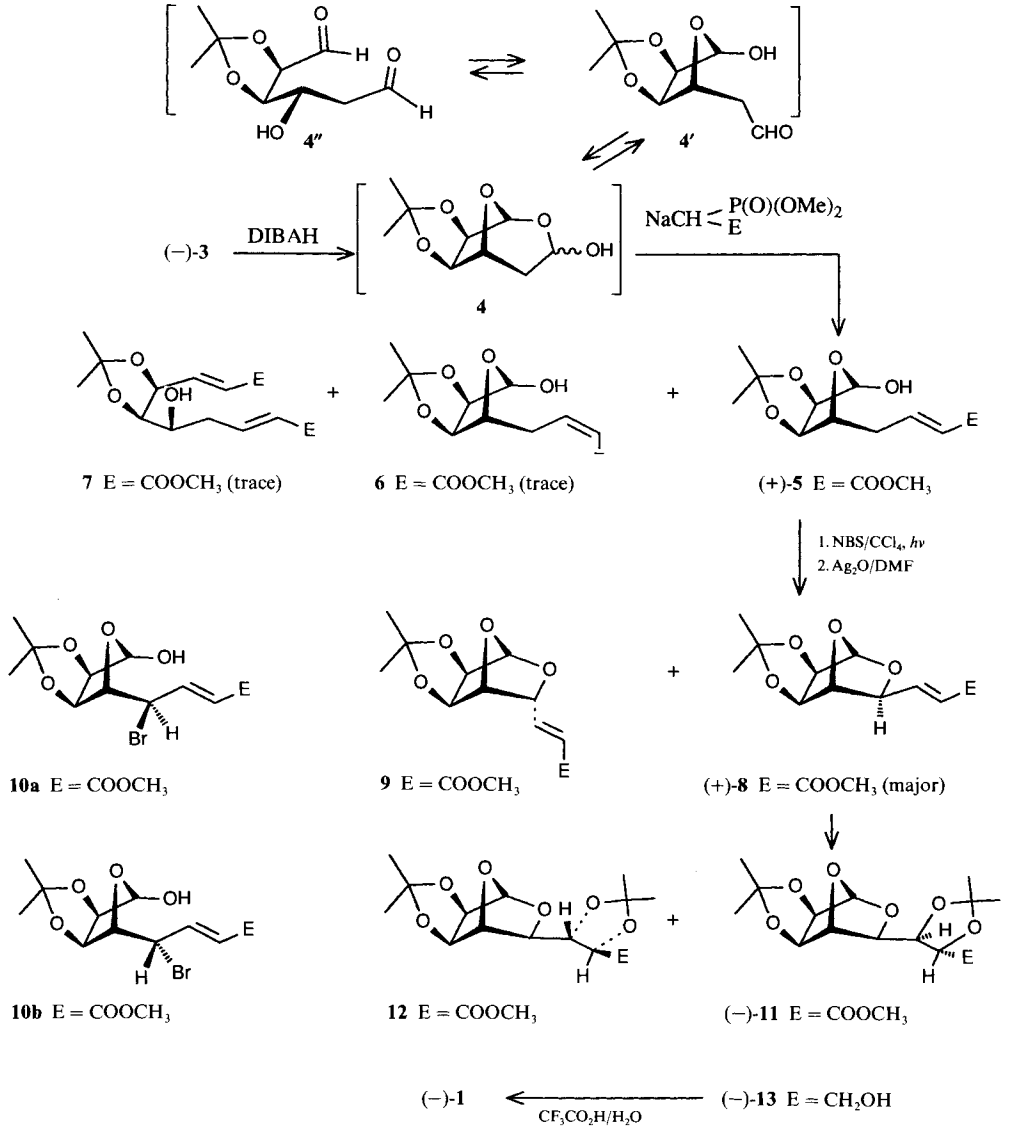
(–)-D-*threo*-L-*talo*-Octose ((–)-**1**) has been described for the first time by *Bilik* and coworkers [30] in 1976. Recently, we presented a first total, asymmetric synthesis of (–)-**1** based on the stereoselective *Mukaiyama* cross-aldolisation of (*R*)-2,3-*O*-isopropylideneglyceraldehyde with (1*R*,4*R*,5*R*,6*R*)-5-*exo*,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**2**) [28b], a compound obtained readily from furan and 1-cyanovinyl (1′*S*)-camphanate [1]. We report here a shorter route for the total synthesis of (–)-**1** which makes use of the chemoselective *Wittig-Horner* olefination of the hemiacetal obtained by partial reduction of (–)-5-deoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hexofuranurono-6,1-lactone [31] ((–)-**3**).



