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TOTAL ASYMMETRIC SYNTHESES OF 3- AND 4-DEOXY-HEXOSES AND DERIVATIVES.[1]

Daniela Fattori and Pierre Vogel*
Section de chimie de l'Université de Lausanne, 2, rue de la Barre, CH 1005 Lausanne, Switzerland

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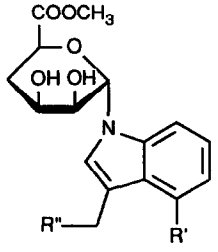
Summary: *(1S,4S)-7-Oxabicyclo[2.2.1]hept-5-en-2-one ((-)-5, a "naked sugar") has been converted to (-)-(1R,4S,6S)-6-endo-benzyloxy-2-bromo-7-oxabicyclo[2.2.1]hept-2-ene ((-)-12) in a highly stereoselective fashion. Double hydroxylation of the C=C double bond of (-)-12, followed by acetylation and Baeyer-Villiger oxidation of the resulting α-acetoxyketone (-)-14 afforded (-)-5-O-acetyl-2-O-benzyl-3-deoxy-β-D-arabino-hexofuranurono-6,1-lactone ((-)-15). This compound was converted readily into (+)-methyl 3-deoxy-α-D-arabino-hexofuranoside ((+)-6) and (+)-methyl 3-deoxy-β-L-xylo-hexofuranoside ((+)-7) and partially protected derivatives. (-)-15 was also converted into 4-deoxy-D-lyxo-hexopyranose (34) and several partially protected derivatives such as (+)-methyl 4-deoxy-2,3-O-isopropylidene-α-D-lyxo-hexopyranoside ((+)-8).*

Among the deoxy-hexoses, the most frequently occurring in Nature are the 2-deoxy, 6-deoxy and 2,6-dideoxy-hexoses. They are, for instance, components of cardiac glycosides, of antibiotics and of antigenic determinants in bacteria.[2] In contrast, the 3-deoxy and 4-deoxy-hexoses are rare compounds. They are extremely useful tools in the study of biological and biochemical properties of mono-[3] and oligosaccharides,[4] of glycoproteins[5] and glycolipids,[6] and of antibodies.[7] Because some pathogenic bacteria are able of deactivating aminoglycoside antibiotics such as kanamycin or neomycin through phosphorylation at C(3') of the aminocyclitol glycosides,[8] antibiotics incorporating the corresponding 3'-deoxy-glycosides are of medicinal significance.[9] Recently, Buchanan and co-workers[10] have recognized methyl 4-deoxy-D-*lyxo*-hexopyranuronate to be the sugar part of neosidomycin (**1**) and SF-2140 (**2**), two indole nucleoside antibiotics.[11]

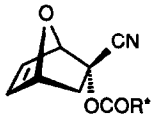


1: R'=H, R"=$CONH_2$
2: R'=OCH_3, R"=CN

One usual approach to the synthesis of 3-deoxy and 4-deoxy-D-hexoses is the selective deoxygenation and natural D-hexoses. The method implies selective protection of the hydroxy groups (or

other functions) at C(1), C(2), C(4) or C(3), C(5) and C(6). Deoxygenation of the remaining unprotected alcohol moiety can be achieved following a large variety of protocols such as hydride reduction of the corresponding tosylate (para-toluenesulfonate)[12] or triflate (trifluoromethanesulfonate),[13] Barton and McCombie[14] radical deoxygenation,[4d,15] halogenation followed by reductive dehalogenation,[7b,16] Na/NH_3 reduction of corresponding O-N,N-dimethylsulfamoyl derivatives,[17] photo-induced[18] or radical-induced reduction[19] of corresponding O-acetyl or O-pivaloyl derivatives,[20] or Raney-nickel desulfurization of corresponding thiosugars.[7c,21] The unprotected alcohol moiety can also be oxydized to the corresponding ulose whose tosylhydrazone can be reduced.[21] Other approaches involve reduction of 2,3-anhydro-hexose derivatives,[23] double hydroxylation[24] or hydrogenation of carbohydrate derived olefins,[25] the Kiliani-Fischer homologation of 2-deoxy and 3-deoxy-pentoses[5a,26] or the cross-aldolisation of 1,1-dimethoxypropan-2-one with O-isopropylidene-D-glyceraldehyde.[27] Chmielewski[28] has prepared the four 3-deoxy-DL-*arabino*, -*ribo*, -*lyxo* and -*xylo*-hexoses via epoxidation of n-butyl 2-hydroxy-6-oxohex--4(E)-enoate. The 3-deoxy-DL-*lyxo* and -*xylo*-hexoses have been prepared via epoxidation of (±)-dihydropyranyl derivatives.[29]

In 1988, Boger and Robarge[30] derived 4-deoxy-DL-*lyxo*-hexose from the hetero-Diels-Alder adduct of methyl 4-methoxy-2-oxobut-3(E)-enoate to (Z)-2-benzyloxyvinyl acetate. Earlier, Danishefsky and co-workers[31] had prepared 4-deoxy-DL-*lyxo* and -*xylo*-hexoses via a Lewis-acid-catalysed hetero-Diels-Alder addition of benzyloxyethanol to (E)-1-methoxy-3-(trimethylsilyl)oxybutadiene. This cycloaddition can be carried out with high enantioselectivity using optically pure europium complexes as catalyst.[32] Wong and co-workers[33] prepared 3-deoxy-D-*ribo*-hexose applying an enzymatic process that combined fructose diphosphate aldolase and glucose isomerase. Fuganti and co-workers[34] obtained 4-deoxy-D-*lyxo*-hexose via a baker's yeast enantioselective reduction of (±)-6,7-isopropylidene-dioxy-4-oxo-1-phenylhept-1(E)-en-3-yl acetate.



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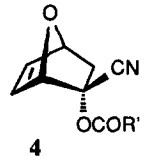

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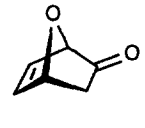
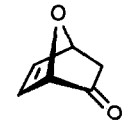


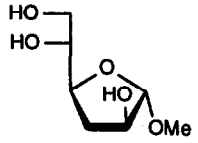
(+)-**5** (1*R*,4*R*)



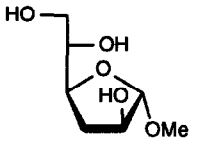
(-)-**5** (1*S*,4*S*)

When deoxy-L-hexoses have to be prepared, the methods starting from common natural carbohydrates may not be economical. In these cases, synthesis using other chiral, non-carbohydrate precursors or total, asymmetric synthesis starting from a chiral compounds might represent suitable alternatives. Optically pure 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives **3**, **4**, (+)-**5** and (-)-**5** can be obtained readily via Diels-Alder addition of furan to 1-cyanovinyl esters.[35] These systems have been shown to be useful chirons for the preparation of natural products and complicated compounds of biological interest.[36] We report here on the conversion of (-)-**5** into methyl 3-deoxy-D-*arabino*-hexofuranoside ((+)-**6**),[37] methyl 3-deoxy-L-*xylo*-hexofuranoside ((+)-**7**) and methyl 4-deoxy-2,3-O-isopropylidene-α-D-

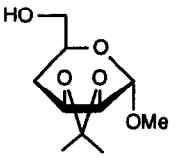
lyxo-hexopyranoside ((+)-**8**)[37] and derivatives.



(+)-**6**



(+)-**7**

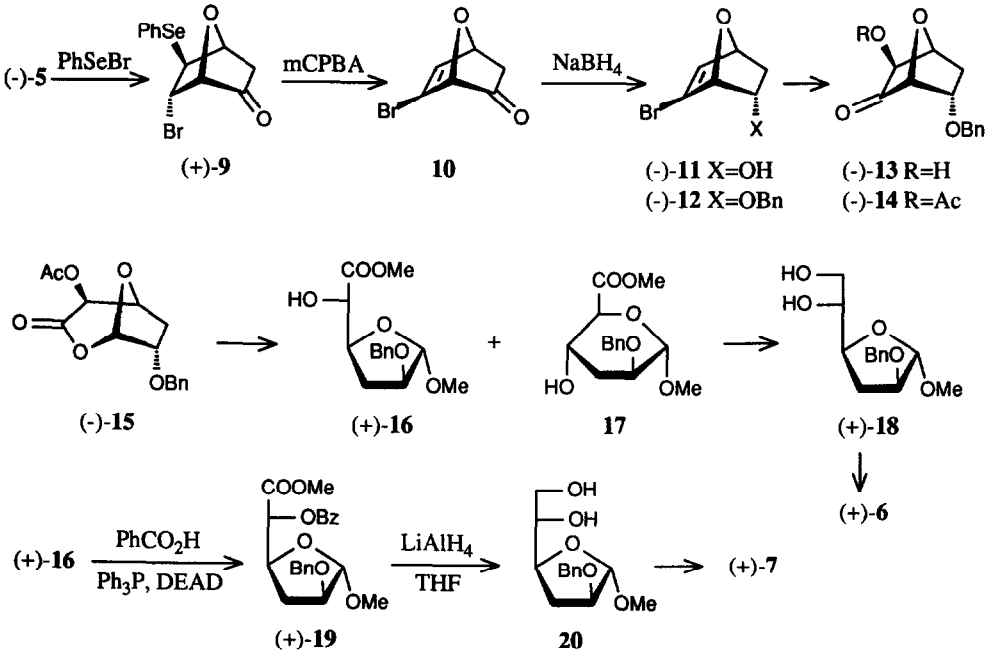


(+)-**8**

Results and Discussion

Addition of benzeneselenyl bromide to enone (-)-**5** gave adduct (+)-**9** nearly quantitatively.[38] The high regioselectivity of this *anti* addition was interpreted in terms of electron-releasing homoconjugated carbonyl group due to favourable n(CO) ↔ σ(C(1),C(2)) ↔ π(C(6)) through-bond interaction that makes 6-oxo-7-oxabicyclo[2.2.1]hept-2-yl cation more stable than 5-oxo-7-oxabicyclo[2.2.1]hept-2-yl cation limiting structure.[39] Treatment of (+)-**9** with mCPBA (metachloroperbenzoic acid) in CH_2Cl_2 afforded unstable bromoenone **10** (91%) whose reduction with $NaBH_4$ in MeOH at 0°C was highly stereoselective giving *endo* alcohol (-)-**11** in 95% yield. Attempts to carry out a double hydroxylation of the olefinic moiety

