Chiral Pool Synthesis of 4a-Substituted Carbocyclic Cyclopentanoid Nucleoside Precursors, II

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Nucleosides, Carbohydrates, X-Ray Data

Suitable protected 4,4a-anhydro-cyclopentane derivatives have been used for the straightforward of cyclopentanoid nucleoside precursors. Thus, by simple transformations nucleoside precursors modified at the positions C(4), C(4a) and C(4,4a) as well as side-chain modified derivatives were accessible. The structures of the key intermediates were determined by x-ray analyses.

Introduction

Nucleoside analogues have been used quite successfully for the chemotherapy of viral infections. In order to obtain biological activity as well as molecules resisting biodegradation, suitable modifications have to be made. Thus, among others, alterations of the sugar moiety have been performed including deoxygenations, eliminations, chain extensions at C(5') and at the anomeric centre, (hetero)substitutions as well as modifications with replacement of the ribose ring by a carbocyclic ring system. Among these derivatives, analogues possessing a cyclopentane ring [1–3] have been most promising.

Results and Discussion

Recently a straightforward chiral pool approach to the key intermediate **1** has been elaborated [4] starting from commercially available D-ribono-1,4-lactone.

Reduction of the epoxide **1** with lithium aluminiumhydride gave 90% of the 4a-carba-β-L-lyxofuranose (**2**), whereas reduction of **3** under the same conditions gave access to the 4a-carba-β-D-ribofuranose (**4**) in 69% yield. Both reductions follow formally a S_N2 ring opening reaction according to the rule of Fürst-Plattner leading to products with *trans* (*pseudo*)-diaxially oriented substituents. Both compounds are characterized by the presence of a broad signal in the IR spectrum at ν = 3465 (for **2**) and ν = 3508 cm^{-1} (for **4**) indicating the presence of a hydroxy group. The newly created methylene group at C(4a) (carbohydrate numbering has been used throughout this work for convenience) is found in the ^{13}C NMR spectrum at δ = 40.02 ppm (for **2**) and at δ = 42.83 ppm (for **4**), respectively.

No reductive opening of the epoxide ring could be achieved, however, using diborane [5] diborane/boron trifluoride diethyletherate [6] or sodium cyanoborohydride/boron trifluoride diethyletherate [7]. The hydrogenation of **1** in the presence of 5% Pd/C resulted in a reductive debenzylation without any reductive cleavage of the oxirane ring; **5** was obtained in 87% isolated yield after chromatographic purification. Due to the failure of these methods to obtain C(4a)-substi-

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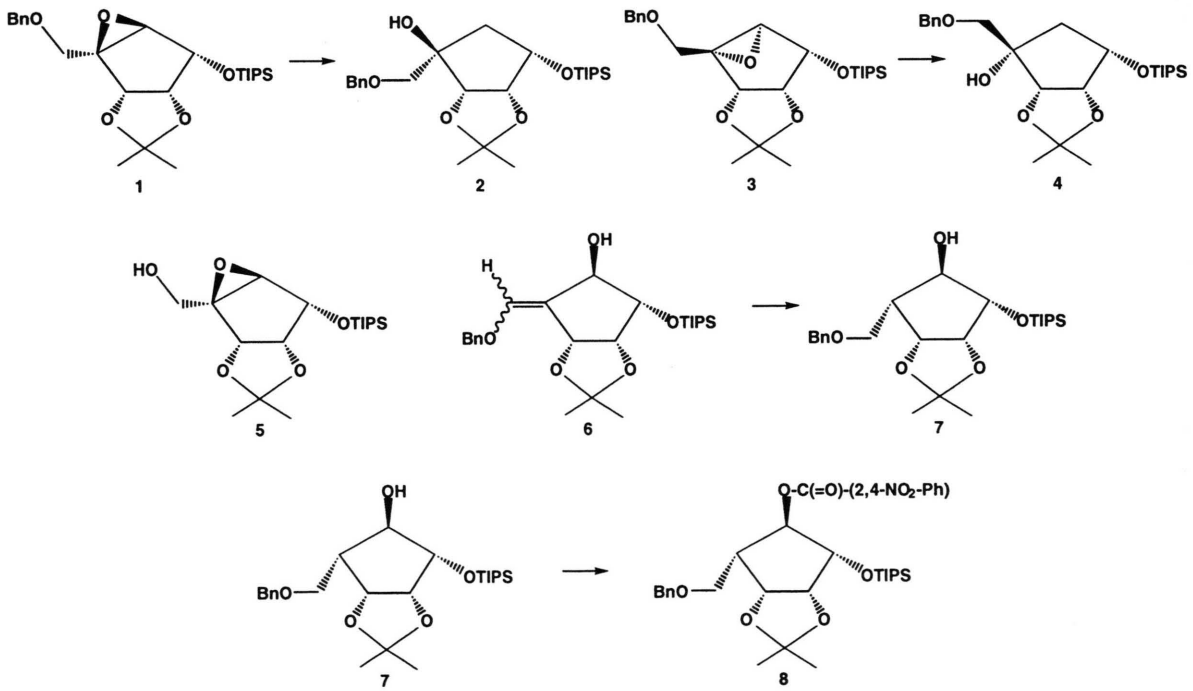
tuted derivatives the rearrangement reaction of these epoxides to the corresponding 4a-oxo-derivatives was investigated.

Thus, treatment of **3** with lithium bromide/hexamethyl phosphoric triamide in refluxing benzene [8] failed as well as the reaction of **3** with lithium perchlorate in benzene [8] did not proceed at all. The reaction of **1** with lithium diethylamide [9] finally gave 60% of an oily **6** that showed in its IR spectrum the presence of a hydroxy group (ν = 3578 cm^{-1}) as well as the presence of a double bond as indicated by the signals at δ = 118.3 and δ = 146.32 ppm in the ^{13}C NMR spectrum; H-C(5) was found in the ^{1}H NMR spectrum at δ = 6.43 ppm. From these findings the structure of **6** as an exocyclic alkene was deduced but neither these data nor further NMR experiments did allow an unambiguous assignment of the configuration of the double bond; after prolonged standing of a solution in $CDCl_3$ the ^{13}C NMR spectrum showed besides huge deterioration the presence of a second isomer albeit in low abundance. Treatment of the isomeric epoxide **3** under the same conditions resulted in huge deterioration of the starting material.

Hydrogenolysis of the alcohol **6** in the presence of Pd/C afforded **7** as a single stereoisomer whose absolute configuration at the newly created stereogenic centre was determined by a single X-ray analysis of its 2,4-dinitro-benzoate (**8**). This analysis revealed **8** to possess the structure of a (4a *R*)-4a-carba-β-L-lyxofuranose. The results of this analysis are depicted in Fig 1.*

Hydroboration of **9** resulted in the formation of two products, **10** and **11**, in a ratio of 6:1. Both compounds possess a hydroxy group as indicated in the IR spectra by the presence of signals at ν = 3465 and 3470 cm^{-1}. In the corresponding ^{1}H NMR spectra the signals for these hydroxy groups were found at δ = 2.50 and 2.61 ppm, respectively. Whereas for **10** an one-proton signal for H-C(4) was found no such signal could be detected for **11**. This compound, however, shows a two-proton signal for HC-(4a) at δ = 1.37 ppm. Thus, the formation of **10** follows the expected pathway for hydroboration reactions, whereas **11** results from a formal addition of water. The absolute configura-

* The atomic coordinates, bond lengths and angles, torsion angles and thermal parameters are available on request from the Director of the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW. Any request should be accompanied by the full literature citation for this communication.



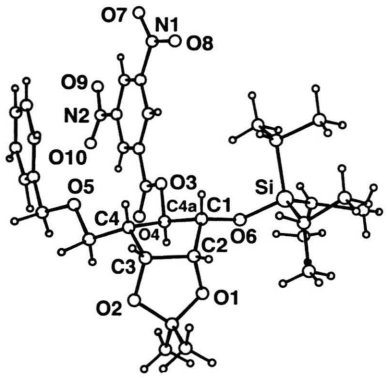


Fig. 1. X-ray analysis of **8**: $C_{32}H_{44}SiN_2O_{10}$, monoclinic, space group $P2_1$, unit cell dimensions: a = 11.159(3) Å, b = 11.825(2) Å, c = 13.685(2) Å, β = 102.04(2)°, F(000) = 688; reflections collected 3638, 2005 observed reflections, I > 3.0 σ(I), 467 parameters refined (H-atoms in disorder area included but not in refinement); R = 0.054; R_w = 0.062; colorless prism; Z = 2; crystal size 0.15 x 0.2 x 0.35 mm; C(1)-C(2) = 1.5526(7)Å, C(1)-C(4a) = 1.516(6)Å, C(2)-C(3) = 1.532(8)Å, C(3)-C(4) = 1.553(7)Å, C(4)-C(4a) = 1.520(8)Å, C(4a)-O(11) = 1.465(5)Å; C(2)-C(1)-C(4a) = 101.3(4)°, C(1)-C(2)-C(3) = 105.7(4)°, C(3)-C(4)-C(4a) = 103.7(4)°, C(1)-C(4a)-C(4) = 102.3(4)°, C(1)-C(4a)-O(11) = 109.2(4)°, C(4)-C(4a)-O(11) = 111.2(4)°.

