hydride (1.01 g, 26.6 mmol) in dry THF (100 mL) was added dropwise a solution of 11 (8.00 g, 22.2 mmol) in dry THF (20 mL) over a period of 10 min. The reaction mixture was refluxed for 2 h, cooled to 0 °C, and then quenched by addition of saturated aqueous NH_4Cl solution (1 mL). The resulting mixture was diluted with ether (300 mL), dried (Na_2SO_4), and concentrated in vacuo to afford a colorless oil, which was purified by flash column chromatography on silica gel (elution with CH_2Cl_2/MeOH, 9:1) to give 7.02 g (100%) of **12** as a colorless waxy solid which was identical with natural one[1,2] in every aspect except optical rotation. The waxy solid slowly changed into a yellow oil on prolonged standing at room temperature. An analytical sample was obtained from silica gel preparative thick-layer chromatography (hexane/ether, 1:4) as a white solid: TLC R_f 0.37 (CH_2Cl_2/MeOH, 9:1); mp 25.5–26.5 °C; $[\alpha]^{25}_D$ +31.08° (*c* 1.0 in $CHCl_3$); IR (NaCl, neat) 3374 (OH), 3040, 2899, 1448, 1147, 695 cm^{-1}; ^1H NMR δ 7.37–7.13 (m, 5 H, aromatic), 3.82 (m, 1 H, H-3), 2.92 (dd, $J_{6,6'}$ = 13.2, $J_{6,2}$ = 10.2 Hz, 1 H, H-6), 2.83 (dd, $J_{6,6'}$ = 13.2, $J_{6',2}$ = 4.5 Hz, 1 H, H-6'), 2.48 (br s, 1 H, OH), 2.33 (s, 3 H, NCH_3), 2.26 (ddd, $J_{2,6}$ = 10.2, $J_{2,6'}$ = 4.5, $J_{2,3}$ = 4.0 Hz, 1 H, H-2), 2.18 (m, 1 H, H-4), 2.10 (m, 1 H, H-5), 1.72 (m, 1 H, H-7), 1.50–1.12 (m, 16 H, H-4', H-7', H-8–H-14), 0.88 (t, $J_{14,15}$ = 6.3 Hz, 3 H, H-15); MS *m/z* (rel intensity) 318 (M^+ + 1, 0.3), 317 (M^+, 0.6), 316 (M^+ - 1, 1.5), 227 (21.0), 226 (100); HRMS calcd for $C_{21}H_{35}NO$ *m/e* 317.2719, found 317.2699. Anal. Calcd for $C_{21}H_{35}NO$: C, 79.44; H, 11.11; N, 4.41. Found: C, 79.43; H, 11.28; N, 4.39.

The ^{13}C NMR ($CDCl_3$), ^{13}C NMR (CD_3COOD), and ^1H NMR (CD_3COOD) spectral data are identical with those in the literature.[1]

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Registry No. **1**, 2457-93-4; **2**, 131013-17-7; **3**, 131013-18-8; **4a**, 131013-19-9; **4b**, 131013-20-2; **5a**, 131013-21-3; **5b**, 131013-22-4; **6a**, 131013-23-5; **6b**, 131013-24-6; **7a**, 131013-25-7; **7b**, 131100-31-7; **8a**, 131013-26-8; **9**, 131013-27-9; **10a**, 131013-28-0; **10b**, 131013-29-1; **11**, 131013-30-4; **12**, 125356-66-3; *n*-$C_8H_{17}P^+Ph_3I^-$, 71344-40-6.

Supplementary Material Available: ^1H NMR spectra of all new compounds including NOE, DEPT, and decoupling experiments (36 pages). Ordering information is given on any current masthead page.

Highly Stereoselective Total Syntheses of Octoses and Derivatives[1a]

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Mukaiyama cross aldolizations of (*R*)-2,3-*O*-isopropylideneglyceraldehyde (**10**) with (1*R*,4*S*,5*R*,6*R*)-5-*exo*,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**8**) and to its enantiomer ((−)-**8**) were highly diastereoselective and led to the corresponding u,u,l or SYNCAT ((+)-**11**) and u,u,u or ANCAT ((−)-**21**) aldols, respectively. The results were interpreted in terms of extended open transition state models with (ul,lk) and (ul,ul) topicities, respectively, which minimize steric repulsions. Aldols (+)-**11** and (−)-**21** were converted into (*tert*-butyl)dimethylsilyl 6-*O*-acetyl-2,3:7,8-di-*O*-isopropylidene-D-*glycero*-L-*talo*-α-octofuranosid-5-ulose ((−)-**18**) and its D-*talo* diastereomer ((+)-**28**), respectively. Reduction of (−)-**18** with $LiEt_3BH$ in THF gave, after deprotection, the known D-*threo*-L-*talo*-octose ((−)-**4**). Reduction of (−)-**18** with $(i\text{-Bu})_2AlH$/THF gave, after deprotection, the unknown D-*threo*-D-*allo*-octose ((+)-**5**) with high stereoselectivity. Similarly, the unknown D-*erythro*-D-*talo*-octose ((+)-**6**) and D-*erythro*-L-*allo*-octose ((−)-**7**) were derived from (+)-**28** through reduction with $LiB(s\text{-Bu})_3H$ and $(i\text{-Bu})_2AlH$, respectively.

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

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(2) (a) Danishefsky, S. J.; DeNinno, M. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 15. (b) Kishi, Y. *Pure Appl. Chem.* **1989**, *61*, 313. (c) Hanessian, S.; Sato, K.; Liak, T. J.; Danh, N.; Dixit, D.; Cheney, B. V. *J. Am. Chem. Soc.* **1984**, *106*, 6114. (d) Kominato, K.; Ogawa, S.; Suami, T. *Carbohydr. Res.* **1988**, *174*, 360. (e) Rosenbrook, W.; Lartey, P. A.; Riley, D. A. U.S. Patent; *Chem. Abstr.* **1987**, *106*, 50600y. (f) Secrist, J. A. III; Barnes, K. D.; Wu, S.-R. In *Trends in Synthetic Carbohydrate Chemistry*; ACS Symposium Series 386; Horton, D., Hawkins, L. D., McGarvey, G. J., Eds.; American Chemical Society: Washington, D.C., 1989; pp 93–106 and references cited therein.

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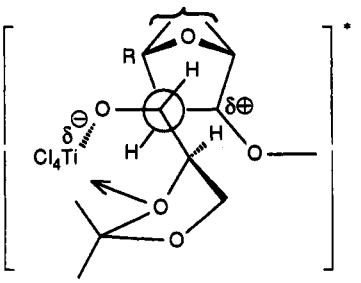
drates, *N*-acetylneuraminic acid (NANA) must be cited. It is a constituent in glycoconjugates that play an important role in the regulation of biological phenomena.[11] Calditol, a branched nonitol, has been found to be part of complex macrocyclic tetraether lipids isolated from the membrane of thermoacidophilic bacteria.[12] A 1,2:8,9-bis(anhydro)nonitol (WF-3405) isolated from the culture of *Amouroascus aureus* F-3405 has been shown to exhibit antitumor activity.[13,14] Higher carbon sugars and analogues can also serve as chiral synthons for the preparation of macrolide antibiotics such as erythromycine[15] or streptovaricin.[16]

One of the earlier methods for the synthesis of higher carbon sugars is the Kiliani–Fischer cyanohydration reaction which was used to extend the aldose chain by one carbon from the reducing end.[17] A similar iterative but more stereoselective homologation method employing 2-(trimethylsilyl)thiazole as formyl anion equivalent has been proposed recently by Dondoni and co-workers.[18] Other approaches for the one-carbon chain extension of aldoses rely on the condensation of nitromethane[19] and sulfur[20] or silicon[21] stabilized methide anions.[22] These methods have been augmented by procedures that permit extension of the sugar chain by two or more carbon atoms; they include the Wittig–Horner olefination of sugar-derived aldehydes,[23] followed by hydroxylation of the newly created



(R,Si,Re,R)

Figure 1.

double bond,[24] the Reformatsky reaction,[25] the Ivanov reaction,[26] the Darzens reaction,[27] the Henry reaction,[28] the Knoevenagel–Doebner condensation,[29] and other nucleophilic additions involving various organometallic reagents.[30] Other methods involving radical C–C bond formation,[31] cycloadditions of sugar-derived aldehydes to dienes,[32] cross-aldolizations,[33] and related condensation reactions[34] have been proposed recently. In many instances, the stereoselectivity of these reactions needs to be improved for the development of practical synthetic methods.

In the last few years, we have shown that 7-oxabicyclo[2.2.1]hept-5-en-2-yl (7-oxanorbornenyl) derivatives such as **1**, **2**, (+)-**3**, and (−)-**3** can be considered as chirons equivalent to hexoses.[35–45] These bicyclic systems can be

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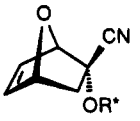
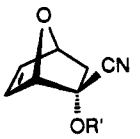
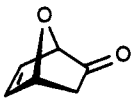
prepared optically pure readily[36] with the help of chiral auxiliaries (e.g. (1*S*)- or (1*R*)-camphanic acid) that are recovered at early stages of the syntheses. The methods exploit the high exo-facial selectivity of the bicyclic systems **1**–**3** and the control of the regioselectivity of the electro-



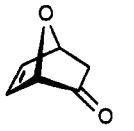
1 R*=(1*S*)-camphanoyl



2 R'=(1*R*)-camphanoyl

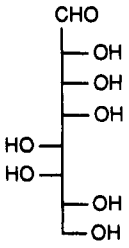


(+)-**3**

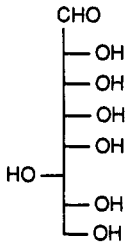


(-)-**3**

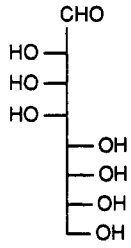
philic reactions occurring at C(5) and C(6) by the remote substituents at C(2).[35] High stereoselectivity has also been observed for the cross-aldolization of 7-oxabicyclo[2.2.1]-octan-2-one derivatives with sugar aldehydes.[1a] This principle is applied here in the development of the first total, asymmetric syntheses of D-*threo*-L-*talo*-octose ((-)-**4**), D-*threo*-D-*allo*-octose ((+)-**5**), D-*erythro*-D-*talo*-octose ((+)-**6**), and D-*erythro*-L-*allo*-octose ((-)-**7**). While octose (-)-**4** has already been described,[46] the stereoisomers (+)-**5**, (+)-**6**, and (-)-**7** are new carbohydrates.