Results and Discussion. – Treatment of urono-6,1-lactone (–)-**3** with 1 equiv. of DIBAH (diisobutylaluminium hydride) in CH_2Cl_2 (–90°) [32] afforded the unstable hemiacetal **4** which reacted with 1 equiv. of Na[$(MeO)_2$POCHCOOMe] [33] in THF at –78° to give the (*E*)-α,β-unsaturated methyl ester (+)-**5** in 72% yield (*Scheme*). Under these conditions, only traces of the (*Z*)-stereoisomer **6** and the product of double olefination **7** were formed, as shown by 250-MHz ^{1}H-NMR of the crude reaction mixture. The structure of (+)-**5** was given by its spectral data (see *Exper. Part*). The (*E*)-configuration of the alkene moiety was expected and confirmed by the typical vicinal coupling constant ^3J(H–C(6), H–C(7)) of 15.7 Hz. The β-D-configuration of the anomeric center of the furanose was suggested by the small vicinal coupling constant ^3J(H–C(1),H–C(2)) = 0 Hz [28b] [34] [35]. The high chemoselectivity observed for the *Wittig-Horner* olefination of hemiacetal **4** can be interpreted in terms of steric factors: the reacting intermediate **4′** with an aldehydic moiety at C(6) is less sterically hindered (adjacent to CH_2(5)) than the isomeric intermediate **4″** with an aldehyde moiety at C(1) (adjacent to substituted centres). It is also possible that the concentration of **4′** is higher than that of **4″**.

Allylic bromination (*N*-bromosuccinimide (NBS)/CCl_4, UV light) of the crude alkenoate (+)-**5** gave a 7:3 bromide mixture **10a**/**10b** which upon treatment with Ag_2O in DMF (60°, 12 h) led to a 13.3:1 mixture of the *exo*- and *endo*-2,7-dioxabicyclo[2.2.1]heptane derivatives (–)-**8** and **9**, respectively, in 58% yield. Since the minor isomer **9** was found to be stable under the conditions of its formation, we propose that the

Scheme

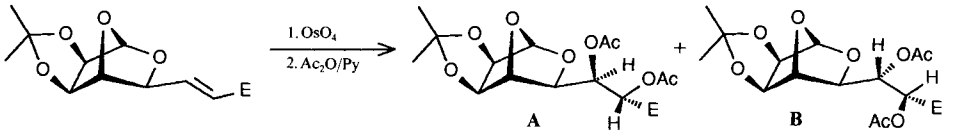


high stereoselectivity observed in the transformation of (+)-**5** into (−)-**8** arises from the incomplete intramolecular displacement of the Br-atom by the anomeric OH group of the furanose moiety in the minor bromide **10b** [35]. Allylic bromination of the (*tert*-butyl)dimethylsilyl furanoside derived from (+)-**5** gave also a 7:3 mixture of the corresponding bromides whose treatment with Bu_4NF (THF, −78°, 2 h) afforded, after column chromatography on silica gel, 53% of (−)-**8** and 16% of **9**. The relative *exo*- and *endo*-configurations of the 2,7-dioxabicyclo[2.2.1]heptane derivatives (−)-**8** and **9** were

given by their ^{1}H-NMR spectra (^3J(H–C(5),H–C(4)) = 0 Hz in (–)-**8** and ^3J(H–C(5), H–C(4)) = 3.8 Hz in **9**; carbohydrate numbering) [36].