Scheme 1

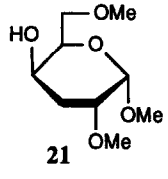


in (-)-**11** failed to give the expected α-hydroxyketone and led to complete decomposition, probably because of possible retro-aldolisation and subsequent fragmentation. However, protection of the *endo* alcoholic

function as a benzylic ether gave (-)-**12** (83%) whose treatment with an excess of 30% H_2O_2 and a catalytic amount of OsO_4 produced (-)-**13** (99%). Baeyer-Villiger oxidation of (-)-**13** gave the desired furanurono-6,1-lactone in mediocre yield (46%). We thus converted the α-hydroxyketone (-)-**13** into the corresponding acetate (-)-**14** which then underwent smooth oxidation with mCPBA/$NaHCO_3$ in CH_2Cl_2 giving the fully protected 3-deoxy-β-D-furanurono-6,1-lactone (-)-**15** (85%). The high regioselectivity of this reaction is not fully understood yet, but it is the same as that observed for the Baeyer-Villiger oxidation of several 7-oxabicyclo[2.2.1]heptan-2-ones with various substituents at C(3).[36a,40]

Acidic methanolysis of (-)-**15** gave uronate (+)-**16** (86%) in which the alcoholic moiety at C(5) is unprotected. The ^{1}H-NMR spectrum of (-)-**16** showed that this α-D-furanoside is contaminated by about 8% of the corresponding methyl α-D-pyranoside **17**. Reduction of (+)-**16** with $LiAlH_4$ in ether afforded (+)-**18** (75%) whose hydrogenolysis over 5% Pd on charcoal furnished the known furanoside (+)-**6**.[41]

Inversion of configuration of centre C(5) in methyl uronate (+)-**16** was carried out by the Mitsunobu[42] technique ($PhCO_2H$, Ph_3P, EtOOCN=NCOOEt) that yielded (+)-**19** (52%). Reduction of this diester with $LiAlH_4$ in THF afforded the partially protected methyl 3-deoxy-α-L-*xylo*-hexopyranoside **20**. Catalytic hydrogenation of **20** produced (+)-**7**, a 4-deoxy-L-hexose that had never been described yet. However, derivatives **21**,[15e] **22**,[15g,43c,d] **23**,[7b] **24α**[23c,43a] and **24β**[43b] with the D-configuration have been reported.



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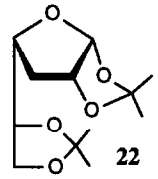

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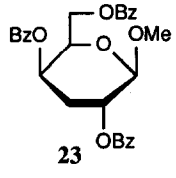

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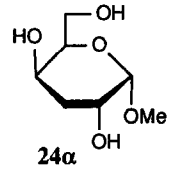
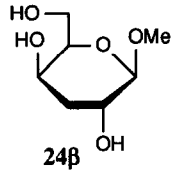


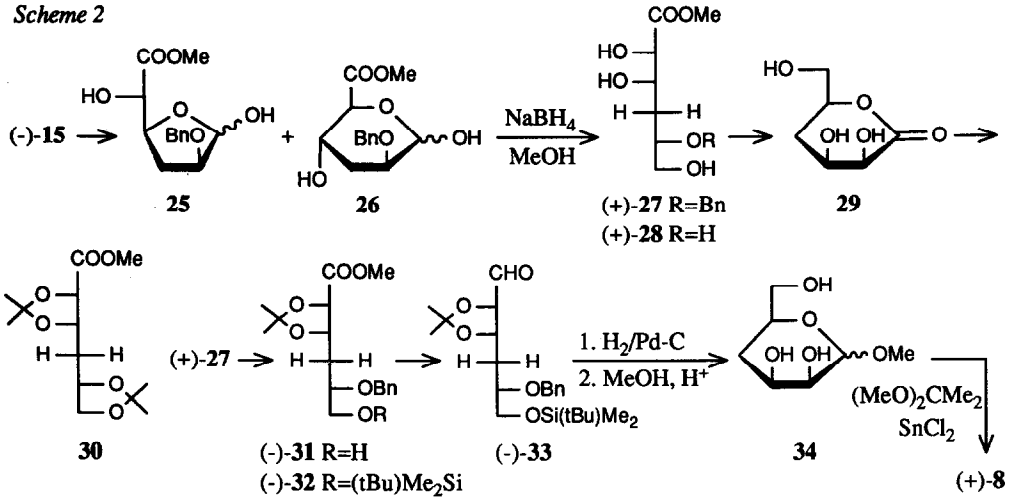
24α



24β

When alkaline rather than acidic methanolysis was applied to urono-6,1-lactone (-)-**15**, a mixture of the furanuronate and pyranuronate **25** + **26** was formed. Without isolation, this mixture was reduced with $NaBH_4$ in MeOH affording methyl 5-O-benzyl-4-deoxy-D-*lyxo*-hexonate ((+)-**27**) in 83% yield. Debenzylation (H_2/Pd-C) of (+)-**27** gave (+)-**28**, then acidic treatment (e.g.: CF_3COOH) yielded the corresponding aldonolactone **29**. Attempts to achieve a selective acetalisation of the vicinal diol moiety of **29** with acidic acetone failed to produce the expected 2,3-O-isopropylidene derivative. Treatment of **29** with $(MeO)_2CMe_2/SnCl_2$ led to the completely protected 4-deoxy-D-*lyxo*-hexonate **30** which was also obtained in one step from (+)-**28** under the same conditions. Other partially or completely protected forms of this sugar were obtained in the following way. Treatment of (+)-**27** with $(MeO)_2CMe_2/SnCl_2$ yielded (-)-**31** which was then fully protected into (-)-**32** on treatment with (tBu)Me_2SiCl/imidazole. Reduction of the ester moiety of (-)-**32** with DIBAH (toluene, -65°C) produced (-)-**33** which furnished **34** by catalytic hydrogenolysis (Pd-C/MeOH, 48 h) and boiling with acidic MeOH (Dowex). This treatment removed the acetonide and silyl protective groups. The methyl pyranosides **34** were converted into the known[15b,44] derivative (+)-**8** by treatment with $(MeO)_2CMe_2/SnCl_2$.

Scheme 2



Conclusion

Compared with classical synthetic methods using natural carbohydrates as starting materials, our approach to the total synthesis of rare 3-deoxy- and 4-deoxy-hexoses presents certain advantages: a) since both starting enones (+)-**5** and (-)-**5** ("naked sugars") are readily available from the Diels-Alder addition of furan to optically pure 1-cyanovinyl esters, both enantiomeric forms of a given targeted compound can be attained with the same ease, the chiral auxiliaries[35] (R*COOH and R'COOH, see **3** and **4**) being recovered at an early stage of the synthesis; b) protected or partially protected polyfunctional systems with different protective groups can be obtained selectively; c) these compounds can be viewed as potential precursors for the synthesis of more complicated systems incorporating a high density of stereochemical information.

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Experimental Part.

General remarks, see ref. 45.

(+)-(1*R*,4*S*,5*S*,6*S*)-5-*exo*-Benzeneselenyl-6-*endo*-bromo-7-oxabicyclo[2.2.1]heptan-2-one ((+)-**9**). A solution of benzeneselenyl bromide (17.79 g, 75.38 mmol) in $CHCl_3$ (60 mL) was added dropwise to a solution of (-)-**5** (8.30 g, 75.38 mmol) in $CHCl_3$ (50 mL) stirred under Ar atm. and cooled to 0°C. The mixture was stirred for one additional hour at 0°C and then allowed to warm to 20°C. After complete disappearance of (-)-**5** (TLC control; silica gel, light petroleum/EtOAc 8:2), the yellow solution was diluted with $CHCl_3$ (100 mL), washed with 5% aq. Na_2CO_3 (100 mL, twice), H_2O (60 mL, twice) and then with brine (50 mL), dried ($MgSO_4$), filtered and concentrated to give a pale yellow solid. The solid was washed with light petroleum to

give 21.16 g (81%) of yellow crystals. A small portion of the product was recrystallized from Et_2O/light petroleum to give an analytical sample, m.p. 71.5-72.5°C. $[\alpha]^{25}_D$ = +34, $[\alpha]^{25}_{578}$ = +36, $[\alpha]25_{546}$ = +41, $[\alpha]^{25}_{436}$ = +75, $[\alpha]^{25}_{365}$ = +134 (*c* = 1.5, $CHCl_3$). IR (CH_2Cl_2) ν: 3040, 3000, 1765, 1570, 1470, 1430, 1400, 1300, 1225, 1155, 1130, 1095, 1065, 1020, 1000, 935, 880, 830 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.61, 7.32 (m, Ph); 4.94 (d, H-C(4), *J* = 6.0 Hz); 4.42 (d, H-C(1), *J* = 5.5 Hz), 4.14 (dd, H-C(6), *J* = 3.0, 5.5 Hz); 2.70 (dd, H_{exo}-C(3), *J* = 6.0, 18.0 Hz); 2.23 (d, H_{endo}-C(3), *J* = 18.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 204.1 (s), 134.7 (d, ^1J(C,H) = 160 Hz), 129.5 (d, ^1J(C,H) = 165 Hz); 128.5 (d, ^1J(C,H) = 160 Hz), 128.0 (s); 82.7 (d, ^1J(C,H) = 170 Hz); 82.4 (d, ^1J(C,H) = 170 Hz), 51.3 (d, ^1J(C,H) = 155 Hz); 44.3 (d, ^1J(C,H) = 165 Hz), 42.8 (t, ^1J(C,H) = 135 Hz). MS (70 eV) m/z: 348 (M^++2, 5), 346 (M^+, 7), 345 (1), 344 (3), 236 (1), 225 (3), 223 (2), 191 (4), 189 (3), 159 (5), 158 (8), 157 (23), 155 (11), 154 (5), 153 (5), 119 (3), 117 (4), 116 (3), 115 (5), 109 (8), 82 (7), 81 (100), 78 (10), 77 (22), 68 (18), 53 (35), 51 (29), 50 (14). Anal. calc. for $C_{12}H_{11}BrO_2Se$ (346.08): C 41.65, H 3.20; found: C 41.64, H 3.26.

(±)-(1*RS*,4*SR*,5*SR*,6*SR*)-5-*exo*-Benzeneselenyl-6-*endo*-bromo-7-oxabicyclo[2.2.1]heptan-2-one ((±)-**9**). Same procedure as for (+)-**9**, starting with (±)-**5**, m.p. 65-66°C.