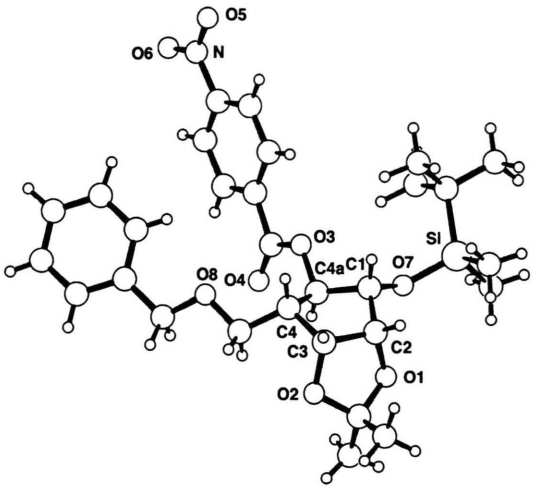


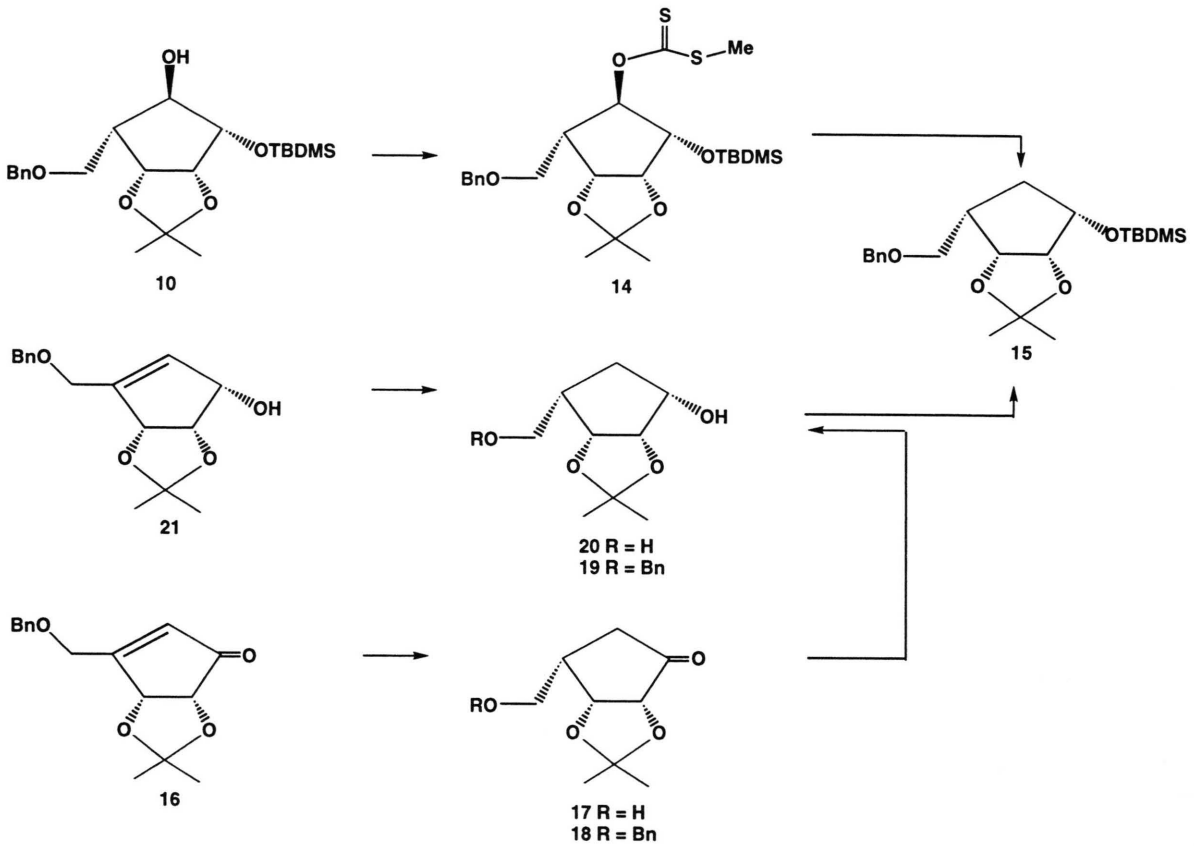
Fig. 2. X-ray analysis of **13**: $C_{29}H_{39}O_8NSi$, space group P_1, unit cell dimensions: a = 10.652(2) Å, b = 14.265(1) Å, c = 10.456(1) Å, α = 99.22(1)°, β = 96.98(1)°, γ = 74.56(1)°, F (000) = 596; 7204 independent reflections, 4345 observed I > 2.5 σ(I) 487 parameters refined; R = 0.045 R_w = 0.054; Z = 2; yellowish needle; crystal size 0.5 x 0.35 x 0.24 mm; C(1)-C(4a) = 1.517(2)Å, C(4)-C(4a) = 1.520(3)Å, C(1)-C(2) = 1.524(2)Å, C(2)-C(3) = 1.541(3)Å, C(3)-C(4) = 1.537(2)Å; O(3)-C(4a)-C(1) = 108.8(1)°, O(3)-C(4a)-C(4) = 112.0(2)°, C(1)-C(4a)-C(4) = 104.2(1)°, C(4a)-C(1)-C(2) = 103.4(1)°, C(1)-C(2)-C(3) = 105.3(1)°, C(2)-C(3)-C(4) = 106.9(1)°.

tion of **11** was deduced from the similarity in the ^{1}H, ^{13}C and CD/ORD spectra of **11** as compared with **2**; both compounds differ only in the protective group at C(1).

In order to determine the absolute configuration of the two newly created stereogenic centres, **10** was transformed into the corresponding 2,4-dinitrobenzoate (**12**) and the 4-nitro-benzoate (**13**), the latter of which gave suitable crystals for a X-ray analysis that revealed **13** to possess a (4a *R*)-β-L-lyxofuranoid structure. The results of this X-ray analysis are depicted in Fig. 2*. The central cyclopentane ring is substituted by five groups that are all in a *pseudoequatorial* position.

Barton deoxygenation [10, 11] of **10** *via* **14** [12] with phenylsilane in the presence of dibenzoyl peroxide gave **15**. Hydrogenation of (−)-**16** with Pd/C afforded a mixture of the cyclopentanes **17**/**18**. Reduction of **18** with sodium borohydride in the presence of $CeCl_3$ gave **19** that upon silylation again gave **15**; reduction of **17** under similar conditions yielded **20**. Hydrogenation of **21** with Raney-nickel afforded **19/20**. From these results the absolute configuration of all centres in **19** as well as in **15** can be deduced quite unambiguously.

Treatment of **9** with catalytic amounts of osmium tetroxide in the presence of *N*-methyl-morpholine *N*-oxide gave a *si*-face attack of the oxidant from the sterically less hindered side to afford **22** whose ^{13}C NMR spectrum shows the presence of a quaternary carbon at δ = 75.85 ppm that was assigned to C(4). Oxidation of **22** with pyridinium chlorochromate did not result in the formation of a keto group at C(4a) but gave the epoxides **23** and **24** in a 1:1 ratio [13]. These epoxides are the product of an elimination reaction of an intermediary chromate ester whose epoxidation from the less hindered *re*-face then affords the epoxides **23** and **24**, respectively. The absolute configuration of **23** was deduced from ^{1}H{^{1}H} nO-experiments that showed a strong nOe at H-C-(3) and at H_A-C(benzylic) upon irradiation of H-C(5). Hydrogenolysis of **23/24** resulted in a reductive opening of the oxirane ring as well as a deprotection and afforded **25** and **26** in a 8:1 ratio, the latter product resulting from an additional methanolysis of the silyl protecting group during the reaction;



26 was also obtained by the fluoride mediated desilylation of **36**.

The formation of a single stereoisomer from the hydrogenolysis starting from a 1:1 mixture **23**/**24** gives an additional proof for the assigned absolute configuration for these epoxides. Reaction of dimethyldioxirane with **22** did not give any trace of a compound possessing a keto group at C(4), instead a smooth debenzylation reaction took place and afforded **25**. Similarly, **10** gave upon treatment with dimethyldioxirane **27** [14].

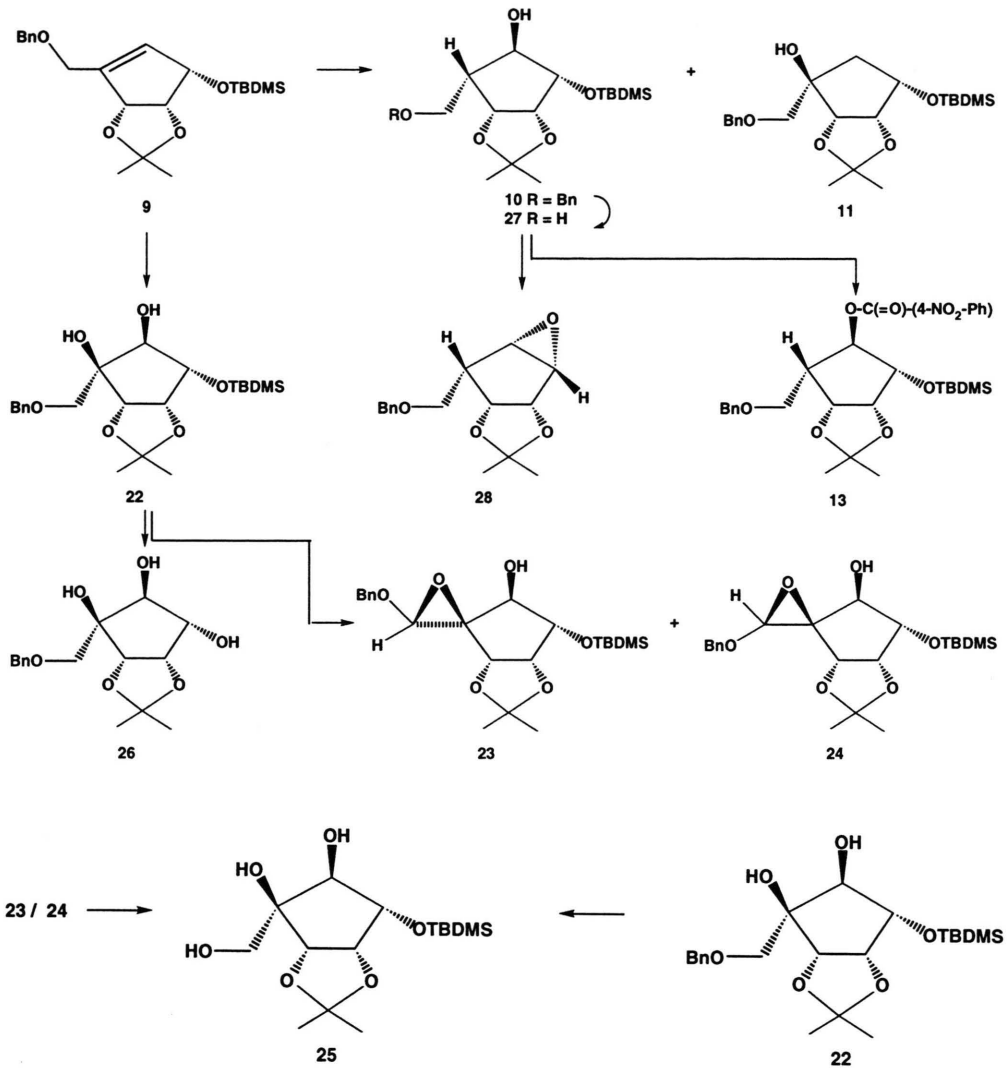
Attempted fluorination of **10** by its treatment with diethylaminosulur trifluoride (DAST) did not result in the formation of a C(4a) mono-fluorinated cyclopentane, but gave the epoxide **28**, the formation of which can be explained by a neighboring group participating reaction starting by a fluoride-mediated desilylation of **10** and finally an intramolecular S_N2 reaction.

The synthetic potential of these novel synthetic precursors for the synthesis of cyclopentanoid nucleoside analogues is currently under investigation in our laboratories.

Experimental

General methods

Melting points are uncorrected (*Leica* hot stage microscope), optical rotations were obtained using a Perkin-Elmer 341 polarimeter (1 cm micro cell), NMR spectra (internal Me_4Si) were recorded using the Varian spectrometers XL300, Gemini 200, Gemini 2000 or Unity 500 (δ given in ppm, J in Hz, internal Me_4Si for ^1H and ^{13}C NMR spectra, internal CCl_3F was used for ^{19}F NMR spectra, C' correspond to the atoms of the heterocycle), IR spectra (film or KBr pellet) on a Perkin-Elmer FT-IR spectrometer Spectrum 1000, MS spectra were taken on a Intectra GmbH AMD 402 (electron impact, 70 eV) or on a Finnigan MAT LCQ 7000 (electrospray, voltage 4.5 kV, under nitrogen) instrument; for elemental analysis a Foss-Heraeus Vario EL instrument was used; TLC was performed on silica gel (Merck 5554, detection by



UV absorption or by treatment with a solution of 10% sulfuric acid, ammonium molybdate and cerium$^{(IV)}$ sulfate followed by gentle heating).