Double hydroxylation of the olefinic moiety [37] of (–)-**8** with *N*-methylmorpholine *N*-oxide in the presence of a catalytic amount of OsO_4 (THF/H_2O 9:1) and 0.3 equiv. of *O*-(4-chlorobenzyl)hydroquinidine [38] gave a mixture of the expected diols which were transformed into a mixture of the more readily isolated acetonides (–)-**11** and **12** (75%) on treatment with dimethoxypropane and a trace amount of TsOH. Their ratio was 9.1:1 (by 250-MHz ^{1}H-NMR); they could be separated by flash chromatography (silica gel). Attempts to improve the diastereoselectivity of the double hydroxylation by changing the oxidant ($K_3[Fe(CN)_6]/K_2CO_3$ [39], H_2O_2), the relative amount of the catalyst (OsO_4), or/and the solvent (*t*-BuOH/H_2O, acetone/H_2O) all failed (see also the *Table*). The

Table. *Diastereoselectivity of the Double Hydroxylations with OsO_4* (1 equiv.)[a])



E	Solvent (base)	Base[b])	A/B[c])
COOMe ((–)-**8**)	THF/pyridine 4:1 (*v*/*v*)	–	3 :1
CH_2OH	THF/pyridine 4:1 (*v*/*v*)	–	3.5:1
CH_2OAc	THF/pyridine 4:1 (*v*/*v*)	–	3 :1
$CH_2OSi(t\text{-Bu})Me_2$	THF/pyridine 4:1 (*v*/*v*)	–	3 :1
CH_2OH	THF	$Me_2NCH_2CH_2NMe_2$ (1 equiv.)	3 :1
CH_2OH	THF	DBU (1 equiv.)	4 :1
CH_2OH	THF	$(t\text{-Bu})_2$MePy (1 equiv.)	7 :1
CH_2OAc	THF	$(t\text{-Bu})_2$MePy (1 equiv.)	7 :1
CH_2OH	THF	$NH_2CH_2CH_2CH_2NH_2$ (1 equiv.)	1.5:1

[a]) Experiments run with racemic starting materials.
[b]) DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; $(t\text{-Bu})_2$MePy = 2,6-di(*tert*-butyl)-4-methylpyridine.
[c]) Product ratio determined by 250-MHz ^{1}H-NMR of the crude reaction mixture.

relative configuration of the newly created chiral centres in α and β position to the ester groups in (–)-**11** and **12** was established by the transformation of (–)-**11** into the corresponding alcohol (–)-**13** ($LiBH_4$/THF, 20°) and deprotection by acidic hydrolysis (CF_3CO_2H/H_2O 8:1, 20°, 14 h) which gave the known D-*threo*-L-*talo*-octose ((–)-**1**) [28b] [30]. Accordingly, the diastereoselectivity of the double hydroxylation (–)-**8** → (–)-**11** follows the empirical rule of *Kishi et al.* [40] for the oxidation of allylic ethers.

Conclusion. – The high chemoselectivity of the *Wittig-Horner* condensation of **4** with methyl (dimethoxyphosphoryl)acetate and the stereoselectivity of the allylic bromination of the resulting (*E*)-enoate (+)-**5** have opened a new route to the asymmetric total synthesis of octoses starting from optically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives. Since the latter 'chirons' exist in both enantiomeric forms and can be substituted at C(5) and C(6) by other functions than by protected OH groups [1], our approach is, in principle, applicable to the total synthesis of stereoisomers of (–)-**1** and other octose analogues.

We thank *F. Hoffmann-La Roche AG*, Basel, the *Swiss National Science Foundation*, and the *Fonds Herbette*, Lausanne, for financial support.

Experimental Part

General. See [31].

