Synthesis of All Stereoisomeric Carbapentofuranoses

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All carbocyclic analogs of the pentofuranoses were synthesized starting from norborn-5-en-2-one (**1**). By using either base- or acid-catalyzed Baeyer–Villiger reaction of **1**, the central intermediates **2** and **3** were obtained. The required functionalization of the olefinic double bond was achieved either by *cis*-hydroxylation in the case of the *ribo*, *lyxo*, and α-*xylo* derivatives or by epoxidation and subsequent opening with aqueous perchloric acid. In the latter case, a pronounced selectivity for opening the epoxy alcohol in the 3-position was found. If an epoxy acetate with both functions on the same side of the ring was used, the epoxide was opened in the 2-position by neighboring group participation of the acetate. The requisite side chain degradation was accomplished either by conversion of the ester into an olefin and subsequent dihydroxylation/cleavage reaction or by Curtius rearrangement to the amine and its conversion into an acetate.

Introduction

Polyoxygenated cyclopentanes are a common feature of a number of interesting biologically active compounds as are the carbocyclic nucleoside analogs[1] and a number of enzyme inhibitors (Figure 1).[2]

Although carbocyclic sugar analogs of pyranoses have been the topic of more detailed investigations[3] for some time, the studies on their five-membered counterparts have not been so numerous. After the pioneering synthesis of carbocyclic fructofuranoses by Wilcox,[4] mainly the group of Tadano and Suami[5] was engaged in the synthesis of carbafuranoses. More recently, Parry et al.[6] reported a new synthesis of α-carbaribofuranose which they found to be an intermediate in the biosynthesis of aristeromycin. The studies published so far can roughly be divided into two groups: (a) syntheses starting from carbohydrates[7] and (b) syntheses from noncarbohydrate precursors.[8]

While the first alternative bears the advantage of enantiomerically pure starting materials which also possess the required polyoxygenated framework, it is often difficult to interconvert one configuration to another one without excessive use of protecting groups.

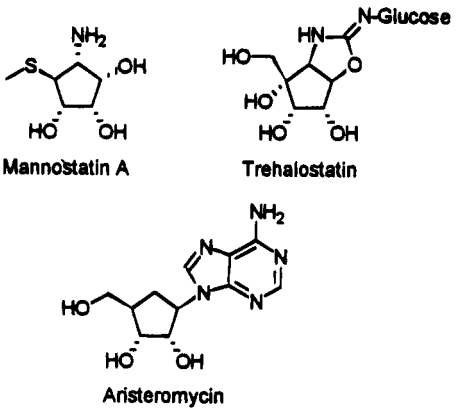

Figure 1.

The second access which usually starts from some cyclopentadiene-derived compound usually suffers from the necessity of getting enantiomerically pure material. The advantage of this approach is that the required configuration often can be introduced in a very straightforward manner.

Results

As reported previously,[9,10] we were able to synthesize the carbocyclic analogs of α- and β-ribofuranose starting from (+)-norborn-5-en-2-one. In addition, we now want to describe the syntheses of the *lyxo*, *arabino*, and *xylo* analogs of the pentofuranoses using the same starting material (Scheme 1) and also add our related synthesis of the free carbasugar analogs of 5-deoxyribohexofuranose (Scheme 2).

The Synthesis of the 5-Deoxycarba-*ribo*-hexofuranoses. The formation of 5-deoxycarba-β-D-ribohexo-

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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(4) (a) Wilcox, C. S.; Gaudino, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3102. (b) Gaudino, J. J.; Wilcox, C. S. *Carbohydr. Res.* **1990**, *206*, 233.

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(6) (a) Parry, R. J.; Haridas, K. *Tetrahedron Lett.* **1993**, *34*, 7013. (b) Parry, R. J.; Haridas, K.; Jong, R. D; Johnson, C. R. *J. Chem. Soc., Chem. Commun.* **1991**, 740. (c) Parry, R. J.; Haridas, K.; Jong, R. D; Johnson, C. R. *Tetrahedron Lett.* **1990**, *31*, 7549.

(7) (a) Yoshikawa, M.; Cha, B. C.; Okaichi, Y.; Kitagawa, I. *Chem. Pharm. Bull.* **1988**, *36*, 3718. (b) Yoshikawa, M.; Murakami, N.; Inoue, Y.; Hatakeyama, S.; Kitagawa, I. *Chem. Pharm. Bull.* **1993**, *41*, 636. (c) Yoshikawa, M.; Yokokawa, Y.; Inoue, Y.; Yamaguchi, S.; Murakami, N.; Kitagawa, I. *Tetrahedron* **1994**, *50*, 9961. (d) Roberts, S. M.; Shoberu, K. A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2625.

(8) Shoberu, K. A., Roberts, S. M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2419.

(9) Marschner, Ch.; Penn, G.; Griengl, H. *Tetrahedron Lett.* **1990**, *31*, 2873.

(10) Marschner, Ch.; Penn, G.; Griengl, H. *Tetrahedron* **1993**, *49*, 5067.

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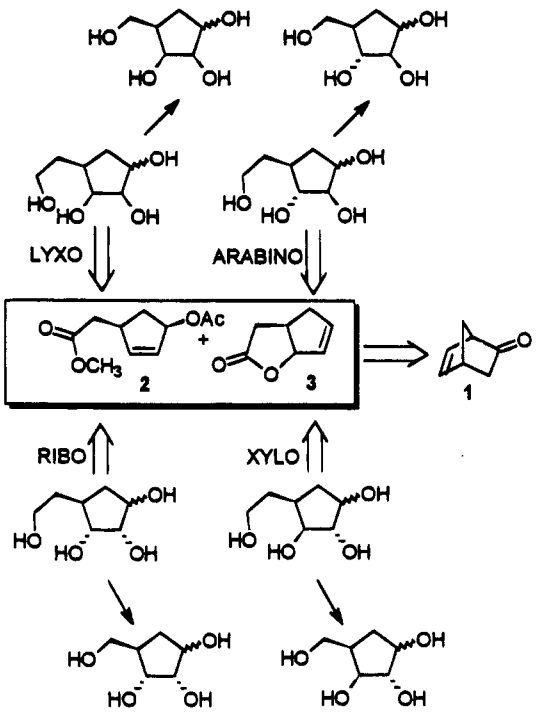
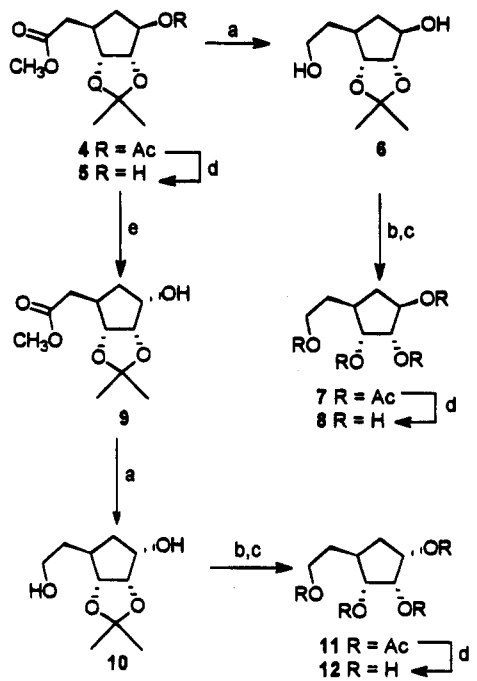
Scheme 1



Scheme 2[a]



[a] Key: (a) $LiAlH_4$, Et_2O, rt; (b) HOAc 80%, reflux; (c) Ac_2O/py/DMAP/CH_2Cl_2, rt; (d) MeONa/MeOH, rt; (e) (i) DMSO/$(COCl)_2$/Et_3N/CH_2Cl_2, −78 °C to rt; (ii) $NaBH_4$, MeOH, 0 °C.

furanose (**8**) was easily accomplished by simple deprotection of compound **6** prepared earlier[9,10] with HOAc. Peracetylation using acetic anhydride/pyridine/DMAP gave tetraacetate **7** which allowed easy chromatographic purification. Tetrol **8** then was released again by reaction of **7** with a catalytic amount of sodium methoxide in methanol. The same convenient purification procedure (acetylation−chromatography−deacetylation) was subsequently used for all carbasugars.

The required inversion of the configuration of C-1 for the formation of the α-isomer was accomplished essentially as already reported[9] for the ribofuranoses by oxidation of **5** to the ketone and subsequent stereoselective reduction with sodium borohydride to alcohol **9**. Further reduction of the ester group to give **10** and deprotection/purification as before led to the desired compound **12**.

As can be seen in Scheme 1 the problem of synthesizing all possible isomers of carbocyclic carbapentofuranoses from the Baeyer−Villiger products of norborn-5-en-2-one consists of three different tasks. First, the double bond of **2** or **3** has to be hydroxylated to the desired pattern. Second, the configuration of the allylic alcohol has to be inverted as required for the α-configuration, and third, the side chain has to be shortened by one carbon atom by a degradative procedure. We will show in this report that all this can be achieved in a different order by alternative methods for the various configurations.

Synthesis of the *lxyo* Configuration. As the problem of *cis*-hydroxylation in the case of the *ribo* series was simply solved by conversion of **2** with OsO_4/NMNO,[9] the *lyxo* configuration required the opposite *cis*-diol (Scheme 3). In order to change the side of preferred attack, we decided to invert the configuration at C-1 of **13** by the Mitsunobu reaction[11] with benzoic acid. Fortunately, on reaction with OsO_4/NMNO the benzoate gave exclusively the desired stereoisomer which was protected with 2,2-dimethoxypropane/TsOH to give dioxolane **14**. Treatment with $LiAlH_4$, yielding the diol **15**, was followed by deprotection with HOAc to give the carbasugar **17** via the corresponding tetraacetate **16**. Removal of the benzoate ester in **14** was achieved by treatment with sodium methoxide giving **18**. Swern oxidation and sodium borohydride reduction resulting in inversion at C-1 (to **19**) was followed again by treatment with $LiAlH_4$ (to **20**) and HOAc to yield carbasugar **22**. In order to effect the side chain degradation, we converted the primary hydroxy group of **15** into the bromide[12] (**23**) which was transformed into olefin **24** by means of reaction with 2-nitrophenylselenolate followed by oxidation with hydrogen peroxide.[13] Cleavage of the double bond was achieved by reaction with $OsO_4/NaIO_4$[14] to give the aldehyde which was reduced with sodium borohydride to yield alcohol **25**.

Deprotection of **25** with HOAc gave carba-α-lyxofuranose **27** via the tetraacetate **26**. The β-isomer **29** was prepared from **25** by protecting the primary alcohol as the trityl ether **28**, repeating the oxidation/reduction protocol described above (**28** → **29**), and subsequently deprotecting the compound with HOAc (**29** → **30** → **31**).

The Synthesis of the Carbasugars with *arabino* Configuration. For this purpose, the conversion of the double bond of **2** into a *trans*-diol was required. Since *trans*-diols are easily formed from epoxides, we chose this approach. Racemic **13** was reduced with $LiAlH_4$ to give diol **32** (Scheme 4), and a vanadium-catalyzed hydroxyl-directed epoxidation[15] cleanly gave epoxide **33**.[16] In the literature,[17] we found some evidence that the epoxide **33** could be opened selectively in the 3-position under acidic conditions. Indeed, treatment of **33** with aqueous perchloric acid resulted in the sole formation of tetrol **35** (via

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(12) Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964.
(13) Sharpless, K. B.; Young, M. W. *J. Org. Chem.* **1975**, *40*, 947.
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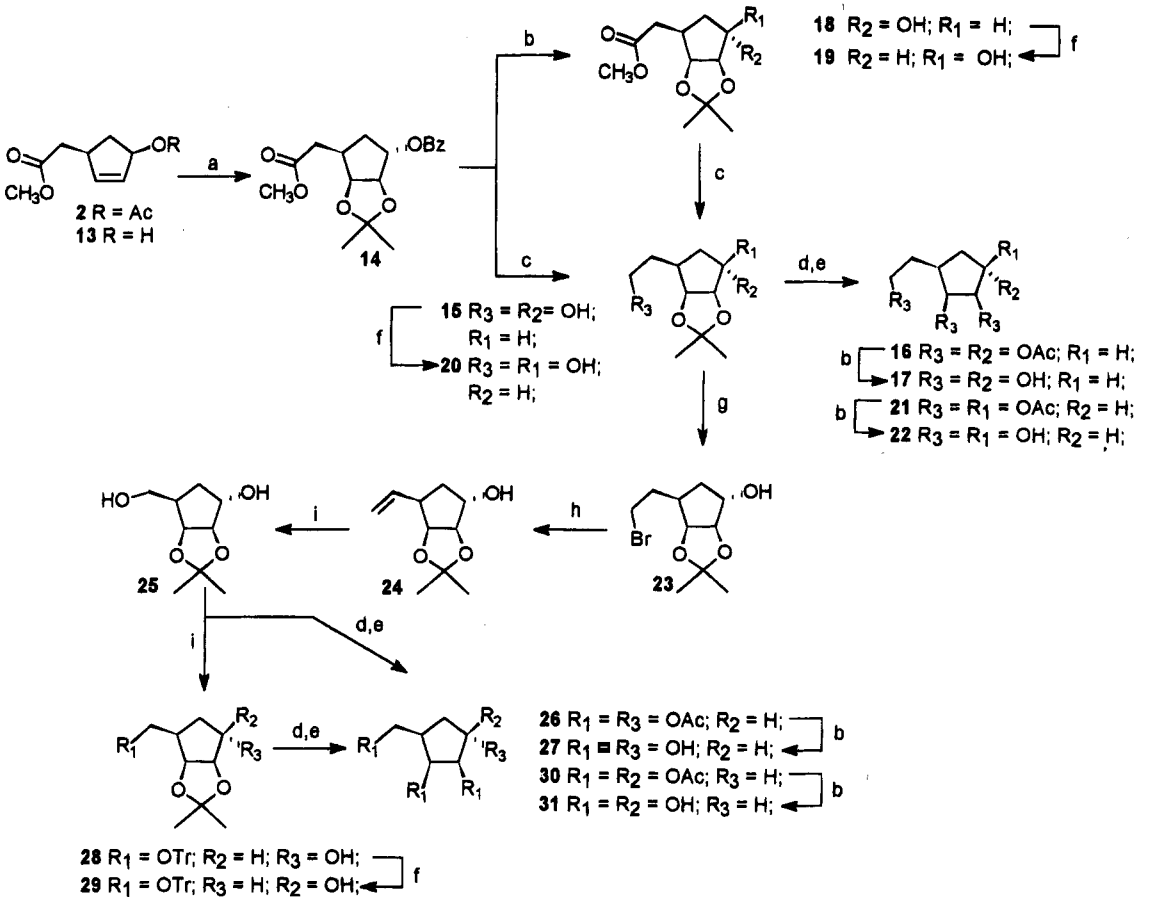
(15) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63.