5-O-Benzyl-4a-carba-2,3-O-isopropylidene-6-O-triisopropylsilyl-pent-4-ulo-β-L-lyxofuranose = (3a S, 4 R, 6 S, 6a R)-4-benzyloxymethyl-2,2-dimethyl-6-triisopropylsilyloxy-tetrahydro-cyclopenta[d]-[1,3]dioxol-4-ol (**2**)

To a 0 °C cold suspension of $LiAlH_4$ (50 mg, 1.26 mmol) in abs. diethyl ether (2 ml) a solution of **1** (90 mg, 0.198 mmol) in abs. diethyl ether (1 ml) was slowly added. After warming to room temperature, stirring was continued for an additional 6 h. The mixture was cooled to 0 °C, and ethanol (96%, 3 ml) and water (2 ml) were carefully added, the mixture was filtered and the aqueous phase extracted with diethyl ether (3 × 10 ml), the combined organic layers were washed with brine, dried ($MgSO_4$), the solvent was removed and the residue subjected to chromatography (silica gel, hexane/ethyl acetate 20:1) to afford **2** (80 mg, 90%); $[\alpha]_D^{20}$ −3.0° (*c*, 1.0 $CHCl_3$); R_F = 0.28 (hexane/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.38 (*m*, 5 H, H-C(ar)), 4.65 (*d*, 1 H, *J* = 12.1 Hz, H_A-CH_2(ar)), 4.57 (*d*, 1 H, *J* = 12.1 Hz, H_B-CH_2(ar)), 4.57 (*d*, 1 H, *J* = 5.2 Hz, H-C(2)), 4.47 (*m* 1 H, H-C(1)), 4.24 (*d*, 1 H, *J* = 5.4 Hz, H-C(3)), 3.70 (*d*, 1 H, *J* = 9.2 Hz, H_A-C(5)),

3.47 (*d*, 1 H, J = 9.2 Hz, H_B-C(5)), 2.65 (*s*, 1 H, OH), 1.79–1.84 (*m*, 2 H, $H_{A/B}$-C(4a)), 1.33, 1.45 (*s*, 3 H, 2 × CH_3(isopropyl)), 1.10 (*s*, 18 H, CH_3-TIPS), 1.09 (*s*, 3 H, CH-TIPS); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.93 (*s*, C_q(ar)), 128.31 (*d*, C_t(ar)), 127.61 (*d*, C_t(ar)), 110.99 (C_q(isopropyl)), 84.47, 79.86 (*d*, C(2), C(3)), 77.67 (*s*, C(4)), 73.49 (*t*, CH_2(ar)), 72.44 (*t*, C(5)), 71.40 (*d*, C(1)), 40.02 (*t*, C(4a)), 26.29, 24.64 (*q*, 2 × CH_3(isopropyl)), 18.06 (*q*, CH_3(TIPS)), 12.32 (*d*, CH(TIPS)); MS (ei, 80 eV, 134 °C): 450 (M, 0.2%), 435 (M–CH_3, 1.3%), 407 (15.2%), 258 (2.7%), 257 (12.9%), 129 (5.4%), 187 (3.3%), 185 (13.4%), 173 (5.5%), 157 (3.6%), 105 (8.1%), 91 (100%); HRMS calcd. for $C_{25}H_{42}O_5Si$: 450.28015; found: 450.2802.

*5-O-Benzyl-4a-carba-4-hydroxy-2,3-O-isopropylidene-6-O-triisopropylsilyl-pent-4-ulo-β-*D*-ribofuranose = (3a* S, *4* S, *6* S, *6a* R*)-4-(benzyloxymethyl)-2,2-dimethyl-6-triisopropylsilyloxy-tetrahydro-cyclopenta[d][1,3] dioxol-4-ol* (**4**)

The preparation was performed according to the synthesis of **2**, starting from **3** (250 mg, 0.56 mmol) to afford **4** (172 mg, 69%) after column chromatography (silica gel, hexane/ethyl acetate 20:1); $[\alpha]_D^{20}$ −6.5° (*c*, 1.4 $CHCl_3$); R_F = 0.55 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.34 (*m*, 5 H, H-C(ar)), 4.53 (*s*, 2 H, CH_2(ar)), 4.45 (*dd*, virt. *t*, 1 H, J =5.0 Hz, H-C(2)), 4.23 (*d*, 1 H, J =5.6 Hz, H-C(3)), 4.17 (*ddd*, 1 H, J = 4.4, 6.4, 10.3 Hz, H-C(1)), 3.42 (*d*, 1 H, J = 9.4 Hz, H_A-C(5)), 3.38 (*d*, 1 H, J = 9.4 Hz, H_B-C(5)), 3.19 (*s*, 1 H, OH), 2.10 (*dd*, 1 H, J = 6.4, 12.6, H_A-C(4a)), 2.00 (*dd*, 1 H, J = 10.3, 12.6, H_B-C(4a)), 1.55, 1.35 (*s*, 3 H, 2 × CH_3(isopropyl)), 1.04 (*s*, 21 H, TIPS); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.78 (*s*, C_q(ar)), 128.19, 127.51 (*d*, C_t(ar)), 111.68 (*s*, C_q(isopropyl)), 81.12, 80.75 (*d*, C(1), C(2)), 75.59 (*t*, C(5)), 74.70 (*s*, C(4)), 73.65 (*t*, CH_2(ar)), 69.64 (*d*, C(3)), 42.83 (*t*, C(4a)), 26.15, 24.79 (*q*, 2 × CH_3(isopropyl)), 17.95 (*q*, CH_3(TIPS)), 12.21 (*d*, CH(TIPS)); MS (ei, 80 eV, 90 °C): 450 (M, 0.1%), 435 (M–CH_3, 1.4%), 407 (4.3%), 349 (10.7%), 257 (10.4%), 241 (10.2%), 229 (4.0%), 185 (13.2%), 157 (3.5%), 143 (2.8%), 91 (100%); HRMS calcd. for $C_{25}H_{42}O_5Si$: 450.28015; found: 450.2802.

(±) (4a SR*) 4,4a-Anhydro-4a-carba-1-O-(triisopropylsilyl)-2,3-O-isopropylidene-β-*L*-lyxofuranose = (1* SR, *2* SR, *3* SR, *4* RS, *5* SR*)-2-hydroxymethyl-7,7-dimethyl-4-triiso-propylsilyloxy-6,8,9-trioxa-tricyclo[3.3.1^{2,3}]nonane* (**5**)

A solution of (±)-**1** (100 mg, 0.22 mmol) in abs. THF (5 ml) was hydrogenated at atmospheric pressure in the presence of catalytic amounts of Pd/C (5%) for 6 h. After filtration and evaporation of the solvents, the residue was purified by chromatography (silica gel, hexane/ethyl acetate 15:1) to afford **5** (69 mg, 87%) as a colorless oil; R_F = 0.31 (hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.62, (*d*, 1 H, J = 4.9 Hz, H-C(3)), 4.52 (*dd*, virt. *t*, 1 H, 5.6 Hz, H-C(2)), 4.22 (*d*, 1 H, J = 5.6 Hz, H-C(1)), 4.16 (*d*, 1 H, J = 12.8 Hz, H_A-C(5)), 3.89 (*d*, 1 H, H_B-C(5)), 3.54 (*s*, 1 H, H-C(4a)), 1.94 (*bs*, 1 H, OH), 1.48, 1.36 (*s*, 3 H, 2 × CH_3(isopropyl)), 1.10 (*s*, 18 H, CH_3(TIPS)), 1.05 (*s*, 3 H, CH(TIPS)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 113.19 (*s*, C_q(isopropyl)), 82.25 (*d*, C(3)), 79.44 (*d*, C(2)), 70.54 (*d*, C(1)), 68.75 (*s*, C(4)), 64.91 (*d*, C(4a)), 59.44 (*t*, C(5)), 26.63, 25.73 (*q*, 2 × CH_3(isopropyl)), 17.88 (*q*, CH_3(TIPS)), 12.15 (*d*, CH(TIPS)); MS (ei, 80 eV, 113 °C): 358 (M, 0.1%), 343 (M–CH_3, 9.2%), 315 (M–isopropyl, 21.3%), 257 (100%); HRMS calcd. for $C_{18}H_{34}O_5Si$: 358.2176; found: 358.2175.

(4a R, *5* Z,E*) 5-O-Benzyl-4a-carba-4a-hydroxy-2,3-O-isopropylidene-1-O-triisopropylsilyl-β-*D*-erythro-pent-4-enofuranose = (3a* R, *5* R, *6* S, *6a* R*) 4-(1-benzyloxy-(Z,E)-methyliden)-6-triisopropylsilyloxy-2,2-dimethylperhydrocyclopenta-[d][1,3]dioxol-5-ol* (**6**)

To a solution of freshly distilled diethylamine (256 mg, 3.50 mmol) in abs. diethyl ether (11 ml) at −10 °C *n*-butyllithium (1.7 ml, 1.6 M in hexane) was slowly added; stirring at this temperature was continued for 10 min, then a solution of **1** (500 mg, 1.11 mmol) in abs. diethyl ether (7 ml) was slowly added and the mixture warmed to room temperature within 6h. The mixture was diluted with diethyl ether (20 ml), washed with a saturated aqueous solution of NH_4Cl (3 × 30 ml), brine (30 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure. After chromatographic purification of the residue (silica gel, hexane/ethyl acetate 20:1 → 10:1 containing 1% of triethylamine) **6** (300 mg, 60%) was obtained as a colorless oil; $[\alpha]_D^{20}$ +64.7° (*c*, 1.2 $CHCl_3$); R_F = 0.45 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29–7.38 (*m*, 5 H, H-C(ar)), 6.43 (*dd*, 1 H, J = 0.9, 2.3 Hz, H-C(5)), 4.86 (*dd*, virt. *t*, 1 H, J = 2.0 Hz, H-C(4a)), 4.82 (*d*, 2 H, J = 1.4 Hz, CH_2(ar)), 4.75 (*d*, 1 H, J = 5.6 Hz, H-C(3)), 4.43 (*dd*, virt. *t*, 1 H, J = 5.3 Hz, H-C(2)), 3.92 (*dd*, 1 H, 4.9, 7.6 Hz, H-C(1)), 3.17 (*d*, 1 H, J = 1.8 Hz, OH), 1.42, 1.28 (*q*, 3 H, 2 × CH_3(isopropyl)), 1.11

(*s*, 21 H, TIPS); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.32 (*d*, C(5)), 136.04 (*s*, C_q(ar)), 128.46 (*d*, C_t(ar)), 128.19 (*d*, C_t(ar)), 127.55 (*d*, C_t(ar)), 118.27 (*s*, C(4)), 110.80 (*s*, C_q(isopropyl)), 78.62 (*d*, C(1)), 78.52 (*d*, C(2)), 77.00 (*d*, C(3)), 76.68 (*d*, C(4a)), 74.79 (*t*, C(5)), 26.81 (*q*, CH_3(isopropyl)), 25.13 (*q*, CH_3(isopropyl)), 17.92 (*q*, CH_3(TIPS)), 12.39 (*d*, CH, TIPS)); MS (ei, 80 eV, 109 °C): 433 (M−CH_3, 0.1%), 405 (M−isopropyl, 0.3%), 348 (1.4%), 347 (4.8%), 297 (1.7%), 256 (1.8%), 255 (8.0%), 239 (4.2%), 213 (2.6%), 185 (1.6%), 173 (1.7%), 157 (1.9%), 131 (2.3%), 129 (1.6%), 91 (100%); HRMS calcd. for $C_{24}H_{37}O_5Si$ (M−CH_3): 433.2410; found: 433.2410.