*(+)-Methyl (E)-5,6,7-Trideoxy-2,3-O-isopropylidene-β-*D*-ribo-oct-6-enofuranuronate* ((+)-**5**). (−)-5-Deoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hexofuranurono-6,1-lactone [31] ((−)-**3**; 0.7 g, 3.5 mmol) was dissolved in anh. CH_2Cl_2 (35 ml). After cooling to −90°, 1.2M DIBAL in toluene (3 ml, 3.5 mmol) was added dropwise under stirring and Ar. The mixture was stirred for another at −90°, and then a soln. of $Na[(MeO)_2P(O)CHCOOMe]$ in THF cooled to −78° (freshly prepared from $(MeO)_2P(O)CH_2COOMe$ (0.56 ml, 3.9 mmol) in anh.THF (10 ml) by dropwise addition to a suspension of NaH (0.17 g, 3.9 mmol) in anh. THF (60 ml) at 0° and stirring 2 h at 0° and 2 h at 20°) was added portionwise under vigourous stirring at −78°. Then the temp. was allowed to rise slowly to 20° and the mixture stirred for 20 h. Sat. aq. NH_4Cl soln. (2 ml) was added and the mixture stirred for 10 min and then filtered through silica gel (10 g) and *Celite* (10 g; washing with CH_2Cl_2 (50 ml)). More sat. aq. NH_4Cl soln. (50 ml) was then added to the filtrate and the mixture extracted with CH_2Cl_2 (40 ml, 3 times). The combined extract was dried ($MgSO_4$) and evaporated and the residue purified by filtration on a short column of silica gel (50 g, petroleum ether/AcOEt 2:1): 0.65 g (72%), of colourless oil which contained a trace amount of **6** and **7**. This crude product can be used directly in the next step without further purification. An anal. sample of (+)-**5** was obtained by FC (silica gel, petroleum ether/Et_2O/CH_2Cl_2 2:3:2). $[\alpha]_D^{25} = +20$, $[\alpha]_{578}^{25} = +20.6$, $[\alpha]_{546}^{25} = +24.2$, $[\alpha]_{476}^{25} = +46.3$, $[\alpha]_{365}^{25} = +83.4$ ($c = 0.64$, $CHCl_3$). UV (EtOH): 208 (14670). UV (MeCN): 208 (15300). IR (film): 3500–3300, 2940, 1712, 1650, 1435, 1380, 1325, 1280, 1200, 1080, 1068, 980, 870. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.96 (*dt*, $^3J = 15.7$, 7.0, H–C(6)); 5.93 (*dt*, $^3J = 15.7$, $^4J = 1.5$, H–C(7)); 5.48 (*d*, ^3J(H–C(1),OH) = 2.7, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 4.68 (*d*, $^3J = 5.9$, H–C(2)); 4.61 (*dd*, $^3J = 5.9$, ^3J(H–C(3),H–C(4)) = 0.9, H–C(3)); 4.33 (*ddd*, $^3J = 7.5$, 7.6, ^3J(H–C(4),H–C(3)) = 0.9, H–C(4)); 3.74 (*s*, MeO); 2.72 (*d*, $^3J = 2.7$, OH); 2.60 (*m*, CH_2(5)); 1.50, 1.32 (2*s*, Me_2C). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 166.9 (*s*, C(8)); 144.7 (*d*, ^1J(C,H) = 157.5, C(6)); 123.3 (*d*, ^1J(C,H) = 162.5, C(7)); 112.6 (*s*); 103.2 (*d*, ^1J(C,H) = 175, C(1)); 86.0 (*d*, ^1J(C,H) = 157.5, C(3)); 85.4 (*d*, ^1J(C,H) = 152.5, C(4)); 84.0 (*d*, ^1J(C,H) = 157.5, C(2)); 51.5 (*q*, ^1J(C,H) = 150, MeO); 38.2 (*t*, ^1J(C,H) = 126, C(5)); 26.4, 24.9 (2*q*, ^1J(C,H) = 128, Me_2C). CI-MS (NH_3): 259 (8, $[M + 1]^+$), 243 (19), 227 (9), 212 (4), 200 (41), 185 (15), 154 (9), 122 (45), 94 (63), 81 (100), 70 (10). Anal. calc. for $C_{12}H_{18}O_6$ (258.27): C 55.81, H 7.02; found: C 55.07, H 6.98.

*(±)-Methyl (E)-5,6,7-Trideoxy-2,3-O-isopropylidene-β-*D,L-ribo-*oct-6-enofuranuronate* ((±)-**5**). The same procedure as described for (+)-**5**, starting with (±)-**3** [31] (1 g), gave 1.2 g (93%) of crude, colourless oil that crystallized from hexane/Et_2O: 0.95 g (74%). M.p. 82–83°.

*(−)-Methyl (E)-1,4-Anhydro-6,7-dideoxy-2,3-O-isopropylidene-β-*L-talo-*oct-6-enopyranuronate* ((−)-**8**). A mixture of (+)-**5** (253 mg, 1 mmol) and *N*-bromosuccinimide (262 mg, 1.5 mmol, 1.5 equiv.) in anh. CCl_4 (40 ml) was irradiated (*Philips HPK-125* UV lamp) in a *Pyrex* vessel at 20° under stirring and Ar. After the disappearance of (+)-**5** (TLC control (petroleum ether/AcOEt 3:1): *ca.* 2.5 h), the mixture was filtered. The filtrate, was evaporated leaving a slightly yellow residue which was dissolved in anh. DMF (25 ml). Ag_2O (0.35 g, 1.5 mmol) was added and the mixture stirred at 60° for 12 h. The precipitate was filtered off over *Celite* (washing with CH_2Cl_2) and the solvent evaported. ^{1}H-NMR (250 MHz, $CDCl_3$) of crude oil: 13.3:1 mixture (−)-**8**/**9**. FC on silica gel (25 g, petroleum ether/AcOEt 3:1) gave 137 mg (54.6%) of (−)-**8** and 9 mg (3.6%) of **9** (total yield 58.2%).