(1*R*,4*S*)-6-Bromo-7-oxabicyclo[2.2.1]hept-5-en-2-one (**10**). A solution of mCPBA (Fluka, pur. 50-60%, 4.62 g, ~14.4 mmol) in CH_2Cl_2 (100 mL) was added dropwise to a solution of (+)-**9** (5.00 g, 14.4 mmol) in CH_2Cl_2 (100 mL) stirred under Ar atm. and cooled to -78°C. After complete disappearance of the starting material (TLC control, silica gel, light petroleum/EtOAc 7:3), the mixture was allowed to warm to 20°C and stirred for an additional 5 h. The solution was then washed with 5% aq. Na_2CO_3 soln. (30 mL, 3 times), H_2O (20 mL, twice) and then with brine (30 mL) and finally dried ($MgSO_4$). Solvent distillation under atmospheric pressure left a yellow oil which was purified by column chromatography on silica gel (light petroleum/EtOAc 7:3) to give 2.50 g (91%), colourless, unstable oil. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 6.75 (d, H-C(5), *J* = 2.0 Hz); 5.36 (dd, H-C(4), *J* = 2.0, 4.0 Hz); 4.35 (s, H-C(1)); 2.29 (dd, H_{exo}-C(3), *J* = 4.0, 16.0 Hz); 2.00 (d, H_{endo}-C(3), *J* = 16.0 Hz). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 204.9 (s), 139.8 (d, ^1J(C,H) = 180 Hz), 122.6 (s), 85.9 (d, ^1J(C,H) = 175 Hz), 81.0 (d, ^1J(C,H) = 175 Hz), 33.4 (t, ^1J(C,H) = 138 Hz).

(-)-(1*R*,2*S*,4*S*)-6-Bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol ((-)-**11**). A solution of **10** (2.50 g, 13.2 mmol) in MeOH (20 mL) was cooled to 0°C and $NaBH_4$ (450 mg, 11.9 mmol) was added portionwise under stirring. The mixture was stirred for an additional hour, then neutralized with ice-cool 10% HCl, concentrated to 10 mL, diluted with CH_2Cl_2 (40 mL), washed with H_2O (20 mL) and then with brine (10 mL, twice). The combined aq. layers were extracted with CH_2Cl_2(10 mL, 7 times). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuo to give 2.39 g (95%) of a colourless oil, which crystallized on standing. A portion of the product was crystallized from light petroleum to give an analytical sample, m.p. 66.5-67.5°C. $[\alpha]^{25}_D$ = -80, $[\alpha]^{25}_{578}$ = -83, $[\alpha]^{25}_{546}$ = -96, $[\alpha]^{25}_{436}$ = -179, $[\alpha]^{25}_{365}$ = -316 (*c* = 1.5, CH_2Cl_2). IR (CH_2Cl_2) ν: 3590, 3450 (br.), 3000, 2940, 1575, 1440, 1380, 1265 (br.) 1205, 1125, 1065, 1050, 1015, 965, 920, 900, 870, 850, 810 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 6.64 (d, H-C(5), *J* = 2.0 Hz); 4.95 (dd, H-C(4), *J* = 2.0, 5.0 Hz,); 4.76 (d, H-C(1), *J* = 4.5 Hz); 4.61 (ddd, H-C(2), *J* = 2.5, 4.5, 8.0 Hz); 2.30 (ddd, H_{exo}-C(3), *J* = 5.0, 8.0, 12.0 Hz); 1.20 (dd, H_{endo}-C(3), *J* = 2.5, 12.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 135.9 (d, ^1J(C,H) = 170 Hz), 122.5 (s), 83.6 (d, ^1J(C,H) = 165 Hz), 81.4 (d, ^1J(C,H) = 155 Hz), 69.1 (d, ^1J(C,H) = 155 Hz), 35.1 (t, ^1J(C,H) = 135 Hz). MS (70 eV) m/z: 190 (0.22), 188 (0.18), 161 (1), 159 (1), 149 (5), 148 (96), 147 (5), 146 (100), 131 (1), 119 (4), 117 (3), 111 (15), 82 (3), 81 (5), 65 (5), 63 (3), 55 (6), 54 (2), 53 (17), 52 (5), 51 (15), 50 (9). Anal. calc. for $C_6H_7BrO_2$: C 37.73, H 3.69; found: C 37.63, H 3.61.

(±)-(1*RS*,2*SR*,4*SR*)-6-Bromo-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol ((±)-**11**). Same procedure as for (-)-**11**, starting with (±)-**9**. Colourless oil that could not be crystallized.

(-)-(1*R*,4*S*,6*S*)-6-*endo*-Benzyloxy-2-bromo-7-oxabicyclo[2.2.1]hept-2-ene ((-)-**12**). A solution of (-)-**11** (340 mg, 1.78 mmol) in dry THF (4 mL) was added dropwise to a suspension of sodium hydride (87 mg, 50% oil suspension, 1.8 mmol) in dry THF (4 mL) under stirring at 0°C and under N_2 atm. The mixture was stirred until the production of H_2 ceased, then allowed to warm to 20°C. Tetrabutylammonium iodide (65 mg, 0.18 mmol) and benzyl bromide (0.21 mL, 1.8 mmol) were added. After stirring for 4 h, the mixture was diluted

with Et_2O (25 mL) and washed with H_2O (5 mL, twice), and then with brine (10 mL). The aq. layers were extracted with Et_2O (20 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated in vacuo to give 415 mg (83%) of a white solid. A portion of the product was crystallized form light petroleum to give an analytical sample, m.p. 84-84.5°C. $[\alpha]^{25}_D$ = -121, $[\alpha]^{25}_{578}$ = -126, $[\alpha]^{25}_{546}$ = -145, $[\alpha]^{25}_{436}$ = -260, $[\alpha]^{25}_{365}$ = -437 (*c* = 1.5, CH_2Cl_2). IR (CH_2Cl_2) ν: 3050, 3000, 2950, 2880, 2860, 1580, 1490, 1450, 1340, 1270 (br.), 1180, 1150, 1090, 1020 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.35 (m, Ph); 6.58 (d, H-C(2), *J* = 2.0 Hz); 4.92 (m, H-C(1) + H-C(4)); 4.67 (d, -C*H*HPh, *J* = 11.5 Hz); 4.51 (d, -CH*H*Ph, *J* = 11.5 Hz); 4.34 (dd, H-C(6), *J* = 2.5, 7.5 Hz); 2.24 (ddd, H_{exo}-C(5), *J* = 4.5, 7.5, 12.0 Hz); 1.30 (dd, H_{endo}-C(5), *J* = 2.5, 12.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 137.7 (s), 135.3 (d, ^1J(C,H) = 180 Hz), 128.3 (d, ^1J(C,H) = 160 Hz), 127.7 (d, ^1J(C,H) = 160 Hz); 127.6 (d, ^1J(C,H) = 160 Hz), 122.7 (s), 82.5 (d, *J* = 165 Hz), 81.1 (d, ^1J(C,H) = 165 Hz), 76.1 (d, ^1J(C,H) = 150 Hz), 72.6 (t, ^1J(C,H) = 140 Hz), 33.0 (t, ^1J(C,H) = 135 Hz). MS (70 eV) m/z: 191 (M^+ -91, 7), 190 (1), 189 (7), 149 (2), 148 (1), 147 (2), 146 (1), 134 (3), 116 (2), 106 (2), 105 (4), 92 (8), 91 (100), 90 (1), 89 (3), 82 (6), 81 (4), 65 (15). Anal. calc. for $C_{13}H_{13}BrO_2$ (281.15): C 55.54, H 4.66, O 11.38; found: C 55.59, H 4.71, O 11.41.

(±)-(1*RS*,4*SR*,6*SR*)-6-*endo*-Benzyloxy-2-bromo-7-oxabicyclo[2.2.1]hept-2-ene ((±)-**12**). Same procedure as for (-)-**12**, starting with (±)-**11**, m.p. 73-74°C.

(-)-(1*R*,3*S*,4*S*,6*S*)-6-*endo*-Benzyloxy-3-*exo*-hydroxy-7-oxabicyclo[2.2.1]heptan-2-one ((-)-**13**). To a solution of (-)-**12** (1.00 g, 3.56 mmol) in THF (100 mL) cooled to 0°C, $NaHCO_3$ (600 mg, 7.14 mmol), OsO_4 (5 drops of a 2.5% soln. in CCl_4), 30% H_2O_2 (5 mL, 44 mmol) were added in succession. The solution became yellow. After 2 h, it was allowed to warm to 20°C and stirred until disappearance of the yellow colour. The solution was concentrated at reduced pressure to 50 mL, diluted with EtOAc (100 mL), washed with 5% aq. Na_2SO_3 (35 mL, 3 times), then with brine (20 mL), and dried ($MgSO_4$). Removal of the solvent in vacuo gave 822 mg (99%) of a thick oil which solidified on standing. An analytical sample was obtained by recrystallization from light petroleum/Et_2O, m.p. 88-89°C. $[\alpha]^{25}_D$ = -38, $[\alpha]^{25}_{578}$ = -40, $[\alpha]^{25}_{546}$ = -47, $[\alpha]^{25}_{436}$ = -98, $[\alpha]^{25}_{365}$ = -235 (*c* = 1.5, CH_2Cl_2). IR (CH_2Cl_2) ν: 3550, 3400 (br.),. 3040, 2910-2860, 1770, 1450, 1175, 1070, 1020, 990, 950 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.29 (m, Ph); 4.64 (d, H-C(4), *J* = 6.0 Hz); 4.55 (d, -C*H*HPh, *J* = 11.5 Hz); 4.48 (d, H-C(1), *J* = 5.5 Hz); 4.43 (d, -CH*H*Ph, *J* = 11.5 Hz); 4.23 (ddd, H-C(6), *J* = 2.0, 5.5, 9.0 Hz); 3.83 (s, H-C(3)); 2.38 (ddd, H_{exo}-C(5), *J* = 6.0, 9.0, 13.5 Hz); 1.67 (dd, H_{endo}-C(5), *J* = 2.0, 13.5 Hz). ^{13}C-NMR (90.55 MHz, $CDCl_3$) δ_C: 207.9 (s), 136.8 (s), 128.5 (d, ^1J(C,H) = 160 Hz), 128.1 (d, ^1J(C,H) = 160 Hz), 128.0 (d, ^1J(C,H) = 160 Hz), 83.3 (d, ^1J(C,H) = 165 Hz), 80.4 (d, ^1J(C,H) = 165 Hz), 75.8 (d, ^1J(C,H) = 160 Hz), 73.6 (d, ^1J(C,H) = 140 Hz), 72.3 (t, *J* = 155 Hz), 34.1 (t, ^1J(C,H) = 135 Hz). MS (70 eV) m/z: 235 (M^+ +1, 0.02), 234 (M^+, 0.1), 190 (1), 91 (100), 90 (1), 89 (3), 86 (5), 65 (8). Anal. calc. for $C_{13}H_{14}O_4$ (234.25): C 66.66, H 6.02; found: C 66.49, H 6.02.