Scheme 3[a]



[a] Key: (a) (i) Ph_3P/DEAD/BzOH/THF, rt, (ii) OsO_4/NMNO/acetone, rt, (iii) 2,2-dimethoxypropane/TsOH, rt; (b) MeONa/MeOH, rt; (c) $LiAlH_4$, Et_2O, rt; (d) HOAc, 80%, reflux; (e) Ac_2O/py/DMAP/CH_2Cl_2, rt; (f) (i) DMSO/$(COCl)_2$/Et_3N/CH_2Cl_2, −78 °C to rt, (ii) $NaBH_4$, MeOH, 0 °C; (g) Ph_3P/Br_2/Et_3N/CH_2Cl_2, rt; (h) (i) 2-nitrophenylselenocyanate/$NaBH_4$/EtOH, 0 °C to rt, (ii) H_2O_2/EtOH, rt; (i) (i) OsO_4/$NaIO_4$/Et_2O/H_2O, rt, (ii) $NaBH_4$, MeOH, rt; (j) TrCl/py/CH_2Cl_2, rt.

34) with the desired *β-arabino* configuration. Compound **35** was converted into the trityl ether **36** with chlorotriphenylmethane in pyridine. Peracetylation of **36** followed by hydrogenolytic removal of the trityl protecting group gave **38** via **37**. Conversion of the alcohol **38** into olefin **40** proceeded as shown above via bromide **39**. The cleavage of the double bond, however, was achieved by means of ozonolysis followed by reduction with sodium borohydride and acetylation giving **42**. The reaction of olefin **40** with OsO_4/$NaIO_4$ outlined above led to the formation of α,β-unsaturated aldehyde **41** which resulted from β-elimination of the intermediate β-acetoxyaldehyde.

In order to also obtain the α-*arabino* configuration, we performed the inversion of C-1 of **33**. The primary hydroxyl group of **33** was protected as the TBDMS ether **44**, and reaction with triflic anhydride was followed by addition of cesium acetate. The reaction gave the inverted alcohol **45** which was converted into the corresponding acetate with acetic anhydride/pyridine. Treatment of this compound with aqueous perchloric acid, however, led to the exclusive formation of the α-*xylo* configuration instead of the expected α-*arabino* configuration (Scheme 5). This result clearly indicated that the attack of the oxygen nucleophile must have taken place at carbon C-2 instead of C-3. The origin of this unexpected selectivity was assigned by us to the neighboring group participation of the acetate which attacks the activated epoxide with the carbonyl oxygen. Repeating the reaction with aqueous perchloric acid and epoxy alcohol **45** resulted only in formation of the expected α-*arabino* configuration. Conversion of **47** into the side-chain-degradated product **54** was carried out in a similar manner to the β-configuration series.

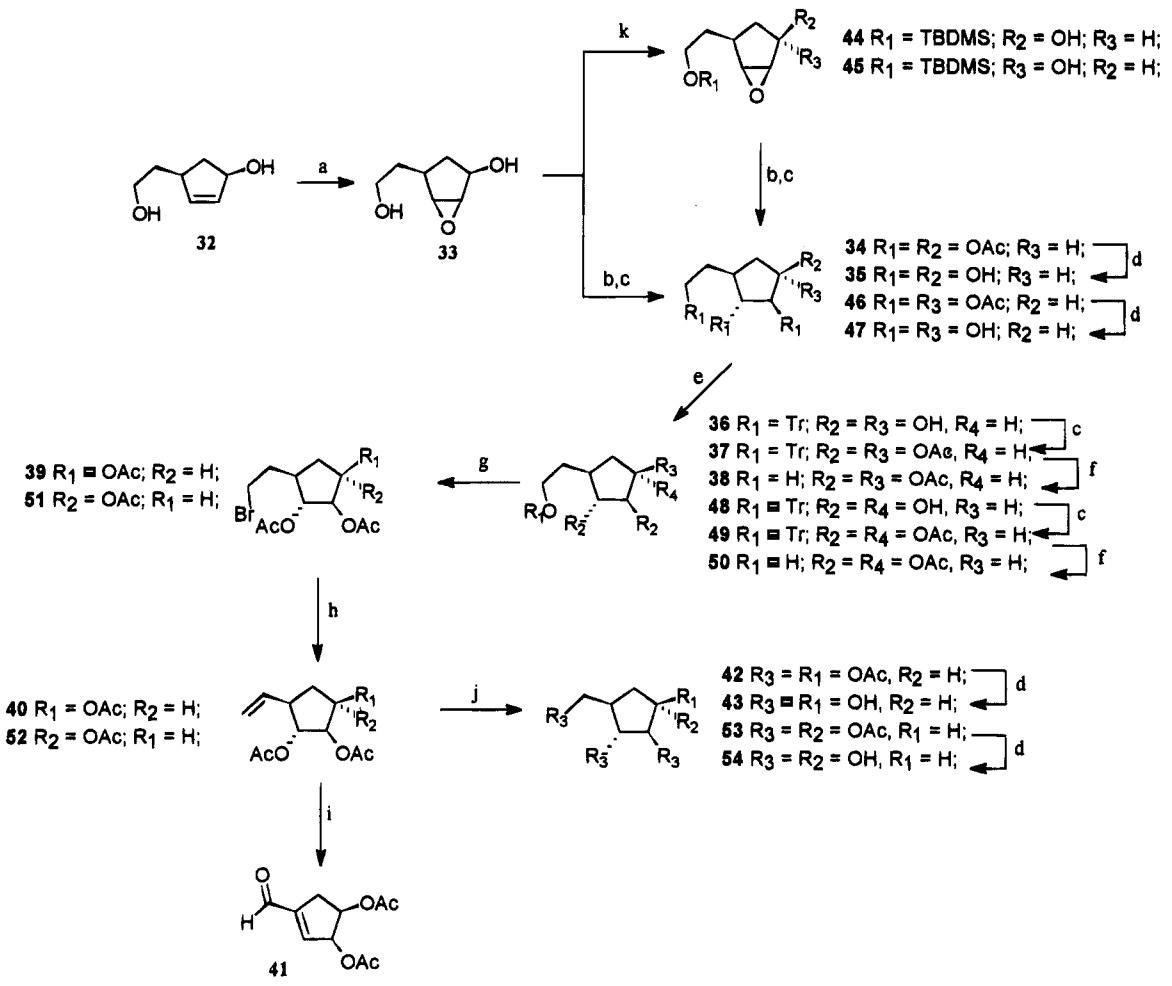
The *xylo* Configuration. The only configuration missing at this point of the study was the *xylo* configuration. Although we were able to introduce the α-*xylo* configuration during our synthesis of the α-*arabino* configuration (see above), we used **3** as a starting material for the *xylo* series rather than **2** because the configuration of C-3 is already existent as required and the bicyclic system of **3** should allow a selective functionalization of the double bond.

cis-Hydroxylation of **3** with OsO_4/NMNO proceeded with excellent stereoselectivity to yield the α-*xylo* configuration (Scheme 6). The resulting diol was protected with 2,2-dimethoxypropane/TsOH to give the 1,3-dioxolane **55**, and subsequently the lactone was reduced with $LiAlH_4$ to diol **56**. Deprotection with HOAc gave carbasugar **58** via **57**. The use of the above-described bromi-

(16) It may be interesting to note that during our study we also tried to epoxidize the diol resulting from reduction of **3** under the same conditions. Instead of the formation of a single product, we got a mixture of both possible epoxides which could be avoided by protecting the primary alcohol as the TBDMS or triphenylmethyl ether. This seems to indicate that the vanadium catalyst when coordinated to the primary alcohol is able to access the double bond from both faces of the ring in this case (Scheme 7).

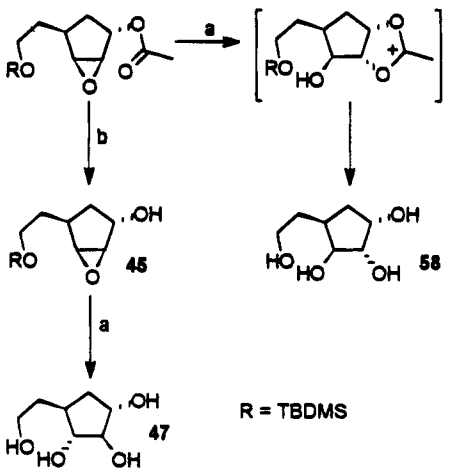
(17) Behrens, C. H.; Sharpless, K. B. *Aldrichim. Acta* **1983**, *16*, 67.

Scheme 4[a]



[a] Key: (a) $VO(acac)_2$/t-BuOOH/CH_2Cl_2, rt; (b) $HClO_4/H_2O$, rt; (c) Ac_2O/pyr/DMAP/CH_2Cl_2, rt; (d) MeONa/MeOH, rt; (e) TrCl/pyr/DMAP/CH_2Cl_2, rt; (f) H_2/Pd–C 10%, EtOH, rt; (g) $Ph_3P/Br_2/Et_3N/CH_2Cl_2$, rt; (h) (i) 2-nitrophenylselenocyanate/$NaBH_4$/EtOH, 0 °C to rt, (ii) H_2O_2/EtOH, rt; (i) $OsO_4/NaIO_4/Et_2O/H_2O$, rt; (j) (i) O_3/MeOH, −80 to 0 °C, (ii) $NaBH_4$, (iii) Ac_2O/pyr/DMAP/CH_2Cl_2, rt; (k) (i) Tf_2O/Et_3N/CH_2Cl_2, 0 °C to rt, (ii) CsOAc/DMF, rt. All compounds are racemic; only the D-enantiomers are shown.

Scheme 5[a]

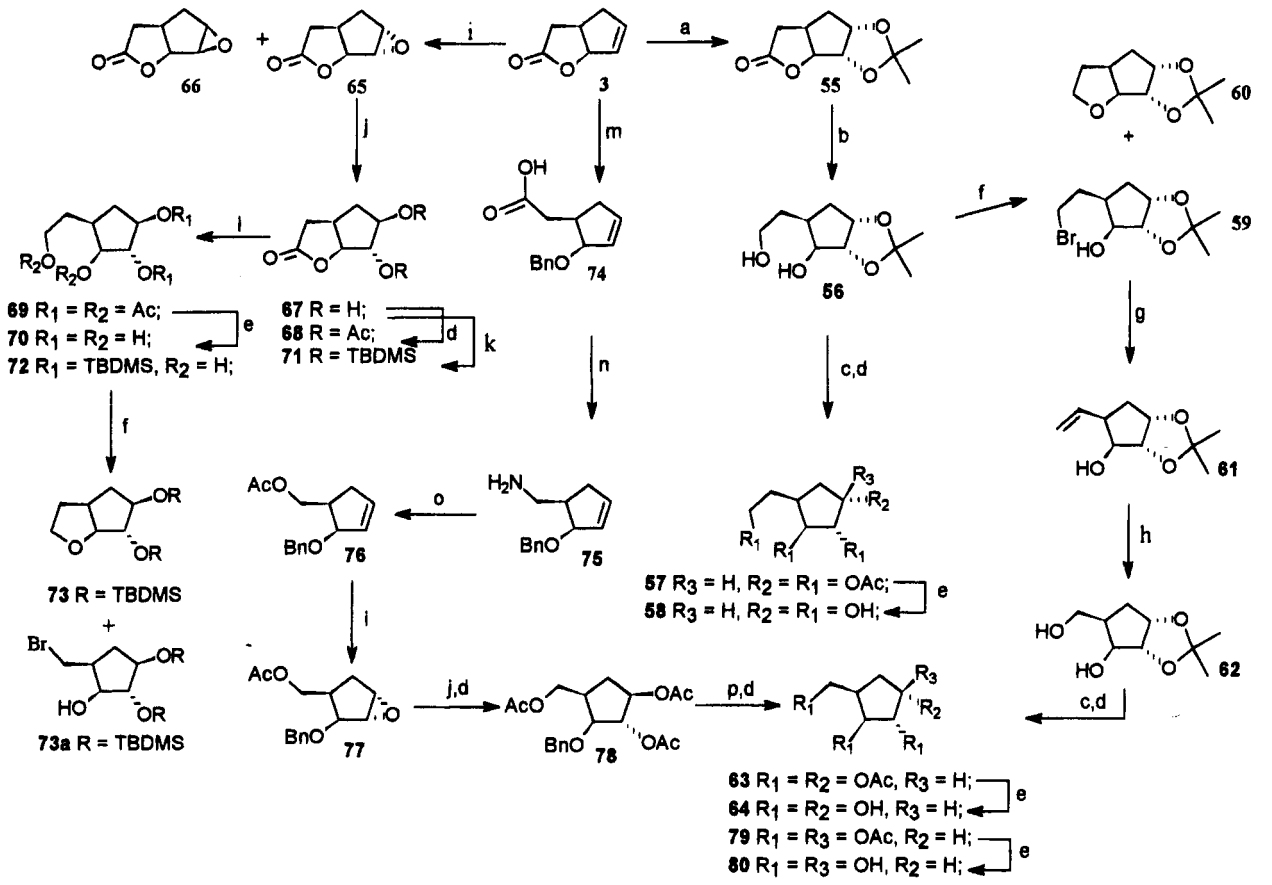


[a] Key: (a) $HClO_4/H_2O$, rt; (b) MeONa/MeOH/rt.

nation procedure for **56** yielded the expected bromide **59** accompanied by with the same amount of the cyclic ether **60** which was formed by the intramolecular attack of the C-3 hydroxy group at the primary bromide. The conversion of the bromide into the olefin **61** and the following cleavage proceeded as expected giving **62**, and carba-α-xylofuranose **64** (via **63**) was obtained by deprotection of **62** with HOAc.

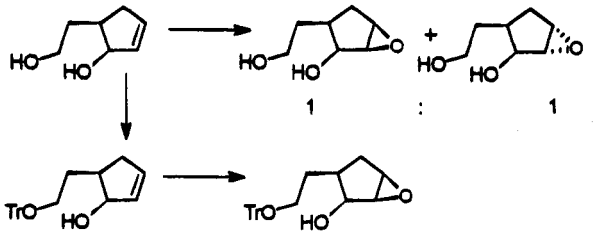
Epoxidation of **3** with *m*-CPBA, however, only gave a mixture of epoxides **65** and **66** with a ratio of about 2:1 in favor of the expected *exo*-epoxide **65**. Because of their easy chromatographic separation, we did not try to improve the selectivity of the epoxidation. Under the usual treatment with perchloric acid, both epoxides behaved as expected. The main product **65** yielded the desired *β-xylo* configuration, i.e., **67**, while **66** led to the *α-lyxo* compound. Diol **67** was protected as the di-TBDMS ether **71** and the lactone reduced with $LiAlH_4$ to give diol **72**. In this case, the bromination gave the same side reaction as described above, but the ratio of bromide **73a** to cyclic ether **73** was almost completely in favor of the ether. While this would require either protection of the secondary alcohol or difficult optimization of the bromination reaction, we sought a different solution. From the beginning of our studies, we were not satisfied with our side-chain degradation protocol. One of the main concerns about the method was that it did not allow the presence of a carbon–carbon double bond in the molecule. We decided to use the procedure we had employed in the synthesis of carbocyclic nucleoside analogs of the *xylo*-configuration.[18] Compound **3** was converted into acid **74** while the secondary alcohol was protected as the benzyl ether. Curtius degradation of the

Scheme 6[a]



[a] Key: (a) (i) OsO_4/NMNO/acetone, rt, (ii) 2,2-dimethoxypropane/TsOH, rt; (b) $LiAlH_4/Et_2O$, rt; (c) HOAc, 80%, reflux; (d) Ac_2O/py/DMAP/CH_2Cl_2, rt; (e) MeONa/MeOH, rt; (f) $Ph_3P/Br_2/Et_3N/CH_2Cl_2$, rt; (g) (i) 2-nitrophenylselenocyanate/$NaBH_4$/EtOH, 0 °C to rt; (ii) H_2O_2/EtOH, rt; (h) (i) $OsO_4/NaIO_4/Et_2O/H_2O$, rt, (ii) $NaBH_4$/MeOH, rt; (i) MCPBA/CH_2Cl_2, rt; (j) $HClO_4/H_2O$, rt; (k) TBDMSCl/imidazole/DMF, rt; (l) for R = Ac: (i) BH_3·Me_2S/THF, rt, (ii) Ac_2O/py/DMAP/CH_2Cl_2, rt; for R = TBDMS: $LiBH_4/Et_2O$, rt; (m) KOH/BnBr/dioxane, reflux; (n) (i) ethyl chloroformate/Et_3N/acetone/NaN_3, (ii) toluene, reflux; (o) $NaNO_2$/HOAc/NaOAc, rt; (p) H_2/Pd–C 10%, EtOH, rt.

