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TOTAL ASYMMETRIC SYNTHESES OF D-LIVIDOSAMINE AND 2-ACETAMIDO-2,3-DIDEOXY-D-*arabino*-HEXOSE DERIVATIVES.[1]

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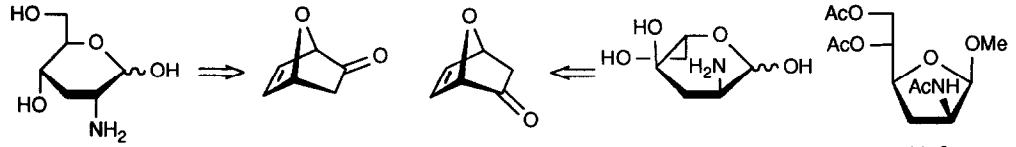
Summary: *The "naked sugar" (+)-(1*R*,4*R*)-7-oxabicyclo[2.2.1]hept-5-en-one ((+)-**2**) has been converted to D-lividosamine ((+)-**1**: 3-deoxy-D-glucosamine) and derivatives via (+)-2-chloro-2,3-dideoxy-5,6-O-isopropylidene-D-*arabino*-hexono-1,4-lactone ((+)-**33**) and (+)-2-azido-2,3-dideoxy-5,6-O-isopropylidene-D-ribo-hexono-1,4-lactone ((+)-**34**) in a highly stereoselective fashion. Similarly, 2-acetamido-2,3-dideoxy-D-arabino-hexose and derivatives were derived from the "naked sugar" (-)-(1*S*,4*S*)-7-oxabicyclo[2.2.1]-hept-5-en-2-one ((-)-**2**) via the double hydroxylation of the C-C double bond in (-)-N-benzyl-N-[(1*R*,2*S*,4*S*)-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-endo-yl]amine ((-)-**40**).*

D-Lividosamine ((+)-**1**: 2-amino-2,3-dideoxy-D-glucose) is present in lividomycin-A and -B isolated form *Streptomyces Lividus*.[2,3] These two aminoglycoside antibiotics have lower toxicity then neomycin.[4] D-Lividosamine is also part of 3'-deoxykanamycin C, an antibiotic extracted from a mutant of *Streptomyces Cremeus Tobramycin*.[5] Umezawa and co-workers[6] have shown that 3'-deoxy-kanamycin A has a better resistance toward enzymatic deactivation than the parent antibiotic. This was also true for streptomycin analogues in which L-glucosamine was exchanged by L-lividosamine ((-)-**1**).[7] These observations have



(+)-**1** (+)-**2** (-)-**2** (-)-**1** (-)-**3**

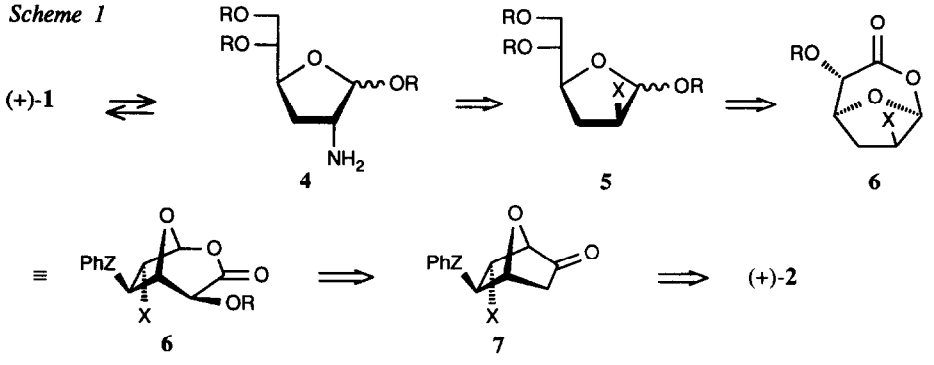
stirred a great interest in the 2-amino-2,3-dideoxyhexoses and their derivatives because their incorporation into aminoglycoside antibiotics make the deactivation process through 3'-hydroxy group phosphorylation impossible.[8,9] Since the first synthesis of D-lividosamine reported by Meyer zu Reckendorf in 1963,[10] several methods starting from D-glucosamine[11-17] have been presented. Other approaches use tri-O-acetyl glucal[18,19] or 1,6-anhydro-β-D-glucose[20] as starting material. In 1984, Jäger and Schohe[21] reported a synthesis of (+)-**1** involving the cycloaddition of a nitrile oxide to 1,2-O-isopropylidene-but-3-en-1,2-diol derived from D-glyceraldehyde (6 steps, 8.7% overall yield.). L-lividosamine was obtained from L-glucosamine,[22,23] a rare carbohydrate that can be prepared from L-arabinose.[23] We wish to report here an alternative approach to the total, asymmetric synthesis of (+)-**1** which can be applied with the same ease to the preparation of (-)-**1**, the starting material being the readily available optically pure "naked sugars" (+)-**2** and (-)-**2**, respectively.[24] Using an approach similar to that developed for the total, asymmetric syntheses of 3- and 4-deoxyhexoses,[25] we have also converted (-)-**2** into 2-acetamido-2,3-dideoxy-D-*arabino*-hexose,

characterized as methyl 2-acetamido-5,6-di-O-acetyl-2,3-dideoxy-β-*arabino*-D-hexofuranoside ((-)-**3**). This rare aminosugar which can be considered as the 2-epimer of N-acetyl D-lividosamine, has been derived in a non-selective fashion from 2-acetamido-5,6-O-isopropylidene-2-deoxy-hexofuranoglucal.[26] It was also present as a minor compound (1:4) in the synthesis of (+)-**1** reported by Jäger and Schohe.[21] To our knowledge there has been no other synthetic approaches to that rare sugar.

Results and discussion

By analogy with our total synthesis of L-daunosamine derived from the "naked sugar" (1*R*,2*S*,4*R*)-2-[(-)-camphanoyloxy]-7-oxabicyclo[2.2.1]hept-5-ene-2-carbonitrile[27] and following the retro-synthetic plan shown in *Scheme 1*, we expected to engender D-lividosamine or a protected derivative via S_N2 type displacement reaction of the chloride or bromide **5** with the azide anion. Halides of type **5** should arise from the corresponding uronolactones **6** which, in turn, should result from the *exo* face stereoselective α-hydroxylation of ketones of type **7**, followed by a Baeyer-Villiger oxidation. Ketones **7** (X=Cl, Br; Z=S, Se) are formed in high yield and complete stereocontrol on adding PhZX electrophic agents to enone (+)-**2** under kinetically-controlled conditions[28] because of the electro-donating ability of the carbonyl moiety.[29]

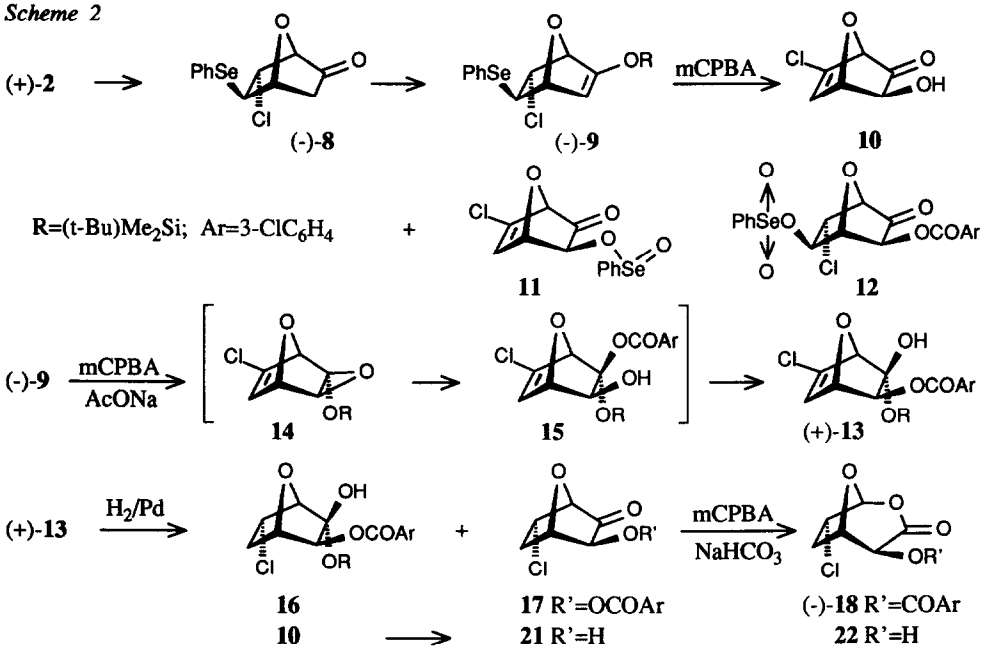
Scheme 1



The product (-)-**8** of addition of benzeneselenyl chloride to (+)-**2** was treated with N-methyl-N-[(tert-butyl)dimethylsilyl]trifluoroacetamide and triethylamine to give the silyl enol ether (-)-**9** (95%). In the presence of unbuffered metachloroperbenzoic acid (mCPBA), or an excess of 90% H_2O_2, (±)-**9** was oxidized into a mixture of compounds containing a maximum of 15% of the desired α-hydroxyketone **10** and small amounts of **11** and **12**. In the presence of 2.5 equivalents of mCPBA and 0.5 equivalent of anhydrous AcONa, (-)-**9** was converted into (+)-**13** (69%). Thus the peracid induces oxidative elimination of the selenide and epoxidation of the enol ether, leading to the hypothetical *exo*-epoxide **14**[30] which probably undergoes acidolysis by meta-chlorobenzoic acid formed during the oxidation with formation of the hemiacylal intermediate **15**.[31] The latter is supposed to undergo an acyl group migration onto the 3-*exo*-hydroxyl group in agreement with results reported for the reactions of peracids with enol ethers and epoxyalkyl ethers.[32] The proposed structure for (+)-**13**, a stable, crystalline compound, is consistent with its spectral data (vicinal coupling constant between H-C(4) and H_{endo}-C(3) being smaller than 0.5 Hz is typical for *endo*-H-C(3)[33]) and its elemental analysis; nevertheless, the configuration of C(2) was not established unambiguously. Catalytic (Pd/C) hydrogenation of (+)-**13** afforded a mixture of the *endo* chlorides **16** and **17** (89%). The high stereoselectively of that reduction can be interpreted in terms of steric hindrance by the

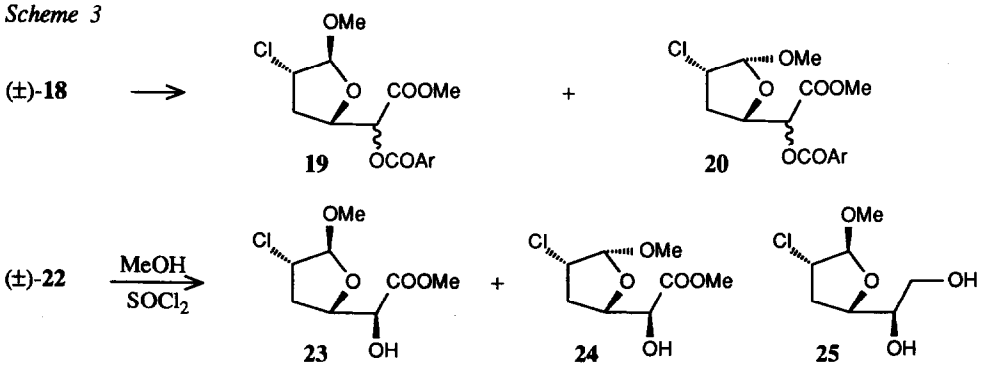
endo (t-Bu)Me_2SiO group at C(2) which retards the hydrogenation of the C(5)=C(6) double bond from its *endo* face. Column chromatography on silica gel allowed one to separate **16** and **17**. Treatment of the crude mixture of **16** + **17** with mCPBA and $NaHCO_3$ provided the lactone (-)-**18** (86%). No trace of the regioisomeric lactone arising from the oxygen atom insertion between C(2) and C(3) of **17** could be detected (^{1}H-NMR) in the reaction mixture.[25]

Scheme 2



Acidic ($MeSO_3H$) methanolysis of (-)-**18**, or its treatment with methyl orthoformiate in CCl_4 in the presence of Nafion-H^+[34] led to mixtures of methyl uronates **19** and **20** that were partially epimerized at C(5). The same deceiving result was obtained under Noyori's conditions ($Me_3SiOSO_2CF_3/Me_3SiOCH_3$).[35] However, when the hydroxylactone **22**, obtained by Baeyer-Villiger oxidation of the hydroxyketone **21** resulting itself from the methanolysis (KOH/MeOH) of **16** + **17** (**21** was also obtained on treatment of **10** with diimide), was treated with MeOH and $SOCl_2$,[36] a 4:1 mixture of **23** and **24** was isolated in 58% yield

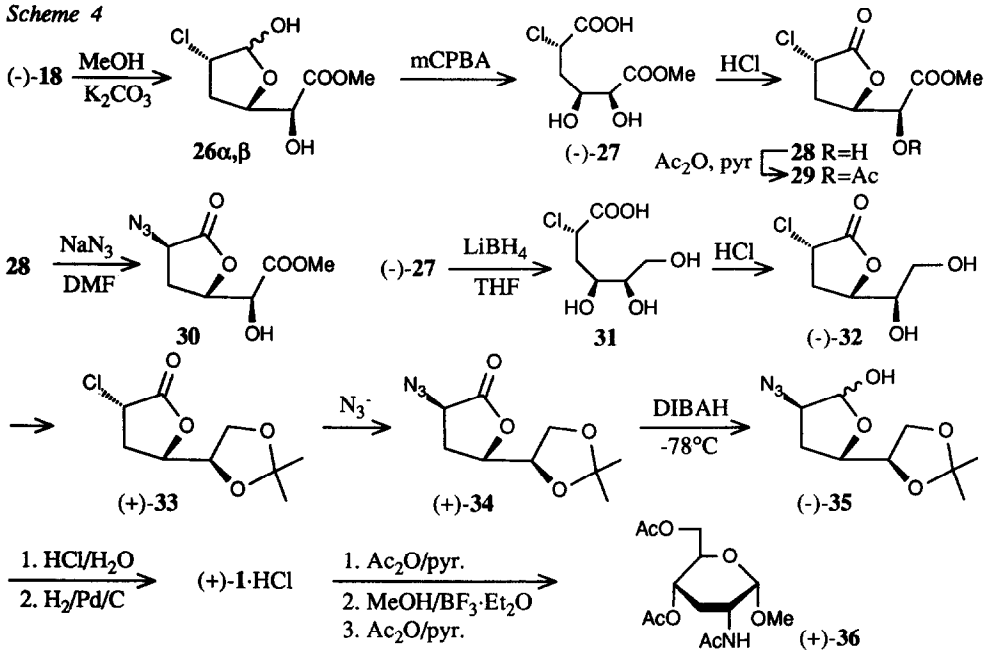
Scheme 3



without epimerization at C(5). Attempts to substitute the chlorides **23** and **24** with NaN_3/DMF (120°C) led to saponification of the methyl uronates, with no formation of the desired azides. Heating **23** and **24** with LiN_3[37] or $(Bu)_4N^+N_3^-$[38] in DMF, DMSO or HMPT (160°C, 7 days) led to the formation of polymers; no trace of the corresponding azides could be seen. Similarly, the diol **25** derived from **23** by reduction with $LiAlH_4$ failed to undergo S_N2 displacement of the chloride under the same conditions.