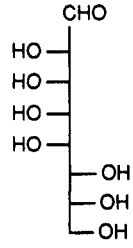
(-)-**4**



(+)-**5**



(+)-**6**



(-)-**7**

Results and Discussion

Double hydroxylation of **1**, followed by protection of the *exo-cis*-diol and saponification of the (1'*S*)-camphanate afforded 7-oxanorbornanones derivative (+)-**8** and (1*S*)-camphanic acid (recovery of the chiral auxiliary).[38] The corresponding silyl ether (-)-**9**[41b] was condensed with (*R*)-2,3-*O*-isopropylideneglyceraldehyde (**10**)[47] in the presence of $TiCl_4$ (CH_2Cl_2, -78 °C) to furnish the product of cross-aldolization (+)-**11** (55–62%) (see Scheme I). No other stereoisomeric aldols could be observed in the 360-MHz ^1H NMR spectrum of the crude reaction mixture. The exo configuration of the newly created C–C bond was indicated by ^3J(H-C(3),H-C(4)) ≃ 0 Hz.[48] The *R* configuration of the alcoholic carbon center was established as shown below (see next section). Taking into consideration the *R* configuration of D-glyceraldehyde derivative **10**, the cross-aldolization (-)-**9** + **10** → (+)-**11** corresponds to a (ul,lk)[49] topicity giving a u,u,l or SYNCAT[50] diastereomer.[49,50] This result can be interpreted in terms of the transition state shown in Figure 1 which minimizes steric repulsions between the reactants.[47] It implies co-coordination of the aldehyde and α-alkoxy functions of **10** to $TiCl_4$ and electrophilic addition of this complex to the less sterically hindered face of the enol silane (-)-**9**, in agreement with Cram's model[51,52] (extended open transition-state model[53] of the cross-aldolization).

Baeyer–Villiger oxidation of ketone (+)-**11** gave exclusively lactone (-)-**12** (86%). Base-catalyzed (K_2CO_3) methanolysis of (-)-**12** afforded hemiacetals **13** as a 1:2.2 mixture of the α- and β-anomers. Under these conditions, about 5–10% of epimerization at C(5) (furanurono-6,1-lactone numbering) was observed. Attempts to generate ester **13** under acidic conditions were not met with success. Treatment of **13** with (*t*-Bu)$Me_2SiOSO_2CF_3$ (1.5 equiv, CH_2Cl_2, 0 °C) in the presence of 2,6-lutidine (1.5 equiv) led to the selective silylation of the hemiacetal, giving (-)-**14** (84%) whose ^1H NMR spectrum indicated that this silyl furanoside consisted mostly of the anomer (see (-)-**19**) in which the (*t*-Bu)Me_2SiO group is trans with respect to the oxy subsituent at C(2) (α-anomer if one considers the carbon atom C(5) bearing the COOMe group to define the L configurational relationship; both the (*t*-Bu)Me_2SiO and COOMe groups are to the left in a Fischer projection formula). Ester (-)-**14** was reduced with $LiAlH_4$ in THF into diol (-)-**15** (94%) whose primary alcohol could be displaced selectively with 2-nitrophenyl selenocyanate and tri-*n*-butylphosphine.[54] Acetylation of the product so-obtained afforded (-)-**16** (63%). Oxidative elimination of the selenide (-)-**16** using 3-chloroperbenzoic acid and $NaHCO_3$ (CH_2Cl_2) led to alkene (-)-**17** (87%). Optimal yield for that reaction was obtained using 2.2 equiv of the peracid. A low yield of (-)-**17** was observed when H_2O_2 was used for the oxidative elimination. Alternatively, ozonolysis of the selenide (-)-**16** at -78 °C followed by warming in the presence of Et_2NH also produced (-)-**17** in a good yield. Ketone (-)-**18** was obtained (92%) upon ozonolysis of (-)-**17**. Thus the conversion of (-)-**16** into (-)-**18** (77%) could be made a one-pot process.[55] Reduction of ketone (-)-**18** with $LiAlH_4$ (THF, 0 °C, 20 min) gave a 1:1 mixture of diols (-)-**19** and (-)-**20**, which could be separated by column chromatography on silica gel. With L-Selectride

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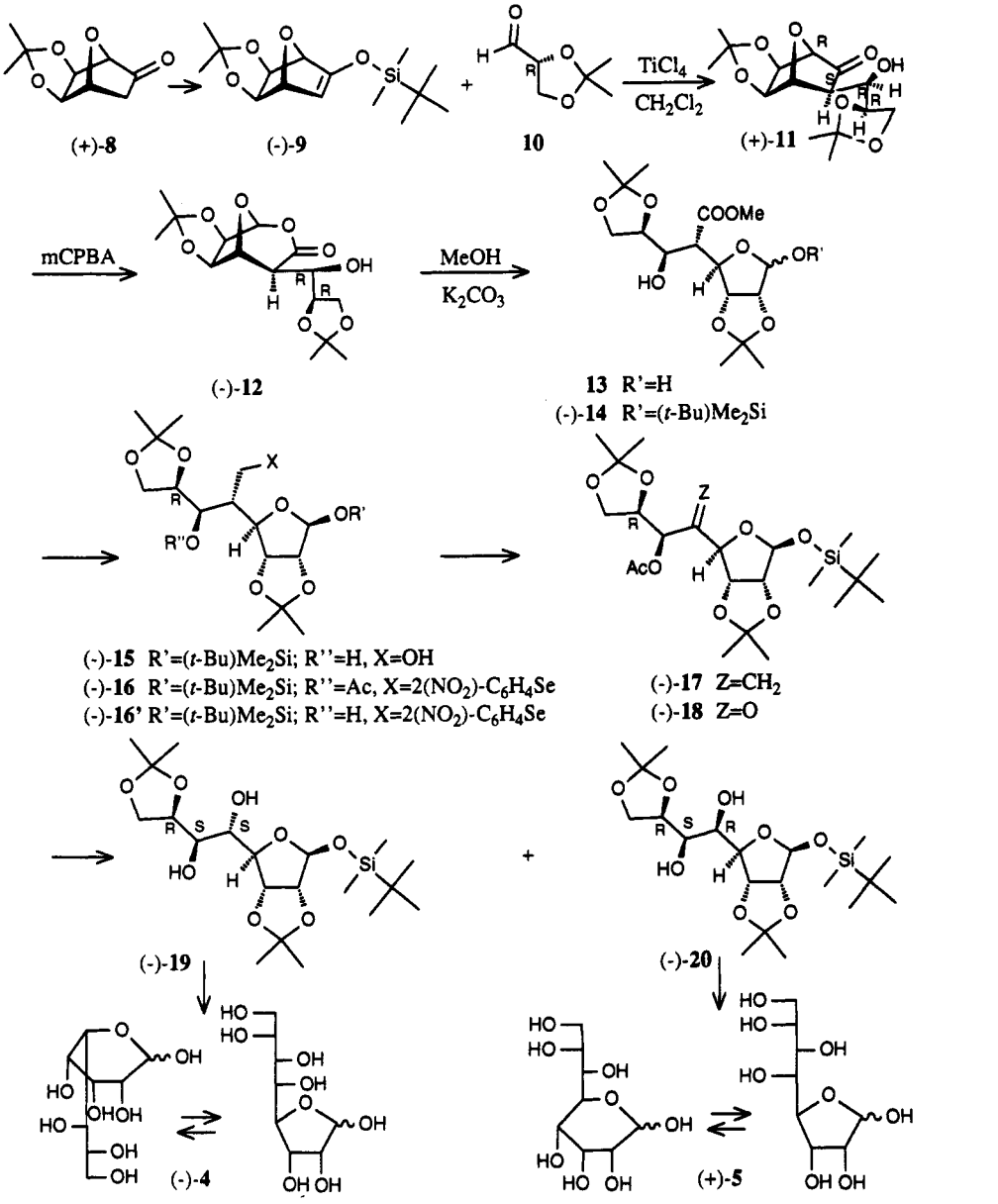
Scheme I



(Aldrich) ($LiB(i\text{-}Bu)_3H$, THF, −78 °C, 1 h) and Superhydride (Aldrich) ($LiB(Et)_3H$, THF, −78 °C, 1 h) the selectivity was 16.3:1.0 and >20:1 (by 250-MHz ^1H NMR of the crude reaction mixture), respectively. Interestingly, reversal of the selectivity was observed with DIBAH ($Al(i\text{-}Bu)_2H$, THF, −20 °C, 4 h) which led to a 1:11.3 mixture of (−)-**19** and (−)-**20**. Deprotection of (−)-**19** and (−)-**20** ($AcOH/H_2O$ 4:1, 60 °C, 5 h) furnished (−)-**4** (79%) and (+)-**5** (87%), respectively. The ^1H NMR spectra of (−)-**4** in D_2O indicated an equilibrium of β-furanose, α-furanose, β-pyranose, and α-pyranose in 2:1:12.7:4 ratio. Similarly, the ^1H NMR spectrum of (+)-**5** in D_2O gave a 1:7.5:2:12.5 ratio for the β-furanose, α-furanose, β-pyranose, and α-pyranose stereomers. The H–C(1) signal assignments were based on the comparison with ^1H NMR spectrum of D-talose and D-allose taken under the same conditions.[56]

Under conditions similar to those used for the cross-aldolization (−)-**9** + **10** → (+)-**11**, the condensation of (+)-**9** derived from "naked sugar" **2** with **10** was a highly diastereoselective process and led to β-hydroxy ketone (−)-**21** (55%). The *S* configuration of the alcoholic carbon center was established as described here below. It corresponds to a (ul,ul) mode of cross-aldolization, as shown with the transition state of Figure 2, which give a u,u,u or ANCAT[50] diastereomer, in agreement with Cram's model[51] in which the carbonyl and β-alkoxy functions of **10** are co-coordinated to $TiCl_4$. For steric reasons, this latter mode of

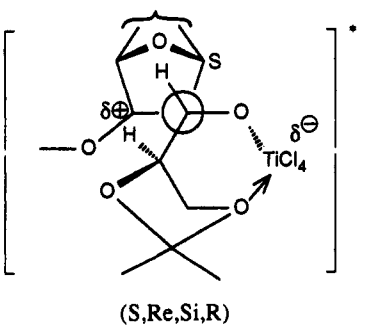


Figure 2.