(4a R*) 5-*O*-Benzyl-4a-carba-2,3-isopropylidene-1-*O*-triisopropylsilyl-4a-hydroxy-β-*L*-lyxofuranose = (3a* R*, 4* R*, 5* R*, 6* S*, 6a R) 4-benzyloxymethyl-6-triisopropylsilyloxy-2,2-dimethylperhydro-cyclopenta[d][1,3]dioxol-5-ol* (**7**)

A solution of **6** (600 mg, 1.34 mmol) in abs. THF (40 ml) was hydrogenated at atmospheric pressure in the presence of Pd/C (5%) for 4 h. After filtration, evaporation of the solvent and chromatographic purification (silica gel, hexane/ethyl acetate 15:1) **7** (456 mg, 76%) was obtained as a colorless oil; $[\alpha]_D^{20}$ −21.5° (*c*, 0.9 $CHCl_3$); R_F = 0.47 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.34 (*m*, 5 H, H-C(ar)), 4.54 (*s*, 2 H, CH_2(ar)), 4.51 (*t*, 1 H, *J* = 5.6 Hz, H-C(2)), 4.40 (*t*, 1 H, *J* = 5.6 Hz, H-C(3)), 3.94 (*dd*, 1 H, *J* = 8.3, 10.2 Hz, H-C(4a)), 3.84 (*dd*, 1 H, *J* = 6.8, 9.0 Hz, H_A-C(5)), 3.79 (*dd*, 1 H, *J* = 5.3, 8.3 Hz, H-C(1)), 3.73 (*dd*, 1 H, *J* = 8.0, 9.0 Hz, H_B-C(5)), 2.42 (*bs*, 1 H, OH), 1.91 (*dddd*, *J* = 5.5, 6.8, 7.9, 10.2 Hz, 1 H, H-C(4)), 1.41, 1.26 (*s*, 3 H, 2 × CH_3(isopropyl)), 1.11 (*s*, 18 H, CH_3(TIPS)), 1.10 (*s*, 3 H, CH(TIPS)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.05 (*s*, C_q(ar)), 128.25, 127.54 (*d*, C_t(ar)), 110.08 (*s*, C_q(isopropyl)), 78.52 (*d*, C(2)), 78.07 (*d*, C(3)), 77.52 (*d*, C(1)), 76.25 (*d*, C(4a)), 73.44 (*t*, CH_2(ar)), 69.50 (*t*, C(5)), 44.19 (*d*, C(4)), 25.93, 24.24 (*q*, 2 × CH_3(isopropyl)) 17.98 (*q*, CH_3(TIPS)), 12.48 (*d*, CH(TIPS)); MS (ei, 80 eV, 144 °C): 450 (M, 0.2%), 435 (M−CH_3, 0.7%), 407 (11.1%), 301 (1.3%), 275 (1.2%), 243 (2.3%), 241 (6.7%), 215 (3.4%), 185 (5.8%), 173 (3.5%), 131 (4.2%), 91 (100%).

Analysis for $C_{25}H_{42}O_5Si$ (450.69)
Calcd C 66.63 H 9.39%,
Found C 66.78 H 9.47%.

(4 a R*) 5-*O*-Benzyl-4a-carba-2,3-*O*-isopropylidene-1-*O*-triisopropylsilyl-4a-*O*-(3,5-dinitrobenzoyl)-β-*L*-lyxofuranose = (3a* R*, 4* S*, 5* R*, 6* S*, 6a* S*) 4-benzyloxymethyl-6-triisopropylsilyloxy-2,2-dimethylperhydro-cyclopenta [d][1,3]dioxol-5-yl-3,5-dinitrobenzoate* (**8**)

Acylation of **7** (84 mg, 0.186 mmol) in pyridine (0.5 ml) with 3,5-dinitrobenzoylchloride (55 mg, 0.24 mmol) for 6 at 25 °C followed by usual work up (*vide supra*) and chromatographic purification (silica gel, hexane/ethyl acetate 20:1 → 10:1) gave **8** (120 mg, 99%); m.p. 100–101 °C; $[\alpha]_D^{20}$ −63° (*c*, 1.0 $CHCl_3$) R_F = 0.64 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.02 (*t*, 1 H, *J* = 2.2 Hz, H-C(4')), 8.85 (*d*, 2 H, *J* = 2.2 Hz, H-C(2')), H-C(6')), 6.95–7.04 (*m*, 5 H, H-C^{ar}(Bn)), 5.58 (*dd*, 1 H, *J* = 8.8, 10.6 Hz, H-C(4a)), 4.63 (*t*, 1 H, *J* = 5.6 Hz, H-C(3)), 4.50 (*t*, 1 H, *J* = 5.6 Hz, H-C(2)), 4.35 (*d*, 1 H, *J* = 11.1 Hz, H_A-CH_2(ar)), 4.24 (*d*, 1 H, *J* = 11.1 Hz, H_B-CH_2(Bn)), 4.22 (*dd*, 1 H, *J* = 5.5, 8.7 Hz, H-C(1)), 3.88 (*dd*, 1 H, *J* = 5.0, 9.2 Hz, H_A-C(5)), 3.70 (*t*, 1 H, *J* = 8.9 Hz, H_B-C(5)), 2.21 (*ddd*, 1 H, *J* = 3.6, 5.2, 10.5 Hz, H-C(4)), 1.52, 1.30 (*s*, 3 H, 2 × CH_3(isopropyl)), 1.00 (*s*, 21 H, TIPS); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.12 (*s*, CO), 148.12 (*s*, C(3'), C(5')), 137.79 (*s*, C_q(bn)), 133.95 (*s*, C(1')), 129.05, 127.71, 127.47, 127.08 (*d*, C_t(ar)), 121.77 (*d*, C(4')), 110.65 (*s*, C_q(isopropyl)), 81.73 (*d*, C(1)), 76.55 (*d*, C(2)), 76.40 (*d*, C(3)), 75.80 (*d*, C(4a)), 73.33 (*t*, CH_2(ar)), 69.34 (*t*, C(5)), 43.13 (*d*, C(4)), 25.99, 24.23 (*q*, 2 × CH_3(isopropyl)),17.84 (*q*, CH_3(TIPS)), 12.32 (*d*, CH(TIPS)); MS (ei, 80 eV, 170 °C): 644 (M, 0.2%), 629 (M−CH_3, 1.1%), 602 (4.1%), 601 (M−isopropyl, 11.9%), 331 (2.6%), 325 (9.2%), 223 (2.3%), 195 (1.7%), 159 (1.2%), 105 (1.4%), 91 (100%).

Analysis for $C_{32}H_{44}N_2O_{10}Si$ (644.79)
Calcd C 59.61 H 6.88 N 4.34%,
Found C 59.43 H 6.78 N 4.56%.

(4a R*) 5-*O*-Benzyl-1-*O*-(tert-butyldimethylsilyl)-4a-carba-4a-hydroxy-2,3-*O*-isopropylidene-β-*L*-lyxofuranose = (3a* R*, 4* R*, 5* R*, 6* S*, 6a* R*) 4-(benzyloxy-methyl)-6-(tert-butyldimethylsilyloxy)-2,2-dimethyl-tetrahydro-cyclopenta[1,3]dioxol-5-ol* (**10**) *and (4a* R*) 5-*O*-benzyl-1-*O*-(tert-butyldimethylsilyl)-4a-carba-4-hydroxy-2,3-*O*-isopropyliden-β-*L*-lyxofuranose = (3a* S *4* R*, 6* S*, 6a* R*) 4-(benzyloxy-methyl)-6-(tert-butyldimethylsilyloxy)-2,2-dimethyl-tetrahydro-cyclopenta[1,3]dioxol-4-ol* (**11**)

A solution of **9** (1.50 g, 3.69 mmol) in abs. THF (33 ml) was cooled to −25 °C and a 1 M solution

of BH_3.THF (4.2 ml, 1.1 equiv.) was slowly added. After stirring at this temperature for an additional 3 h, methanol (5 ml) was added, the mixture allowed to warm to 25 °C and 3 M NaOH solution (10 ml) and 30% H_2O_2 (30%, 10 ml) were added in succession. Stirring at 55 °C was continued for 1h, then the mixture was diluted with diethyl ether (50 ml) and water (30 ml), the phases were separated, the aqueous layer was extracted with diethyl ether (3 × 50 ml), the combined organic layers were washed with brine (20 ml), dried ($MgSO_4$), the solvents removed under reduced pressure and the residue was subjected to chromatography (silica gel, hexane/ethyl acetate 20:1 → 10:1) to afford **10** (0.97 g, 61.8%) and **11** (0.16 g, 10.2%). Data for **10**. – $[\alpha]_D^{20}$ −23.6° (*c*, 0.6 $CHCl_3$); R_F = 0.22 (hexane/ethyl acetate 1:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.37–7.28 (*m*, 5 H, H-C(ar)), 4.54 (*s*, 2 H, CH_2(ar)), 4.50 (*t*, 1 H, *J* = 5.6 Hz, H-C(2)), 4.36 (*t*, 1 H, *J* = 5.6 Hz, H-C(3)), 3.91 (*dd*, 1 H, *J* = 8.6, 10.1 Hz, H-C(4a)), 3.83 (*dd*, 1 H, *J* = 6.9, 9.0 Hz, H_AC(5)), 3.72 (*t*, 1 H, *J* = 8.0 Hz, H_BC(5)), 3.67 (*dd*, 1 H, *J* = 5.4, 8.4Hz, H-C(1)), 2.50 (*bs*, 1 H, OH), 1.96–1.86 (*m*, 1 H, H-C(4)), 1.40 (*s*, 3 H, CH_3(isopropyl)), 1.26 (*s*, 3 H, CH_3(isopropyl)), 0.92 (*s*, 9 H, CH_3(*tert*-butyl)), 0.12 (*s*, 6 H, CH_3-Si); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 138.20 (*s*, C_q(ar)), 128.39 (*d*, C_t(ar)), 127.64 (*d*, C_t(ar)), 110.28 (*s*, C_q(isopropyl)), 78.67, 77.72, 77.47, 76.34 (*d*, C(2), C(3), C(1), C(4a)), 73.48 (*t*, CH_2(ar)), 69.48 (*t*, C(5)), 44.17 (*s*, C(4)), 25.92 (*q*, CH_3(isopropyl)), 25.90 (*q*, CH_3(*tert*-butyl)), 24.23 (*q*, CH_3(isopropyl)), 18.41 (*s*, C_q(*tert*-butyl)), -4.57 (*q*, CH_3-Si), -4.55 (*q*, CH_3-Si); MS (ei, 80 eV, 130 °C): 408 (0.3%), 351 (14.7%), 245 (3.7%), 185 (9.7%), 171 (3.8%), 159 (4.6%), 157 (4.8%), 143 (4.0%), 131 (5.4%), 129 (16.2%), 117 (10.5%), 116 (4.9%), 105 (3.3%), 101 (4.0%), 92 (20.5%), 91 (100%).