The reduced reactivity of **23** - **25** toward the azide anion can be attributed to the bulk and dipole of the acetal moiety adjacent to the chloride.[39] We thus changed our synthetic plan and transformed the (furanosid)uronic system (*Scheme 3*) into an aldaric system (*Scheme 4*) with the hope that the chloride α to the carboxylic function would be displaced more readily in a S_N2 fashion.[40] Alkaline (K_2CO_3) methanolysis of the uronolactone (-)-**18** led to a mixture of the furanoses **26**α + **26**β, the oxidation of which (mCPBA) afforded the 6-methyl hydrogen-*arabino*-hexarate derivative (-)-**27** (95%). Treatment of (-)-**27** with aqueous HCl (40°C) and with Ac_2O/pyridine gave the corresponding γ-lactones **28** and **29**, respectively, with yield

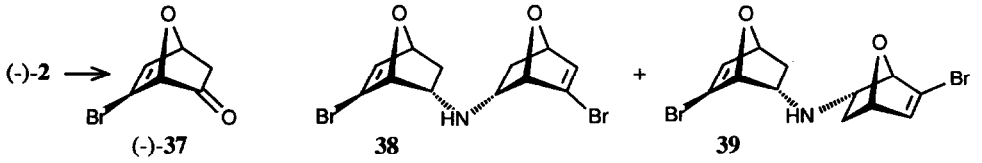
Scheme 4



lower than 60%. Reaction of **28** with NaN_3/DMF furnished the desired azide **30** in moderate yield (26% based on (-)-**27**). For that reason we turn to another reaction sequence which started with the selective reduction of the ester group in (-)-**27** with $LiBH_4$/THF giving the corresponding triol **31**. This compound was not isolated but directly treated with aqueous HCl to give the aldonolactone (-)-**32**. Protection of its diol moiety as an acetonide ($(MeO)_2CMe_2/SnCl_2$/dioxane) provided (+)-**33** (52.5% based on (-)-**27**) the reaction of which with $Bu_4N^+N_3^-$/THF (20°C) furnished the azide (+)-**34**, a known precursor in the synthesis of 4,5,6-trihydroxynorleucine.[41] This compound is also a potential starting material for the synthesis of bulgecinine.[42] Reduction of the lactone (+)-**34** with diisobutylaluminium hydride at -78°C (toluene) led to a 3.5:1 mixture of the α and β-furanoses (-)-**35** (98%). Acidic (HCl) hydrolysis of the acetonide and catalytic (Pd/C) hydrogenation of the azido group provided the chlorhydrate of D-lividosamine ((+)-**1**·HCl) which was

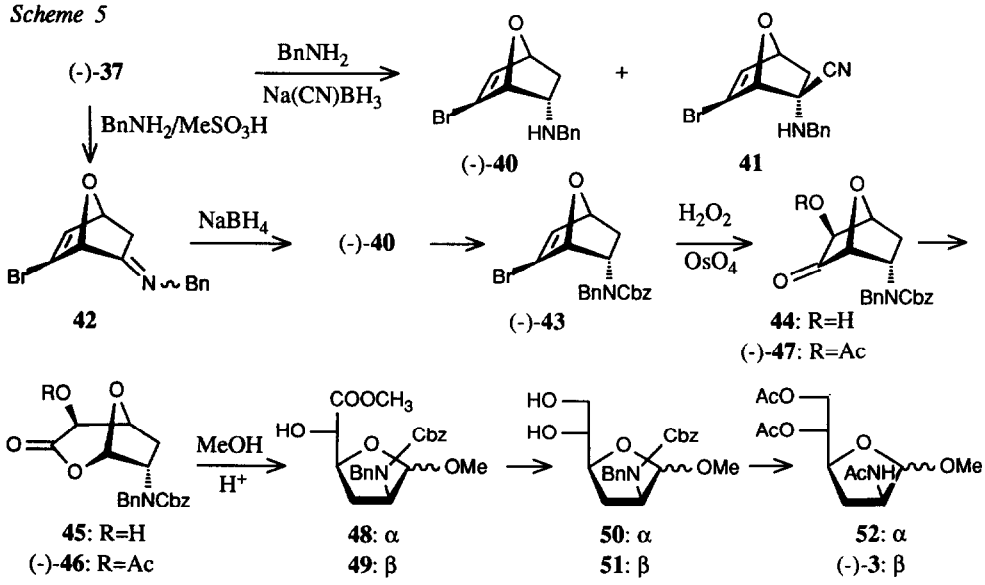
transformed into the peracetylated pyranoside (+)-**36** for complete characterization (see experimental part). The structures of products **16** - **35** were confirmed by their spectral data, elemental analyses and their mode of formation.

Our total synthesis of the 2-epimer of D-lividosamine, starts with the reductive amination of (-)-6-bromobicyclo[2.2.1]hept-5-en-2-one ((-)-**37**).[25] Treatment of (±)-**37** with $NaBH_4/NH_4OAc$ in MeOH, with $Na(CN)BH_3$ or $Li(CN)BH_3$[43] and NH_4OAc in MeOH gave only mixtures of the secondary amines **38** and **39**. No trace of the desired 6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl amine could be observed, even when a large excess of NH_4OAc was used. The reaction of (-)-**37** with benzyl amine and $Na(CN)BH_3$ in absolute MeOH led to a mixture of secondary benzylamines (-)-**40** (49%) and **41** (14%) that could be separated by column chromatography. Compound **41** arises probably from the competitive cyanide anion vs.



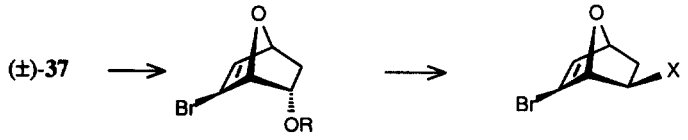
hydride addition to the benzylimine intermediate **42**. We finally found that a two-step procedure implying isolation of **42** followed by its reduction with $NaBH_4$ in methanol gave (-)-**40** with a better overall yield (76%). The secondary amine (-)-**40** was then protected as the benzylcarbamate (-)-**43** (80%) under standard conditions. Oxidation of the bromoalkene moiety of (-)-**43** with H_2O_2/OsO_4 produced the corresponding α-hydroxyketone **44** (88%) the Baeyer-Villiger oxidation of which with $mCPBA/NaHCO_3$ afforded the α-hydroxylactone **45** characterized as the acetate (-)-**46**. The same compound was also obtained by Baeyer-Villiger oxidation of acetate (-)-**47** derived from **44**. Acidic methanolysis (MeOH, $MeSO_3H$) of urono-6,1-lactone **45** yielded a mixture of methyl (methylfuranosid)uronates **48** and **49** contaminated with about 7% of a mixture of the corresponding α- and β-pyranosides. Flash chromatography on silica gel

Scheme 5



allowed one to isolate the mixture of **48** + **49** (76%) which was reduced with $LiBH_4$ in THF to produce a mixture of methyl furanosides **50** + **51** (72%) whose benzyl carbamoyl moieties were intact. These compounds were converted into methyl 2-acetamido-5,6-di-O-acetyl-3-deoxy-α and β-D-hexofuranoside **52** and (-)-**3** by successive catalytic hydrogenolysis (Pd-C/MeOH/AcOH) and acetylation (Ac_2O/pyridine/2-dimethylaminopyridine). Compounds **52** and (-)-**3** in proportion 1:4 were separated and purified by a combination of chromatographic and recrystallization techniques. The β-furanoside (-)-**3** displayed physical and spectral characteristics identical to those already reported for this compound[26] of thus confirming the structures proposed for the synthetic intermediates **43** - **52**.

For reasons that are not clear to us at this moment, the double hydroxylation of the bromoalkene moiety in the 6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl derivatives **55** - **57** with H_2O_2/OsO_4 failed to produce the expected α-hydroxyketones and led instead to the formation of polymers or products of



53 R=H
54 R=SO_2CF_3

55 X=OBn
56 X=N(Bn)H
57 X=N(Bn)Cbz

decomposition. The racemic *exo* benzyloxy derivative **55** was obtained in 59% by reaction of triflate **54** with BnOLi in DMF/HMPT. The triflate **54** was derived from the corresponding alcohol **53** obtained by $NaBH_4$ reduction of (±)-**37**.[25] Similarly, displacement of **54** with benzylamine provided **56** which was protected as the benzylcarbamate **57** (80%) applying standard conditions.

Conclusion

Our work represent the first total, asymmetric syntheses of D-lividosamine ((+)-**1**) and of its 2-epimer derivative (-)-**3** (2-acetamido-2,3-dideoxy-D-*arabino*-hexose) that does not use carbohydrates as starting materials. Our synthesis of (+)-**1** (11% based on (+)-(1*R*,4*R*)-7-oxabicyclo[2.2.1]hept-5-en-2-one ((+)-**2**) requires the isolation of 9 synthetic intermediates) does not compete with some of those starting with D-glucosamine **14** - **17** or tri-O-acetyl-D-glucal.[19] Nevertheless, it can be applied with the same ease to the total, asymmetric synthesis of L-lividosamine, a compound less readily available by the published procedures. Our approach generates a number of homochiral compounds such as (2*R*,4*S*,5*R*)-2-azido-2,3-dideoxy-5,6-O-isopropylidene-D-gluconolactone ((+)-**34**) that are potential synthetic intermediates for other natural products. Compared with the two approaches reported[21,26] for the synthesis of (-)-**3** our method (24% based on (-)-**2**, requires the isolation of 8 intermediates) has the advantage to be highly stereoselective.

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Experimental Part.

General remarks, see ref. 44. Unless indicated otherwise the ^{1}H- and ^{13}C-NMR spectra were measured in $CDCl_3$ with 360 MHz and 90.55 MHz Bruker NMR machines, respectively. Column chromatography (*Lobar* B or C) used silica gel Lichroprep Si60, 40-43 μm. Column flash chromatography (FC) were run on silica gel (Merck 0.040 - 0.063 mm).

(-)-(1*S*,4*R*,5*R*,6*R*)-5-*exo*-Benzeneselenyl-6-*endo*-chloro-7-oxabicyclo[2.2.1]heptan-2-one ((-)-**8**). Obtained by the same procedure as that described for (±)-**8**,[28] starting with (+)-**2**. M.p. 66-67°C. $[\alpha]^{25}_{589}$ = -9.5, $[\alpha]^{25}_{578}$ = -9.5, $[\alpha]^{25}_{546}$ = -10.6, $[\alpha]^{25}_{436}$ = -12.0, $[\alpha]^{25}_{365}$ = +13.8 (*c* = 1.0, CH_2Cl_2).

(-)-(1*S*,4*R*,5*R*,6*R*)-5-*exo*-Benzeneselenyl-2-[(tert-butyl)dimethylsilyloxy]-6-*endo*-chloro-7-oxabicyclo[2.2.1]-hept-2-ene ((-)-**9**). To a soln. of (-)-**8** (0.3 g, 1 mmol) in anh. DMF (dried over 4 Å molecular sieves) Et_3N (0.3 mL, 5 mmol) and N-methyl-N-[(tert-butyl)dimethylsilyl]trifluoroacetamide (MTBSTFA, 1 mL, 4.3 mmol) were added under stirring and Ar atm. at 20°C. After stirring overnight at 40°C, the solvent and volatile reagents were distilled off in vacuo giving 393 mg (95%), yellow oil. $[\alpha]^{25}_{589}$ = -87, $[\alpha]^{25}_{578}$ = -81, $[\alpha]^{25}_{546}$ = -94, $[\alpha]^{25}_{436}$ = -172, $[\alpha]^{25}_{365}$ = -307 (*c* = 1.0, CH_2Cl_2). UV (CH_3CN) λ_{max}: 272 nm (ϵ = 2700); UV (dioxane): 275 (2500), 214 (12500). IR (KBr) ν: 3120, 3060, 3015, 2965, 2940, 2900, 2862, 1631, 1580, 1485, 1350, 1260, 1242, 1212, 1167, 1004, 955, 846, 783, 731, 688, 632 cm^{-1}. ^{1}H-NMR δ_H: 7.59, 7.30 (m, C_6H_5); 5.05 (d, *J* = 2.2 Hz, H-C(3)); 4.82 (dd, *J* = 2.2, 1.3 Hz, H-C(4)); 4.61 (d, *J* = 4.2 Hz, H-C(1)); 4.25 (dd, *J* = 4.2, 2.7 Hz, H-C(6)); 3.25 (d, *J* = 2.7 Hz, H-C(5)); 0.90 (s, t-Bu); 0.18, 0.15 (2s, Me_2Si). ^{13}C-NMR δ_C: 161.0 (s, C(2)); 134.1, 129.3 (2d, ^1J(C,H) = 166 Hz, arom.); 103.2 (d, ^1J(C,H) = 175 Hz, C(3)); 85.6 (d, ^1J(C,H) = 172 Hz, C(1)); 82.0 (d, ^1J(C,H) = 175 Hz, C(4)); 58.7 (d, ^1J(C,H) = 163 Hz, C(6)); 51.0 (d, ^1J(C,H) = 157 Hz, C(5)); 25.8, 25.4 (2q, ^1J(C,H) = 127 Hz, (t-Bu)Me_2Si). MS (70 eV) m/z: 259 (9), 218 (9), 198 (55), 167 (14), 157 (14), 151 (15), 142 (53), 141 (59), 115 (7), 93 (9), 77 (25), 75 (46), 73 (100), 65 (11), 59 (26), 57 (23), 56 (24), 51 (23), 50 (14), 45 (15). Anal. calc. for $C_{18}H_{25}ClO_2SeSi$ (415.9): C 52.05, H 6.02; found: C 52.09, H 6.04.

(±)-(1*RS*,4*SR*,5*SR*,6*SR*)-5-*exo*-Benzeneselenyl-2-[(tert-butyl)dimethylsilyloxy]-6-*endo*-chloro-7-oxabicyclo-[2.2.1]hept-2-ene ((±)-**9**). Obtained by the above procedure from (±)-**8**,[28] (±)-**9** had m.p. 82-83°C, yellow crystals, recrystallized from light petroleum/Et_2O.

(±)-(1*RS*,3*RS*,4*RS*)-6-chloro-3-*exo*-hydroxy-7-oxabicyclo[2.2.1]hept-5-en-2-one (**10**). A soln. of mCPBA (*Fluka*, 85%, 0.2 g, 1.16 mmol) in anh. CH_2Cl_2 (5 mL) was added dropwise to a stirred soln. of (±)-**9** (0.1 g, 0.24 mmol) in anh. CH_2Cl_2 (4 mL) cooled to -15°C under Ar atm. After stirring at 20°C for 2 h, a 40% aq. soln. of $NaHSO_3$ (0.1 mL) was added, followed by the addition of a sat. aq. soln. of $NaHCO_3$ (1 mL). The aq. phase was extracted with CH_2Cl_2. The combined org. extracts were dried ($MgSO_4$), concentrated in vacuo and purified by FC (hexane/CH_2Cl_2), yielding 5.7 mg (15%), colourless oil. IR ($CHCl_3$) ν: 3580, 3125, 3045, 1800, 1593, 1308, 1262, 1249, 1179, 1120, 1052, 1040, 958, 910, 900, 848, 820, 675, 650 cm^{-1}. ^{1}H-NMR δ_H: 6.44 (d, *J* = 2.5 Hz, H-C(5)); 5.26 (dd, *J* = 2.5, 1.0 Hz, H-C(4)); 4.57 (br. s, H-C(1)); 3.92 (s, H-C(3)). MS (70 eV) m/z: 160 (M^+, 5) 117 (28), 115 (89), 104 (32), 102 (100), 87 (33), 85 (12), 76 (16), 74 (11), 73 (22), 61 (13), 60 (12), 51 (83), 50 (53), 49 (17), 48 (13).