(±)-(1*RS*,3*SR*,4*SR*,6*SR*)-6-*endo*-Benzyloxy-3-*exo*-hydroxy-7-oxabicyclo[2.2.1]heptan-2-one ((±)-**13**). Same procedure as for (-)-**13**, starting with (±)-**12**, colourless, viscous oil.

(±)-2-O-Benzyl-3-deoxy-β-DL-*arabino*-hexofuranurono-6,1-lactone. Na_2CO_3 (40 mg, 0.46 mmol) and mCPBA (80 mg, 0.46 mmol) were added portionwise to a solution of (±)-**13** (100 mg, 0.43 mmol) in $CHCl_3$ (5 mL). The mixture was stirred overnight. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 1:1) the mixture was diluted with CH_2Cl_2 (15 mL) and washed with 5% aq. Na_2CO_3 (15 mL, twice) and brine (10 mL), and then dried ($MgSO_4$). Distillation of the solvent at reduced pressure and flash chromatographic purification (silica gel, light petroleum/EtOAc 7:3) afforded 50 mg (46%), colourless solid, m.p. 117-119°C. IR (CH_2Cl_2) ν: 3600-3400, 3050, 2920, 1750, 1450, 1350, 1205, 1070, 1000, 955 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.35 (m, Ph); 5.84 (d, H-C(1), *J* = 3.5 Hz); 4.62 (d, -C*H*HPh, *J* = 11.0 Hz); 4.59 (d, H-C(4), *J* = 8.0 Hz); 4.44 (d, -CH*H*Ph, *J* = 11.0 Hz); 4.24 (ddd, H-C(2), *J* = 3.5, 3.5, 10.0 Hz); 4.06 (s, H-C(5)); 2.53 (ddd, H_{exo}-C(3), *J* = 8.0, 10.0, 14.0 Hz); 1.66 (dd, H_{endo}-C(3), *J* = 3.5, 14.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 189.3 (s), 136.7 (s), 128.6 (d, ^1J(C,H) = 160 Hz), 128.2 (d, ^1J(C,H) = 160 Hz), 128.1 (d, ^1J(C,H) = 160 Hz), 100.0 (d, ^1J(C,H) = 180 Hz), 79.2 (d, ^1J(C,H) = 155 Hz), 78.6 (d, ^1J(C,H) = 155 Hz), 72.8 (d, ^1J(C,H) = 150 Hz), 72.5 (t, ^1J(C,H) = 145 Hz), 31.9 (t, ^1J(C,H) = 135 Hz). MS (70 eV) m/z: 107 (4), 105 (2), 98 (9), 92 (16), 91 (100), 89 (3), 85 (10), 77 (3), 69 (2), 65 (2), 63 (2), 57 (15). MS (CI, NH_3) m/z:

268 (M^+ +18, 1), 250 (M^+, 0.5), 177 (2), 108 (2), 98 (3), 92 (14), 91 (100), 89 (2), 85 (4), 77 (3). Anal. calc. for $C_{13}H_{14}O_5$ (250.25): C 62.39, H 5.64; found: C 62.23, H 5.73.

(-)-(1*R*,3*S*,4*S*,6*S*)-6-*endo*-Benzyloxy-2-oxo-7-oxabicyclo[2.2.1]hept-3-*exo*-yl acetate ((-)-**14**). A solution of (-)-**13** (900 mg, 3.84 mmol) and 4-dimethylaminopyridine (DMAP, 20 mg, 0.2 mmol) in pyridine (8 mL) and Ac_2O (1 mL) was stirred at 20°C for 12 h. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 8:2), toluene was added (20 mL) and the solvent was distilled off under reduced pressure; the remaining brown oil was dissolved in EtOAc and filtered through silica gel. Solvent distillation under reduced pressure gave 1.00 g (94%) pale yellow oil. $[\alpha]^{25}_D$ = -39, $[\alpha]^{25}_{578}$ = -41, $[\alpha]^{25}_{546}$ = -50, $[\alpha]^{25}_{436}$ = -132, $[\alpha]^{25}_{365}$ = -482 (*c* = 1.5, CH_2Cl_2). IR (CH_2Cl_2) ν: 3050, 2900, 1780, 1750, 1370, 1225, 1175, 1095, 1070 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.30 (m, Ph); 4.81 (s, H-C(3)); 4.65 (d, H-C(4), *J* = 6.0 Hz); 4.55 (d, -C*H*HPh, *J* = 11.5 Hz); 4.50 (d, H-C(1), *J* = 5.0 Hz); 4.45 (d, -CH*H*Ph, *J* = 11.5 Hz); 4.25 (ddd, H-C(6), *J* = 2.0, 5.0, 9.0 Hz); 2.40 (ddd, H_{exo}-C(5), *J* = 6.0, 9.0, 13.5 Hz); 2.15 (s, Me); 1.80 (dd, H_{endo}-C(5), *J* = 2.0, 13.5 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 203.2 (s), 170.3 (s), 136.8 (s), 128.5, 128.1, 128.0 (3d, ^1J(C,H) = 160 Hz), 80.8, 80.5, 75.7, 73.8 (4d, ^1J(C,H) = 165 Hz); 72.4 (t, ^1J(C,H) = 140 Hz), 34.4 (t, ^1J(C,H) = 135 Hz), 20.6 (q, ^1J(C,H) = 130 Hz). MS (70 eV) m/z: 276 (M^+, 0.13), 187 (1), 131 (2), 125 (4), 105 (1), 91 (100). MS (CI, NH_3) m/z: 295 (M^+ +18, 16), 294 (M^+ +1, 97), 279 (3), 278 (16), 277 (100), 276 (4), 237 (4), 236 (24), 218 (1), 217 (2), 216 (1), 131 (2), 125 (4), 109 (2), 108 (24), 91 (30). Anal. calc. for $C_{15}H_{16}O_5$ (276.29): C 65.21, H 5.89; found: C 65.16, H 5.87.

(±)-(1*RS*,3*SR*,4*SR*,6*SR*)-6-*endo*-Benzyloxy-2-oxo-7-oxabicyclo[2.2.1]hept-3-*exo*-yl acetate ((±)-**14**). Same procedure as described for (-)-**14**, starting with (±)-**13**. A portion of the yellow oil obtained after column chromatography on silica gel was cristallyzed from hexane, giving pale yellow crystals, m.p. 79-81°C.

(-)-5-O-Acetyl-2-O-benzyl-3-deoxy-β-D-*arabino*-hexofuranurono-6,1-lactone ((-)-**15**). $NaHCO_3$ (510 mg, 6.07 mmol) and mCPBA (1.16 g 80-90%, ~5.4 mmol) were added to a solution of the (-)-**14** (1.45 g, 5.25 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred at 20°C for 14 h. It was then diluted with CH_2Cl_2 (40 mL), washed with 5% aq. $NaHCO_3$ (15 mL, twice) and then brine (25 mL), and dried ($MgSO_4$). Solvent evaporation left 1.68 g of a colourless oil. Crystallization from light petroleum/EtOAc afforded 1.30 g (85%), white crystals, m.p. 85.5-86.5°C. $[\alpha]^{25}_D$ = -128, $[\alpha]^{25}_{578}$ = -133, $[\alpha]^{25}_{546}$ = -153, $[\alpha]^{25}_{436}$ = -271, $[\alpha]^{25}_{365}$ = -454 (*c* = 1.57, CH_2Cl_2). IR (CH_2Cl_2) ν: 3040, 2945, 2900, 2860, 1775, 1445, 1370, 1205, 1180, 1125, 1095, 1045, 1000, 985 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.30 (m, Ph); 5.84 (d, H-C(1), *J* = 3.5 Hz); 5.16 (s, H-C(4)); 4.60 (d, -C*H*HPh, *J* = 11.0 Hz); 4.53 (d, H-C(5), *J* = 8.0 Hz); 4.42 (d, -CH*H*Ph, *J* = 11.0 Hz); 4.20 (ddd, H-C(7), *J* = 3.5, 3.5, 9.5 Hz); 2.51 (ddd, H_{exo}-C(6), *J* = 8.0, 9.5, 14.0 Hz); 2.13 (s, Me); 1.17 (dd, H_{endo}-C(6), *J* = 3.5, 14.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 169.5, 162.9, 136.7 (3s), 128.6, 128.2, 128.1 (3d, ^1J(C,H) = 160 Hz); 99.9 (d, ^1J(C,H) = 185 Hz); 78.6, 78.3 (2d, ^1J(C,H) = 145 Hz); 72.5 (t, ^1J(C,H) = 150 Hz); 72.1 (d, ^1J(C,H) = 150 Hz), 31.8 (t, ^1J(C,H) = 135 Hz); 20.6 (q, ^1J(C,H) = 135 Hz). MS (70 eV) m/z: 201 (2), 159 (1), 141 (1), 140 (12), 130 (1), 118 (1), 113 (2), 105 (11), 99 (2), 98 (6), 92 (10), 91 (100), 87 (3), 77 (6), 65 (14). Anal. calc. for $C_{15}H_{16}O_6$ (292.29): C 61.64, H 5.52; found: C 61.60, H 5.59.

(±)-5-O-Acetyl-2-O-benzyl-3-deoxy-β-DL-*arabino*-hexofuranurono-6,1-lactone ((±)-**15**). Same procedure as for (-)-**15**, starting with (±)-**14**, m.p. 63-65°C.