*Data of (−)-***8**. M.p. 82–83°. $[\alpha]_D^{25} = -12.1$, $[\alpha]_{578}^{25} = -9.3$, $[\alpha]_{546}^{25} = -6.9$, $[\alpha]_{476}^{25} = +8.1$, $[\alpha]_{365}^{25} = +59.3$ ($c = 0.25$, $CHCl_3$). UV (EtOH): 204 (15400). UV (MeCN): 205 (14100). IR (KBr): 2980, 1705, 1660, 1440, 1370, 1310, 1210, 1170, 1105, 1060, 990, 980, 920, 860, 830, 782. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.78 (*dd*, $^3J = 15.5$, 5.2, H–C(6)); 6.05 (*dd*, $^3J = 15.5$, $^4J = 1.5$, H–C(7)); 5.55 (*s*, H–C(1)); 4.50 (*s*, H–C(4)); 4.41, 4.36 (2*d*, $^3J = 5.5$, H–C(2), H–C(3)); 3.98 (*dd*, $^3J = 5.2$, $^4J = 1.5$, H–C(5)); 3.75 (*s*, MeO); 1.46, 1.31 (2*s*, Me_2C). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 166.2 (*s*, C(8)); 143.8 (*d*, ^1J(C,H) = 160, C(6)); 123.1 (*d*, ^1J(C,H) = 165, C(7)); 112.7 (*s*); 100.4 (*d*, ^1J(C,H) = 184, C(1)); 81.0 (*d*, ^1J(C,H) = 164, C(2)); 80.6 (*d*, ^1J(C,H) = 169, C(3)); 79.1 (*d*, ^1J(C,H) = 160, C(4)); 72.1 (*d*, ^1J(C,H) = 150, C(5)); 51.7 (*q*, ^1J(C,H) = 148, MeO); 25.8, 25.3 (2*q*, ^1J(C,H) = 126, Me_2C). MS (70 eV): 257 (3, $[M + 1]^+$), 256 (0.1, $M^{+\cdot}$), 241 (11), 225 (5), 182 (3), 169 (3), 152 (6), 138 (4), 117 (29), 111 (24), 100 (39), 85 (67), 81 (31), 75 (100). Anal. calc. for $C_{12}H_{16}O_6$ (256.26): C 56.25, H 6.29; found: C 56.05, H 6.26.

*Data of Methyl (E)-1,4-Anhydro-6,7-dideoxy-2,3-*O*-isopropylidene-α-*D*-allo-oct-6-enopyranuronate* (**9**). IR (KBr): 2940, 1720, 1658, 1440, 1380, 1310, 1270, 1240, 1210, 1160, 915, 860, 825. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.87 (*ddd*, $^3J = 15.6$, 4.3, $^4J = 0.6$, H–C(6)); 6.15 (*dd*, $^3J = 15.6$, $^4J = 1.9$, H–C(7)); 5.53 (*s*, H–C(1)); 4.72 (*d*, $^3J = 3.8$, H–C(4)); 4.34 (*dd*, $^3J = 4.3$, 3.8, H–C(5)); 4.34, 4.30 (2*d*, $^3J = 5.5$, H–C(2), H–C(3)); 3.78 (*s*, MeO);

1.45, 1.27 (2*s*, Me_2C). MS (70 eV): 256 (0.9, $M^{+\cdot}$), 241 (13), 182 (2), 169 (2), 153 (2), 141 (3), 117 (6), 109 (15), 100 (28), 85 (35), 81 (18), 61 (100).

*(±)-Methyl (E)-1,4-Anhydro-6,7-dideoxy-2,3-*O*-isopropylidene-β-*D,L*-talo-oct-6-enopyranuronate* ((±)-**8**) *and (±)-Methyl (E)-1,4-Anhydro-6,7-dideoxy-2,3-*O*-isopropylidene-α-*D,L*-allo-oct-6-enopyranuronate* ((±)-**9**). Same procedure as described for (−)-**8**, starting with 387 mg of (±)-**5**: 222 mg of (±)-**8**, m.p. 86–87°, and 14.4 mg of (±)-**9**, m.p. 90–91°. Total yield: 62%.