(±)-(1*RS*,2*RS*,4*RS*)-5-Chloro-3-oxo-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl benzeneseleninate (**11**) and (1*RS*,2*SR*,4*SR*,5*SR*,6*RS*)-6-*exo*-benzeneselenonoxy-5-*endo*-chloro-3-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl metachlorobenzoate (**12**). 90% H_2O_2 (1 mL, 30 mmol) was added dropwise to a stirred soln of (±)-**9** (620 mg, 2 mmol) in THF (10 mL) cooled to 0°C. After stirring at 20°C for 6 days, H_2O (10 mL) was added and the mixture extracted with CH_2Cl_2 (10 mL, 5 times). The combined extracts were dried ($MgSO_4$) and the solvent distilled in vacuo. The yellow residue was purified by FC (30 g, CH_2Cl_2/hexane 3:2) yielding a first fraction containing 84 mg (15%) of **11** and a second fraction giving 20-50 mg (4-10%) of **12**. Characteristics of **11**: colourless oil. IR ($CHCl_3$) ν: 3062, 2935, 2938, 1765, 1585, 1478, 1439, 1249, 1212, 1173, 1132, 1070, 1035, 940, 900, 888, 815, 632 cm^{-1}. ^{1}H-NMR δ_H: 7.67 (2H), 7.31 (3H, C_6H_5); 6.49 (d, *J* = 2.0, H-C(5)); 5.30 (dd, *J* = 2.0, 1.0, H-C(4)); 4.49 (d, *J* = 1.0, H-C(1)); 3.45 (s, H-C(3)). ^{13}C-NMR δ_C: 202.2 (s, C(2)); 138.3 (s, C(6)); 134.9 (dm, ^1J(C,H) = 163 Hz); 134.7 (dm, ^1J(C,H) = 183 Hz, C(5)); 129.4, 128.6 (2 dm, ^1J(C,H) = 160 Hz, H-C(arom)); 86.0 (dm, C(4)); 84.5 (dm, C(1)); 40.7 (d, C(3)). MS (70 eV) m/z: 200 (5), 198 (29), 172 (5), 170 (30), 157 (14), 129 (3), 117 (9), 115 (18), 105 (11), 102 (11), 93 (5), 89 (10), 87 (15), 77 (34), 73 (11), 63 (8), 51 (11), 50 (37). Characteristics of **12**: colourless crystals, m.p. 131-133°C. ^{1}H-NMR δ_H: 8.03, 7.94, 7.66, 7.58, 7.39 (5m, 10H arom.); 5.08 (s, H-C(3)); 4.81 (s, H-C(4)); 4.63 (dm, *J* = 6.0 Hz, H-C(1)); 4.35 (ddm, *J* = 6.0, 3.0 Hz, H-C(6)); 3.70 (d, *J* = 3.0 Hz, H-C(5)). ^{13}C-NMR δ_C: 199.4 (s, C(2)); 164.5, 134.8 (2s, arom.); 134.6 (dm, ^1J(C,H) = 162 Hz); 133.9 (dm, ^1J(C,H) = 167 Hz); 130.1, 129.7 (2dm, ^1J(C,H) = 165 Hz); 128.8, 128.2 (2dm, ^1J(C,H) = 162 Hz); 86.9, 82.0 (2dm, ^1J(C,H) = 170 Hz, C(4), C(3)); 72.4 (dm, ^1J(C,H) = 155 Hz, C(1)); 54.2 (dm, ^1J(C,H) = 170 Hz, C(6)); 47.9 (dm, ^1J(C,H) = 155 Hz, C(5)). Anal. calc. for $C_{19}H_{14}Cl_2O_7Se$

(504.2): C 45.26, H 2.80; found: C 45.34, H 2.83.

(+)-(1*S*,2*S*,3*R*,4*S*)-5-Chloro-3-*exo*-hydroxy-3-*endo*-[(tert-butyl)dimethylsilyloxy]-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl metachlorobenzoate ((+)-**13**). A mixture of (-)-**9** (10 g, 24 mmol) and AcONa (0.98 g, 12 mmol) was dried under vacuum (10^{-3} Torr) for 30 min. and storred under Ar atm. The mixture was dissolved in anh. CH_2Cl_2 (200 mL, <0.004% H_2O) and the soln. was cooled to 0°C. A soln. of mCPBA (*Fluka*, 85%, dried under vacuum for 30 min., 12.2 g, 60 mmol) in anh. CH_2Cl_2 (120 mL) was added slowly though a syringe. After stirring for 5 min. at 0°C, the mixture was allowed to warm slowly to 20°C. After stirring for 30 min. at 20°C, the yellow soln. was poured into a 5% aq. soln. of $NaHCO_3$ (500 mL). After the addition of a 40% aq. soln. of $NaHSO_3$ (6 mL) the org. phase was collected and washed with 5% aq. soln. of $NaHCO_3$ containing 0.5% $NaHSO_3$ (300 mL, twice), then with brine (100 mL). The aq. phases were combined and extracted with CH_2Cl_2 (60 mL, twice). The combined org. extracts were dried ($MgSO_4$), the solvent was distilled in vacuo and the residue purified by FC at -25°C (hexane/CH_2Cl_2 3:2) yielding 7.2 g (69%), colourless crystals, m.p. 97-98°C. $[\alpha]^{25}_{589}$ = +111, $[\alpha]^{25}_{578}$ = +117, $[\alpha]^{25}_{546}$ = +134, $[\alpha]^{25}_{436}$ = +250, $[\alpha]^{25}_{365}$ = +451 (*c* = 1.0, CH_2Cl_2). UV (CH_3CN) λ_{max}: 207 (ε 24000), 230 (11500), 282 (1100); UV (dioxane): 212 (13000), 230 (10500), 282 (1100). IR (KBr) ν: 3500, 2912, 1708, 1596, 1570, 1470, 1345, 1292, 1255, 1130, 1002, 862, 834, 743. ^{1}H-NMR ($CDCl_3$ filtered through Na_2CO_3) δ_H: 8.04 (t, 1H, *J* = 1.8, 1.8 Hz), 7.96 (ddd, 1H, *J* = 8.0, 1.8, 1.5 Hz); 7.61 (ddd, 1H, *J* = 8.0, 1.8, 1.5 Hz); 7.44 (t, 1H, *J* = 8.0, 8.0 Hz); 6.29 (d, *J* = 2.2 Hz, H-C(5)); 4.90 (dd, *J* = 2.2, 1.4 Hz, H-C(4)); 4.80 (s, H-C(3)); 4.30 (d, *J* = 1.4 Hz, H-C(1)); 3.69 (s, O-H); 0.88 (t-Bu); 0.18, 0.09 (2s, Me_2Si). ^{13}C-NMR ($CDCl_3$ filtered through Na_2CO_3) δ_C: 164.4 (s); 141.5 (d, ^1J(C,H) = 8.0 Hz, C(5)); 134.9 (s); 133.8 (dm, ^1J(C,H) = 168 Hz); 130.8 (s); 130.0 (d, ^1J(C,H) = 165 Hz); 129.7 (dm, ^1J(C,H) = 180 Hz); 127.8 (dm, ^1J(C,H) = 170 Hz); 126.5 (dd, ^1J(C,H) = 179 Hz, ^3J(C,H) = 5.0 Hz, C(6)); 99.8 (s, C(2)); 87.7, 84.5 (2dm, ^1J(C,H) = 170 Hz, C(4), C(1)); 78.8 (dm, ^1J(C,H) = 164 Hz, C(3)); 25.6 (qm, ^1J(C,H) = 126 Hz, t-Bu); 17.7 (s); -3.1, -3.6 (2q, ^1J(C,H) = 120 Hz, Me_2Si). MS (70 eV) m/z: 375 (11), 373 (19), 330 (9), 328 (26), 309 (29), 307 (20), 294 (10), 292 (7), 279 (13), 277 (10), 270 (9), 252 (11), 235 (12), 233 (12), 219 (16), 217 (34), 215 (21), 213 (60), 198 (32), 197 (10), 196 (100), 189 (24), 173 (8), 169 (10), 159 (8), 158 (22), 156 (58), 141 (24), 139 (71), 113 (8), 111 (23), 75 (100), 57 (23), 56 (22), 51 (18), 50 (16), 47 (13), 45 (17). Anal. calc. for $C_{19}H_{24}Cl_2O_5Si$ (431.4): C 52.90, H 5.61; found: C 52.76, H 5.55.

(±)-(1*RS*,2*RS*,3*SR*,4*SR*)-5-Chloro-3-*exo*-hydroxy-3-*endo*-[(tert-butyl)dimethylsilyloxy]-7-oxabicyclo[2.2.1]-hept-5-en-2-*exo*-yl metachlorobenzoate ((±)-**13**). Prepared by the above procedure from (±)-**9**, (±)-**13** had m.p. 102-103°C.

[(1*S*,2*S*,3*S*,4*S*,5*S*)-5-*endo*-Chloro-3-*exo*-hydroxy-3-*endo*-[(tert-butyl)dimethylsilyloxy]-7-oxabicyclo[2.2.1]-hept-2-*exo*-yl metachlorobenzoate (**16**) and (1*S*,3*S*,4*S*,5*S*)-5-*endo*-chloro-3-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl metachlorobenzoate (**17**). A suspension of (+)-**13** (1.75 g, 4 mmol), Na_2CO_3 (0.2 g) and 10% Pd on charcoal (0.4 g) in EtOAc (60 mL) was shaken under H_2 atm. for 15 h, then filtered through Celite. 10% Pd on charcoal (1.3 g) and Na_2CO_3 (0.2 g) were added to the filtrate which was then pressurized (1 atm.) with H_2 and shaken at 20°C for 24 h. After filtration through Celite, the solvent was distilled in vacuo, yielding 1.58 g of a mixture containing **16** (major), **17** (minor) and (t-Bu)Me_2SiOH. This mixture can be used directly in the next synthetic step. Separation by column chromatography (Lobar, light petroleum/EtOAc 9:1, R_f (**16**) = 0.25, R_f (**17**) = 0.20) gave 1.15 g (66.7%) of **16** and 0.16 g (13.2%) of **17**, both as unstable colourless oils.

(1*RS*,2*RS*,3*RS*,4*RS*,5*RS*)-5-*endo*-Chloro-3-*exo*-hydroxy-3-*endo*-[(tert-butyl)dimethylsilyloxy]-7-oxabicyclo-[2.2.1]hept-5-en-2-*exo*-yl metachlorobenzoate ((±)-**16**). Obtained by the above procedure from (±)-**13**, (±)-**16** could be crystallized from light petroleum/Et_2O, m.p. 134-135°C. IR ($CHCl_3$) ν: 3575, 2950, 2922, 2850, 1720, 1450, 1350, 1268, 1250, 1169, 1137, 1100, 1067, 1030, 982, 900, 858, 837 cm^{-1}. ^{1}H-NMR ($CDCl_3$ filtered through K_2CO_3) δ_H: 8.08 (dm, 2H, *J* = 8.1 Hz); 7.61 (dm, 1H, *J* = 8.0 Hz); 7.46 (dd, 1H, *J* = 8.1, 8.0 Hz); 4.87 (s, H-C(3)); 4.46 (d, *J* = 6.7 Hz, H-C(4)); 4.15 (ddd, *J* = 10.7, 5.7, 5.0 Hz, H-C(6)); 4.09 (d, *J* = 5.0, H-C(1)); 2.67 (ddd, *J* = 13.5, 10.7, 6.7 Hz, H_{exo}-C(5)); 1.86 (dd, *J* = 13.5, 5.7 Hz, H_{endo}-C(5)); 0.92 (s, tBu); 0.17, 0.09 (2s, Me_2Si). ^{13}C-NMR ($CDCl_3$ filtered through K_2CO_3) δ_C: 165.2 (s); 133.7 (d, ^1J(C,H) = 164 Hz); 129.7 (dm, ^1J(C,H) = 178 Hz); 129.2 (s), 128.7 (dm, ^1J(C,H) = 165 Hz); 127.8 (s); 104.5 (s, C(3)); 83.6 (d, ^1J(C,H) = 165 Hz, C(4), C(2)); 82.2 (d, ^1J(C,H) = 168 Hz, C(1)); 50.8 (d, ^1J(C,H) = 161 Hz, C(5)); 36.0 (t, ^1J(C,H) = 140 Hz, C(6)); 25.9 (q, ^1J(C,H) = 126 Hz, t-Bu); 17.9 (s); -2.8, -3.1 (2q, Me_2Si). MS (70 eV) m/z: 341 (4), 179 (8), 106 (7), 105 (100), 93 (5), 81 (8), 77 (48). Anal. calc. for $C_{19}H_{26}Cl_2O_5Si$ (433.4): C 52.66, H 6.05; found: C 52.52, H 5.75.

(1*RS*,2*RS*,4*RS*,5*RS*)-5-*endo*-Chloro-3-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl metachlorobenzoate ((±)-**17**). Obtained by the above procedure form (±)-**13**, (±)-**17** could be crystallized from light petroleum/Et_2O 3:1, m.p. 105-107°C. IR ($CHCl_3$) ν: 1780, 1723, 1448, 1292, 1260, 1108, 1089, 1068, 1021, 987, 950, 700. ^{1}H-NMR δ_H: 8.07 (m, 2H); 7.61 (m, 1H), 7.46 (m, 1H); 5.06 (m, H-C(2)); 4.87 (d, *J* = 6.1 Hz, H-C(1)); 4.57 (d, *J* = 5.3 Hz, H-C(4)); 4.36 (dd, *J* = 10.0, 5.3, 3.0 Hz, H-C(5)); 2.84 (ddd, *J* = 14.0, 10.0, 6.1 Hz, H_{exo}-C(6));

2.09 (dd, J = 14.0, 3.0 Hz, H_{endo}-C(6)).

(-)-(1*S*,4*S*,5*S*,7*S*)-7-*endo*-Chloro-3-oxo-2,8-dioxabicyclo[3.2.1]oct-4-*exo*-yl metachlorobenzoate ((-)-**18**). The crude mixture of **16** + **17** derived from (+)-**13** obtained above (2.16 g, 5 mmol) was dissolved in CH_2Cl_2 (125 mL). Solid $NaHCO_3$ (2.73 g, 32.5 mmol) and mCPBA (5.17 g, 30 mmol) were added and the suspension was stirred at 20°C for 66 h. After the addition of CH_2Cl_2 (100 mL), the soln. was washed with 5% aq. soln. of Na_2CO_3 containing 4% $NaHSO_3$ (50 mL, 3 times), then with brine (50 mL). After drying ($MgSO_4$), the solvent was distilled and the residue purified by FC (150 g, hexane/CH_2Cl_2 2:3) yielding 1.25 g (79%), colourless crystals, m.p. 160-161°C. $[\alpha]^{25}_{589}$ = -57, $[\alpha]^{25}_{578}$ = -59, $[\alpha]^{25}_{546}$ = -69, $[\alpha]^{25}_{436}$ = -126, $[\alpha]^{25}_{365}$ = -224 (c = 1.0, CH_2Cl_2). UV (CH_3CN) λ_{max}: 205 (ϵ = 25000), 232 (10000), 283 (1000); UV (dioxane): 212 (17000), 233 (10000), 284 (1000). IR (KBr) v: 1768, 1729, 1450, 1250, 1215, 1167, 1100, 1000, 908 cm^{-1}. ^{1}H-NMR δ_H: 8.11, 7.98, 7.63, 7.49 (4m, 4H arom.); 5.94 (d, J = 3.8 Hz, H-C(1)); 5.43 (s, H-C(4)); 4.86 (dd, J = 8.4, 2.0 Hz, H-C(5)); 4.40 (ddd, J = 11.0, 5.6, 3.8 Hz, H-C(7)); 3.05 (ddd, J = 14.8, 11.0, 8.4 Hz, H_{exo}-C(6)); 2.01 (ddd, J = 14.8, 5.6, 2.0 Hz, H_{endo}-C(6)). ^{13}C-NMR δ_C: 134.0 (dm, ^1J(C,H) = 170 Hz); 130.0, 128.4 (2dm, ^1J(C,H) = 150 Hz, C arom.); 100.7 (dm, ^1J(C,H) = 190 Hz, C(1)); 78.9 (dm, ^1J(C,H) = 150 Hz, C(4)); 72.9 (dm, ^1J(C,H) = 145 Hz, C(7)); 55.1 (dm, ^1J(C,H) = 160 Hz, C(5)); 33.9 (t, ^1J(C,H) = 140 Hz, C(6)); the quarternary signals for C(3) and ClC_6H_5 were not visible. MS (70 eV) m/z: 316 (0.3), 237 (0.3), 158 (0.3), 156 (0.7), 142 (3), 141 (30), 140 (7), 139 (100), 113 (8), 112 (2), 111 (22), 105 (4), 104 (1), 81 (9), 77 (4), 76 (6), 75 (18). Anal. calc. for $C_{19}H_{10}O_5Cl_2$ (317.1): C 49.24, H 3.18, Cl 22.36; found: C 49.30, H 3.25, Cl 22.28.

