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TETRAHEDRON

Stereocontrolled Synthesis of *O*- and *C*-Furanosides through 1,4-Iodocyclisation of D-Galactal

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Dedicated to Professor Pierre Sinaÿ on the occasion of his 62nd birthday

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Abstract: Iodocyclisation of 6-*O*-protected-D-galactal, followed by radical reduction, gives [2.2.1] bicyclic acetals which are regioselectively opened by various nucleophiles (alcohols, allyltrimethylsilane, triphenylphosphine) to give furanosyl compounds. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

2,5-Disubstituted tetrahydrofurans are the core motifs of natural compounds such as polyether antibiotics[1] and annonaceous acetogenins.[2,3] Numerous stereocontrolled approaches to such valuable units have been reported.[4] Among them, the nucleophilic substitution at the anomeric centre of a glycofuranose appears as an excellent strategy to prepare the corresponding tetrahydrofuran. Unfortunately, unlike their pyranoside counterparts, hexo-furanosides are not readily attainable. Moreover, furanoid glycals and furanosyl halides are often unstable compounds.

The conversion of a pyranose form to a furanose one would be a contrathermodynamic process as it is demonstrated by the composition of a Fischer glycosidation mixture at equilibrium.[5] However, stereoelectronic factors should allow regioselective openings of 1,4-anhydro-pyranoses by various nucleophiles in the presence of a Brönsted or Lewis acid. These strained bicyclic [2.2.1] acetals can be obtained from pyranose derivatives[6,7] and have a well-defined geometry; X-ray analysis of 2,7-dioxabicyclo[2.2.1]heptane derivatives[8-10] have shown that bond angles at *O*-4 and *O*-5 (carbohydrate numbering) are near 95 and 105° respectively. Therefore, lone pairs at *O*-5 have a higher p character giving more nucleophilicity to that oxygen atom. Furthermore, cleavage of the *C*-1–*O*-5 bond would be facilitated[11] by the antiperiplanar arrangement of a lone pair at *O*-4 with this bond, whereas neither orbital at *O*-5 is accurately positioned for breaking of the other bond (Scheme 1). When considering transi-

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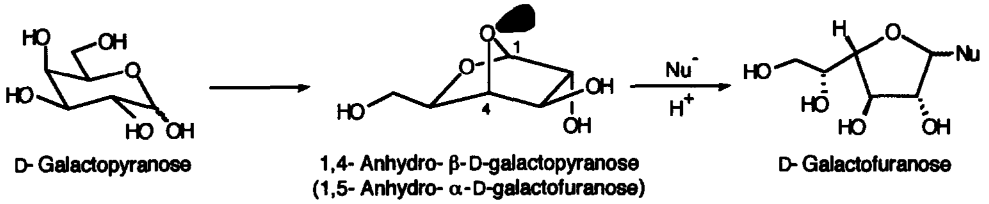
tion states of the reverse cyclisation processes, it is also highly probable that a transannular reaction from a pyrano compound in a boat conformation requires more energy than an intramolecular one from an envelope conformer of the furano isomer.

Among hexoses, galactose gives the highest percentage of furanosides (22%) at equilibrium in methanol under Fischer glycosidation conditions.[5] The vicinal *trans*-relationship for the *C*-2, *C*-3 and *C*-4 groups in the furanose form minimizes steric interactions and it is noteworthy that, although absent in mammalian glycoconjugates, D-galactofuranoses occur in bacteria, protozoa and fungi.[12] A mutase enzyme catalysing a pyrano ↔ furano interconversion at the nucleotide sugar (UDP-Gal) level has been recently identified and cloned.[13,14] It is therefore tempting to postulate a 1,4-anhydro-β-D-galactopyranose as a plausible intermediate in the equilibrium between the two tautomeric forms.



Scheme 1

1,4-Anhydro-pyranoses have been submitted to cationic polymerisation[15,16] and stereoregular polymers mainly made of (1→5)-β-D-galactofuranosidic units have been obtained from 1,4-anhydro-2,3,6-tri-*O*-benzyl-β-D-galactopyranose.[17] A trialkyloxonium ion mechanism (S_N2 type) rather than an oxycarbenium one (S_N1 type) would be responsible for the observed β-configuration.

Oxidative iodocyclisation of *O*-tributylstannylated D-glucal has been shown[18] to give [3:2:1] bicyclic acetals-(1,6-anhydro derivatives) in high yield. When applied to D-galactal **1**, this procedure gave[19] a mixture of 1,6- and 1,4-anhydro-2-deoxy-2-iodo-β-D-galactopyranoses. We now report[20] our results concerning the 1,4-iodocyclisation of D-galactal and the use of derived bicyclic acetals in regioselective synthesis of furanose compounds.