*(−)-Methyl 1,4-Anhydro-2,3:6,7-di-*O*-isopropylidene-*D-threo-*β-*L-talo-octopyranuronate* ((−)-**11**) *and Methyl 1,4-Anhydro-2,3:6,7-di-*O*-isopropylidene-*L-threo-*β-*L-talo-octopyranuronate* (**12**). A mixture of (−)-**8** (108 mg, 0.42 mmol), *N*-methylmorpholine *N*-oxide (114 mg, 0.84 mmol), *O*-(4-chlorobenzyl)hydroquinidine (59 mg, 0.13 mmol), THF (27 ml), H_2O (3 ml), and 2.5% OsO_4 soln. in CCl_4 (1.3 ml, 0.13 mmol) was stirred at 20° for 3.5 d. After the addition of sat. aq. $Na_2S_2O_5$ soln. (30 ml), the mixture was heated under reflux for 2 h. After cooling to 20°, the mixture was extracted with AcOEt (30 ml, 5 times), the combined extract dried ($MgSO_4$), and the solvent evaporated. The white solid residue was dissolved in acetone (8 ml) and 2,2-dimethoxypropane (8 ml). After the addition of TsOH (1 mg), the soln. was stirred at 20° for 20 h. Sat. aq. $NaHCO_3$ soln. (20 ml) was added and the mixture extracted with CH_2Cl_2 (20 ml, 4 times). The combined org. extracts were washed with sat. aq. NaCl soln. (20 ml, twice), dried ($MgSO_4$), and evaporated: white solid, (−)-**11**/**12** 9.1:1. FC (silica gel, petroleum ether/AcOEt 3:1) afforded 94 mg (68%) of (−)-**11** and 10 mg (7.2%) of **12**. Total yield: 75%.

Data of (−)-**11**. M.p. 110.5–111°. $[\alpha]_D^{25} = -11.3$, $[\alpha]_{578}^{25} = -12.9$, $[\alpha]_{546}^{25} = -14.7$, $[\alpha]_{476}^{25} = -26.4$, $[\alpha]_{365}^{25} = -47$ ($c = 1.15$, $CHCl_3$). IR (KBr): 2980, 2960, 1765, 1430, 1375, 1210, 1110, 1055, 1000, 950, 915, 860, 840, 820. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.47 (*s*, H–C(1)); 4.74 (*s*, H–C(4)); 4.49 (*d*, $^3J = 5.8$, H–C(7)); 4.37, 4.32 (2*d*, $^3J = 5.5$, H–C(2), H–C(3)); 4.19 (*dd*, $^3J = 6.8, 5.8$, H–C(6)); 3.8 (*s*, MeO); 3.48 (*d*, $^3J = 6.8$, H–C(5)); 1.46, 1.41, 1.30 (3*s*, 2 Me_2C). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 171.1 (*s*, C(8)); 112.6, 111.8 (2*s*); 110.5 (*d*, ^1J(C,H) = 182.5, H–C(1)); 81.1 (*d*, ^1J(C,H) = 165, C(4)); 79.0, 78.9 (2*d*, ^1J(C,H) = 156, C(2), C(3)); 78.0 (*d*, ^1J(C,H) = 150, C(5)); 76.4 (*d*, ^1J(C,H) = 155, C(6)); 73.7 (*d*, ^1J(C,H) = 153, C(7)); 52.6 (*q*, ^1J(C,H) = 148, MeO); 27.2, 25.2 (2*q*, ^1J(C,H) = 125, Me_2C); 25.8 (*q*, ^1J(C,H) = 125, Me_2C). CI-MS (NH_3): 348 (100, $[M + NH_4]^+$), 331 (60, $[M + 1]^+$), 330 (0.2, $M^{+\cdot}$), 315 (14), 290 (1), 273 (4), 257 (6), 226 (2), 213 (1), 197 (1), 168 (3), 159 (13), 130 (4), 97 (2), 85 (4), 73 (5). Anal. calc. for $C_{15}H_{22}O_8$ (330.34): C 54.54, H 6.71; found: C 54.50, H 6.57.