Analysis for $C_{22}H_{36}O_5Si$ (408.61)
Calcd C 64.67 H 8.88%,
Found C 64.44 H 8.99%.

Data for **11**. – $[\alpha]_D^{20}$ −4.7° (*c*, 0.8 $CHCl_3$); R_F = 0.44 (hexane/ethyl acetate 1:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.35–7.28 (*m*, 5 H, H-C(ar)), 4.63 (*d*, 1 H, *J* = 12.2 Hz, H_A-CH_2(ar)), 4.55 (*d*, 1 H, *J* = 11.9 Hz, H_B-CH_2(ar)), 4.53 (*t*, 1 H, *J* = 5.2 Hz, H-C(2)), 4.41–4.32 (*m*, 1 H, H-C(1)), 4.22 (*d*, 1 H, *J* = 4.9 Hz, H-C(3)), 3.68 (*d*, 1 H, *J* = 9.0 Hz, H_A-C(5)), 3.43 (*d*, 1 H, *J* = 8.2 Hz, H_B-C(5)), 2.61 (*s*, 1 H, OH), 1.47–1.26 (*m*, 2 H, $H_{A/B}$C(4a)), 1.43 (*s*, 3 H, CH_3(isopropyl)), 1.31 (*s*, 3 H, CH_3(isopropyl)), 0.90 (*s*, 9 H, CH_3(*tert*-butyl)), 0.09 (*s*, 6 H, CH_3-Si); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 138.08 (*s*, C_q(ar)), 128.45, 127.77, 127.72 (*d*, C_t(ar)), 111.17 (*s*, C_q(isopropyl)), 84.56, 79.89 (*d*, C(2), C(3)), 77.76 (*s*, C(4)), 73.54 (*t*, CH_2(ar)), 72.45 (*t*, C(5)), 71.58 (*d*, C(1)), 39.79 (*t*, C(4a)), 26.23 (*q*, CH_3(isopropyl)), 26.01 (*q*, CH_3(*tert*-butyl)), 24.55 (*q*, CH_3(isopropyl)), 18.41 (*s*, C_q(*tert*-butyl)), -4.48 (*q*, CH_3-Si), -4.68 (*q*, CH_3-Si); MS (ei, 80 eV, 102 °C): 408 (M, 0.2%), 351 (4.0%), 129 (5.7), 101 (4.6%), 92 (7.6%), 91 (100%); HRMS calcd. for $C_{22}H_{36}O_5Si$ (408.61): 408.2333; found: 408.2332.

(4a R*) 5-*O*-Benzyl-1-*O*-(tert-butyldimethylsilyl)-4a-carba-4a-*O*-(4-nitrobenzoyl)-2,3-*O*-isopropylidene-β-*L*-lyxofuranose = [(3a* R*, 4* S*, 5* R*, 6* S*, 6a* R*) 4-(benzyloxy-methyl)-4-hydroxy-6-(tert-butyldimethylsilyl-oxy)-2,2-dimethyl-tetrahydrocyclopenta[1,3]dioxol-5-yl] 4-nitro-benzoate* (**13**)

Compound **10** (100 mg, 0.25 mmol) was acylated in dry dichloromethane (5 ml) with pyridine (0.2 ml) and 4-nitrobenzoylchloride (55 mg, 0.27 mmol); after usual work up (*vide supra*) and chromatography (silica gel, hexane/ethyl acetate 20:1) **13** (127 mg, 93%) was obtained; m.p. 111 °C; R_F = 0.40 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22 (*td*, 2 H, *J* = 2.1, 9.0 Hz, H-C(3′), H-C(5′)), 8.09 (*td*, 2 H, *J* = 2.1, 9.0 Hz, H-C(2′)), H-C(6′)), 7.16(*s*, 5 H, H-C(ar)), 5.46 (*dd*, 1 H, *J* = 8.6, 10.7 Hz, H-C(4a)), 4.66 (*t*, 1 H, *J* = 5.5 Hz, H-C(3)), 4.45 (*t*, 1 H, *J* = 5.6 Hz, H-C(2)), 4.44 (*d*, 1 H, *J* = 11.6 Hz, H_A-CH_2(ar)), 4.39 (*d*, 1 H, *J* = 11.7 Hz, H_B-CH_2(ar)), 4.04 (*dd*, 1 H, *J* = 5.6, 8.6 Hz, H-C(1)), 3.88 (*dd*, 1 H, *J* = 7.2, 9.2 Hz, H_A-C(5)), 3.62 (*dd*, 1 H, *J* = 6.7, 9.2 Hz, H_B-C(5)), 2.21–2.18 (*m*, 1 H, H-C(4)), 1.52 (*s*, 3 H, CH_3(isopropyl)), 1.33 (*s*, 3 H, CH_3(isopropyl)), 0.82 (*s*, 9 H, CH_3(*tert*-butyl)), 0.07 (*s*, 6 H, CH_3-Si); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.01 (s, CO), 150.15 (*s*, C_q(ar)), 138.08 (*s*, C_q(ar)), 128.45, 127.77, 127.72 (*d*, C_t(ar)), 111.17 (*s*, C_q(isopropyl)), 84.56, 79.89 (*d*, C(2), C(3)), 77.76 (*s*, C(4)), 73.54 (*t*, CH_2(ar)), 72.45 (*t*, C(5)), 71.58 (*d*, C(1)), 39.79 (*t*, C(4a)), 26.23 (*q*, CH_3(isopropyl)), 26.01 (*q*, CH_3(*tert*-butyl)), 24.55 (*q*, CH_3(isopropyl)), 18.41 (*s*, C_q(*tert*-butyl)), -4.48 (*q*, CH_3-Si), -4.68 (*q*, CH_3-Si); MS (ei, 80 eV, 72 °C): 557 (1.4%), 500 (11.4%), 275 (2.1%), 225 (2.4%), 224 (11.2%), 150 (8.3%), 120 (3.9%), 92 (9.1%), 91 (100%).

Analysis for $C_{29}H_{39}NO_8Si$ (557.71)
Calcd C 62.45 H 7.05 N 2.51%,
Found C 62.80 H 6.76 N 2.36%.

(4a R*) 5-*O*-Benzyl-1-*O*-(tert-butyldimethylsilyl)-4a-carba-4a-*O*-(3',5'-dinitrobenzoyl)-2,3-*O*-isopropylidene-β-*L*-lyxofuranose = [(3a* R*, 4* S*, 5* R*, 6* S*, 6a* R*) 4-(benzyloxy-methyl)-4-hydroxy-6-(tert-butyldimethylsilyloxy)-2,2-dimethyl-tetrahydro-cyclopenta [1,3]dioxol-5-yl] 3,5-dinitro-benzoate* (**12**)

Compound **10** (100 mg, 0.25 mmol) was acylated in dry dichloromethane (5 ml) in the presence of pyridine (0.2 ml) and 3,5-dinitrobenzoylchloride (63 mg, 0.27 mmol) for 12 h to afford after usual work up and chromatography (silica gel, hexane/ethyl acetate 20:1) **12** (138 mg, 90%); m.p. 150–153 °C; R_F = 0.41 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.00 (*t*, 1 H, *J* = 2.2 Hz, H-C(4')), 8.88 (*d*, 2 H, *J* = 2.2 Hz, H-C(2'), H-C(6')), 7.09–6.97 (*m*, 5 H, H-C(ar)), 5.57 (*dd*, 1 H, *J* = 8.7, 10.4 Hz, H-C(4a)), 4.65 (*t*, 1 H, *J* = 5.6 Hz, H-C(3)), 4.48 (*t*, 1 H, *J* = 5.6 Hz, H-C(2)), 4.38 (*d*, 1 H, *J* = 11.0 Hz, H_A-CH_2(ar)), 4.28 (*d*, 1 H, *J* = 11.0 Hz, H_B-CH_2(ar)), 4.11 (*dd*, 1 H, *J* = 5.7, 8.6 Hz, H-C(1)), 3.90 (*dd*, 1 H, *J* = 5.2, 9.3 Hz, H_A-C(5)), 3.62 (*t*, 1 H, *J* = 8.8 Hz, H_B-C(5)), 2.28–2.21 (*m*, 1 H, H-C(4)), 1.54 (*s*, 3 H, CH_3(isopropyl)), 1.33 (*s*, 3 H, CH_3(isopropyl)), 0.84 (*s*, 9 H, CH_3(*tert*-butyl)), 0.10, 0.02 (*s*, 6 H, CH_3-Si); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.97 (s, CO), 148.10 (*s*, C(3'), C(5')), 137.71(s, C_q(benzyl)), 133.87 (s, C(1')), 128.97, 128.95, 127.64, 127.43, 127.41, 127.04 (*d*, C_t(ar)), 121.72 (s, C(4')), 110.69 (*s*, C_q(isopropyl)), 81.47, 76.48, 76.38, 75.87 (*d*, C(1), C(2), C(3), C(4a)), 73.26 (*t*, CH_2(ar)), 69.17 (*t*, C(5)), 43.00(*t*, C(4)), 25.91 (*q*, CH_3(isopropyl)), 25.60 (*q*, CH_3(*tert*-butyl)), 24.25 (*q*, CH_3(isopropyl)), 18.20 (*s*, C_q(*tert*-butyl)), -4.57 (*q*, CH_3-Si), -4.82 (*q*, CH_3-Si); MS (ei, 80 eV, 144 °C): 602 (0.8%), 587 (1.8%), 546 (3.2%), 545 (11.1%), 269 (7.5%), 195 (3.0%), 167 (2.6%), 155 (2.1%), 129 (2.3%), 105 (2.7%), 92 (13.1%), 91 (100%).

Analysis for $C_{29}H_{38}N_2O_{10}Si$ (602.71)
Calcd C 57.79 H 6.35 N 4.65%,
Found C 58.12 H 6.03 N 4.33%.

