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TOTAL, ASYMMETRIC SYNTHESIS OF HEXOSES AND AZASUGARS BRANCHED AT C(5).[1]

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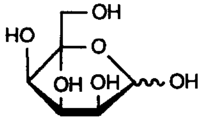
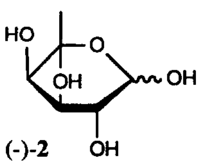
Summary: The *Diels-Alder* adduct (-)-**5** (a "naked sugar") of furan to 1-cyanovinyl (1*R*')-camphanate was converted into (+)-(1*R*,5*S*,6*S*,7*S*)-6-*exo*,7-*exo*-(isopropylidenedioxy)-2,8-dioxabicyclo[3.2.1]octan-3-one and into (+)-(1*R*,5*S*,6*S*,7*R*)-7-*endo*-(benzyloxy)-6-*exo*-{[(*t*-butyl)dimethylsilyl]oxy}-2,8-dioxabicyclo[3.2.1]-octan-3-one ((+)-**17**). Double methylation at C(4) gave the corresponding 5-deoxy-5-*C*-dimethyl furanurono-6,1-lactones (+)-**42** and (+)-**19**, respectively. Stereoselective and successive methylation and benzyloxymethylation of (+)-(1*R*,5*S*,6*S*,7*S*)-6-*exo*,7-*exo*-(isopropylidenedioxy)-2,8-dioxabicyclo[3.2.1]octan-3-one gave (+)-(1*R*,4*R*,5*S*,6*S*,7*S*)-4-*exo*-[(benzyloxy)methyl]-6-*exo*,7-*exo*-(isopropylidenedioxy)-4-*endo*-methyl-2,8-dioxabicyclo[3.2.1]octan-3-one ((+)-**9**). Highly stereoselective oxydative decarboxylation of lactones (+)-**9** and (+)-**19** led to 5-*C*-methyl-αβ-D-*talo*-hexose ((-)-**1**) and to 6-deoxy-5-*C*-methyl-αβ-L-*arabino*-hexose ((-)-**2**), respectively. Transformation of lactones (+)-**9** and (+)-**42** into the corresponding acyl azides and their *Curtius* rearrangements led to (5-ammonio-1,5-*N*-anhydro-5-deoxy-5-*C*-methyl-αβ-D-*talo*-hexitol)-1-sulfonate ((+)-**3**) and to (5-ammonio-1,5-*N*-anhydro-5,6-dideoxy-5-*C*-methyl-αβ-L-*ribo*-hexitol)-1-sulfonate ((+)-**4**), respectively.

During the last three decades numerous branched-chain sugars have been discovered as glycosidic components of antibiotics.[2-6] The chemical syntheses of branched-chain sugars apply nucleophilic addition of various carbon nucleophiles to aldosuloses,[3,5] additions to *C*-alkylidene glycosides,[3,6] nucleophilic reactions of sugar oxiranes,[3,7] additions[3,8] and cycloadditions[3,9] to unsaturated carbohydrates, cyclization of dialdehydes with nitroalkanes[3,10] and rearrangement reactions,[3,11] including the *Claisen* rearrangement.[12] More recently rare branched-chain carbohydrates have been prepared through alkylation of stabilized anions derived from sugars,[13] via a *Kornblum* reaction of nitromethane with a 4-nitro-D-*gluco*-L-*erythro*-nonulopyranose derivative,[14] via addition of radicals derived from a carbohydrate to an olefinic moiety,[15] radical cyclizations[16] and via *de novo* syntheses based on the aldol condensation,[17] on the *Henry* reaction,[18] on the hetero *Diels-Alder* addition[19] and other cycloadditions.[20]

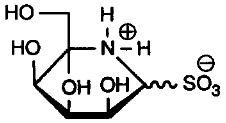
Except for noviose[21] (6-deoxy-5-*C*-methyl-4-*O*-methyl-L-*lyxo*-hexose), the aldose moiety of noviosylcoumarin antibiotics, and for 5-*C*-aryl glucosidic antibiotics such as nogalamycin-related anthracyclines,[22] branched-chain carbohydrates with tertiary C(5) carbon atoms are rare compounds. In 1958, *Walton* and co-workers[23] reported on the conversion of D-ribose into methyl 6-deoxy-2,3-*O*-isopropylidene-5-*C*-methyl-D-*ribo*-hexofuranoside. Ten years later, *Nutt* and *Walton*[24] prepared 5',5'-di-*C*-methyladenosine via methyl



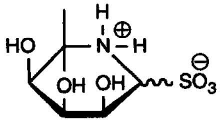
(-)-**1**



(-)-**2**

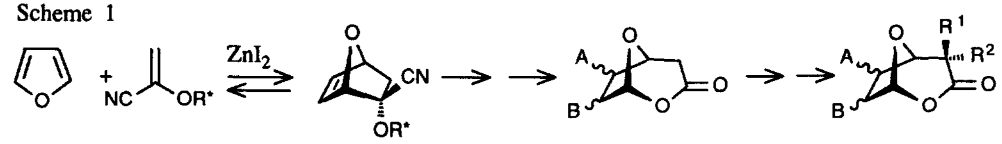


(+)-**3**



(+)-**4**

Scheme 1



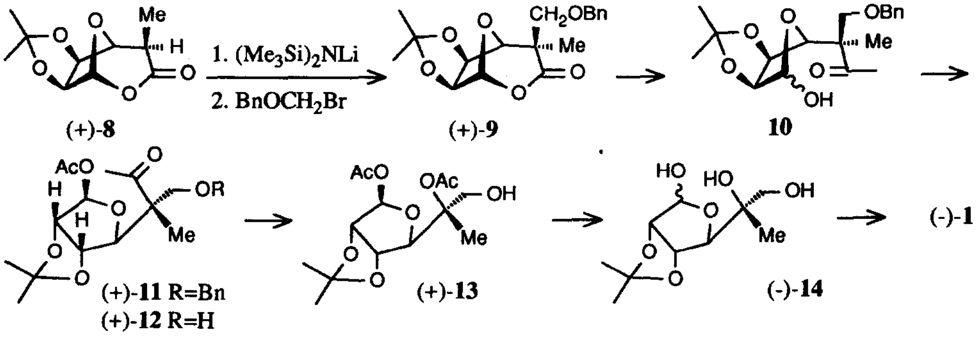
R*=(1*R*)-camphanoyl (-)-**5** **6** **7**

2,3,5-tri-*O*-benzoyl-6-deoxy-5-*C*-methyl-β-D-*ribo*-hexofuranoside. D-glucose has been converted into 6-deoxy-5-*C*-methyl-D-*xylo*-hexose[25] and into 5-*C*-methyl-D-*gluco*-hexose.[26] We report on the first syntheses of 5-*C*-methyl-D-*talo*-hexose ((-)-**1**), 6-deoxy-5-*C*-methyl-L-*arabino*-hexose ((-)-**2**), (5-ammonio-1,5-*N*-anhydro-5-deoxy-5-*C*-methyl-D-*talo*-hexitol)-1-sulfonate ((+)-**3**) and (5-ammonio-1,5-*N*-anhydro-5,6-di-deoxy-5-*C*-methyl-L-*ribo*-hexitol)-1-sulfonate ((+)-**4**). Our approach is based on the highly stereoselective methylation and benzyloxymethylation of the conjugated bases (enolates) of the optically pure furanurono-6,1 lactones **6** derived readily from the *Diels-Alder* adduct (-)-**5** (a "naked sugar"[27]) of furan to 1-cyanovinyl (1*R*')-camphanate (*Scheme 1*).

SYNTHESES OF HEXOSES BRANCHED AT C(5)

The α-methyl-lactone (+)-**8** derived from (-)-**5**[28-30] was deprotonated with $(Me_3Si)_2NLi$ (THF, -65°C). Quenching of the corresponding enolate with $BnOCH_2Br$[29] afforded (+)-**9** in 97% yield (5 steps from (-)-**5**, 55.7% overall yield). The configuration of C(4) in (+)-**9** was confirmed by NOE measurements in its ^{1}H-NMR spectrum between *exo*-CH_2OBn and H-C(5) protons, and between *endo*-Me and H-C(6) protons. The high *exo*-face selectivity of the transformation (+)-**8** → (+)-**9** can be attributed to a steric factor, the *endo* face of the enolate intermediate being less accessible than the *exo* face.[30] Lactone (+)-**9** added Me_3SiCH_2Li in THF and led, after *in situ* methanolysis of the TMS group, to a mixture of the α- and β-furanose **10** whose acetylation gave (+)-**11** (94% based on (+)-**9**). Debenzylation (H_2/Pd/C) furnished (+)-**12** (98%) which was oxidized into (+)-**13** (50%) on treatment with CF_3CO_3H and Na_2HPO_4 in CH_2Cl_2. The yield of the latter *Baeyer-Villiger* reaction could not be improved with the use of other peracids such as *m*-chloroperbenzoic acid (mCPBA), magnesium monoperoxyphthalate (MMPP),[32] 4-nitroperbenzoic acid[33] or 3,5-dinitroperbenzoic acid[34] in the presence or absence of various buffers. Transesterification (MeOH/K_2CO_3) of (+)-**13** gave a mixture of the partially protected α- and β-furanose (-)-**14** (97%) whose acidic hydrolysis (1N H_2SO_4, 80°C) afforded the unprotected 5-*C*-methyl-D-*talo*-hexose ((-)-**1**) in 95% yield (10 steps, 23.6% overall yield based on (-)-**5**, *Scheme 2*).

Scheme 2

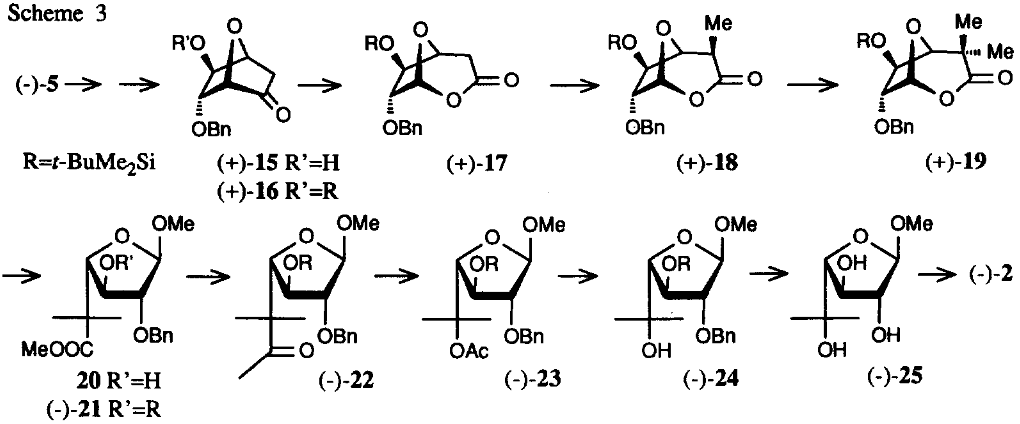


(+)-**8** (+)-**9** **10**

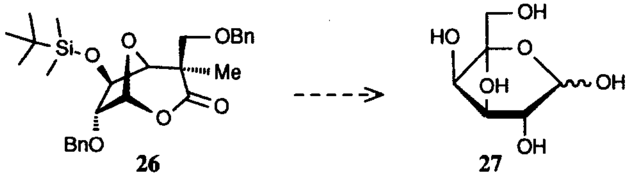
(+)-**11** R=Bn
(+)-**12** R=H
(+)-**13**
(-)-**14**

As an illustration of the flexibility of the approach shown above to the synthesis of rare hexoses branched at C(5), we have also prepared 6-deoxy-5-*C*-methyl-L-*arabino*-hexose ((-)-**2**) (*Scheme 3*: 14 steps from (-)-**5**, 22% overall yield, see Experimental Part) via alcohol (+)-**15**.[35]

Scheme 3

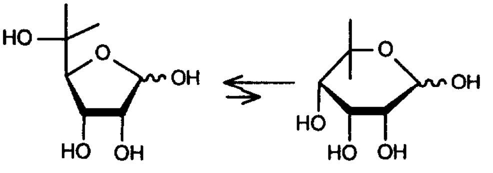


As in the case of (+)-**8** (*Scheme 2*), stereoselective benzyloxymethylation of (+)-**18** could be carried out by deprotonation with $(Me_3Si)_2NLi$ and quenching of the conjugated base with $BnOCH_2Br$; this afforded **26** in 87% yield (reactions tested with racemic (±)-**18** derived from (±)-**5**, with R*=Ac). In principle **26** should allow one to prepare the yet unknown branched hexose **27** (5-*C*-methyl-D-*galacto*-hexose).

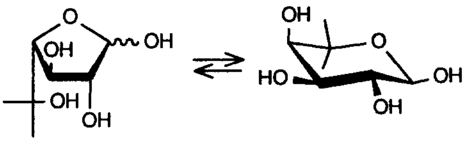


26 **27**

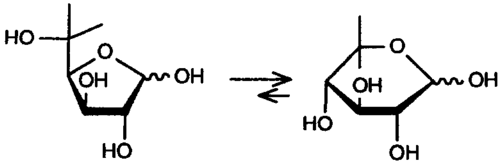
The ^1H- and ^{13}C-NMR spectra of the new sugars (-)-**1** and (-)-**2** taken in D_2O allowed one to determine their structure in aqueous solutions. As for most hexoses,[36] their acyclic forms could not be detected (<1%). The branched *talo*-hexose (-)-**1** was a 54 ± 0.5 : 40 ± 1 : 3.5 ± 0.5 : 2.0 ± 0.5 mixture of the corresponding α-furanose/β-furanose/α-pyranose/β-pyranose form, whereas for (-)-**2**, a 37 ± 1 : 24.5 ± 0.5 : 38.5 ± 0.5 : <1 mixture of the corresponding α-furanose/β-furanose/α-pyranose/β-pyranose form was



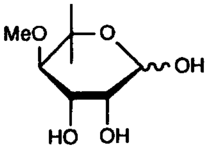
(α/β 37:52) **28** (α/β 4:7)



(α/β 37:24) (-)-**2** (α/β 39:1)



29 (α/β 8:92)



30 (α/β 26:74)

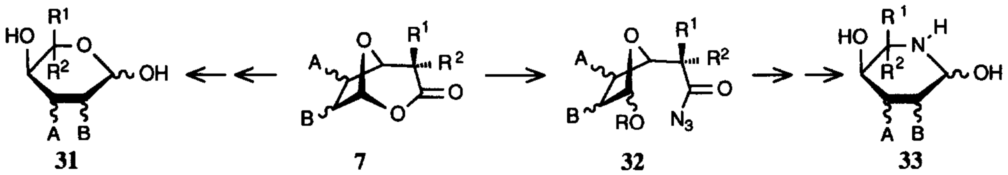
observed (the reported proportions did not vary with the age of the solutions: 1-15 days). As in the case of 6-deoxy-5-*C*-methyl-D-*ribo*-hexose (**28**),[37] the furanose forms are preferred for (-)-**1**. In the case of (-)-**2**, the α-pyranose form, which has the $^4C_1$ conformation (see vicinal H-H coupling constants in its ^{1}H-NMR spectrum, Experim. Part), has nearly the same stability as the corresponding α- and β-furanose forms. These results must be compared with those reported for 6-deoxy-5-*C*-methyl-D-*xylo*-hexose (**29**) and noviose (**30**) for which the furanose forms were not detected in aqueous solutions.[37]

SYNTHESES OF AZASUGARS BRANCHED AT C(5)

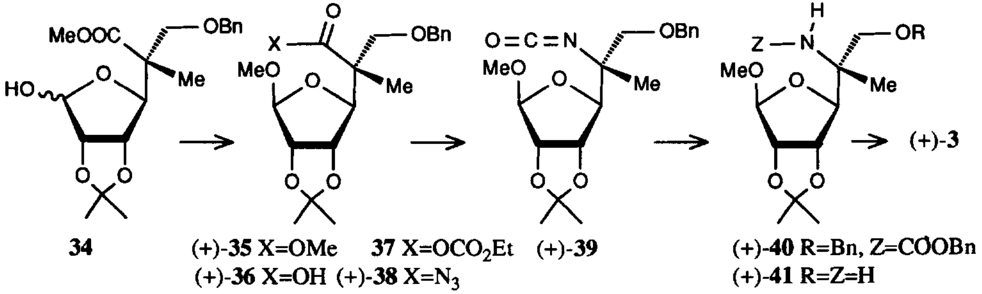
The substitution of the ring oxygen of pyranoses by nitrogen (azasugars)[38] leads to powerful and specific glycosidase inhibitors whose chemotherapeutic potential is well recognized.[39] Because some derivatives have exhibited anti-HIV-activity,[40] there has been recently a large effort in the search of new azasugars.[41] Instead of performing a stereoselective oxidative decarboxylation of the furanurono-6,1-lactones of type **7** which permitted one to generate the corresponding hexoses of type **31**, a *Curtius* rearrangement of the acyl azides of type **32** derived from **7** should allow one to prepare the corresponding azasugars **33** branched at C(5) (*Scheme 4*).[42]

The alkaline methanolysis (MeOH, K_2CO_3) of lactone (+)-**9** gave a mixture of the α- and β-furanose **34** (93%) which was treated with $HC(OMe)_3$ and Amberlyst 15 to yield (+)-**35** (91%; 22:1 mixture of β- and α-anomer which could be separated by column chromatography). Saponification of (+)-**35** gave (+)-**36** (100%) whose mixed anhydride **37**, obtained by treatment with $EtOCOCl/Et_3N$, reacted with NaN_3 to furnish the unstable azide (+)-**38** that underwent *Curtius* rearrangement (benzene, 80°C) into the isocyanate (+)-**39** which added $PhCH_2OH$ to give (+)-**40** (72%, based on (+)-**36**). Debenzylation of (+)-**40** gave the partially protected methyl furanoside (+)-**41** (99%). Treatment of (+)-**41** with SO_2 afforded (+)-**3** (53%; 11 steps from "naked sugar" (-)-**5**, 17.8% overall yield) whose ^{1}H- and ^{13}C-NMR were consistent with a 1:1 mixture of α- and β-anomer.