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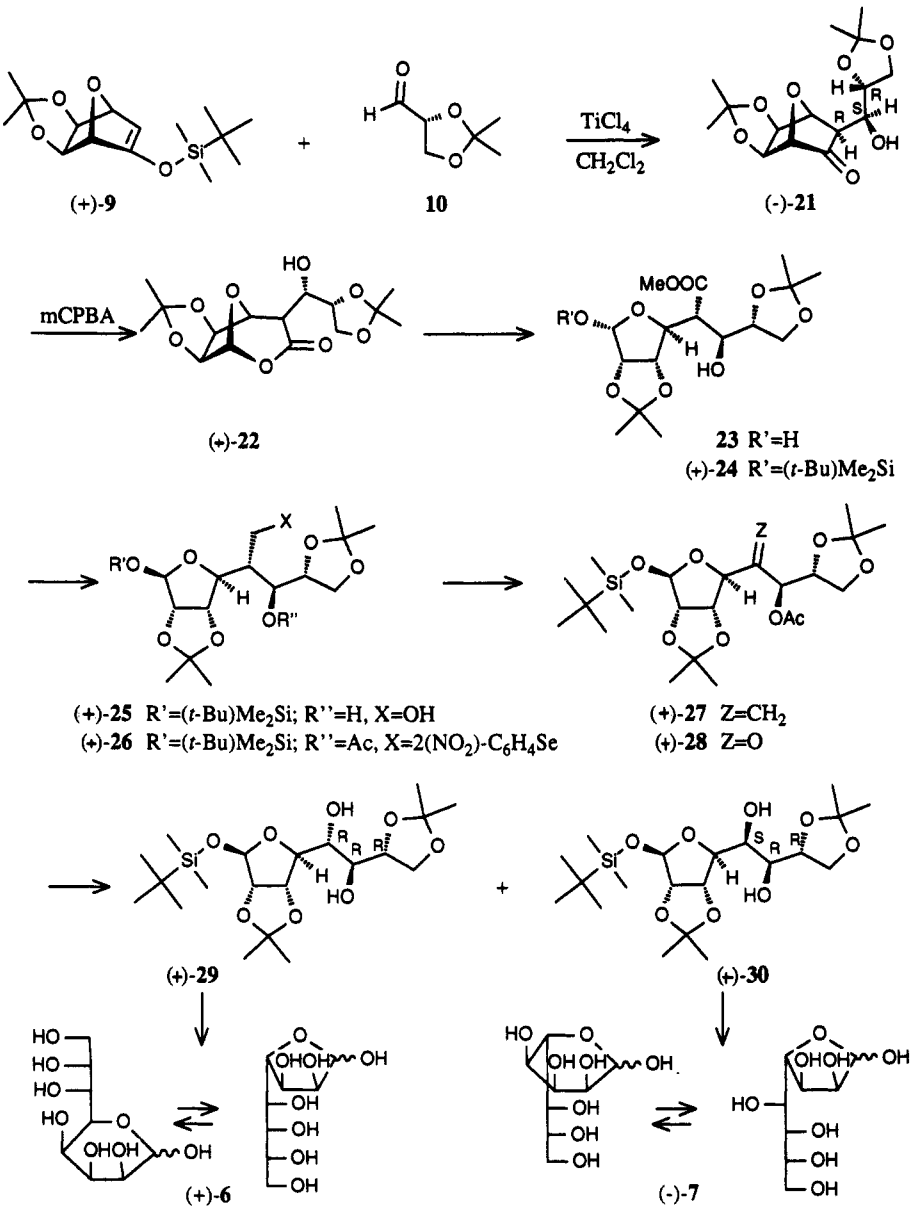
Scheme II



complexation is preferred to that employing the α-alkoxy group.

Baeyer–Villiger oxidation of (−)-**21** gave (+)-**22** (81%). The lactone was converted into hemiacetal **23** (83%, 2:1 mixture of α- and β-anomers (in the major α-anomer the hemiacetal hydroxyl group and the oxy substituent at C(2) are in a trans relative configuration, see (+)-**25**), less than 7% of epimerization at C(5)) by treatment with MeOH and K_2CO_3. After selective silylation to (+)-**24** (83%), ester reduction to diol (+)-**25** (92%), selenation into (+)-**26** (73%), oxidative elimination giving alkene (+)-**27** (91%), and ozonolysis (91%), the ketone (+)-**28** was obtained in similar fashion as (−)-**18** (Scheme II). Reductions of (+)-**28** with various reducing agent have been examined (see Table I). With L-Selectride, diols (+)-**29** and (+)-**30** were obtained with a ratio >20:1 whereas with DIBAH, this ratio was reversed. Deprotection of (+)-**29** furnished (+)-**6** (94%) whose ^1H NMR spectrum in D_2O indicated a 5:1:28:8 mixture of the corresponding β-furanose, α-furanose, β-pyranose, and α-pyranose stereomers. Similarly, (+)-**30** gave (−)-**7** (85%) as a 1:1:2.8:13.5 mixture of the corresponding β-furanose, α-furanose, β-pyranose, and α-pyranose stereomers. The octoses (−)-**4**, (+)-**5**, (+)-**6**, and (−)-**7** were obtained as pure, hygroscopic solid materials.

Table I. Selectivity of the Hydride Reductions of Ketone (+)-28 into (+)-29 and (+)-30, As Determined by 250-MHz ^1H NMR Spectral Analysis of the Crude Reaction Mixtures

reagent[a]	conditions	ratio (+)-29/(+)-30
$NaBH_4$	MeOH, 0 °C, 15 min	2:1[b]
$NaBH_4/CeCl_3$	MeOH, −78 °C, 1 h	6:1[b]
$LiAlH(Ot\text{-}Bu)_3$	THF, −78 °C, 5 h	3.8:1
Alpine hydride	THF, −78 °C, 1 h	10:1
L-Selectride	THF, −78 °C, 1 h	>20:1[b]
Superhydride	THF, −78 °C, 1 h	>20:1[b]
$LiAlH_4$	THF, 0 °C, 10 min	2.7:1
$LiAlH_4/LiI$	THF, −78 °C, 1 h	2.4:1
DIBAH	THF, 20 °C, 1 h	1:7
$DIBAH/ZnI_2$	THF, 0 °C, 2 h	1:5.7
DIBAH	THF, −25 °C, 3 h	<1:20

[a] 3–5-fold excess of the reducing agent was used. [b] For the diacetates obtained by acetylation with Ac_2O/pyridine.

The $TiCl_4$-mediated cross-aldolization of (±)-**9** with **10** gave a 1:1 mixture of (+)-**11** and (−)-**21** in 55–62%. After Baeyer–Villiger oxidation, the corresponding lactones (−)-**12** and (+)-**22** were obtained and separated by column chromatography on silica gel. Mixtures of alkenes (−)-**17**

Scheme III

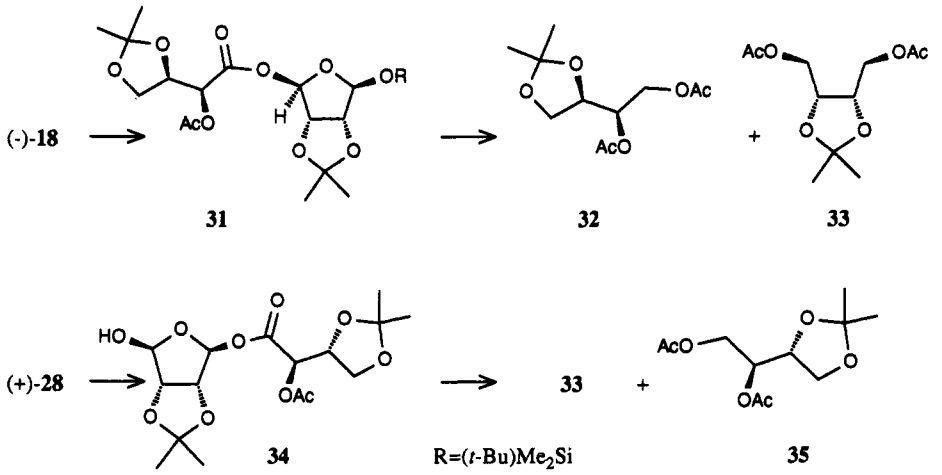
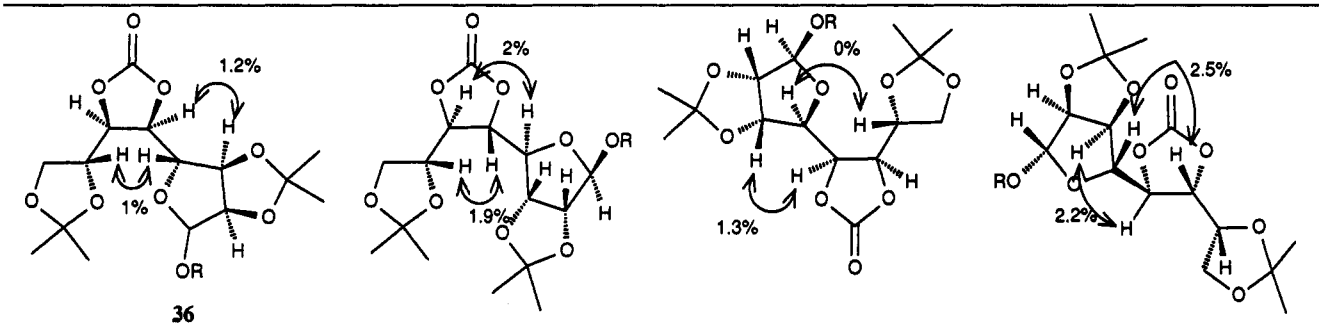


Table II. Selected NOE's[a] and Vicinal H,H Coupling Constants Measured in the 360-MHz ^{1}H NMR Spectra (CD_3COCD_3) of Carbonates 36, 37, 38, and 39 Derived from Diols (-)-19, (-)-20, (+)-29, and (+)-30, Respectively



36 37 38 39

NOE's (%); ^3J (Hz)	NOE's (%); ^3J (Hz)	NOE's (%); ^3J (Hz)	NOE's (%); ^3J (Hz)
HC(4),HC(5): 1; 10	0.5; 9.5	2.6; 4.0	1.8; 6.8
HC(5),HC(6): 2.5; 7.8	0.5; 4.0	2.9; 8.0	0; 4.0
HC(6),HC(7): 0.8; 1.0	1.6; 1.5	0.2; 9.2	1.3; 5.0

[a] Average for both NOE's (±0.5%).

and (+)-27 could also be separated readily by column chromatography.

Structural Determinations

The *S* configuration of C(6) in ketone (-)-18 (corresponds to the *R* configuration of the unprotected alcoholic carbon center in (+)-11) was established as shown in Scheme III. The Baeyer–Villiger oxidation of (-)-18 gave exclusively 31. Reduction with $LiBH_4$ (THF, 45 °C, 1 h) followed by acetylation (Ac_2O, pyridine) gave a 1:1 mixture of diacetates 32 and 33, which were separated by column chromatography on silica gel. The nonsymmetrical diacetate 32 was hydrolyzed ($AcOH/H_2O$ 9:1, 60 °C) and then acetylated to give pure D-threitol tetracetate. Similarly (Scheme III), the *R* configuration of C(6) in ketone (+)-28 (corresponds to the *S* configuration of the unprotected alcoholic carbon center of (-)-21) was established in the same way by transformation of (+)-28 into 34 and then into a separable 1:1 mixture of diacetates 33 and 35. The nonsymmetrical diacetate 35 was hydrolyzed, and then acetylated into *meso*-erythritol tetracetate.

The configuration of centers C(5) in diols (-)-19, (-)-20, (+)-29, and (+)-30 was determined by the vicinal coupling constant between H–C(5) and H–C(6) in the ^{1}H NMR spectra of the corresponding carbonates 36, 37, 38, and 39 obtained by treatment with phosgene and pyridine. The cis carbonates show larger vicinal coupling constant than their trans isomers.[57] Our assignments were confirmed by NOE measurements as shown in Table II.

Conclusion

The $TiCl_4$-promoted condensations of (*R*)-2,3-*O*-isopropylideneglyceraldehyde to (-)-(1*R*,4*R*,5*R*,6*R*)-5,6-(isopropylidenedioxy)-2-((*tert*-butyldimethylsilyl)oxy)-7-oxabicyclo[2.2.1]hept-2-ene and to its enantiomer are highly stereoselective processes. The products so-obtained are readily converted into octose stereomers with high stereoselectivity. The method allows one to obtain not only the free carbohydrates but also partially protected derivatives that are potential chirons.[58] The alkenes (-)-17 and (+)-27, as well as the corresponding 5-ulose derivatives (-)-18 and (+)-28 can also be considered as potentially useful synthetic intermediates. Using (*S*)-2,3-*O*-isopropylideneglyceraldehyde instead of its *R* enantiomer 10, the 7-epimers of (-)-4, (+)-5, (+)-6, and (-)-7 should be accessible with the same ease.[59] Further octose stereomers

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and analogues are also attainable, in principle, since centers C(5) and C(6) of our "naked sugars" **1–3** can be substituted by other functions than hydroxy groups and with other relative configurations than the cis-exo stereochemistry.[35,40]

Experimental Section

General remarks, see ref 41c. Optical rotations, α_D (c in g/100 mL).