*(4a S) 5-*O*-Benzyl-1-*O*-(tert-butyldimethylsilyl)-4a-carba-4a-*O*-[(S-methyl)-dithiocarboxyl]-2,3-*O*-isopropylidene-β-*L*-lyxofuranose = (3a* R*, 4* S*, 5* R*, 6* S*, 6a* R*) O-[4-(benzyloxy-methyl)-6-(tert-butyldimethylsilyloxy)-2,2-dimethyl-tetrahydro-cyclopenta[1,3] dioxol-5-yl]methansulfanyl methanthioate* (**14**)

To a 0 °C cold solution of **10** (250 mg, 0.61 mmol) in diethyl ether (2 ml) sodium hydride (hexane washed, 16 mg, 0.67 mmol) was added in four portions, the reaction warmed to 25 °C and stirred for another 2 h. Then carbon disulfide (74 mg, 0.98 mmol) and after 1 h iodomethane (207 mg, 0.1 ml, 1.46 mmol) was added and stirring continued overnight. The solvents were removed under reduced pressure and the residue subjected to column chromatography (silica gel, hexane/ethyl acetate 20:1) to afford **14** (135 mg, 44%) besides unchanged starting material **10** (80 mg, 32%); m.p. 94–95 °C; $[\alpha]_D^{20}$ −8.5° (*c*, 1.0 $CHCl_3$); R_F = 0.68 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.25 (*m*, 5 H, H-C(ar)), 6.12 (*dd*, 1 H, *J* = 8.3, 10.6, H-C(4a)), 4.65 (*t*, 1 H, *J* = 5.5 Hz, H-C(3)), 4.48 (*s*, 2 H, CH_2(ar)), 4.41 (*t*, 1 H, *J* = 5.7 Hz, H-C(2)), 4.03 (*dd*, 1 H, *J* = 5.8, 8.3 Hz, H-C(1)), 3.84 (*t*, 1 H, *J* = 8.9 Hz, H_A-C(5)), 3.60 (*dd*, 1 H, *J* = 5.6, 9.3 Hz, H_B-C(5)), 2.52 (*s*, 3 H, S-CH_3), 2.23–2.17 (*m*, 1 H, H-C(4)), 1.49 (*s*, 3 H, CH_3(isopropyl)), 1.32 (*s*, 3 H, CH_3(isopropyl)), 0.87 (*s*, 9 H, CH_3(*tert*-butyl)), 0.09, 0.06 (*s*, 3 H, 2 × Si-CH_3); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 196.38 (*s*, C=S), 138.54 (*s*, C_q(ar)), 128.23, 127.59, 127.41 (*d*, C_t(ar)), 110.76 (*s*, C_q(isopropyl)), 86.34 (*d*, C(4a)), 76.40, 76.38, 76.37 (*d*, C(1), C(2), C(3)), 73.34 (*t*, CH_2(ar)), 67.61 (*t*, C(5)), 43.86 (*d*, C(4)), 26.08 (*q*, CH_3(isopropyl)), 25.68 (*q*, CH_3(*tert*-butyl)), 24.63 (*q*, CH_3(isopropyl)), 19.12 (*q*, S-CH_3), 18.20 (*s*, C_q(*tert*-butyl)), -4.73, -4.96 (*q*, Si-CH_3); MS (ei, 80 eV, 104 °C): 498 (0.1%), 483 (0.8%), 441 (12.2%), 165 (20.0%), 155 (14.5%), 105 (13.0%), 91 (100%); HRMS calcd. for $C_{24}H_{38}O_5S_2Si$: 498.1930; found 498.1929.

*5-*O*-Benzyl-1-*O*-(tert-butyldimethylsilyl)-4a-carba-2,3-*O*-isopropylidene-β-*L*-lyxofuranose = 4-(benzyloxy-methyl)-6-(tert-butyldimethylsilyloxy)-2,2-dimethyl-tetrahydro-cyclopenta[1,3]dioxol* (**15**)

A solution of **14** (80 mg, 0.16 mmol) and phenylsilane (40 μl, 0.32 mmol) in toluene (2 ml) was heated under reflux and a solution of dibenzoylperoxide (155 mg, dissolved in 2 ml toluene) was added in several portions within 20 min. The solvents were removed under reduced pressure and the residue subjected to chromatography (hexane/ethyl acetate 20:1) to afford **15** (53 mg, 84%); $[\alpha]_D^{20}$ −21.8° (*c*, 1.0 $CHCl_3$); **15** was also obtained by silylation of **19** with *tert*-butyl-dimethylchlorosilane under usual conditions in 90% yield; $[\alpha]_D^{20}$ −22.5° (*c*, 1.0 $CHCl_3$).

Data for **15**. – R_F = 0.75 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (*m*, 5 H, H-C(ar)), 4.56 (*d*, 1 H, *J* = 11.8 Hz, H_A-CH_2(ar)), 4.51 (*t*, 1 H, *J* = 4.9 Hz, H-C(3)), 4.50 (*d*, 1 H, *J* = 12.0 Hz, H_B-CH_2(ar)), 4.36 (*t*, 1 H, *J* = 5.2 Hz, H-C(2)), 3.86 (*dt*, 1 H, *J* = 5.4, 10.9 Hz, H-

C(1)), 3.70 (*t*, 1 H, J = 7.8 Hz, H_A-C(5)), 3.45 (*dd*, 1 H, J = 7.0, 8.5 Hz, H_B-C(5)), 1.92–1.86 (*m*, 1 H, H_A-C(4a)), 1.81–1.73 (*m*, 1 H, H_B-C(4a)), 1.60 (*m*, 1 H, H-C(4)), 1.44, 1.30 (*s*, 3 H, CH_3(isopropyl)), 0.90 (*s*, 9 H, 3 × CH_3(*tert*-butyl)), 0.09 (*s*, 6 H, 2 × Si-CH_3)); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.54 (*s*, C_q(ar)), 128.24, 128.23, 127.55, 127.39 (*d*, C_t(ar)), 112.45 (*s*, C_q(isopropyl)), 79.90, 78.89 (*d*, C(2,3)), 73.57 (*d*, C(1)), 73.18 (*t*, CH_2(ar)), 69.50 (*t*, C(5)), 39.01 (*d*, C(4)), 33.35 (*t*, C(4a)), 26.10 (*q*, CH_3(*tert*-butyl)), 25.89, 24.42 (*q*, 2 × CH_3(isopropyl)); MS (ei, 80 eV, 93 °C): 392 (0.4%), 377 (1.3%), 335 (8.1%), 169 (4.6%), 149 (4.5%), 92 (7.5%), 91 (100%).

Analysis for $C_{22}H_{36}O_4Si$ (392.24)
Calcd C 67.30 H 9.24%,
Found C 67.48 H 9.51%.

(1a R, *3a* R, *6* S*) 6-(Hydroxymethyl)-2,2-dimethyl-tetrahydrocyclopenta-[1,3]dioxol-4-on* (**17**)

Hydrogenation of (–)-**16** (100 mg, 0.36 mmol) in methanol in the presence of hydrogen (atmospheric pressure) with Pd/C (10%, catalytical) for 24 h gave after usual work up and chromatography (silica gel, hexane/ethyl acetate 3:1 → 1:1) **17** (36 mg, 53%) and **18** (2.4 mg, 2.4%). Data for **17**: m.p. 87–89 °C; $[\alpha]_D^{20}$ –173.3° (*c*, 1.0 $CHCl_3$); ^{1}H NMR (250 MHz, acetone-d_6): δ = 4.88 (*dd*, 1 H, J = 4.3, 4.5 Hz, H-C(3)), 4.28 (*d*, 1 H, J = 4.5 Hz, H-C(2)), 3.83 (*dd*, 1 H, J = 8.6, 10.8 Hz, H_A-C(5)), 3.74 (*dd*, 1 H, J = 6.8, 11.1 Hz, H_B-C(5)), 3.62 (*bs*, 1 H, OH), 2.55 (*m*, 1 H, H-C(4)), 2.25 (*d*, 2 H, J = 11.7 Hz, H_2C(4a)), 1.34, 1.31 (*s*, 3 H, CH_3(isopropyl)); ^{13}C NMR (62.89 MHz, acetone-d_6): δ = 213.69 (*s*, C(1)), 112.35 (*s*, C_q(isopropyl)), 81.12, 78.82 (*d*, C(2), C(3)), 62.33 (*t*, C(5)), 38.56 (*d*, C(4)), 37.30 (*t*, C(4a)), 27.06, 25.24 (*q*, CH_3(isopropyl)); MS (FAB, matrix glycerol): 186 (31.2%, M), 185 (34.7%), 127 (32.8%), 111 (62.2%), 83 (41.8%), 69 (50.7%), 59 (100%); HRMS calcd. for $C_9H_{14}O_4$: 186.0893; found: 186,0894.

*5-*O*-Benzyl-4a-carba-2,3-*O*-isopropylidene-β-*L*-lyxofuranose = (3a* S, *4* S, *6* S, *6a* R*) 6-(benzyloxymethyl)-2,2-dimethyl-tetrahydro-cyclopenta[1,3]dioxol-4-ol* (**19**)

Reduction of **18** (55 mg, 0.2 mmol) with sodium borohydride (10 mg, 0.26 mmol) and $CeCl_3 \cdot 7\ H_2O$ (60 mg, 0.16 mmol) in methanol (2 ml) as described (*vide supra*) gave **19** (35 mg, 66%). Data for **19**.– $[\alpha]_D^{20}$ –88.0° (*c*, 1.0 $CHCl_3$); R_F = 0.51 (hexane/ethyl acetate 1:1); ^{1}H NMR (300 MHz, MeOH-d_4): δ = 7.33–7.25 (*m*, 5 H, H-C(ar)), 4.57 (*t*, 1 H, J = 5.5 Hz, H-C(2)), 4.50 (*s*, 2 H, CH_2(ar)), 4.43 (*t*, 1 H, J = 5.1 Hz, H-C(3)), 3.85 (*dt*, 1 H, J = 5.6, 11.2, H-C(1)), 3.67 (*dd*, 1 H, J = 7.9, 9.2 Hz, H_A-C(5)), 3.47 (*dd*, 1 H, J = 6.5, 9.3 Hz, H_B-C(5)), 1.99–1.94 (*m*, 1 H, H-C(4)), 1.80–1.77 (*m*, 1 H, H_A-C(4a)), 1.48–1.27 (*m*, 1 H, H_B-C(4a)), 1.43 (*s*, 3 H, CH_3(isopropyl)), 1.31 (*s*, 3 H, CH_3(isopropyl)); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 139.67 (*s*, C_q(ar)), 129.14, 128.66, 128.42 (*d*, C_t(ar)), 111.18 (*s*, C_q(isopropyl)), 80.61, 80.41 (*d*, C(2,3)), 74.06 (*t*, CH_2(ar)), 73.35 (*d*, C(1)), 70.32 (*t*, C(5)), 40.27 (*d*, C(4)), 33.59 (*t*, C(4a)), 25.92, 24.26 (*q*, 2 × CH_3(isopropyl)); MS (ei, 80 eV, 80 °C): 278 (0.1%), 277 (0.3%), 263 (4.5%), 92 (12.1%), 91 (100%); HRMS calcd. for $C_{16}H_{22}O_4$: 278.1518; found: 278.1518.