(+)-Methyl (methyl 2-O-benzyl-3-deoxy-α-D-*arabino*-hexofuranosid)uronate ((+)-**16**). Freshly distilled $SOCl_2$ (0.45 mL, 6.2 mmol) was added dropwise at 20°C to a stirred solution of (-)-**15** (301 mg, 1.03 mmol) in MeOH (10 mL). At the end of the reaction (TCL control, silica gel, light petroleum/EtOAc 7:3) the solvent was distilled off under reduced pressure and the crude product was dissolved in EtOAc (20 mL), washed with a sat. aq. soln. of Na_2CO_3 (5 mL), dried ($MgSO_4$). filtered and then concentrated in vacuo to afford 320 mg of a yellow oil. Chromatographic purification (silica gel, light petroleum/EtOAc 7:3) gave 262 mg (86%), colourless oil (contaminated with 8% of the corresponding hexopyranoside **17** by ^{1}H-NMR). $[\alpha]^{25}_D$ = +50, $[\alpha]^{25}_{578}$ = +52, $[\alpha]^{25}_{546}$ = +58, $[\alpha]^{25}_{436}$ = +94, $[\alpha]^{25}_{365}$ = +140 (*c* = 0.95, CH_2Cl_2). IR (film) ν: 3600-3150, 3060, 2940 (br.), 1740, 1450, 1100, 1045, 950 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.30 (m, Ph); 5.00 (s, H-C(1)); 4.47 (d, H-C(5), *J* = 3.0 Hz); 4.58 (d, -C*H*HPh, *J* = 12.0 Hz); 4.53 (ddd, H-C(4), *J* = 3.0, 4.5, 8.5

Hz); 4.50 (d, -CH*H*Ph, J = 12.0 Hz); 3.95 (dd, H-C(2), J = 1.5, 5.5 Hz); 3.75 (s, CO_2Me); 3.31 (s, MeO); 2.20 (ddd, H_α-C(3), J = 5.5, 8.5, 14.0 Hz); 1.98 (ddd, H_β-C(3), J = 1.5, 4.0, 14.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 172.2 (s), 137.1 (s), 128.5, 128.0, 127.9 (3d, ^1J(C,H) = 160 Hz), 106.9 (d, ^1J(C,H) = 170 Hz); 81.6 (d, ^1J(C,H) = 150 Hz); 79.0 (d, ^1J(C,H) = 155 Hz), 72.5 (d, ^1J(C,H) = 150 Hz), 71.5 (t, ^1J(C,H) = 145 Hz), 54.6 q, ^1J(C,H) = 140 Hz), 52.6 (q, ^1J(C,H) = 150 Hz), 29.7 (t, ^1J(C,H) = 125 Hz). MS (70 eV) m/z: 175 (4), 172 (1), 158 (1), 133 (3), 129 (2), 128 (2), 127 (5), 113 (1), 108 (5), 105 (2), 92 (11), 91 (100). MS (CI, NH_3) m/z: 314 (M^+ +18, 1), 297 (M^+ +1, 2), 265 (2), 248 (1), 247 (7), 229 (4), 197 (1), 192 (1), 175 (8), 174 (1), 133 (2), 129 (2), 127 (4), 108 (7), 105 (3), 92 (11), 91 (100).

(±)-Methyl (methyl 2-O-benzyl-3-deoxy-α-DL-*arabino*-hexofuranosid)uronate ((±)-**16**). Obtained by the above procedure from (±)-**15**, (±)-**16** was a colourless oil.

(+)-Methyl 2-O-benzyl-3-deoxy-α-D-*arabino*-hexofuranoside ((+)-**18**). A solution of (+)-**17** (262 mg, 0.88 mmol), in dry Et_2O (9 mL) was added dropwise to a suspension of $LiAlH_4$ (60 mg, 1.6 mmol) in dry Et_2O (4 mL) stirred at 20°C under N_2 atm. After 30 min., EtOAc (1 mL) was added and stirring continued an additional 5 min. The mixture was cooled to 0°C and neutralized with 5% aq. HCl. EtOAc (40 mL) was added, the two phases were separated and the organic layer was washed with water (5 mL) and then with brine (7 mL), and dried ($MgSO_4$). Distillation of the solvent under reduced pressure gave a colourless oil (229 mg). Flash chromatographic purification (silica gel, Et_2O) afforded 178 mg (75%), colourless oil. $[\alpha]^{25}_D$ = +53, $[\alpha]^{25}_{578}$ = +55, $[\alpha]^{25}_{546}$ = +63, $[\alpha]^{25}_{436}$ = +101, $[\alpha]^{25}_{365}$ = +149 (c = 1.5, CH_2Cl_2). IR (CH_2Cl_2) v: 3700-3400, 3050, 2925, 1450, 1180, 1105, 1050, 960 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.29 (m, Ph); 4.94 (s, H-C(1)); 4.52 (AB syst., -CH_2Ph); 4.17 (ddd, H-C(4), J = 4.0, 4.5, 8.5 Hz); 3.95 (dd, H-C(2), J = 2.0, 5.5 Hz); 3.84 (ddd, H-C(5), J = 4.0, 4.0, 6.0 Hz); 3.61 (ddd, H_2C(6), J = 4.0, 6.0, 11.0 Hz); 3.31 (s, Me); 2.22 (ddd, H-C(3), J = 5.5, 8.5, 13.0 Hz); 2.01 (ddd, H-C(3), J = 2.0, 4.5, 13.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 137.2 (s), 128.4, 127.8 (2d, ^1J(C,H) = 160 Hz); 127.7 (d, ^1J(C,H) = 155 Hz); 106.4 (d, ^1J(C,H) = 170 Hz); 82.2 (d, ^1J(C,H) = 150 Hz); 79.0, 72.7 (2d, ^1J(C,H) = 145 Hz); 71.3, 63.7 (2t, ^1J(C,H) = 145 Hz); 54.4 (q, ^1J(C,H) = 145 Hz), 30.4 (t, ^1J(C,H) = 135 Hz). MS (70 eV) m/z: 133 (1), 117 (1), 108 (5), 100 (4), 92 (11), 91 (100).

(±)-Methyl 2-O-benzyl-3-deoxy-α-DL-*arabino*-hexofuranoside ((±)-**18**). Obtained by the above procedure from (±)-**16**, (±)-**18** was a colourless oil.

(+)-Methyl 3-deoxy-α-D-*arabino*-hexofuranoside ((+)-**6**). A solution of (+)-**18** (140 mg, 0.522 mmol) in MeOH (15 mL) was stirred for 14 h under H_2 atm. in the presence of Pd/C (50 mg, 5% Pd). Filtration through Celite, distillation of the solvent under reduced pressure, and chromatographic purification (silica gel, EtOAc) afforded 72 mg (77%) of a colourless solid. A portion of it was crystallized from Et_2O/MeOH at -30°C to give an analytical sample, m.p. 92-93°C; lit 81-83°C.[40] $[\alpha]^{25}_D$ = +100, $[\alpha]^{25}_{578}$ = +105, $[\alpha]^{25}_{546}$ = +118, $[\alpha]^{25}_{436}$ = +189, $[\alpha]^{25}_{365}$ = +279 (c = 0.44, H_2O); lit. $[\alpha]^{25}_D$ = 47.6 (c = 0.3, H_2O).[40] IR (CH_2Cl_2) v: 3950, 3500-3100, 3050, 2940, 1450, 1180, 1100, 1050 cm^{-1}. ^{1}H-NMR (250 MHz, D_2O) δ_H: 4.94 (s, H-C(1)); 4.26 (dd, H-C(2), J = 2.5, 6.0 Hz); 4.23 (ddd, H-C(4), J = 5.0, 5.5, 8.0 Hz); 3.84 (ddd, H-C(5), J = 4.0, 5.0, 6.5 Hz); 3.72 (dd, H-C(6), J = 4.0, 12.0 Hz); 3.55 (dd, H'-C(6), J = 6.5, 12.0 Hz); 3.27 (s, Me); 2.36 (ddd, H-C(3), J = 6.0, 8.0, 14.0 Hz); 1.84 (ddd, H'-C(3), J = 2.5, 5.5, 14.0 Hz). ^{13}C-NMR (90 MHz, D_2O) δ_C: 109.8 (d, ^1J(C,H) = 170 Hz), 79.3 (d, ^1J(C,H) = 155 Hz), 75.0 (d, ^1J(C,H) = 145 Hz), 73.4 (d, ^1J(C,H) = 145 Hz), 63.6 (t, ^1J(C,H) = 140 Hz), 55.4 (q, ^1J(C,H) = 140 Hz), 33.3 (t, ^1J(C,H) = 130 Hz). MS (CI, NH_3) m/z: 196 (M^+ +18, 15), 179 (M^+ +1, 20), 164 (33), 147 (38), 146 (37), 129 (22), 117 (100). Anal. calc. for $C_7H_{14}O_5$ (178.18): C 47.18, H 7.92; found: C 47.09, H 7.97.

(±)-Methyl 3-deoxy-α-DL-*arabino*-hexofuranoside ((±)-**6**). Obtained by the above procedure form (±)-**18**. (±)-**6** had m.p. 79-80°C (from Et_2O/MeOH at -30°C).

(+)-Methyl (methyl 5-O-benzoyl-2-O-benzyl-3-deoxy-β-L-*xylo*-hexofuranosid)uronate ((+)-**19**). A solution of Ph_3P (870 mg, 3.32 mmol) in dry THF (2 mL) was added dropwise to a solution of the (+)-**17** (890 mg, 3.00 mmol) and benzoic acid (405 mg, 3.32 mmol) in dry THF (11 mL) stirred at -10°C under Ar atm. A solution

of diethyl azodicarboxylate (0.6 mL, 90%, 3.4 mmol) in dry THF (2 mL) was added dropwise. The mixture was allowed to warm to 20°C and stirred overnight. The mixture was filtered through silica gel and the solvent distilled under reduced pressure. The residue was purified by flash chromatography (silica gel, light petroleum/EtOAc, 4:1) giving 630 mg (52%) of a colourless solid, m.p. 82-83°C. $[\alpha]^{25}_{D}$ = +50, $[\alpha]^{25}_{578}$ = +52 $[\alpha]^{25}_{546}$ = +58, $[\alpha]^{25}_{436}$ = +87, $[\alpha]^{25}_{365}$ = +110 (*c* = 1.06, $CHCl_3$). IR (KBr) ν: 3060, 2980, 2920, 2900, 1770, 1715, 1450, 1370, 1320, 1295, 1255 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 8.12, 7.72, 7.49, 7.31 (m, 2 Ph); 5.36 (d, H-C(5), *J* = 4.0 Hz); 5.10 (s, H-C(1)); 4.69 (ddd, H-C(4), *J* = 4.0, 6.5, 8.0 Hz); 4.52 (s, -CH_2Ph); 4.04 (dd, H-C(2), *J* = 2.5, 6.5 Hz); 3.77, 3.34 (2s, 2 Me); 2.40 (ddd, H_α-C(3), *J* = 6.5, 8.0, 14.0 Hz); 2.05 (dd, H_β-C(3), *J* = 2.5, 14.0 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 168.4, 166.0, 152.2, 137.6 (4s), 133.3, 132.1, 130.0, 128.2, 128.1, 127.6 (6d, ^1J(C,H) = 160 Hz); 107.4 (d, ^1J(C,H) = 175 Hz); 82.8, 76.5, 73.2 (3d, ^1J(C,H) = 150 Hz), 71.6 (t, ^1J(C,H) = 140 Hz), 54.6 (q, ^1J(C,H) = 140 Hz); 52.5 (q, ^1J(C,H) = 145 Hz); 31.9 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 419 (M^+ +19, 29), 418 (M^+ +18, 100), 403 (M^+ +3, 3) 402 (M^+ +2, 11), 401 (M^+ +1, 5), 387 (2), 386 (10), 385 (9), 370 (1), 369 (10), 299 (2), 298 (10), 281 (3), 279 (2), 266 (3), 249 (1), 212 (5), 211 (31), 195 (3), 194 (20). Anal. calc. for $C_{22}H_{24}O_7$ (400.42): C 65.99, H 6.04; found: C 66.04, H 5.98.