Data of **12**. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.52 (*s*, H–C(1)); 4.80 (*s*, H–C(4)); 4.42 (*d*, $^3J = 6.8$, H–C(7)); 4.38, 4.34 (2*d*, $^3J = 5.5$, H–C(2), H–C(3)); 4.19 (*dd*, $^3J = 6.8, 6.4$, H–C(6)); 3.82 (*s*, MeO); 3.53 (*d*, $^3J = 6.4$, H–C(5)); 1.49, 1.46, 1.43, 1.30 (4*s*, 2 Me_2C). CI-MS (NH_3): 331 (25, $[M + 1]^+$), 315 (89), 271 (19), 257 (30), 244 (3), 226 (4), 214 (11), 198 (6), 185 (5), 169 (18), 159 (100), 141 (37), 136 (11), 130 (30), 109 (21), 97 (18), 85 (44), 73 (55).

*(±)-Methyl 1,4-Anhydro-2,3-*O*-isopropylidene-*D,L-threo-β-*L,D-talo-octopyranuronate*. A mixture of (±)-**8** (92 mg, 0.36 mmol), 2.5% OsO_4 soln. in CCl_4 (0.1 ml), and *N*-methylmorpholine *N*-oxide (85 mg, 0.65 mmol) in THF/H_2O 9:1 (10 ml) was stirred at 20° for 7 d. After filtration over silica gel (10 g, AcOEt), the soln. was evaporated: slightly yellow solid. FC (30 g, SiO_2, AcOEt/petroleum ether 4:1) gave 64 mg (61.5%) of (±)-methyl 1,4-anhydro-2,3-*O*-isopropylidene-D,L-*threo*-β-L,D-*talo*-octopyranuronate. M.p. 158–159°. IR (KBr): 3550–3350, 2960, 1740, 1290, 1260, 1210, 1130, 1090, 1060, 910, 860, 825. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.46 (*s*, H–C(1)); 4.80 (*s*, H–C(4)); 4.39 (*dd*, $^3J = 4.3$,[4]) 1.5, H–C(7)); 4.38, 4.32 (2*d*, $^3J = 5.5$, H–C(2), H–C(3)); 3.85 (*s*, MeO); 3.74 (*dddd*, $J = 10$[4]), 9, 1.5, 0.5[4]), H–C(6)); 3.40 (*d*, $^3J = 9.0$, H–C(5)); 3.07[4]) (*dd*, $^3J = 4.3$, $^4J = 0.5$, OH–C(7)); 2.20[4]) (*d*, $^3J = 10.0$, OH–C(6)); 1.47, 1.31 (2*s*, Me_2C). CI-MS (NH_3): 291 (56, $[M + 1]^+$), 290 (9, $M^{+\cdot}$), 275 (26), 233 (6), 214 (7), 197 (2), 186 (5), 168 (20), 155 (9), 136 (2), 124 (3), 97 (13), 86 (5), 71 (6).

*(±)-Methyl 1,4-Anhydro-2,3-*O*-isopropylidene-*L,D-threo-β-*L,D-talo-octopyranuronate*. The 2nd fraction of the above FC gave 10 mg (9.6%) of colourless crystals. M.p. 119–120°. IR (KBr): 3540–3340, 2960, 1760, 1380, 1210, 1130, 1090, 1065, 1050, 985, 950, 915, 860, 830. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.51 (*s*, H–C(1)); 4.67 (*s*, H–C(4)); 4.39, 4.34 (2*d*, $^3J = 5.5$, H–C(2), H–C(3)); 4.25 (*dd*, $^3J = 6.3$[4]), 1.8, H–C(7)); 3.85 (*m*, H–C(6)); 3.84 (*s*, MeO); 3.64 (*d*, $^3J = 7$, H–C(5)); 3.13[4]) (*d*, $^3J = 6.3$, OH–C(7)); 2.53[4]) (*d*, $^3J = 5.6$, OH–C(6)); 1.46, 1.29 (2*s*, Me_2C). CI-MS (NH_3): 291 (49, $[M + 1]^+$), 275 (21), 240 (9), 215 (39), 204 (10), 180 (9), 168 (17), 156 (10), 145 (8), 121 (10), 109 (10), 97 (10), 85 (12).