Scheme 4



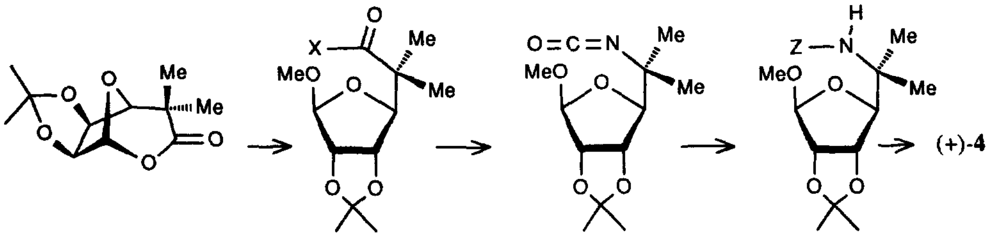
Scheme 5



The preparation of azasugar (+)-**4** followed a similar method starting with uronolactone (+)-**42** (5 steps from (-)-**5**, 49.2 % overall yield) obtained by methylation of (+)-**8** ($(Me_3Si)_2NLi$, then MeI).[30]

Methanolysis of (+)-**42** with $HC(OMe)_3$ and Nafion 117 in CCl_4 gave the methyl furanosiduronate (+)-**43** (70%) whose saponification afforded acid (+)-**44** (100%). Treatment of (+)-**44** with $ClCO_2Et/Et_3N$ led to the unstable mixed anhydride **45** which reacted, after filtration, with NaN_3/H_2O to give the corresponding acyl azide (+)-**46**. On heating (+)-**46** in C_6H_6 a *Curtius* rearrangement was induced with formation of the corresponding isocyanate (+)-**47** which could be isolated in nearly quantitative yield. In the presence of $PhCH_2OH$ and a small amount of Et_3N, the corresponding benzyl carbamate (+)-**48** (89%) was obtained. Other alcohols such as allylic alcohol or ethanol were reacted with (+)-**47** and led to the corresponding allyl and ethyl carbamate, respectively, in high yields. Hydrogenolysis (H_2/Pd/C) of (+)-**48** afforded (+)-**49** (91%) which gave the crystalline sulfonate (+)-**4** (62%); 10 steps from (-)-**5**, 17.2% overall yield) on bubbling with SO_2 (aqueous solution, 55°C). The ^1H- and ^{13}C-NMR spectra of (+)-**4** were consistent with a 2:1 mixture of α- and β-anomer.

We also explored the possibility to apply the *Hofmann* degradation on the carboxamide **50** derived from (±)-**42**. This compound was not formed on heating lactone (±)-**42** with NH_3 but it could be isolated in 92% yield by bubbling gaseous NH_3 into a CH_2Cl_2 solution of the mixed anhydride (±)-**45** (-20°C).



(+)-**42** (+)-**43** X=OMe (+)-**46** X=N_3 (+)-**47** (+)-**48** R=Bn, Z=COOBn
(+)-**44** X=OH **50** X=NH_2 (+)-**49** R=Z=H
45 X=OCO_2Et

Unfortunately, the expected amine (±)-**49** could not be obtained in a yield better than 45% on treating **50** with phenyliodosyl bis(trifluoroacetate)[43] in aqueous CH_3CN.

Conclusion.

Stereoselective methylation and oxymethylation of the hexofuranurono-6,1-lactones derived from 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives ("naked sugars") and their stereoselective oxidative decarboxylation has opened a new way to the synthesis of rare carbohydrates branched at C(5). Similarly, the transformation of the 5,5-*C*-disubstituted urono-6,1-lactones into the corresponding acyl azides and their *Curtius* rearrangement has allowed one to generate the first members of a new class of azasugars branched at C(5). The advantages of our total synthesis methodology are numerous: (1) since the 7-oxabicyclo-[2.2.1]hept-5-en-2-yl derivatives ("naked sugars") can be substituted at C(5) and C(6) by other groups than hydroxy moieties,[27] a large variety of yet unknown branched carbohydrates and azasugars can be prepared in principle, (2) both enantiomers of a given system can be obtained with the same ease as both enantiomeric forms of the starting "naked sugar" are available and (3) the chiral auxiliaries (*e.g.* (1*S*)- or (1*R*)-camphanic acid) are recovered at an early stage of the synthesis.

Acknowledgments. We thank *F. Hoffmann-La Roche & Co. AG*, Basel, the *Fonds Herbette*, Lausanne, and the *Swiss National Science Foundation* for generous support. We are grateful also to Miss Nadia Larbi for her technical assistance.

Experimental Part

General remarks, see ref. 28a. The glassware was dried in a flame with a flow of Ar. THF was dried over K just before use. Unless indicated otherwise the ^{1}H- and ^{13}C-NMR spectra were measured in $CDCl_3$ with 250 MHz and 62.9 MHz Bruker NMR machines, respectively. Column chromatography (*Lobar* B or C) used silica gel Lichroprep Si 60, 40 - 63 μm.

(1*R*,4*R*,5*S*,6*S*,7*S*)-4-*exo*-[(Benzyloxy)methyl]-6-*exo*,7-*exo*-(isopropylidenedioxy)-4-*endo*-methyl-2,8-dioxabicyclo[3.2.1]octan-3-one ((+)-**9**). In a 1 L three-necked flask, a 1.6M soln. of BuLi in hexane (32 mL, 1.1 equiv.) was added dropwise to a stirred soln. of hexamethyldisilazane (12.6 mL, 1.3 equiv.) in anh. THF (400 mL) cooled to 0°C under Ar atm. After stirring at 0°C for 15 min, the soln. was cooled to -60°C and a soln. of (+)-**8** (10.0 g, 46.7 mmol) in anh. THF (200 mL) cooled to -40°C was added slowly. After stirring at -60°C for 2 h, freshly distilled $PhCH_2OCH_2Br$[29] (22 mL, 6 equiv.) was added and the mixture allowed to warm to -10°C in *ca.* 30 min (control by tlc, CH_2Cl_2/Et_2O/petroleum ether 3:1:4, R_f (+)-**8**: 0.33, R_f (+)-**9**: 0.51, vanilline as revelator. The mixture was poured onto a vigourously stirred ice-cold sat. aq. soln. of NH_4Cl (400 mL). The mixture was extracted with CH_2Cl_2 (400 mL, then 200 mL, twice), the extracts were combined, dried ($MgSO_4$) and the solvent evaporated. The residue was immediately purified by flash column chromatography on silica gel (*Merck* 9385, CH_2Cl_2/Et_2O/petroleum ether 3:1:4) and recrystallized from AcOEt/pentane 1:10. The mother liquor was concentrated and purified by column chromatography (*Lobar* C, Et_2O/petroleum ether 2:3) giving a total of 15.1 g (97%), colourless crystals, m.p. 91.5-92°C. $[\alpha]^{25}_{589} = +7.5$, $[\alpha]^{25}_{578} = +6.7$, $[\alpha]^{25}_{546} = +8.2$, $[\alpha]^{25}_{436} = +17.0$, $[\alpha]^{25}_{365} = +33.8$ ($c = 0.70$, CH_2Cl_2). UV (EtOH 95%) λ_{max}: 264 nm (ϵ, 200), 258 (240), 252 (220), 207 (7900). IR (KBr) ν: 2980, 2940, 2905, 2860, 1730, 1370, 1075, 980, 860, 695 cm^{-1}. ^{1}H-NMR δ_H: 7.28-7.42 (m, 5H); 5.67 (d, $^4J = 0.5$ Hz, H-C(1)); 4.87, 4.80 (2d, $^3J = 5.5$ Hz, H-C(6), H-C(7)); 4.67 (d, $^4J = 0.5$ Hz, H-C(5)); 4.61, 4.54 (2d, $^2J = 12.0$ Hz, $-CH_2OCH_2C_6H_5$); 3.88, 3.45 (2d, $^2J = 8.5$ Hz, $-CH_2OBn$); 1.50, 1.36, 1.34 (3s, 3 Me). ^{13}C-NMR (90.55 MHz) δ_C: 169.7 (s, C(3)); 137.6 (s); 128.4, 127.8 (2d, ^1J(C,H) = 160 Hz); 127.5 (d, ^1J(C,H) = 158 Hz); 113.2 (s); 103.6 (d, ^1J(C,H) = 186 Hz, C(1)); 83.6, 82.9 (2d, ^1J(C,H) = 162 Hz), 78.4 (d, ^1J(C,H) = 156 Hz, C(5), C(6), C(7)); 73.6 (t, ^1J(C,H) = 143 Hz), 73.5 (t, ^1J(C,H) = 143 Hz, $-CH_2OCH_2C_6H_5$); 48.9 (s, C(4)); 26.0 (q, ^1J(C,H) = 128 Hz, $-CH_3$); 25.0 (q, ^1J(C,H) = 127 Hz, $-CH_3$); 16.7 (q, ^1J(C,H) = 131 Hz, $-CH_3$). MS (70 eV) m/z: 319 ($M^{+\cdot}$-15, 6), 259 (3), 213 (2), 185 (1), 155 (2), 113 (3), 105 (4), 91 (100), 85 (16), 65 (10), 59 (11). Anal. calc. for $C_{18}H_{22}O_6$ (334.33): C 64.67, H 6.63; found: C 64.71, H 6.53.

(1*RS*,4*RS*,5*SR*,6*SR*,7*SR*)-4-*exo*-[(Benzyloxy)methyl]-6-*exo*,7-*exo*-(isopropylidenedioxy)-4-*endo*-methyl-2,8-dioxabicyclo[3.2.1]octan-3-one ((±)-**9**). Same procedure as described for (+)-**9**, starting with (±)-2-*exo*-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl acetate, see ref. 28a. M.p. 71-71.5°C.

5-[(Benzyloxy)methyl]-5,7-dideoxy-2,3-*O*-isopropylidene-5-*C*-methyl-αβ-L-*allo*-heptos-6-ulofuranosyl acetate ((+)-**11**). A 1.0M soln. of $LiCH_2SiMe_3$ in pentane (*Aldrich*, 19 mL, 3.2 equiv.) was added dropwise to a stirred soln. of (+)-**9** (2.0 g, 6.0 mmol) in anh. THF (100 mL) cooled to -65°C under Ar atm. After stirring at -65°C for 5-10 min (disappearance of (+)-**9**), MeOH (10 mL) was added dropwise and the mixture was stirred at -40°C for 15 min (tlc, Et_2O/petroleum ether 2:1, R_f (+)-**9**: 0.54, R_f **10**: 0.39). The mixture was poured into a stirred mixture of ice-cold sat. aq. soln. of NH_4Cl (150 mL). The aq. phase was extracted with CH_2Cl_2 (150 mL, then 100 mL, twice). The org. extracts were combined, dried ($MgSO_4$) and the solvent evaporated. The residue (**10**, oil that can be distilled, b.p. -150°C, 0.1 Torr) was dissolved in THF (20 mL), mixed with Ac_2O (10 mL) and pyridine (10 mL). After stirring at 20°C for 2 h, the solvent was evaporated. The residue was taken with toluene (30 mL) and the solvent evaporated (3 times). The residue was distilled (*Büchi* bulb-to-bulb) giving 2.2 g (94%), colourless oil, b.p. -180°C, 0.5 Torr, 1:17.5 mixture of α- and β-anomer. $[\alpha]^{25}_{589} = +39.5$, $[\alpha]^{25}_{578} = +42.6$, $[\alpha]^{25}_{546} = +47.7$, $[\alpha]^{25}_{436} = +79.1$, $[\alpha]^{25}_{365} = +115.6$ (c = 0.78, CH_2Cl_2). UV (EtOH 95%) λ_{max}: 208 (ϵ, 6700), 252 (215), 258 (245), 264 (205). IR (film) ν: 3090, 3060, 3030, 2985, 2940, 2865, 1745, 1705, 1450, 1370, 1210, 1100, 1005, 970, 860, 740, 700 cm^{-1}. ^{1}H-NMR (C_6D_6, 250 MHz) δ_H: 7.08-7.20 (m, 5H); 6.52 (d, $^4J = 1.0$ Hz, H-C(1)); 4.96 (dd, $^3J = 6.2$, 2.7 Hz, H-C(3)); 4.68 (d, $^3J = 2.7$ Hz, H-C(4)); 4.38 (dd, $^3J = 6.2$ Hz, $^4J = 1.0$ Hz, H-C(2)); 4.22, 4.16 (2d, $^2J = 12.0$ Hz, $-OCH_2C_6H_5$); 3.59, 3.33 (2d, $^2J = 9.2$ Hz, $-CH_2OBn$); 2.02 (s, $-OCOCH_3$); 1.60 (s, $-COCH_3$); 1.41, 1.12, 1.10 (3s, 3 Me). ^{13}C-NMR (C_6D_6, 62.9 MHz) δ_C: 210.1, 169.2, 137.4 (3s); 128.3, 127.7 (2d, ^1J(C,H) = 161 Hz); 127.4 (d, ^1J(C,H) = 160 Hz); 112.9 (s); 102.5 (d, ^1J(C,H) = 180 Hz, C(1)); 91.7 (d, ^1J(C,H) = 153 Hz), 85.2 (d, ^1J(C,H) = 158 Hz), 80.8 (d, ^1J(C,H) = 159 Hz, C(2), C(3), C(4)); 73.4 (t, ^1J(C,H) = 141 Hz), 72.6 (t, ^1J(C,H) = 143 Hz, $-CH_2OCH_2C_6H_5$); 54.4 (s, C(5)); 27.1 (q, ^1J(C,H) = 129 Hz, $-CH_3$); 26.8 (q, ^1J(C,H) = 127 Hz, $-CH_3$); 25.0 (q, ^1J(C,H) = 128 Hz, $-CH_3$); 21.0 (q, ^1J(C,H) = 129 Hz, $-OCOCH_3$); 17.3 (q, ^1J(C,H) = 129 Hz, $-COCH_3$). MS (CI, NH_3) m/z: 410 ($M^{+\cdot}$+18, 16), 350 (2), 333 (30), 245 (3), 227 (6), 168 (9), 137 (7), 125 (7), 106 (22), 91 (100). Anal. calc. for $C_{21}H_{28}O_7$ (392.45): C 64.27, H 7.19; found: C 64.08, H 7.03.

5,7-Dideoxy-5-(hydroxymethyl)-2,3-*O*-isopropylidene-5-*C*-methyl-αβ-L-*allo*-heptos-6-ulofuranosyl acetate

((+)-**12**). A mixture of (+)-**11** (0.50 g, 1.27 mmol), THF (10 mL), H_2O (1.7 mL), 10% Pd/C (750 mg) was pressurized with H_2 (1 atm.) and shaken at 20°C for 5 h (tlc, AcOEt/petroleum ether 1:1, R_f (+)-**11**: 0.93, R_f (+)-**12**: 0.23). After filtration through *Celite*, the filtrate was dried ($MgSO_4$) and the solvent evaporated, yielding 376 mg (98%), colourless oil that can be distilled (*Büchi*, bulb-to-bulb, 150°C, 0.08 Torr); 1:17.5 mixture of α- and β-anomer. $[\alpha]^{25}_{589}$ = +29.8, $[\alpha]^{25}_{578}$ = +31.1, $[\alpha]^{25}_{546}$ = +34.5, $[\alpha]^{25}_{436}$ = +51.0, $[\alpha]^{25}_{365}$ = +52.9 (c = 1.84, CH_2Cl_2). UV (EtOH, 95%) λ_{max}: 202 (ϵ, 215), 283 (26). IR (film) v: 3500 (broad), 2985, 2940, 2890, 1745, 1705, 1370, 1210, 1155, 1105, 1005, 970, 860 cm^{-1}. ^{1}H-NMR δ_H: 6.11 (d, ^3J = 0.7 Hz, H-C(1)); 4.97 (dd, ^3J = 2.5, 6.2 Hz, H-C(3)); 4.77 (dd, ^3J = 0.7, 6.2 Hz, H-C(2)); 4.37 (d, ^3J = 2.5 Hz, H-C(4)); 3.79 (s, -CH_2OH); 2.76 (s, -OH); 2.23 (s, -$OCOCH_3$); 2.05 (s, -$COCH_3$); 1.49, 1.31, 1.10 (3s, 3 Me). ^{13}C-NMR δ_C: 210.9, 169.5, 113.3 (3s); 102.5 (d, ^1J(C,H) = 180 Hz, C(1)); 92.9 (d, ^1J(C,H) = 151 Hz), 85.3 (d, ^1J(C,H) = 160 Hz), 80.6 (d, ^1J(C,H) = 162 Hz, C(2), C(3), C(4)); 66.7 (t, ^1J(C,H) = 144 Hz, -CH_2OH); 55.1 (s, C(5)); 27.2, 26.8 (2q, ^1J(C,H) = 128 Hz, 2 Me); 25.0 (q, ^1J(C,H) = 126 Hz, Me); 21.0, 17.1 (2q, ^1J(C,H) = 129 Hz, 2 CH_3CO). MS (CI, NH_3) m/z: 320 ($M^{+\cdot}$+18, 3), 243 (99), 227 (33), 213 (13), 199 (40), 182 (11), 167 (12), 155 (26), 142 (32), 137 (72), 125 (93), 111 (37), 97 (100), 85 (94). Anal. calc. for $C_{14}H_{22}O_7$ (302.33): C 55.62, H 7.33; found: C 55.64, H 7.27.

