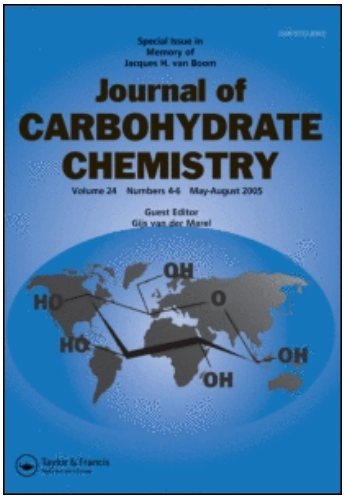


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# EASY SYNTHESIS OF 1-ALLYL-1-DEOXY-β- AND α- d-LYXOFURANOSES

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# EASY SYNTHESIS OF 1-ALLYL-1-DEOXY-β- AND α-D-LYXOFURANOSES

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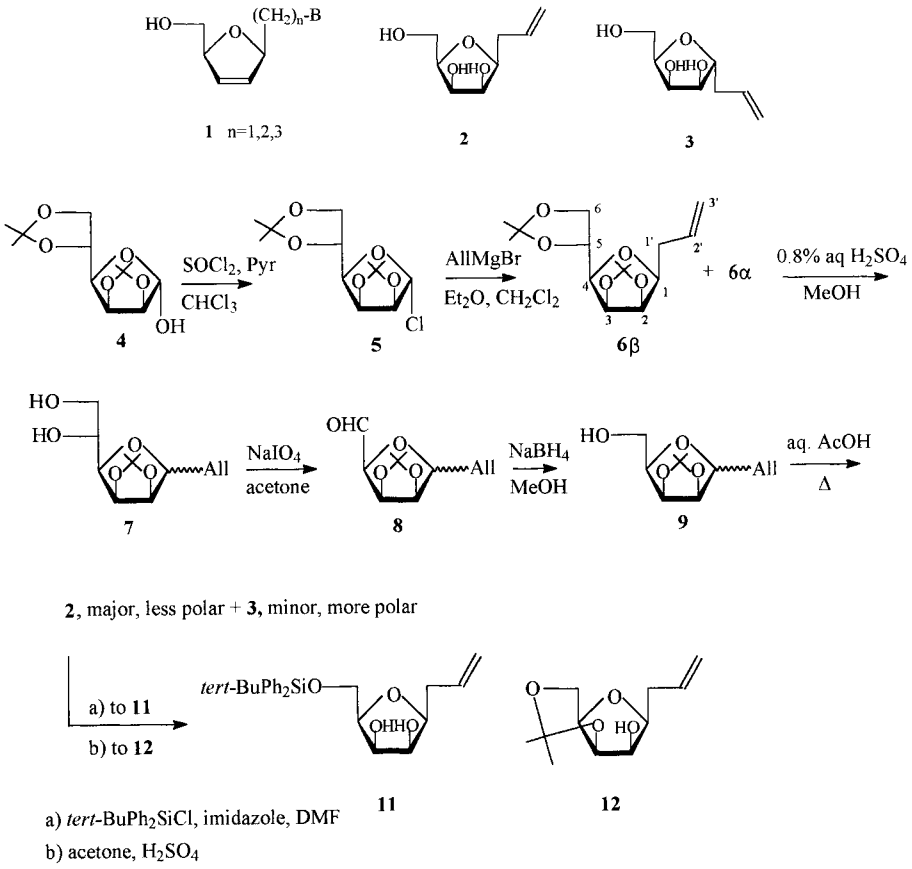
## ABSTRACT

2,3;5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl chloride reacted with allylmagnesium bromide with preferential inversion of the anomeric configuration to furnish a mixture of the 1-allyl-1-deoxy-β- and α-D-mannofuranoses. Separation of β and α derivatives was possible only after conversion to the 1-allyl-1-deoxylyxofuranoses **2** and **3**. The β configuration of the predominant product **2** was proved using the NOE method.