Scheme 7



acid gave amine **75** which was treated with HOAc/$NaNO_2$ to give the analogous acetate **76** in a moderate yield. Epoxidation with *m*-CPBA proceeded stereoselectively to the desired epoxide **77**. Treatment of **77** with perchloric acid gave the triol which was peracetylated (**78**), subjected to hydrogenolysis to remove the benzyl ether, and converted to the tetraacetate **79**. Deprotection of **79** in the usual manner finally gave β-xylocarbapentofuranose **80**.

Experimental Section

Melting points are uncorrected. If not mentioned otherwise ^1H and ^{13}C spectra were measured at 300 and 75 MHz, respectively. Assignments of signals, if reported, were done on the basis of H,H- and H,C-COSY (HETCOR) experiments. Reactions were performed with predried solvents under an inert gas atmosphere. While all compounds of the *ribo, lyxo,* and α-*xylo* series were prepared from (+)-norborn-5-en-2-one with an ee of 86%, the β-*xylo* and *arabino* compounds were formed from racemic norborn-5-en-2-one. For nomenclature all molecule were treated as carbohydrate derivatives, where the furanose ring oxygen is formally replaced by a methylene group (carba-prefix).[19] The new carbon was numbered as 4a rather than 1a to emphasize that it replaced the oxygen which belonged to C-4.[20]

1,2,3,6-Tetra-*O*-acetyl-5-deoxycarba-β-D-*ribo*-hexofuranose (7). Diol **6**[9,10] (0.59 g, 2.92 mmol) was treated with acetic acid (20 mL, 80% in water) and heated to 80 °C for 20 min, and then the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (20 mL) and treated with acetic anhydride (2.21 mL, 23.4 mmol), pyridine (2.36 mL, 29.2 mmol), and a few crystals of DMAP for 2 h at 20 °C. Then methanol (2 mL) was added, and stirring was continued for 15 min. The

(18) (a) Baumgartner, H.; Marschner, Ch.; Pucher, R.; Griengl, H. *Tetrahedron Lett.* **1991**, *32*, 611. (b) For a modified procedure which gives greatly improved yields in the transformation of the amine to the ester: Kapeller, H.; Neufellner, E.; Griengl, H. Unpublished results.

(19) For the use of the carba prefix, see: Balzarini, J.; Baumgartner, H.; Bodenteich, M.; De Clercq, E.; Griengl, H. *Nucleosides Nucleotides* **1989**, 855. This nomenclature is in accordance with: (a) International Union of Pure and Applied Chemistry, Nomenclature of Organic Chemistry, rules F-4.12 and F-4.13. (b) Tentative Rules for Carbohydrate Nomenclature; Part I; 1969. *Biochem. J.* **1971**, 637. The use of the "carba" system of nomenclature for carbocyclic analogs of carbohydrates and nucleosides has been recommended by Professor D. Horton on the occasion of the Symposium on Developments in Carbohydrate Nomenclature, 199th National Meeting of the American Chemical Society, Boston, MA, April 22–27. 1990.

(20) The change in the numbering of the methylene group from 1a to 4a was suggested to us by Professor M. J. Robbins. For further discussion on this nomenclature we thank Professors W. A. Szarek, Canada, and E. B. Pedersen, Denmark, and Dr. E. J. Prisbe, USA.

solution was diluted with 0.1 N HCl, the layers were separated, and the organic layer was washed with saturated aqueous $NaHCO_3$. The aqueous washings were reextracted twice with CH_2Cl_2, and the combined CH_2Cl_2 extracts were dried over Na_2SO_4 and concentrated. Flash chromatography (60% hexane/40% ethyl acetate) provided fully protected **7** as a colorless oil (0.9 g, 93%). NMR ($CDCl_3$) δ: ^1H and COSY 1.18 (ddd, 1H, H4a, J = 4.2, 7.0, 12.5 Hz), 1.57 (ddd, 1H, H5, J = 6.3, 8.6, 14.8 Hz), 1.80 (ddd, 1H, H5′, J = 6.5, 13.3, 20.3 Hz), 1.92 (s, 3H), and 1.94 (s, 9H, CH_3-ester), 2.12 (m, 1H, H4), 2.45 (dt, 1H, H4a′, J = 8.3, 14.0 Hz), 3.97 (m, 2H, 2H6), 4.87 (dd, 1H, H3, J = 5.5, 7.3 Hz), 4.98 (ddd, 1H, H1, J = 4.3, 6.2, 7.8 Hz), 5.09 (t, 1H, H2, J = 4.6 Hz); ^{13}C and HETCOR 20.59, and 20.84 (CH_3-ester), 32.33 (C4a), 33.07 (C5), 37.38 (C4), 62.48 (C6), 75.19, 75.30, and 75.48 (C1, C2, C3), 169.55, 168.99, 170.76 (C=O ester). $[\alpha]_{20}^{D}$ +1.2° (c 3.7, CH_2Cl_2). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.41; H, 6.79.

5-Deoxycarba-β-D-*ribo*-hexofuranose (8). To a solution of **7** (0.16 g, 0.48 mmol) in methanol (7 mL) was added at room temperature a catalytic amount of a freshly prepared sodium methoxide solution. After 2 h, weakly acidic ionic exchange resin (Amberlite IRC-84) was used to neutralize the solution which was filtered, and the resin was washed with methanol and the solvent removed *in vacuo*. Tetrol **8** (78 mg, 100%) was obtained as a colorless oil. NMR (d_6-DMSO) δ: ^1H and COSY 0.95 (ddd, 1H, H4a, J = 5.9, 8.7, 13.4 Hz), 1.38 (m, 1H, H5), 1.72 (m, 2H, H4, H5′), 2.11 (ddd, 1H, H4a′, J = 7.7, 13.1, 15.1 Hz), 3.41 (m, 2H, H6), 3.53 (m, 2H, H2, H3), 3.76 (t, 1H, H1, J = 5.5 Hz); ^{13}C and HETCOR 36.41 (C4a), 37.65 (C5), 39.13 (C4), 59.95 (C6), 75.06 (C1), 76.41, 77.99 (C2, C3). $[\alpha]_{20}^{D}$ +22.2° (c 3.9, CH_3OH). HRMS: calcd for $C_7H_{15}O_4$ M + H m/z 163.0970, found 163.0978.

Methyl 5-Deoxy-2,3-*O*-isopropylidenecarba-α-D-*ribo*-hexofuranuronate (9). Oxidation: To a solution of oxalyl chloride (4.4 mL, 51.3 mmol) in CH_2Cl_2 (150 mL) at −78 °C was added DMSO (4.4 mL, 61.7 mmol) dropwise, followed after 15 min by alcohol **5**[9,10] (10.9 g, 46.1 mmol) in 100 mL of CH_2Cl_2 and after an additional 15 min by dry triethylamine (38.0 mL, 0.27 mol). The mixture was allowed to warm to room temperature and diluted with 0.1 N HCl, and the workup used for **7** was followed. A total of 10.4 g (45.3 mmol) of the intermediary ketone was obtained as a white foam, which was not subjected to further purification. NMR (90 MHz) ($CDCl_3$) δ: ^1H 1.34 (s, 3H), 1.43 (s, 3H), 2.1−2.8 (m, 5H), 3.65 (s, 3H), 4.45 (d, 1H), 4.61 (d, 1H); ^{13}C (22.6 MHz) 24.8, 26.9, 34.9, 37.5, 39.7, 52.0, 78.8, 82.2, 112.2, 172.1, 219.9. $[\alpha]_{20}^{D}$ −106.1° (c 3.0, CH_2Cl_2).

Reduction: To a solution of the crude product (10.0 g, 43.6 mmol) in methanol (200 mL) at 0 °C was added $NaBH_4$ (2.0 g, 52.9 mmol). After 30 min at room temperature, the solution was diluted with CH_2Cl_2 and washed with water. The layers were separated, the aqueous washings were reextracted twice with CH_2Cl_2, and the combined CH_2Cl_2 extracts were dried over Na_2SO_4 and concentrated. Flash chromatography (70% hexane/30% ethyl acetate) of the residue provided a white foam of **9** (9.3 g, 93%). NMR ($CDCl_3$) δ: ^1H 1.09 (s, 3H), 1.26 (s, 3H), 1.45 (m, 1H), 1.72 (m, 1H), 2.06 (m, 1H), 2.23 (m, 1H), 2.67 (d, 1H, J = 6.4 Hz), 3.45 (s, 3H), 3.83 (m, 1H), 4.15 (d, 1H, J = 6.0 Hz), 4.27 (t, 1H, J = 5.5 Hz); ^{13}C 24.08, 25.80, 36.12, 36.32, 37.81, 51.29, 70.87, 79.08, 83.99, 111.32, 171.97. $[\alpha]_{20}^{D}$ −9.9° (c 3.6, CH_2Cl_2). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.21; H, 7.86.

5-Deoxy-2,3-*O*-isopropylidenecarba-α-D-*ribo*-hexofuranose (10). A suspension of LAH (0.1 g, 2.6 mmol) in 40 mL of ether under nitrogen atmosphere was cooled to 0 °C, and a solution of **9** (0.42 g, 1.82 mmol) in 5 mL of ether was added dropwise. After being refluxed for 10 min, the mixture was cooled to 0°C and treated with 0.4 mL of a saturated aqueous solution of $MgSO_4$. The precipitate was removed by filtration, washed with CH_2Cl_2, triturated twice with CH_2Cl_2, heated to reflux, and filtered. The combined organic layers were concentrated, and diol **10** (0.37 g, 100%) was obtained as a colorless oil. NMR (90 MHz) ($CDCl_3$) δ: ^1H 1.36 (s, 3H), 1.50 (s, 3H), 1.70 (m, 1H), 1.5−2.0 (m, 3H), 2.0−2.3 (bs, 2H, exchangeable with D_2O), 3.70 (t, 2H), 4.09 (q, 1H), 4.48 (m, 3H); ^{13}C (22.6 MHz) 24.54, 26.23, 35.27, 37.38, 38.65, 61.21, 70.76, 79.61, 85.27, 112.32. Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.50; H, 8.86.

1,2,3,6-Tetra-*O*-acetyl-5-deoxycarba-α-D-*ribo*-hexofuranose (11). Diol **10** (0.38 g, 1.82 mmol) was treated according to the procedure used for **7**. Flash chromatography (60% hexane/40% ethyl acetate) gave fully protected **11** as a colorless oil (0.43 g, 72%). NMR ($CDCl_3$) δ: ^1H and COSY 1.67−1.49 (m, 2H, H4a, H5), 1.77 (m, 1H, H5′), 1.93 (s, 9H), and 1.95 (s, 3H, CH_3 ester), 2.01 (m, 1H, H4a′), 2.25 (m, 1H, H4), 3.97 (m, 2H, 2H6), 4.78 (dd, 1H, H3, J = 5.0, 7.8 Hz), 5.11 (dt, 1H, H1, J = 4.9, 7.4 Hz), 5.22 (t, 1H, H2, J = 4.7 Hz); ^{13}C and HETCOR 20.48, 20.57, 20.67, and 20.78 (CH_3 ester), 32.47 (C4a), 37.68 (C4), 62.67 (C6), 71.03 (C1), 71.69 (C2), 75.77 (C3), 169.63, 169.96, 170.11, and 170.77 (C=O ester). $[\alpha]_{20}^{D}$ +29.0° (c 2.3, CH_2Cl_2). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.59; H, 6.75.

5-Deoxycarba-α-D-*ribo*-hexofuranose (12). Cleavage of the acetyl groups of **11** (0.25 g, 0.76 mmol) was done according to the preparation of **8**. Tetrol **12** (0.13 g, 100%) was obtained as a colorless oil, which required no further purification. NMR (d_6-DMSO) δ: ^1H 1.37 (m, 2H), 1.68 (m, 2H), 1.95 (m, 1H), 3.38 (m, 3H), 3.67 (t, 1H, J = 4.1 Hz), 3.91 (dd, 1H, J = 6.4, 10.7 Hz); ^{13}C 36.68, 37.91, 40.36, 60.68, 70.84, 73.90, 77.57. $[\alpha]_{20}^{D}$ +40.9° (c 1.0, CH_2Cl_2) (lit.[6c] $[\alpha]_{25}^{D}$ +47.1° (c 0.85, CH_3OH); lit.[7d] $[\alpha]_{25}^{D}$ +48.3° (c 0.74, CH_3OH)). HRMS: calcd for $C_7H_{15}O_4$ M + H m/z 163.0970, found 163.0982.

Methyl 1-*O*-Benzoyl-5-deoxy-2,3-*O*-isopropylidenecarba-α-D-*lyxo*-hexofuranuronate (14). Diethyl azodicarboxylate (4.35 mL, 27.9 mmol) was added dropwise to a stirred solution of **13**[9] (2.77 g, 17.75 mmol), triphenylphosphine (9.30 g, 35.5 mmol), and benzoic acid (4.34 g, 35.5 mmol) in 50 mL of THF, and stirring was continued for 15 min at room temperature. The solution was concentrated and treated with ether, and the resulting precipitate was removed by filtration. The filtrate was evaporated to give 5.4 g of a light orange oil. An analytical sample was obtained by flash chromatography (90% hexane/10% ethyl acetate) to give **14** as a colorless liquid. NMR ($CDCl_3$) δ: ^1H 1.98 (ddd, 1H, J = 6.0, 7.3, 14.5 Hz), 2.22 (ddd, 1H, J = 2.5, 7.7, 14.4 Hz), 2.38 (dd, 1H, J = 8.0, 15.6 Hz), 2.44 (dd, 1H, J = 7.1, 15.6 Hz), 3.36 (m, 1H), 3.68 (s, 1H), 5.93 (dt, 1H, J = 2.2, 7.0 Hz), 5.98 (dt, 1H, J = 2.1, 5.4 Hz), 6.10 (dd, 1H, J = 1.8, 5.5 Hz), 7.40 (m, 2H), 7.51 (m, 1H), 7.99 (d, 2H); ^{13}C 37.21, 39.86, 41.08, 51.72, 80.47, 128.47, 129.78, 130.27, 132.96, 141.14, 166.67.

cis-Dihydroxylation and protection of the diol: The crude product (5.0 g) was dissolved in acetone and treated with 4.80 g (35.5 mmol) of *N*-methylmorpholine *N*-oxide and a catalytic amount of osmium tetraoxide. The mixture was stirred at room temperature for 24 h, and then sodium thiosulfate was added to destroy the osmium tetraoxide and the solvent removed. The residue was dissolved in 1 N HCl, saturated with NaCl, and extracted several times with CH_2Cl_2, and the combined extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was treated with 50 mL of 2,2-dimethoxypropane and a few crystals of PTSA. After 6 h at 20 °C, the mixture was neutralized with $NaHCO_3$, filtered, and concentrated. Purification by flash chromatography (90% hexane/10% ethyl acetate) gave **14** as white needles (2.35 g, 40%). Mp: 80−81 °C. NMR ($CDCl_3$) δ: ^1H 1.30 (s, 3H), 1.45 (s, 3H), 1.91 (m, 2H), 2.47 (m, 1H), 2.66 (m, 2H), 3.70 (s, 3H), 4.61 (d, 1H, J = 5.5 Hz), 4.77 (t, 1H, J = 4.3 Hz), 5.23 (d, 1H, J = 3.9 Hz), 7.44 (m, 2H), 7.57 (m, 1H), 8.01 (d, 2H); ^{13}C 24.19, 26.23, 33.25, 34.18, 38.06, 51.80, 78.69, 80.67, 84.94, 110.88, 128.60, 129.84, 133.30, 165.77, 173.42. $[\alpha]_{20}^{D}$ −5.8° (c 1.1, CH_2Cl_2). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.61; H, 6.78. The enantiomeric excess (ee) of **14** thus obtained was determined by use of chiral shift reagent (Eu-hfc) to be 90%.