5-*O*-Acetyl-2,3-*O*-isopropylidene-5-*C*-methyl-α-D-*talo*-hexofuranosyl acetate ((+)-**13**). A mixture of 2.2M CF_3CO_3H (2.9 mL, 5.6 equiv., prepared by mixing 84% H_2O_2 with $(CF_3CO)_2O$ in CH_2Cl_2 at 0°C) and CH_2Cl_2 (6 mL) was added dropwise in 30 min to a vigourously stirred mixture of (+)-**12** (350 mg, 1.16 mmol), CH_2Cl_2 (7 mL) and Na_2HPO_4 (1.6 g, 9.7 equiv.). After stirring at 20°C for 5 h (tlc, CH_2Cl_2/Et_2O 1:1, R_f (+)-**12**: 0.30, R_f (+)-**13**: 0.48), the mixture was poured into a 1M aq. soln. of $NaHSO_3$. The aq. layer was extracted with CH_2Cl_2 (20 mL, twice). The org. extracts were combined, dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by column chromatography (*Lobar* B, CH_2Cl_2/Et_2O 3:1), yielding 184 mg (50%) of colourless crystals (recrystallization from AcOEt/pentane 1:5), m.p. 79.5-80.5°C. $[\alpha]^{25}_{589}$ = +18.2, $[\alpha]^{25}_{578}$ = +18.6, $[\alpha]^{25}_{546}$ = +21.0, $[\alpha]^{25}_{436}$ = +33.3, $[\alpha]^{25}_{365}$ = +49.1 (c = 1.10, CH_2Cl_2). IR (KBr) v: 3530, 2980, 2950, 1740, 1730, 1375, 1280, 1230, 1105, 1060, 960, 850, 800 cm^{-1}. ^{1}H-NMR δ_H: 6.26 (s, H-C(1)); 4.94 (dd, ^3J = 1.6, 6.1 Hz, H-C(3)); 4.65 (d, ^3J = 6.1 Hz, H-C(2)); 4.25 (d, ^3J = 1.6 Hz, H-C(4)); 4.26, 3.80 (2d, ^2J = 11.3 Hz, -CH_2OH); 2.72 (s, -OH); 2.11, 2.07 (2s, 2 $COCH_3$); 1.49, 1.32, 1.26 (3s, 3 Me). ^{13}C-NMR δ_C: 171.0, 168.7, 112.9 (3s); 102.7 (d, ^1J(C,H) = 180 Hz, C(1)); 92.8 (d, ^1J(C,H) = 151 Hz), 85.5 (d, ^1J(C,H) = 161 Hz), 80.1 (d, ^1J(C,H) = 159 Hz, C(2), C(3), C(4)); 71.9 (s, C(5)); 67.9 (t, ^1J(C,H) = 149 Hz, -CH_2OH); 26.4 (q, ^1J(C,H) = 127 Hz, -CH_3); 24.8 (q, ^1J(C,H) = 125 Hz, -CH_3); 21.0, 20.8, 20.6 (3q, ^1J(C,H) = 130 Hz, 3 Me). MS (CI, NH_3) m/z: 336 ($M^{+\cdot}$+18, 72), 276 (65), 259 (100), 134 (25), 117 (45), 85 (62), 77 (24). Anal. calc. for $C_{14}H_{22}O_8$ (318.32): C 52.83, H 6.97; found: C 52.95, H 6.83.

5-*O*-Acetyl-2,3-*O*-isopropylidene-5-*C*-methyl-α-DL-*talo*-hexofuranosyl acetate ((±)-**13**). Same procedure as described for (+)-**13**, starting with (±)-**9**. Colourless crystals, m.p. 65-65.5°C.

2,3-*O*-Isopropylidene-5-*C*-methyl-αβ-D-*talo*-hexofuranose ((-)-**14**). A mixture of (+)-**13** (80 mg, 0.25 mmol), anh. MeOH (3 mL) and anh. K_2CO_3 (15 mg, 0.43 equiv.) was stirred at 20°C for 12 h. After solvent evaporation, the residue was filtered through silica gel ($MeOH/CH_2Cl_2$ 1:10, R_f (-)-**14**: 0.41) giving 57 mg (97%), colourless oil which crystallizes slowly, m.p. 102-103°C. $[\alpha]^{25}_{589}$ = -0.2, $[\alpha]^{25}_{578}$ = -0.3, $[\alpha]^{25}_{546}$ = -0.7, $[\alpha]^{25}_{436}$ = -3.6, $[\alpha]^{25}_{365}$ = -10.7 (c = 0.95, CH_2Cl_2). IR (KBr) v: 3250 (broad), 2980, 2950, 1370, 1205, 1090, 1055, 940, 865, 840, 795, 660 cm^{-1}. ^{1}H-NMR δ_H: α-anomer: 6.16 (s, -OH); 5.40 (s, H-C(1)); 4.94 (dd, ^3J = 1.0, 6.0 Hz, H-C(3)); 4.57 (s, -OH); 4.55 (d, ^3J = 6.0 Hz, H-C(2)); 4.20 (d, ^3J = 1.0 Hz, H-C(4)); 3.75 (s, -OH); 3.69, 3.46 (2d, ^2J = 11.0 Hz, -CH_2OH); 1.47, 1.33, 1.24 (3s, 3Me); β-anomer: 5.41 (d, ^3J = 4.3 Hz, H-C(1)); 4.87 (dd, ^3J = 6.9, 2.9 Hz, H-C(3)); 4.65 (dd, ^3J = 6.9, 4.3 Hz, H-C(2)); 4.00 (d, ^3J = 2.9 Hz, H-C(4)); 1.57, 1.40, 1.17 (3s, 3Me). ^{13}C-NMR δ_C: α-anomer: 112.3 (s); 102.7 (d, ^1J(C,H) = 176 Hz, C(1)); 92.9 (d, ^1J(C,H) = 148 Hz), 86.3 (d, ^1J(C,H) = 157 Hz), 80.8 (d, ^1J(C,H) = 157 Hz, C(2), C(3), C(4)); 71.9 (s, C(5)); 68.4 (t, ^1J(C,H) = 145 Hz, -CH_2OH); 26.4, 24.7, 20.8 (3q, 3Me); β-anomer: 114.5 (s); 96.9 (d, ^1J(C,H) = 176 Hz, C(1)); 86.8 (d, ^1J(C,H) = 148 Hz), 80.5 (d, ^1J(C,H) = 157 Hz), 79.3 (d, ^1J(C,H) = 160 Hz, C(2), C(3), C(4)); 72.1 (s, C(5)); 68.7 (t, ^1J(C,H) = 146 Hz); 26.2 (q, ^1J(C,H) = 129 Hz). MS (CI, NH_3) m/z: 252 ($M^{+\cdot}$+18, 14), 234 ($M^{+\cdot}$, 16), 217 (32), 207 (13), 185 (19), 159 (15), 101 (24), 85 (100), 75 (30), 71 (29). Anal. calc. for $C_{10}H_{18}O_6$ (234.25): C 51.27, H 7.75; found: C 51.41, H 7.62.

5-*C*-Methyl-αβ-D-*talo*-hexose ((-)-**1**). A soln. of (-)-**14** (97 mg, 0.41 mmol) in 1N aq. H_2SO_4 (2 mL) was heated to 80°C for 2 h. After cooling to 20°C, $BaCO_3$ (*ca.* 550 mg) was added until pH = 6. The precipitate was filtered off (*Celite*) and the solvent was evaporated. The residue was dissolved in a minimum amount of H_2O and filtered through Acrodisc 0.2 µm. After solvent evaporation 76 mg (95%) of colourless oil was obtained, mostly a mixture of α- and β-furanoses. $[\alpha]^{25}_{589}$ = -18.5, $[\alpha]^{25}_{578}$ = -19.3, $[\alpha]^{25}_{546}$ = -21.9, $[\alpha]^{25}_{436}$ = -35.9, $[\alpha]^{25}_{365}$ = -53.4 (c = 4.40, H_2O, after 3 d at 25°C). ^{1}H-NMR (D_2O, 250 MHz, int. ref: DSS (sodium 2,2-dimethyl-2-silapentan-5-sulfonate) δ_H: β-furanose: 5.34 (d, ^3J = 4.15 Hz, H-C(1)); 4.22 (dd, ^3J = 6.2, 4.3 Hz, H-C(3)); 4.01 (dd, ^3J = 6.2, 4.15 Hz, H-C(2)); 4.00 (d, ^3J = 4.3 Hz, H-C(4)); 3.56, 3.50 (2d, ^2J = 11.4 Hz,

$H_2C(6)$); 1.21 (s, $-CH_3$); α-furanose: 5.21 (d, ^3J = 2.0 Hz, H-C(1)); 4.38 (dd, ^3J = 6.6, 5.0 Hz, H-C(3)); 3.92 (dd, ^3J = 5.0, 2.0 Hz, H-C(2)); 3.89 (d, ^3J = 6.6 Hz, H-C(4)); 3.55, 3.51 (2d, ^2J = 11.1 Hz, $H_2C(6)$); 1.21 (s, $-CH_3$). ^{13}C-NMR (D_2O, 62.9 MHz, int. ref: MeOH) δ_C: α-furanose: 101.0 (d, ^1J(C,H) = 173 Hz, C(1)); 85.3 (d, ^1J(C,H) = 147 Hz, C(4)); 76.1 (d, ^1J(C,H) = 153 Hz, C(2)); 73.3 (s, C(5)); 70.3 (d, ^1J(C,H) = 147 Hz, C(3)); 67.3 (t, ^1J(C,H) = 144 Hz, C(6)); 19.1 (q, ^1J(C,H) = 127 Hz, $-CH_3$); β-furanose: 96.9 (d, ^1J(C,H) = 172 Hz, C(1)); 86.8 (d, ^1J(C,H) = 147 Hz, C(4)); 73.7 (s, C(5)); 71.8 (d, ^1J(C,H) = 150 Hz, C(2)); 70.0 (d, ^1J(C,H) = 153 Hz, C(3)); 66.8 (t, ^1J(C,H) = 144 Hz, C(6)); 19.8 (q, ^1J(C,H) = 127 Hz, $-CH_3$). MS (CI, NH_3) m/z: 212 ($M^{+\cdot}$+18, 12), 194 ($M^{+\cdot}$, 100), 177 (23), 159 (9), 128 (15), 111 (82), 110 (73), 97 (26), 87 (32), 82 (30), 75 (30), 71 (44).

Racemic (±)-**14** and (±)-**1** were obtained from (±)-**13** and were both colourless oils.

(1*S*,4*S*,5*S*,6*R*)-6-*endo*-(Benzyloxy)-5-*exo*-{[(*t*-butyl)dimethylsilyl]oxy}-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**16**). A mixture of (+)-**15** (prepared from (-)-**5** according to ref. 35) (7 g, 29.9 mmol), anh. DMF (28 mL), imidazole (4.1 g, 2 equiv.), t-$BuMe_2SiCl$ (4.5 g, 1 equiv.) was stirred at 20°C for 1 h. The soln. was poured into a stirred mixture of H_2O (100 mL) and hexane (100 mL). The aq. phase was extracted with hexane (100 mL, 3 times). The org. extracts were combined, dried ($MgSO_4$) and the solvent was evaporated, giving 10.05 g (96%), white solid, recrystallized from pentane, m.p. 80-80.5°C. $[\alpha]^{25}_{589}$ = +51.2, $[\alpha]^{25}_{578}$ = +53.1, $[\alpha]^{25}_{546}$ = +60.1, $[\alpha]^{25}_{436}$ = +98.2, $[\alpha]^{25}_{365}$ = +141.1 (c = 0.98, CH_2Cl_2). UV (isooctane) λ_{max}: 208 nm (ε, 8300), 252 (200), 258 (245), 264 (195). IR (KBr) ν: 3060, 3020, 2945, 2920, 2885, 2850, 1765, 1250, 1105, 1020, 990, 850, 835, 775, 695 cm^{-1}. ^1H-NMR δ_H: 7.28-7.40 (m, 5H); 4.60, 4.42 (2d, ^2J = 11.2 Hz, $-OCH_2C_6H_5$); 4.57 (dd, ^3J = 6.8 Hz, ^4J = 1.8 Hz, H-C(4)); 4.48 (dd, ^3J = 5.0 Hz, ^4J = 1.7 Hz, H-C(1)); 4.05 (d, ^3J = 1.0 Hz, H-C(5)); 3.94 (ddd, ^3J = 5.0, 1.0 Hz, ^4J = 1.8 Hz, H-C(6)); 2.48 (ddd, ^2J = 17.7 Hz, ^3J = 6.8 Hz, ^4J = 1.7 Hz, H_{exo}-C(3)); 2.11 (d, ^2J = 17.7 Hz, H_{endo}-C(3)); 0.91 (s, $-SiC(CH_3)_3$); 0.11, 0.10 (2s, Me_2Si). ^{13}C-NMR δ_C: 207.7 (s, C(2)); 136.7 (s); 128.4, 128.2, 128.1 (3d, ^1J(C,H) = 160 Hz); 85.3 (d, ^1J(C,H) = 156 Hz), 83.0 (d, ^1J(C,H) = 163 Hz), 80.7 (d, ^1J(C,H) = 167 Hz), 79.9 (d, ^1J(C,H) = 147 Hz, C(1), C(4), C(5), C(6)); 72.5 (t, ^1J(C,H) = 142 Hz, $-OCH_2C_6H_5$); 39.1 (t, ^1J(C,H) = 135 Hz, C(3)); 25.7 (q, ^1J(C,H) = 125 Hz); 18.0 (s); -4.8 (q, ^1J(C,H) = 119 Hz). MS (CI, NH_3) m/z: 366 ($M^{+\cdot}$+18, 76), 263 (3), 207 (27), 175 (5), 106 (11), 91 (100), 83 (64), 73 (14). Anal. calc. for $C_{19}H_{28}O_4Si$ (348.51): C 65.48, H 8.10; found: C 65.54, H 8.22.

(1*RS*,4*RS*,5*RS*,6*SR*)-6-*endo*-(Benzyloxy)-5-*exo*-{[(*t*-butyl)dimethylsilyl]oxy}-7-oxabicyclo[2.2.1]heptan-2-one ((±)-**16**). Same procedure as described for (+)-**16**, starting with 2-*exo*-cyano-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl acetate.[35] Colourless crystals (pentane), m.p. 50-50.5°C.

(1*R*,5*S*,6*S*,7*R*)-7-*endo*-(Benzyloxy)-6-*exo*-{[(*t*-butyl)dimethylsilyl]oxy}-2,8-dioxabicyclo[3.2.1]octan-3-one ((+)-**17**). A mixture of (+)-**16** (10.0 g, 28.7 mmol), CH_2Cl_2 (250 mL), *m*-chloroperbenzoic acid (80%, *Aldrich*, 6.2 g, 1 equiv.) and $NaHCO_3$ (4.8 g, 2 equiv.) was stirred at 20°C for 15 h (tlc, Et_2O/petroleum ether, R_f (+)-**16**: 0.48, R_f (+)-**17**: 0.38). The soln. was washed with H_2O (100 mL), then with a sat. aq. soln. of $NaHCO_3$ (100 mL). The aq. phases were combined and extracted with CH_2Cl_2 (75 mL, 3 times). The org. extracts were combined, dried ($MgSO_4$) and the solvent was evaporated, giving 10.33 g (98%), colourless oil which was purified by column chromatography (*Lobar* C, Et_2O/petroleum ether 1:2). $[\alpha]^{25}_{589}$ = +108, $[\alpha]^{25}_{578}$ = +112, $[\alpha]^{25}_{546}$ = +128, $[\alpha]^{25}_{436}$ = +220, $[\alpha]^{25}_{365}$ = +355 (c = 1.62, CH_2Cl_2). UV (isooctane) λ_{max}: 207 nm (ε, 8300), 252 (205), 258 (240), 264 (195). IR ($CHCl_3$) ν: 3020, 2955, 2930, 2890, 2860, 1755, 1255, 1200, 1115, 1010, 945, 850, 700 cm^{-1}. ^1H-NMR δ_H: 7.33-7.37 (m, 5H); 5.89 (dd, ^3J = 4.1 Hz, ^4J = 0.9 Hz, H-C(1)); 4.67, 4.43 (2d, ^2J = 11.3 Hz, $-OCH_2C_6H_5$); 4.34 (ddd, ^3J = 7.0 Hz, ^4J = 1.0, 0.9 Hz, H-C(5)); 4.09 (d, ^3J = 1.3 Hz, H-C(6)); 4.05 (ddd, ^3J = 4.1, 1.3 Hz, ^4J = 1.0 Hz, H-C(7)); 3.04 (dd, ^2J = 18.3 Hz, ^3J = 7.0 Hz, H_{exo}-C(4)); 2.54 (d, ^2J = 18.3 Hz, H_{endo}-C(4)); 0.89 (s, 9 H); 0.08 (s, 6H). ^{13}C-NMR δ_C: 165.0 (s, C(3)); 136.5 (s); 128.5, 128.3, 128.1 (3d, ^1J(C,H) = 160 Hz); 100.0 (d, ^1J(C,H) = 183 Hz, C(1)); 89.4 (d, ^1J(C,H) = 150 Hz), 80.7 (d, ^1J(C,H) = 159 Hz), 80.3 (d, ^1J(C,H) = 148 Hz, C(5), C(6), C(7)); 72.4 (t, ^1J(C,H) = 143 Hz, $-OCH_2C_6H_5$); 35.5 (t, ^1J(C,H) = 131 Hz, C(4)); 25.6 (q, ^1J(C,H) = 125 Hz); 17.9 (s); -4.9, -5.0 (2q, ^1J(C,H) = 119 Hz, Me_2Si). MS (CI, NH_3) m/z: 382 ($M^{+\cdot}$+18, 13), 307 (2), 129 (3), 105 (4), 91 (100), 75 (17). Anal. calc. for $C_{19}H_{28}O_5Si$ (364.51): C 62.61, H 7.74; found: C 62.59, H 7.56.