## INTRODUCTION

Modified nucleosides[1] have received much attention as potential chemotherapeutic agents due to their ability to interfere with the polymerases engaged in replication processes in metastatic or virus invaded cells. In fact, most of the antiviral compounds approved for commercialization are nucleoside analogs which were obtained by modifications of the ribonucleosides or 2′-deoxyribonucleosides at a nucleobase moiety (iododeoxyuridine, trifluoromethylthymidine, ribavirin), at a carbohydrate moiety (arabinoadenosine, acyclovir, ganciclovir, azidothymidine, dideoxyinosine, dideoxycitidine, dideoxydidehydrothymidine, ''L'' 3′-thia-2′,3′-dideoxycytidine) or at both moieties (famcilcovir, abacavir).[2] Continuing research in this field has resulted in synthesis of C1′-O-N nucleosides[3] and homo-*C*-nucleosides[4] by insertion, respectively, of an oxygen atom or a methylene group between a carbohydrate and a nucleobase, i.e. by changing the connection mode between them. Other possibilities have also been described.[5] Recently 2′-deoxyhomo-*C*-nucleosides received attention[6] as substrates for antiviral screening




***Scheme 1.*** Outline of the synthetic procedure.

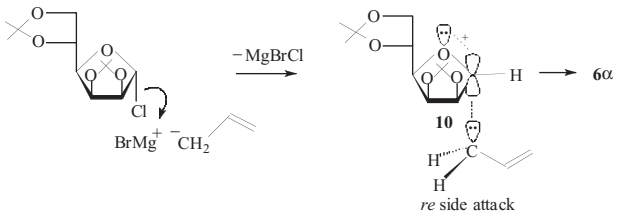
and for anti-sense probes with favorable hybridization properties. We published a synthesis of **1** (n = 1, B = thymin-1-yl),[6a] a homo-*C*-analog of the active anti-HIV drug dideoxydidehydrothymidine,[1b,c] which is the first example of such a group of compounds. To explore this field further we have been working on compounds having two and three methylene groups as linkers (**1** n = 2,3). For this reason we needed easy access to 1-allyl-1-deoxy-β-D-lyxofuranose **2**, which can be a precursor of both targets **1** (n = 2,3). The subject of this communication is a synthesis of **2** together with 1-allyl-1-deoxy-α-D-lyxofuranose **3** as shown in Scheme 1. Both products are easily separable by gravitational column chromatography.

## RESULTS AND DISCUSSION

Recent literature[7] indicates that the 2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranosyl chloride **5**[8] can be a convenient starting material for the synthesis of 1-allyl-1-deoxy-D-mannofuranoses **6**. Since the chlorine and hydrogen atoms at C1 and C2 are in a *cis* arrangement in **5**, elimination by an E2 path should not take place during a

reaction with a basic reagent such as allylmagnesium bromide. At the same time the 2,3-*O*-isopropylidene group is considered to be a non-participating moiety.[9] One could therefore expect that allylmagnesium bromide would react preferentially with inversion of configuration at C1 of **5** to furnish a necessary β-derivative **6**. This compound was in fact formed as the principal product as shown after conversion to the *lyxo* product **2** (see below).

2,3;5,6-Di-*O*-isopropylidene-α-D-mannofuranose **4**[10] (H1: $\delta = 5.35$ ppm, s, $CDCl_3$, 400 MHz) was reacted with $SOCl_2$ in the presence of pyridine[8] to furnish the α chloride **5** as the only detectable anomer (H1: $\delta = 6.78$ ppm, s, $CDCl_3$, 400 MHz). Compound **5** was prepared in quantities over 20 g in ca. 88% yield and because of its high purity, judged by TLC, was subsequently used without distillation.[8] Other methods of chlorination of **4** [$Ph_3P$-$CCl_4$,[11a] $CH_3SO_2Cl$-collidine,[11b] TlOEt-$SOCl_2$,[11c] 2-chlorobenzoxazolium tetrafluoroborate-$Et_4NCl$],[11d] triphosgene[11e] were much less convenient for larger scale preparations. Compound **5** was treated with an excess of freshly prepared ethereal allylmagnesium bromide to furnish an inseparable mixture of the 1-allyl-1-deoxy-β- and α-mannofuranoses **6** in 83% yield in batches of ca 18 g. The same mixture was previously obtained during a free-radical process[12] and reported to contain predominantly **6**α, although no evidence was presented to support this configuration. Selective hydrolysis of the 5,6-*O*-isopropylidene group in **6** was accomplished by the treatment with diluted $H_2SO_4$ in MeOH to furnish a diol **7**, which was cleaved with $NaIO_4$ to give the aldehydes **8**. The aldehydes **8** were reduced with $NaBH_4$ to furnish 1-allyl-1-deoxy-2,3-*O*-isopropylidene-α,β-D-lyxofuranoses **9**. Final removal of the acetonide function with aqueous AcOH yielded an easily separable mixture of the 1-allyl-1-deoxy-β-D-lyxofuranose **2** as the principal, less polar product, and the α derivative **3**. Only at this stage was it possible to separate both products. The proportion of **2** to **3** was ca. 3.5:1.0, which shows that allylmagnesium bromide reacted preferentially with inversion of configuration at the anomeric center of **5** as expected. Formation of **6**α can be rationalized as a consequence of the halide-ion catalysis,[9] where either a chloride or a bromide ion acted as a nucleophile and formed a transient 2,3;5,6-di-*O*-isopropylidene-β-D-mannofuranosyl halide, which then reacted in the $S_N2$ fashion to furnish **6**α. Alternatively, one can consider a mechanism shown in Scheme 2, where the cation **10** was approached by the allyl anion from the *re* side to get maximum overlap of the orbitals in the transition state. This stereoelectronic effect is responsible for predominant formation of α-*C*-glycosides during Lewis acid catalyzed reactions.[7c–e] Magnesium bromide resulting from the Schlenk equilibrium[13] can act like a Lewis acid and independently contribute to formation of **10**. Steric factors also favor the attack on **10** from the *re* side.