5-Deoxy-2,3-*O*-isopropylidenecarba-α-D-*lyxo*-hexofuranose (15). Reduction of **14** (1.00 g, 2.99 mmol) was done according to the procedure for **10**. After flash chromatography (5% hexane/95% ethyl acetate) **15** was obtained as a colorless oil (0.52 g, 86%). NMR ($CDCl_3$) δ: ^1H 1.29 (s, 3H), 1.40 (s, 3H), 1.68 (m, 3H), 1.83 (m, 1H), 2.37 (m, 1H), 2.67 (bs, 2H), 3.70 (m, 2H), 4.09 (t, 1H, J = 2.1), 4.38 (d, 1H, J = 5.5 Hz),

4.64 (t, 1H, J = 5.2 Hz); ^{13}C 24.18, 26.22, 31.85, 36.70, 38.23, 61.85, 75.77, 81.28, 87.10, 110.24. $[\alpha]_{20}^{D}$ −40.2° (*c* 0.6, CH_2Cl_2). Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.33; H, 9.04.

1,2,3,6-Tetra-*O*-acetyl-5-deoxycarba-α-D-*lyxo*-hexofuranose (16). Cleavage of the isopropylidene group in **15** (0.12 g, 0.59 mmol) and peracetylation was done according to the procedure for **7**. Flash chromatography (33% hexane/67% ethyl acetate) afforded **16** as a colorless oil (0.16 g, 83%). NMR ($CDCl_3$) δ: ^{1}H and COSY 1.50 (m, 1H, H5), 1.67 (m, 2H, H5′, H4a), 1.88, 1.90, 1.93, and 1.97 (s, each 3H, CH_3-ester), 2.05 (m, 1H, H4a′), 2.28 (m, 1H, H4), 2.91 (m, 2H, 2H6), 5.08 (m, 2H, H1, H2), 5.27 (t, 1H, H3, J = 2.9); ^{13}C and HETCOR 20.52, 20.59, 20.82, and 20.89 (CH_3-ester), 28.34 (C5), 34.25 (C4a), 35.48 (C4), 62.60 (C6), 74.06 (C3), 75.74 (C1), 77.79 (C2), 170.82, 170.50, and 170.06 (C=O ester). $[\alpha]_{20}^{D}$ +38.4° (*c* 3.4, CH_2Cl_2). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.62; H, 6.83.

5-Deoxycarba-α-D-*lyxo*-hexofuranose (17). Cleavage of the protecting groups of **16** (0.14 g, 0.42 mmol) was done according to the procedure for **8**. A white foam of **17** was obtained which was not subjected to further purification (65 mg, 96%). NMR (d_6-DMSO) δ: ^{1}H 1.41 (m, 2H), 1.64 (m, 2H), 2.06 (m, 1H), 3.40 (m, 2H), 3.54 (t, 1H, J = 4.4 Hz), 3.82 (m, 2H); ^{13}C 33.56, 36.43, 38.16, 48.50, 59.44, 72.85, 76.49, 80.74. $[\alpha]_{20}^{D}$ +14.7° (*c* 3.2, CH_3OH). HRMS Calcd for $C_7H_{15}O_4$ M + H m/z 163.0970. Found: 163.0968.

Methyl 5-Deoxy-2,3-*O*-isopropylidenecarba-α-D-*lyxo*-hexofuranuronate (18). Compound **14** (0.5 g, 1.50 mmol) was allowed to react according to the procedure described for **8**. Flash chromatography (33% hexane/67% ethyl acetate) afforded **18** as a colorless oil (0.33 g, 96%). NMR ($CDCl_3$) δ: ^{1}H 1.27 (s, 3H), 1.39 (s, 3H), 1.68 (2 dd, AB-system, 2H), 2.21 (bs, 1H), 2.38 (t, 1H, J = 9.1 Hz), 2.61 (m, 2H), 3.68 (s, 3H), 4.10 (d, 1H, J = 3.2 Hz), 4.38 (dd, 1H, J = 1.0, 5.5 Hz), 4.69 (t, 1H, J = 5.1 Hz); ^{13}C 24.31, 26.61, 33.83, 37.09, 37.73, 52.18, 76.07, 81.27, 87.27, 110.75, 174.16. $[\alpha]_{20}^{D}$ −25.8° (*c* 2.0, CH_2Cl_2). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.52; H, 7.81.

Methyl 5-Deoxy-2,3-*O*-isopropylidenecarba-β-D-*lyxo*-hexofuranuronate (19). Oxidation of the hydroxyl group of **18** (0.3 g, 1.31 mmol) was done according to the procedure for **9**. A light yellow oil was obtained which was not subjected to further purification (0.23 g, 78%). NMR ($CDCl_3$) δ: ^{1}H 1.33 (s, 3H), 1.39 (s, 3H), 2.29 (dd, 1H, J = 11.6, 18.4 Hz), 2.42 (dd, 1H, J = 6.9, 18.4 Hz), 2.57 (dd, 1H, J = 6.2, 14.5 Hz), 2.66 (m, 1H), 2.75 (dd, 1H, J = 6.1, 14.6 Hz), 3.70 (s, 3H), 4.23 (d, 1H, J = 4.9 Hz), 4.79 (t, 1H, J = 4.1 Hz); ^{13}C 25.26, 26.99, 31.94, 34.62, 39.26, 51.95, 78.92, 80.36, 112.75, 172.63, 213.16. $[\alpha]_{20}^{D}$ +144.4° (*c* 1.0, CH_2Cl_2). Following the procedure for the preparation of **9**, the ketone was reduced, and after flash chromatography (50% hexane/50% ethyl acetate) **19** was obtained as a colorless oil (0.17 g, 84%). NMR ($CDCl_3$) δ: ^{1}H 1.26 (s, 3H) 1.33 (m, 1H), 1.39 (s, 3H), 1.87 (dt, 1H, J = 5.7, 12.6 Hz), 1.97 (m, 1H), 2.30 (m, 2H), 2.53 (dd, 1H, J = 7.7, 16.5 Hz), 3.61 (s, 3H), 3.81 (m, 1H), 4.38 (t, 1H, J = 5.5), 4.51 (t, 1H, J = 5.0 Hz); ^{13}C 24.46, 25.90, 33.04, 34.96, 35.92, 51.80, 72.31, 79.10, 80.29, 110.82, 173.02. $[\alpha]_{20}^{D}$ −16.0° (*c* 0.9, CH_2Cl_2). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.44; H, 7.83.

5-Deoxy-2,3-*O*-isopropylidenecarba-β-D-*lyxo*-hexofuranose (20). Compound **19** (0.15g, 0.65 mmol) was reduced with LAH according to the procedure for **10**. Flash chromatography (30% hexane/70% ethyl acetate) afforded **20** as a colorless oil (0.12 g, 94%). NMR ($CDCl_3$) δ: ^{1}H 1.33 (s, 3H), 1.40 (m, 1H), 1.47 (s, 3H), 1.71 (m, 3H), 1.87 (m, 2H), 2.45 (bs, 1H), 3.69 (m, 2H), 3.87 (bs, 1H), 4.44 (t, 1H, J =5.4 Hz), 4.53 (t, 1H, J = 4.3 Hz); ^{13}C 24.47, 25.91, 31.83, 35.91, 36.15, 61.71, 72.45, 79.14, 80.79, 110.69. $[\alpha]_{20}^{D}$ −16.7° (*c* 0.7, CH_2Cl_2). Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.42; H, 8.89.

1,2,3,6-Tetra-*O*-acetyl-5-deoxycarba-β-D-*lyxo*-hexofuranose (21). Following the procedure identical to that used for the preparation of **7**, **20** (0.1 g, 0.50 mmol) was deprotected and acetylated to give **21**. After chromatography (75% hexane/25% ethyl acetate) a colorless oil (0.13 g, 78%) was obtained. NMR ($CDCl_3$) δ: ^{1}H and COSY 1.58 (m, 2H, H5, H4a), 1.78 (m, 1H, H5′), 1.89, 1.92, 1.94, and 2.00 (s, each 3H, CH_3-ester), 2.32 (m, 1H, H4a′), 3.98 (m, 2H, H6), 5.01 (dd, 1H, H2, J = 4.0, 10.5 Hz), 5.17 (ddd, 1H, H1, J = 6.5, 7.4, 19.1 Hz), 5.22 (t, 1H, H3, J = 8.5 Hz); ^{13}C and HETCOR 20.37, 20.62, 20.72, and 20.83 (CH_3-ester), 28.57 (C5), 34.70 (C4), 35.16 (C4a), 62.80 (C6), 70.23 (C1), 72.42 (C2), 73.31 (C3), 169.54, 170.21, and 170.90 (C=O ester). $[\alpha]_{20}^{D}$ −3.4° (*c* 0.7, CH_2Cl_2). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.50; H, 6.66.

5-Deoxycarba-β-D-*lyxo*-hexofuranose (22). Cleavage of the acetyl groups of **21** (0.12 g, 0.36 mmol) was done according to the preparation of **8**. Tetrol **22** (50 mg, 86%) was obtained as a light yellow oil, which required no further purification. NMR (d_6-DMSO) δ: ^{1}H 1.32 (m, 1H), 1.48 (m, 1H) 1.73 (m, 2H) 2.03 (td, 1H, J = 7.3, 13.3 Hz), 3.45 (m, 2H), 3.62 (dd, 1H, J = 4.1, 5.9 Hz), 3.73 (t, 1H, J = 3.9 Hz), 3.86 (dd, 1H, J = 6.2, 11.6 Hz); ^{13}C 33.53, 35.37, 38.14, 59.90, 70.49, 73.37, 73.93. $[\alpha]_{20}^{D}$ −17.6° (*c* 0.3, CH_3OH). HRMS: calcd for $C_7H_{15}O_4$ M + H m/z 163.0970, found 163.0971.

6-Bromo-5,6-dideoxy-2,3-*O*-isopropylidenecarba-α-D-*lyxo*-hexofuranose (23). To a solution of triphenylphosphine (1.21 g, 4.63 mmol) in CH_2Cl_2 (20 mL) was added bromine (2 mL) in CH_2Cl_2 (10 mL) dropwise until a light yellow color was sustained. Then the solution was treated with triethylamine (0.74 mL, 5.34 mmol) and stirred for 15 min at room temperature before **15** (0.72 g, 3.56 mmol) dissolved in CH_2Cl_2 (5 mL) was added. After 5 min, the reaction was quenched with 0.1 N HCl, and the extractive workup described for **7** was followed. The residue obtained was diluted with ether, the insoluble triphenylphosphine oxide was removed by filtration, and the ether layer was concentrated. Column chromatography (33% hexane/67% ethyl acetate) afforded 0.74 g (76%) of **23** as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 1.29 (s, 3H), 1.40 (s, 3H), 1.68 (d, 1H, J = 3.4 Hz), 1.71 (d, 1H, J = 2.4 Hz), 1.98 (dd, 1H, J = 6.9, 14.0 Hz), 2.05 (bs, 1H), 2.15 (q, 1H, J = 7.0, 14.0 Hz), 2.46 (m, 1H), 3.51 (m, 2H), 4.12 (t, 1H, J = 2.3 Hz), 4.39 (d, 1H, J = 5.6 Hz), 4.63 (t, 1H, J = 5.2 Hz); ^{13}C and DEPT 24.15 (q), 26.26 (q), 32.20 (t), 32.86 (t), 32.86 (t), 39.71 (d), 75.84 (d), 80.49 (d), 87.01 (d), 110.39 (s). $[\alpha]_{20}^{D}$ −28.4° (*c* 2.7, CH_2Cl_2). Anal. Calcd for $C_{10}H_{17}BrO_3$: C, 45.30; H, 6.46; Br, 30.14. Found: C, 45.21; H, 6.50; Br, 30.16.

5,6-Dideoxy-2,3-*O*-isopropylidenecarba-α-D-*lyxo*-hex-5-enofuranose (24). To a solution of 2-nitrophenylselenocyanate (0.56 g, 2.49 mmol) in ethanol (20 mL) was added $NaBH_4$ (0.10 g, 2.71 mmol) at 0 °C under nitrogen. After 15 min the mixture was allowed to warm to room temperature, and stirring was continued until no more gas evolution was observed (about 10 min). A solution of **23** (0.6 g, 2.26 mmol) in ethanol (10 mL) was added dropwise over a period of 30 min. After a total time of 16 h, the reaction mixture was diluted to double the volume with CH_2Cl_2, washed with water, and dried (Na_2SO_4), and the solvent was removed in vacuo. The dark brown residue was taken up in THF (30 mL) and cooled to 0 °C, and H_2O_2 (0.3 mL, 2.71 mmol, 30% in water) was added dropwise over 30 min. Stirring was continued over 16 h at room temperature. Excess H_2O_2 was destroyed by addition of MnO_2, the reaction mixture was filtrated over Celite, and the filtrate was concentrated. The residue was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. Flash chromatography (20% hexane/80% ethyl acetate) afforded olefin **24** as a colorless oil (0.36 g, 86%). NMR ($CDCl_3$) δ: ^{1}H 1.28 (s, 3H), 1.41 (s, 3H), 1.68 (dd, 1H, J = 3.1, 10.7 Hz), 1.93 (ddd, 1H, J = 4.2, 13.1, 17.3 Hz), 2.16 (bs, 1H), 2.89 (m, 1H), 4.12 (d, 1H, J = 4.2 Hz), 4.38 (dd, 1H, J = 1.7, 5.6 Hz), 4.64 (t, 1H, J = 5.1 Hz), 5.10 (dd, 1H, J = 1.4, 10.3 Hz), 5.15 (dd, 1H, J = 1.4, 17.6 Hz), 5.92 (ddd, 1H, J = 7.5, 10.3, 17.6 Hz); ^{13}C 24.06, 26.21, 36.63, 45.37, 75.91, 82.83, 87.17, 110.46, 116.21, 136.70. $[\alpha]_{20}^{D}$ −62.9° (*c* 2.6, CH_2Cl_2). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.24; H, 8.79.