(1*R*,3*S*,4*R*,5*R*,6*R*)-3-*exo*-((1′*R*,2′*R*)-1′-Hydroxy-2′,3′-(isopropylidenedioxy)propyl)-5-*exo*,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one ((+)-11). A precooled (−78 °C) solution of $TiCl_4$ (113 mg, 0.6 mmol) in anhydrous CH_2Cl_2 (4 mL) was added dropwise to a stirred solution of enol silane (−)-9[41b] (180 mg, 0.6 mmol) and (*R*)-2,3-*O*-isopropylideneglyceraldehyde (**10**) in anhydrous CH_2Cl_2 (4 mL) cooled to −78 °C under Ar atmosphere. After being stirred at −78 °C for 5 min, the mixture was poured at once into a vigourously stirred mixture of ice (3 g) and a saturated aqueous soloution of $NaHCO_3$ (5 mL) and CH_2Cl_2 (10 mL). The aqueous layer was extracted with CH_2Cl_2 (15 mL, twice), and the combined organic extracts were washed with saturated aqueous $NaHCO_3$ solution (10 mL). After drying ($MgSO_4$), the solvent was evaporated and the residue was purified by filtration on Florisil (20 g, EtOAc/petroleum ether, 1:4) and recrystallization from EtOAc/petroleum ether: 97 mg (51%); colorless crystals; mp 125–127 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 5.02 (d, *J* = 1.2, HC(4)), 4.55 and 4.42 (2 d, *J* = 5.5, HC(5), HC(6)), 4.39 (ddd, *J* = 7.0, 6.5, 2.0, HC(2′)), 4.29 (d, *J* = 1.2, HC(1)), 4.04 (dd, ^2J = 8.2, ^3J = 7.0) and 3.88 (dd, ^2J = 8.2, ^3J = 6.5, $H_2C(3')$), 3.73 (ddd, *J* = 9.2, 8.5, 2.0, HC(1′)), 2.47 (d, *J* = 9.2, HOC(1′)), 2.06 (d, *J* = 8.5, HC(3)), 1.52, 1.45, 1.38, and 1.32 (4 s, 2 CMe_2); $[\alpha]^{25}_{589}$ = +108.6° (*c* = 1, CH_2Cl_2).

(1*S*,4*S*,5*R*,6*R*,7*R*)-4-*exo*-((1′*R*,2′*R*)-1′-Hydroxy-2′,3′-(isopropylidenedioxy)propyl)-6-*exo*,7-*exo*-(isopropylidenedioxy)-2,8-dioxabicyclo[3.2.1]octan-2-one ((−)-12). A mixture of (+)-11 (90 mg, 0.29 mmol), metachloroperbenzoic acid (61 mg, 0.3 mmol), and $NaHCO_3$ (50 mg, 0.6 mmol) in CH_2Cl_2 (5 mL) was stirred at 20 °C for 30 h. The precipitate was filtered off, and the solution was concentrated in vacuo. The white residue was treated with ether, and the solid was collected and recrystallized from EtOAc/petroleum ether, giving 81 mg (86%) of (−)-**12** as colorless crystals: mp 141–143 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 5.73 (s, HC(1)), 4.99 (s, HC(5)), 4.83 amp 4.68 (2 d, *J* = 5.5, HC(6), HC(7)), 4.47 (ddd, *J* = 6.8, 6.7, 2.5, HC(2′)), 4.07 (dd, *J* = 8.0, 6.8, HC(3′)), 3.88 (m, 2 H, HC(1′), HC(3′)), 2.78 (d, *J* = 9.0, HOC(1′)), 2.66 (d, *J* = 7.5, HC(4)), 1.50, 1.48, 1.40, 1.34 (4 s, 2 Me_2C); $[\alpha]^{25}_{589}$ = −20.8° (*c* = 0.9, CH_2Cl_2).

Mixture of (−)-12 and (+)-22. A solution of $TiCl_4$ (380 mg, 2 mmol) in anhydrous CH_2Cl_2 (6 mL) was added dropwise to a stirred solution of (±)-**9** (0.6 g, 2 mmol) and **10** (0.6 g, 4.6 mmol) in anhydrous CH_2Cl_2 (6 mL) cooled to −78 °C. After the mixture was stirred at −78 °C for 5 min, a precooled (−78 °C) solution of triethanolamine (0.3 g, 2 mmol) and ethanolamine (0.49 g, 8 mmol) in anhydrous CH_2Cl_2 (6 mL) was added dropwise. After being warmed to −20 °C, the mixture was filtered through a pad of Florisil (50 g). The precipitate was rinsed with CH_2Cl_2/MeOH, 10:1 (20 mL). The solution was concentrated in vacuo, and the residue was purified by column chromatography on Florisil (100 g, EtOAc/petroleum ether, 1:5): 0.39 g (62%), 1:1 mixture of (+)-11 and (−)-**21**. The 1:1 mixture of (+)-11 and (−)-**21** (1.81 g, 5.8 mmol) was stirred with metachloroperbenzoic acid (1.42 g, 7 mmol, 85%) and $NaHCO_3$ (1.2 g, 14 mmol) in CH_2Cl_2 (50 mL) at 20 °C for 30 h. The solution was filtered, and the solvent was evaporated. The white residue solidified and was washed with cold Et_2O, giving 1.6 g of a 1:1 mixture of lactones (−)-**12** and (+)-**22**. An additional 0.2 g of these lactones was collected by evaporation of the filtrate and purification by filtration on a short column of silica gel (50 g, EtOAc/petroleum ether, 1:2). The combined solid products were recrystallized from EtOAc/petroleum ether to give 1.65 g (87%) of white crystals. Column chromatography on silica gel (Lobar (see ref 41c), column C; EtOAc/petroleum ether, 1:2) gave a first fraction of 0.8 g (42%) of (+)-**22**. The second fraction yielded 0.78 g (41%) of (−)-**12**.

***tert*-Butyldimethylsilyl 5-Deoxy-5-*C*-(methoxycarbonyl)-2,3:7,8-di-*O*-isopropylidene-D-*threo*-L-*talo*-α-octofuranoside ((−)-14).** A mixture of (−)-**12** (785 mg, 2.4 mmol) and anhydrous K_2CO_3 (28 mg, 0.2 mmol) in anhydrous MeOH (25 mL) was stirred at 20 °C for 20 min. The solution was filtered through a short column of silica gel (15 g, CH_2Cl_2/MeOH) and evaporated to give 860 mg (99%) of a gum consisting of a 1.0:2.2 mixture of the β- and α-furanoses **13** (with ca. 5% of epimerization at C(5)). This compound was dissolved in CH_2Cl_2 (15 mL) and 2,6-lutidine (0.86 g, 3.6 mmol). *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.91 g, 3.6 mmol) was added dropwise to the above solution cooled to 0 °C. After the mixture was stirred at 0 °C for 1 h, saturated aqueous NaCl solution (5 mL) was added, followed by CH_2Cl_2 (5 mL). The organic layer was concentrated in vacuo, and the residue was purified by filtration on a short column of silica gel (50 g, EtOAc/petroleum ether, 1:5), giving 0.94 g (84%) of a colorless gum consisting mostly of the α-anomer: ^1H NMR (360 MHz, $CDCl_3$) δ 5.34 (s, HC(1)), 5.10 (dd, *J* = 6.0, 2.2, HC(3)), 4.51 (d, *J* = 6.0, HC(2)), 4.47 (dd, *J* = 10.2, 2.2, HC(4)), 4.08 (ddd, *J* = 7.0, 6.5, 4.0, HC(7)), 4.00 (dd, *J* = 8.2, 7.0, HC(8)), 3.86 (ddd, *J* = 8.8, 6.5, 4.0, HC(6)), 3.78 (dd, *J* = 8.2, 6.5, HC(8)), 3.69 (s, MeO), 2.93 (dd, *J* = 10.2, 8.8, HC(5)), 2.71 (d, *J* = 6.5, HOC(6)), 1.49, 1.42, 1.35, and 1.33 (4 s, 2 Me_2C), 0.89 (s, 9 H, *t*-BuSi), 0.09 (s, Me_2Si); $[\alpha]^{25}_{589}$ = −9.7° (*c* = 1.67, CH_2Cl_2).

***tert*-Butyldimethylsilyl 5-Deoxy-5-*C*-(hydroxymethyl)-2,3:7,8-di-*O*-isopropylidene-D-*threo*-L-*talo*-α-octofuranoside ((−)-15).** $LiAlH_4$ (106 mg, 2.8 mmol) was added to a stirred solution of (−)-**14** (0.67 g, 1.41 mmol) in anhydrous tetrahydrofuran (THF, 6 mL). The mixture was stirred at 20 °C for 30 min. After cooling to 0 °C, EtOAc (10 mL) and saturated aqueous NH_4Cl solution (1 mL) were added successively. The organic layer was separated and dried ($MgSO_4$). The solvent was evaporated, giving 590 mg (94%) of a colorless oil, containing 5–10% of the β-anomer: ^1H NMR (360 MHz, $CDCl_3$) δ 5.40 (s, HC(1)), 4.87 (dd, *J* = 6.0, 2.8, HC(3)), 4.51 (d, *J* = 6.0, HC(2)), 4.43 (dd, *J* = 6.8, 2.8, HC(4)), 4.35 (ddd, *J* = 7.0, 6.5, 3.2, HC(7)), 4.08 (dd, ^2J = 8.5, ^3J = 6.5) & 3.93 (dd, ^2J = 8.5, ^3J = 7.0, $H_2C(8)$), 3.85 (m, 2 H, $HOCH_2C(5)$), 3.75 (ddd, ^3J = 8.0, 6.5, 3.2, HC(6)), 2.87 (dd, *J* = 7.5, 6.0, $HOCH_2$), 2.49 (d, *J* = 8.0, HOC(6)), 1.98 (m, HC(5)), 1.50, 1.45, 1.38, and 1.33 (4 s, 2 Me_2C), 0.90 (s, *t*-BuSi), 0.15 and 0.13 (2 s, Me_2Si); $[\alpha]^{25}_{589}$ = −11.4° (*c* = 1, CH_2Cl_2).