***Scheme 2.*** Possible mechanism of formation of 6α.

The major less polar lyxofuranose **2** was shown to have a β configuration by spectroscopic methods, i.e., $^{1}H$, $^{13}C$, COSY, HETCOR, and NOE. A coupling constant 4.2 Hz was found between the hydrogen atoms H1′ and H2′ (300 MHz, DMSO-$d_6$), a value close to the $J_{1,2}$ in the tetra-*O*-benzoyl-β-D-lyxofuranose[14] ($J_{1,2} = 4.6$ Hz, $CDCl_3$, 100 MHz), but the corresponding coupling in the α anomer **3** was impossible to obtain due to superimposed H1′ and H2′ signals. The values of the H1′–H2′ couplings in the anomeric *C*-glycofuranosides alone cannot be used in general as indicators of the anomeric configuration because they can be close to each other making such identification difficult if not impossible.[15] Several newer approaches were suggested[16] but the Nuclear Overhauser Effect (NOE) spectroscopy is considered the best procedure for this purpose.[15] We therefore examined **2** by a differential NOE method, Figure 1. Selective irradiation of the atom H3′ gave enhancements of signals of H2′, H4′ and H1′, and also much weaker increase of 2′OH, 3′OH and both H3 signals; all other signals were cancelled. Irradiation of the H1 atoms multiplet in turn gave enhancement of signals of the H1′, H2′, H2 and H3; all other signals were cancelled. These results can be interpreted in terms of β configuration and the preferential S type puckering of the sugar moiety. Particularly important is a NOE between H3′ and H1′ atoms, which must be oriented *syn* and must be spatially close to influence each other's relaxation. Although a conformation $_3T^2$ is shown in Figure 1, a blend of the *S* type conformations is consistent with the described NOE pattern, but an α configuration can be unequivocally excluded. Also, the proton–proton coupling constants in **2**: $J_{1',2'} = 4.2$ Hz, $J_{2',3'} = 5.1$ Hz and $J_{3',4'} = 6.6$ Hz (300 MHz, DMSO-$d_6$) are comparable with the values calculated for the *S* type β-lyxofuranosyl nucleosides having a puckering amplitude $\Phi = 40°$ and a phase angle $P = 198°$:[17] $J_{1',2'} = 4.00$ Hz, $J_{2',3'} = 4.66$ Hz, $J_{3',4'} = 6.98$ Hz. The proximity of these values suggests that a β oriented 1-allyl-1-deoxy moiety and a β-oriented nucleobase influence a puckering mode of the lyxofuranosyl ring in a similar way. Interestingly, the type of nucleobase does not influence significantly the distribution of a phase angle.[18] It remains to be determined if the same applies in general to *C*-aglycons.

Compounds **2** and **3** violate Hudson's rules of isorotation which is a known characteristic of *C*-glycosides.[19]

The β product **2** was additionally characterized by its conversion to 1-allyl-5-*O*-*tert*-butyldiphenylsilyl-1-deoxy-β-D-lyxofuranose **11** and 1-allyl-1-deoxy-3,5-*O*-isopropylidene-β-D-lyxofuranose **12**. The position of the isopropylidene group in **12** was inferred from the presence of an exchangeable doublet in the $^{1}H$ NMR spectrum, since the OH proton is coupled to the H2′ proton only.