2,3-*O*-Isopropylidenecarba-α-D-lyxofuranose (25). To a solution of **24** (0.34 g, 1.8 mmol) in 50% water/50% ether were added sodium metaperiodate (0.85 g, 3.98 mmol) and a catalytic amount of OsO_4. The vigorous stirring was continued

for 16 h. The ether layer was dried (Na_2SO_4) and concentrated. The obtained aldehyde was a dark oil, which was used without further purification. NMR ($CDCl_3$) δ: ^{13}C 24.07, 26.04, 32.14, 54.04, 74.86, 79.89, 86.68, 111.49, 201.18. $NaBH_4$ reduction of the aldehyde was done according to the procedure for **9** and yielded after flash chromatography (30% hexane/70% ethyl acetate) 0.22 g (61%) of **25** as a colorless oil. NMR ($CDCl_3$) δ: ^1H 1.27 (s, 3H), 1.42 (s, 3H), 1.61 (dd, 1H, J = 5.7, 13.3 Hz), 1.87 (ddd, 1H, J = 4.1, 13.3, 17.3 Hz), 2.39 (m, 1H), 2.87 (bs, 2H), 3.74 (m, 1H), 3.86 (m, 1H) 4.15 (d, 1H, J = 3.8 Hz), 4.39 (dd, 1H, J = 1.2, 5.7 Hz), 4.76 (t, 1H, J = 5.3 Hz); ^{13}C and DEPT 23.92 (q), 26.12 (q), 33.19 (t), 42.85 (d), 62.02 (t), 75.42 (d), 81.43 (d), 87.00 (d), 110.59 (s). $[\alpha]_{20}^{D}$ +40.2° (*c* 2.35, CH_2Cl_2). Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.37; H, 8.57.

1,2,3,5-Tetra-*O*-acetylcarba-α-D-lyxofuranose (26). Diol **25** (47 mg, 0.25 mmol) was reacted according to the procedure for **7**. Flash chromatography (33% hexane/67% ethyl acetate) afforded the peracetylated compound **26** (59 mg, 75%) as a colorless oil. NMR ($CDCl_3$) δ: ^1H 1.76 (ddd, 1H, J = 3.4, 9.4, 13.8 Hz), 1.99 (s, 6H), 2.03 (s, 3H), 2.07 (s, 3H), 2.12 (m, 1H), 2.68 (m, 1H), 4.04 (2 dd, AB-system, 2H, J = 6.6, 10.9, 8.6; 10.9 Hz), 5.20 (m, 2H), 5.44 (t, 1H, J = 3.8 Hz); ^{13}C 20.63 (2C), 20.76, 20.97, 31.10, 37.38, 62.51, 72.31, 75.46, 76.75, 169.93, 170.54, 170.79. $[\alpha]_{20}^{D}$ +33.6° (*c* 2.95, CH_2Cl_2). Anal. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.06; H, 6.31.

Carba-α-D-lyxofuranose (27). Cleavage of the acetyl groups of **26** (40 mg, 0.13 mmol) was done according to the preparation of **8**. Tetrol **27** (18 mg, 94%) was obtained as a light yellow oil, which required no further purification. NMR (CD_3OD) δ: ^1H 1.63 (ddd, 1H, J = 4.2, 9.5, 13.7 Hz), 1.94 (dd, 1H, J = 8.8, 13.7 Hz), 2.32 (m, 1H), 3.59 (dd, 1H, J = 6.1, 10.6 Hz), 3.72 (dd, 1H, J = 7.2, 10.6 Hz), 3.81 (t, 1H, J = 5.0 Hz), 4.14 (m, 2H); ^{13}C and DEPT 34.29 (t), 42.57 (d), 63.16 (t), 74.62 (d), 77.40 (d), 82.24 (d). $[\alpha]_{20}^{D}$ +21.4° (*c* 1.12, CH_3OH). HRMS: calcd for $C_6H_{13}O_4$: M + H *m/z* 149.0814, found 149.0810.

2,3-*O*-Isopropylidene-5-*O*-triphenylmethylcarba-α-D-lyxofuranose (28). To a solution of **25** (95 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) was added pyridine (60 μL, 0.765 mmol), chlorotriphenylmethane (0.16 g, 0.56 mmol), and a few crystals of DMAP. After being stirred for 2 h at room temperature, the mixture was diluted with 0.1 N HCl and extractive workup as described for **7** was followed. Flash chromatography (70% hexane/30% ethyl acetate) provided **28** (0.14 g, 62%) as a white foam. NMR ($CDCl_3$) δ: ^1H 1.32 (s, 3H), 1.35 (s, 3H), 1.63 (dd, 1H, J = 3.9, 13.1 Hz), 1.71 (dt, 1H, J = 6.0, 13.1 Hz), 2.58 (m, 1H), 3.13 (dd, 1H, J = 7.0, 8.6 Hz), 3.47 (dd, 1H, J = 7.5, 8.6 Hz), 4.17 (dd, 1H, J = 7.1, 14.2 Hz), 4.42 (bs, 1H), 4.43 (dd, 1H, J = 1.6, 4.8 Hz), 4.82 (t, 1H, J = 5.1 Hz), 7.30 (m, 12H), 7.55 (d, 3H); ^{13}C 24.24, 26.20, 34.76, 42.01, 62.74, 75.81, 80.34, 86.65, 87.08, 110.20, 126.99, 127,82, 129.09, 144,64. $[\alpha]_{20}^{D}$ −17.9° (*c* 6.5, CH_2Cl_2). Anal. Calcd for $C_{28}H_{30}O_4$: C, 78.11; H, 7.02. Found: C, 78.30; H, 6.91.

2,3-*O*-Isopropylidene-5-*O*-triphenylmethylcarba-β-D-lyxofuranose (29). Oxidation of **28** (0.14 g, 0.31 mmol) provided 0.11 g (0.26 mmol) of the intermediate ketone as a white foam, under conditions identical to those used for the preparation of **9**. NMR ($CDCl_3$) δ: ^1H 1.49 (s, 3H), 1.50 (s, 3H), 2.25 (dd, 1H, J = 12.5, 18.5 Hz), 2.34 (dd, 1H, J = 8.0, 18.5 Hz), 2.50 (m, 1H), 3.29 (dd, 1H, J = 6.6, 8.8 Hz), 3.57 (t, 1H, J = 8.8 Hz), 4.25 (d, 1H, J = 4.8 Hz), 4.82 (t, 1H, J = 4.2 Hz), 7.34 (m, 12H), 7.52 (d, 3H); ^{13}C 25.38, 27.03, 36.31, 37.29, 63,26, 77.88, 80.41, 86.94, 112.56, 127.24, 128.09, 128.96, 144.27, 213.85. $[\alpha]_{20}^{D}$ +54.7° (*c* 5.5, CH_2Cl_2). The reduction of the ketone was done as described for **9**, at −5 °C. A white foam of **29** (0.10 g, 76%) was obtained after flash chromatography (70% hexane/30% ethyl acetate). NMR ($CDCl_3$) δ: ^1H 1.32 (s, 3H), 1.44 (s, 3H), 1.90 (dt, 1H, J = 12.1, 5.6 Hz), 1.98 (dt, 1H, J = 11.4, 5.7 Hz), 2.48 (bd, 1H, J = 9.3 Hz), 3.15 and 3.42 (two m, 1H, caused by restricted rotation), 3.88 (bs, 1H), 4.48 (t, 1H, J = 5.5 Hz) 4.71 (t, 5.0 Hz), 7.39 (m, 12H), 7.52 (d, 3H); ^{13}C 24.51, 25.85, 33.80, 39.55, 62.28, 72.35, 78.88, 79.57, 86.64, 110.58, 127.25, 127.95, 129.00, 144.49. $[\alpha]_{20}^{D}$ −11.7° (*c* 3.5, CH_2Cl_2). Anal. Calcd for $C_{28}H_{30}O_4$: C, 78.11; H, 7.02. Found: C, 78.18; H, 6.97.

1,2,3,5-Tetra-*O*-acetylcarba-β-D-lyxofuranose (30). Alcohol **29** (70 mg, 0.16 mmol) was reacted according to the procedure for **7**. Flash chromatography (33% hexane/67% ethyl acetate) afforded fully acetylated compound **30** (32 mg, 62%) as a colorless oil. NMR ($CDCl_3$) δ: ^1H 1.69 (ddd, 1H, J = 5.2, 9.3, 13.9 Hz), 2.02 (s, 6H), 2.04 (s, 3H), 2.08 (s, 3H), 2.35 (dd, 1H, J = 7.5, 8.6 Hz), 2.45 (m, 1H), 4.09 (dd, 1H, J = 6.6, 11.0 Hz), 4.17 (dd, 1H, J = 8.2, 11.0 Hz), 5.15 (dd, 1H, J = 4.3, 5.8 Hz), 5.26 (dd, 1H, J = 5.7, 12.9 Hz), 5.38 (t, 1H, J = 4.8 Hz); ^{13}C and DEPT 20.66 (q), 20.79 (q), 20.95(q), 32.17 (t), 36.95 (d), 63.46 (t), 70.57 (d), 71.83 (d), 72.68 (d), 169.76 (s), 170.12 (s), 170.27 (s), 170.96 (s). $[\alpha]_{20}^{D}$ −5.8° (*c* 1.6, CH_2Cl_2). Anal. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.17; H, 6.37.

Carba-β-D-lyxofuranose (31). Cleavage of the acetyl groups of **30** (32 mg, 0.10 mmol) was done according to the preparation of **8**. Tetrol **31** (14 mg, 94%) was obtained as a light yellow oil, which required no further purification. NMR (CD_3OD) δ: ^1H 1.55 (ddd, 1H, J = 4.3, 7.8, 12.8 Hz), 2.09 (m, 1H), 2.13 (ddd, 1H, J = 6.9, 9.0, 12.8 Hz), 3.65 (dd, 1H, J = 5.4, 10.6 Hz), 3.78 (dd, 1H, J = 6.8, 10.6 Hz), 3.81 (t, 1H, J = 4.7 Hz), 4.05 (dd, 1H, J = 5.5, 6.3 Hz), 4.09 (t, 1H, J = 4.6 Hz); ^{13}C and DEPT 35.41 (t), 42.95 (d), 63.26 (t), 72.85 (d), 74.78 (d), 75.83 (d). $[\alpha]_{20}^{D}$ −12.9 (*c* 1.0; CH_3OH); (lit.[5b] for the enantiomer $[\alpha]_{25}^{D}$ +11.3° (*c* 0.84, CH_3OH)). HRMS: calcd for $C_6H_{13}O_4$ M + H *m/z* 149.0814, found 149.0809.

***rac*-2,3,5-Trideoxycarba-β-*glycero*-hex-2-enofuranose (32).** Compound **13** (3.0 g, 15.1 mmol) was reduced with LAH according to the procedure for **10**. Diol **32** (2.1 g, 90%) was obtained after flash chromatography (50% hexane/50% ethyl acetate) as a colorless oil. NMR ($CDCl_3$) δ: ^1H 1.44 (dt, 1H, J = 4.4, 13.7 Hz), 1.64 (m, 1H), 1.81 (m, 1H), 2.45 (m, 2H), 2.76 (bs, 1H), 3.71 (t, 2H, J = 6.2), 4.81 (bs, 1H), 5.84 (m, 1H), 5.90 (m, 1H); ^{13}C 38.89, 40.02, 41.56, 61.38, 77.40, 133.69, 138.48. Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.72; H, 9.57.

***rac*-2,3-Anhydro-5-deoxycarba-β-*lyxo*-hexofuranose (33).** *tert*-Butyl hydroperoxide (7.2 mL, 21.6 mmol, 3 M in isooctane) was added dropwise to a solution of **32** (2.0 g, 15.6 mmol) and vanadyl(IV) acetylacetonate (0.1 g, 0.4 mmol) in CH_2Cl_2 (50 mL). After the addition was complete, the mixture was refluxed for 48 h and then cooled to 20 °C, filtered over Celite, and concentrated. Column chromatography (80% toluene/20% ethyl acetate) gave epoxide **33** (1.6 g, 70%) as a colorless oil. NMR ($CDCl_3$) δ: ^1H 0.98 (dt, 1H, J = 8.5, 12.0 Hz), 1.74 (m, 1H), 1.85 (m, 1H), 2.08 (m, 3H), 2.35 (bs, 1H), 3.45 (d, 1H, J = 2.7 Hz), 3.50 (d, 1H, J = 2.4 Hz), 3.70 (m, 2H), 4.21 (t, 1H, J = 7.9 Hz); ^{13}C 33.40, 33.95, 35.61, 58.83, 59.50, 61.31, 73.38. Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.19; H, 8.28.

***rac*-1,2,3,6-Tetra-*O*-acetyl-5-deoxycarba-β-*arabino*-hexofuranose (34).** Epoxide **33** (0.1 g, 0.7 mmol) was suspended in water (5 mL), treated with a few drops of $HClO_4$ (70% in water), and stirred for 12 h at 20 °C. After neutralization with weakly basic ionic exchange resin (Amberlite IRA-68), the mixture was filtered and concentrated. The obtained tetrol was acetylated following the method for **7** to give after flash chromatography (90% hexane/10% ethyl acetate) **34** as a colorless oil (0.23 g, 99%). NMR ($CDCl_3$) δ: ^1H and COSY 1.51 (m, 1H, H4a), 1.70 (m, 1H, H5), 1.99 (m, 14H, 4 CH_3-ester, H4, H5'), 2.36 (m, 1H, H4a'), 4.03 (m, 2H, 2H6), 5.04 (m, 2H, H2, H3), 5.18 (q, 1H, H1, J = 5.3, 11.0 Hz); ^{13}C 20.59, 20.76, 20.82, 20.91, 33.05 (2C), 36.96, 62.52, 70.99, 76.07, 79.86, 169.79, 169.89, 170.24, 170.79. Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.69; H, 6.62.

***rac*-5-Deoxycarba-β-*arabino*-hexofuranose (35).** Cleavage of the acetyl groups of **34** (41 mg, 0.124 mmol) was done according to the procedure for **8**. Tetrol **35** (19 mg, 94%) was obtained as a colorless oil, which required no further purification. NMR (d_6-DMSO) δ: ^1H and COSY 1.13 (m, 1H, H4a), 1.41 (m, 1H, H5), 1.48 (m, 1H, H4), 1.70 (m, 1H, H5'), 2.05 (m, 1H, H4a'), 3.45 (m, 4H, H2, H3, 2H6), 3.84 (m, 1H, H1);

^{13}C 36.73, 38.28, 39.19, 61.16, 70.46, 79.27, 82.20. HRMS: calcd for $C_7H_{15}O_4$ M + H m/z 163.0970, found 163.0962.

***rac*-5-Deoxy-6-*O*-triphenylmethylcarba-β-*arabino*-hexofuranose (36).** The same method used for tritylation of **25** was used for **35** (1.2 g, 7.4 mmol) to give after flash chromatography (90% $CHCl_3$/10% methanol) **36** (2.7 g, 90%) as a colorless oil. NMR (CD_3OD) δ: ^{1}H 1.25 (m, 2H), 1.58 (m, 1H), 1.76 (m, 1H), 2.07 (m, 2H), 3.15 (m, 2H), 3.34 (m, 1H), 3.98 (m, 1H), 4.12 (m, 1H), 7.24 (m, 12H), 7.45 (m, 3H); ^{13}C 36.32, 37.01, 40.24, 63.86, 71.43, 80.13, 82.17 and 82.80 (caused upon restricted rotation), 128.20, 128.86, 128.97, 129.53, 130.05, 145.96, 149.07. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98. Found: C, 77.97; H, 7.11.