(1*RS*,5*SR*,6*SR*,7*RS*)-7-*endo*-(Benzyloxy)-6-*exo*-{[(*t*-butyl)dimethylsilyl]oxy}-2,8-dioxabicyclo[3.2.1]octan-3-one ((±)-**17**). Same procedure as described for (+)-**17**, starting with (±)-**16**. Colourless crystals recrystallized from pentane, m.p. 61.5-62°C.

(1*R*,4*R*,5*S*,6*S*,7*R*)-7-*endo*-(Benzyloxy)-4-*exo*-methyl-6-*exo*-{[(*t*-butyl)dimethylsilyl]oxy}-2,8-dioxabicyclo[3.2.1]octan-3-one ((+)-**18**). A 1.6M soln. of BuLi in hexane (9.4 mL, 1.1 equiv.) was added to a stirred soln. of $(Me_3Si)_2NH$ (3.7 mL, 1.3 equiv.) in anh. THF (60 mL) cooled to 0°C under Ar atmosphere. After stirring at 0°C for 15 min, the mixture was cooled to -65°C and a soln. of (+)-**17** (5.0 g, 13.7 mmol) in anh. THF (30 mL) cooled to -40°C was added slowly. After stirring at -65°C for 30 min, MeI (15 mL, 17.6 equiv.) was added. After stirring at -65°C for 5 min (tlc, Et_2O/petroleum ether 1:1, R_f (+)-**17**: 0.35, R_f (+)-**18**: 0.55), the mixture was poured into an ice-cold sat. aq. soln. of NH_4Cl (150 mL). The mixture was extracted with CH_2Cl_2 (100 mL, 3 times). The combined extracts were dried ($MgSO_4$) and the solvent evaporated. The residue was immediately filtered through silica gel (AcOEt/petroleum ether 1:1), yielding 4.79 g (92%), colourless crystals, m.p. 57.5-58°C (pentane). $[\alpha]^{25}_{589}$ = +111, $[\alpha]^{25}_{578}$ = +114, $[\alpha]^{25}_{546}$ = +131, $[\alpha]^{25}_{436}$ = +224, $[\alpha]^{25}_{365}$ = +359 (c = 1.27, CH_2Cl_2). UV (isooctane) λ_{max}: 207 nm (ϵ, 8000), 252 (200), 258 (240), 264 (190). IR ($CHCl_3$) ν: 3000, 2950, 2925, 2880, 2860, 1750, 1375, 1250, 1190, 1110, 1000, 945, 865, 835, 695 cm^{-1}. ^1H-NMR δ_H: 7.31-7.38 (m, 5H); 5.83 (dd, ^3J = 3.9 Hz, ^4J = 1.0 Hz, H-C(1)); 4.67, 4.45 (2d, ^2J = 11.3 Hz, -$OCH_2C_6H_5$); 4.07 (d, ^3J = 1.5 Hz, H-C(6)); 4.02 (ddd, ^3J = 3.9, 1.5 Hz, ^4J = 1.0 Hz, H-C(7)); 4.00 (dd, ^4J = 1.0, 1.0 Hz, H-C(5)); 2.60 (q, ^3J = 7.5 Hz, H-C(4)); 1.49 (d, ^3J = 7.5 Hz, -CH_3); 0.89 (s, 9H); 0.08 (s, Me_2Si). ^{13}C-NMR δ_C: 169.1 (s, C(3)); 136.5 (s); 128.2, 128.0, 127.8 (3d, ^1J(C,H) = 162 Hz); 99.8 (d, ^1J(C,H) = 182 Hz, C(1)); 89.0 (d, ^1J(C,H) = 150 Hz), 86.5 (d, ^1J(C,H) = 159 Hz), 79.8 (d, ^1J(C,H) = 149 Hz, C(5), C(6), C(7)); 72.1 (t, ^1J(C,H) = 143 Hz, -$OCH_2C_6H_5$); 41.1 (t, ^1J(C,H) = 132 Hz, C(4)); 25.4 (q, ^1J(C,H) = 126 Hz); 18.2 (q, ^1J(C,H) = 130 Hz); 17.7 (s); -5.1, -5.2 (2q, ^1J(C,H) = 118 Hz). MS (CI, NH_3) m/z: 396 ($M^{+\cdot}$+18, 5), 361 (4), 321 (3), 247 (3), 185 (3), 157 (3), 129 (2), 91 (100), 73 (10). Anal. calc. for $C_{20}H_{30}O_5Si$ (378.55): C 63.46, H 7.99; found: C 63.48, H 7.95.

(1*RS*,4*RS*,5*SR*,6*SR*,7*RS*)-7-*endo*-(Benzyloxy)-4-*exo*-methyl-6-*exo*-{[(*t*-butyl)dimethylsilyl]oxy}-2,8-dioxabicyclo[3.2.1]octan-3-one ((±)-**18**). Same procedure as above, starting with (±)-**17**. Colourless crystals, m.p. 64.5-65°C (pentane).

(1*R*,5*S*,6*S*,7*R*)-7-*endo*-(Benzyloxy)-4,4-dimethyl-6-*exo*-{[(*t*-butyl)dimethylsilyl]oxy}-2,8-dioxabicyclo-[3.2.1]octan-3-one ((+)-**19**). A 1.6M soln. of BuLi in hexane (4.3 mL, 1.3 equiv.) was added to a stirred soln. of $(Me_3Si)_2NH$ (1.65 mL, 1.5 equiv.) in anh. THF (40 mL) cooled to 0°C under Ar atmosphere. After stirring at 0°C for 15 min, the soln. was cooled to -65°C and a soln. of (+)-**18** (2.0 g, 5.3 mmol) in anh. THF (20 mL) cooled to -40°C was added. The mixture was stirred at -65°C for 30 min and then MeI (6 mL, 18.2 equiv.) was added. The temperature was allowed to reach 5°C in 30 min (tlc, Et_2O/petroleum ether 1:1, R_f (+)-**18**: 0.50, R_f (+)-**19**: 0.60). The soln. was poured into an ice-cold sat. aq. soln. of NH_4Cl (100 mL). The mixture was extracted with CH_2Cl_2 (50 mL, 4 times). The org. extracts were combined, dried ($MgSO_4$) and the solvent was evaporated. The residue was immediately filtered (AcOEt/petroleum 1:1) through silica gel, giving 2.0 g (97%), colourless crystals, m.p. 91-91.5°C (pentane). $[\alpha]^{25}_{589}$ = +104, $[\alpha]^{25}_{578}$ = +108, $[\alpha]^{25}_{546}$ = +124, $[\alpha]^{25}_{436}$ = +212, $[\alpha]^{25}_{365}$ = +339 (c = 2.13, CH_2Cl_2). UV (isooctane) λ_{max}: 207 nm (ϵ, 8050), 252 (190), 258 (220), 264 (180). IR ($CHCl_3$) ν: 3060, 3010, 2955, 2930, 2890, 2860, 1745, 1390, 1255, 1150, 1100, 1015, 865, 835, 695 cm^{-1}. ^1H-NMR δ_H: 7.33-7.37 (m, 5H); 5.80 (dd, ^3J = 3.9 Hz, ^4J = 0.9 Hz, H-C(1)); 4.67 , 4.44 (2d, ^2J = 11.5 Hz, -$OCH_2C_6H_5$); 4.28 (d, ^3J = 1.5 Hz, H-C(6)); 3.99 (ddd, ^3J = 3.9, 1.5 Hz, ^4J = 1.0 Hz, H-C(7)); 3.85 (dd, ^4J = 1.0, 0.9 Hz, H-C(5)); 1.49, 1.28 (2s, 2 Me); 0.89 (s, 9H); 0.09 (s, Me_2Si). ^{13}C-NMR δ_C: 172.8 (s, C(3)); 136.7 (s); 128.4, 128.2, 128.0 (3d, ^1J(C,H) = 162 Hz); 100.3 (d, ^1J(C,H) = 182 Hz, C(1)); 90.4 (d, ^1J(C,H) = 158 Hz), 89.2 (d, ^1J(C,H) = 150 Hz), 76.2 (d, ^1J(C,H) = 148 Hz, C(5), C(6), C(7)); 72.2 (t, ^1J(C,H) = 143 Hz, -$OCH_2C_6H_5$); 43.7 (s, C(4)); 27.8 (q, ^1J(C,H) = 130 Hz); 25.6 (q, ^1J(C,H) = 125 Hz); 20.6 (q, ^1J(C,H) = 129 Hz); 17.9 (s); -4.8, -4.9 (2q, ^1J(C,H) = 119 Hz). MS (CI, NH_3) m/z: 410 ($M^{+\cdot}$+18, 10), 393 ($M^{+\cdot}$+1, 1), 375 (6), 335 (8), 199 (7), 171 (4), 91 (100), 73 (11). Anal. calc. for $C_{21}H_{32}O_5Si$ (392.57): C 64.25, H 8.22; found: C 64.14, H 8.11.

(1*RS*,5*SR*,6*SR*,7*RS*)-7-*endo*-(Benzyloxy)-4,4-dimethyl-6-*exo*-{[(*t*-butyl)dimethylsilyl]oxy}-2,8-dioxabicyclo-[3.2.1]octan-3-one ((±)-**19**). Same procedure as described for (+)-**19**, starting with (±)-**18**; colourless crystals, m.p. 87.5-88°C (pentane).

Methyl (methyl 2-*O*-benzyl-5-deoxy-5,5-*C*-dimethyl-3-*O*-[*t*-butyl)dimethylsilyl]-α-L-*arabino*-hexofuranoside)uronate ((-)-**21**). Freshly distilled $SOCl_2$ (1 mL) was added dropwise to a soln. of (+)-**19** (2.3 g, 5.86 mmol) in anh. MeOH (25 mL). After stirring at 20°C for 4 days, $NaHCO_3$ (*ca.* 2 g) was added portionwise. The solvent was evaporated and the residue taken in H_2O (20 mL). The mixture was extracted with CH_2Cl_2 (20 mL, 4 times). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated, yielding 1.935 g of a colourless oil that was dissolved in anh. DMF (10 mL). Imidazole (0.8 g, 2 equiv.) and *t*-$BuMe_2SiCl$ (0.97 g, 1.1 equiv.) were added and the mixture heated to 55°C for 4 days. The mixture was poured into H_2O (30 mL) and extracted with hexane (20 mL, 4 times). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by column chromatography (*Lobar* C, Et_2O/petroleum ether 1:1), giving 2.038 g (79%), colourless oil. $[\alpha]^{25}_{589}$ = -41, $[\alpha]^{25}_{578}$ = -42, $[\alpha]^{25}_{546}$ = -48, $[\alpha]^{25}_{436}$ = -78, $[\alpha]^{25}_{365}$ = +115 (c = 1.22, CH_2Cl_2). UV (isooctane) λ_{max}: 207 nm (ϵ, 8150), 252 (180), 258 (220), 264 (175). IR (film) ν: 3060, 3030, 2950, 2925, 2855, 1735, 1465, 1250, 1140, 1105, 1035, 855, 835, 775 cm^{-1}. ^1H-NMR δ_H: 7.32-7.37 (m, 5H); 4.81 (d, ^3J = 1.1 Hz, H-C(1)); 4.51 (s, -$OCH_2C_6H_5$); 4.12 (d, ^3J = 2.0 Hz, H-C(3)); 4.11 (d, ^4J = 1.0, H-C(4)); 3.78 (ddd, ^3J = 2.0, 1.1 Hz, ^4J = 1.0 Hz, H-C(2)); 3.69 (s, -CO_2CH_3); 3.32 (s, -OCH_3);

1.24, 1.23 (2s, 2 Me); 0.87 (s, 9H); 0.09, 0.07 (2s, Me_2Si). ^{13}C-NMR δ_C: 176.3 (s, -CO_2CH_3); 137.5 (s); 128.3, 127.8, 127.7 (3d, ^1J(C,H) = 160 Hz); 105.5 (d, ^1J(C,H) = 170 Hz, C(1)); 91.5 (d, ^1J(C,H) = 147 Hz), 85.8 (d, ^1J(C,H) = 147 Hz), 77.7 (d, ^1J(C,H) = 149 Hz, C(2), C(3), C(4)); 72.3 (t, ^1J(C,H) = 141 Hz); 54.2 (q, ^1J(C,H) = 143 Hz); 51.8 (q, ^1J(C,H) = 147 Hz); 44.1 (s, C(5)); 25.7 (q, ^1J(C,H) = 126 Hz); 22.5, 19.8 (2q, ^1J(C,H) = 128 Hz); 17.7 (s); -4.3, -5.2 (q, ^1J(C,H) = 119 Hz). MS (CI, NH_3) m/z: 456 ($M^{+\cdot}$+18, 1), 439 ($M^{+\cdot}$+1, 1), 407 (14), 381 (45), 349 (18), 259 (22), 199 (8), 129 (7), 91 (100), 73 (17). Anal. calc. for $C_{23}H_{38}O_6Si$ (438.64): C 62.98, H 8.73, Si 6.40; found: C 63.32, H 8.59, Si 6.60.

Methyl 2-*O*-benzyl-5,7-dideoxy-5,5-dimethyl-3-*O*-[(*t*-butyl)dimethylsilyl]-α-L-*arabino*-heptos-6-ulofuranoside ((-)-**22**). A 1M soln. of $LiCH_2SiMe_3$ (34 mL, 8.3 equiv.) in pentane was added dropwise to a stirred soln. of (-)-**21** (1.793 g, 4.09 mmol) in anh. THF (75 mL) cooled to -60°C. The temperature was allowed to reach -20°C in 30 min MeOH (15 mL) was added *dropwise* and the mixture was stirred at -15°C for 20 min (tlc, Et_2O/petroleum ether 1:1, R_f (-)-**21**: 0.73, revealed as a yellow spot with vanillin, R_f (-)-**22**: 0.73; brown spot with vanillin). The mixture was poured into an ice-cold sat. aq. soln. of NH_4Cl (180 ml) and extracted with CH_2Cl_2 (180 mL, twice). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by column chromatography (*Lobar* C, Et_2O/petroleum ether 1:1) yielding 1.544 g (89%), colourless oil. $[\alpha]^{25}_{589}$ = -48, $[\alpha]^{25}_{578}$ = -51, $[\alpha]^{25}_{546}$ = -57, $[\alpha]^{25}_{436}$ = -91, $[\alpha]^{25}_{365}$ = -134 (c = 1.26, CH_2Cl_2). UV (isooctane) λ_{max}: 207 nm (ϵ, 8050), 252 (206), 258 (250), 264 (204). IR (film) ν: 3060, 3030, 2950, 2925, 2855, 1710, 1465, 1360, 1250, 1105, 1035, 855, 835, 775 cm^{-1}. ^{1}H-NMR δ_H: 7.32-7.37 (m, 5H); 4.79 (dd, ^3J = 1.3 Hz, ^4J = 0.4 Hz, H-C(1)); 4.51 (s, -$OCH_2C_6H_5$); 4.14 (d, ^3J = 7.5 Hz, H-C(4)); 4.03 (ddd, ^3J = 7.5, 3.5 Hz, ^4J = 0.4 Hz, H-C(3)); 3.79 (dd, ^3J = 3.5, 1.3 Hz, H-C(2)); 3.34 (s, -OCH_3); 2.21 (s, -$COCH_3$); 1.18, 1.16 (2s, 2 Me); 0.87 (s, 9H); 0.09, 0.07 (s, Me_2Si). ^{13}C-NMR δ_C: 211.3 (s, -$COCH_3$); 137.5 (s); 128.4, 127.9, 127.8 (3d, ^1J(C,H) = 162 Hz); 106.0 (d, ^1J(C,H) = 171 Hz, C(1)); 91.3 (d, ^1J(C,H) = 149 Hz), 85.5 (d, ^1J(C,H) = 150 Hz), 77.8 (d, ^1J(C,H) = 147 Hz, C(2), C(3), C(4)); 72.4 (t, ^1J(C,H) = 143 Hz); 54.6 (q, ^1J(C,H) = 143 Hz); 49.4 (s, C(5)); 26.1 (q, ^1J(C,H) = 129 Hz); 25.8 (q, ^1J(C,H) = 126 Hz); 21.3, 19.3 (2q, ^1J(C,H) = 129 Hz); 17.8 (s); -4.3, -5.1 (2q, ^1J(C,H) = 119). MS (CI, NH_3) m/z: 440 ($M^{+\cdot}$+18, 27), 423 ($M^{+\cdot}$+1, 5), 393 (11), 392 (38), 391 (100), 365 (14), 333 (11), 259 (6), 243 (16), 157 (6), 129 (5), 108 (12), 91 (69), 73 (9). Anal. calc. for $C_{23}H_{38}O_5Si$ (422.64): C 65.36, H 9.06, Si 6.65; found: C 65.29, H 8.90, Si 6.57.