***tert*-Butyldimethylsilyl 5-Deoxy-5-*C*-(((2-nitrophenyl)selenyl)methyl)-2,3:7,8-di-*O*-isopropylidene-D-*threo*-L-*talo*-α-octofuranoside ((−)-16′).** A mixture of (−)-**15** (0.54 g, 1.21 mmol), (2-nitrophenyl)seleno cyanate (0.41 g, 1.8 mmol), and tri-*n*-butylphosphine (0.43 g, 1.8 mmol, 85%) in anhydrous THF (6 mL) was stirred at 50 °C for 1 h. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (50 g), eluting first with CH_2Cl_2 (50 mL) and then with EtOAc/petroleum ether, 1:4, to yield 0.42 g (55%) of (−)-**16′**, yellow gum. A second fraction afforded 0.134 g of a mixture of C(5)-epimer and β-anomers. Total yield: 0.554 g (73%). The combined fractions are used in the following steps. Characteristics of pure (−)-16′: ^1H NMR (360 MHz, $CDCl_3$) δ 8.29 and 7.64 (2 dd, 2 H, ^3J = 8.5, ^4J = 1.5), 7.51 and 7.33 (2 ddd, 2 H, ^3J = 8.5, 7.0, ^4J = 1.5), 5.41 (s, HC(1)), 4.92 (dd, *J* = 6.2, 3.0, HC(3)), 4.50 (d, *J* = 6.2, HC(2)), 4.47 (dd, *J* = 6.5, 3.0, HC(4)), 4.35 (ddd, *J* = 7.2, 6.5, 3.8, HC(7)), 4.07 (dd, ^2J = 8.5, ^3J = 6.5) and 3.89 (dd, ^2J = 8.5, ^3J = 7.2, $H_2C(8)$), 3.82 (ddd, *J* = 8.0, 5.0, 3.8, HC(6)), 3.26 (dd, ^2J = 12.0, ^3J = 8.5) & 3.12 (dd, ^2J = 12.0, ^3J = 4.5, $H_2CC(5)$), 2.79 (d, *J* = 8.0, HOC(6)), 2.23 (dddd, *J* = 8.5, 6.5, 5.0, 4.5, HC(5)), 1.51, 1.45, 1.38, 1.33 (4 s, Me_2C), 0.91 (s, *t*-Bu), 0.14, 0.13 (2, s, Me_2Si); $[\alpha]^{25}_{589}$ = −29.3°, $[\alpha]^{25}_{578}$ = −31.0°, $[\alpha]^{25}_{546}$ = −37.7° (*c* = 1.36, CH_2Cl_2).

***tert*-Butyldimethylsilyl 6-*O*-Acetyl-5-deoxy-5-*C*-(((2-nitrophenyl)selenyl)methyl)-2,3:7,8-di-*O*-isopropylidene-D-*threo*-L-*talo*-α-octofuranoside ((−)-16).** A mixture of (−)-16′ (0.16 g, 0.25 mmol), pyridine (1 mL), Ac_2O (0.8 mL), and 2-(dimethylamino)pyridine (10 mg) in CH_2Cl_2 (3 mL) was stirred at 20 °C for 2 h. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (30 g, EtOAc/petroleum ether, 1:5), yielding 156 mg (92%) of a yellow gum: ^1H NMR (360 MHz, $CDCl_3$) δ 8.28 (dd, 1 H, ^3J = 8.5, ^4J = 1.5), 7.61 (dd, 1 H, ^3J = 8.0, ^4J = 1.5), 7.51 and 7.31 (2 ddd, ^3J = 8.5, 8.0, ^4J = 1.5), 5.38 (s, HC(1)), 5.16 (dd, *J* = 6.5, 3.0, HC(6)), 4.94

(59) This implies ul,ul topicity for the reaction with (−)-**9** (transition state analogous to that in Figure 2) and ul,lk topicity for the cross-aldolization with (+)-**9** (transition state analogous to that in Figure 1).

(dd, J = 6.0, 2.5, HC(3), 4.49 (d, J = 6.0, HC(2)), 4.44 (ddd, J = 7.0, 6.0, 3.0, HC(7)), 4.09 (dd, J = 9.0, 2.5, HC(4)), 4.03 (dd, ^2J = 8.8, ^3J = 7.0) and 3.65 (dd, ^2J = 8.8, ^3J = 6.0, $H_2C(8)$), 3.34 (dd, ^2J = 11.5, ^3J = 7.0) and 3.24 (dd, ^2J = 11.5, ^3J = 4.0, $H_2CC(5)$), 2.58 (dddd, J = 11.5, 7.0, 6.5, 4.0, HC(5)), 2.17 (s, Ac), 1.48, 1.46, 1.36, 1.32 (4 s, 2 Me_2C), 0.88 (s, t-Bu), 0.11, 0.07 (2 s, Me_2Si); $[\alpha]^{25}_{589}$ = −21.4 (c = 1, CH_2Cl_2).

***tert*-Butyldimethylsilyl 6-*O*-Acetyl-5-deoxy-5-*C*-methylidene-2,3:7,8-di-*O*-isopropylidene-D-*glycero*-L-*talo*-α-octofuranoside ((−)-17).** Metachloroperbenzoic acid (67 mg, 85%, 0.33 mmol) was added to a stirred mixture of (−)-**16** (100 mg, 0.15 mmol), saturated aqueous $NaHCO_3$ solution (1 mL), and CH_2Cl_2 (5 mL) cooled to 0 °C. After stirring at 20 °C for 30 min, CH_2Cl_2 (10 mL) was added, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution (2 mL), dried ($MgSO_4$), and evaporated. The residue was purified by filtration on a short column of silica gel (20 g, EtOAc/petroleum ether, 1:8): 61 mg (87%), colorless gum; ^1H NMR (360 MHz, $CDCl_3$) δ 5.57 (dd, J = 1.0, 0.9) and 5.43 (br s, $H_2C{=}C(5)$), 5.29 (d J = 6.2, HC(6)), 5.27 (s, HC(1)), 4.85 (dd, J = 6.0, 3.0, HC(3)), 4.57 (dd, J = 3.0, 1.0, HC(4)), 4.47 (d, J = 6.0, HC(2)), 4.37 (ddd, J = 6.5, 6.2, 6.0, HC(7)), 4.03 (dd, ^2J = 8.5, ^3J = 6.5) and 3.82 (dd, ^2J = 8.5, ^3J = 6.0, $H_2C(8)$), 2.12 (s, Ac), 1.52, 1.44, 1.36, 1.34 (4 s, 2 Me_2C), 0.87 (s, t-Bu), 0.14, 0.12 (2 s, Me_2Si); $[\alpha]^{25}_D$ = −25.5° (c = 0.2, CH_2Cl_2).

***tert*-Butyldimethylsilyl 6-*O*-Acetyl-2,3:7,8-di-*O*-isopropylidene-D-*glycero*-L-*talo*-α-octofuranosid-5-ulose ((−)-18). Procedure A.** Ozone (3% in O_2) was bubbled through a solution of (−)-**17** (200 mg, 0.42 mmol) in CH_2Cl_2 (10 mL) cooled to −78 °C until persistence of the blue color. Me_2S (156 mg, 2.52 mmol) was added, and the mixture was stirred at 20 °C for 1 h. CH_2Cl_2 (10 mL) was added, and the solution was washed with brine (5 mL). After drying ($MgSO_4$), the solvent was evaporated and the residue was purified by filtration on a short column of silica gel (20 g, EtOAc/petroleum ether, 1:8): 184 mg (92%), colorless gum; ^1H NMR (250 MHz, $CDCl_3$) δ 5.63 (d, J = 5.2, HC(6)), 5.34 (dd, J = 6.0, 1.0, HC(3)), 5.33 (s, HC(1), 4.69 (br s, HC(4)), 4.54 (ddd, J = 7.0, 5.2, 5.0, HC(7)), 4.41 (d, J = 6.0, HC(2)), 4.11 (dd, ^2J = 9.0, ^3J = 7.0) and 3.79 (dd, ^2J = 9.0, ^3J = 5.0, $H_2C(8)$), 2.20 (s, Ac), 1.47, 1.40 (2 s, Me_2C), 1.32 (s, Me_2C), 0.85 (s, t-Bu), 0.13 (s, Me_2Si); $[\alpha]^{25}_D$ = −50.8° (c = 0.3, CH_2Cl_2).

Procedure B. A solution of (−)-**16** (100 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) was ozonized at −78 °C until a blue color remained. Et_2NH (33 mg, 0.45 mmol) was added, and the solution was warmed to 20 °C. After stirring at 20 °C for 30 min, the reaction mixture was cooled to −78 °C and ozonized again. Me_2S (62 mg, 1 mmol) was added, and the mixture was stirred at 20 °C for 1 h. CH_2Cl_2 (10 mL) was added, and the solution was washed with brine (5 mL) and dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (15 g, EtOH/petroleum ether, 1:8): 54 mg (77%).

***tert*-Butyldimethylsilyl 2,3:7,8-Di-*O*-isopropylidene-D-*threo*-L-*talo*-α-octofuranoside ((−)-19) and *tert*-Butyldimethylsilyl 2,3:7,8-Di-*O*-isopropylidene-D-*threo*-D-*allo*-β-octofuranoside ((−)-20).** A 1 M solution of $LiAlH_4$ (0.8 mL, 0.8 mmol) in anhydrous THF was added dropwise to a stirred solution of (−)-**18** (190 mg, 0.4 mmol) in anhydrous THF (4 mL) cooled to −20 °C. After stirring at −20 °C for 20 min, saturated aqueous NH_4Cl solution (1 mL) was added, and the mixture was extracted with AcOEt (10 mL) twice. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:4). The first fraction gave 71 mg (41%) of (−)-**19**; the second fraction yielded 78 mg (45%) of (−)-**20**. Characteristics of (−)-**19**: colorless solid, mp 100–102 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 5.43 (s, HC(1)), 4.91 (dd, J = 6.0, 1.0, HC(3)), 4.81 (br s, HC(4)), 4.51 (d, J = 6.0, HC(2)), 4.35 (ddd, J = 7.0, 6.5, 4.0, HC(7)), 4.08 (dd, ^2J = 8.2, ^3J = 6.5) and 3.88 (dd, ^2J = 8.2, ^3J = 7.0, $H_2C(8)$), 3.90 (d, J = 11.0, HO); 3.46 (m, 2 H, HC(5), HC(6)), 2.39 (d, J = 6.5, OH), 1.49, 1.43, 1.39, 1.33 (4 s, 2 Me_2C), 0.91 (s, t-Bu), 0.19, 0.17 (2 s, Me_2Si); $[\alpha]^{25}_D$ = −14.4° (c = 1, CH_2Cl_2). Characteristics of (−)-**20**: colorless gum; ^1H NMR (250 MHz, $CDCl_3$) δ 5.39 (s, HC(1)), 5.08 (dd, J = 6.0, 1.0, HC(3)), 4.51 (d, J = 6.0, HC(2)), 4.29 (dd, J = 6.2, 1.0, HC(4)), 4.24 (ddd, J = 6.8, 6.5, 5.0, HC(7)), 4.05 (dd, ^2J = 8.5, ^3J = 6.5) and 3.89 (dd, ^2J = 8.5, ^3J = 6.8, $H_2C(8)$), 3.77 (ddd, J = 6.2, 5.0, 2.5, HC(6)), 3.66 (ddd, J = 6.2, 3.8, 2.5, HC(5)), 3.47 (d, J = 3.8, HOC(5)), 2.58 (d, J = 6.2, HOC(6)), 1.49, 1.44, 1.38, 1.33 (4 s, 2 Me_2C), 0.9 (s, t-Bu), 0.16, 0.13 (2 s, Me_2Si); $[\alpha]^{25}_D$ = −25.2° (c = 1, CH_2Cl).