Application of **2** to obtain analogs of nucleosides with ethylene and propylene linkers **1** n = 2,3 will be published in due course.

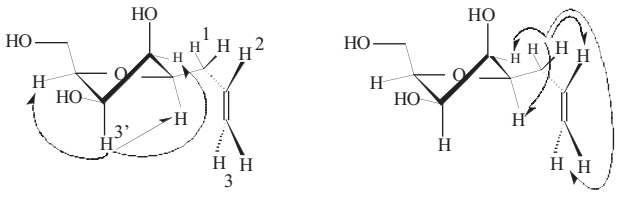



***Figure 1.*** Principal NOEs during irradiation of the proton H3′ and both H1 in **2**.

In summary, we obtained both 1-allyl-1-deoxy-α- and β-lyxofuranoses starting from the readily available mannofuranose **4**. Even though inseparable mixtures of the intermediates **6**, **7**, **8** and **9** resulted, separation of the final products **2** and **3** was easy. The β configuration of the predominant product **2** was proved using the NOE method.

## EXPERIMENTAL

**General Methods.** Column chromatography was performed on a silica gel G 70–230 mesh, and TLC chromatography on aluminum plates precoated with silica gel 60 $F_{254}$, both from Merck. 10% $H_2SO_4$ in MeOH was used to char the TLC chromatograms. NMR spectra were recorded on a Bruker 400 MHz, Varian 200 MHz or Varian 300 MHz instruments in DMSO-$d_6$ as solvent unless otherwise stated; exact mass measurements were performed on a Jeol SX 102A spectrometer using electron impact or a chemical ionization mode (with methane as reagent gas). Optical rotations were measured on a Perkin Elmer 241 automatic polarimeter at 24 °C. $MgSO_4$ was used for drying extracts.

**2,3;5,6-Di-*O*-isopropylidene-α-D-mannofuranosyl chloride (5).** To a cold (ca. 4 °C) solution of 2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranose **4**[10] (23.0 g, 88.5 mmol), in $CHCl_3$ (140 mL) and pyridine (60 mL, 742 mmol), was added $SOCl_2$ (24 mL, 330 mmol), using a syringe under the atmosphere of argon. The mixture was incubated in a refrigerator for 4 h, whereupon TLC (hexane-EtOAc 3:1) showed complete conversion of **4** to a less polar **5**. The mixture was poured into a separatory funnel, charged with crushed ice and water, and extraction was performed with $CH_2Cl_2$. The organic phase was washed with ice-cooled water until neutrality. Drying, filtration and evaporation of the solvents furnished oily **5** (21.6 g, 87.7 %), which was used without distillation[8] due to its purity. To avoid any exposure of **5** to humidity, **5** was kept under argon using a balloon. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.78 (s,1H, H-1); 4.96 (d, 1H, $J_{2,3}$=5.8 Hz, H-2); 4.89 (dd, 1H, $J_{3,4}$ = 3.7 Hz, $J_{3,2}$ = 5.7 Hz, H-3); 4.44 (ddd, 1H, $J_{5,6a}$ = 4.3 Hz, $J_{5,6b}$ = 6.0 Hz, $J_{5,4}$ = 7.7 Hz, H-5); 4.21 (dd, 1H, $J_{4,3}$ = 3.6 Hz, $J_{4,5}$ = 7.7 Hz, H-4); 4.10 (dd, 1H, $J_{6a,5}$ = 6.0 Hz, $J_{6a,6b}$ = 9.0 Hz, H-6a); 4.02 (dd, 1H, $J_{6b,5}$ = 4.6 Hz, $J_{6b,6a}$ = 8.8 Hz, H-6b); 1.46 (s, 6H); 1.38 and 1.33 (two s, 3H each).