***rac*-1,2,3-Tri-*O*-acetyl-5-deoxy-6-*O*-(triphenylmethyl)-carba-β-*arabino*-hexofuranose (37).** Triol **36** (3.8 g, 9.4 mmol) in CH_2Cl_2 (20 mL) was treated with acetic anhydride (1.18 mL, 12.5 mmol), pyridine (1.26 mL, 15.6 mmol), and a catalytic amount of DMAP. After 2 h at rt methanol (2mL) was added, and stirring was continued for a further 15 min. The solution was washed with 1 N HCl and saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated to give **37** (4.3 g, 87%) as a colorless oil after flash chromatography (96% toluene/4% ethyl acetate). NMR ($CDCl_3$) δ: ^{1}H 1.48 (ddd, 1H, J = 6.0, 7.5, 13.5 Hz), 1.70 (m, 1H), 1.98−2.14 (m, 11H), 2.21 (m, 1H), 3.13 (m, 2H), 5.10 (ddd, 2H, J = 6.0, 11.1, 17.6 Hz), 5.23 (dd, 1H, J = 4.4, 11.2 Hz), 7.27 (m, 9H), 7.46 (m, 6H); ^{13}C 20.72, 20.90, 21.05, 33.24, 34.64, 36.89, 61.87, 71.06, 76.17, 80.28, 86.81, 127.10, 127.26, 127.90, 128.12, 128.77, 144.36, 169.96, 170.02, 170.36. Anal. Calcd for $C_{32}H_{34}O_7$: C, 72.43; H, 6.46. Found: C, 72.40; H, 6.40.

***rac*-1,2,3-Tri-*O*-acetyl-5-deoxycarba-β-*arabino*-hexofuranose (38).** Compound **37** (3.7 g, 7.0 mmol) was dissolved in ethanol (50 mL) and after addition of Pd−C (50 mg, 10%) was subjected to hydrogenation in a Parr apparatus for 2 d (50 psi; room temperature). The catalyst was removed by filtration, and the filtrate was concentrated to yield alcohol **38** (2.02 g, 84%) as a colorless oil after column chromatography (96% toluene/4% ethyl acetate). NMR ($CDCl_3$) δ: ^{1}H 1.63−1.46 (m, 2H), 1.85 (dd, 1H, J = 6.8, 13.5 Hz), 1.98 (s, 6H), 1.99 (s, 3H), 2.09 (m, 1H), 2.33 (ddd, 1H, J = 6.7, 9.0, 15.2 Hz), 2.44 (bs, 1H), 3.58 (m, 2H), 4.99 (t, 1H, J = 5.7 Hz), 5.06 (t, 1H, J = 5.2 Hz), 5.19 (dd, 1H, J = 6.2, 11.6 Hz); ^{13}C 20.66, 20.84, 21.04, 33.31, 36.90, 37.09, 60.68, 71.25, 76.26, 80.15, 169.99, 170.15, 170.63. Anal. Calcd for $C_{13}H_{20}O_7$: C, 54.16; H, 6.99. Found: C, 54.03; H, 7.08.

***rac*-1,2,3-Tri-*O*-acetyl-6-bromo-5-deoxycarba-β-*arabino*-hexofuranose (39).** The procedure for the preparation of **23** was followed using alcohol **38** (1.52 g, 5.27 mmol) to give after flash chromatography (90% toluene/10% ethyl acetate) bromide **39** (1.78 g, 85%) as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 1.50 (ddd, 1H, J = 5.6, 7.3, 13.4 Hz), 1.91−2.09 (m, 11H), 2.19 (m, 1H), 2.39 (ddd, 1H, J = 6.3, 8.9, 15.0 Hz), 3.38 (m, 2H), 5.05 (t, 1H, J = 5.9), 5.12 (t, 1H, J = 5.2), 5.24 (dd, 1H, J = 5.6, 11.1 Hz); ^{13}C 20.79, 20.97, 21.11, 31.06, 32.84, 37.45, 38.70, 71.22, 76.33, 79.57, 169.97, 170.07, 170.44. Anal. Calcd for $C_{13}H_{19}BrO_6$: C, 44.46; H, 5.45. Found: C, 44.48; H, 5.58.

***rac*-1,2,3-Tri-*O*-acetyl-5,6-dideoxycarba-β-*arabino*-hex-5-enofuranose (40).** Bromide **39** (0.83 g, 2.3 mmol) provided under conditions similar to those used for **24** after flash chromatography (96% toluene/4% ethyl acetate) 0.79 g (88%) of **40** as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 1.73 (ddd, 1H, J = 5.4, 8.5, 14.1 Hz), 2.06 (s, 6H), 2.08 (s, 3H), 2.41 (m, 1H), 2.56 (ddd, 1H, J = 8.6, 16.6 Hz), 5.04−5.28 (m, 5H), 5.85 (ddd, 1H, J = 7.7, 10.1, 17.3 Hz); ^{13}C 20.84, 21.04, 21.13, 33.63, 43.77, 70.56, 75.97, 79.29, 116.18, 138.56, 170.45, 170.22. Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.61; H, 6.58.

***rac*-1,2-Di-*O*-acetyl-3-deoxycarba-β-*glycero*-pent-3-enodialdo-1,4-furanose (41).** Compound **40** (0.79 g, 2.9 mmol) was reacted according to the first part of procedure for **25** to give unsaturated aldehyde **41** (0.33 g, 43%) as a colorless oil after flash chromatography (75% toluene/25% ethyl acetate). NMR 200 MHz ($CDCl_3$) δ: ^{1}H 2.02−2.08 (m, 6H), 2.73 (m, 1H), 2.82 (m, 1H), 5.49 (ddd, 1H, J = 3.7, 6.2, 9.9 Hz), 5.88 (m, 1H), 6.72 (m, 1H), 9.83 (s, 1H); ^{13}C 20.62, 20.70, 33.52, 71.39, 75.62, 144.17, 146.42, 169.85, 170.13, 189.09. Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.69; H, 5.58.

***rac*-1,2,3,5-Tetra-*O*-acetylcarba-β-arabinofuranose (42).** A solution of **40** (50 mg, 0.019 mmol) in 5 mL of CH_3OH was cooled to −78 °C, and O_3 was bubbled through the solution for 5 min. The solution was flushed with argon while warming to 0 °C, the aldehyde was reduced (procedure **9**), and the alcohol was protected according to the procedures for **37**. Purification by flash chromatography (80% toluene/20% ethyl acetate) afforded **42** as a colorless oil (26 mg, 44%). NMR ($CDCl_3$) δ: ^{1}H 1.68 (m, 2H), 2.06 (bs, 12H), 2.31 (m, 2H), 4.10 (d-AB system, 1H, J = 6.8, 11.1 Hz), 4.22 (d-AB system, 1H, J = 6.5, 11.1 Hz), 5.17 (m, 2H), 5.28 (m, 1H); ^{13}C 20.81, 20.96, 21.00, 21.09, 30.46, 39.70, 65.60, 71.35, 76.38, 76.84, 170.07, 170.13, 170.24, 171.00. Anal. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.11; H, 6.33.

***rac*-Carba-β-arabinofuranose (43).** Cleavage of the acetyl groups of **42** (15 mg, 0.047 mmol) was done according to the preparation of **8**. Tetrol **43** (6 mg, 83%) was obtained as a colorless oil, which required no further purification. NMR (CD_3OD) δ: ^{1}H and COSY 1.51 (ddd, 1H, H4a, J = 4.7, 7.3, 12.0 Hz), 1.91 (m, 1H, H5), 2.19 (m, 1H, H4a'), 3.57 (dd, 1H, H3, J = 7.1, 10.5 Hz), 3.80−3.69 (m, 3H, H2, 2H6), 4.06 (m, 1H, H1); ^{13}C 33.87, 46.04, 66.01, 72.38, 79.59, 80.84. HRMS: calcd for $C_6H_{13}O_4$ M + H m/z 149.0814, found 149.0806.

***rac*-2,3-Anhydro-6-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-carba-β-*lyxo*-hexofuranose (44).** A solution of **33** (1.7 g, 11.9 mmol), *tert*-butyldimethylsilyl chloride (1.96 g, 13.0 mmol), and pyridine (1.9 mL, 23.8 mmol) in CH_2Cl_2 (20 mL) was stirred for 16 h at room temperature. The reaction was quenched with 0.1 N HCl, and the extractive workup described for **7** was followed. After flash chromatography (90% toluene/10% ethyl acetate) **44** (1.7 g, 55%) was obtained as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 0.03 (s, 6H), 0.86 (s, 9H), 1.45 (m, 1H), 1.60 (m, 1H), 1.76 (m, 1H), 1.96 (m, 2H), 3.40 (d, 1H, J = 2.7 Hz), 3.46 (dd, 1H, J = 1.2, 2.6 Hz), 3.62 (m, 2H), 4.16 (m, 1H). Anal. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14. Found: C, 60.38; H, 10.08.

***rac*-2,3-Anhydro-6-*O*-(*tert*-butyldimethylsilyl)-5-deoxy-carba-α-*lyxo*-hexofuranose (45).** To a solution of **44** (1.56 g, 6.0 mmol) and pyridine (0.97 mL, 12.0 mmol) in CH_2Cl_2 (25 mL) was added trifluoromethane sulfonic anhydride (1.15 mL, 7.0 mmol) dropwise at 0 °C under argon atmosphere. After 10 min the reaction was quenched with cold 0.1 N HCl, and the extractive workup described for **7** was followed. The residue was diluted in DMF (25 mL) and treated with cesium acetate (1.5 g, 7.8 mmol). The mixture was stirred for 12 h at room temperature, diluted with 0.1 N HCl, and worked up as above. Flash chromatography (70% toluene/30% ethyl acetate) afforded **45** (0.61 g, 39%) as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 0.03 (s, 6H), 0.91 (s, 9H), 1.30 (ddd, 1H, J =5.4, 9.8, 15.2 Hz), 1.56−1.83 (m, 4H), 3.41 (d, 1H, J = 2.3 Hz), 3.50 (dd, 1H, J = 1.0, 2.2 Hz), 3.69 (m, 2H), 4.36 (d, 1H, J = 5.4 Hz); ^{13}C −5.07, 18.55, 26.21, 34.11, 34.99, 36.48, 58.80, 59.41, 62.16, 72.20. Anal. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14. Found: C, 60.46; H, 10.02.

***rac*-1,2,3,6-Tetra-*O*-acetyl-5-deoxycarba-α-*arabino*-hexofuranose (46).** Epoxide **45** (0.51 g, 1.97 mmol) was allowed to react according to the procedure for **34**. The obtained tetrol was acetylated following the method for **7** to give after flash chromatography (90% toluene/10% ethyl acetate) **46** as a colorless oil (0.33 g, 51%). NMR ($CDCl_3$) δ: ^{1}H 1.67 (m, 1H), 1.88 (m, 2H); 2.16−1.97 (m, 13H), 2.30 (m, 1H), 4.07 (ddd, 2H, J = 2.8, 6.6, 9.4 Hz), 4.95 (dd, 1H, J = 5.7, 8.7 Hz), 5.05 (ddd, 1H, J = 3.3, 6.9, 10.4 Hz), 5.18 (t, 1H, J = 5.1 Hz); ^{13}C 21.09, 21.14, 21,21, 31.88, 34.60, 38.63, 62.75, 76,11, 81.12, 81.93. Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.71; H, 6.88.

***rac*-5-Deoxycarba-α-*arabino*-hexofuranose (47).** Cleavage of the acetyl groups of **46** (0.10 g, 0.30 mmol) was done according to the procedure for **8**. Tetrol **47** (46 mg, 94%) was obtained as a colorless oil, which required no further purification. NMR (CD_3OD) δ: ^{1}H 1.51 (m, 1H), 1.67 (m, 1H), 1.81 (m, 1H), 1.94 (m, 1H), 3.35 (m, 1H), 3.71−3.55 (m, 2H), 3.87 (m, 1H); ^{13}C and DEPT 30.96 (t), 38.52 (t), 40.63 (d), 62.21 (t),

76.20 (d), 83.33 (d), 86.36 (d). HRMS: calcd for $C_7H_{15}O_4$ M + H *m/z* 163.0970, found 163.0976.

***rac*-5-Deoxy-6-*O*-(triphenylmethyl)carba-α-*arabino*-hexofuranose (48).** The same method for protection as for **28** was used for **47** (1.1 g, 6.8 mmol) to give after flash chromatography (80% $CHCl_3$/20% methanol) **48** (2.47 g, 90%) as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 1.71–1.44 (m, 3H), 1.88 (m, 2H), 2.96 (dd, 1H, *J* = 8.3, 13.4 Hz), 3.22 (m, 1H), 3.45 (t, 1H, *J* = 6.0), 3.77 (t, 1H, *J* = 6.8), 3.87 (dd, 1H, *J* = 6.2, 14.2 Hz), 4.21 (bs, 1H), 4.44 (bs, 1H), 5.04 (bs, 1H), 7.26 (m, 10H), 7.45 (m, 5H); ^{13}C 34.87, 35.37, 39.58, 63.29, 74.49, 76.87, 81.33, 84.57, 87.51, 127.29, 128.14, 128.86, 144.28. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98. Found: C, 77.07; H, 7.10.

***rac*-1,2,3-Tri-*O*-acetyl-5-deoxy-6-*O*-(triphenylmethyl)-carba-α-*arabino*-hexofuranose (49).** Triol **48** (1.44 g, 3.6 mmol) was acetylated according to the method for **37**. Flash chromatography (96% toluene/4% ethyl acetate) provided **49** (1.63 g, 86%) as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 1.59 (m, 1H), 1.96–1.77 (m, 2H), 2.02 (s, 3H), 2.06 (s, 6H), 2.41 (m, 1H), 3.11 (m, 2H), 4.92 (dd, 1H, *J* = 5.9, 8.7 Hz), 5.02 (m, 1H), 5.19 (t, 1H, *J* = 4.1 Hz), 7.21 (m, 9H), 7.44 (m, 6H); ^{13}C 20.96, 21.04, 21.12, 33.16, 34.43, 38.42, 61.88, 76.14, 81.36, 81.95, 86.88, 127.15, 127.96, 128.57, 129.20, 144.39, 170.15, 170.57. Anal. Calcd for $C_{32}H_{34}O_7$: C, 72.43; H, 6.46. Found: C, 72.41; H, 6.41.

***rac*-1,2,3-Tri-*O*-acetyl-5-deoxycarba-α-*arabino*-hexofuranose (50).** Cleavage of the trityl group of **49** (1.5 g, 2.8 mmol) was done according to the procedure for **38**. Alcohol **50** (0.66 g, 81%) was obtained as a colorless oil after column chromatography (20% toluene/80% ethyl acetate). NMR ($CDCl_3$) δ: ^{1}H 1.57 (m, 1H), 1.83 (m, 2H), 2.10–1.97 (m, 10H), 2.36 (ddd, 1H, *J* = 8.1, 16.0 Hz), 3.65 (m, 2H), 4.93 (dd, 1H, *J* = 5.4, 8.0, 13.4 Hz), 5.04 (m, 1H), 5.18 (t, 1H, *J* = 4.5 Hz); ^{13}C 21.02, 21.15, 34.65, 35.68, 38.39, 60.95, 76.35, 81.38, 82.00, 170.23, 170.40, 170.91. Anal. Calcd for $C_{13}H_{20}O_7$: C, 54.16; H, 6.99. Found: C, 54.26; H, 6.93.