(±)-Methyl (methyl 2-chloro-5-O-metachlorobenzoyl-2,3-dideoxy-β-DL-*arabino*- and α-DL-*xylo*-hexofuranosid)uronate (**19**) and (±)-methyl (methyl 2-chloro-5-O-metachlorobenzoyl-2,3-dideoxy-α-DL-*arabino*- and β-DL-*xylo*-hexofuranosid)uronate (**20**). A mixture of Nafion-H$^+$ (5.2 g), CCl_4 (40 mL), (±)-**18** (0.54 g, 1.7 mmol) and $HC(OMe)_3$ (0.37 mL, 3.4 mmol) was stirred at 20°C for 6 days. After filtration through Celite, the solvent was distilled in vacuo. The residue was purified by column chromatography (Lobar, light petroleum/EtOAc 1:9, R_f (**19**) = 0.21, R_f (**20**) = 0.13), yielding 195 mg (31%) of **19** and 126 mg (20%) of **20**. The major isomers are the *arabino* derivatives, the minor the *xylo* derivatives; their proportions varied between 5:1 to 3:2. Characteristics of **19**: colourless crystals, m.p. 89-91°C. IR ($CHCl_3$) v: 3000, 2942, 2823, 1750, 1722, 1570, 1461, 1340, 1290, 1242, 1128, 1096, 1038, 945, 889 cm^{-1}. ^{1}H-NMR (of the *arabino* isomer) δ_H: 8.17, 8.05, 7.57, 7.40 (4m, 4H arom.); 5.59 (d, J = 4.0 Hz, H-C(1)); 5.11 (s, H-C(5)); 4.68 (ddd, J = 5.8, 6.0, 4.0 Hz, H-C(2)); 4.23 (dd, J = 7.5, 2.5 Hz, H-C(4)); 3.81, 3.39 (2s, 2 Me); 2.74 (ddd, J = 15.0, 8.0, 7.5 Hz, H_{syn}-C(3)); 2.41 (ddd, J = 15.0, 6.0, 2.5 Hz, H_{anti}-C(3)). MS (70 eV) m/z: 363 ($M^{+\cdot}$, 0.7), 362 (M^{+}-1, 0.6), 361 (M^{+}-2, 1.3), 333 (1), 332 (2), 331 (2), 330 (3), 302 (1), 194 (3), 172 (1), 171 (7), 170 (9), 147 (3), 146 (2), 142 (3), 141 (24), 140 (8), 139 (89), 138 (2), 137 (22), 136 (5), 135 (96), 133 (2), 115 (3), 113 (23), 112 (8), 111 (100), 105 (77), 99 (70), 77 (71), 76 (32), 75 (100), 74 (14), 71 (91). Anal. calc. for $C_{15}H_{16}O_6Cl_2$ (363.2): C 49.61, H 4.44; found: C 49.68, H 4.49. Characteristics of **20**: colourless oil. ^{1}H-NMR (of the *arabino* isomer) δ_H: 8.15 (m, 2H), 7.61 (m, 1H), 7.50 (m, 1H); 5.39 (d, J = 5.0 Hz, H-C(1)); 4.89 (d, J = 4.2 Hz, H-C(5)); 4.62 (ddd, J = 9.0, 8.5, 5.0 Hz, H-C(2)); 4.18 (ddd, J = 10.0, 9.0, 4.2 Hz, H-C(4)); 3.82, 3.34 (2s, 2 Me); 2.54 (m, H_2C(3)).

(±)-(1*RS*,3*SR*,4*SR*,6*SR*)-6-*endo*-Chloro-3-*exo*-hydroxy-7-oxabicyclo[2.2.1]heptan-2-one (**21**). (A) A mixture of **17** (0.964 g, 2.2 mmol), MeOH (100 mL) and methanolic 0.1N KOH (50 mL, 5 mmol) was stirred at 20°C for 30 min. After the addition of H_2O (20 mL), the soln. was concentrated in vacuo to ca. 20 mL, extracted with EtOAc (100 mL). The org. extract was washed with 5% aq. soln. of $NaHCO_3$ (10 mL, 3 times). The aq. layers were combined and extracted with EtOAc (10 mL, 3 times). The combined org. extracts were washed with 1N HCl (10 mL, twice), then with brine (10 mL). The acidic aq. phases were extracted with EtOAc (10 mL, twice). The combined org. phases were dried $MgSO_4$ and the solvent was distilled in vacuo yielding 500 mg, yellowish oil which was purified by FC (45 g, Et_2O, -25°C), giving 250 mg (69.3%), colourless oil. (B) AcOH (0.9 mL, 15.7 mmol) in anh. dioxane (4 mL) was added dropwise (1 h) to a stirred suspension of (±)-**10** (10 mg, 0.06 mmol) and potassium azodicarboxylate (0.6 g, 3 mmol) in anh. dioxane (5 mL). The precipitate (K_2CO_3) was filtered off and 2N HCl (3 mL) was added and the mixture stirred vigourously for 15 h. The org. layer was washed with sat. aq. soln. of $NaHCO_3$ (3 mL, 3 times) and then with H_2O (3 mL, 3 times). The aq. phases were combined and extracted with $CHCl_3$. The combined org. extracts were dried ($MgSO_4$) and the solvent distilled in vacuo. The residue was purified by FC (3 g, CH_2Cl_2), yielding 8 mg (80%), colourless oil. IR ($CHCl_3$) v: 3500, 2960, 2920, 1700, 1597, 1430, 1405, 1330, 1285, 1260, 1145, 1075, 985 cm^{-1}. ^{1}H-NMR δ_H: 4.82 (d, J = 6.0 Hz, H-C(4)); 4.58 (d, J = 5.5 Hz, H-C(1)); 4.32 (ddd, J = 10.0, 5.5, 3.5 Hz, H-C(6)); 3.93 (s, H-C(3)); 2.83 (ddd, J = 14.5, 10.0, 6.0 Hz, H_{exo}-C(5)); 1.92 (dd, J = 14.5, 3.5 Hz, H_{endo}-C(5)). ^{13}C-NMR δ_C: 205.2 (s, C(2)); 82.9 (d, ^1J(C,H) = 170 Hz, C(1)); 81.0 (d, ^1J(C,H) = 172 Hz, C(4)); 73.2 (d, ^1J(C,H) = 151 Hz, C(3)); 49.9 (d, ^1J(C,H) = 168 Hz, C(6)); 37.2 (t, ^1J(C,H) = 139 Hz, C(5)). Anal. calc. for $C_6H_7ClO_3$ (162.6): C 44.33, H 4.34; found: C 44.34; H 4.39.

(±)-(1*RS*,4*RS*,5*RS*,7*RS*)-7-*endo*-Chloro-4-*exo*-hydroxy-2,8-dioxabicyclo[3.2.1]octan-3-one (**22**). A mixture of **21** (1.35 g, 8.3 mmol), CH_2Cl_2 (225 mL), $NaHCO_3$ (0.2 g) and mCPBA (2.52 g, 12 mmol) was stirred at 20°C for 15 h. The soln. was concentrated in vacuo to ca. 40 mL and purified twice by FC (100 g, Et_2O, R_f (**22**) = 0.31) yielding 783 mg (53%), colourless oil. IR ($CHCl_3$) ν: 3440, 2960, 1750, 1450, 1370, 1200, 1160, 1070, 1005, 950, 853, 820, 792 cm^{-1}. ^{1}H-NMR δ_H: 5.89 (d, J = 3.7 Hz, H-C(1)), 4.81 (ddm, J = 8.0, 2.0 Hz, H-C(5)), 4.37 (ddd, J = 10.5, 5.5, 3.7 Hz, H-C(7)); 4.25 (s, H-C(4)); 3.05 (ddd, J = 14.5, 10.5, 8.0 Hz, H_{exo}-C(6)); 1.85 (ddd, J = 14.5, 5.5, 2.0 Hz, H_{endo}-C(6)). ^{13}C-NMR δ_C: 167.0 (s, C(3)); 100.4 (d, ^1J(C,H) = 190 Hz, C(1)); 79.8 (d, ^1J(C,H) = 162 Hz, C(5)); 72.8 (d, ^1J(C,H) = 151 Hz, C(7)); 55.1 (d, ^1J(C,H) = 160 Hz, C(4)); 33.2 (t, ^1J(C,H) = 132 Hz, C(6)).

Methyl (methyl 2-chloro-2,3-dideoxy-α-DL-*arabino*-hexofuranosid)uronate (**23**) and methyl (methyl 2-chloro-2,3-dideoxy-β-DL-*arabino*-hexofuranosid)uronate (**24**). Freshly distilled $SOCl_2$ (9.46 g, 79.8 mmol) was added dropwise under vigourous stirring to a soln. of **22** (1.42 g, 7.98 mmol) in MeOH (45 mL). The temperature was maintained at 20°C by a water bath. After stirring at 20°C for 10 min. the mixture was poured onto ice (750 g) covered by 5% aq. $NaHCO_3$ soln. The mixture was extracted with CH_2Cl_2 (140 mL, 7 times). The combined org. extracts were dried ($MgSO_4$) and the solvent distilled in vacuo. The residue was purified by column chromatography (Lobar, Et_2O/light petroleum 1:1) yielding 791 mg (43.7%) of **23** and 192 mg (10.6%) of **24**, both colourless oils. Characteristics of **23**: IR ($CHCl_3$) ν: 3540, 2945, 1730, 1438, 1254, 1130, 1096, 1052, 950 cm^{-1}. ^{1}H-NMR δ_H: 5.08 (s, H-C(1)); 4.49 (d, J = 4.0 Hz, H-C(5)); 4.44 (ddd, J = 8.0, 6.2, 4.0 Hz, H-C(4)); 4.23 (dd, J = 7.0, 3.0 Hz, H-C(2)); 3.83, 3.37 (2s, 2 Me); 2.59 (ddd, J = 14.7, 8.0, 7.0 Hz, H_a-C(3)); 2.24 (ddd, J = 14.7, 6.2, 3.0 Hz, H_s-C(3)). ^{13}C-NMR δ_C: 172.2 (s, CO_2Me); 110.1 (d, ^1J(C,H) = 178 Hz, C(1)); 79.1 (d, ^1J(C,H) = 152 Hz, C(5)); 71.3 (d, ^1J(C,H) = 150 Hz, C(4)); 59.3 (dm, ^1J(C,H) = 160 Hz, C(2)); 54.9, 52.5 (2q, ^1J(C,H) = 147 Hz, 2 Me); 34.2 (t, ^1J(C,H) = 135 Hz, C(3)). Characteristics of **24**: ^{1}H-NMR δ_H: 4.87 (d, J = 4.0 Hz, H-C(1)); 4.43 (ddd, J = 9.0, 7.4, 4.0 Hz, H-C(2)); 4.34 (d, J = 4.5 Hz, H-C(5)); 4.14 (ddd, J = 11.2, 8.8, 4.5 Hz, H-C(4)); 3.83, 3.51 (2s, 2 Me); 2.40 (dd, J = 8.8, 7.4 Hz, H_s-C(3)); 2.39 (dd, J = 11.2, 9.0 Hz, H_a-C(3)). ^{13}C-NMR δ_C: 172.2 (s), 99.9 (d, ^1J(C,H) = 174 Hz, C(1)); 79.1 (d, ^1J(C,H) = 152 Hz, C(5)); 72.0 (d, ^1J(C,H) = 150 Hz, C(4)); 62.8 (dm, ^1J(C,H) = 160 Hz, C(2)); 55.2, 52.6 (2q, ^1J(C,H) = 147 Hz); 33.8 (t, ^1J(C,H) = 135 Hz, C(3)).

(±)-Methyl 2-chloro-2,3-dideoxy-α-DL-*arabino*-hexofuranoside (**25**). A soln. of **23** (50 mg, 0.23 mmol) in anh. THF (1.2 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (18 mg, 0.46 mmol) in anh. THF (1.2 mL) cooled to -78°C. After stirring at -78°C for 20 min., EtOAc (138 μL) was added and the mixture was allowed to warm slowly to 20°C. After stirring at 20°C for 1 h, H_2O (170 μL) was added. At the end of H_2 evolution, the mixture was filtered through Celite (150 mg, THF) and the solvent distilled in vacuo. The residue was dissolved in EtOAc (2 mL) and purified by FC (1.5 g, Et_2O, R_f (**25**) = 0.29) yielding 12.5 mg (27%), colourless oil. ^{1}H-NMR δ_H: 5.04 (s, H-C(1)); 4.38 (dd, J = 7.0, 2.6 Hz, H-C(2)); 4.19 (ddd, J = 8.0, 5.8, 5.5 Hz, H-C(4)); 3.94 (ddd, J = 6.0, 5.5, 4.0 Hz, H-C(5)); 3.80 (dd, J = 11.5, 4.0 Hz, H-C(6)); 3.69 (dd, J = 11.0, 5.5 Hz, H'-C(6)); 3.37 (s, MeO); 3.64 (ddd, J = 15.0, 8.0, 7.0 Hz, H_a-C(3)); 3.24 (ddd, J = 15.0, 5.8, 2.6 Hz, H_s-C(3)).

(-)-6-Methyl hydrogen 2-chloro-2,3-dideoxy-D-*arabino*-hexarate ((-)-**27**). A soln. of K_2CO_3 (42 mg, 0.3 mmol, dried in a flame) in anh. MeOH (15 mL) was added to a soln. of (-)-**18** (1 g, 3.15 mmol) in anh. MeOH (60 mL) under Ar atm. After stirring at 20°C for 90 min, a soln. of mCPBA (2.58 g, 12.7 mmol, *Fluka*, 85%, dried under vacuum) in anh. MeOH (30 mL) was added slowly. After stirring at 20°C for 3 h, the solvent was distilled in vacuo. The residue was triturated with CH_2Cl_2 (45 mL, then 30 mL, twice, in a ultra-sound bath). The org. extracts were combined and filtered through silica gel (8g, rinsing with MeOH, 30 mL, 3 times). The combined methanolic extracts were concentrated in vacuo and mixed with the oily residue left after the trituration with CH_2Cl_2, yielding 681 mg (95.6%), viscous oil. $[\alpha]^{25}_{589}$ = -15.7, $[\alpha]^{25}_{578}$ = -16.2, $[\alpha]^{25}_{546}$ = -18.5, $[\alpha]^{25}_{436}$ = -29, $[\alpha]^{25}_{365}$ = -38 (c = 1.0, MeOH). IR (KBr) ν: 3410, 1735, 1600, 1440, 1253, 1124, 1080, 1022, 750, 712 cm^{-1}. ^{1}H-NMR (CD_3OD) δ_H: 4.67 (dd, J = 11.0, 3.0, Hz, H-C(2)); 4.31 (d, J = 5.0 Hz, H-C(5)); 4.24 (ddd, J = 10.5, 5.0, 2.0 Hz, H-C(4)); 3.92 (s, MeO); 2.25 (ddd, J = 14.0, 10.5, 3.0 Hz, H_a-C(3)); 2.12 (ddd, J = 14.0, 11.0, 2.0 Hz, H_b-C(3)). ^{13}C-NMR (CD_3OD) δ_C: 174.4 (s, C(1), C(6)); 76.0 (d, ^1J(C,H) = 146 Hz, C(2)); 70.7 (d, ^1J(C,H) = 145 Hz, C(5)); 57.6 (d, ^1J(C,H) = 153 Hz, C(4)); 52.4 (q, ^1J(C,H) = 148 Hz, Me); 39.0 (t, ^1J(C,H) = 130 Hz, C(3)). MS (CI, NH_3) m/z: 228 (M^++2, 29), 226 (M^+, 100), 208 (41), 192 (26), 191 (23), 164 (10), 139 (16), 100 (13) 88 (18), 86 (13), 74 (16). Anal. calc. for $C_7H_{11}ClO_6$ (226.6): C 37.10, H 4.89; found: C 37.13, H 4.23.