Methyl 5-*O*-acetyl-2-*O*-benzyl-6-deoxy-5-*C*-methyl-3-*O*-[(*t*-butyl)dimethylsilyl]-α-L-*arabino*-hexofuranoside ((-)-**23**). A mixture of a 2.1M soln. of CF_3CO_3H in CH_2Cl_2 (2.55 mL, 4.5 equiv., prepared from 65% H_2O_2 and $(CF_3CO)_2O$ in CH_2Cl_2, 0°C) and CH_2Cl_2 (10 mL) was added dropwise in 30 min to a vigourously stirred mixture of (-)-**22** (0.5 g, 1.18 mmol), CH_2Cl_2 (15 mL) and Na_2HPO_4 (1.34 g, 8 equiv.). After stirring at 20 °C for 4 h (tlc, CH_2Cl_2/Et_2O/petroleum ether 3:1:8, R_f (-)-**22**: 0.41, revealed on a yellow spot with vanillin, R_f (-)-**23**: 0.38; violet spot with vanillin), a 1M aq. soln. of $NaHSO_3$ (50 mL) was added and the mixture was extracted with CH_2Cl_2 (30 mL, 4 times). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by column chromatography (*Lobar* B, Et_2O/petroleum ether/CH_2Cl_2 1:8:3) yielding 64 mg of (-)-**22** and 310 mg (69%) of (-)-**23**, colourless oil. $[\alpha]^{25}_{589}$ = -42, $[\alpha]^{25}_{578}$ = -43, $[\alpha]^{25}_{546}$ = -49, $[\alpha]^{25}_{436}$ = -77, $[\alpha]^{25}_{365}$ = -111 (c = 1.26, CH_2Cl_2). UV (isooctane) λ_{max}: 207 nm (ϵ, 7950), 252 (180), 258 (220), 264 (173). IR (film) ν: 3060, 2930, 2860, 1735, 1365, 1250, 1110, 1040, 855, 835, 775, 695 cm^{-1}. ^{1}H-NMR δ_H: 7.30-7.38 (m, 5H); 4.89 (dd, ^3J = 1.2 Hz, ^4J = 0.6 Hz, H-C(1)); 4.58, 4.52 (2d, ^2J = 11.0 Hz, -$OCH_2C_6H_5$); 4.19 (ddd, ^3J = 6.8, 3.1 Hz, ^4J = 0.6 Hz, H-C(3)); 3.98 (d, ^3J = 6.8 Hz, H-C(4)); 3.82 (dd, ^3J = 3.1, 1.2 Hz, H-C(2)); 3.37 (s, -OCH_3); 2.01 (s, -$OCOCH_3$); 1.58, 1.53 (2s, 2 Me); 0.88 (s, 9H); 0.09, 0.08 (2s, Me_2Si). ^{13}C-NMR δ_C: 170.2 (s, -$OCOCH_3$); 137.6 (s); 128.3, 127.8, 127.7 (3d, ^1J(C,H) = 161 Hz); 106.0 (d, ^1J(C,H) = 171 Hz, C(1)); 91.3 (d, ^1J(C,H) = 147 Hz), 87.4 (d, ^1J(C,H) = 150 Hz), 77.5 (d, ^1J(C,H) = 147 Hz, C(2), C(3), C(4)); 81.5 (s, C(5)); 72.3 (t, ^1J(C,H) = 141 Hz); 54.5 (q, ^1J(C,H) = 143 Hz); 25.7 (q, ^1J(C,H) = 125 Hz); 22.6 (q, ^1J(C,H) = 127 Hz); 22.4 (q, ^1J(C,H) = 129 Hz); 22.3 (q, ^1J(C,H) = 127 Hz); 17.8 (s); -4.3, -5.1 (2q, ^1J(C,H) = 119 Hz). MS (CI, NH_3) m/z: 456 ($M^{+\cdot}$+18, 2), 439 ($M^{+\cdot}$+1, 10), 407 (8), 379 (76), 364 (9), 347 (32), 321 (7), 289 (6), 277 (8), 273 (16), 215 (25), 199 (43), 129 (27), 117 (24), 91 (100), 73 (18). Anal. calc. for $C_{23}H_{38}O_6Si$ (438.64): C 62.98, H 8.73, Si 6.40; found: C 63.07, H 8.58, Si 6.06.

Methyl 2-*O*-benzyl-6-deoxy-5-*C*-methyl-3-*O*-[(*t*-butyl)dimethylsilyl]-α-L-*arabino*-hexofuranoside ((-)-**24**). A soln. of (-)-**23** (0.60 g, 1.37 mmol) and K_2CO_3 (215 mg, 1.1 equiv.) in anh. MeOH (25 mL) was heated to 60°C for 36 h. After solvent evaporation the residue was filtered through silica gel (Et_2O/petroleum ether 1:1), yielding 487 mg (90%), colourless oil. $[\alpha]^{25}_{589}$ = -44, $[\alpha]^{25}_{578}$ = -46, $[\alpha]^{25}_{546}$ = -52, $[\alpha]^{25}_{436}$ = -84, $[\alpha]^{25}_{365}$ = -122 (c = 1.23, CH_2Cl_2). UV (isooctane) λ_{max}: 207 nm (ϵ, 8100), 252 (175), 258 (215), 264 (170). IR (film) ν: 3480 (broad), 3065, 3035, 2930, 2860, 1465, 1370, 1250, 1110, 1035, 860, 835, 775, 695 cm^{-1}. ^{1}H-NMR δ_H: 7.30-7.37 (m, 5H); 4.87 (dd, ^3J = 1.2 Hz, ^4J = 0.6 Hz, H-C(1)); 4.55 (s, -$OCH_2C_6H_5$); 4.22 (ddd, ^3J = 6.8, 3.2 Hz, ^4J = 0.6 Hz, H-C(3)); 3.84 (dd, ^3J = 3.2, 1.2 Hz, H-C(2)); 3.76 (d, ^3J = 6.8 Hz, H-C(4)); 3.37 (s, -OCH_3); 2.29 (s, -OH); 1.30, 1.24 (2s, 2 Me); 0.88 (s, 9H); 0.12, 0.08 (2s, Me_2Si). ^{13}C-NMR δ_C: 137.5 (s); 128.3, 127.8 (2d, ^1J(C,H) = 161 Hz); 106.2 (d, ^1J(C,H) = 171 Hz, C(1)); 91.2 (d, ^1J(C,H) = 149 Hz), 88.4 (d,

${}^{1}J$(C,H) = 147 Hz), 77.0 (d, ${}^{1}J$(C,H) = 147 Hz, C(2), C(3), C(4)); 72.3 (t, ${}^{1}J$(C,H) = 141 Hz); 70.2 (s, C(5)); 54.4 (q, ${}^{1}J$(C,H) = 143 Hz); 27.3 (q, ${}^{1}J$(C,H) = 127 Hz); 25.7 (q, ${}^{1}J$(C,H) = 125 Hz); 25.0 (q, ${}^{1}J$(C,H) = 127 Hz); 17.7 (s); -4.3, -5.1 (2q, ${}^{1}J$(C,H) = 119 Hz). MS (CI, NH_3) m/z: 414 ($M^{+\cdot}$+18, 20), 397 ($M^{+\cdot}$+1, 2), 379 (28), 365 (37), 347 (41), 307 (21), 289 (15), 215 (25), 199 (20), 129 (24), 91 (100), 73 (17). Anal calc. for $C_{21}H_{36}O_5Si$ (396.60): C 63.60, H 9.15, Si 7.08; found: C 63.48, H 8.87, Si 6.93.

Methyl 6-deoxy-5-*C*-methyl-3-*O*-[(*t*-butyl)dimethylsilyl]-α-L-*arabino*-hexofuranoside ((-)-**25**). A mixture of (-)-**24** (188 mg, 0.47 mmol), THF (3 mL), H_2O (0.6 mL) and 10% Pd on charcoal (230 mg) was degassed and then pressurized with H_2 (1 atm.). After shaking at 20°C for 5 h, the precipitate was filtered off (*Celite*), the soln. dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by column chromatography (*Lobar* B, AcOEt/petroleum ether 1:1), yielding 143 mg (quant.), colourless oil which crystallized slowly, m.p. 67-68°C. $[\alpha]^{25}_{589}$ = -90, $[\alpha]^{25}_{578}$ = -94, $[\alpha]^{25}_{546}$ = -106, $[\alpha]^{25}_{436}$ = -174, $[\alpha]^{25}_{365}$ = -261 (c = 0.80, CH_2Cl_2). UV (isooctane): final absorption, ϵ_{200} = 130. IR (film) ν: 3420 (broad), 2950, 2930, 2860, 1465, 1250, 1110, 1045, 1020, 860, 835, 775 cm^{-1}. ^{1}H-NMR δ_H: 4.81 (d, ${}^{4}J$ = 0.5 Hz, H-C(1)); 4.05 (ddd, ${}^{3}J$ = 4.6, 1.5 Hz, ${}^{4}J$ = 0.5 Hz, H-C(3)); 3.93 (m, H-C(2)); 3.74 (d, ${}^{3}J$ = 4.6 Hz, H-C(4)); 3.36 (s, $-OCH_3$); 3.30 (s, -OH); 2.56 (s, -OH); 1.32, 1.23 (2s, 2 Me); 0.88 (s, 9H); 0.13, 0.10 (2s, Me_2Si). ^{13}C-NMR δ_C: 109.4 (d, ${}^{1}J$(C,H) = 171 Hz, C(1)); 91.2 (d, ${}^{1}J$(C,H) = 149 Hz), 82.1 (d, ${}^{1}J$(C,H) = 153 Hz), 78.6 (d, ${}^{1}J$(C,H) = 147 Hz, C(2), C(3), C(4)); 70.8 (s, C(5)); 54.6 (q, ${}^{1}J$(C,H) = 142 Hz, $-OCH_3$); 27.4 (q, ${}^{1}J$(C,H) = 127 Hz); 25.7 (q, ${}^{1}J$(C,H) = 125 Hz); 25.5 (q, ${}^{1}J$(C,H) = 127 Hz); 17.8 (s); -4.2, -5.0 (2q, ${}^{1}J$(C,H) = 118 Hz). MS (CI, NH_3) m/z: 324 ($M^{+\cdot}$+18, 100), 307 ($M^{+\cdot}$+1, 26), 292 (91), 275 (48), 257 (16), 217 (37), 199 (30), 159 (13), 129 (28), 115 (16), 92 (25), 75 (46). Anal. calc. for $C_{14}H_{30}O_5Si$ (306.48): C 54.87, H 9.87, Si 9.16%; found: C 55.00, H 9.84, Si 9.53.

6-Deoxy-5-*C*-methyl-αβ-L-*arabino*-hexose ((-)-**2**). A mixture of (-)-**25** (100 mg, 0.33 mmol) and 1N H_2SO_4 (2 mL) was heated to 80°C for 2 h. After cooling to 20°C, $BaCO_3$ (*ca.* 550 mg) was added (pH 7-8). The precipitate was filtered off (*Celite*) and the solvent was evaporated. The residue was taken with acetone (20 mL), dried ($MgSO_4$) and the solvent was evaporated giving 54 mg (93%), colourless oil. $[\alpha]^{25}_{589}$ = -12.8, $[\alpha]^{25}_{578}$ = -13.4, $[\alpha]^{25}_{546}$ = -15.1, $[\alpha]^{25}_{436}$ = -24.0, $[\alpha]^{25}_{365}$ = -34.7 (c = 2.6, acetone). ^{1}H-NMR (D_2O, DSS as int. ref., 250 MHz): β-furanose, δ_H: 5.25 (d, ${}^{3}J$ = 4.5 Hz, H-C(1)); 4.09 (dd, ${}^{3}J$ = 7.2, 7.0 Hz, H-C(3)); 4.05 (dd, ${}^{3}J$ = 7.2, 4.5 Hz, H-C(2)); 3.64 (d, ${}^{3}J$ = 7.0 Hz, H-C(4)); α-furanose, δ_H: 5.20 (d, ${}^{3}J$ = 3.1 Hz, H-C(1)); 4.05 (dd, ${}^{3}J$ = 6.2, 4.1 Hz, H-C(3)); 3.98 (dd, ${}^{3}J$ = 4.1, 3.1 Hz, H-C(2)); 3.85 (d, ${}^{3}J$ = 6.2 Hz, H-C(4)); α-pyranose, δ_H: 4.77 (d, ${}^{3}J$ = 8.1 Hz, H-C(1)); 3.93 (d, ${}^{3}J$ = 3.4 Hz, H-C(4)); 3.63 (dd, ${}^{3}J$ = 10.1, 3.4 Hz, H-C(3)); 3.44 (dd, ${}^{3}J$ = 10.1, 8.1 Hz, H-C(2)); and for the methyl signals, δ_H: 1.31, 1.27, 1.26, 1.24, 1.23; ^{13}C-NMR (D_2O, MeOH as int. ref., 62.9 MHz): β-furanose, δ_C: 95.1 (d, ${}^{1}J$(C,H) = 174 Hz, C(1)); 87.4 (d, ${}^{1}J$(C,H) = 147 Hz, C(4)); 77.6 (d, ${}^{1}J$(C,H) = 147 Hz, C(2)); 74.6 (d, ${}^{1}J$(C,H) = 148 Hz, C(3)); 71.6 (s, C(5)); α-furanose, δ_C: 101.3 (d, ${}^{1}J$(C,H) = 173 Hz, C(1)); 89.1 (d, ${}^{1}J$(C,H) = 146 Hz, C(4)); 82.6 (d, ${}^{1}J$(C,H) = 150 Hz, C(2)); 76.5 (d, ${}^{1}J$(C,H) = 149 Hz, C(3)); 71.7 (s, C(5)); α-pyranose, δ_C: 93.3 (d, ${}^{1}J$(C,H) = 162 Hz, C(1)); 76.9 (s, C(5)); 74.7 (d, ${}^{1}J$(C,H) = 147 Hz, C(4)); 72.9 (d, ${}^{1}J$(C,H) = 149 Hz, C(2)); 71.0 (d, ${}^{1}J$(C,H) = 142 Hz, C(3)); and for the methyl signals: 26.1, 25.9, 24.4, 24.0, 22.2 (5q, ${}^{1}J$(C,H) = 126 Hz). The ^{1}H- and ^{13}C-NMR signals attributions were confirmed by a 2D-NMR (^{13}C, ^{1}H correlated, 400 MHz, Bruker AM, 400) spectrum, measured with the programm XHCORRDC.AUR, see ref. 44. MS (CI, NH_3) m/z: 196 ($M^{+\cdot}$+18, 74), 178 ($M^{+\cdot}$, 100), 161 (16), 143 (8), 85 (12), 73 (13).

Racemic (±)-**21**, (±)-**22**, (±)-**23**, (±)-**24**, (±)-**25** and (±)-**2**, all colourless oils, were prepared starting from (±)-**19**, following the same procedures as above given for the optically pure systems.