(±)-Methyl (methyl 5-O-benzoyl-2-O-benzyl-3-deoxy-β-DL-*xylo*-hexofuranosid)uronate ((±)-**19**). Obtained by the above procedure from (±)-**16**, (±)-**19** was a colourless oil.

(-)-Methyl 2-O-benzyl-2-deoxy-β-L-*xylo*-hexofuranoside (**20**). A solution of (+)-**19** (243 mg, 0.61 mmol) in dry THF (4 mL) was added dropwise to a suspension of $LiAlH_4$ (60 mg, 1.6 mmol) in dry THF (2 mL) stirred at 20°C under Ar atm. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 7:3) EtOAc (1 mL) was added and the mixture was stirred an additional 5 min. It was then neutralized with 10% aq. HCl, filtered and extracted 3 times with EtOAc. The combined organic extracts were dried ($MgSO_4$), concentrated in vacuo and purified by flash chromatography (silica gel, light petroleum/EtOAc 7:3) giving 150 mg (92%), colourless oil. IR (film) ν: 3400 (br.), 2920, 1495, 1450, 1360, 1180, 1105, 1040, 900 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.33 (m, Ph); 4.98 (s, H-C(1)); 4.54 (AB syst., -CH_2Ph); 4.26 (ddd, H-C(4), *J* = 3.5, 5.0, 8.5 Hz); 3.98 (dd, H-C(2), *J* = 2.0, 6.0 Hz); 3.67 (m, H- and H'-C(6) + H-C(5)); 3.32 (s, Me); 2.31 (ddd, H_α-C(3), *J* = 6.0, 8.5, 14.0 Hz); 1.02 (ddd, H_β-C(3), *J* = 2.0, 5.0, 13.5 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 137.1 (s), 128.4, 127.9, 127.7 (3d, ^1J(C,H) = 160 Hz), 106.9 (d, ^1J(C,H) = 170 Hz), 82.1, 78.4 (2d, ^1J(C,H) = 150 Hz), 73.2 (d, ^1J(C,H) = 145 Hz), 71.4 (t, ^1J(C,H) = 140 Hz), 64.3 (t, ^1J(C,H) = 145 Hz); 54.5 (q, ^1J(C,H) = 140 Hz); 32.1 (t, ^1J(C,H) = 135 Hz). MS (CI, NH_3) m/z: 286 (M^+ +18, 18), 270 (M^+ +2, 8), 269 (M^+ +1, 48), 268 (M^+, 0.35), 254 (12), 238 (4), 237 (27), 219 (13), 201 (6), 189 (6), 175 (9), 171 (6), 108 (13), 92 (11), 91 (100).

(±)-Methyl 2-O-benzyl-3-deoxy-β-DL-hexofuranoside ((±)-**20**). Obtained by the above procedure form (±)**19**, (±)-**20** was a colourless oil.

(+)-Methyl 3-deoxy-β,L-*xylo*-hexofuranoside ((+)-**7**). A solution of **20** (189 mg, 0.704 mmol) in MeOH (5 mL) was sitrred at 20 °C under H_2 atm. in the presence of a catalytic amount of 5% Pd/C. After stirring for 20 h, the mixture was filtered through a Celite pad and concentrated under reduced pressure. Flash chromatographic purification (silica gel, EtOAc) afforded 120 mg (96%), colourless oil. $[\alpha]^{25}_{D}$ = +65, $[\alpha]^{25}_{578}$ = +68 $[\alpha]^{25}_{546}$ = +74, $[\alpha]^{25}_{436}$ = +128, $[\alpha]^{25}_{365}$ = +192 (*c* = 1.0, $CHCl_3$). IR (CH_2Cl_2) ν: 3420 (br.), 3040, 2930 (br.), 2830, 1440, 1180, 1100, 1045, 975, 950, 890 cm^{-1}. ^{1}H-NMR (250 MHz, MeOH-d_4) δ_H: 4.82 (s, H-C(1)); 4.30 (ddd, H-C(4), *J* = 3.0, 4.5, 9.0 Hz); 4.07 (dd, H-C(2), *J* = 2.0, 6.0 Hz); 3.71-3.57 (m, H-C(5) + H_2C(6)); 3.35 (s, OMe); 2.40 (ddd, H_α-C(3), *J* = 6.0, 9.0, 13.5 Hz); 1.79 (ddd, H_β-C(3), *J* = 2.0, 4.5, 13.5 Hz). ^{13}C-NMR (62.9 MHz, MeOH-d_4) δ_C: 110.8 (d, ^1J(C,H) = 170 Hz), 79.1 (d, ^1J(C,H) = 150 Hz), 75.5 (d, ^1J(C,H) = 155 Hz), 74.4 (d, ^1J(C,H) = 140 Hz), 64.4 (t, ^1J(C,H) = 145 Hz); 54.8 (q, ^1J(C,H) = 140 Hz); 35.3 (t, ^1J(C,H) = 135 Hz). MS (CI): 197 (M^+ +19, 11), 196 (M^+ +18, 100), 179 (M^+ +1, 58), 165 (3), 164 (23), 148 (2), 147 (24), 146 (10), 129 (9), 117 (20), 102 (3), 100 (3), 99 (2), 85 (5), 82 (4), 81 (3), 74 (3), 71 (6).

(±)-Methyl 3-deoxy-β-DL-*xylo*-hexofuranoside ((±)-**7**). Obtained by the above procedure form (±)-**20**, (±)-**7** was a colourless oil.

Methyl 2,3,6-O-tri-O-acetyl-3-deoxy-β-DL-*xylo*-hexofuranoside. A solution of (±)-**7** (22 mg, 0.12 mmol) in a mixture of CH_2Cl_2 (0.5 mL), Ac_2O (0.2 mL) and pyridine (0.5 mL) was stirred overnight at 20°C. The mixture was then diluted with toluene (10 mL) and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, light petroleum/EtOAc 3:2) affording 32 mg (85%) pale yellow oil. This compound was prepared with the hope to obtain a crystalline derivative that could be fully characterized by an element analysis. Unfortunately, this oil could not be crystallized. IR (CH_2Cl_2) v: 3050, 2990, 2960, 2930, 2840, 1740, 1440, 1370, 1230, 1105, 1050, 955, 905 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 5.24 (ddd, H-C(5), J = 3.5, 5.0, 7.0 Hz); 5.05 (dd, H-C(2), J = 2.0, 7.0 Hz); 4.94 (s, H-C(1)); 4.88 (dd, H-C(6), J = 3.5, 12.0 Hz); 4.30 (ddd, H-C(4), J = 5.0, 6.0, 8.5 Hz); 4.17 (dd, H'-C(6), J = 7.0, 12.0 Hz); 3.34 (s, MeO); 2.48 (ddd, H_α-C(3), J = 7.0, 8.5, 14.5 Hz); 2.13, 2.07, 2.06 (3s, 3 Me); 1.71 (ddd, H_β-C(3), J = 2.0, 6.0, 14.5 Hz). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 170.7, 170.4, 170.2 (3s); 107.0 (d, ^1J(C,H) = 175 Hz); 77.2 (d, ^1J(C,H) = 160 Hz), 75.8, 71.5 (2d, ^1J(C,H) = 150 Hz), 63.1 (t, ^1J(C,H) = 150 Hz), 56.6 (q, ^1J(C,H) = 145 Hz), 31.8 (t, ^1J(C,H) = 135 Hz), 21.0 (q, ^1J(C,H) = 130 Hz), 20.7 (q, ^1J(C,H) = 130 Hz). MS (CI, NH_3)m/z: 322 (M^+ +18, 2), 273 (M^+ -31, 41), 171 (3), 159 (51), 125 (3), 113 (3), 99 (100), 81 (5).

(+)-Methyl 5-O-benzyl-4-deoxy-*lyxo*-D-hexonate ((+)-**27**). A solution of (-)-**15** (790 mg, 2.70 mmol) and Na_2CO_3 (240 mg, 2.26 mmol) in MeOH (40 mL) was stirred for 5 h at 20°C. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 7:3) the mixture was neutralized with AcOH, concentrated to 20 mL, diluted with EtOAc (100 mL) and filtered through silica gel. Distillation of the solvent under reduced pressure gave a colourless oil (770 mg), which was carried through the next reaction without further purification. The crude product was dissolved in MeOH (30 mL) and cooled to 0°C; $NaBH_4$ (220 mg, 5.81 mmol) was then added portionwise. At the end of the reaction (TLC control, silica gel, EtOAc) the mixture was neutralized with AcOH and concentrated in vacuo. The crude product was dissolved in EtOAc (20 mL), filtered through silica gel and concentrated in vacuo another time, to yield 638 mg (83%), colourless oil which later crystallized on standing, m.p. 53.5-54.5°C. $[\alpha]^{25}_D$ = +2, $[\alpha]^{25}_{578}$ = +2 $[\alpha]^{25}_{546}$ = +3, $[\alpha]^{25}_{436}$ = +8, $[\alpha]^{25}_{365}$ = +21 (c = 1.3, CH_2Cl_2). IR (CH_2Cl_2) v: 3550 (br.), 3050, 2950-2850, 1735, 1450, 1240, 1070, 1055 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.34 (m, Ph); 4.62 (AB syst., CH_2Ph); 4.22 (d, H-C(2), J = 4.0 Hz); 4.10 (m; H-C(3)); 3.79 (s, Me); 3.79 (m, H-C(5) + H-C(6)); 3.58 (dd, H'-C(6), J = 5.5, 12.5 Hz); 1.75 (m, H- and H'-C(4)). ^{13}C-NMR (62.9 MHz, MeOH-d_4) δ_C: 174.5 (s), 140.2 (s), 129.2, 128.9, 128.5 (3d, ^1J(C,H) = 160 Hz); 78.2 (d, ^1J(C,H) = 140 Hz), 76.4 (d, ^1J(C,H) = 145 Hz), 73.3 (t, ^1J(C,H) = 140 Hz), 71.0 (d, ^1J(C,H) = 145 Hz), 65.2 (t, ^1J(C,H) = 140 Hz), 52.4 (q, ^1J(C,H) = 145 Hz), 35.6 (t, ^1J(C,H) = 125 Hz). MS (CI, NH_3) m/z: 302 (M^+ +18, 34), 286 (M^+ +2, 6), 285 (M +1, 36), 267 (3), 212 (1), 194 (4), 177 (4), 175 (2), 162 (3), 159 (3), 108 (14), 107 (2), 106 (3), 92 (12), 91 (100), 90 (3). Anal. calc. for $C_{14}H_{20}O_6$ (284.30): C 59.14, H 7.09; found: C 59.06, H 7.16.