***rac*-1,2,3-Tri-*O*-acetyl-6-bromo-5,6-dideoxycarba-α-*arabino*-hexofuranose (51).** The procedure for the preparation of **23** was followed using alcohol **50** (0.71 g, 2.5 mmol) to give after flash chromatography (90% toluene/10% ethyl acetate) bromide **51** (0.60 g, 70%) as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 1.87 (m, 1H), 2.16–2.00 (m, 12H), 2.47 (m, 1H), 3.39 (m, 2H), 4.94 (dd, 1H, *J* = 5.6, 8.4 Hz), 5.04 (m, 1H), 5.20 (t, 1H, *J* = 4.2); ^{13}C 21.04, 21.13, 30.83, 34.15, 36.17, 40.07, 75.94, 81.85, 81.89, 170.13, 170.34, 170.71. Anal. Calcd for $C_{13}H_{19}BrO_6$: C, 44.46; H, 5.45. Found: C, 44.46; H, 5.51.

***rac*-1,2,3-Tri-*O*-acetyl-5,6-dideoxycarba-α-*arabino*-hex-5-enofuranose (52).** Bromide **51** (0.86 g, 2.5 mmol) was converted under conditions similar to those used for **24** and after flash chromatography (90% toluene/10% ethyl acetate) into 0.49 g (74%) of **52** as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 2.08–1.97 (m, 11H), 2.87 (ddd, 1H, *J* = 7.9, 18.2 Hz), 5.23–5.02 (m, 5H), 5.75 (ddd, 1H, *J* = 7.5, 10.1, 17.4 Hz); ^{13}C 21.07, 21.23, 34.59, 45.35, 76.06, 80.33, 81.98, 116.81, 137.20, 170.25, 170.30, 170.57. Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.72; H, 6.64.

***rac*-1,2,3,5-Tetra-*O*-acetylcarba-α-arabinofuranose (53).** Compound **52** (0.20 g, 0.74 mmol) was reacted according to the procedure for the preparation of **25** to give the alcohol, which was acetylated according to the procedure for **37**. After flash chromatography (96% toluene/4% ethyl acetate), fully protected **53** was obtained as a colorless oil (0.18 g, 78%). NMR ($CDCl_3$) δ: ^{1}H 2.08–1.96 (m, 14H), 2.57 (m, 1H), 4.11 (m, 2H), 5.06 (m, 2H), 5.24 (t, 1H, *J* = 4.5 Hz); ^{13}C and DEPT 21.05 (q), 21.18 (q), 31.75 (t), 40.91 (d), 64.36 (t), 75.73 (d), 77.93 (d), 81.60 (d), 170.16 (s), 170.30 (s), 170.48 (s), 170.97 (s). Anal. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.21; H, 6.42.

***rac*-Carba-α-arabinofuranose (54).** Cleavage of the acetyl groups of **53** (0.1 g, 0.32 mmol) was done according to the preparation of **8**. Tetrol **54** (40 mg, 87%) was obtained as a colorless oil, which required no further purification. NMR (CD_3OD) δ: ^{1}H and COSY 1.89–1.67 (m, 2H, 4a), 2.03 (m, 1H, H4), 3.49 (m, 2H, 2H5), 3.62 (m, 2H, H3, H2), 3.79 (q, 1H, H1, *J* = 6.5, 7.9 Hz); ^{13}C 33.44, 45.39, 64.95, 75.96, 79.16, 86.01. HRMS: calcd for $C_6H_{13}O_4$ M + H *m/z* 149.0814, found 149.0811.

5-Deoxy-1,2-*O*-isopropylidenecarba-α-D-*xylo*-hexofuranurono-6,3-lactone (55). Lactone **3**[9,10] (0.4 g, 3.22 mmol) was *cis*-dihydroxylated, and the obtained diol was protected according to the preparation of **14**. Flash chromatography (90% hexane/10% ethyl acetate) gave compound **55** as white needles (0.47 g, 74%). Mp: 51–53 °C. NMR ($CDCl_3$) δ: ^{1}H 1.27 (s, 3H), 1.39 (s, 3H), 1.55 (ddd, 1H, *J* = 4.4, 11.0, 14.6 Hz), 2.32 (dd, 1H, *J* = 7.7, 14.6 Hz), 2.33 (d, 1H, *J* = 17.7 Hz), 2.70 (dd, 1H, *J* = 7.5, 17.7 Hz), 3.11 (m, 1H), 4.62 (d, 1H, *J* = 5.3 Hz), 4.67 (d, 1H, *J* = 5.3 Hz), 4.75 (t, 1H, *J* = 4.8 Hz); ^{13}C 24.28, 26.64, 34.96, 37.06, 37.60, 81.67, 83.84, 89.76, 110.95, 176.03. $[\alpha]_{20}^{D}$ +83.3° (*c* 1.3, CH_2Cl_2). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.53; H, 7.18. The enantiomeric excess (ee) of this compound was determined by use of chiral shift reagent (Eu-hfc) to be 91%.

5-Deoxy-1,2-*O*-isopropylidenecarba-α-D-*xylo*-hexofuranose (56). Lactone **55** (0.4 g, 2.02 mmol) was reduced with LAH according to the procedure for **10**. A colorless oil was obtained which was not subjected to further purification (0.38 g, 93%). NMR ($CDCl_3$) δ: ^{1}H 1.29 (s, 3H), 1.43 (s, 3H), 1.77 (m, 4H), 2.26 (m, 1H), 2.74 (m, 2H), 4.06 (d, 1H, *J* = 3.4 Hz), 4.43 (d, 1H, *J* = 5.7 Hz), 4.71 (t, 1H, *J* = 5.2 Hz); ^{13}C 23.98, 26.34, 30.68, 36.23, 39.35, 61.99, 77.10, 79.73, 86.46, 109.79. $[\alpha]_{20}^{D}$ −11.3° (*c* 1.1, CH_2Cl_2). Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.46; H, 8.91.

***rac*-1,2,3,6-Tetra-*O*-acetyl-5-deoxycarba-α-*xylo*-hexofuranose (57).** Diol **56** (0.27 g, 1.27 mmol) was reacted according to the procedure for **7**. Flash chromatography (33% hexane/67% ethyl acetate) afforded the fully acetylated compound **57** (0.34 g, 81%) as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H and COSY 1.48 (m, 1H, H5′), 1.70 (m, 1H, H5), 1.76 (m, 1H, H4a), 1.94 (m, 1H, H4a′), 1.97 (s, 6H, CH_3-ester), 1.98 and 2.02 (s, each 3H, CH_3-ester), 2.50 (m, 1H, H4), 3.98 (m, 2H, 2H6), 5.09 (t, 1H, H2, *J* = 4.6 Hz), 5.21 (dd, 1H, H3, *J* = 4.5, 7.0 Hz), 5.28 (ddd, 1H, H1, *J* = 3.1, 6.4, 7.9 Hz); ^{13}C and HETCOR 20.92, 20.61, and 20.63 (CH_3-ester), 28.51 (C5), 34.41 (C4a), 35.01 (C4), 62.88 (C6), 71.58 (C1), 76.69 (C2, C3), 169.68, 170.07, and 170.89 (C=O ester). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.39; H, 6.79.

***rac*-5-Deoxycarba-α-*xylo*-hexofuranose (58).** Cleavage of the acetyl groups of **57** (0.4 g, 1.21 mmol) was done according to the preparation of **8**. Tetrol **58** (0.19 g, 97%) was obtained as a colorless oil, which required no further purification. NMR (d_6-DMSO) δ: ^{1}H 1.55 (m, 3H), 2.19 (m, 2H), 3.64 (m, 2H), 3.75 (m, 2H), 4.05 (m,1H); ^{13}C 33.09, 36.06, 37.07, 60.39, 77.26, 78.73. HRMS: calcd for $C_7H_{15}O_4$ M + H *m/z* 163.0970, found 163.0967.

6-Bromo-5,6-dideoxy-1,2-*O*-isopropylidenecarba-α-D-*xylo*-hexofuranose (59). The procedure for the preparation of **23** was followed using diol **56** (0.25 g, 1.26 mmol) to give after flash chromatography (33% hexane/67% ethyl acetate) bromide **59** (0.15 g, 46%) as a colorless oil. NMR ($CDCl_3$) δ: ^{1}H 1.28 (s, 3H), 1.42 (s, 3H), 1.65 (dt, 1H, *J* = 5.0, 13.2 Hz), 1.87 (dd, 1H, *J* = 6.3, 13.4 Hz), 1.93–2.16 (2dd, AB-system, *J* = 7.2, 14.4 Hz), 2.24 (bs, 1H), 2.26–2.40 (m, 1H), 3.38–3.52 (2dd, AB-system, 2H, *J* = 7.1, 9.9, 16.8 Hz), 4.04 (d, 1H, *J* = 3.8 Hz), 4.38 (d, 1H, *J* = 5.8 Hz), 4.71 (t, 1H, *J* = 5.3 Hz); ^{13}C and DEPT 24.05 (q), 26.32 (q), 31.46 (t), 32.51 (t), 35.54 (t), 39.49 (d), 76.46 (d), 79.63 (d), 86.62 (d), 110.10 (s). $[\alpha]_{20}^{D}$ −15.1° (*c* 1.6, CH_2Cl_2). Anal. Calcd for $C_{10}H_{17}BrO_3$: C, 45.30; H, 6.46. Found: C, 45.22; H, 6.42. As a byproduct **3,6-anhydro-5-deoxy-1,2-*O*-isopropylidenecarba-α-D-*xylo*-hexofuranose (60)** was obtained as a colorless oil (90 mg, 40%). NMR ($CDCl_3$) δ: ^{1}H 1.29 (s, 3H), 1.42 (s, 3H), 1.53 (ddd, 1H, *J* = 4.9, 10.4, 14.4 Hz), 1.74 (ddd, 1H, *J* = 4.0, 7.1, 12.5 Hz), 2.04 (m, 2H), 2.91 (m, 1H), 3.83 (ddd, 1H, *J* = 3.8, 8.4, 15.6 Hz), 3.89 (dd, 1H, *J* = 8.4, 15.4 Hz), 4.10 (d, 1H, *J* = 4.9 Hz), 4.50 (d, 1H, *J* = 5.3 Hz), 4.73 (t, 1H, *J* = 5.1 Hz); ^{13}C 24.45, 26.87, 30.80, 37.16, 41.69, 67.94, 82.74, 85.07, 90.08, 110.07. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.22; H, 8.71.

5,6-Dideoxy-1,2-*O*-isopropylidenecarba-α-D-*xylo*-hex-5-enofuranose (61). Bromide **59** (0.15 g, 0.57 mmol) was converted under conditions similar to those used for **24** followed by flash chromatography (90% hexane/10% ethyl acetate) into 80 mg (77%) of olefin **61** as a light yellow oil. NMR ($CDCl_3$) δ: ^1H 1.30 (s, 3H), 1.43 (s, 3H), 1.70 (bs, 1H), 1.88 (dd, 1H, J = 6.5, 13.4 Hz), 1.93 (dt, 1H, J = 4.9, 13.4 Hz), 2.96 (m, 1H), 3.99 (d, 1H, J = 3.6 Hz), 4.43 (d, 1H, J = 5.6 Hz), 4.74 (t, 1H, J = 5.3 Hz), 5.19 (dd, 1H, J = 1.5, 17.0 Hz), 5.25 (dd, 1H, J = 1.5, 10.6 Hz), 5.94 (ddd, 1H, J = 6.0, 10.6, 17.0 Hz); ^{13}C 23.73, 26.09, 33.52, 44.21, 76.61, 79.74, 85.51, 109.78, 117.71, 135.40. $[\alpha]_{20}^{D}$ −23.1° (*c* 3.5, CH_2Cl_2). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.28; H, 8.63.

1,2-*O*-Isopropylidenecarba-α-D-xylofuranose (62). Olefin **61** (70 mg, 0.38 mmol) was reacted according to the procedure for the preparation of **25** to give in the first step the aldehyde as a yellow oil. NMR ($CDCl_3$) δ: ^1H 1.27 (s, 3H), 1.42 (s, 3H), 2.08 (dd, 1H, J = 6.8, 13.7 Hz), 2.19 (ddd, 1H, J = 5.0, 13.7, 18.5 Hz), 3.11 (ddd, 1H, J = 3.8, 6.8, 11.5 Hz), 4.38 (d, 1H, J = 5.5 Hz), 4.47 (d, 1H, J = 3.8 Hz), 4.79 (t, 1H, J = 5.25 Hz), 9.88 (s, 1H); ^{13}C 23.93, 26.32, 30.91, 53.62, 76.14, 79.34, 86.10, 110.36, 203.70. The aldehyde was reduced, and compound **62** (39 mg, 54%) was obtained as a colorless oil after flash chromatography (90% $CHCl_3$/10% methanol). NMR (CD_3OD) δ: ^1H 1.29 (s, 3H), 1.42 (s, 3H), 1.74 (dd, 1H, J = 6.4, 13.6 Hz), 1.96 (dt, 1H, J = 4.9, 13.4 Hz), 2.28−2.40 (m, 1H), 3.12 (bs, 1H), 3.62 (bs, 1H), 3.79 (dd, 1H, J = 6.4, 10.8 Hz), 3.97 (dd, 1H, J = 2.7, 10.9 Hz), 4.18 (d, 1H, J = 3.5 Hz), 4.37 (d, 1H, J = 5.7 Hz), 4.77 (t, 1H, J = 5.4 Hz); ^{13}C and DEPT 24.05 (q), 26.35 (q), 32.01 (t), 41.85 (d), 61.85 (t), 77.93 (d), 79.92 (d), 86.63 (d), 110.04 (s). $[\alpha]_{20}^{D}$ −18.5° (*c* 1.6, 90% $CHCl_3$/10% CH_3OH). Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.25; H, 8.68.

1,2,3,5-Tetra-*O*-acetylcarba-α-D-xylofuranose (63). Diol **62** (37 mg, 0.20 mmol) was reacted according to the procedure for **7**. Flash chromatography (33% hexane/67% ethyl acetate) afforded fully acetylated compound **63** (51 mg, 82%) as a colorless oil. NMR ($CDCl_3$) δ: ^1H 1.97 (m, 2H), 2.03 (s, 9H), 2.07 (s, 3H), 2.84 (m, 1H), 3.96 (dd, 1H, J = 7.0, 11.2 Hz), 4.09 (dd, 1H, J = 5.4, 11.2 Hz), 5.18 (dd, 1H, J = 4.7, 6.0 Hz), 5.37 (m, 2H); ^{13}C 20.79, 21.01, 31.28, 35.90, 62.97, 71.19, 75.29, 76.58. 170.03, 170.19, 170.34, 171.09. $[\alpha]_{20}^{D}$ +23.3° (*c* 1.8, CH_2Cl_2) (lit.[5b] $[\alpha]_{21}^{D}$ +24.7° (*c* 1.02, $CHCl_3$)). Anal. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.21; H, 6.56.