(1*RS*,4*RS*,5*SR*,6*SR*,7*RS*)-7-*endo*-(Benzyloxy)-4-*exo*-[(benzyloxy)methyl]-4-*endo*-methyl-6-*exo*-{[(*t*-butyl)-dimethylsilyl]oxy}-2,8-dioxabicyclo[3.2.1]octan-3-one ((±)-**26**). A 1.6M soln. of BuLi in hexane (1.65 ml, 2.0 equiv.) was added to a stirred soln. of $(Me_3Si)_2NH$ (0.61 mL, 2.2 equiv.) in anh. THF (10 mL) cooled to 0°C. After stirring at 0°C for 15 min, the mixture was cooled to -65°C and a soln. of (±)-**18** (0.50 g, 1.32 mmol) in anh. THF (5 mL) cooled to -30°C was added slowly. The mixture was stirred at -65°C for 150 min and then [(bromomethoxy)methyl]benzene (1 mL, 9.6 equiv.) was added. The temperature was allowed to reach +10°C in 30 min. The mixture was poured into an ice-cold sat. aq. soln. of NH_4Cl (50 ml) and extracted with CH_2Cl_2 (50 mL, twice). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated. The residue was immediately filtered through silica gel (Et_2O/petroleum ether 1:1) and purified by column chromatography (*Lobar* B, CH_2Cl_2/Et_2O/petroleum ether 3:1:2) yielding 571 mg (87%), colourless crystals, m.p. 45.5-46.5°C. UV (isooctane) λ_{max}: 206 nm (ε, 15300), 252 (380), 258 (400), 264 (320). IR ($CHCl_3$) ν: 3085, 3060, 3030, 2950, 2925, 2855, 1750, 1455, 1355, 1255, 1185, 1100, 1010, 865, 835, 775, 735, 695 cm^{-1}. ^{1}H-NMR δ_H: 7.33-7.43 (m, 10H); 5.84 (dd, ${}^{3}J$ = 3.9 Hz, ${}^{4}J$ = 0.9 Hz, H-C(1)); 4.71, 4.49 (2d, ${}^{2}J$ = 11.5 Hz, $-OCH_2C_6H_5$); 4.65, 4.59 (2d, ${}^{2}J$ = 12.3 Hz, $-OCH_2C_6H_5$); 4.43 (dd, ${}^{4}J$ = 1.3, 0.9 Hz, H-C(5)); 4.35 (d, ${}^{3}J$ = 1.4 Hz, H-C(6)); 4.08 (ddd, ${}^{3}J$ = 3.9, 1.4 Hz, ${}^{4}J$ = 1.3 Hz, H-C(7)); 3.94, 3.52 (2d, ${}^{2}J$ = 8.5 Hz, $-CH_2OBn$); 1.40 (s, $-CH_3$); 0.95 (s, *t*-BuSi); 0.14 (s, Me_2Si). Irradiation of δ_H = 1.40 ppm (Me-C(4-*endo*) led to significant NOE's at δ_H = 4.43

(H-C(5)) and 4.35 (H-C(6)) thus confirming the structure of (±)-**26**. ^{13}C-NMR δ_C: 170.1 (s, C(3)); 137.8, 136.7 (2s), 128.4, 128.3, 128.1, 128.0, 127.6, 127.3 (6d, ^1J(C,H) = 161 Hz); 100.3 (d, ^1J(C,H) = 182 Hz, C(1)); 89.5 (d, ^1J(C,H) = 150 Hz), 85.2 (d, ^1J(C,H) = 160 Hz), 76.5 (d, ^1J(C,H) = 149 Hz, C(5), C(6), C(7)); 73.8 (t, ^1J(C,H) = 146 Hz); 73.4 (t, ^1J(C,H) = 146 Hz); 72.3 (t, ^1J(C,H) = 143 Hz); 49.0 (s, C(4)); 25.6 (q, ^1J(C,H) = 125 Hz); 17.9 (s); 16.7 (q, ^1J(C,H) = 130 Hz); -4.8 (q, ^1J(C,H) = 119 Hz). MS (CI, NH_3) m/z: 516 ($M^{+\cdot}$+18, 28), 499 ($M^{+\cdot}$+1, 8), 243 (17), 181 (29), 91 (100). Anal. calc. for $C_{28}H_{38}O_6Si$ (498.70): C 67.44, H 7.68, Si 5.63; found: C 67.60, H 7.90, Si 5.63.

Methyl {methyl 5-[(benzyloxy)methyl]-5-deoxy-2,3-*O*-isopropylidene-5-methyl-β-L-*allo*-hexofuranosid}-uronate ((+)-**35**). A mixture of (+)-**9** (0.50 g, 1.5 mmol), K_2CO_3 (115 mg, 0.55 equiv.) and anh. MeOH (20 mL) was stirred at 20°C for 2 h. After solvent evaporation, the residue was filtered through silica gel and purified by column chromatography (*Lobar* B, Et_2O/petroleum ether 1:1) giving 509 mg (93%) of a mixture of α- and β-L-*allo*-hexofuranuronate **34**, a colourless oil. **34** (420 mg, 1.14 mmol) was dissolved in CCl_4 (8.5 mL). Trimethylorthoformate (0.9 mL, 1.5 equiv.) and Amberlyst 15 (0.42 g, strongly acidic ion-exchange resin, *Fluka*) were added and the mixture was stirred at 20°C for 24 h. After filtration (paper), the solvent was evaporated. The residue was purified by column chromatography (*Lobar* C, Et_2O/petroleum ether 1:1) giving 0.38 g (87%) of (+)-**35** and 17 mg (4%) of its α-anomer, colourless oils. $[\alpha]^{25}_{589}$ = +41.9, $[\alpha]^{25}_{578}$ = +44.0, $[\alpha]^{25}_{546}$ = +49.5, $[\alpha]^{25}_{436}$ = +81, $[\alpha]^{25}_{365}$ = +123 (c = 0.85, CH_2Cl_2). UV (isooctane) λ_{max}: 206 nm (ε, 8000), 252 (165), 258 (200), 264 (145). IR (film) ν: 3060, 3025, 2980, 2935, 1730, 1450, 1370, 1205, 1155, 1085, 865, 735, 695 cm^{-1}. ^{1}H-NMR δ_H: 7.29-7.35 (m, 5H); 5.15 (dd, ^3J = 6.1, 1.8 Hz, H-C(3)); 4.94 (s, H-C(1)); 4.58, 4.52 (2d, ^2J = 12.2 Hz, -$CH_2OCH_2C_6H_5$); 4.47 (d, ^3J = 1.8 Hz, H-C(4)); 4.46 (d, ^3J = 6.1 Hz, H-C(2)); 3.72, 3.64 (2d, ^2J = 9.0 Hz, -CH_2OBn); 3.68 (s, -CO_2CH_3); 3.30 (s, -OCH_3); 1.50, 1.33, 1.30 (3s, 3 Me). ^{13}C-NMR δ_C: 174.0 (s, -CO_2CH_3); 138.3 (s); 128.1, 127.3 (2d, ^1J(C,H) = 161 Hz); 112.1 (s); 110.4 (d, ^1J(C,H) = 173 Hz, C(1)); 90.4 (d, ^1J(C,H) = 153 Hz), 85.8 (d, ^1J(C,H) = 157 Hz), 81.1 (d, ^1J(C,H) = 159 Hz, C(2), C(3), C(4)); 73.3 (t, ^1J(C,H) = 142 Hz); 72.2 (d, ^1J(C,H) = 145 Hz); 55.4 (q, ^1J(C,H) = 143 Hz); 51.7 (q, ^1J(C,H) = 142 Hz); 50.0 (s, C(5)); 26.7, 25.0 (2q, ^1J(C,H) = 127 Hz); 18.1 (q, ^1J(C,H) = 129 Hz). MS (CI, NH_3) m/z: 398 ($M^{+\cdot}$+18, 35), 381 ($M^{+\cdot}$+1, 3), 366 (10), 349 (67), 333 (21), 315 (3), 291 (8), 273 (8), 173 (8), 91 (100). Anal. calc. for $C_{20}H_{28}O_7$ (380.44): C 63.14, H 7.42; found: C 63.33, H 7.46.

Characteristics of methyl{methyl 5-[benzyloxy)methyl]-5-deoxy-2,3-*O*-isopropylidene-5-methyl-α-L-*allo*-hexofuranosid}uronate. IR (film) ν: 3060, 2980, 2940, 1730, 1450, 1370, 1210, 1135, 1090, 1035, 1020, 860, 735, 695 cm^{-1}. ^{1}H-NMR δ_H: 7.26-7.33 (m, 5H); 4.84 (dd, ^3J = 7.1, 3.6 Hz, H-C(3)); 4.79 (d, ^3J = 4.4 Hz, H-C(1)); 4.56 (dd, ^3J = 7.1, 4.4 Hz, H-C(2)); 4.55, 4.49 (2d, ^2J = 11.2 Hz, -$CH_2OCH_2C_6H_5$); 4.31 (d, ^3J = 3.6 Hz, H-C(4)); 3.70 (s, -CO_2CH_3); 3.67, 3.62 (2d, ^2J = 9.1 Hz, -CH_2OBn); 3.41 (s, -OCH_3); 1.56, 1.34, 1.29 (3s, 3 Me). ^{13}C-NMR δ_C: 174.0 (s, -CO_2CH_3); 138.0 (s), 128.2, 127.4, 127.3 (3d, ^1J(C,H) = 161 Hz); 115.2 (s); 102.1 (d, ^1J(C,H) = 171 Hz, C(1)); 83.6 (d, ^1J(C,H) = 151 Hz), 80.6 (d, ^1J(C,H) = 158 Hz), 80.4 (d, ^1J(C,H) = 159 Hz, C(2), C(3), C(4)); 73.3 (t, ^1J(C,H) = 141 Hz); 72.4 (d, ^1J(C,H) = 144 Hz); 55.3, 51.8 (2q, ^1J(C,H) = 142 Hz); 49.3 (s, C(5)); 25.9, 25.7 (2q, ^1J(C,H) = 127 Hz); 17.2 (q, ^1J(C,H) = 129 Hz). MS (CI, NH_3) m/z: 398 ($M^{+\cdot}$+18, 45), 366 (100), 349 (88), 333 (13), 108 (16), 91 (52).

{Methyl 5-[(benzyloxy)methyl]-5-deoxy-2,3-*O*-isopropylidene-5-methyl-β-L-*allo*-hexofuranosid}uronic acid ((+)-**36**). A mixture of (+)-**35** (415 mg, 1.09 mmol), MeOH (8 mL), THF (2 mL) and 1N aq. KOH (8 mL) was heated to 50°C for 24 h. After acidification until pH=1 with 1N H_2SO_4 (*ca.* 15 mL), the mixture was extracted with Et_2O (20 mL, 3 times). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated to yield 398 mg (quant.), colourless paste. $[\alpha]^{25}_{589}$ = +39.0, $[\alpha]^{25}_{578}$ = +40.7, $[\alpha]^{25}_{546}$ = +45.8, $[\alpha]^{25}_{436}$ = +74.3, $[\alpha]^{25}_{365}$ = +112 (c = 1.62, CH_2Cl_2). IR (film) ν: 3440 (broad), 3060, 3030, 2980, 2935, 1705, 1450, 1375, 1210, 1080, 865, 735, 695 cm^{-1}. ^{1}H-NMR δ_H: 7.27-7.34 (m, 5H); 5.16 (dd, ^3J = 6.2, 1.7 Hz, H-C(3)); 4.97 (s, H-C(1)); 4.53 (s, -$CH_2OCH_2C_6H_5$); 4.50 (d, ^3J = 6.2 Hz, H-C(2)); 4.48 (d, ^3J = 1.7 Hz, H-C(4)); 3.72, 3.64 (2d, ^2J = 9.0 Hz, -CH_2OBn); 3.32 (s, -OCH_3); 1.51, 1.32, 1.31 (3s, 3 Me). ^{13}C-NMR δ_C: 179.8 (s, -CO_2H); 138.2 (s); 128.2, 127.5 (2d, ^1J(C,H) = 161 Hz); 112.3 (s); 110.5 (d, ^1J(C,H) = 174 Hz, C(1)); 90.6 (d, ^1J(C,H) = 153 Hz), 85.7 (d, ^1J(C,H) = 159 Hz), 81.3 (d, ^1J(C,H) = 159 Hz, C(2), C(3), C(4)); 73.4 (t, ^1J(C,H) = 142 Hz); 72.4 (t, ^1J(C,H) = 145 Hz); 55.6 (q, ^1J(C,H) = 142 Hz); 49.9 (s, C(5)); 26.8 (q, ^1J(C,H) = 128 Hz); 25.1 (q, ^1J(C,H) = 127 Hz); 18.3 (q, ^1J(C,H) = 130 Hz). MS (CI, NH_3) m/z: 384 ($M^{+\cdot}$+18, 100), 352 (50), 335 (44), 319 (15), 308 (6), 291 (8), 262 (3), 213 (5), 108 (13), 91 (36). Anal. calc. for $C_{19}H_{26}O_7$ (366.41): C 62.28, H 7.15; found: C 62.28, H 7.08.

{Methyl 5-[(benzyloxy)methyl]-5-deoxy-2,3-*O*-isopropylidene-5-methyl-β-L-*allo*-hexofuranosid}uronoyl azide ((+)-**38**). Ethyl chloroformate (85 μL, 1.09 equiv.) was added to a stirred soln. of (+)-**36** (0.30 g, 0.82 mmol), Et_3N (126 μL, 1.1 equiv.) in acetone (13 mL) cooled to 0°C. After stirring at 0°C for 20 min, the white precipitate (Et_3NHCl) was filtered off and the soln. (containing the mixed anhydride **37**) cooled to -10°C. A soln. of NaN_3 (107 mg, 2 equiv.) in H_2O (0.5 mL) was added *dropwise* (tlc, Et_2O/petroleum ether

1:1, R_f **37**: 0.43, R_f (+)-**38**: 0.69). After stirring at +10°C for 15 min, the solvent was evaporated at 10°C in vacuo and the residue dissolved in CH_2Cl_2 (20 mL). After drying ($MgSO_4$), the soln. was filtered through silica gel and the solvent was evaporated yielding 233 mg (73%), colourless oil. $[\alpha]^{25}_{589}$ = +48, $[\alpha]^{25}_{578}$ = +51, $[\alpha]^{25}_{546}$ = +58, $[\alpha]^{25}_{436}$ = +93, $[\alpha]^{25}_{365}$ = +145 (c = 0.84, CH_2Cl_2). IR (CH_2Cl_2) ν: 3050, 2990, 2930, 2870, 2135, 1705, 1450, 1375, 1200, 1090, 1040, 1005, 860 cm^{-1}. ^{1}H-NMR δ_H: 7.28-7.36 (m, 5H); 5.06 (dd, ^3J = 6.2, 2.1 Hz, H-C(3)); 4.96 (s, H-C(1)); 4.54 (s, $-CH_2OCH_2C_6H_5$); 4.50 (d, ^3J = 6.2 Hz, H-C(2)); 4.45 (d, ^3J = 2.1 Hz, H-C(4)); 3.66, 3.61 (2d, ^2J = 9.2 Hz, $-CH_2OBn$); 3.33 (s, $-OCH_3$); 1.51, 1.32, 1.28 (3s, 3 Me). ^{13}C-NMR δ_C: 181.4 (s, $-CON_3$); 137.9 (s); 128.2, 127.5, 127.4 (3d, ^1J(C,H) = 160 Hz); 112.3 (s); 110.3 (d, ^1J(C,H) = 174 Hz, C(1)); 90.3 (d, ^1J(C,H) = 153 Hz), 85.6, 80.8 (2d, ^1J(C,H) = 159 Hz, C(2), C(3), C(4)); 73.3 (t, ^1J(C,H) = 142 Hz); 72.0 (t, ^1J(C,H) = 146 Hz); 55.6 (q, ^1J(C,H) = 142 Hz); 51.9 (s, C(5)); 26.7, 25.0, 17.5 (3q, ^1J(C,H) = 128 Hz). MS (CI, NH_3) m/z: 409 ($M^{+\cdot}$+18, 66), 381 (12), 360 (13), 334 (10), 242 (8), 108 (36), 91 (100), 85 (11).

Methyl 6-*O*-benzyl-5-deoxy-5-isocyanato-2,3-*O*-isopropylidene-5-methyl-α-D-*talo*-hexofuranoside ((+)-**39**. (+)-**38** (140 mg, 0.36 mmol) was heated in benzene (6 mL) to 80°C for 15 h. The solvent was evaporated yielding 128 mg (quant.), colourless oil. $[\alpha]^{25}_{589}$ = +35.6, $[\alpha]^{25}_{578}$ = +37.0, $[\alpha]^{25}_{546}$ = +41.7, $[\alpha]^{25}_{436}$ = +68.1, $[\alpha]^{25}_{365}$ = +105 (c = 1.27, CH_2Cl_2). UV (isooctane) λ_{max}: 207 nm (ε, 8000), 252 (360), 258 (395), 264 (345). IR (CH_2Cl_2) ν: 3030, 2980, 2935, 2860, 2250, 1450, 1375, 1210, 1110, 1085, 860 cm^{-1}. ^{1}H-NMR δ_H: 7.30-7.38 (m, 5H); 5.02 (s, H-C(1)); 4.85 (dd, ^3J = 6.2, 2.6 Hz, H-C(3)); 4.61 (s, $-CH_2O$, $CH_2C_6H_5$); 4.55 (d, ^3J = 6.2 Hz, H-C(2)); 4.08 (d, ^3J = 2.6 Hz, H-C(4)); 3.57, 3.50 (2d, ^2J = 9.0 Hz, $-CH_2OBn$); 3.36 (s, $-OCH_3$); 1.51, 1.37, 1.34 (3s, 3 Me). ^{13}C-NMR δ_C: 137.7 (s); 128.4, 127.7, 127.6 (3d, ^1J(C,H) = 159 Hz); 125.4 (s, -N=C=O); 112.8 (s); 109.9 (d, ^1J(C,H) = 171 Hz, C(1)); 90.7 (d, ^1J(C,H) = 150 Hz), 85.4 (d, ^1J(C,H) = 161 Hz), 80.6 (d, ^1J(C,H) = 159 Hz, C(2), C(3), C(4)); 74.4 (t, ^1J(C,H) = 144 Hz); 73.5 (t, ^1J(C,H) = 142 Hz); 61.8 (s, C(5)); 55.6 (q, ^1J(C,H) = 142 Hz); 26.8, 25.1 (2q, ^1J(C,H) = 127 Hz); 22.3 (q, ^1J(C,H) = 129 Hz). MS (CI, NH_3) m/z: 381 ($M^{+\cdot}$+18, 100), 364 ($M^{+\cdot}$+1, 31), 316 (5), 242 (5), 173 (7), 136 (8), 108 (15), 91 (63), 77 (10). Anal. calc. for $C_{19}H_{25}NO_6$ (363.41): C 62.80, H 6.93, N 3.85; found: C 62.66, H 6.87, N 3.47.