*(−)-1,4-Anhydro-2,3:6,7-di-*O*-isopropylidene-*D-threo-β-*L-talo-octopyranose* ((−)-**13**). A soln. of (−)-**11** (111 mg, 0.34 mmol) in anh. THF (10 ml) was added dropwise to a stirred soln. of $LiBH_4$ (36.7 mg, 1.68 mmol) in anh. THF (10 ml) at 20° and under Ar. The mixture was stirred at 20° for 22 h and then cooled to 0°. After slow addition of sat. aq. NH_4Cl soln. (10 ml), the mixture was extracted with AcOEt (20 ml, 3 times), the combined extract dried (Na_2SO_4) and evaporated, and the residue filtered through a short column of silica gel (8 g, petroleum ether/AcOEt

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[4]) Disappears on mixing with D_2O.

1:1) and then recrystallized from petroleum ether/AcOEt: 98 mg (96.5%). Colourless crystals. M.p. 106–107°. $[\alpha]_D^{25} = -22.2$, $[\alpha]_{578}^{25} = -23.0$, $[\alpha]_{546}^{25} = -26.6$, $[\alpha]_{476}^{25} = -50.1$, $[\alpha]_{365}^{25} = -83.8$ ($c = 0.73$, $CHCl_3$). IR (KBr): 3470, 2980, 2930, 1468, 1372, 1255, 1162, 1140, 1090, 1060, 1035, 990, 950, 910, 860, 825. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.45 (*s*, H–C(1)); 4.72 (*s*, H–C(4)); 4.38, 4.29 (2*d*, $^3J = 5.5$, H–C(2), H–C(3)); 3.99 (*dt*, $^3J = 7.8$, 4.5, H–C(7)); 3.88–3.66 (*m*; after mixing with D_2O, 2*dd*, $^2J = 12$, $^3J = 4.5$; CH_2(8)); 3.65 (*dd*, $^3J = 8.1$, 7.8, H–C(6)); 3.41 (*d*, $^3J = 8.1$, H–C(5)); 2.15 (*dd*, $^3J = 8.0$, 4.5, disappeared after mixing with D_2O, OH–C(8)); 1.46 (3 H), 1.40 (6 H), 1.26 (3 H, 3*s*, 2 Me_2C). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 112.5, 109.5 (2*s*); 100.3 (*d*, ^1J(C,H) = 183, C(1)); 81.0 (*d*, ^1J(C,H) = 160, C(4)); 80.1 (*d*, ^1J(C,H) = 145, C(5)); 79.3 (*d*, ^1J(C,H) = 166, C(2)); 78.9 (*d*, ^1J(C,H) = 164, C(3)); 76.1 (*d*, ^1J(C,H) = 148, C(6)); 74.4 (*d*, ^1J(C,H) = 153, C(7)); 62.6 (*t*, ^1J(C,H) = 141, C(8)); 26.9, 25.8, 25.2 (3*q*, ^1J(C,H) = 125, 2 Me_2C). CI-MS (NH_3): 320 (100, $[M + NH_4]^+$), 303 (78, $[M + 1]^+$), 287 (35), 271 (4), 262 (3), 245 (18), 229 (13), 207 (4), 185 (3), 169 (4), 155 (5), 140 (4), 131 (30), 123 (7), 114 (15), 97 (15), 85 (17). Anal. calc. for $C_{14}H_{22}O_7$ (302.3): C 53.60, H 7.33; found: C 55.59, H 7.29.

D-threo-L-talo-*Octose* ((–)-**1**). A mixture of (–)-**13** (26 mg, 0.086 mmol) and CF_3COOH/H_2O 8:1 (2 ml) was stirred at 20° for 14 h. The solvent was evaporated, the crude octose dissolved in H_2O, the solvent evaporated, and the white crystalline residue washed with anh. Et_2O and dried *in vacuo* to give 21 mg (100%) of colourless solid. M.p. 144–147° (N_2, sealed tube; [30]: 138–140°) $[\alpha]_D^{25} = -14.1$, $[\alpha]_{578}^{25} = -14.5$, $[\alpha]_{546}^{25} = -15.5$, $[\alpha]_{476}^{25} = -23.1$, $[\alpha]_{365}^{25} = -32.5$ ($c = 0.815$, H_2O, after 4 d; [30]: $[\alpha]_D^{25} = -14.4$ ($c = 3.0$, H_2O)). Other spectral data were identical to those reported in [28b] for (–)-**1**.

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