(±)-Methyl 5-O-benzyl-4-deoxy-*lyxo*-DL-hexonate ((±))-**27**). Obtained by the above procedure form (±)**15**, (±)-**27** had m.p. 79-80°C.

(±)-Methyl 4-deoxy-DL-*lyxo*-hexonate ((±)-**28**). A solution of (±)-**27** (100 mg, 0.352 mmol) in MeOH (5 mL) was stirred und H_2 atm. in the presence of a catalytic amount of Pd/C (Pd 10%) for 20 h. The mixture was filtered and concentrated in vacuo yielding 63 mg (92%), colourless oil that crystallized on standing. A portion of the product was crystallized form MeOH/Et_2O to give an analytical sample. IR (KBr) v: 3270 (br.), 1960, 1930, 1890, 1735, 1435, 1280, 1220, 1130, 1100, 1070, 1000, 975, 920, 885, 855, 785 cm^{-1}. ^{1}H-NMR (250 MHz, MeOH-d_4) δ_H: 4.18 (d, H-C(2), J = 4.5 Hz); 4.10 (ddd, H-C(5), J = 2.5, 5.0, 10.0 Hz); 3.88 (m, H-C(3)); 3.77 (s, Me); 3.53 (dd, H-C(6), J = 5.0, 11.5 Hz); 3.47 (dd, H'-C(6), J = 6.0, 11.5 Hz); 1.69 (ddd, H-C(4), J = 2.0, 10.0, 14.5 Hz); 1.53 (ddd, H'-C(4), J = 2.5, 10.0, 14.5 Hz). ^{13}C-NMR (62.9 MHz, MeOH-d_4) δ_C: 174.6 (s), 76.4 (d, J = 150 Hz), 70.8, 69.8 (2d, J = 145 Hz), 67.9 (t, J = 140 Hz), 52.4 (q, J = 150 Hz), 36.8 (t, J = 125 Hz). MS (CI, NH_3) m/z: 213 (M^+ +19, 4), 212 (M^+ +18, 46) 196 (M^+ +2, 9), 195 (M^+ +1, 100), 194 (M^+, 2), 192 (5), 190 (2), 187 (5), 186 (9), 182 (2), 181 (7), 180 (79), 179 (3), 178 (5), 177 (29), 175 (6), 174 (2), 163 (17), 162 (14), 159 (15), 157 (3), 145 (6), 141 (6), 127 (13). Anal. calc. for $C_7H_{14}O_6$ (194.18): C 43.30, H 7.27; found: C 43.31, H 7.30.

(±)-Methyl 2,3:5,6-O-diisopropylidene-4-deoxy-DL-*lyxo*-hexonate ((±)-**30**). A mixture of (±)-**28** (149 mg, 0.767 mmol), a catalytic amount of $SnCl_2$ and 2,2-dimethoxypropane (10 mL) was stirred 1.5 h at 20°C under N_2 atm. The mixture was diluted with CH_2Cl_2, filtered through Celite and concentrated to afford 139 mg (66%) of a white solid, m.p. 45-46°C. IR (KBr) ν: 2980, 2940, 2880, 1760, 1740, 1455, 1440, 1380, 1210 (br.), 1160, 1095, 1065, 890, 860, 835 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.61 (d, H-C(2), J = 7.0 Hz); 4.51 (ddd, H-C(3), J = 2.5, 7.0, 10.5 Hz); 4.22 (dddd, H-C(5), J = 4.5, 6.0, 8.0, 8.5 Hz); 4.07 (dd, H-C(6), J = 6.0, 8.5 Hz); 3.75 (s, Me); 3.55 (dd, H'-C(6), J = 7.0, 8.5 Hz); 1.84 (ddd, H-C(4), J = 2.5, 8.0, 13.5 Hz); 1.59 (s, Me); 1.51 (ddd, H'-C(4), J = 4.5, 10.5, 13.5 Hz); 1.38, 1.37, 1.34 (3s, 3 Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 170.5, 110.8, 108.8 (3s); 77.0 (d, ^1J(C,H) = 155 Hz), 74.5 (d, ^1J(C,H) = 145 Hz); 73.4 (d, ^1J(C,H) = 150 Hz); 69.7 (t, ^1J(C,H) = 150 Hz); 52.0 (q, ^1J(C,H) = 150 Hz); 34.7 (t, ^1J(C,H) = 125 Hz); 27.0 (q, ^1J(C,H) = 125 Hz); 25.7 (q, ^1J(C,H) = 125 Hz); 25.6 (q, ^1J(C,H) = 125 Hz). One quartet is not visible, probably because it is superposed with another one. MS (CI, NH_3) m/z: 292 (M^+ +18, 13), 276 (M^+ +2, 10), 275 (M^+ +1, 48), 273 (3), 260 (21), 259 (100), 218 (19), 217 (85), 215 (12), 202 (15), 201 (75), 195 (3), 176 (4), 169 (11), 159 (26), 158 (5), 157 (17), 156 (15), 155 (11), 142 (4), 141 (34), 140 (9), 137 (8), 130 (6), 122 (12), 121 (5), 116 (7), 109 (5), 101 (27), 100 (6), 99 (24), 98 (16), 97 (6), 96 (3), 86 (2), 85 (11), 83 (11), 81 (14), 78 (3), 77 (3), 76 (3), 73 (20), 72 (19), 71 (7).

(-)-Methyl 5-O-benzyl-4-deoxy-2,3-O-isopropylidene-D-*lyxo*-hexonate ((-)-**31**). 2,2-dimethoxypropane (1 mL) and $SnCl_2$ (200 mg, 1.05 mmol) were added to a solution of (+)-**27** (660 mg, 2.32 mmol) in dioxane (10 mL) stirred at 20°C under N_2 atm. Stirring was continued for 24 h, then the solution was diluted with CH_2Cl_2, filtered, washed with 5% aq. $NaHCO_3$ (10 mL), dried ($MgSO_4$), filtered and concentrated in vacuo to afford a colourless oil. Chromatographic purification (silica gel, light petroleum/EtOAc 6:4) gave 553 mg (73%), colourless oil. $[\alpha]^{25}_D$ = -9, $[\alpha]^{25}_{578}$ = -9, $[\alpha]^{25}_{546}$ = -10, $[\alpha]^{25}_{436}$ = -15, $[\alpha]^{25}_{365}$ = -17 (c = 1.22, CH_2Cl_2). IR (CH_2Cl_2) ν: 3250 (br.), 3050, 2950, 2880, 1730, 1748, 1450, 1205, 1090 cm^{-1}. ^{1}H-NMR (250 MHz, C_6D_6) δ_H: 7.23 (m, Ph); 4.58 (d, -C*H*HPh, J = 12.0 Hz); 4.55 (ddd, H-C(3), J = 2.5, 7.0, 10.5 Hz); 4.44 (d, -CH*H*Ph, J = 12.0 Hz); 4.44 (d, H-C(2), J = 7.0 Hz); 3.75 (dddd, H-C(5), J = 3.5, 4.0, 4.5, 9.5 Hz); 3.63 (dd, H-C(6), J = 4.0, 11.5 Hz); 3.43 (dd, H'-C(6), J = 4.5, 11.5 Hz); 3.31 (s, CO_2Me); 2.04 (ddd, H-C(4), J = 2.5, 9.5, 14.0 Hz); 1.73 (s, Me); 1.67 (ddd, H'-C(4), J = 3.5, 10.5, 14.0 Hz); 1.29 (s, Me). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 170.6 (s), 138.1 (s), 128.4, 127.8 (2d, ^1J(C,H) = 160 Hz); 110.5 (s); 78.0 (d, ^1J(C,H) = 155 Hz); 76.8 (d, ^1J(C,H) = 140 Hz); 74.1 (d, ^1J(C,H) = 150 Hz); 72.3, 64.1 (2t, ^1J(C,H) = 140 Hz); 51.9 (q, ^1J(C,H) = 145 Hz); 32.2 (t, ^1J(C,H) = 130 Hz); 26.9, 25.5 (2q, ^1J(C,H) = 125 Hz). MS (70 eV) m/z: 309 (M^+ -15, 1), 235 (4), 177 (5), 157 (1), 129 (1), 127 (3), 107 (2), 105 (2), 100 (1), 99 (2), 92 (9), 91 (100), 89 (2), 85 (3), 77 (3), 73 (3), 65 (6), 59 (11). MS (CI, NH_3) m/z: 342 (M^+ +18, 19), 326 (M^+ +2, 5), 325 (M^+ +1, 25), 324 (M^+, 1) 309 (2), 284 (3), 268 (3), 267 (29), 266 (1), 235 (5), 217 (2), 203 (2), 177 (9), 175 (3), 159 (2), 157 (3), 127 (2), 108 (12), 106 (2), 92 (10), 91 (100). Anal. calc. for $C_{17}H_{24}O_6$ (324.37): C 62.95, H 7.46; found: C 62.40, H 7.34.

(±)-Methyl 5-O-benzyl-4-deoxy-2,3-O-isopropylidene-DL-*lyxo*-hexonate ((±)-**31**). Obtained by the above procedure form (±)-**27**, (±)-**31** was a colourless oil.