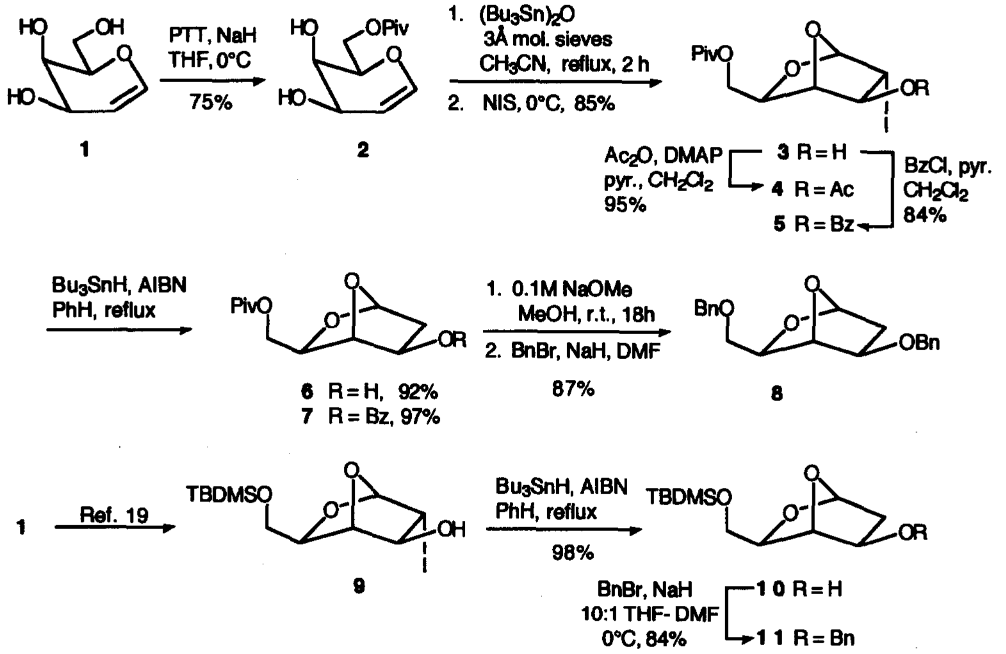
DISCUSSION

Synthesis of [2.2.1] bicyclic acetals from D-*galactal*

D-Galactal **1** was prepared by action of Zn–Cu couple on acetobromo-α-D-galactose[21] in refluxing ethyl acetate and in the presence of *N*-methylimidazole.[22] Deacetylation was performed with a strongly basic ion-exchange resin in methanol.[23] These modifications of Fischer's procedure gave higher and more reproducible yields of a crystalline material without need for chromatographic purification. Regioselective protection at *O*-6 of D-galactal **1** was achieved by 3-pivaloyl-1,3-thiazolidine-2-thione (PTT), a stable reagent readily obtained[24] by treatment of commercially available 2-thiazoline-2-thiol with pivaloyl chloride and triethylamine. 6-*O*-Pivaloyl-D-galactal **2** was obtained in 75% yield and was contaminated by less than 5% of the 3-*O*-pivaloyl isomer as shown by NMR and gas-liquid chromatography of a trimethylsilylated sample. Treatment of D-galactal with dibutyltin oxide[25] in boiling acetonitrile, then pivaloyl chloride at room temperature gave a 17:3 mixture of 3- and 6-*O*-

pivaloyl-D-galactal (47%) and some 3,6-disubstituted product (10%). Pivaloyl chloride in pyridine at low temperature also gave mixtures of products.

6-*O*-Pivaloyl-D-galactal **2** was treated with bis(tributyltin)oxide (0.8 mol. eq.) in boiling acetonitrile and in the presence of powdered 3 Å molecular sieves, then *N*-iodosuccinimide (NIS, 2 eq.) at 0°C. The crystalline iodoacetal **3** was isolated in 85% yield (Scheme 2). Its structure was ascertained by ^{1}H NMR spectroscopy; typical[7] coupling constants ($J_{1,2}$ 2.6, $J_{2,3}$ 2, $J_{3,4} = J_{4,5} = 0$, and $J_{2,4}$ 1 Hz) indicated that H-2 is *exo*, whereas H-3 and H-5 are *endo*, bridgehead hydrogens of bicyclo[2.2.1]heptane derivatives having nearly 90° dihedral angles with vicinal *endo* hydrogens. Conventional *O*-acetylation of **3** gave **4** where H-3 was shifted downfield ($\Delta\delta$ +0.69 ppm).