**1-Allyl-1-deoxy-2,3;5,6-di-*O*-isopropylidene-α,β-D-mannofuranoses (6).** The obtained chloride **5** (ca. 77 mmol) in $CH_2Cl_2$ (55 mL) under argon, was cooled in an ice-salt bath and treated with freshly prepared allylmagnesium bromide (from Mg turnings 8.0 g, 329 mmol) in $Et_2O$ (100 mL) and AllBr (11.0 mL, 127 mmol) in $Et_2O$ (60 mL), transferred via a cannula over ca. 4h under an argon atmosphere, with magnetic stirring. The cooling bath was removed and the mixture was left overnight at rt under an atmosphere of argon. TLC (hexane-EtOAc 85:10) showed complete conversion of **5** to slightly more polar **6**. The solution was cautiously transferred to a separatory funnel charged with aq $NH_4Cl$, and extraction was performed using EtOAc. Drying, evaporation and chromatography in hexane-EtOAc 8:1 furnished **6** (18.4 g, 83%); $^1$H NMR (400 MHz, $CDCl_3$, data for the major β product only) δ 5.71 (ddt, 1H, $J_{2,1b}$ = 7.0 Hz, $J_{2,1a}$ = 7.0 Hz, $J_{2,3cis}$ = 10.3 Hz, $J_{2,3trans}$ = 17.0 Hz, H-2); 4.99 (d of apparent quartettes [ΣJ = 5Hz], 1 H, $J_{3trans,2}$ = 17 Hz, H-3) and 4.91 (d of apparent quintets [ΣJ = 5 Hz, 1 H, $J_{3cis,2}$ = 10 Hz, H-3); 4.58 (dd, 1H, $J_{3',4'}$ = 3.9 Hz, $J_{3',2'}$ = 6.1 Hz, H-3′); 4.47 (dd, 1H, $J_{2',1'}$ = 3.4 Hz,

$J_{2',3'} = 6.0$ Hz, H-2′); 4.24 (ddd, 1H, $J_{5',6a'} = 5.0$ Hz, $J_{5',6b'} = 5.9$ Hz, $J_{5',4'} = 7.3$ Hz, H-5′); 3.93 (dd, 1H, $J_{6b',5'} = 5.9$ Hz, $J_{6a',6b'} = 9.0$ Hz, H-6b′); 3.89 (dd, 1H, $J_{6a',5'} = 4.9$ Hz, $J_{6a',6b'} = 8.9$ Hz, H-6a′); 3.34 (ddd, 1H, $J_{1',2'} = 3.5$ Hz, $J_{1',1a} = 7.0$ Hz, $J_{1',1b} = 7.0$ Hz, H-1′); 3.32 (dd, 1H, $J_{4',3'} = 3.6$ Hz, $J_{4',5'} = 7.5$ Hz, H-4′); 2.31 (apparent t, 2H, J = 7 Hz, H1a, H1b); 1.34, 1.29, 1.23, 1.20 (four s, 3H each) C(**Me**)$_2$; $^{13}$C NMR (100 MHz, $CDCl_3$) **6**β δ 133.9 C2; 116.6 C3; 111.8 and 108.5 **C**(Me)$_2$; 81.2 C1′,4′; 80.8 C3′; 80.3 C2′; 72.8 C5′; 66.5 C6′; 32.4 C1; 26.6, 25.4, 25.0, 24.3 C(**Me**)$_2$; **6**α δ 133.2 C2; 117.4 C3; 112.1, 108.6 **C**(Me)$_2$; 84.2; 83.2; 80.4; 80.1; 73.0 C5′; 66.6 C6′; 35.0 C1; 25.8, 24.8 C(**Me**)$_2$.