Methyl 6-*O*-benzyl-5-{[(benzyloxy)carbonyl]amino}-5-deoxy-2,3-*O*-isopropylidene-5-methyl-α-D-*talo*-hexofuranoside ((+)-**40**). Ethyl chloroformate (285 µL, 1.1 equiv.) was added to a soln. of (+)-**36** (1.0 g, 2.73 mmol) and Et_3N (0.42 mL, 1.1 equiv.) in acetone (40 mL) cooled to 0°C. After stirring at 0°C for 20 min, the precipitate was filtered off and the filtrate cooled to -10°C. A soln. of NaN_3 (356 mg, 2 equiv.) in H_2O (1.5 mL) was added dropwise. After stirring at -10°C for 30 min, the solvent was evaporated at 10°C and the residue taken in CH_2Cl_2 (70 mL). After drying ($MgSO_4$), the solvent was evaporated and the residue dissolved in benzene (50 mL) after filtration through silica gel. Benzylic alcohol (1.13 mL, 4.0 equiv.) and Et_3N (0.38 mL, 1.0 equiv.) were added and the mixture heated to 80°C for 2 days. The solvent was evaporated and the residue purified by column chromatography (*Lobar* C, Et_2O/petroleum ether 1:1), giving 924 mg (72%), yellowish oil. $[\alpha]^{25}_{589}$ = +11.9, $[\alpha]^{25}_{578}$ = +12.4, $[\alpha]^{25}_{546}$ = +13.8, $[\alpha]^{25}_{436}$ = +20.8, $[\alpha]^{25}_{365}$ = +27.1 (c = 2.15, CH_2Cl_2). UV (isooctane) λ_{max}: 208 nm (ε, 16400), 252 (660), 258 (725), 264 (625). IR (CH_2Cl_2) ν: 3320, 3030, 2980, 2940, 1725, 1535, 1450, 1375, 1235, 1210, 1100, 1070, 860 cm^{-1}. ^{1}H-NMR δ_H: 7.30-7.37 (m, 10H); 6.12 (s, $-NHCO_2Bn$); 5.09, 5.02 (2d, ^2J = 12.5 Hz, $-OCH_2C_6H_5$); 5.02 (s, H-C(1)); 4.87 (dd, ^3J = 6.2, 2.4 Hz, H-C(3)); 4.56 (s, $-CH_2OCH_2C_6H_5$); 4.53 (d, ^3J = 6.2 Hz, H-C(2)); 4.46 (d, ^3J = 2.4 Hz, H-C(4)); 3.73, 3.50 (2d, ^2J = 8.5 Hz, $-CH_2OBn$); 3.38 (s, $-OCH_3$); 1.59, 1.52, 1.33 (3s, 3 Me). ^{13}C-NMR δ_C: 155.5 (s, $-NHCO_2Bn$); 138.2, 136.7 (2s); 128.3, 128.2, 127.8, 127.6, 127.3 (5d, ^1J(C,H) = 160 Hz); 112.6 (s); 109.0 (d, ^1J(C,H) = 174 Hz, C(1)); 91.3 (d, ^1J(C,H) = 153 Hz), 85.2 (d, ^1J(C,H) = 158 Hz), 80.1 (d, ^1J(C,H) = 157 Hz, C(2), C(3), C(4)); 73.2 (t, ^1J(C,H) = 142 Hz); 72.2 (t, ^1J(C,H) = 145 Hz); 65.9 (t, ^1J(C,H) = 147 Hz); 55.9 (s, C(5)); 55.3 (q, ^1J(C,H) = 143 Hz); 26.6, 25.0, 18.2 (3q, ^1J(C,H) = 126-128 Hz). MS (CI, NH_3) m/z: 472 ($M^{+\cdot}$+1, 77), 440 (92), 350 (36), 338 (18), 298 (17), 91 (100). Anal. calc. for $C_{26}H_{33}NO_7$ (471.56): C 66.23, H 7.05, N 2.97; found: C 66.16, H 7.03, N 3.08.

Methyl 5-amino-5-deoxy-2,3-*O*-isopropylidene-5-methyl-α-D-*talo*-hexofuranoside ((+)-**41**). A mixture of (+)-**40** (0.20 g, 0.42 mmol), THF (5 mL), H_2O (1 mL) and 10% Pd on charcoal (0.4 g) was degassed and then pressurized with H_2 (1 atm.). After shaking for 3 d, the precipitate was filtered off (*Celite*) and the soln. dried ($MgSO_4$). Solvent evaporation yielded 104 mg (quant.), white solid recrystallized from AcOEt/petroleum ether 1:4, m.p. 82.5-83.5°C. $[\alpha]^{25}_{589}$ = +36.9, $[\alpha]^{25}_{578}$ = +38.0, $[\alpha]^{25}_{546}$ = +42.9, $[\alpha]^{25}_{436}$ = +67.1, $[\alpha]^{25}_{365}$ = +94.1 (c = 0.74, CH_2Cl_2). UV (EtOH 95%) λ_{max}: 204 nm (ε, 365), 276 (14). IR (KBr) ν: 3340, 3280, 3160 (broad), 2970, 2950, 2910, 2840, 1590, 1460, 1375, 1210, 1105, 1075, 1050, 985, 865 cm^{-1}. ^{1}H-NMR δ_H: 5.00 (s, H-C(1)); 4.87 (dd, ^3J = 6.2, 2.0 Hz, H-C(3)); 4.54 (d, ^3J = 6.2 Hz, H-C(2)); 4.16 (d, ^3J = 2.0 Hz, H-C(4)); 3.48, 3.38 (2d, ^2J = 10.8 Hz, $-CH_2OH$); 3.41 (s, $-OCH_3$); 1.91 (s, $-NH_2$); 1.49, 1.33, 1.08 (3s, 3 Me). ^{13}C-NMR δ_C: 112.5 (s); 110.4 (d, ^1J(C,H) = 173 Hz, C(1)); 93.2 (d, ^1J(C,H) = 150 Hz), 85.6 (d, ^1J(C,H) = 157 Hz), 80.6 (d, ^1J(C,H) = 156 Hz, C(2), C(3), C(4)); 69.8 (t, ^1J(C,H) = 142 Hz, $-CH_2OH$); 55.8 (q, ^1J(C,H) = 142 Hz, $-OCH_3$); 53.8 (s, C(5)); 26.7, 25.0, 21.5 (3q, ^1J(C,H) = 126 Hz). MS (CI, NH_3) m/z: 248 ($M^{+\cdot}$+1, 100), 216 (18), 74 (16). Anal. calc. for $C_{11}H_{21}NO_5$ (247.29): C 53.43, H 8.56, N 5.66; found: C 53.34, H 8.48, N 5.56.

Methyl 5-amino-5-deoxy-2,3-*O*-isopropylidene-5-methyl-α-DL-*talo*-hexofuranoside ((±)-**41**). Same procedure as described for (+)-**41** derived from (+)-**9** starting with (±)-**9**, colourless crystals, m.p. 86.5-87°C (AcOEt/pentane 1:4). All the racemic synthetic intermediates (±)-**34** - (±)-**40** are oils.

(5-Ammonio-1,5-*N*-anhydro-5-deoxy-5-*C*-methyl-αβ-D-*talo*-hexitol)-1-sulfonate ((+)-**3**). SO_2 was bubbled slowly for 36 h through a soln. of (+)-**41** (91 mg, 0.37 mmol) in H_2O (2 mL) heated to 55°C (the apparatus must be metal free). After the addition of EtOH (3 mL) and cooling to 0°C, the soln. was saturated further with SO_2. The solvent was evaporated and the residue dissolved in EtOH (2 mL). On trituration 50 mg (53%) of a white powder was formed and collected. M.p. 115-116°C (dec.). $[\alpha]^{25}_{589} = +11.6$, $[\alpha]^{25}_{578} = +11.6$, $[\alpha]^{25}_{546} = +12.3$, $[\alpha]^{25}_{436} = +16.1$, $[\alpha]^{25}_{365} = +21.0$ (c = 0.69, H_2O, after 24 h in solution at 25°C). IR (KBr) ν: 3460 (broad), 3390 (broad), 3060, 2960, 1580, 1430, 1220, 1200, 1095, 1055, 1030, 1000, 800 cm^{-1}. ^{1}H-NMR (D_2O, DSS int. ref., 250 MHz): β-anomer δ_H: 4.59 (ddd, ^3J = 3.2, 1.6 Hz, ^4J = 1.2 Hz, H-C(2)); 4.55 (d, ^3J = 1.6 Hz, H-C(1)); 4.08 (dd, ^3J = 3.2, 3.2 Hz, H-C(3)); 3.98 (d, ^2J = 11.8 Hz, H-C(6)); 3.95 (dd, ^3J = 3.2 Hz, ^4J = 1.2 Hz, H-C(4)); 3.93 (d, ^2J = 11.8 Hz, H-C(6)); 1.45 (s, $-CH_3$); α-anomer, δ_H: 4.42 (d, ^2J = 13.1 Hz, H-C(6));. 4.30 (d, ^3J = 10.7 Hz, H-C(1)); 4.22 (dd, ^3J = 3.2, 3.0 Hz, H-C(3)); 4.14 (dd, ^3J = 10.7, 3.0 Hz, H-C(2)); 3.85 (d, ^3J = 3.2 Hz, H-C(4)); 3.67 (d, ^2J = 13.1 Hz, H-C(6)); 1.54 (s, CH_3). ^{13}C-NMR (D_2O, MeOH int. ref., 62.9 MHz): β-anomer, δ_C: 72.2 (d, ^1J(C,H) = 150 Hz), 69.0 (d, ^1J(C,H) = 154 Hz), 68.1 (d, ^1J(C,H) = 149 Hz), 65.6 (d, ^1J(C,H) = 144 Hz, C(1), C(2), C(3), C(4)); 66.3 (s, C(5)); 64.2 (t, ^1J(C,H) = 147 Hz, C(6)); 16.3 (q, ^1J(C,H) = 129 Hz); α-anomer, δ_C: 71.7 (d, ^1J(C,H) = 141 Hz), 71.4 (d, ^1J(C,H) = 150 Hz), 67.7 (d, ^1J(C,H) = 147 Hz), 65.0 (d, ^1J(C,H) = 153 Hz, C(1), C(2), C(3), C(4)); 64.8 (s, C(5)); 59.8 (t, ^1J(C,H) = 145 Hz, C(6)); 20.7 (q, ^1J(C,H) = 129 Hz). MS (CI, NH_3) m/z: 158 (7), 123 (13), 109 (100), 108 (83), 95 (21), 80 (48). Anal. calc. for $C_7H_{15}NO_7S$ (257.26): C 32.68, H 5.88, N 5.44, S 12.46; found: C 32.68, H 6.03, N 5.52, S 12.28.

Racemic (±)-**3** was prepared form (±)-**41**: white powder, m.p. 105-106°C (dec.).

Methyl (methyl 5-deoxy-5,5-dimethyl-2,3-*O*-isopropylidene-β-L-*ribo*-hexofuranosid)uronate ((+)-**43**). A mixture of lactone (+)-**42**[29] (1.156 g, 5.07 mmol), CCl_4 (50 mL), Nafion 117 (1.2 g, *Fluka*) and trimethyl orthoformate (0.64 mL, 1.15 equiv.) was stirred at 20°C for 9 d. After filtration (paper), the solvent was evaporated and the residue purified by column chromatography (*Lobar* C, Et_2O/petroleum ether 1:1) yielding 53 mg (+)-**42** and 925 mg (70%) (+)-**43**, colourless oil. $[\alpha]^{25}_{589} = +59.2$, $[\alpha]^{25}_{578} = +62.5$, $[\alpha]^{25}_{546} = +70.5$, $[\alpha]^{25}_{436} = +114$, $[\alpha]^{25}_{365} = +174$ (c = 0.65, CH_2Cl_2). UV (EtOH 95%) λ_{max}: 204 nm (ε, 160), 215 (sh, 140); UV (isooctane) λ_{max}: 216 nm (ε, 180). IR (film) ν: 2980, 2940, 2840, 1735, 1370, 1240, 1210, 1150, 1110, 1080, 1035, 1010, 865 cm^{-1}. ^{1}H-NMR δ_H: 4.96 (dd, ^3J = 6.1, 2.2 Hz, H-C(3)); 4.91 (s, H-C(1)); 4.47 (d, ^3J = 6.1 Hz, H-C(2)); 4.18 (d, ^3J = 2.2 Hz, H-C(4)); 3.65 (s, $-CO_2CH_3$); 3.28 (s, $-OCH_3$); 1.48, 1.32, 1.24, 1.22 (4s, 4 Me). ^{13}C-NMR δ_C: 175.9, 112.5 (2s); 109.9 (d, ^1J(C,H) = 171 Hz, C(1)); 93.8 (d, ^1J(C,H) = 151 Hz), 85.9 (d, ^1J(C,H) = 157 Hz), 80.6 (d, ^1J(C,H) = 157 Hz, C(2), C(3), C(4)); 55.4 (q, ^1J(C,H) = 143 Hz, $-OCH_3$); 51.9 (q, ^1J(C,H) = 147 Hz, $-CO_2CH_3$); 45.6 (s, C(5)); 26.8, 25.2, 22.5, 22.1 (4q, ^1J(C,H) = 126-128 Hz). MS (CI, NH_3) m/z: 292 ($M^{+\cdot}$+18, 2), 273 (1), 259 (39), 243 (100), 185 (22), 173 (35), 158 (15), 128 (25), 113 (25), 97 (19), 85 (26), 73 (16). Anal. calc. for $C_{13}H_{22}O_6$ (274.17): C 56.95, H 8.09; found: C 57.08, H 7.93.

(Methyl 5-deoxy-5,5-dimethyl-2,3-*O*-isopropylidene-β-L-*ribo*-hexofuranosid)uronic acid ((+)-**44**). A mixture of (+)-**43** (925 mg, 3.37 mmol), THF (15 mL), H_2O (30 mL) and 1N KOH (7.5 mL, 2.2 equiv.) was stirred at 20°C for 36 h. After acidification (pH = 1) with 1N HCl (*ca.* 10 mL), the mixture was extracted with Et_2O (50 mL, 4 times). The combined extracts were dried ($MgSO_4$), the solvent was evaporated yielding 877 mg (quant.), colourless oil. $[\alpha]^{25}_{589} = +49.5$, $[\alpha]^{25}_{578} = +51.3$, $[\alpha]^{25}_{546} = +58.1$, $[\alpha]^{25}_{436} = +95.2$, $[\alpha]^{25}_{365} = +142$ (c = 1.17, CH_2Cl_2). UV (EtOH 95%) λ_{max}: 215 nm (ε, 85). IR (KBr) ν: 3200 (broad), 2980, 2940, 2840, 1735, 1370, 1245, 1135, 1095, 1060, 1010, 860, 815, 645 cm^{-1}. ^{1}H-NMR δ_H: 4.96 (s, H-C(1)); 4.94 (dd, ^3J = 6.15, 2.15 Hz, H-C(3)); 4.52 (d, ^3J = 6.15 Hz, H-C(2)); 4.25 (d, ^3J = 2.15 Hz, H-C(4)); 3.33 (s, $-OCH_3$); 1.51, 1.34, 1.28, 1.26 (4s, 4 Me). ^{13}C-NMR δ_C: 180.9, 112.7 (2s); 109.9 (d, ^1J(C,H) = 171 Hz, C(1)); 93.3 (d, ^1J(C,H) = 151 Hz), 85.8 (d, ^1J(C,H) = 157 Hz), 80.5 (d, ^1J(C,H) = 157 Hz, C(2), C(3), C(4)); 55.5 (q, ^1J(C,H) = 143 Hz, $-OCH_3$); 45.4 (s, C(5)); 26.8, 25.2, 22.2, 21.5 (4q, ^1J(C,H) = 126-128 Hz). MS (CI, NH_3) m/z: 278 ($M^{+\cdot}$+18, 81), 261 ($M^{+\cdot}$+1, 7), 246 (100), 234 (57), 232 (53), 229 (16), 215 (31), 202 (41), 200 (19), 185 (8), 98 (11), 85 (14). Anal. calc. for $C_{12}H_{20}O_6$ (260.29): C 55.37, H 7.74; found: C 55.34, H 7.56.

(Methyl 5-deoxy-5,5-dimethyl-2,3-*O*-isopropylidene-β-DL-*ribo*-hexofuranosid)uronic acid ((±)-**44**). Same procedure as described for (+)-**44**, starting with (±)-**42**. White solid, recrystallized from $CHCl_3$/pentane, m.p. 104.5-105.5°C.