Scheme 2

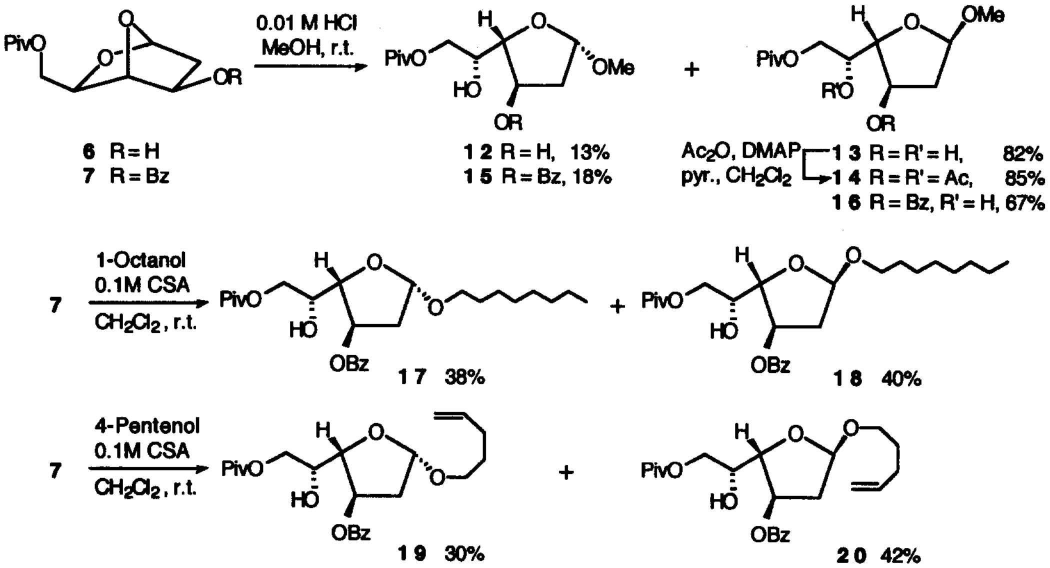
When stannylation of the glycal was omitted no cyclisation occurred, although an iodonium species was certainly formed, but led only to intractable mixtures. The main role of stannylation seems therefore to enhance the nucleophilicity of *O*-4, since a $^4H_5$ half-chair conformation of the glycal and the iodonium intermediate already places *O*-4 in a favorable axial orientation. To this respect, Miljkovic *et al.*[26] have stressed the higher reactivity of *galacto* oxycarbenium ions where a through-space electron donation from the axial *O*-4 to the electron-deficient anomeric centre is all the more efficient as the electron density at this oxygen atom is higher (with an axial methoxy group the distance between *O*-4 and the ring oxygen is 2.88 Å).

Compound **3** and its 3-*O*-benzoyl derivative **5** were reduced with tributyltin hydride and catalytic amounts of azobisisobutyronitrile (AIBN) in boiling benzene to give the 2-deoxy acetals **6** (92%) and **7** (97%) respectively (Scheme 2). Removal of the pivaloyl group in **6** was achieved with 0.1M sodium methoxide in methanol at room temperature. The crude 3,6-diol was then benzylated to give **8** in 87% overall yield. As expected, in compounds **6**, **7** and **8** H-2endo has a very small coupling constant with H-1 ($J_{1,2endo} \leq 0.5$ Hz) and a large one with H-3 ($J_{2endo,3} \sim 7$ Hz).

6-*O*-*tert*-Butyldimethylsilyl-D-galactal also underwent a 1,4-iodocyclisation reaction to give **9** in 79% yield as it has been previously reported.[19] Acetal **9** was similarly reduced into **10** (98%) and the hydroxyl group was benzylated at 0°C to give **11** (84%).

Synthesis of O-furanosides

The reactivity of these [2.2.1] bicyclic acetals towards nucleophiles was first tested with alcohols. Compound **6** with unprotected 3-OH was treated at room temperature with a 10^{-2} M HCl solution in methanol (readily obtained by addition of acetyl chloride to methanol). A 1:4 mixture of methyl α-**12** and β-**13** furanosides was isolated in 95% yield (Scheme 3). The major component was isolated by chromatography, then converted to its 3,5-di-*O*-acetyl derivative **14**. NMR signals of H-3 (δ 4.31) and H-5 (δ ~ 4.15) in **13** were shifted downfield (δ 4.97 and 5.39 respectively) in **14**, therefore establishing the furano structure of these products. It has been reported[27] that in *O*-furanosides a coupling constant ≤ 4 Hz between two vicinal ring hydrogens is indicative of a *trans* relationship. The following values $J_{2a,3}$ 8.1 and 8.6 and $J_{2b,3}$ 3.6 and 2.5 Hz in **13** and **14** respectively established the *trans* relationship between H-2b and H-3. The values $J_{1,2b}$ 1.5 and 1 Hz also give a *trans* relation between H-1 and H-2b and therefore establish the β-configuration of these compounds.