Reduction of (−)-18 with Superhydride. $LiEt_3BH$ (1 M, 30 μL, 0.03 mmol) in THF was added dropwise to a stirred solution of (−)-**18** (5 mg, 0.01 mmol) in anhydrous THF (0.5 mL) cooled to −78 °C. After stirring at −78 °C for 1 h, saturated aqueous NH_4Cl solution (0.2 mL) was added, and the mixture was extracted with EtOAc (5 mL, twice). The extracts were combined and dried ($MgSO_4$), and the solvent evaporated. The residue was treated with pyridine (0.1 mL), Ac_2O (0.1 mL) and 2-(dimethylamino)-pyridine (2 mg) at 20 °C for 2 h. The solvent was evaporated in vacuo. The ^1H NMR (360 MHz, $CDCl_3$) spectrum showed a ratio >20:1 for the diacetates of (−)-**19** and (−)-**20**. The crude residue was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:6) yielding 5.2 mg (96%) of the diacetate of (−)-**19**.

Reduction of (−)-18 with DIBAL. A 2 M solution of $(i\text{-Bu})_2AlH$ (20 μL, 0.04 mmol) in toluene was added to a stirred solution of (−)-**18** (5 mg, 0.01 mmol) in anhydrous THF (0.5 mL) cooled to −20 °C. After stirring at −20 °C for 4 h, saturated aqueous NH_4Cl solution (0.2 mL) was added and the mixture was extracted with EtOAc (5 mL, twice). The extracts were combined and dried ($MgSO_4$), and the solvent was evaporated. The ^1H NMR (360 MHz, $CDCl_3$) spectrum showed a 1:11.3 mixture of (−)-**19** and (−)-**20**. Purification by column chromatography as above afforded 4.1 g (89%) of pure (−)-**20**.

D-*threo*-L-*talo*-Octose ((−)-4). A solution of (−)-**19** (60 mg, 0.13 mmol) in AcOH/H_2O, 8:2 (2 mL), was heated to 60 °C for 5 h. The solvent was evaporated, and the white residue was washed with cold Et_2O (5 mL): 26 mg (79%) of a white, hygroscopic solid; mp 140–146 °C (under Ar) (lit.[46] mp 138–140 °C); ^1H NMR (250 MHz, D_2O/CD_3COCD_3 as internal standard) δ 5.25 (br s, HC(1), α-furanose), 5.18 (d, J = 4.0, HC(1), β-furanose), 5.19 (d, J = 1.5, HC(1), β-pyranose), 5.17 (d, J = 2.2, HC(1), α-pyranose), ratio 1:2:12.7:4 (determined by integration of the signals assigned to the anomeric protons in the ^1H NMR spectrum); $[\alpha]^{25}_D$ = −14.1° (c = 1, H_2O, after 4 days at 25 °C) (lit.[46] $[\alpha]^{25}_D$ = −14.4° (c = 3, H_2O).

D-*threo*-D-*allo*-Octose ((+)-5). Same procedure as for (−)-**4** starting with (−)-**20** (50 mg, 0.11 mmol): yield 24 mg (87%) of a white hygroscopic solid; mp 127–130 °C; ^1H NMR (250 MHz, D_2O/CD_3COCD_3 as internal standard) δ 5.15 (d, J = 4.0), 5.11 (br s), 5.08 (d, J = 2.0), 4.95 (d, J = 4.0, HC(1)) of the β-furanose, α-furanose, β-pyranose, and α-pyranose, respectively; ratio 1:7.5:2:12.5 (by ^1H NMR integration of the H–C(1) signals; after staying 4 days at 25 °C); $[\alpha]^{25}_D$ = +7.4° (c = 1.2, H_2O, after 4 days at 25 °C).

(1*S*,3*R*,4*S*,5*S*,6*S*)-3-*exo*-((1′*S*,2′*R*)-1′-Hydroxy-2′,3′-(isopropylidenedioxy)propyl)-5-*exo*,6-*exo*-(isopropylidenedioxy)-7-oxabicyclo[2.2.1]heptan-2-one ((−)-21). Same procedure as for (+)-**11**, starting with (+)-**9**[41b] (260 mg, 0.87 mmol), **10** (260 mg, 2 mmol), and $TiCl_4$ (167 mg, 0.88 mmol): yield 151 mg (55%), colorless needles; mp 131–132 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 4.97 (d, J = 1.2, HC(4)), 4.56 and 4.50 (2 d, J = 5.5, HC(5), HC(6)), 4.31 (d, J = 1.2, HC(1)), 4.12 (m, 2 H, HC(2′), HC(3′)), 4.02 (ddd, J = 6.8, 5.0, 3.8, HC(1′)), 3.93 (dd, ^2J = 8.2, ^3J = 6.0, HC(3′)), 2.67 (d, J = 3.8, HOC(1′)), 1.96 (d, J = 6.8, HC(3)), 1.51, 1.41, 1.34, and 1.32 (4 s, 2 Me_2C); $[\alpha]^{25}_D$ = −110.2° (c = 0.62, CH_2Cl_2).

(1*R*,4*R*,5*S*,6*S*,7*S*)-4-*exo*-((1′*S*,2′*R*)-1′-Hydroxy-2′,3′-(isopropylidenedioxy)propyl)-6-*exo*,7-*exo*-(isopropylidenedioxy)-2,8-dioxabicyclo[3.2.1]octan-2-one ((+)-22). Same procedure as for (−)-**12**, starting with (−)-**21** (158 mg, 0.5 mmol): yield 135 mg (81%) of colorless crystals, recrystallized from EtOAc/petroleum ether; mp 159–160 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 5.76 (s, HC(1)), 4.94 (s, HC(5)), 4.85, 4.72 (2 d, J = 5.5, HC(6), HC(7)), 4.19 (m, 3 H, HC(1′), $H_2C(3')$), 4.06 (m, HC(2′)), 2.73 (d, J = 5.0, HC(4)), 2.58 (d, J = 4.8, HOC(1′)), 1.49, 1.44, 1.35, 1.34 (4 s, 2 Me_2C); $[\alpha]^{25}_D$ = +21.8° (c = 0.84, CH_2Cl_2).

***tert*-Butyldimethylsilyl 5-Deoxy-5-*C*-(methoxycarbonyl)-2,3:7,8-di-*O*-isopropylidene-D-*erythro*-D-*talo*-α-octofuranoside ((+)-24).** A mixture of (+)-**22** (115 mg, 0.35 mmol), anhydrous K_2CO_3 (5 mg, 0.03 mmol), and anhydrous MeOH (5 mL) was stirred at 20 °C for 20 min and worked up as described for (−)-**14**. The hemiacetal **23** was obtained as a colorless gum (125 mg, 99%, 5–7% epimerization at C(5), α:β anomeric ratio 2:1 from ^1H NMR (360 MHz, $CDCl_3$); the hemi-

acetal hydroxyl group and the oxy substituent at C(2) are in a trans relative configuration in the major product. This product (125 mg, 0.35 mmol), mixed at 0 °C with anhydrous CH_2Cl_2 (3 mL), 2,6-lutidine (192 mg, 1.8 mmol), and *tert*-butyldimethylsilyl trifluoromethanesulfonate (185 mg, 0.7 mmol), was stirred at 0 °C for 1 h. After the addition of brine (2 mL) and CH_2Cl_2 (10 mL), the organic layer was dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by filtration on a short column of silica gel (20 g, EtOAc/petroleum ether, 1:5): yield 137 mg (83%), colorless oil (mostly α-anomer); ^1H NMR (360 MHz, $CDCl_3$) δ 5.35 (s, HC(1)), 5.16 (dd, J = 6.0, 2.0, HC(3)), 4.51 (dd, J = 10.0, 2.0, HC(4)), 4.51 (d, J = 6.0, HC(2)), 4.05 (m, 3 H), 3.96 (dd, ^2J = 7.0, ^3J = 5.5, HC(8)), 3.71 (s, MeO), 2.80 (dd, J = 10.0, 8.0, HC(5)), 2.80 (d, J = 2.5, HOC(6)), 1.50, 1.41, 1.35, 1.33 (4 s, 2 Me_2C), 0.90 (s, *t*-Bu), 0.10 and 0.09 (2 s, Me_2Si); $[\alpha]^{25}_D$ = +11.4° (c = 1.4, CH_2Cl_2).

***tert*-Butyldimethylsilyl 5-Deoxy-5-*C*-(hydroxymethyl)-2,3:7,8-di-*O*-isopropylidene-D-*erythro*-D-*talo*-α-octofuranoside ((+)-25).** $LiAlH_4$ (15 mg, 0.4 mmol) was added to a stirred solution of (+)-**24** (90 mg, 0.19 mmol) in anhydrous THF (1 mL) cooled to 0 °C. After being stirred at 20 °C for 30 min, the solution was cooled to 0 °C and EtOAc (10 mL) was added, followed by saturated aqueous NH_4Cl solution (1 mL). The organic layer was separated and dried ($MgSO_4$), and the solvent was evaporated to give 78 mg (92%) of colorless oil which was purified by column chromatography on silica gel (30 g, EtOAc/petroleum ether, 1:2). The first fraction yielded 65 mg (77%) of pure (+)-**25** and the second fraction gave 8 mg (9%) of its β-anomer. Characteristics of (+)-**25**: ^1H NMR (360 MHz, $CDCl_3$) δ 5.42 (s, HC(1)), 5.02 (dd, J = 6.0, 2.0, HC(3)), 4.58 (dd, J = 7.5, 2.0, HC(4)), 4.51 (d, J = 6.0, HC(2)), 4.21 (ddd, J = 7.5, 6.5, 6.2, HC(7)), 4.12 (dd, ^2J = 8.5, ^3J = 6.5) and 3.94 (dd, ^2J = 8.5, ^3J = 6.2, $H_2C(8)$), 4.05 (ddd, ^2J = 11.8, ^3J = 5.0, 4.5) and 3.80 (ddd, ^2J = 11.8, ^3J = 7.0, 4.5, $H_2CC(5)$), 3.89 (ddd, J = 7.5, 5.0, 3.8, HC(6)), 3.18 (d, J = 3.8, *H*OC(6)), 2.48 (dd, J = 7.5, 5.0, *H*OCH$_2$C(5)), 2.01 (dddd, J = 9.5, 7.5, 5.0, 4.5, HC(5)), 1.51, 1.41, 1.36, 1.33 (4 s, 2 Me_2C), 0.90 (s, *t*-Bu), 0.16 and 0.13 (2 s, Me_2Si); $[\alpha]^{25}_D$ = +14.4° (c = 1, CH_2Cl_2).