(Methyl 5-deoxy-5,5-dimethyl-2,3-*O*-isopropylidene-β-L-*ribo*-hexofuranosid)uronoyl azide ((±)-**46**). Ethyl chloroformate (80 µL, 1.1 equiv.) was added to a stirred soln. of (+)-**44** (200 mg, 0.77 mmol), Et_3N (120 µL, 1.1 equiv.) in acetone (8 mL) cooled to 0°C. After stirring at 0°C for 20 min, the precipitate was filtered off, the filtrate cooled to 0°C and a soln. of NaN_3 (100 mg, 2 equiv.) in H_2O (0.5 mL) was added. After 10 min at 0°C, the solvent was evaporated at 10°C, the residue taken in CH_2Cl_2 (20 mL) and the soln. dried ($MgSO_4$) and filtered through silica gel. The solvent was evaporated yielding 150 mg (68%), unstable, colourless oil. $[\alpha]^{25}_{589} = +57.4$, $[\alpha]^{25}_{578} = +59.4$, $[\alpha]^{25}_{546} = +67.5$, $[\alpha]^{25}_{436} = +110$, $[\alpha]^{25}_{365} = +163$ (c = 1.24, CH_2Cl_2). IR (film) ν: 2980, 2930, 2835, 2130, 1710, 1465, 1370, 1210, 1180, 1105, 1090, 1040, 1010, 920, 865 cm^{-1}. ^{1}H-NMR δ_H: 4.93 (s, H-C(1)); 4.86 (dd, ^3J = 6.1, 2.5 Hz, H-C(3)); 4.49 (d, ^3J = 6.1 Hz, H-C(2)); 4.20 (d, ^3J = 2.5 Hz, H-C(4)); 3.30 (s, $-OCH_3$); 1.49, 1.31, 1.22, 1.20 (4s, 4 Me). ^{13}C-NMR δ_C: 183.2, 112.7 (2s); 109.7 (d, ^1J(C,H) = 174 Hz, C(1)); 93.3 (d, ^1J(C,H) = 153 Hz), 85.7 (d, ^1J(C,H) = 158 Hz), 80.2 (d, ^1J(C,H) = 158 Hz, C(2), C(3), C(4)); 55.5 (q, ^1J(C,H) = 143 Hz, $-OCH_3$); 47.4 (s, C(5)); 26.7, 25.1, 22.3, 20.9 (4q, ^1J(C,H) = 129 Hz). MS (CI, NH_3) m/z: 303 ($M^{+\cdot}$+18, 100), 271 (30), 259 (42), 234 (31), 232 (34), 228 (44), 215 (22), 202 (30).

Methyl 5,6-dideoxy-5-isocyanato-2,3-*O*-isopropylidene-5-*C*-methyl-β-L-*ribo*-hexofuranoside ((+)-**47**). A soln. of (+)-**46** (772 mg, 2.71 mmol) in benzene (30 mL) was heated to 80°C for 6 h. The solvent was evaporated yielding 696 mg (quant.), colourless oil. $[\alpha]^{25}_{589} = +46.3$, $[\alpha]^{25}_{578} = +48.1$, $[\alpha]^{25}_{546} = +54.6$, $[\alpha]^{25}_{436} = +90$, $[\alpha]^{25}_{365} = +136$ (c = 1.25, CH_2Cl_2). UV (EtOH 95%) λ_{max}: 240 nm (sh, 48), final absorption: $\epsilon_{201} = 235$; UV (isooctane) λ_{max}: 235 nm (sh, 53), final absorption: $\epsilon_{200} = 195$. IR (film) ν: 2980, 2930, 2835, 2250, 1370, 1210, 1155, 1110, 1080, 1040, 860, 735 cm^{-1}. ^{1}H-NMR δ_H: 5.29 (s, H-C(1)); 4.67 (dd, ^3J = 6.2, 2.8 Hz, H-C(3)); 4.53 (d, ^3J = 6.2 Hz, H-C(2)); 3.91 (d, ^3J = 2.8 Hz, H-C(4)); 3.40 (s, $-OCH_3$); 1.48, 1.40, 1.32, 1.31 (4s, 4 Me). ^{13}C-NMR δ_C: 124.0 (s, -N=C=O); 112.9 (s); 109.5 (d, ^1J(C,H) = 174 Hz, C(1)); 93.5 (d, ^1J(C,H) = 152 Hz), 85.6 (d, ^1J(C,H) = 158 Hz), 80.6 (d, ^1J(C,H) = 158 Hz, C(2), C(3), C(4)); 58.9 (s, C(5)); 55.5 (q, ^1J(C,H) = 143 Hz, $-OCH_3$); 27.3, 26.8, 26.4, 25.1 (4q, ^1J(C,H) = 127 Hz). MS (CI, NH_3) m/z: 275 ($M^{+\cdot}$+18, 99), 258 ($M^{+\cdot}$+1, 60), 243 (100), 226 (11), 215 (7), 179 (18), 158 (12), 91 (15), 74 (11). Anal. calc. for $C_{12}H_{19}NO_5$ (257.29): C 56.02, H 7.44; found: C 56.10, H 7.68.

Methyl 5-{[(benzyloxy)carbonyl]amino}-5,6-dideoxy-2,3-*O*-isopropylidene-5-*C*-methyl-β-L-*ribo*-hexofuranoside ((+)-**48**). Same procedure as described for (+)-**46** and (+)-**47** starting with 1.00 g (3.84 mmol) of (+)-**46**. The crude azide (+)-**50** (1.04 g) was dissolved in benzene (60 mL). Et_3N (535 µL, 1 equiv.) and benzyl alcohol (1.6 mL, 4 equiv.) were added and the mixture heated to 80°C for 2 days. The solvent was evaporated and the residue purified by column chromatography (*Lobar* C, Et_2O/petroleum ether 1:1) yielding 1.247 g (89%), white solid recrystallized from AcOEt/petroleum ether 1:5, m.p. 55.5-56°C. $[\alpha]^{25}_{589} = +17.9$, $[\alpha]^{25}_{578} = +18.2$, $[\alpha]^{25}_{546} = +20.4$, $[\alpha]^{25}_{436} = +31.1$, $[\alpha]^{25}_{365} = +40.7$ (c = 1.64, CH_2Cl_2). UV (EtOH 95%) λ_{max}: 208 nm (ε, 7980), 252 (150), 257 (195), 263 (160), 267 (100). UV (isooctane) λ_{max}: 207 (ε, 8200), 252 (160), 258 (195), 264 (155). IR (film) ν: 3320, 3060, 3030, 2980, 2935, 2835, 1730, 1530, 1455, 1380, 1370, 1245, 1210, 1155, 1095, 1070, 860, 740, 695 cm^{-1}. ^{1}H-NMR δ_H: 7.29-7.36 (m, 5H); 6.03 (s, $-N\mathit{H}CO_2Bn$); 5.10, 5.03 (2d, ^2J = 12.5 Hz, $-OC\mathit{H}_2C_6H_5$); 5.01 (s, H-C(1)); 4.80 (dd, ^3J = 6.1, 2.6 Hz, H-C(3)); 4.52 (d, ^3J = 6.1 Hz, H-C(2)); 4.00 (d, ^3J = 2.6 Hz, H-C(4)); 3.40 (s, $-OCH_3$); 1.51 (s, 2 Me); 1.39, 1.32 (2s, Me). ^{13}C-NMR δ_C: 155.6 (s, $-NH\mathit{C}O_2Bn$); 136.9 (s); 128.3 (d, ^1J(C,H) = 162 Hz); 127.7, 127.6 (2d, ^1J(C,H) = 159 Hz); 112.7 (s); 108.5 (d, ^1J(C,H) = 174 Hz, C(1)); 95.9 (d, ^1J(C,H) = 151 Hz), 85.1 (d, ^1J(C,H) = 160 Hz), 79.8 (d, ^1J(C,H) = 158 Hz, C(2), C(3), C(4)); 65.7 (t, ^1J(C,H) = 147 Hz, $-O\mathit{C}H_2C_6H_5$); 55.1 (q, ^1J(C,H) = 143 Hz, $-OCH_3$); 53.4 (s, C(5)); 26.6, 25.0, 24.2, 22.3 (4q, ^1J(C,H) = 126-127 Hz). MS (CI, NH_3) m/z: 383 ($M^{+\cdot}$+18, 40), 366 ($M^{+\cdot}$+1, 100), 334 (60), 275 (25), 258 (11), 243 (21), 232 (43), 192 (31), 148 (9), 108 (8), 91 (20). Anal. calc. for $C_{19}H_{27}NO_6$ (365.43): C 62.45, H 7.45, N 3.83; found: C 62.64, H 7.37, N 4.25.

Methyl 5-amino-5,6-dideoxy-2,3-*O*-isopropylidene-5-*C*-methyl-β-L-*ribo*-hexofuranoside ((+)-**49**). A mixture of (+)-**48** (200 mg, 0.55 mmol), THF (5 mL), H_2O (1 mL) and 10% Pd on charcoal (200 mg) was degassed and then pressurized with H_2 (1 atm). After shaking at 20°C for 4 h, the mixture was filtered (*Celite*), dried ($MgSO_4$) and the solvent evaporated. The residue was purified by column chromatography on silica gel (*Merck* 7734, $MeOH/CH_2Cl_2$ 1:4) yielding 116 mg (91%), colourless oil. $[\alpha]^{25}_{589} = +47.9$, $[\alpha]^{25}_{578} = +48.9$, $[\alpha]^{25}_{546} = +55.4$, $[\alpha]^{25}_{436} = +87$, $[\alpha]^{25}_{365} = +121$ (c = 1.17, CH_2Cl_2). UV (EtOH 95%): final absorption: ϵ_{203} = 280 nm. IR (film) ν: 3370 (broad), 2970, 2930, 2835, 1470, 1380, 1370, 1210, 1155, 1080, 1030, 1005, 865 cm^{-1}. ^{1}H-NMR δ_H: 4.92 (s, H-C(1)); 4.74 (dd, ^3J = 6.2, 2.0 Hz, H-C(3)); 4.49 (d, ^3J = 6.2 Hz, H-C(2)); 3.93 (d, ^3J = 2.0 Hz, H-C(4)); 3.36 (s, $-OCH_3$); 1.62 (s, $-NH_2$); 1.44, 1.27, 1.13, 1.08 (4s, 4 Me). ^{13}C-NMR δ_C: 112.3 (s); 110.2 (d, ^1J(C,H) = 173 Hz, C(1)); 95.6 (d, ^1J(C,H) = 149 Hz), 86.0 (d, ^1J(C,H) = 159 Hz), 80.7 (d, ^1J(C,H) = 158 Hz, C(2), C(3), C(4)); 55.5 (q, ^1J(C,H) = 143 Hz, $-OCH_3$); 50.8 (s, C(5)); 28.9, 26.7, 26.5, 25.0 (4q, ^1J(C,H) = 126-129 Hz). MS (CI, NH_3) m/z: 232 ($M^{+\cdot}$+1, 100), 200 (63), 98 (5). Anal. calc. for $C_{11}H_{21}NO_4$ (231.29): C 57.12, H 9.15, N 6.06; found: C 56.95, H 9.12, N 6.56.

Methyl 5-amino-5,6-dideoxy-2,3-*O*-isopropylidene-5-*C*-methyl-β-DL-*ribo*-hexofuranoside ((±)-**49**) (a) Same procedure as described for (+)-**46**, (+)-**47**, (+)-**48** and (+)-**49**, starting with (±)-**44**. Colourless solid, m.p.

34-35°C. The racemic intermediates (±)-**46**, (±)-**47** and (±)-**48** are all oils. (b) A mixture of amide **50** (100 mg, 0.39 mmol), CH_3CN (2 mL), H_2O (2 mL) and phenyliodosyl bis(trifluoroacetate (340 mg, 2 equiv.) was stirred in the dark at 20°C for 5 h. Water (10 mL) and conc. aq. HCl (1 mL) were added successively. The mixture was extracted with Et_2O (10 mL, twice). The aq. phase was alkalinized (pH = 14) with 20% aq. NaOH and extracted with Et_2O (10 mL, 4 times). The second org. extract was dried ($MgSO_4$) and the solvent evaporated yielding 37 mg (41%) of (±)-**49**.

(Methyl 5-deoxy-5,5-dimethyl-2,3-*O*-isopropylidene-β-DL-*ribo*-hexofuranosid)uronamide ((±)-**50**). Ethyl chloroformate (400 μL, 1.1 equiv.) was added to a stirred soln. of (±)-**44** (1.00 g, 3.84 mmol) and Et_3N (600 μL, 1.1 equiv.) in acetone (40 mL) cooled to 0°C. After stirring at 0°C for 20 min, the precipitate was filtered off and the solvent was evaporated. The residue (mixed anhydride **45**, *ca.* 1.34 g) was dissolved in CH_2Cl_2 (50 mL). The soln. was cooled to -20°C and gaseous NH_3 was bubbled through it for 10 min. The solvent was evaporated and the residue purified by filtration on silica gel (Et_2O/petroleum ether/MeOH 25:15:4) yielding 915 mg (92%), colourless solid recrystallized from MeOH/pentane 1:5, m.p. 118.5-119°C. UV (EtOH 95%) λ_{max}: 221 nm (sh, 115), final absorption: ϵ_{203} = 415. IR (KBr) ν: 3440, 3340, 3240, 3190, 2980, 2930, 2910, 2840, 1645, 1600, 1475, 1370, 1270, 1245, 1205, 1160, 1100, 1075, 1030, 1005, 950, 855, 815 cm^{-1}. ^1H-NMR (CD_3OD, 250 MHz) δ_H: 4.96 (d, ^3J = 1.0 Hz, H-C(1)); 4.81 (dd, ^3J = 6.3, 2.9 Hz, H-C(3)); 4.51 (dd, ^3J = 6.3, 1.0 Hz, H-C(2)); 4.29 (d, ^3J = 2.9, H-C(4)); 3.41 (s, $-OCH_3$); 1.52, 1.35, 1.23, 1.22 (4s, 4 Me). ^{13}C-NMR (CD_3OD, 62.9 MHz) δ_C: 181.2 (s, $-CONH_2$); 114.1 (s); 110.9 (d, ^1J(C,H) = 173 Hz, C(1)); 93.5 (d, ^1J(C,H) = 151 Hz), 86.8 (d, ^1J(C,H) = 159 Hz), 81.6 (d, ^1J(C,H) = 159 Hz, C(2), C(3), C(4)); 56.0 (q, ^1J(C,H) = 143 Hz, $-OCH_3$); 45.8 (s, C(5)); 27.3, 25.4, 22.5, 21.5 (4q, ^1J(C,H) = 126-128 Hz). MS (CI, NH_3) m/z: 277 ($M^{+\cdot}$+18, 4), 260 ($M^{+\cdot}$+1, 17), 244 (3), 232 (5), 229 (12), 228 (100), 215 (3), 154 (2). Anal calc. for $C_{12}H_{21}NO_5$ (259.31): C 55.58, H 8.16, N 5.40; found: C 55.64, H 8.06, N 5.42.

(5-Ammonio-1,5-*N*-anhydro-5,6-dideoxy-5-*C*-methyl-αβ-L-*ribo*-hexitol)-1-sulfonate ((+)-**4**). SO_2 was bubbled through a soln. of (+)-**49** (106 mg, 0.46 mmol) in H_2O (2 mL) heated to 55°C for 5 days (the apparatus must be metal free). EtOH (3 mL) was added and the soln. cooled to 0°C was saturated with SO_2 (bubbling for 10 min). The solvent was evaporated and the residue taken with EtOH (2 mL) at 0°C. Trituration yielded 68 mg (62%), colourless crystals, m.p. 120°C (dec.). $[\alpha]^{25}_{589}$ = +6.8, $[\alpha]^{25}_{578}$ = +6.7, $[\alpha]^{25}_{546}$ = +7.6, $[\alpha]^{25}_{436}$ = +12.1, $[\alpha]^{25}_{365}$ = +17.6 (c = 0.96, H_2O, after the soln. has stayed at 25°C for 24 h). IR (KBr) ν: 3440 (broad), 3030, 2980, 1600, 1430, 1375, 1230, 1205, 1100, 1055, 620 cm^{-1}. ^1H-NMR (D_2O, DSS int. ref., 250 MHz): α-anomer, δ_H: 4.56 (ddd, ^3J = 3.2, 1.5 Hz, ^4J = 1.0 Hz, H-C(2)); 4.50 (d, ^3J = 1.5 Hz, H-C(1)); 4.10 (dd, ^3J = 3.3, 3.2 Hz, H-C(3)); 3.78 (dd, ^3J = 3.3 Hz, ^4J = 1.0 Hz, H-C(4)); 1.58, 1.45 (2s, 2 Me); β-anomer, δ_H: 4.34 (d, ^3J = 10.6 Hz, H-C(1)); 4.21 (dd, ^3J = 3.3, 3.2 Hz, H-C(3)); 4.12 (dd, ^3J = 10.6, 3.3 Hz, H-C(2)); 3.67 (d, ^3J = 3.2 Hz, H-C(4)); 1.51, 1.49 (2s, 2 Me). ^{13}C-NMR (D_2O, MeOH int. ref., 62.9 MHz): α-anomer, δ_C: 74.6 (d, ^1J(C,H) = 150 Hz), 68.4 (d, ^1J(C,H) = 154 Hz), 68.0 (d, ^1J(C,H) = 147 Hz), 65.7 (d, ^1J(C,H) = 141 Hz, C(1), C(2), C(3), C(4)); 63.7 (s, C(5)); 23.7, 20.6 (2q, ^1J(C,H) = 126 Hz); β-anomer, δ_C: 71.6 (d, ^1J(C,H) = 150 Hz), 71.5 (d, ^1J(C,H) = 141 Hz), 67.8 (d, ^1J(C,H) = 144 Hz), 65.1 (d, ^1J(C,H) = 154 Hz, C(1), C(2), C(3), C(4)); 62.1 (s, C(5)); 25.7, 18.5 (2q, ^1J(C,H) = 126 Hz). MS (CI, NH_3) m/z: 160 (20), 144 (48), 142 (100), 126 (72), 124 (46), 110 (16), 96 (37), 88 (14). Anal. calc. for $C_7H_{15}NO_6S$ (241.26): C 34.85, H 6.27, N 5.87, S 13.23; found: C 34.69, H 6.20, N 6.03, S 13.40.

(5-Ammonio-1,5-*N*-anhydro-5,6-dideoxy-5-*C*-methyl-αβ-DL-*ribo*-hexitol)-1-sulfonate ((±)-**4**). Same procedure as described for (+)-**4**, starting with (±)-**49**. M.p. 120°C (dec.).

References and Notes

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