(±)-Methyl 2-chloro-2,3-dideoxy-DL-*arabino*-hexarate 1,4-lactone (**28**). (±)-**27** (100 mg) prepared by the above procedure form (±)-**18** was dissolved in 1N HCl (10 mL) and stirred at 20°C for 30 min. After solvent evaporation at 40°C, the residue was dissolved in EtOAc (1 mL) and purified by FC (EtOAc/light petroleum 1:2, R_f (**28**) = 0.1) yielding 47 mg (51%) colourless oil. IR (CH_2Cl_2) ν: 3230, 3053, 1800, 1744, 1450, 1162, 1129, 1034, 960, 935, 890 cm^{-1}. ^{1}H-NMR ($CDCl_3$ filtered through K_2CO_3) δ_H: 4.78 (ddd, J = 9.0, 6.5, 3.4 Hz,

H-C(4)); 4.61 (dd, J = 5.0, 3.4 Hz, H-C(5)); 4.60 (dd, J = 10.0, 9.0 Hz, H-C(2)); 3.86 (s, CH_3); 3.31 (d, J = 5.0, O-H); 2.78 (ddd, J = 13.8, 9.0, 6.5 Hz, H_{anti}-C(3)); 2.56 (ddd, J = 13.8, 10.0, 9.0 Hz, H_{syn}-C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$ filtered through K_2CO_3) δ_C: 171.5 (s, C(1)); 170.8 (s, C(6)); 77.2 (d, ^1J(C,H) = 157 Hz, C(4)); 70.3 (d, ^1J(C,H) = 150 Hz, C(2)); 53.3 (q, ^1J(C,H) = 147 Hz); 50.5 (d, ^1J(C,H) = 152 Hz, C(5)); 32.1 (t, ^1J(C,H) = 137 Hz, C(3)). MS (70 eV) m/z: 209 (M^++1, 0.6), 151 (44), 149 (15), 121 (24), 120 (6), 119 (75), 118 (1), 115 (2), 111 (25), 105 (10), 91 (13), 90 (89), 89 (20), 75 (15), 63 (100). Anal. calc. for $C_7H_9ClO_5$ (208.6): C 40.31, H 4.35; found: C 40.48, H 4.28.

(±)-Methyl 5-O-acetyl-2-chloro-2,3-dideoxy-DL-*arabino*-hexarate 1,4-lactone (**29**). A mixture of **28** (60 mg, 0.24 mmol), pyridine (2.5 mL) and Ac_2O (0.25 mL, 2.6 mmol) was stirred at 20°C for 15 h. The solvent was distilled in vacuo (co-distillation with toluene, 3 times). The residue was purified by column chromatography (Lobar, EtOAc/light petroleum 1:2, R_f (**29**) = 0.28) yielding 39 mg (59%), colourless oil. IR (CH_2Cl_2) ν: 3260, 3055, 1800, 1755, 1436, 1218, 1160, 1122, 1007, 966, 890 cm^{-1}. ^{1}H-NMR ($CDCl_3$ filtered through K_2CO_3) δ_H: 5.48 (d, J = 3.0 Hz, H-C(5)); 4.91 (ddd, J = 9.8, 6.5, 3.0 Hz, H-C(4)); 4.62 (dd, J = 9.5, 9.0 Hz, H-C(2)); 3.81 (s, MeO); 2.88 (ddd, J = 13.5, 9.5, 6.5 Hz, H_a-C(3)); 2.61 (ddd, J = 13.5, 9.8, 9.0 Hz, H_b-C(3)); 2.20 (s, Ac). ^{13}C-NMR (62.9 MHz, $CDCl_3$ filtered through K_2CO_3) δ_C: 170.8 (s, C(1)); 169.5 (s, C(6)); 166.6 (s, Ac); 75.0 (d, ^1J(C,H) = 155 Hz, C(5)); 70.9 (d, ^1J(C,H) = 150 Hz, C(4)); 53.0 (q, ^1J(C,H) = 148 Hz); 49.9 (d, ^1J(C,H) = 154 Hz, C(2)); 32.7 (t, ^1J(C,H) = 135 Hz, C(3)); 20.4 (q, ^1J(C,H) = 130 Hz, Ac). MS (70 eV)) m/z: 193 (9), 191 (M^+-CH_3CO_2, 16), 155 (14), 132 (85), 121 (11), 119 (30), 111 (83), 91 (12), 83 (14), 75 (11), 63 (54).

(±)-Methyl 2-azido-2,3-dideoxy-DL-*ribo*-hexarate 1,4-lactone (**30**). A mixture of (±)-**27** (36 mg, 0.16 mmol) and 1N HCl (3.6 mL) was stirred at 20°C for 30 min. After solvent evaporation in vacuo (40°C), tetrabutylammonium azide (100 mg, 0.48 mmol) was added and the mixture dried in vacuo for 45 min. After pressurization with Ar, anh. THF (1 mL) was added and the mixture stirred at 20°C for 15 h. The solvent was distilled in vacuo, the residue was dissolved in EtOAc and the soln. washed successively with H_2O (3.5 mL, 3 times) and brine (1 mL). The solvent was distilled in vacuo, yielding 21 mg of an oil purified by column chromatography (Lobar, EtOAc/light petroleum, -30°C, R_f (**30**) = 0.1) yielding 9 mg (26%), colourless oil. IR ($CHCl_3$) ν: 3698, 3530, 3275, 2115, 1790, 1740, 1455, 1255, 1772, 1014, 970, 805 cm^{-1}. ^{1}H-NMR ($CDCl_3$ filtered through K_2CO_3) δ_H: 4.93 (ddd, J = 8.8, 2.3, 2.3 Hz, H-C(4)); 4.57 (dd, J = 3.8, 2.4 Hz, H-C(5)); 4.56 (dd, J = 9.0, 8.8 Hz, H-C(2)); 3.87 (s, MeO); 3.18 (d, J = 3.8 Hz, O-H); 2.39 (ddd, J = 13.2, 9.0, 2.3 Hz, H_s-C(3)), 2.12 (ddd, J = 13.2, 8.8. 8.8 Hz, H_a-C(3)). MS (CI, NH_3) m/z: 235 (1), 234 (9), 233 (M^++18, 100), 224 (6), 207 (6), 207 (5), 205 (8), 192 (4), 190 (5), 117 (2).

(-)-2-Chloro-2,3-dideoxy-D-*arabino*-hexono-1,4-lactone ((-)-**32**). A 2M soln. of $LiBH_4$ in anh. THF (5 mL, 10 mmol) was added dropwise to a stirred suspension of (-)-**27** (250 mg, 1.1 mmol) in anh. THF under Ar atm. The temperature of the mixture was kept below 20°C with a water bath. After stirring at 20°C for 1 h, the mixture was cooled to 0°C and 1N HCl (5 mL) was added dropwise. Solvent evaporation gave the crude aldonic acid **31** which was immediately treated with 1N HCl (20 mL) and stirred at 20°C for 15 min. The solvent was distilled off and the residue taken with H_2O (15 mL) and extracted with EtOAc (75 mL, 3 times). The combined org. extracts were washed with brine (5 mL) and dried ($MgSO_4$). The solvent was distilled yielding 366 mg of crude (-)-**32** that was used in the next synthetic step. FC purification of 47 mg of that oil (EtOAc/light petroleum 1:1, R_f ((-)-**32**) = 0.29) afforded 10 mg (26.7%), colourless oil. $[\alpha]^{25}_{589}$ = -0.1, $[\alpha]^{25}_{578}$ = -0.1, $[\alpha]^{25}_{546}$ = -0.1, $[\alpha]^{25}_{436}$ = -0.6, $[\alpha]^{25}_{365}$ = -1.8 (c = 1.2, CH_2Cl_2). ^{1}H-NMR (250 MHz, CD_3COCD_3) δ_H: 4.94 (dd, J = 10.2, 9.0 Hz, H-C(2)); 4.64 (ddd, J = 9.5, 5.5, 4.5 Hz, H-C(4)); 3.94 (dm, J = 4.5 Hz, H-C(5)); 3.58 (m, H_2C(6)); 2.89 (ddd, J = 12.5, 8.7, 5.5 Hz, H_a-C(3)); 2.49 (ddd, J = 12.5, 9.5, 9.0 Hz, H_s-C(3)). ^{13}C-NMR (62.9 MHz, CD_3COCD_3) δ_C: 171.3 (d, C(1)); 78.7 (d, ^1J(C,H) = 152 Hz, C(4)); 72.1 (d, ^1J(C,H) = 142 Hz, C(2)); 63.3 (t, ^1J(C,H) = 140 Hz, C(6)); 52.7 (d, ^1J(C,H) = 152 Hz, C(5)); 33.9 (t, ^1J(C,H) = 138 Hz, C(3)). MS (CI, NH_3) m/z: 200 (33), 199 (11), 198 (M^++18, 100), 187 (4), 186 (5), 164 (15), 162 (5), 139 (9), 114 (6), 112 (8), 106 (6), 105 (6), 94 (8), 91 (11).

(+)-2-Chloro-2,3-dideoxy-5,6-O-isopropylidene-D-*arabino*-hexono-1,4-lactone ((+)-**33**). A mixture of crude (-)-**32** (derived from 54 mg (0.24 mmol) of (-)-**27**) and $SnCl_2$ (10 mg) was dried under vacuum (10^{-3} Torr) for 10 min. After the addition of anh. dioxane (1 mL) and dimethoxypropane (0.5 mL), the mixture was heated to 50°C for 4 h. Pyridine (0.1 mL) was added and the solvent was distilled off. The residue was taken with CH_2Cl_2 (1 mL) and filtered through silica gel (315 mg), rinsing with CH_2Cl_2 (1 mL, 3 times). The combined CH_2Cl_2 extracts were washed with H_2O (1 mL) and dried ($MgSO_4$). Solvent evaporation yielded 27.6 mg (52.5%), colourless oil. $[\alpha]^{25}_{589}$ = +4.5, $[\alpha]^{25}_{578}$ = +4.8, $[\alpha]^{25}_{546}$ = +5.0, $[\alpha]^{25}_{436}$ = +9.5, $[\alpha]^{25}_{365}$ = +13.3 (c = 1.0, CH_2Cl_2). IR ($CHCl_3$) ν: 3260, 2995, 1794, 1452, 1373, 1175, 1058, 947, 841 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$ filtered through K_2CO_3) δ_H: 4.54 (dd, J = 8.8, 8.6 Hz, H-C(2)); 4.36 (ddm, J = 7.5, 6.2 Hz, H-C(4)); 4.23 (m, H-C(5)); 4.17 (m, H_a-C(6)); 3.95 (dd, J = 8.7, 3.9 Hz, H_b-C(6)); 2.97 (ddd, J = 13.8, 8.6, 6.2 Hz, H_a-C(3)); 2.44 (ddd, J = 13.8, 8.8, 7.5 Hz, H_s-C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$ filtered through K_2CO_3)

δ_C: 171.5 (s, C(1)); 110.2 (s, $C(CH_3)_2$); 77.6 (d, ^1J(C,H) = 156 Hz, C(4)); 76.4 (d, ^1J(C,H) = 154 Hz, C(2)); 66.8 (t, ^1J(C,H) = 148 Hz, C(6)); 50.2 (d, ^1J(C,H) = 153 Hz, C(5)); 35.3 (t, ^1J(C,H) = 138 Hz, C(3)); 26.7, 24.9 (2q, ^1J(C,H) = 128 Hz, Me_2C). MS (70 eV) m/z: 220 ($M^{+\cdot}$, 1), 217 (9), 207 (27), 205 (M^+-15, 100), 152 (14), 101 (48), 83 (19), 75 (14), 73 (16), 69 (15), 62 (13), 61 (25). Anal. calc. for $C_9H_{13}ClO_4$ (220.7): C 48.99, H 5.94; found: 49.02, H 5.98.

(+)-2-Azido-2,3-dideoxy-5,6-O-isopropylidene-D-*ribo*-hexono-1,4-lactone ((+)-**34**). A mixture of (+)-**33** (27.6 mg, 0.12 mmol), tetrabutylammonium azide (90 mg, 0.31 mmol) and anh. THF (1 mL) was stirred at 20°C for 15 h. The solvent was distilled and the residue dissolved in EtOAc (15 mL). The soln. was washed with H_2O (3 mL, 3 times) and dried ($MgSO_4$). The solvent was distilled off yielding 23.5 mg of an oil purified by FC (10 g, Et_2O, R_f ((+)-**34**) = 0.2) yielding 16.5 mg (58%), colourless crystals, m.p. 60-61°C; lit.[45]: 60-61°C. $[\alpha]^{25}_{589}$ = +131, $[\alpha]^{25}_{578}$ = +136, $[\alpha]^{25}_{546}$ = +157, $[\alpha]^{25}_{436}$ = +282, $[\alpha]^{25}_{365}$ = +486 (*c* = 1.0, MeOH); lit.[41a]: $[\alpha]^{25}_{589}$ = +134 (*c* = 1.06, MeOH). IR (KBr) ν: 3350, 3065, 3000, 2955, 2900, 2110, 1778, 1453, 1380, 1310, 1250, 1178, 990, 943, 868, 824, 680 cm^{-1}. ^{1}H-NMR δ_H: 4.51 (ddd, *J* = 8.0, 4.8, 3.0 Hz, H-C(4)); 4.43 (dd, *J* = 9.0, 8.5 Hz, H-C(2)); 4.28 (ddd, *J* = 7.0, 5.0, 4.8 Hz, H-C(5)); 4.14 (dd, *J* = 9.0, 7.0 Hz, H_a-C(6)); 3.76 (dd, *J* = 9.0, 5.0 Hz, H_b-C(6)); 2.53 (ddd, *J* = 13.5, 9.0, 3.0 Hz, H_s-C(3)); 2.19 (ddd, *J* = 13.5, 8.5, 8.0 Hz, H_a-C(3)); 1.47, 1.35 (2s, Me_2C). ^{13}C-NMR δ_C: 173.2 (s, C(1)); 110.5 (s, $C(CH_3)_2$); 78.0 (d, ^1J(C,H) = 155 Hz, C(4)); 75.8 (d, ^1J(C,H) = 143 Hz, C(2)); 65.8 (t, ^1J(C,H) = 150 Hz, C(6)); 56.4 (d, ^1J(C,H) = 143 Hz, C(5)); 29.3 (t, ^1J(C,H) = 137 Hz, C(3)); 26.2, 24.4 (2q, ^1J(C,H) = 128 Hz). MS (70 eV) m/z: 214 (1.5), 212 (M^+-15, 100), 185 (1), 102 (3), 101 (45), 98 (3), 97 (2), 96 (4), 83 (5), 73 (9), 72 (7). Anal. calc. for $C_9H_{13}N_3O_4$ (227.2): C 47.57, H 5.77; found: C 47.68, H 5.90.

(±)-2-Azido-2,3-dideoxy-5,6-O-isopropylidene-DL-*ribo*-hexono-4,1-lactone ((±)-**34**). Prepared by the above procedures form (±)-**27**, (±)-**34** had m.p. 66-67°C. The intermediate products (±)-**31**, (±)-**32** and (±)-**33** were all colourless oils.