***tert*-Butyldimethylsilyl 6-*O*-Acetyl-5-deoxy-5-*C*-(((2-nitrophenyl)selenyl)methyl)-2,3:7,8-di-*O*-isopropylidene-D-*erythro*-D-*talo*-α-octofuranoside ((+)-26).** (+)-**25** (1 g, 2.2 mmol) was treated with (2-nitrophenyl)seleno cyanate (0.75 g, 3.3 mmol) and Bu_3P (0.79 g, 3.3 mmol) in THF (10 mL) at 50 °C for 1 h. Following the procedure described for (−)-**16'**, and then acetylation with Ac_2O/pyridine as for (−)-**16**, 1.1 g (73%) of pure (+)-**26** was obtained as a yellow gum: ^1H NMR (360 MHz, $CDCl_3$) δ 8.29 (dd, 1 H, ^3J = 8.5, ^4J = 1.5), 7.59 (dd, 1 H, ^3J = 8.0, ^4J = 1.5), 7.52 (ddd, 1 H, ^3J = 8.5, 8.0, ^4J = 1.5), 7.32 (td, 1 H, ^3J = 8.0, ^4J = 1.5), 5.37 (s, HC(1)), 5.17 (dd, J = 6.0, 1.5, HC(3)), 5.00 (dd, J = 9.0, 2.0, HC(6)), 4.53 (d, J = 6.0, HC(2)), 4.49 (ddd, J = 9.0 6.2, 5.0, HC(7)), 4.43 (dd, J = 11.0, 1.5, HC(4)), 4.14 (dd, J = 9.0, 6.2) and 3.82 (dd, J = 9.0, 5.0, $H_2C(8)$), 3.40 (dd, ^2J = 11.0, ^3J = 3.5) and 3.08 (dd, ^2J = 11.0, ^3J = 10.5, $H_2CC(5)$), 2.42 (dddd, J = 11.0, 11.0, 3.5, 2.0, HC(5)), 2.15 (s, Ac), 1.47, 1.46, 1.38, 1.37 (4 s, 2 Me_2C), 0.79 (s, *t*-Bu), 0.06–0.05 (2 s, Me_2Si); $[\alpha]^{25}_D$ = +45.2° (c = 1.1, CH_2Cl_2).

***tert*-Butyldimethylsilyl 6-*O*-Acetyl-5-deoxy-5-*C*-methylidene-2,3:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-α-octofuranoside ((+)-27).** Same procedure as for (−)-**17**, starting with (+)-**26** (200 mg, 0.3 mmol) and metachloroperbenzoic acid (134 mg, 85%, 0.66 mmol): yield 128 mg (91%), colorless gum; ^1H NMR (360 MHz, $CDCl_3$) δ 5.55, 5.47 (2 br s, $H_2C{=}C(5)$), 5.25 (d, J = 6.0, HC(6)), 5.21 (s, HC(1)), 4.94 (dd, J = 6.0, 3.0, HC(3)), 4.65 (br s, HC(4), becomes a doublet (J = 3.0) on irradiating the olefinic signals), 4.48 (d, J = 6.0, HC(2)), 4.30 (ddd, J = 6.5, 6.4, 6.0, HC(7)), 4.05 (dd, ^2J = 8.5, ^3J = 6.5) and 3.92 (dd, ^2J = 8.5, ^3J = 6.4, $H_2C(8)$), 2.10 (s, Ac), 1.52, 1.44, 1.35, 1.34 (4 s, 2 Me_2C), 0.89 (s, *t*-Bu), 0.15, 0.13 (2 s, Me_2Si); $[\alpha]^{25}_D$ = +18.9° (c = 0.18, CH_2Cl_2).

***tert*-Butyldimethylsilyl 6-*O*-Acetyl-2,3:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-α-octofuranosid-5-ulose ((+)-28).** Same procedure as for (−)-**18**, starting with (+)-**27** (90 mg, 0.19 mmol): yield 82 mg (91%), colorless gum; ^1H NMR (360 MHz, $CDCl_3$) δ 5.76 (d, J = 4.5, HC(6)), 5.41 (s, HC(1)), 5.36 (dd, J = 6.0, 1.5, HC(3)), 4.73 (d, J = 1.5, HC(4)), 4.47 (td, J = 6.5, 4.5, HC(7)), 4.43 (d, J = 6.0, HC(2)), 4.08 and 3.86 (2 dd, ^2J = 8.8, ^3J = 6.5, $H_2C(8)$), 2.16 (s, Ac), 1.48, 1.39, 1.34, 1.33 (4 s, 2 Me_2C), 0.87 (s, *t*-Bu), 0.16 (s, Me_2Si); $[\alpha]^{25}_D$ = +42.4° (c = 0.35, CH_2Cl_2).

***tert*-Butyldimethylsilyl 2,3:7,8-Di-*O*-isopropylidene-D-*erythro*-D-*talo*-α-octofuranoside ((+)-29) and *tert*-Butyldimethylsilyl 2,3:7,8-Di-*O*-isopropylidene-D-*erythro*-L-*allo*-β-octofuranoside ((+)-30).** Same procedure as for the $LiAlH_4$ reduction of (−)-**18** → (−)-**19** + (−)-**20**, using 500 mg (1.05 mmol) of (+)-**28** and 2.2 mL of 1 M $LiAlH_4$ solution in THF. The diols (+)-**29** and (+)-**30** (more polar) were separated by flash chromatography on silica gel (100 g, EtOAc/petroleum ether, 1:4). Yield: 210 mg (46%) of (+)-**29**; 95 mg (22%) of (+)-**30**. Characteristics of (+)-**29**: colorless gum, which solidified in the freezer, mp 97–98 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 5.43 (s, HC(1)), 4.93 (dd, J = 6.0, 1.0, HC(3)), 4.78 (dd, J = 2.0, 1.0, HC(4)), 4.53 (d, J = 6.0, HC(2)), 4.27 (td, J = 6.5, 6.0, HC(7)), 4.10 and 3.98 (2 dd, ^2J = 8.5, ^3J = 6.5, $H_2C(8)$), 3.93 (d, J = 11.2, HOC(5)), 3.82 (ddd, J = 7.0, 6.0, 5.5, HC(6)), 3.55 (ddd, J = 11.2, 7.0, 2.2, HC(5)), 2.56 (d, J = 5.5, HOC(6)), 1.50, 1.43, 1.37, 1.33 (4 s, 2 Me_2C), 0.93 (s, *t*-Bu), 0.20, 0.19 (2 s, Me_2Si); $[\alpha]^{25}_D$ = +26.1° (c = 0.23 g/dm^3, CH_2Cl_2).

Characteristics of (+)-**30**: colorless gum which solidified in the freezer, mp 75–76 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 5.40 (s, HC(1)), 5.10 (dd, J = 6.0, 1.0, HC(3)), 4.52 (d, J = 6.0, HC(2)), 4.41 (dd, J = 3.2, 1.0, HC(4)), 4.12 (m, 2 H), 4.02 (m, 1 H), 3.79 (br s, 3 H), 2.58 (d, J = 6.0, HO), 1.49, 1.42, 1.37, 1.33 (4 s, 2 Me_2C), 0.92 (s, *t*-Bu), 0.18, 0.16 (2 s, Me_2Si); $[\alpha]^{25}_D$ = +35.5° (c = 0.2, CH_2Cl_2).

Reduction of (+)-28 with Superhydride. Same procedure as for the reduction of (−)-**18**. The crude reaction residue (95%) was acetylated with Ac_2O/pyridine and a trace of 2-(dimethylamino)pyridine to yield a >20:1 mixture of the diacetates of (+)-**29** and (+)-**30** (by 360-MHz ^1H NMR).

Reduction of (+)-28 with DIBAH. Same procedure as for the reduction of (−)-**18**. Yield 93% of a <1:20 mixture of (+)-**29** and (+)-**30** (by 360-MHz ^1H NMR).

D-*erythro*-D-*talo*-Octose ((+)-6). A solution of (+)-**29** (60 mg, 0.13 mmol) in AcOH/H_2O, 4:1 (2 mL), was heated to 60 °C for 5 h. The solvent was evaporated. Acetone (3 mL) was added to the residue which solidified. The solid was washed with Et_2O (1 mL) and dried under high vacuum: yield 30 mg (94%) highly hygroscopic, white solid; ^1H NMR (360 MHz, D_2O/CD_3COCHD_2 as internal standard) δ 5.24 (br s, HC(1) of α-furanose), 5.18 (d, J = 4.0, HC(1) of β-furanose), 5.07 (d, J = 1.2, HC(1) of β-pyranose), 5.05 (d, J = 1.8, HC(1) of α-pyranose), 3.32–4.21 (m); β-furanose/α-furanose/β-pyranose/α-pyranose ratio: 5:1:28:8 (after staying at 25 °C for 6 days); $[\alpha]^{25}_D$ = +8.7° (c = 1.5, H_2O, after 6 days at 25 °C).

D-*erythro*-L-*allo*-Octose ((−)-7). Same procedure as for (+)-**6**, starting with (+)-**30** (60 mg, 0.13 mmol): yield 28 mg (85%), highly hygroscopic, white solid; ^1H NMR (250 MHz, D_2O/CD_3COCHD_2 as internal standard) δ 5.17 (d, J = 4.5, HC(1) of α-furanose), 5.12 (d, J = 1.5, HC(1) of β-furanose), 5.07 (d, J = 2.5, HC(1) of β-pyranose), 4.96 (d, J = 4.0, HC(1) of α-pyranose); ratio 1:1:2.8:13.5. $[\alpha]^{25}_D$ = −11.7° (c = 1.3, H_2O, after 6 days at 25 °C).

1,2-*O*-Diacetyl-3,4-*O*-isopropylidene-D-threitol (32) and 1,4-Diacetyl-2,3-*O*-isopropylidene-*meso*-erythrol (33). A mixture of (−)-**18** (15 mg, 0.032 mmol) and $NaHCO_3$ (4 mg, 0.5 mmol) metachlorperbenzoic acid (9 mg, 0.045 mmol) in CH_2Cl_2 (2 mL) was stirred at 20 °C overnight. After solvent evaporation the residue was purified by column chromatography on silica gel (10 g, EtOAc/petroleum ether, 1:8): 14.2 mg (92% of ester **31** (Scheme III)); ^1H NMR (250 MHz, $CDCl_3$) δ 6.28 (s, HC(4)), 5.54 (s, HC(1)), 5.10 (d, J = 5.0, HC(7)), 4.77, 4.57 (2 d, J = 5.5, HC(2), HC(3)), 4.53 (ddd, J = 6.5, 6.0, 5.0, HC(8)), 4.08 (dd, ^2J = 9.0, ^3J = 6.5, HC(9)), 3.94 (dd, ^2J = 9.0, ^3J = 6.0, HC(9)), 2.19 (s, $COCH_3$), 1.48, 1.44, 1.36, 1.31 (4 s, 2 Me_2C), 0.89 (s, *t*-Bu), 0.16, 0.12 (2 s, Me_2Si); MS (CI, NH_3) m/z 508 (13, $[M + NH_4]^+$), 475 (7), 375 (6), 317 (9), 273 (81), 217 (50), 175 (17), 158 (39), 129 (60), 101 (38).

$LiBH_4$ (2.7 mg, 0.12 mmol) was added to a stirred solution of the ester **31** (11.8 mg, 0.02 mmol) in THF (0.5 mL) at 40 °C. After the mixture was stirred at 40 °C for 1 h, a saturated aqueous NH_4Cl solution (0.2 mL) was added, and the mixture was stirred for 10 min. EtOAc (5 mL) was added. The organic layer was separated and dried ($MgSO_4$), and the solvent was evaporated.