**1-Allyl-1-deoxy-β-D-lyxofuranose (2) and 1-Allyl-1-deoxy-α-D-lyxofuranose (3).** A solution of **6** (32 g, 113 mmol) in MeOH (350 mL) was cooled to ∼0 °C and treated with cold (ca. 4 °C) aq $H_2SO_4$ (0.8%, 170 mL). The mixture was left at rt overnight. TLC (toluene-EtOAc 5:8) showed a single spot of **7**. The solution was neutralized with 1 N NaOH, most of the MeOH was evaporated, EtOAc and water were added to the residue and extraction was performed. The organic phase was dried and solvent evaporated to furnish 23.9 g, 87% of oily **7**. Acetone (400 mL) was added followed by a solution of $NaIO_4$ (32.0 g, 150 mmol) in $H_2O$ (180 mL) added dropwise with magnetic stirring. After 2 h TLC (toluene-EtOAc 5:8) showed a single purple-blue spot of **8** located higher than that of **7**. Inorganic material was filtered and acetone was evaporated. The residue was partitioned between $CHCl_3$ and $H_2O$, and exhaustive extraction was performed. The organic phase was dried to furnish 17.1 g, 82.3% of oily **8**. The crude aldehydes were dissolved in MeOH (250 mL), cooled in an ice-bath and treated with $NaBH_4$ (5.2 g, 137.5 mmol), added portionwise during 10 min. The mixture was stirred overnight. TLC showed a single spot of the alcohols **9**, which were more polar than the aldehydes **8**. Methanol was evaporated and the residue was partitioned between $CHCl_3$ and water. The organic phase was concentrated to furnish 20.8 g of oily **9**, which were evidently contaminated with inorganic material (theoretical yield is 17.3 g). This residue was dissolved in 80% AcOH (500 mL) and kept at 100 °C for 3 h. Glacial AcOH (100 mL) was added and heating was maintained for 45 min. and then the acetic acid was evaporated. The residue was co-evaporated with xylenes to remove the residual AcOH. TLC showed two spots: $R_f = 0.32$ (major) of **2** and $R_f = 0.21$ of **3** ($CH_2Cl_2$-MeOH 15:1). Column chromatography in the same system furnished **2** (6.65 g), **3** (1.91 g), and 1.2 g of mixed fractions, which were re-chromatographed to give a total of 7.25 g of **2** (37%) and 2.07 g of **3** (10.6%). The yields are based on **6**. **2**: oil, $[\alpha_D]$+38.1° (*c* 2.4, chloroform); $^1$H NMR (300MHz, after $D_2O$ exchange) δ 5.81 (ddt, 1H, $J_{2,1a} = J_{2,1b} = 4.8$ Hz, $J_{2,3cis} = 10.2$ Hz, $J_{2,3trans} = 17.4$ Hz, H-2); 5.10 (d of multiplets [ΣJ = 5 Hz], 1H, $J_{2,3trans} = 17.4$ Hz) and 4.98 (d of multiplets [ΣJ = 5Hz), 1H, $J_{2,3cis} = 10.4$ Hz, H-3); 4.84 (t, J = 5.4 Hz, residual 5′-OH); 4.83 (d, J = 6.9 Hz, residual OH); 4.76 (d, J = 5.4 Hz, residual OH); 4.19 (dd, 1H, $J_{3',2'} = 5.1$ Hz, $J_{3',4'} = 6.6$ Hz, H-3′); 3.84 (t, 1H, $J_{2',3'} = J_{2',1'} = 4.6$ Hz, H-2′); 3.73 (ddd, 1H, $J_{4',5'a} = 4.2$ Hz, $J_{4',5'b} = 4.8$ Hz, $J_{4',3'} = 6.6$ Hz, H-4′); 3.63 (ddd, 1H, $J_{1',2'} = 4.2$ Hz, $J_{1',1a} = 6.3$ Hz, $J_{1',1b} = 7.8$ Hz, H-1′); 3.52 (dd, partially superimposed on the HOD signal, $J_{5'a,4'} = 4.2$ Hz, $J_{5'a,5'b} = 11.4$ Hz, H-5′a); 3.42 (dd, 1H, $J_{5'b,4'} = 4.8$ Hz, $J_{5'b,5'a} = 11.4$ Hz, H-5′b); 2.36–2.17 (m, 2H, H-1a, H-1b); $^{13}$C NMR (75 MHz) δ 136.1 C2; 116.5 C3; 80.0 C4′; 79.5 C1′; 71.6 C3′; 71.1 C2′; 60.2 C5′; 34.3 C1. HRMS: Calcd. for M+H ($C_8H_{15}O_4$): 175.0970. Found: 175.0966. **3**: oil, $[\alpha_D]$+32.2° (*c* 2.5, chloroform); $^1$H NMR (300MHz, after $D_2O$ exchange) δ 5.80 (ddt, 1H, $J_{2,1a} = J_{2,1b} = 6.9$ Hz, $J_{2,3cis} = 10.2$ Hz, $J_{2,3trans} = 17.1$ Hz, H-2); 5.06 (d of multiplets [ΣJ = 7.5 Hz], $J_{trans} = 17.4$ Hz) and 5.02 (d of multiplets