(-)-Methyl 5-O-benzyl-6-O-t-butyldimethylsilyl-4-deoxy-2,3-O-isopropylidene-D-*lyxo*-hexonate ((-)-**32**). A solution of (-)-**31** (296 mg, 0.912 mmol) and imidazole (200 mg, 2.94 mmol) in DMF (3.4 mL) was cooled to 0°C and a solution of (t-Bu)Me_2SiCl (139 mg, 0.922 mmol) in DMF (2.2 mL) was added dropwise under stirring. At the end of the reaction (TLC control, silica gel light petroleum/EtOAc 7:3) the mixture was diluted with H_2O (30 mL) and extracted with Et_2O (10 mL, 3 times). The combined ethereal layers were washed with H_2O (10 mL, twice) and then with brine (15 mL), dried ($MgSO_4$), filtered and concentrated in vacuo to give 394 mg (98%), a colourless oil. A portion of the oil was distilled bulb to bulb (0.1 mm Hg) for analysis. $[\alpha]^{25}_D$ = -25, $[\alpha]^{25}_{578}$ = -26, $[\alpha]^{25}_{546}$ = -30, $[\alpha]^{25}_{436}$ = -48, $[\alpha]^{25}_{365}$ = -71 (c = 2.62, CH_2Cl_2). IR (CH_2Cl_2) ν: 3040, 2940, 2920, 2880, 2850, 1750, 1450, 1365, 1200, 1090, 830 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 7.41-7.22 (m, Ph); 4.76 (d, -C*H*HPh, J = 12.0 Hz); 4.65 (ddd, H-C(3), J = 2.0, 7.0, 10.5 Hz); 4.54 (d, -C*H*Ph, J = 12.0 Hz); 4.43 (d, H-C(2), J = 7.0 Hz); 3.88 (ddt, H-C(5), J = 2.5, 5.0, 10.0 Hz); 3.60 (d, H_2C(6), J = 5.0 Hz); 3.33 (s, Me); 1.94 (ddd, H-C(4), J = 2.0, 10.0, 14.0 Hz); 1.73 (s, Me); 1.73 (ddd, H'-C(4), J = 2.5, 10.5, 14.0 Hz); 1.29 (s, Me); 0.98 (s, t-Bu); 0.05 (s, $SiMe_2$). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 171.0 (s), 138.9 (s), 128.5 (d, ^1J(C,H) = 160 Hz), 128.1, 127.8 (2d, ^1J(C,H) = 155 Hz); 110.6 (s); 110.6

(s); 77.2 (d, ^1J(C,H) = 155 Hz); 77.0 (d, ^1J(C,H) = 140 Hz); 74.2 (d, ^1J(C,H) = 140 Hz); 73.1, 66.0 (2t, ^1J(C,H) = 140 Hz); 51.9 (q, ^1J(C,H) = 145 Hz); 32.9 (t, ^1J(C,H) = 125 Hz); 27.2, 26.1, 25.9 (3q, ^1J(C,H) = 125 Hz); 18.4 (s); -4.2 (m, not defined). MS (CI, NH_3) m/z: 458 (M^+ +20, 3), 457 (M^+ +19, 11), 456 (M^+ +18, 36), 455 (2), 440 (6), 439 (17), 438 (2), 398 (1), 382 (2), 381 (9), 334 (2), 291 (1), 273 (1), 271 (1), 231 (3), 220 (2), 217 (2), 215 (3), 213 (1), 203 (2), 199 (4), 173 (4), 171 (1), 159 (2), 145 (1), 141 (2), 132 (3), 131 (2), 129 (2), 117 (8), 108 (16), 106 (11), 102 (16), 91 (100). Anal. calc. for $C_{23}H_{38}O_6Si$ (438.63): C 62.98, H 8.73; found: C 62.81, H 8.60.

(±)-Methyl 5-O-benzyl-t-butyldimethylsilyl-4-deoxy-2,3-O-isopropylidene-DL-*lyxo*-hexonate ((±)-**32**). Obtained by the above procedure from (±)-**31**, (±)-**32** was a colourless oil.

(-)-5-O-Benzyl-6-O-(t-butyl)dimethylsilyl-4-deoxy-2,3-O-isopropylidene-D-*lyxo*-hexose ((-)-**33**). A solution of (-)-**32** (394 mg, 0.898 mmol) in dry toluene (20 mL) was cooled to -65°C under N_2 atm. A 1.2 N solution of DIBAL (diisobutylaluminium hydride) in toluene (0.75 mL, 0.90 mmol) was added dropwise. At the end of the reaction (TLC control, silica gel, toluene/EtOAc 8:2), 5% aq. HCl (1 mL) was added dropwise and the mixture was allowed to warm to 20°C. The reaction mixture was then diluted with toluene (15 mL), washed with water (10 mL, twice) and brine (15 mL), and dried ($MgSO_4$). Distillation of the solvent under reduced pressure afforded 345 mg (94%), colourless oil. $[\alpha]^{25}_D$ = -40, $[\alpha]^{25}_{578}$ = -42, $[\alpha]^{25}_{546}$ = -48, $[\alpha]^{25}_{436}$ = -80, $[\alpha]^{25}_{365}$ = -87 (*c* = 1.89, CH_2Cl_2). IR (CH_2Cl_2) ν: 2960, 2930, 2890, 2860, 2356, 1730, 1460, 1380, 1220, 1100, 835 cm^{-1}. ^{1}H-NMR (250 MHz, C_6D_6) δ_H: 9.74 (d, -C*H*O, *J* = 3.0 Hz); 7.48 (m, Ph); 4.90, 4.68 (2d, CH_2Ph, *J* = 10.5 Hz); 4.68 (ddd, H-C(3), *J* = 3.0, 7.0, 10.5 Hz); 4.13 (dd, H-C(2), *J* = 3.0, 7.0 Hz); 3.92 (dddd, H-C(5), *J* = 3.0, 5.0, 5.0, 10.5 Hz); 3.76 (dd, H-C(6), *J* = 5.0, 10.5 Hz); 3.68 (dd, H'-C(6), *J* = 5.0, 10.0 Hz); 2.00 (ddd, H-C(4), *J* = 3.0, 10.0, 13.5 Hz); 1.84 (ddd, H'-C(4), *J* = 3.0, 10.5, 13.5 Hz); 1.68 (s, Me); 1.39 (s, Me); 1.16 (s, t-Bu); 0.23 (s, $SiMe_2$). ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 202.2 (d, ^1J(C,H) = 175 Hz); 138.7 (s); 128.6 (d, ^1J(C,H) = 160 Hz); 128.1 (d, ^1J(C,H) = 155 Hz); 127.9 (d, ^1J(C,H) = 160 Hz); 110.4 (s); 82.0 (d, ^1J(C,H) = 150 Hz); 77.0, 75.0 (2d, ^1J(C,H) = 140 Hz), 73.1, 65.9, 32.4 (3t, ^1J(C,H) = 140 Hz); 27.8, 26.0, 25.6 (3q, ^1J(C,H) = 130 Hz); 18.4 (s); -4.3 (q, ^1J(C,H) = 115 Hz). MS (CI, NH_3) m/z: 427 (M^+ +20, 7), 427 (M^+ +19, 32), 426 (M^+ +18, 100), 425 (M^+ +17, 14), 409 (M^+ +7), 408 (2), 379 (2), 351 (3), 302 (5), 301 (20), 293 (2), 245 (3), 243 (3), 117 (2), 109 (2), 108 (20), 106 (6), 92 (5), 91 (46).

(±)-5-O-Benzyl-6-O-(t-butyl)dimethylsilyl-4-deoxy-2,3-O-isopropylidene-DL-*lyxo*-hexose ((±)-**33**). Obtained by the above procedure from (±)-**32**, (±)-**33** was a colourless oil.

Mixture of methyl 4-Deoxy-D-*lyxo*-hexopyranosides (**34**). A solution of (-)-**33** (239 mg, 0.585 mmol) in anhydrous MeOH (5 mL) was stirred together with Pd/C (100 mg, 10% Pd) under H_2 atm. at 20°C. At the end of the reaction (TLC control, silica gel, MeOH/EtOAc 2:8) the solution was filtered and concentrated at reduced pressure; Dowex (50 Wx8, *Fluka*, 110 mg) was added and the mixture heated under reflux (3 h). After filtration, the solvent was evaporated to afford 90 mg (96%), colourless syrup. ^{13}C-NMR (62.9 MHz, MeOH-d_4) of the major pyranoside δ_C: 103.3 (d, ^1J(C,H) = 155 Hz); 70.4 (d, ^1J(C,H) = 145 Hz); 70.1 (d, ^1J(C,H) = 140 Hz); 66.7 (d, ^1J(C,H) = 140 Hz); 66.0 (t, ^1J(C,H) = 140 Hz); 55.1 (q, ^1J(C,H) = 140 Hz); 31.1 (t, ^1J(C,H) = 125 Hz). MS (CI, NH_3) m/z: 196 (M^+ +18, 100), 194 (M^+ +16, 13), 179 (M^+ +1, 31), 178 (M^+, 3) 177 (2), 166 (2), 164 (17), 162 (1), 159 (2), 148 (3), 147 (24), 146 (4), 132 (3), 130 (3), 129 (16), 128 (2), 120 (4), 114 (3), 113 (2), 100 (11), 98 (3), 97 (3), 86 (4), 85 (4).

(+)-Methyl 4-deoxy-2,3-O-isopropylidene-α-D-*lyxo*-hexopyranoside ((+)-**8**). A mixture of **34** (93 mg, 0.56 mmol), 2,2-Dimethoxypropane (1 mL), $SnCl_2$ (50 mg, 0.26 mmol) and THF (5 mL) was stirred at 20°C under N_2 atm. for 12 h. At the end of the reaction (TLC control, silica gel, light petroleum/EtOAc 1:1) the solvents were distilled under reduced pressure and the residue was purified by flash chromatography (silica gel, Et_2O) giving 90 mg (73%) of a colourless oil. A portion of the oil was crystallized from light petroleum at -20°C for analysis, m.p. 58-59°C; lit. 59-60°C.[15b] $[\alpha]^{25}_D$ = +65, $[\alpha]^{25}_{578}$ = +68, $[\alpha]^{25}_{546}$ = +124, $[\alpha]^{25}_{365}$ = +184 (*c* = 1.5, $CHCl_3$); lit. $[\alpha]^{25}_D$ = +66 (*c* = 1.5 $CHCl_3$).[15b] IR (CH_2Cl_2) ν: 3250 (br.), 3050, 2990, 1455, 1240, 1220, 1080 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ_H: 4.90 (s, H-C(1)); 4.37 (ddd, H-C(3), *J* = 6.0, 6.0, 8.5 Hz); 3.95 (d, H-C(2), *J* = 6.0 Hz); 3.81 (dddd, H-C(5), *J* = 3.5, 3.5, 6.5, 9.5 Hz); 3.63 (m, H_2C(6)); 3.40 (s, Me); 1.87

(ddd, 1H, H-C(4), J = 3.5, 6.0, 13.5 Hz); 1.61 (ddd, 1H, H'-C(4), J = 8.5, 9.5, 13.5 Hz); 1.51 (s, Me); 1.34 (s, Me).^{13}C-NMR (62.9 MHz, $CDCl_3$) δ_C: 109.2 (s); 98.8 (d, ^1J(C,H) = 145 Hz); 73.0, 70.3 (2d, ^1J(C,H) = 150 Hz); 66.7 (d, ^1J(C,H) = 140 Hz); 65.6 (t, ^1J(C,H) = 140 Hz); 55.1 (q, ^1J(C,H) = 140 Hz); 29.0 (t, ^1J(C,H) = 130 Hz); 27.9, 26.0 (2q, ^1J(C,H) = 125 Hz). Anal. calc. for $C_{10}H_{18}O_5$ (218.24): C 55.03, H 8.31; found: C 54.98, H 8.36.

(±)-Methyl 4-deoxy-2,3-O-isopropylidene-α-DL-*lyxo*-hexopyranoside ((±)-**8**). Obtained by the above procedure from (±)-**33** via (±)**34**, (+)-**8** was a colourless oil.

References and Notes

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