(-)-2-Azido-2,3-dideoxy-5,6-O-isopropylidene α-D- and β-D-*ribo*-hexofuranose ((-)-**35**). A 1.2M soln. of diisobutylaluminium hydride in toluene (0.17 mL, 0.2 mmol) was added slowly to a stirred soln. of (+)-**34** (39 mg, 0.17 mmol) in anh. toluene (0.8 mL) cooled to -78°C. After stirring at -78°C for 1 h, AcOH (51 μL) was added and the mixture allowed to warm to 20°C. After the addition of EtOAc (4 mL) and filtration through Celite (rinsing with EtOAc), the solvent was distilled to give 38.5 mg (98%) of a 3.5:1 mixture of the α and β furanoses (-)-**35**, colourless oil. $[\alpha]^{25}_{589}$ = -29, $[\alpha]^{25}_{578}$ = -30, $[\alpha]^{25}_{546}$ = -34, $[\alpha]^{25}_{436}$ = -56, $[\alpha]^{25}_{365}$ = -82 (*c* = 1.0, MeOH). ^{1}H-NMR (250 MHz, $CDCl_3$ of (-)-**35**α) δ_H: 5.26 (s, H-C(1)); 4.31 (dd, *J* = 12.2, 8.5 Hz, H-C(6)), 4.25 (dd, *J* = 12.2, 5.2 Hz, H'-C(6)); 4.10 (dd, *J* = 8.0, 6.5 Hz, H-C(4)); 3.96 (d, *J* = 5.2 Hz, H-C(5)); 2.24 (ddd, *J* = 13.2, 8.0, 5.2 Hz, H-C(3)); 2.11 (dd, *J* = 13.2, 6.5 Hz, H'-C(3)); 1.46, 1.36 (2s, Me_2C). The anomeric protons of (-)-**35**β was visible: δ_H: 5.41 (d, *J* = 4.0 Hz, H-C(1)). Acylation (pyridine/Ac_2O) of (-)-**35** gave the corresponding 1-O-acetyl derivative, colourless oil. Anal. calc. for $C_{11}H_{17}N_3O_5$ (271.3): C 48.70, H 6.32, N 15.49; found: C 48.79, H 6.33, N 15.42.

Chlorhydrate of D-lividosamine ((+)-**1**·HCl). A mixture of (-)-**35** (37 mg, 0.16 mmol), 1N HCl (5 mL), 10% Pd on charcoal (20 mg) was pressurized with H_2 (1 atm.) and shaken for 4 h. After filtration, solvent distillation gave 30 mg (94%) of crude (+)-**1**·HCl which was recrystallized from EtOH (0.5 mL) and acetone (2 mL), yielding 18 mg (55.4%) white solid, characterized as (+)-**36**.

(+)-Methyl N-acetyl-4,6-O-diacetyl-α-D-lividosamide (methyl 2-acetamido-4,6-O-diacetyl-2,3-dideoxy-D-*ribo*-hexopyranoside: (+)-**36**). A mixture of (+)-**1**·HCl (18 mg, 0.09 mmol), pyridine (1 mL) and Ac_2O (135 mg, 13 mmol) was stirred at 20°C for 1 h. The solvent was distilled off (several co-distillation with toluene). The residue was dissolved in anh. MeOH (1 mL) and BF_3·Et_2O (15 μL) was added. The soln. was heated to 70°C for 5 h; it was then concentrated to dryness. The residue was dissolved in pyridine (1 mL) and Ac_2O (125 μL) and stirred at 20°C for 15 h. The solvent was distilled off (co-distillation in vacuo with toluene, 3 times) yielding a viscous residue which was taken with acetone and filtered through silica gel. The solvent was distilled and the residue purified by column chromatography (Lobar, Merck type B, acetone/(t-Bu)OMe 1:4, R_f ((+)-**36**) = 0.34), yielding 9 mg (33%), colourless crystals, m.p. 133-134°C; lit.[46]: 134-135°C; lit.[21]: 139°C. $[\alpha]^{25}_{589}$ = +90, $[\alpha]^{25}_{578}$ = +92, $[\alpha]^{25}_{546}$ = +103, $[\alpha]^{25}_{436}$ = +167, $[\alpha]^{25}_{365}$ = +245 (*c* = 0.17, MeOH); lit.[45]: $[\alpha]^{25}_{589}$ = +90 (*c* = 0.12, MeOH); lit.[21]: $[\alpha]^{25}_{589}$ = +90.2, $[\alpha]^{25}_{365}$ = +250.8 (*c* = 0.6, MeOH). IR (KBr) ν: 2115, 1788, 1458, 1262, 1180, 1057, 1000 cm^{-1}; lit.[21]: 2100, 1790 cm^{-1}.

(±)-Methyl 2-acetamido-4,6-O-diacetyl-2,3-dideoxy-α-DL-*ribo*-hexopyranoside ((±)-**36**). Prepared by the above procedures form (±)-**34**; (±)-**36** had m.p. 125-127°C. ^{1}H-NMR δ_H: 5.61 (d, *J* = 9.0 Hz, N-H); 4.84 (ddd, *J* = 11.0, 10.0, 5.0, Hz, H-C(4)); 4.62 (d, *J* = 3.4 Hz, H-C(1)); 4.28 (dddd, *J* = 12.5, 9.0, 4.8, 3.4 Hz, H-C(2)); 4.22 (dd, *J* = 12.2, 5.0 Hz, H_a-C(6)); 4.15 (dd, *J* = 12.2, 2.5 Hz, H_b-C(6)); 3.84 (ddd, *J* = 10.0, 5.0, 2.5 Hz,

H-C(5)); 3.42 (s, OMe); 2.25 (ddd, J = 11.5, 5.0, 4.8 Hz, $H_{equat.}$-C(3)); 2.10, 2.04 (2s, 2 AcO); 1.98 (s, ($NCOCH_3$); 1.66 (dd, 1H, H_{axial}-C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 170.8 (s, NCO); 169.4 (s, OCO); 169.2 (s, OCO); 97.2 (d, ^1J(C,H) = 170 Hz, C(1)); 67.9 (d, ^1J(C,H) = 142 Hz, C(5)); 66.0 (d, ^1J(C,H) = 147 Hz, C(4)); 62.5 (t, ^1J(C,H) = 148 Hz, C(6)); 55.0 (q, ^1J(C,H) = 140 Hz, OCH_3); 46.6 (d, ^1J(C,H) = 140 Hz, C(2)); 30.6 (t, ^1J(C,H) = 132 Hz, C(3)); 23.3, 20.9 (2q, ^1J(C,H) = 128 Hz). MS (CI, NH_3) m/z: 321 (M^++18, 17), 305 (M^++2, 17), 304 (M^++1, 100), 272 (23), 244 (11), 184 (7), 85 (28). Anal. calc. for $C_{13}N_{21}NO_7$ (303.3): C 51.48, H 6.98, N 4.62; found: C 51.50, H 7.06, N 4.62.

Mixture of (±)-[(1*RS*,2*SR*,4*SR*)-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl] [(1*SR*,2*RS*,4*RS*)-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl amine (**38**) and di[(1*RS*,2*SR*,4*SR*)-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl]amine (**39**). A mixture of ketone (±)-**37**[25] (148 mg, 0.783 mmol), $NaBH_3CN$ (24 mg, 0.32 mmol) NH_4OAc (600 mg, 7.8 mmol) and 4 Å molecular sieves in dry MeOH (6 mL) was stirred at 0°C for 1 h. Conc. HCl was added until pH <2. The solvent was distilled off and the residue dissolved in H_2O (5 mL). The soln. was extracted with Et_2O (10 mL, 3 times). The aq. layer was alkalinized to pH ~10 with solid KOH and then extracted with Et_2O (10 mL, 3 times). The ethereal extracts were dried ($MgSO_4$) and the solvent was distilled off to afford 99 mg of a colourless oil, that was purified by FC (light petroleum/EtOAc 8:2) yielding 27 mg (20%) of **38** (or **39**) and 33 mg (24%) of **39** (or **38**).Characteristics of **38** (or **39**):IR (KBr) v: 3300 (br.), 3100, 3060, 3020, 3000, 2940, 2850, 1580, 1450, 1300, 1280, 1200, 1155, 1045, 1030, 1000, 985, 910, 875, 835, 785, 750, 710, 660 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 6.55 (d, J = 2.0 Hz, H-C(5)); 4.96 (d, J = 4.0 Hz, H-C(1)); 4.90 (ddd, J = 1.0, 2.0, 5.0 Hz, H-C(4)); 3.62 (ddd, J = 4.0, 4.5, 8.0 Hz, H-C(2)); 2.26 (ddd, J = 4.5, 8.0, 11.5 Hz, H_{exo}-C(3)); 0.90 (dd, J = 2.0, 11.5 Hz, H_{endo}-C(3)). MS (70 eV) m/z: 367 (5), 366 (24), 365 (35), 364 (100), 363 (40), 262 (63), 361 (12), 288 (3), 287 (2), 286 (18), 285 (3), 284 (18), 282 (3), 268 (2), 239 (3), 237 (2), 234 (2), 220 (2), 219 (3), 218 (34), 217 (4), 216 (35), 209 (3), 208 (2), 207 (3), 206 (4), 197 (6), 192 (10), 190 (11), 174 (5), 172 (3), 158 (3), 157 (5), 156 (3), 155 (3), 154 (4), 148 (10), 146 (12), 119 (3), 115 (3), 114 (4), 112 (13), 111 (3), 110 (99), 94 (24), 78 (68). Characteristics of **39** (or **38**): IR (KBr) v: 3360 (br.), 3300, 3080, 3000, 2980, 2940, 2920, 2850, 1580, 1475, 1440, 1350, 1290, 1250, 1215, 1195, 1110, 1050, 1020, 1000, 910, 850, 830, 785, 710, 690 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 6.56 (d, J = 2.0 Hz, H-C(5)); 4.92 (ddd, J = 1.0, 2.0, 5.0 Hz, H-C(4)); 4.80 (d, J = 4.5 Hz, H-C(1)); 3.55 (ddd, J = 3.5, 4.5, 8.0 Hz, H-C(2)); 2.24 (ddd, J = 5.0, 8.0, 11.5 Hz, H_{exo}-C(3)); 1.01 (dd, J = 3.5, 11.5 Hz, H_{endo}-C(3)). MS (70eV) m/z: 367 (5), 366 (28), 365 (25), 369 (100), 363 (34), 362 (65), 361 (10), 287 (2), 286 (20), 285 (3), 284 (17), 270 (2), 223 (2), 219 (3), 218 (39), 217 (5), 216 (41), 210 (14), 209 (6), 208 (23), 207 (6), 206 (15), 204 (3), 192 (9), 190 (13), 188 (4), 148 (21), 146 (2), 140 (37), 139 (6), 138 (26), 136 (5), 112 (12), 110 (8).

(-)-N-Benzyl-N-[(1*R*,2*S*,4*S*)-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl] amine ((-)-**40**). Benzylamine (14.7 mL, 98%, 134 mmol) and $MeSO_3H$ (3.15 mL, 48.6 mmol) were added to a soln. of (-)-**37**[25] (4.20 g, 2.22 mmol) in benzene (50 mL) and stirred at 20°C under Ar atm. A colourless salt precipitated. Stirring was continued for 24 h. The mixture was filtered, concentrated to 20 mL under reduced pressure and diluted with MeOH (10 mL). Cooling to 0°C was followed by portionwise addition of $NaBH_4$ (820 mg, 21.7 mmol). At the end of the reaction (TLC control, silica gel, toluene/EtOAc 4:1) the soln. was diluted with EtOAc (100 mL) and 5% aq. Na_2CO_3 (50 mL); the two phases were separated and the aq. one was extracted two times with EtOAc. The combined org. layers were washed with brine, dried ($MgSO_4$), filtered and concentrated to afford 4.70 g (76%) of the amine. A portion of the product was crystallized from light petroleum for analysis. M.p. 52-53°C. $[\alpha]^{25}_D$ = -104, $[\alpha]^{25}_{578}$ = -109, $[\alpha]^{25}_{546}$ = -125, $[\alpha]^{25}_{436}$ = -229, $[\alpha]^{25}_{365}$ = -401 (*c* = 1.0, $CHCl_3$). IR (KBr) v: 3420 (br.), 3300, 3070, 3030, 3010, 2980, 2940, 2920, 2880, 1575, 1490 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.34 (m, Ph); 6.60 (d, J = 2.0 Hz, H-C(5)); 4.96 (d, J = 4.0 Hz, H-C(1)); 4.92 (dd, J = 2.0, 5.0 Hz, H-C(4)); 3.87 (AB syst., 2H, J = 12.5 Hz); 3.60 (ddd, J = 3.5, 4.0, 8.0 Hz, H-C(2)); 2.31 (ddd, J = 5.0, 8.5, 12.0 Hz, H_{exo}-C(3)); 1.00 (dd, J = 3.0, 12.0 Hz, H_{endo}-C(3)). ^{13}C-NMR (62.9 MHz) δ_H: 139.7 (s); 135.7 (d, ^1J(C,H) = 180 Hz); 128.4, 128.2, 127.2 (3d, ^1J(C,H) = 160 Hz); 122.3 (s); 83.5 (d, ^1J(C,H) = 165 Hz); 56.7 (d, ^1J(C,H) = 145 Hz); 53.4 (t, ^1J(C,H) = 130 Hz); 33.6 (t, ^1J(C,H) = 135 Hz). MS (70 eV) m/z: 283 (13), 282 (90), 281 (63), 280 (96), 279 (47), 202 (7), 200 (4), 134 (18), 133 (100), 132 (41), 118 (6), 116 (4), 108 (5), 104 (7), 92 (8), 91 (93). Anal. calc. for $C_{13}H_{14}BrNO$ (280.16): C 55.73, H 5.04, Br 28.52; found: 55.65, H 5.09, Br 28.53.

(±)-N-Benzyl-N-[(1*RS*,2*SR*,4*SR*)-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl]amine ((±)-**40**) and (1*RS*,2*SR*,4*SR*)-2-*endo*-Benzylamino-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-carbonitrile (**41**). $Na(CN)BH_3$ (109 mg, 1.73 mmol) was added to a soln. of (±)-**37** (546 mg, 2.89 mmol), benzylamine (1.9 mL, 98%, 17 mmol) and $MeSO_3H$ (0.4 mL, 6.2 mmol) in dry MeOH (8 mL) under Ar atm. in the presence of activated 3 Å molecular sieves. The mixture was stirred for 14 h; it was diluted with Et_2O (30 mL) and extracted with 5% aq. HCl (10 mL, 4 times). The acidic extracts were neutralized (pH ~10) with Na_2CO_3 and extracted with EtOAc until all the product had portioned into the org. phase form the aq. phase (TLC control, silica gel, light petroleum/EtOAc 6:4). Drying ($MgSO_4$) and concentration of the org. extracts followed by FC (light petroleum/EtOAc 3:2) afforded 125 mg (14%) of (±)-**40** and 138 mg (49%) of **41**. Characteristics of

(±)-**40**: m.p. 89-90°C. Characteristics of **41**: colourless crystals, m.p. 99-100°C. IR (KBr) v: 3430 (br.), 3320, 3100, 3060, 3030, 2950, 2850, 2220, 1585, 1455, 1200, 1010, 875 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.36 (m, C_6H_5); 6.67 (d, J = 2.0 Hz, H-C(5)); 5.14 (d, J = 1.0 Hz, H-C(1)); 5.09 (ddd, J = 1.0, 2.0, 5.0 Hz, H-C(4)); 4.06 (dd, J = 4.0, 12.0 Hz, -C*H*HPh); 3.94 (dd, J = 9.0, 1.20 Hz, -CH*H*Ph); 2.18 (dd, J = 5.0, 11.5 Hz, H_{exo}-C(3)); 1.53 (d, J = 11.5 Hz, H_{endo}-C(3)). ^{13}C-NMR (62.9 MHz) δ_H: 138.0 (s); 136.3 (d, ^1J(C,H) = 190 Hz); 128.6 (d, ^1J(C,H) = 160 Hz); 128.3 (d, ^1J(C,H) = 160 Hz); 127.7 (d, ^1J(C,H) = 160 Hz); 122.3 (s); 121.6 (s); 87.5 (d, ^1J(C,H) = 170 Hz); 80.7 (d, ^1J(C,H) = 170 Hz); 60.8 (s); 51.4 (t, ^1J(C,H) = 135 Hz); 41.1 (t, ^1J(C,H) = 140 Hz). MS (CI, NH_3) m/z: 308 (M^+ +3, 4), 307 (M^+ +2, 26), 306 (M^+ +1, 6), 305 (M^+, 27), 281 (2), 280 (19), 279 (3), 278 (20), 159 (18), 158 (34), 91 (100). Anal. calc. for $C_{14}H_{13}OBrN_2$ (305.17): C 55.10, H 4.29, Br 26.18; found: C 55.16, H 4.26, Br 26.13.