[ΣJ = 4.9 Hz], $J_{cis}$ = 10.2 Hz) H-3a, H-3b; 4.80 (d, J = 6.8 Hz, residual OH); 4.64 (d, J = 4.3 Hz, residual OH); 4.46 (t, J = 5.6 Hz, residual 5′-OH); 3.93 (t, 1H, $J_{3',2'} = J_{3',4'}$ = 3.9 Hz, H-3′); 3.83 (ddd, 1H, $J_{4',3'}$ = 3.9 Hz, $J_{4',5'a}$ = 5.1 Hz, $J_{4',5'b}$ = 6.3 Hz, H-4′); 3.68–3.65 (unresolved, 2H, H-1′,2′); 3.56 (ddd, 1H, $J_{5'a,4'}$ = 5.4 Hz, $J_{5'a,5'b}$ = 11.4 Hz, H-5′a); 3.41 (dd, 1H, $J_{5'b,4'}$ = 6.6 Hz, $J_{5'b,5'a}$ = 11.4 Hz, H-5′b); 2.35–2.24 (unresolved, 1H) and 2.18–2.08 (unresolved, 1H) H-1a, H-1b; $^{13}$C NMR (50 MHz) δ 135.6; 116.8; 80.9; 79.8; 75.7; 71.2; 60.4; 37.7. HRMS: Calcd. for M+H ($C_8H_{15}O_4$) 175.0970. Found: 175.0965.

**1-Allyl-5-*O*-*tert*-butyldiphenylsilyl-1-deoxy-β-D-lyxofuranose (11).** Compound **2** (0.45 g, 2.59 mmol) in DMF (5.5 mL), imidazole (0.50 g, 7.3 mmol) and *tert*-butyldiphenylsilyl chloride (1.0 g, 3.6 mmol) were allowed to react during 36 h with exclusion of moisture. Extraction ($CH_2Cl_2$-$H_2O$), evaporation of solvents and chromatography with $CH_2Cl_2$-MeOH 10:0.1 furnished **11** (0.85 g, 78%); mp 75–77 °C (spontaneous crystallization); [$\alpha_D$] 68.4° (*c* 0.94, chloroform); $^1$H NMR (200 MHz, after $D_2O$ exchange) δ 7.69–7.42 (H aromatic, 10H); 4.80 (d, J = 5.4 Hz, residual OH); 4.62 (d, J = 5.8 Hz, residual OH); 5.84 (ddt, 1H, J = 7.0 Hz, J = 7.0 Hz, J = 10.1 Hz, J = 17.0 Hz); 5.06 (d, 1H, J = 18 Hz); 4.99 (d, 1H, J = 10.6 Hz); 4.16 (t, 1H, J = 5.7 Hz); 3.94–3.86 (unresolved, 2H); 3.79 (dd, 1H, J = 2.8 Hz, J = 10.9 Hz); 3.68 (apparent dd, 2H, J = 6.2 Hz, J = 10.4 Hz); 2.29 (t, 2H, J = 6.5 Hz); 0.95 (s, 9 H). HRMS: Calcd. for M+H ($C_{24}H_{33}O_4Si$) 413.2148. Found: 413.2130.

**1-Allyl-1-deoxy-3,5-*O*-isopropylidene-β-D-lyxofuranose (12).** Compound **2** (0.30 g, 1.7 mmol) in dry acetone (50 mL) and 2 drops of concd $H_2SO_4$ were incubated overnight. Neutralization with $K_2CO_3$, filtration, concentration and chromatography with hexane-EtOAc 3:1 furnished **12** (0.28g, 76%); mp. 38–40 °C (spontaneous crystallization in a refrigerator); $^1$H NMR (200 MHz) δ 5.84 (ddd, 1H, J = 6.9 Hz, J = 10.2 Hz, J = 17.2 Hz); 5.12 (d of unresolved signals [ΣJ = 5.8 Hz], 1H, J = 18 Hz); 5.04 (d of unresolved signals [ΣJ = 4.6 Hz], 1H, J = 11 Hz); 4.68 (d, partially overlapped, exchangeable, J = 3.1 Hz, OH); 4.66 (dd, 1H, J = 3.0 Hz, J = 6.1 Hz); 4.59 (dd, 1H, J = 3.5 Hz, J = 6.1 Hz); 3.70–3.41 (m, 4H); 2.35 (dt, 2H, J = 1.1Hz, J = 6.7 Hz, J = 6.7 Hz); 1.37 and 1.26 (two s, 3H each); $^{13}$C NMR (50 MHz) δ 135.2; 117.1; 111.1; 82.0; 81.0; 80.7; 80.4; 59.2; 32.9; 26.2; 25.2. HRMS (EI): Calcd. for M+H ($C_{11}H_{19}O_5$): 214.1204. Found: 214.1204.

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