*4a-Carba-2,3-*O*-isopropylidene-β-*L*-lyxofuranose = (3a* S, *4* S, *6* S, *6a* R*) 6-(hydroxymethyl)-2,2-dimethyl-tetrahydro-cyclopenta[1,3]dioxol-4-ol* (**20**)

Reduction of **17** (50 mg, 0.3 mmol) with sodium borohydride (12 mg, 0.32 mmol) and $CeCl_3 \cdot 7\ H_2O$ (85 mg, 0.23 mmol) in methanol (3 ml) as described (*vide supra*) gave **20** (45 mg, 89%). Hydrogenation of **21** (0.5 g, 1.81 mmol) with Raney-nickel (catalytical) in water (10 ml) at 25 °C for 24 h gave **20** (0.18 g 52%) and **19** (0.18 g, 36%); reduction at 3 °C for 24 h gave **20** (traces) and **19** (94%). Data for **20**.– $[\alpha]_D^{20}$ –77.0° (*c*, 1.0 $CHCl_3$); R_F = 0.06 (hexane/ethyl acetate 1:1); ^{1}H NMR (300 MHz, MeOH-d_4): δ = 4.5 (*t*, 1 H, J = 5.4 Hz, H-C(2)), 4.44 (*t*, 1 H, J = 5.3 Hz, H-C(3)), 3.85 (*dt*, 1 H, J = 5.5, 11.1, H-C(1)), 3.74 (*dd*, 1 H, J = 7.5, 10.6 Hz, H_A-C(5)), 3.56 (*dd*, 1 H, J = 6.2, 10.6 Hz, H_B-C(5)), 1.90–1.74 (*m*, 2 H, H_A-C(4a), H-C(4)), 1.51–1.39 (*m*, 1 H, H_B-C(4a)), 1.44 (*s*, 3 H, CH_3-(isopropyl)), 1.30 (*s*, 3 H, CH_3(isopropyl)); ^{13}C NMR (75 MHz, MeOH-d_4): δ = 111.18 (*s*, C_q(isopropyl)), 80.68, 80.40 (*d*, C(2, 3)), 73.42 (*d*, C(1)), 61.93 (*t*, C(5)), 42.51 (*d*, C(4)), 33.30 (*t*, C(4a)), 25.91, 24.21 (*q*, 2 × CH_3(isopropyl)); MS (ei, 80 eV, 50 °C): 173 (52.6%), 112 (19.7%), 99 (23.1%), 95 (25.1%), 84 (15.2%), 83 (39.5%), 71 (21.6%), 69 (30.6%), 67 (22.2%), 59 (90.6%), 57 (17.3%), 55 (27.4%), 44 (19.5%), 43 (100%); MS (FAB, matrix glycerol): 189 (46.0%); MS (FAB, matrix glycerol + LiCl): 195 (100%); HRMS calcd. for $C_9H_{16}O_4$: 188.1049; found: 188.1050.

*(4a S) 5-O-Benzyl-1-O-(tert-butyldimethylsilyl)-4a-carba-4,4a-dihydroxy-2,3-O-isopropylidene-β-*L*-lyxofuranose = (3a* S, *4* S, *5* S, *6* S, *6a* R*) 4-(benzyloxy-methyl)-6-(tert-butyldimethylsilyloxy)-2,2-dimethyl-tetrahydro-cyclopenta[1,3]dioxol-4,5-diol* (**22**).

To a solution of **9** (1.00 g, 2.56 mmol) and *N*-methylmorpholine-*N*-oxide (0.70 g, 5.12 mmol, 2 equiv.) in acetone/water 8:1 (51 ml) a catalytical amount of osmiumtetroxide (*ca.* 50 mg) was added and stirring of the mixture was continued for 2 days at 25 °C. Then solid sodium hydrogensulfite (100 mg) was addded, the mixture diluted with acetone (30 ml), filtered and the solvents were removed *in vacuo* to afford a residue that was subjected to chromatography (silica gel, hexane/ethyl acetate 10:1) to yield **22** (1.05 g, 93%); $[\alpha]_D^{20}$ −25.4 (*c*, 1.2 $CHCl_3$), R_F = 0.48 (hexane/ethyl acetate 3:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.32–7.28 (*m*, 5 H, H-C(ar)), 4.60 (*d*, 1 H, *J* = 11.7 Hz, H_A-CH_2(ar)), 4.53 (*d*, 1 H, *J* = 11.8 Hz, H_B-CH_2(ar)), 4.46 (*t*, 1 H, *J* = 5.5 Hz, H-C(2)), 4.28 (*d*, 1 H, *J* = 5.8 Hz, H-C(3)), 4.00 (*dd*, 1 H, *J* = 5.3, 8.7 Hz), 3.91 (*dd*, 1 H, *J* = 5.4, 8.7 Hz), 3.74 (*d*, 1 H, *J* = 9.5 Hz, H_AC(5)), 3.68 (*d*, 1 H, *J* = 9.5 Hz, H_BC(5)), 3.11 (*s*, 1 H, *tert*-OH), 2.35 (*d*, 1 H, *J* = 5.3 Hz, *sec*-OH), 1.41 (*s*, 3 H, CH_3(isopropyl)), 1.28 (*s*, 3 H, CH_3(isopropyl)), 0.92 (*s*, 9 H, CH_3(*tert*-butyl)), 0.12 (*s*, 6 H, CH_3-Si); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 137.73 (*s*, C_q(ar)), 128.50 (*d*, C_t(ar)), 127.91 (*d*, C_t(ar)), 127.77 (*d*, C_t(ar)), 111.25 (*s*, C_q(isopropyl)), 81.53, 78.27, 76.15 (*d*, C(1), C(2), C(3)), 75.85 (*s*, C(4)), 73.87 (*t*, CH_2(ar)), 73.04 (*t*, C(5)), 26.12 (*q*, CH_3(isopropyl)), 25.90 (*q*, CH_3(*tert*-butyl)), 25.65 (*q*, CH_3(isopropyl)), 18.40 (*s*, C_q(*tert*-butyl)), -4.58 (*q*, CH_3-Si), -4.62 (*q*, CH_3-Si); MS (ei, 80 eV, 125 °C): 424 (0.1%, M), 409 (0.5%), 367 (5.9%), 91 (100%).

Analysis for $C_{22}H_{36}O_6Si$ (424.61)
Calcd C 62.23 H 8.55%,
Found C 62.33 H 8.53%.

(4a S, *5* R*) 4,5-Anhydro-5-O-benzyl-1-O-(tert-butyldimethylsilyl)-4a-carba-4a-hydroxy-2,3-O-isopropylidene-β-*L*-lyxofuranose* (**23**) *and (4a* S, *5* S*) 4,5-anhydro-5-O-benzyl-1-O-(tert-butyldimethylsilyl)-4a-carba-4a-hydroxy-2,3-O-isopropylidene-β-*L*-lyxofuranose* (**24**)

To a solution of **22** (0.50 g, 1.18 mmol) in abs. dichloromethane (45 ml) pyridinium chlorochromate (0.375 g, 1.74 mmol), anhydrous sodium acetate (0.375 g, 4.57 mmol) and powdered molecular sieves 3 Å (0.70 g) were added and the stirring was continued for 18 h. Approx. 2/3 of the solvents were removed under reduced pressure and the resulting suspension poured onto the top of a chromatographic column containing diethylether. Chromatography with diethyl ether and re-chromatography of the combined product-containing fractions (silica gel, hexane/ethyl acetate 20:1) gave **23** (0.12 g, 25%) and **24** (0.13 g, 26%). Data for **23**.– $[\alpha]_D^{20}$ −34.7 (*c*, 1.4 $CHCl_3$); R_F = 0.68 (hexane/ethyl acetate 3:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.60–7.32 (*m*, 5 H, H-C(ar)), 5.84 (*s*, 1 H, H-C(5)), 4.50 (*dd*, 1 H, *J* = 5.6, 5.7 Hz, H-C(2)), 4.41 (*d*, 1 H, *J* = 6.0 Hz, H-C(3)), 4.36 (*d*, 1 H, *J* = 8.9 Hz, H_A-CH_2(ar)), 4.12 (*d*, 1 H, *J* = 8.9 Hz, H_B-CH_2(ar)), 3.97 (*dd*, 1 H, *J* = 9.3, 9.5 Hz, H-C(4a)), 3.84 (*dd*, 1 H, *J* = 5.0, 8.9 Hz, H-C(1)), 1.95 (*bs*, 1 H, OH), 1.44, 1.32 (*s*, 3 H, CH_3(isopropyl)), 0.92 (*s*, 9 H, CH_3(*tert*-butyl)), 0.10, 0.11 (*s*, 3 H, Si-CH_3); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 137.10 (*s*, C_q(ar)), 130.09, 128.95, 127.05 (*d*, C_t(ar)), 111.82 (*s*, C_q(isopropyl)), 104.15 (*d*, C(5)), 84.35 (*s*, C(4)), 80.52, 77.19, 77.00. 76.74 (*d*, C(1), C(2), C(3), C(4a)), 68.46 (*t*, CH_2(ar)), 26.41 (*q*, CH_3(isopropyl)), 26.22 (*q*, CH_3(*tert*-butyl)), 24.61 (*q*, CH_3(isopropyl)), 18.67 (*s*, C_q(*tert*-butyl)), -4.19, -4.25 (*q*, Si-CH_3); MS (FAB, glycerol): 424 (1.8%, M+1). 423 (7.4%, M), 422 (0.8%), 129 (9.5%), 107 (10.0%), 105 (16.4%), 93 (11.7%), 75 (48.6%), 73 (100%).

Analysis for $C_{22}H_{34}O_6Si$ (422.59)
Calcd C 62.53 H 8.11%,
Found C 62.63 H 8.23%.

Data for **24**.– $[\alpha]_D^{20}$ −31.2° (*c*, 2.0 $CHCl_3$); R_F = 0.62 (hexane/ethyl acetate 3:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.65–7.30 (*m*, 5 H, H-C(ar)), 5.93 (*s*, 1 H, H-C(5)), 4.64 (*d*, 1 H, *J* = 9.0 Hz, H_A-CH_2(ar)), 4.47 (*dd*, 1 H, *J* = 4.7, 5.8 Hz, H-C(2)), 4.36 (*d*, 1 H, *J* = 6.0 Hz, H-C(3)), 4.03 (d, 1 H, *J* = 9.0 Hz, H_B-CH_2(ar)), 3.98–3.89 (*m*, 2 H, H-C(1), H-C(4a)), 2.05 (*bs*, 1 H, OH), 1.45, 1.32 (*s*, 3 H, CH_3(isopropyl)), 0.95 (*s*, 9 H, CH_3(*tert*-butyl)), 0.14 (*s*, 6 H, 2 × Si-CH_3); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 137.03 (*s*, C_q(ar)), 129.63, 128.43, 126.77 (*d*, C_t(ar)), 111.33 (*s*, C_q(isopropyl)), 106.07 (*d*, C(5)), 84.16 (*s*, C(4)), 81.20,76.52,76.38 (*d*, C(1), C(2), C(3), C(4a)), 67.99 (*t*, CH_2(ar)), 26.07,24.32 (*q*, CH_3(isopropyl)), 25.83 (*q*, CH_3(*tert*-butyl)), 18.28 (*s*, C_q(*tert*-butyl)), -4.58 (*q*, 2x CH_3-Si); MS (ei, 80 eV, 141 °C): 408 (0.5%, M+1), 407 (2.2%, M), 365 (22.6%), 307 (21.5%), 259 (11.0%), 201 (28.5%), 183 (15.95%), 155 (28.9%), 129 (65.4%), 107 (31.3%), 105 (29.4%), 75 (100.0%).