(-)-Benzyl N-benzyl,N-[(1*R*,2*S*,4*S*)-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl]carbamate ((-)-**43**). Benzylchloroformate (20 mL, 90-95% ca. 12.7 mmol) was added dropwise to a stirred soln. of (-)-**40** (3.15 g, 11.2 mmol) and $NaHCO_3$ (2.25 g, 26.8 mmol) in EtOH (40 mL) and H_2O (26 mL). At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 7:3), CH_2Cl_2 (220 mL) and brine (75 mL) were added and the resulting two phases were separated. The aq. phase was extracted with CH_2Cl_2 (50 mL). The combined org. extracts were washed with brine (60 mL, twice), dried ($MgSO_4$), filtered and concentrated to give a yellow oil. Two successive FC (light petroleum/EtOAc 4:1 and then toluene) gave 3.70 g (80%) of a colourless oil which crystallized on standing. A portion of the product was recrystallized from hexane/Et_2O for analysis. M.p. 67-68°C. $[\alpha]^{25}_D$ = -157, $[\alpha]^{25}_{578}$ = -164, $[\alpha]^{25}_{546}$ = -191, $[\alpha]^{25}_{436}$ = -350, $[\alpha]^{25}_{365}$ = -611 (c = 1.0, $CHCl_3$). IR (KBr) v: 3030, 2940, 1695, 1575, 1405, 1290, 1220, 1195, 1100 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.30 (m, Ph); 7.07 (m, Ph); 6.52 (d, J = 2.0 Hz, H-C(5)); 5.26-4.64 (m, H-C(1), H-C(2), -CH_2-(Cbz), -C*H*H(Bn)); 4.90 (dd, J = 2.0, 4.5 Hz, H-C(4)); 3.98 (d, J = 170 Hz, -CH*H*(Bn)); 2.10 (ddd, J = 4.5, 9.5, 13.0 Hz, H_{exo}-C(3)); 1.43 (dd, J = 2.0, 4.5 Hz, H_{endo}-C(3)). ^{13}C-NMR (62.9 MHz) δ_C: 157.0 (s); 138.6 (s); 135.5 (d, ^1J(C,H) = 180 Hz); 128.6, 128.5, 128.0 (3d, ^1J(C,H) = 155 Hz); 126.9 (d, ^1J(C,H) = 160 Hz); 125.8 (d, ^1J(C,H) = 155 Hz); 123.9 (s); 83.0 (d, ^1J(C,H) = 175 Hz); 80.9 (d, ^1J(C,H) = 160 Hz); 67.6 (d, ^1J(C,H) = 150 Hz); 53.8 (d, ^1J(C,H) = 155 Hz); 48.0 (t, ^1J(C,H) = 135 Hz); 28.9 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 434 (4), 433 (19), 432 (23), 431 (16), 430 (17), 417 (6), 416 (34), 415 (26), 414 (31), 413 (21), 268 (25), 267 (14), 224 (4), 176 (16), 146 (5), 134 (8), 133 (22), 108 (29), 106 (14), 105 (3), 92 (11), 91 (100). Anal. calc. for $C_{21}H_{20}BrNO_3$ (414.30): C 60.88, H 4.87, Br 19.29; found: C 60.94, H 4.90, Br 19.13.

Benzyl N-benzyl,N-[(1*R*,2*S*,4*S*,5*S*)-5-*exo*-hydroxy-6-oxo-7-oxabicyclo[2.2.1]hept-2-*endo*-yl] carbamate (**44**). $NaHCO_3$ (1.88 g, 22 mmol), OsO_4 (0.34 mL, soln. 2.5% in CCl_4, 0.87 mmol) and 30% H_2O_2 (5.0 mL, 44 mmol) were added in succession to a soln. of (-)-**43** (3.60 g, 8.69 mmol) in THF/H_2O 5:1 (220 mL) with stirring at 20°C. The soln. became yellow. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 7:3) the mixture was diluted with EtOAc (200 mL), washed with 5% aq. Na_2SO_3 (50 mL, 3 times), H_2O (50 mL) and brine (60 mL), dried ($MgSO_4$), filtered and concentrated to give a yellow oil (3.40 g). A portion of the oil was acetylated to have an analytical sample (Ac_2O, Et_3N, CH_2Cl_2), the remaining product was immediately carried through the next reaction.

(-)-(1*R*,2*S*,4*S*,5*S*)-5-*endo*-(N-Benzyl,N-benzyloxycarbonyl)amino-3-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl acetate ((-)-**47**). M.p. 72-74.5°C. $[\alpha]^{25}_D$ = -35, $[\alpha]^{25}_{578}$ = -37, $[\alpha]^{25}_{546}$ = -44, $[\alpha]^{25}_{436}$ = -106, $[\alpha]^{25}_{365}$ = -339 (c = 1.0, $CHCl_3$). IR (KBr) v: 3060, 3020, 2960, 1775, 1735, 1700, 1470, 1430, 1360, 1230, 1120 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.33 (m, Ph); 7.17 (m, Ph); 5.14 (AB syst., -CH_2(Cbz)); 5.12 (s, H-C(2)); 4.62 (d, J = 6.5 Hz, H-C(1)); 4.54 (AB syst., -CH_2(Bn)); 4.08 (d, J = 5.5 Hz, H-C(4)); 3.75 (ddd, J = 5.5, 5.5, 11.0 Hz, H-C(5)); 2.37 (m, H_{endo}-C(6)); 2.22 (ddd, J = 6.5, 11.0, 13.0 Hz, H_{exo}-C(6)); 2.14 (s, Me). ^{13}C-NMR (62.9 MHz) δ_C: 202.3, 170.4, 155.7, 137.0, 135.7 (5s); 128.9, 128.5, 128.3, 127.8, 127.1 (5d, ^1J(C,H) = 160 Hz); 81.7 (d, ^1J(C,H) = 165 Hz); 78.8 (d, ^1J(C,H) = 170 Hz); 75.0 (d, ^1J(C,H) = 165 Hz); 67.7 (t, ^1J(C,H) = 150 Hz); 58.4 (d, ^1J(C,H) = 145 Hz); 53.1 (t, ^1J(C,H) = 140 Hz); 28.0 (t, ^1J(C,H) = 135 Hz); 20.7 (q, ^1J(C,H) = 130 Hz). MS (CI, NH_3) m/z: 429 (M^+ +20, 3), 428 (M^+ +19, 16), 427 (M^+ +18, 57), 411 (M^+ +2, 26), 410 (M^+ +1, 100), 409 (M^+, 26), 369 (2), 352 (8), 274 (2), 133 (2), 108 (3), 91 (3). Anal. calc. for $C_{23}H_{23}NO_6$ (409.43): C 67.47, H 5.66, N 3.42; found: C 67.49, H 5.74, N 3.49.

(±)-(1*RS*,2*SR*,4*SR*,5*SR*)-5-*endo*-(N-Benzyl,N-benzyloxycarbonyl)amino-3-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl acetate ((±)-**47**). Obtained by the above procedures form (±)-**40**; (±)-**47** was a colourless solid, m.p. 71-72 °C. The intermediates (±)-**43** and (±)-**44** were colourless oils.

2-(N-Benzyl,N-benzyloxycarbonyl)amino-2,3-dideoxy-β-D-*arabino*-furanurono-6,1-lactone (**45**). H_2O (1 mL), $NaHCO_3$ (710 mg, 8.45 mmol) and mCPBA (1.82 g, 80%, 8.44 mmol) were added in succession to a soln. of crude **44** (2.82 g, 7.67 mmol) in CH_2Cl_2 (110 mL) and the mixture was stirred at 20°C for 14 h. At the end of the reaction (TLC control, silica gel, toluene/EtOAc 7:3) the mixture was washed with 5% aq. Na_2CO_3 (50 mL, twice), H_2O (50 mL) and brine (50 mL) and dried ($MgSO_4$). The solvent was distilled giving 2.5 g of

colourless oil. A portion of it was acetylated (Ac_2O, Et_3N, CH_2Cl_2) and crystallized form pentane/CH_2Cl_2 for analysis. The remaining product was carried through the next reaction.

(-)-5-O-Acetyl-2-(N-benzyl,N-benzyloxycarbonyl)amino-2,3-dideoxy-β-D-*arabino*-furanurono-6,1-lactone ((-)-**46**). M.p.: 122-123°C. $[\alpha]^{25}_{D}$ = -115, $[\alpha]^{25}_{578}$ = -120, $[\alpha]^{25}_{546}$ = -137, $[\alpha]^{25}_{436}$ = -243, $[\alpha]^{25}_{365}$ = -405 (*c* = 1.0, $CHCl_3$). IR (KBr) v: 3010, 2775, 2730, 2700, 1430, 1390, 1360, 1230, 1205 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.33 (m, Ph); 7.19 (m, Ph); 5.55 (d, *J* = 4.0 Hz, H-C(1)); 5.16 (m, H-C(4) + -CH_2); 4.86 (d, *J* = 16.0 Hz, -C*H*H-); 4.60 (d, *J* = 8.5 Hz, H-C(5)); 4.37 (d, *J* = 16.0 Hz, -CH*H*-); 4.07 (m, H-C(7)); 2.57 (m, H_{endo}-C(6)); 2.35 (ddd, *J* = 8.5, 12.5, 13.5 Hz, H_{exo}-C(6)); 2.41 (s, Me). ^{13}C-NMR (62.9 MHz) δ_C: 169.6, 162.9, 155.3, 137.2, 135.1 (5s); 129.0, 128.6, 128.3, 127.8, 126.9 (5d, ^1J(C,H) = 160 Hz); 100.6 (d, ^1J(C,H) = 185 Hz); 79.1 (d, ^1J(C,H) = 160 Hz); 72.7 (d, ^1J(C,H) = 155 Hz); 67.9 (t, ^1J(C,H) = 150 Hz); 61.3 (d, ^1J(C,H) = 145 Hz); 52.5 (t, ^1J(C,H) = 140 Hz); 25.4 (t, ^1J(C,H) = 135 Hz); 20.7 (q, ^1J(C,H) = 130 Hz). MS (CI, NH_3) m/z: 445 (M^+ +20, 6), 444 (M^+ +19, 36), 443 (M^+ +18, 100), 442 (M^+ +17, 5), 428 (M^+ +5, 1), 427 (M^+ +2, 7), 426 (M^+ +1, 25), 425 (M^+, 1), 385 (4), 384 (1), 368 (3), 292 (3), 290 (5), 232 (2), 176 (2), 132 (2), 92 (2), 91 (12). Anal. calc. for $C_{23}H_{23}NO_7$ (425.43): C 64.93, H 5.45, N 3.29; found: C 64.91, H 5.49, N 3.34.

(±)-5-O-Acetyl-2-(N-benzyl,N-benzyloxycarbonyl)amino-2,3-dideoxy-β-DL-*arabino*-furanurono-6,1-lactone ((±)-**46**). Obtained by the above procedures form (±)-**44**; (±)-**46** had m.p. 108-109°C; the intermediate (±)-**45** was a colourless oil.

Methyl [methyl-2-(N-benzyl,N-benzyloxycarbonyl)amino-2,3-dideoxy-α- and β-D-*arabino*-furanosid]uronate (**48** + **49**). The crude lactone **45** (1.40 g, 3.65 mmol) was dissolved in dry MeOH (170 mL); $MeSO_3H$ (0.24 mL, 3.70 mmol) was added and the mixture was stirred at 20°C. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 1:1) NaOAc (304 mg, 3.70 mmol) was added and the soln. was stirred for an additional 15 min. The solvent was distilled and the residue diluted with EtOAc (50 mL), filtered through Celite and concentrated to afford a yellow oil (1.60 g). FC (toluene/EtOAc 7:3) gave a first fraction yielding 1.32 g (76% based on (-)-**43**) of a mixture of α- and β-furanosiduronates, colourless oil. A second fraction afforded 116 mg (7%) of the corresponding α- and β-pyranosiduronates, colourless oil. Characteristics of **48**: IR (KBr) v: 3450 (br.), 3030, 2950, 1740, 1700, 1450, 1420, 1240, 1215, 1100, 1040, 1000, 735, 700 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.24 (m, Ph); 5.17 (br. s, CH_2(Cbz)); 5.00 (br.s, H-C(1)); 4.69 (d, 1H, *J* = 16.0 Hz, Bn); 4.45 (m, H-C(2), H-C(4), H-C(5)); 4.38 (d, 1H, *J* = 16.0 Hz, Bn); 3.75, 3.26 (2s, OMe); 2.07 (m, H_2-C(3)). ^{13}C-NMR (62.9) δ_C: 170.2, 155.3, 139.1, 138.1 (4s); 128.5, 128.3, 128.0, 127.9, 127.1, 126.7 (6d, ^1J(C,H) = 160 Hz); 107.1 (d, ^1J(C,H) = 175 Hz); 79.0, 71.0 (2d, ^1J(C,H) = 145 Hz); 67.5 (t, ^1J(C,H) = 145 Hz); 64.8 (d, ^1J(C,H) = 140 Hz); 57.7 (d, ^1J(C,H) = 155 Hz); 55.2 (q, ^1J(C,H) = 155 Hz); 52.5 (q, ^1J(C,H) = 160 Hz); 50.2 (t, ^1J(C,H) = 150 Hz); 29.6 (t, ^1J(C,H) = 130 Hz). MS (CI, NH_3) m/z: 448 (M^+ +19, 7), 447 (M^+ +18, 27), 446 (M^+ +17, 16), 431 (M^+ +2, 25), 430 (M^+ +1, 100), 429 (M^+, 52), 399 (10), 398 (41), 397 (13), 296 (23), 236 (6), 234 (11), 188 (12), 108 (16), 91 (50).

Methyl 2-(N-benzyl,N-benzyloxycarbonyl)amino-2,3-dideoxy-α- and β-D-*arabino*-hexofuranosides (**50** + **51**). A soln. of **48** + **49** (808 mg, 1.88 mmol) in dry THF (8 mL) was added dropwise to a stirred suspension of $LiBH_4$ (60 mg, 2.7 mmol) in dry THF (8 mL) under Ar atm. at 20°C. At the end of the reaction (TLC control, silica gel, EtOAc), the soln was neutralized with sat. aq. soln. of NH_4Cl and made slightly (pH ~5) acidic with 5% HCl. EtOAc (40 mL) was added and the two phases separated; the aq. one was extracted with EtOAc (20 mL, twice). The combined org. extracts were dried ($MgSO_4$), filtered and concentrated to afford 544 mg (72%) of **50** + **51**, colourless oil. The α/β ratio could not be determined, but the α-epimer **50** predominated. Characteristics of **50**: IR (CH_2Cl_2) v: 3500 (br.), 3050, 2980, 1695, 1465, 1420, 1250 (br.), 1100, 1040, 890 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.28 (m, Ph); 5.14 (br.s, CH_2(Cbz)); 5.00 (br.s, H-C(1)); 4.70, 4.36 (2d, *J* = 16.0 Hz, CH_2Ph); 4.29-3.42 (m, H_2-C(6), H-C(5), H-C(2)); 3.25 (s, Me), 2.08 (m, H_2-C(3)). ^{13}C-NMR (62.9 MHz) δ_C: 155.7, 137.9, 136.0 (3s); 128.5, 128.4, 128.0, 127.9, 127.2, 126.8 (6d, ^1J(C,H) = 160 Hz); 106.8 (d, ^1J(C,H) = 170 Hz); 78.6, 72.2 (2d, ^1J(C,H) = 145 Hz); 67.5 (t, ^1J(C,H) = 150 Hz); 65.8 (d, ^1J(C,H) = 145 Hz); 63.5 (t, ^1J(C,H) = 140 Hz); 55.2 (q, ^1J(C,H) = 140 Hz); 51.1 (d, ^1J(C,H) = 140 Hz); 29.8 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 419 (M^+ +18, 5), 403 (M^+ +2, 11), 402 (M^+ +1, 42), 371 (16), 370 (67), 369 (8), 280 (3), 269 (3), 268 (20), 266 (4), 250 (4), 236 (6), 234 (3), 108 (13), 106 (19), 92 (17), 91 (100).