The residue was acetylated with pyridine (0.1 mL), Ac_2O (0.1 mL), and DMAP (2 mg, catalytic). The resulting two diacetates were separated by column chromatography on silica gel (10 g, EtOAc/petroleum ether, 1:5). The less polar, unsymmetrical diacetate **32** was obtained in 68% yield (4 mg). The symmetrical diacetate **33** (more polar) was otained in 76% yield (4.5 mg): ^1H NMR (360 MHz, $CDCl_3$) of **32** δ 5.09 (ddd, J = 6.5, 6.5, 3.0, HC(2)), 4.51 (dd, ^2J = 12.5, ^3J = 3.0, HC(1)), 4.26 (ddd, J = 6.0, 5.5, 5.0, HC(3)), 4.11 (m, 2 H, HC(1), HC(4)), 3.88 (dd, ^2J = 9.0, ^3J = 5.5, HC(4)), 2.12, 2.10 (2 s, 6 H, 2 Ac), 1.45, 1.37 (2 s, Me_2C).

The diacetate **32** (4 mg, 0.016 mmol) in AcOH/H_2O 9:1 (3 mL) was heated to 60 °C, for 5 h. The solvent was evaporated under vacuum, and the residue was acetylated using pyridine (0.1 mL), Ac_2O (0.1 mL), and DMAP (1 mg) for 2 h at 20 °C. The solvent was evaporated, and the residue was filtered through a short silica gel column (5 g, EtOAc/petroleum ether, 1:1) to afford D-threitol tetraacetate (3.5 mg, 65%) **33** as a colorless gum. It was identical with an authentic sample made from D-threitol (Fluka), ^1H NMR, TLC, mixed ^1H NMR (360 MHz): ^1H NMR (360 MHz, $CDCl_3$) δ 5.34 (m, 2 H), 4.35 (dd, J = 12.0, 4.5, 2 H), 4.07 (dd, J = 12.0, 6.0, 2 H), 2.11, 2.07 (2 s, 4 Ac); $[\alpha]^{25}_D$ = +22.1°, $[\alpha]^{25}_{578}$ = +23.6°, $[\alpha]^{25}_{546}$ = +25.3°, $[\alpha]^{25}_{436}$ = +40.0°, $[\alpha]^{25}_{365}$ = +62.6° (c = 1.9, $CHCl_3$).

1,2-*O*-Diacetyl-3,4-*O*-isopropylidene-*meso*-erythrol (35). The ketone (+)-**28** (12 mg, 0.025 mmol) was oxidized with mCPBA (6 mg, 0.03 mmol, 85%) and $NaHCO_3$ (5 mg, 0.06 mmol) as for (−)-**18**, see above: yield 11.8 mg (95%) of ester **34**, colorless gum; ^1H NMR (250 MHz, $CDCl_3$) δ 6.29 (s, HC(4)), 5.54 (s, HC(1)), 5.12 (d, J = 4.2, HC(7)), 4.79, 4.59 (2 d, J = 5.5, HC(2), HC(3)), 4.46 (dt, J = 6.2, 4.2, HC(8)), 4.07 (d, J = 6.2, $H_2C(9)$), 2.17 (s, $COCH_3$), 1.48, 1.43, 1.36, 1.31 (4 s, 2 Me_2C), 0.90 (s, t-Bu), 0.16, 0.14 (2 s, Me_2Si). MS (CI, NH_3) m/z 508 (14, $[M + NH_4]^+$), 490 (2, $M^{\bullet+}$), 475 (11), 317 (9), 273 (59), 217 (36), 158 (26), 129 (45), 115 (42), 101 (30). Ester **34** (15 mg, 0.03 mmol) was then reduced with $LiBH_4$ (4 mg, 0.12 mmol) as before to afford 5 mg of **35** (67%): ^1H NMR (360 MHz, $CDCl_3$) δ 5.28 (m, 2 H), 4.34 (dd, 2 H, J = 12.5, 2.5), 4.19 (dd, 2 H, J = 12.5, 5.0), 2.10, 2.07 (2 s, 4 Ac). The diacetate **35** (5 mg, 0.02 mmol) was hydrolyzed as before to afford 4 mg (60%) of *meso*-erythritol tetraacetate, mp 85–86 °C. This sample was idential with authentic *meso*-erythritol tetraacetate (mixed mp, ^1H NMR, TLC): ^1H NMR (360 MHz, $CDCl_3$) of *meso*-erythritol tetraacetate δ 5.28 (m, 2 H), 4.34 (dd, 2 H, J = 12.5, 2.5), 4.19 (dd, 2 H, J = 12.5, 5.0), 2.10, 2.07 (2 s, 4 Ac).

***tert*-Butyldimethylsilyl 5,6-*O*-Carbonyl-2,3:7,8-di-*O*-isopropylidene-D-*threo*-L-*talo*-α-octofuranoside (36).** $COCl_2$ (1.8 M) in toluene (44 mL, 0.08 mmol) was added to a stirred solution of (−)-**19** (7 mg, 0.016 mmol), pyridine (0.2 mL), CH_2Cl_2 (0.2 mL), and 2-(dimethylamino)pyridine (2 mg) cooled to 0 °C. After stirring at 0 °C for 30 min, the solvent was evaporated and the residue was filtered through a short column of silica gel (10 g, EtOAc/petroleum ether, 1:6) to yield 5.1 mg (69%) colorless crystals: mp 204–205 °C; ^1H NMR (250 MHz, CD_3COCD_3) δ 5.58 (s, HC(1)), 5.19 (dd, J = 7.8, 1.0, HC(6)), 5.09 (dd, J = 10.0, 7.8, HC(5)), 5.0 (dd, J = 6.0, 2.0, HC(3), 4.80 (dd, J = 10.0, 2.0, HC(4)), 4.74 (d, J = 6.0, HC(2)), 4.61 (ddd, J = 7.0, 6.8, 1.0, HC(7)), 4.30 (dd, ^2J = 8.0, ^3J = 6.8) & 4.02 (dd, ^2J = 8.0, ^3J = 7.0, $H_2C(8)$), 1.56, 1.48, 1.46, 1.42 (4 s, 2 Me_2C), 1.02 (s, t-Bu), 0.30, 0.27 (2 s, Me_2Si); MS (CI, NH_3) m/z 478 (100, $[M + NH_4]^+$), 477 (31), 403 (59), 329 (54), 101 (49). Anal. Calcd for $C_{21}H_{36}O_9Si$ (460.60): C, 54.76; H, 7.88. Found: C, 54.98; H, 7.98.

***tert*-Butyldimethylsilyl 5,6-*O*-Carbonyl-2,3:7,8-di-*O*-isopropylidene-D-*threo*-D-*allo*-β-octofuranoside (37).** Same procedure as for **36**, starting with (−)-**20** (6 mg, 0.014 mmol): yield 4.8 mg (76%), colorless oil; ^1H NMR (250 MHz, CD_3COCD_3) δ 5.55 (s, HC(1)), 5.07 (dd, J = 6.0, 1.2, HC(3)), 4.91 (dd, J = 4.0, 1.5, HC(6)), 4.82 (d, J = 6.0, HC(2)), 4.77 (dd, J = 9.5, 4.0, HC(5)), 4.43 (ddd, J = 7.2, 6.0, 1.5, HC(7)), 4.35 (dd, J = 9.5, 1.2, HC(4)), 4.31 (d, ^2J = 8.5, ^3J = 7.2) & 4.10 (dd, ^2J = 8.5, ^3J = 6.0, $H_2C(8)$), 1.54, 1.46 (2 s, Me_2C), 1.43 (s, Me_2C), 1.05 (s, t-Bu), 0.31, 0.28 (2 s, Me_2Si); MS (CI, NH_3) m/z 478 (100, $[M + NH_4]^+$), 477 (60), 460 (3, M^+), 445 (35), 329 (26), 129 (6), 101 (40). Anal. Calcd for $C_{21}H_{36}O_9Si$ (460.60): C, 54.76; H, 7.88. Found: C, 54.53; H, 7.69.

***tert*-Butyldimethylsilyl 5,6-*O*-Carbonyl-2,3:7,8-di-*O*-isopropylidene-D-*erythro*-D-*talo*-α-octofuranoside (38).** $COCl_2$ (1.8 M) in toluene (67 μL, 0.12 mmol) was added to a stirred solution of (+)-**29** (9 mg, 0.02 mmol) and pyridine (0.5 mL) in CH_2Cl_2 (0.5 mL) cooled to 0 °C. After the mixture was stirred at 15 °C for 30 min, the solvent was evaporated and the residue was filtered through a short column of silica gel (10 g, EtOAc/petroleum ether, 1:6) to yield 7.1 mg (75%) of a colorless gum: ^1H NMR (360 MHz, CD_3COCD_3) δ 5.42 (d, J = 1.5, HC(1)), 5.06 (dd, J = 8.0, 4.0, HC(5)), 4.87 (dd, J = 6.2, 2.0, HC(3)), 4.79 (dd, J = 9.2, 8.0, HC(6)), 4.64 (ddd, J = 9.2, 6.0, 4.9, HC(7)), 4.54 (dd, J = 4.0, 2.0, HC(4)), 4.51 (J = 6.2, 1.5, HC(2)), 4.20 (dd, ^2J = 9.0, ^3J = 6.0) and 3.97 (dd, ^2J = 9.0, ^3J = 4.0, $H_2C(8)$), 1.44, 1.40, 1.32, 1.30 (4 s, 2 Me_2C), 0.89 (s, t-Bu), 0.13, 0.11 (2 s, Me_2Si); MS (CI, NH_3) m/z 478 (93, $[M + NH_4]^+$), 477 (83), 461 (4, $M^+ + H$), 460 (4, M^+), 445 (12), 403 (93), 397 (17), 378 (18), 361 (13), 346 (14), 303 (19), 245 (6), 143 (22), 129 (30), 101 (100), 85 (16).

***tert*-Butyldimethylsilyl 5,6-*O*-Carbonyl-2,3:7,8-di-*O*-isopropylidene-D-*erythro*-D-*allo*-β-octofuranoside (39).** Same procedure as for **38**, starting with (+)-**30** (4 mg, 0.01 mmol): yield 3 mg (70%), colorless gum; ^1H NMR (360 MHz, $CDCl_3$) δ 5.46 (s, HC(1)), 4.89 (dd, J = 6.0, 2.5, HC(3)), 4.72 (dd, J = 5.0, 4.0, HC(6)), 4.65 (dd, J = 6.8, 4.0, HC(5)), 4.63 (d, J = 6.0, HC(2)), 4.47 (t, J = 7.0, 5.0, HC(7)), 4.29 (dd, J = 6.8, 2.5, HC(4)), 4.18 (dd, ^2J = 9.2, ^3J = 7.0) and 3.92 (dd, ^2J = 9.2, ^3J = 5.0, $H_2C(8)$), 1.44, 1.41, 1.33, 1.31 (4 s, 2 Me_2C), 0.93 (s, t-Bu), 0.17, 0.16 (2 s, Me_2Si); MS (CI, NH_3) m/z 478 (66, $[M + NH_4]^+$), 477 (60), 461 (3, $M^+ + H$), 460 (2), 445 (22), 403 (12), 346 (10), 329 (10), 201 (5), 171 (8), 143 (20), 101 (100), 85 (12). Anal. Calcd for $C_{21}H_{36}O_9Si$ (460.60): C, 54.76; H, 7.88. Found: C, 54.79; H, 7.72.

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Supplementary Material Available: IR, ^{13}C NMR, optical rotations at λ = 578, 546, 436, and 365 nm, mass spectra data, and elemental analyses of new compounds; NOE measurements in the ^1H NMR spectra of **36–39** (10 pages). Ordering information is given on any current masthead page.