Analysis for $C_{22}H_{34}O_6Si$ (422.59)
Calcd C 62.53 H 8.11%,
Found C 62.65 H 8.19%.

(4a S) 1-O-(tert-Butyldimethylsilyl)-4a-carba-4,4a-dihydroxy-2,3-O-isopropylidene-β-L-lyxofuranose = (3a S, 4 S, 5 S, 6 S, 6a R)-6-tert-butyldimethylsilyloxy-4-hydroxymethyl-2,2-dimethyltetrahydro-cyclopenta [1,3] di–oxol-4,5-diol (**25**) *and (4a S) 4a-carba-4,4a-dihydroxy-2,3-O-isopropylidene-β-L-lyxofuranose* (**26**)

A 1:1 mixture of the epoxides **23** and **24** (0.26 g, 0.60 mmol) was dissolved in methanol (25 ml) and hydrogenolyzed at atmospheric pressure in the presence of Pd/C (10%) for 24 h. After filtration and evaporation of the solvents, the residue was subjected to chromatography (hexane/ethyl acetate 5:1 → 3:1) to afford **25** (0.17 g, 84%) and **26** (13 mg, 10%).

A solution of **22** (0.43 g, 1.0 mmol) in dichloromethane (25 ml) and acetone (10 ml) was debenzylated with dimethyldioxirane (*ca.* 0.1 M, 25 ml) as previously described to afford **25** (0.28 g, 85%). Desilylation of **22** (043 g, 1.0 mmol) in THF/methanol/water (9:1:1, 5 ml) with tetra-*n*-butyl-ammonium fluoride trihydrate (20 mg) for 48h at 25 °C gave after usual work up **26** (0.19 g, 87%). Data for **25**.– white solid; m.p. 72–74 °C; $[\alpha]_D^{20}$ −29.0° (*c*, 1.0 $CHCl_3$); R_F = 0.37 (hexane/ethyl acetate 1:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.47 (*dd*, *J* = 4.9, 5.9 Hz, 1 H, H-C(2)), 4.31 (*d*, *J* = 6.1 Hz, 1 H, H-C(3)), 4.03 (*dd*, *J* = 4.8, 8.8 Hz, 1 H, H-C(1)), 3.96 (*d*, *J* = 8.8 Hz, 1 H, H-C(4a)), 3.74 (*s*, 2 H, $H_2C(5)$), 3.25 (*bs*, OH), 2.90 (*bs*, 2 H, OH), 1.45 (*s*, 3 H, CH_3(isopropyl)), 1.29 (*s*, 3 H, CH_3(isopropyl)), 0.93 (*s*, 9 H, 3 × CH_3(*tert*-butyl)), 0.13 (*s*, 6 H, 2 × CH_3-Si); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 111.07 (*s*, C_q(isopropyl)), 81.65 (*d*, C(1)), 76.55, 76.54, 76.00 (*d*, C(2), C(3), C(4a)), 76.10 (*s*, C(4)), 64.55 (*t*, C(5)), 25.85 (*q*, CH_3(*tert*-butyl)), 25.75 (*q*, CH_3(isopropyl)), 23.96 (*q*, CH_3(isopropyl)), 18.21 (*s*, C_q(*tert*-butyl)), -4.69 (*q*, CH_3-Si), -4.76 (*q*, CH_3-Si); MS (FAB, glycerol): 337 (M+2, 2.0%), 336 (M+1, 6.0%), 335 (M, 29.1%), 73 (100%); MS (FAB, glycerol + LiCl): 341 (M+Li, 68.0%), 99 (100%); HRMS calcd. for $C_{15}H_{30}O_6Si$: 334.1811 found: 334.1812.

Analysis for $C_{15}H_{30}O_6Si$ (334.49)
Calcd C 53.86 H 9.04%,
Found C 53.92 H 9.04%.

Data for **26**. – white solid; m.p. 78–81 °C; $[\alpha]_D^{20}$ −25.7° (*c*, 1.0 $CHCl_3$); R_F = 0.07 (hexane/ethyl acetate 1:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.59 (*m*, 1 H), 4.38 (*m*, 2 H), 4.05 (*m*, 2 H), 3.84 (*m*, 1 H), 3.77 (*m*, 4 H), 1.47 (*s*, 3 H, CH_3(isopropyl)), 1.33 (*s*, 3 H, CH_3(isopropyl)); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 111.15 (*s*, C_q(isopropyl)), 81.22, 77.19, 75.63, 74.72 (*d*, C(1), C(2), C(3), C(4a)), 76.85 (*s*, C(4)), 60.89 (*t*, C(5)), 25.82, 23.75 (*q*, CH_3(isopropyl)); MS (ei, 80 eV, 118 °C): 220 (0.05%), 205 (25.5%, M-15), 171 (1.4%), 144 (7.4%), 127 (5.0%), 109 (11.7%), 103 (31.1%), 100 (39.0%), 85 (49.6%), 73 (56.5%), 72 (55.0%), 71 (34.4%), 59 (100%); HRMS calcd. for $C_9H_{16}O_6$: 220.0947; found: 220.0947.

(4a R) 1-O-(tert-Butyldimethylsilyl)-4a-carba-4a-hydroxy-2,3-O-isopropylidene-β-L-lyxofuranose = (3a R, 4 R, 5 R, 6 S, 6a R) 6-(tert-butyldimethylsilyloxy)-4-hydroxymethyl-2,3-dimethyl-tetrahydro-cyclopenta [1,3]dioxol-5-ol (**27**)

Following the debenzylation procedure given for **22**, from **10** (0.41 g, 1.0 mmol) **27** (0.28 g, 88%) was obtained after chromatographic work up (silica gel, hexane/ethyl acetate 20:1 → 10:1); m.p. 92–94 °C; $[\alpha]_D^{20}$ −15.9° (*c*, 1.1 $CHCl_3$); R_F = 0.60 (hexane/ethyl acetate 3:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.56 (*t*, 1 H, *J* = 5.8 Hz), 4.34 (*t*, 1 H, *J* = 5.7 Hz), 4.10–3.70 (*m*, 1 H), 3.63 (*dd*, 1 H, *J* = 5.4, 8.5 Hz), 2.60 (*bs*, 2 H, exchangeable with D_2O, HO-C(4a), HO-C(5)), 1.65 (*m*, 1 H, H-C(4)), 1.42 (*s*, 3 H, CH_3(isopropyl)), 1.25 (*s*, 3 H, CH_3(isopropyl)), 0.93 (s, 9 H, 3 × CH_3(*tert*-butyl)), 0.10 (*s*, 6 H, 2 × CH_3-Si); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 110.31 (*s*, C_q(isopropyl)), 78.58, 77.53, 77.14, 75.00 (*d*, C(1), C(2), C(3), C(4a)), 60.65 (*t*, C(5)), 44.92 (*d*, C(4)), 25.86 (*q*, 3 × CH_3(*tert*-butyl)), 25.76 (*q*, CH_3(isopropyl)), 23.82 (*q*, CH_3(isopropyl)), 18.33 (*s*, C_q(*tert*-butyl)), −4.56 (*q*, CH_3-Si); MS (ei, 80 eV, 62 °C): 318 (0.1%)303 (3.8%), 262 (2.5%), 261 (14.4%), 203 (43.5%), 185 (33.6%), 161 (19.9%), 157 (20.4%), 155 (10.2%), 129 (35.8%), 117 (18.7%), 111 (11.6%).

Analysis for $C_{15}H_{30}SiO_5$ (318.49)
Calcd C 56.57 H 9.49%,
Found C 56.88 H 9.22%.

(4a S) 1,4a-Anhydro-5-O-benzyl-1-O-(tert-butyldimethylsilyl)-4a-carba-2,3-O-isopropylidene-β-L-lyxofuranose = (1 S, 1a R, 4a R, 5 R, 6 S) 5-(benzyloxy-methyl)-3,3-dimethyl-tetrahydro-1,2,4-trioxy-cyclopropa[a] pentalene (**28**)

To a solution of **10** (35 mg, 0.1 mmol) in abs. dichloromethane (2 ml) DAST (70 µl) was slowly added at −78 °C . The mixture was allowed to

warm to room temperature and stirred for an additional 2 h, then cooled to 0 °C, and ice water (2 ml) was added. After extraction with dichloromethane (3 × 10 ml), the mixture was dried ($MgSO_4$), the solvent removed and the residue purified by chromatography (silica gel, hexane/ethyl acetate 5:1) to afford **28** (15 mg, 63%); $[\alpha]_D^{20}$ −16.7° (*c*, 0.6 $CHCl_3$); R_F = 0.28 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.70 (*dd*, 1 H, *J* = 1.6, 6.7 Hz), 4.62 (*d*, 1 H, *J* = 11.5 Hz, H_A-CH_2(ar)), 4.61 (*t*, 1 H, *J* = 6.9 Hz), 4.55 (*d*, 1 H, *J* = 11.9 Hz, H_B-CH_2(ar)), 3.84 (*dd*, 1 H, *J* = 6.2, 9.2 Hz), 3.79 (*t*, 1 H, *J* = 8.8 Hz), 3.65 (*d*, 1 H, *J* = 1.3 Hz, H_A-C(5)), 3.51 (*d*, 1 H, *J* = 1.3 Hz, H_B-C(5)), 2.50 (*ddt*, 1 H, *J* = 1.4, 6.7, 7.5 Hz, H-C(4)), 1.52, 1.27 (*s*, 3 H, CH_3(isopropyl)); ^{13}C NMR (62 MHz, $CDCl_3$): δ = 138.46 (*s*, C_q(ar)), 128.37, 127.69, 127.60 (*d*, C_t(ar)), 112.21 (*s*, C_q(isopropyl)), 80.58, 78.71 (*d*, C(2), C(3)), 73.46 (*t*, CH_2(ar)), 66.59 (*t*, C(5)), 60.61, 57.36 (*d*, C(1), C(4a)), 43.26 (*d*, C(4)), 26.44, 25.45 (*q*, CH_3(isopropyl)); MS (ei, 80 eV, 90 °C): 276 (0.5%), 275 (0.6%), 262 (3.2%), 261 (18.8%), 145 (7.2%), 98 (11.1%), 91 (100%); HRMS calcd. for $C_{16}H_{20}O_4$: 276.1361; found: 276.1360.

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