Methyl 2-acetamido-5,6-di-O-acetyl-2,3-dideoxy-α- and β-D-*arabino*-hexofuranoside (**52** and (-)-**3**). Crude mixture of **50** + **51** (544 mg, 1.35 mmol was dissolved in MeOH (12 mL) and AcOH (2 mL) and stirred under H_2 atm. for 24 h in the presence of 10% Pd on charcoal (120 mg). At the end of the reaction (TLC control, silica gel, EtOAc) the mixture was filtered and concentrated in vacuo. The residue was dissolved in pyridine (5 mL) and Ac_2O (1 mL) together with 4-dimethylaminopyridine (10 mg, 0.08 mmol) and the soln. was stirred for 15 h. The solvent was distilled and FC (EtOAc) gave 349 mg (85%) of a mixture of **52** and (-)-**3**, colourless oil. Crystallization from light petroleum/Et_2O at -20°C, afforded a crystalline 3.4:1 mixture of (-)-**3**

and **52**. A second crystallization form Et_2O/EtOH at -20°C gave (60% yield for the recrystallization) pure (-)-**3**, colourless crystals, m.p. 134°C; lit.[26]: 141°C; $[\alpha]^{25}_D$ = -3, $[\alpha]^{25}_{546}$ = -3, $[\alpha]^{25}_{436}$ = -4, $[\alpha]^{25}_{365}$ = -4 (*c* = 0.5, $CHCl_3$); lit.[26]: $[\alpha]^{20}_D$ = -4.0 (c = 0.5, $CHCl_3$). IR (KBr) v: 3270 (br.), 3090, 3000, 2960, 2930, 1735, 1639, 1560, 1370, 1300, 1240, 1180 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 6.90 (d, *J* = 9.0 Hz, NH); 5.07 (ddd, *J* = 3.0, 6.0, 9.5 Hz, H-C(5)); 4.77 (d, *J* = 4.5 Hz, H-C(1)); 4.48 (dd, *J* = 3.0, 12.0 Hz, H-C(6)); 4.48 (ddd, *J* = 4.5, 8.0, 9.5 Hz, H-C(2)); 4.23 (ddd, *J* = 6.5, 9.5, 9.5 Hz, H-C(4)); 4.12 (dd, *J* = 6.0, 12.0 Hz, H'-C(6)); 3.40 (s, Me); 2.46 (ddd, *J* = 6.5, 8.0, 12.0 Hz, H_β-C(3)); 2.10, 2.07, 2.00, (3s, 3 Me); 1.64 (ddd, *J* = 9.5, 9.5, 12.0 Hz, H_α-C(3)). ^{13}C-NMR (62.9 MHz) δ_C: 170.7, 170.2, 169.8 (3s); 101.8 (d, ^1J(C,H) = 175 Hz); 76.2, 73.4 (2d, ^1J(C,H) = 150 Hz); 62.9 (t, ^1J(C,H) = 150 Hz); 55.0 (q, ^1J(C,H) = 145 Hz); 51.7 (d, ^1J(C,H) = 140 Hz); 32.0 (t, ^1J(C,H) = 135 Hz); 23.2, 20.9, 20.8 (3q, ^1J(C,H) = 130 Hz). MS (CI, NH_3) m/z: 305 (M^+ +2, 15), 304 (M^+ +1, 100), 303 (M^+, 77), 273 (10), 272 (69), 271 (29), 183 (13), 158 (11), 142 (2), 116 (3), 98 (3), 99 (2). Anal. calc. for $C_{13}H_{21}NO_7$ (303.31): C 51.48, H 6.98, N 4.62; found: C 51.58, H 7.03, N 4.65.

(±)-Methyl 2-acetamido-5,6-di-O-acetyl-2,3-dideoxy-α-DL-*arabino*-hexofuranoside ((±)-**52**). Crystallization of the crude mixture of (±)-**3**/(±)-**52** obtained by the above procedures from (±)-**46**, from Et_2O/EtOH at -20°C afforded pure (±)-**52**, colourless crystals. M.p. 99-100°C. IR (KBr) v: 3270 (br.), 3090, 3000, 2960, 2930, 1735, 1630, 1560, 1450, 1370, 1300, 1240, 1180 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 6.00 (d, *J* = 7.0 Hz, NH); 5.14 (ddd, *J* = 3.0, 6.5, 6.5 Hz, H-C(5)); 4.83 (s, H-C(1)); 4.40 (dd, *J* = 3.0, 12.0 Hz, H-C(6)); 4.30 (dd, *J* = 2.0, 7.5 Hz, H-C(2)); 4.23 (ddd, *J* = 2.0, 4.5, 9.0 Hz, H-C(4)); 4.14 (dd, *J* = 6.5, 12.0 Hz, H'-C(6)); 3.33 (s, OMe), 2.49 (ddd, *J* = 7.5, 9.0, 14.0 Hz, H_α-C(3)); 2.14 (s, Me); 2.07 (s, Me); 1.99 (s, Me); 1.60 (ddd, *J* = 2.0, 4.5, 14.0 Hz, H_β-C(3)). ^{13}C-NMR (62.9 MHz) δ_C: 170.6, 170.5, 169.6 (3s); 108.2 (d, ^1J(C,H) = 175 Hz); 75.6, 72.6 (2d, ^1J(C,H) = 150 Hz); 63.0 (t, ^1J(C,H) = 150 Hz); 54.7 (q, ^1J(C,H) = 145 Hz); 54.5 (d, ^1J(C,H) = 150 Hz); 31.2 (t, ^1J(C,H) = 135 Hz); 23.2, 21.1, 20.9 (3q, ^1J(C,H) = 130 Hz). MS (CI, NH_3) m/z: 305 (M^+ +2, 15), 304 (M^+ +1, 100), 303 (M^+, 77), 273 (10), 272 (69), 271 (29), 183 (13), 158 (11), 116 (3), 99 (3), 84 (3). Anal. calc. for $C_{13}H_{21}NO_7$ (303.31): C 51.48, H 6.98, N 4.62; found: C 51.53, H 6.92, N 4.69.

(1*RS*,2*SR*,4*SR*)-6-Bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl trifluoromethanesulfonate (**54**). A soln. of Tf_2O (4.2 mL, 25 mmol) in dry CH_2Cl_2 (34 mL) was added dropwise to a soln. of dry pyridine (2.5 mL) in dry CH_2Cl_2 (68 mL) cooled to -10°C and stirred under Ar atm. The mixture was stirred for an additional 10 min. and a soln. of (±)-**53** (2.869 g, 15.02 mmol)[25] was added dropwise. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 7:3) the soln. was transferred in a separatory funnel containing H_2O (150 mL) and ice. The two phases were separated and the aq. one was extracted with CH_2Cl_2 (150 mL). The combined org. layers were washed successively with sat. aq. soln. of $NaHCO_3$ (50 mL), ice-cooled H_2O (100 mL) and brine (200 mL), dried ($MgSO_4$), filtered through basic alumina (Merck I) and concentrated under reduced pressure at 20°C, yielding 3.157 g (65%) of a yellow oil which solidified on standing at -20°C. The product was used without further purification. IR (KBr) v: 3040, 3000, 2960, 1580, 1410, 1360, 1290, 1245, 1210, 1135, 1050, 1025, 1000, 970, 910, 880, 865, 850, 820, 805, 775, 760, 715 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 6.72 (d, *J* = 2.0 Hz, H-C(5)); 5.47 (ddd, *J* = 2.0, 4.5, 8.0 Hz, H-C(2)); 5.04 (dd, *J* = 2.0, 4.5 Hz, H-C(4)); 5.00 (d, *J* = 4.5 Hz, H-C(1)); 2.50 (ddd, *J* = 4.5, 8.0, 12.5 Hz, H_{exo}-C(3)); 1.60 (dd, *J* = 2.0, 12.5 Hz, H_{endo}-C(3)).

(1*RS*,4*SR*,6*RS*)-6-*exo*-Benzyloxy-2-bromo-7-oxabicyclo[2.2.1]hept-2-ene (**55**). 1.6M BuLi in hexane (1.5 mL, 2.4 mmol) was added dropwise to a soln. of BnOH (0.25 mL, 98%, 2.4 mmol) in dry THF (2 mL) cooled to -78°C. A soln. of **54** (508 mg, 1.57 mmol) in dry THF (2 mL) and dry hexamethylphosphortriamide (2 mL) was added dropwise. The mixture was allowed to warm to 20°C and stirred overnight. The org. phase was diluted with Et_2O, washed 3 times with H_2O and once with brine, dried ($MgSO_4$) filtered and concentrated in vacuo. FC (light petroleum/EtOAc 9:1) gave 258 mg (59%) of a colourless oil that crystallized on standing. A portion of the product was recrystallized from light petroleum for analysis. M.p. 40°C. IR (KBr) v: 3060, 3020, 3000, 2950, 2900, 2860, 1580, 1500, 1450, 1350, 1280 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.36 (m, Ph); 6.42 (d, *J* = 2.0 Hz, H-C(3)); 5.01 (ddd, *J* = 1.0, 2.0, 4.0 Hz, H-C(4)); 4.77 (d, *J* = 1.0 Hz, H-C(1)); 4.70 (AB syst., -CH_2Ph); 3.91 (dd, *J* = 2.5, 6.5 Hz, H-C(6)); 2.91 (dd, *J* = 2.5, 6.5 Hz, H_{exo}-C(5)); 1.75 (ddd, *J* = 2.5, 4.0, 12.0 Hz, H_{endo}-C(5)). ^{13}C-NMR (62.9 MHz) δ_C: 137.6 (s); 137.6 (d, ^1J(C,H) = 180 Hz); 128.4, 127.8, 127.7 (3d, ^1J(C,H) = 160 Hz); 123.9 (s), 86.0 (d, ^1J(C,H) = 170 Hz); 79.6 (d, ^1J(C,H) = 165 Hz); 77.5 (d, ^1J(C,H) = 155 Hz); 71.8 (t, ^1J(C,H) = 145 Hz); 34.6 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 300 (M^+ +18, 58), 299 (10), 298 (57), 222 (2), 221 (3), 220 (7), 191 (1), 189 (6), 188 (1), 148 (2), 146 (2), 134 (3), 116 (5), 108 (13), 106 (4), 105 (5), 92 (9), 91 (100). Anal. calc. for $C_{13}H_{13}BrO_2$ (281.15): C 55.54, H 4.66, Br 28.42; found: C 55.67, H 4.47, Br 28.36.

N-Benzyl-N-[(1*RS*,2*RS*,4*SR*)-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl]amine (**56**). A mixture of **54** (2.755 g, 8.53 mmol) and $BnNH_2$ (2.0 mL, 18 mmol) in DMF (40 mL) was stirred at 60°C for 12 h and then diluted with Et_2O (100 mL) and 5% aq. Na_2CO_3 (50 mL). The two phases were separated and the aq. one was extracted with Et_2O (50 mL). The combined org. layers were washed with H_2O (50 mL, twice) and then with

brine (50 mL), dried ($MgSO_4$), filtered and concentrated in vacuo to afford a brown oil. FC (toluene/EtOAc 1:1) gave (1.735 g) of a 10:1 mixture of **56** and **53**. A portion of the oil was crystallized form light petroleum/Et_2O at -20°C to give an analytical sample. M.p. 54-55°C. IR (KBr) ν: 3280 (br.), 3050, 3030, 2920, 2880, 1650, 1530, 1500, 1450, 1385, 1350, 1240, 1125, 1080, 1030, 755, 740, 695 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.31 (m, Ph); 6.34 (d, J = 2.0 Hz, H-C(3)); 4.93 (ddd, J = 1.0, 2.0, 4.5 Hz, H-C(4)); 4.65 (d, J = 1.0 Hz, H-C(1)); 3.85 (AB syst., J_{gem} = 13.0 Hz, -CH_2Ph); 3.04 (dd, J = 3.0, 7.5 Hz, H-C(6)); 1.88 (dd, J = 7.5, 12.0 Hz, H_{endo}-C(5)); 1.44 (ddd, J = 3.0, 4.5, 12.0 Hz, H_{exo}-C(5)). MS (CI, NH_3) m/z: 280 (M^+, 0.04), 136 (18), 135 (67), 134 (29), 133 (4), 132 (2), 118 (6), 117 (3), 116 (2), 107 (7), 106 (44), 105 (2), 104 (7), 92 (19), 91 (100), 90 (9), 89 (13), 80 (3), 79 (36), 78 (13), 77 (37), 75 (2), 74 (6).

Benzyl N-benzyl,N-[(1*RS*,2*RS*,4*SR*)-6-bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*exo*-yl]carbamate (**57**). Benzyl chloroformate (1.1 mL, 90-95%, ~7.0 mmol) was added dropwise to a stirred soln. of **56** (1.730 g, 6.17 mmol) and $NaHCO_3$ (1.30 g, 15.5 mmol) in EtOH (23 mL) and H_2O (14 mL). At the end of the reaction (TLC control, silica gel, toluene/EtOAc 7:3) the mixture was diluted with CH_2Cl_2 (50 mL) and washed successively with 5% aq. Na_2CO_3 (25 mL, twice), H_2O (25 mL) and brine (30 mL), dried ($MgSO_4$), filtered and concentrated in vacuo to afford a brown oil. FC (silica gel, toluene/EtOAc 9:1) gave 2.05 g (80%), pale yellow oil. IR (CH_2Cl_2) ν: 3080, 3060, 3010, 3020, 2950, 1700, 1580, 1495, 1450, 1415, 1335, 1305, 1285, 1260, 1240, 1220, 1175, 1135, 1110, 1070, 1025, 975, 925, 900, 870, 860, 805, 790, 750, 730, 695 cm^{-1}. ^{1}H-NMR (250 MHz) δ_H: 7.28 (m, Ph); 6.38 (d, J = 2.0 Hz, H-C(5)); 5.18 (m, -CH_2-(Cbz)); 4.95 (ddd, J = 1.5, 4.0, 4.0 Hz, H-C(2)); 4.71-4.51 (m, -CH_2(OBn) + H-C(4)); 4.54 (d, J = 1.0 Hz, H-C(1)); 1.90 (m, H_{endo}-C(3)); 1.67 (ddd, J = 4.0, 4.0, 12.0 Hz, H_{exo}-C(3)). MS (CI, NH_3) m/z: 414 (M^+, 0.15), 267 (2), 176 (5), 132 (6), 108 (1), 107 (2), 106 (1), 105 (2), 104 (1), 92 (9), 91 (100), 89 (3), 79 (2), 78 (1), 77 (4).

References and Notes

1. Enantiomerically Pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl Derivatives ("Naked Sugars") as Synthetic Intermediates, Part XX. For Part XIX, see: Fattori, D.; Vogel P., preceding paper.
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