Carba-α-D-xylofuranose (64). Cleavage of the acetyl groups of **63** (36 mg, 0.11 mmol) was done according to the preparation of **8**. Tetrol **64** (14 g, 83%) was obtained as a colorless oil, which required no further purification. NMR (CD_3OD) δ: ^1H 1.79 (m, 2H), 2.48 (m, 1H), 3.59 (dd, 1H, J = 6.5, 10.9 Hz), 3.72 (dd, 1H, J = 6.7, 10.9 Hz), 3.83 (t, 1H, J = 4,5 Hz), 4.16 (m, 2H); ^{13}C 34.25, 42.06, 63.60, 72.59, 78.59, 80.74. $[\alpha]_{20}^{D}$ +12.1° (*c* 0.7, CH_3OH) (lit.[5b] $[\alpha]_{22}^{D}$ +13.4° (*c* 0.78, CH_3OH)). HRMS: calcd for $C_6H_{13}O_4$ M + H *m*/*z* 149.0814, found 149.0816.

***rac*-1,2-Anhydro-5-deoxycarba-β-*lyxo*-hexofuranurono-6,3-lactone (66) and *rac*-1,2-Anhydro-5-deoxy-carba-α-*xylo*-hexofuranurono-6,3-lactone (65).** Racemic lactone **3**[9,10] (10 g, 80.5 mmol) was treated with *m*-CPBA (30g, 96.6 mmol, 55% containing 35% water and 10% chlorobenzoic acid) in benzene (200 mL). After 1 h at room temperature, the reaction mixture was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. The obtained mixture of the epoxides was separated by column chromatography (50% hexane/50% ethyl acetate) to give 2.70 g (24%) of epoxide **66** as a colorless oil and 5.20 g (52%) of compound **65** as white needles. **65**. Mp: 47−49 °C. NMR ($CDCl_3$) δ: ^1H 1.54 (ddd, 1H, J = 1.2, 7.2, 14.5 Hz), 2.29 (d, 1H, J = 17.1 Hz), 2.45 (dd, 1H, J = 8.5, 14.5 Hz), 2.68 (m, 2H), 3.59 (s, 1H), 3.69 (d, 1H, J = 2.2 Hz), 4.86 (d, 1H, J = 5.7 Hz); ^{13}C 33.97, 34.69, 34.87, 56.68, 58.58, 82.99, 176.02. Anal. Calcd for $C_7H_8O_3$: C, 60.00; H, 5.75. Found: C, 59.81; H, 5.88. **66**. NMR ($CDCl_3$) δ: ^1H 2.11 (d, 2H), 2.32 (dd, 1H, J = 9.5, 18.0 Hz), 2.58 (dd, 1H, J = 11.4, 18.0 Hz), 2.92 (m, 1H), 3.64 (s, 2H), 5.03 (d, 1H, J = 8.6 Hz); ^{13}C 32.56, 33.56, 36.14, 57.93, 59.61, 83.57, 177.51.

***rac*-5-Deoxycarba-β-*xylo*-hexofuranurono-6,3-lactone (67).** Epoxide **65** (1.42 g, 10.1 mmol) was reacted according to the procedure for **34**. Without further purification compound **67** was obtained as white needles (1.34 g, 84%). Mp: 83−84 °C. NMR ($CDCl_3$) δ: ^1H 1.71 (dt, 1H, J = 3.7, 13.3 Hz), 2.28 (ddd, 1H, J = 4.5, 8.8, 13.3 Hz), 2.46 (dd, 1H, J = 3.5, 18.5 Hz), 2.83 (dd, 1H, J = 11.4, 18.5 Hz), 3.11 (m, 1H), 4.02 (t, 1H, J = 3.6 Hz), 4.07 (bs, 1H), 4.77 (d, 1H, J = 7.7 Hz); ^{13}C and DEPT 36.15 (d), 37.41 (t), 39.77 (t), 78.26 (d), 81.87 (d), 91.49 (d), 180.58 (s). Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.31; H, 6.45.

***rac*-1,2-Di-*O*-acetyl-5-deoxycarba-β-*xylo*-hexofuranurono-6,3-lactone (68).** Diol **67** (0.30 g, 1.90 mmol) was acetylated according to the procedure for **37**. After recrystallization (33% 2-propanol/33% ether/34% pentane), lactone **68** was obtained as white needles (0.33 g, 90%). Mp: 89−91 °C. NMR ($CDCl_3$) δ: ^1H 1.84 (td, 1H, J = 14.5 Hz), 2.02 (s, 3H), 2.07 (s, 3H), 2.41 (m, 2H), 2.85 (dd, 1H, J = 11.0, 18.4 Hz), 3.17 (m, 1H), 4.81 (d, 1H, J = 7.3 Hz), 5.12 (s, 1H), 5.22 (s, 1H); ^{13}C 20.86, 20.94, 35.61, 35.94, 37.29, 77.09, 79.64, 86.58, 169.15, 169.85, 176.04. Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.54; H, 5.83. Found: C, 54.61 H, 5.85.

***rac*-1,2,3,6-Tetra-*O*-acetyl-5-deoxycarba-β-*xylo*-hexofuranose (69).** To a solution of **68** (0.15 g, 0.62 mmol) in THF (8 mL) was added 0.7 mL (5.6 mmol) of borane dimethyl sulfide complex. After 2 h of stirring at room temperature, methanol (2 mL) was added dropwise (strong gas evolution) and the solvent removed *in vacuo*. The crude tetrol was acetylated according to the procedure for the preparation of **37** to obtain after column chromatography (67% hexane/33% ethyl acetate) **69** as a colorless oil (0.19 g, 93%). NMR ($CDCl_3$) δ: ^1H and COSY 1.53 (m, 2H, H5, H4a), 1.76 (ddd, 1H, H5′, J = 6.9, 14.0, 20.8 Hz), 1.98, 1.97, 1.99, and 2.04 (s, each 3H, CH_3-ester), 2.24 (m, 1H, H4), 2.35 (m, 1H, H4a′), 4.00 (m, 2H, 2H6), 4.97 (m, 3H, H1, H2, H3); ^{13}C and HETCOR 20.88 and 20.97 (CH_3-ester), 27.65 (C5), 35.04 (C4a), 37.19 (C4), 62.91 (C6), 77.47 and 77.70 (C1 and C3), 82.04 (C2). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.71 H, 6.55.

***rac*-5-Deoxycarba-β-*xylo*-hexofuranose (70).** Cleavage of the acetyl groups of **69** (0.1 g, 0.3 mmol) was done according to the preparation of **8**. Tetrol **70** (47 mg, 96%) was obtained as a colorless oil, which required no further purification. NMR (d_6-DMSO) δ: ^1H 1.28 (m, 2H), 1.39 (m, 1H), 1.66 (m, 1H), 1.93 (m, 1H), 3.43 (m, 2H), 3.58 (dd, 1H, J = 3.5, 4.5 Hz), 3.64 (m, 1H), 3.71 (m, 1H); ^{13}C 32.69, 36.69, 37.68, 60.22, 77.38, 77.61, 85.22. HRMS: calcd for $C_7H_{15}O_4$ M + H *m*/*z* 163.0970, found 163.0966.

***rac*-1,2-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxycarba-β-*xylo*-hexofuranurono-6,3-lactone (71).** The diol **67** was reacted similarly to the procedure for **44** (imidazole was used instead of pyridine and DMF instead of CH_2Cl_2). After flash chromatography (80% hexane/20% ethyl acetate) compound **71** was obtained as a colorless oil (0.72 g, 98%). NMR ($CDCl_3$) δ: ^1H 0.03, 0.05, 0.05, and 0.09 (s, each 3H) 0.85 (s, 18H) 1.62 (d, 1H, J = 13.5 Hz), 1.99 (ddd, 1H, J = 4.1, 8.8, 13.5 Hz), 2.39 (dd, 1H, J = 3.7, 18.3 Hz), 2.72 (dd, 1H, J = 11.5, 18.3 Hz), 3.03 (m, 1H), 3.96 (bs, 1H), 4.03 (s, 1H), 4.59 (d, 1H, J = 7.7 Hz); ^{13}C −4.89, −4.70, 18.04, 25.84, 36.58, 36.70, 40.03, 79.02, 81.42, 90.04, 177.51. Anal. Calcd for $C_{19}H_{38}O_4Si_2$: C, 59.02; H, 9.91. Found: C, 59.15; H, 10.07.

***rac*-1,2-Bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxycarba-β-*xylo*-hexofuranose (72).** To a solution of lactone **71** (0.72 g, 1.87 mmol) in ether (10 mL) at 0 °C was added lithium borohydride (42 mg, 1.93 mmol). After 1 h, the mixture was diluted with saturated aqueous ammonium sulfate, and the extractive workup described for **7** was followed. Diol **72** (0.68 g, 93%) was obtained without further purification as a colorless oil. NMR ($CDCl_3$) δ: ^1H 0.09 (s, 12H), 0.89 (s, 18H), 1.33 (m, 1H), 1.74 (m, 1H), 1.90 (m, 1H), 2.28 (m, 2H), 2.3−3.0 (exchangeable with D_2O, 2H), 3.70 (m, 2H), 3.83 (d, 1H, J = 4.4 Hz), 3.98 (s, 2H); ^{13}C −4.53. 18.16, 26.00, 33.47, 39.05, 39.33, 62.52, 79.54, 79.63, 83.41. Anal. Calcd for $C_{19}H_{42}O_4Si_2$: C, 58.41; H, 10.83. Found: C, 58.22; H, 10.91.

***rac*-3,6-Anhydro-1,2-bis-*O*-(*tert*-butyldimethylsilyl)-5-deoxycarba-β-*xylo*-hexofuranose (73).** The procedure for the preparation of **23** was followed using diol **72** (0.75 g, 1.9 mmol) to give after flash chromatography (95% hexane/5% ethyl acetate) mainly bicyclic compound **73** (0.45 g, 64%) and as a minor product ***rac*-6-bromo-1,2-bis-*O*-(*tert*-butyldimethylsilyl)-5,6-dideoxycarba-β-*xylo*-hexofuranose (73a)** (70 mg, 9%), both as colorless oils. **73**. NMR ($CDCl_3$) δ: ^1H 0.07 (s, 6H), 0.09 (s, 3H), 0.11 (s, 3H), 0.89 (s, 18H), 1.32 (dt, 1H, J = 8.9, 12.7 Hz), 1.62 (m, 1H), 1.88 (ddd, 1H, J = 8.6, 12.3, 16.8 Hz), 2.03 (ddd, 1H, J = 6.1, 8.5, 13.0 Hz), 2.61 (ddt, 1H, J = 2.4, 16.8, 8.5 Hz), 3.78 (m, 4H), 4.09 (dd, 1H, J = 4.5, 8.0 Hz); ^{13}C −4.47, −4.34, −4.29, 18.30, 26.14, 33.08, 37.72, 38.05, 67.27, 78.35, 84.36, 89.07. Anal. Calcd for $C_{19}H_{40}O_3Si_2$: C, 61.23; H, 10.82. Found: C, 61.04; H, 10.48. **73a**: NMR ($CDCl_3$) δ: ^1H 0.09 (s, 18H), 0.94 (s, 27H), 1.45 (q, 1H, J = 6.5, 12.3 Hz), 1.72 (ddd, 1H, J = 5.9, 6.8, 13.6 Hz), 1.85 (q, 1H, J = 6.6, 13.2 Hz), 2.03 (q, 1H, J = 7.0, 12.1 Hz), 2.32 (m, 1H), 3.11 (t, 2H), 3.63 (d, 1H, J = 2.8 Hz), 3.79 (s, 1H), 3.96 (t, 1H, J = 6.6 Hz), 7.29 (m, 12H), 7.47 (m, 3H); ^{13}C −4.74, −4.34, −4.07, 17.95, 25.93, 31.40, 38.81, 39.10, 62.24, 79.38, 81.18, 86.17, 127.06, 127.81, 128.76, 144.61.

***rac*-1,2,5-Tri-*O*-acetyl-3-*O*-benzylcarba-β-xylofuranose (78).** Epoxide **77**[18a] was treated with $HClO_4$ according to the method for the preparation of **34** to give after acetylation and chromatography (80% hexane/20% ethyl acetate) **78** (104 mg, 62%) as a colorless oil. NMR ($CDCl_3$) δ: ^1H 1.75 (m, 1H), 1.96 (s, 3H), 2.06 (s, 3H), 2.08(s, 3H), 2.33 (m, 2H), 3.71 (d, 1H, J = 4.4 Hz), 4.15 (dd, 1H, J = 6.0, 10.8 Hz), 4.28 (dd, 2H, J = 7.5, 10.8 Hz), 4.55 (d, 1H, J = 12.2 Hz), 4.77 (d, 1H, J = 12.2 Hz), 5.08 (dt, 1H, J = 2.6, 7.7 Hz), 5.17 (s, 1H), 7.32 (m, 5H); ^{13}C 21.04, 21.14, 21.21, 32.76, 40.49, 62.94, 71.26, 78.24, 81.12, 81.52, 127.90, 128.06, 128.54, 138.21, 140.10, 170.63, 171.02. Anal. Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.69; H, 6.45.

***rac*-1,2,3,5-Tetra-*O*-acetylcarba-β-xylofuranose (79).** Benzylether **78** was dissolved in ethanol (5 mL), and Pd−C (10%, 20 mg) was added. The solution was hydrogenated under atmospheric pressure for 16 h. After removal of the catalyst by filtration and concentration of the solvent, the expected alcohol (67 mg, 88%) was obtained as a colorless oil. The alcohol was acetylated according to the procedure for product **37**, and fully protected **79** (74 mg, 96%) was obtained as a colorless oil. NMR ($CDCl_3$) δ: ^1H and COSY 1.62 (ddd, 1H, H4a, J = 7.8, 10.7, 13.3 Hz), 1.99, 2.01, 2.02, and 2.04 (s, each 3H, CH_3-ester), 3.38 (dt, 1H, H4a′, J = 13.2, 7.5 Hz), 2.58 (m, 1H, H4), 4.07 (m, 2H, 2H5), 5.01 (d, 1H, H1, J = 3.1), 5.11 (m, 2H, H2, H3); ^{13}C 20.82, 20.89, 20.98, 32.20, 38.55, 62.45, 75.83, 76.56, 81.40, 169.70, 169.88, 170.32, 170.79. Anal. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 53.02; H, 6.39.

***rac*-Carba-β-xylofuranose (80).** Cleavage of the acetyl groups of **79** (59 mg, 0.19 mmol) was done according to the procedure for the preparation of **8**. Tetrol **80** (27 mg, 97%) was obtained as a colorless oil. NMR (CD_3OD) δ: ^1H 1.55 (dt, 1H, J = 8.8, 12.6 Hz), 2.15 (dd, 1H, J = 7.5, 12.8 Hz), 2.23 (m, 1H), 3.66 (dd, 1H, J = 6.1, 10.5 Hz), 3.79 (m, 2H), 3.91 (dd, 1H, J = 7.5, 13.1 Hz), 3.98 (dd, 1H, J = 4.8, 6.4 Hz); ^{13}C 34.78, 42.55, 63.43, 77.75, 78.57, 85.94. HRMS: calcd for $C_6H_{13}O_4$ M + H m/z 149.0814, found 149.0817.

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Supporting Information Available: NMR spectra of **7**, **8**, **11**, **12**, **16**, **17**, **21**, **22**, **26**, **27**, **30**, **31**, **34**, **35**, **42**, **43**, **46**, **47**, **53**, **54**, **57**, **58**, **63**, **64**, **69**, **70**, **79**, and **80** (81 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current page for ordering information.

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