Scheme 3

This analysis was confirmed by the low value of optical rotation in **14**, $[\alpha]_D$ -88, the isomeric α-furanoside **12** having a much higher optical rotation, $[\alpha]_D$ +30. The values $J_{1,2a}$ 2, $J_{1,2b}$ 5.6, $J_{2a,3}$ 7.1 and $J_{2b,3}$ 6.6 Hz in **12** confirmed the *trans* relation of H-1 and H-2a, but obviously not the one of H-2b and H-3. However, a consistent downfield shift was always observed for H-2a as compared to H-2b (Δδ ~ + 0.1 and + 0.25 ppm in α- and β-furanosides respectively) and could be attributed to anisotropic effects.

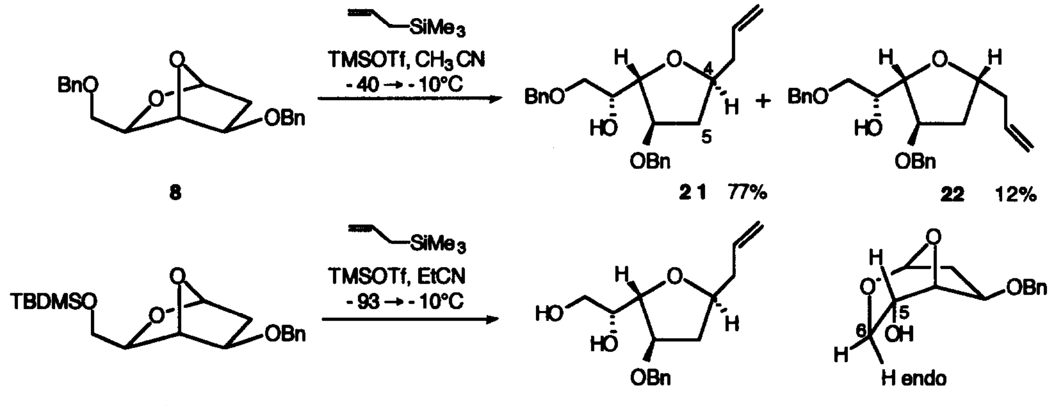
The benzoyl derivative **7** was similarly treated and gave also a 1:4 mixture of methyl α-**15**, $[\alpha]_D$ +30.5, and β-**16** furanosides, $[\alpha]_D$ -98.5, in 85% yield. Longer reaction time led to increasing amounts of methyl pyranosides as a result of thermodynamic equilibration. Study[28] of 2-deoxy-D-galactose has indeed shown that in methanolic 0.05% HCl a mixture of furanosides was initially formed, which evolved rapidly to more stable pyranosides.

1-Octanol and 4-pentenol (5 eq.) reacted at room temperature with a solution of acetal **7** in dichloromethane containing 10^{-1} M (±)-10-camphorsulfonic acid (CSA) to give a 1:1 mixture of n-octyl α-**17**, $[\alpha]_D$ +23, and β-**18** furanosides, $[\alpha]_D$ -75, and a 2:3 mixture of pent-4-enyl α-**19**, $[\alpha]_D$ +30, and β-**20** furanosides, $[\alpha]_D$ -99, in 78 and 72% yields respectively (Scheme 3). Pent-4-enyl glycosides are useful glycosylating reagents[29] and have been recently reported in furano sugars.[30-32] The lack of stereoselectivity in dichloromethane may reflect a S_N1 mechanism, whereas the use of methanol as reagent and solvent mostly involved a S_N2 reaction. To this respect, it is noteworthy that *N*-glycosylation of the 3,6-di-*O*-benzyl acetal **8** with silylated uracile[33] gave a 1:1 mixture of α and β-nucleosides. Unprotected acetal **6** could not be used in glycosylation reactions with limited amounts of alcohol, intractable mixtures of polar products being obtained possibly by polycondensation.

2-Deoxy-D-galactofuranosides could probably be equally obtained by a Brönsted acid promoted addition of alcohols to furanoid D-galactal as it has been reported[28,34,35] for the synthesis of 2-deoxy-pyranosides from pyranoid glycals. The interconversion pyrano → furano herein reported avoids however the preparation of furanoid glycals which are not readily attainable and are even unknown in the galacto series.

Synthesis of C-allyl furanosides

Next was studied the behavior of [2.2.1]bicyclic acetals towards a *C*-nucleophile. In the absence of substituent at C-2 stereoselectivity at the newly created stereogenic centre was hard to predict, since it is usually[4] governed by steric interactions with a vicinal group.



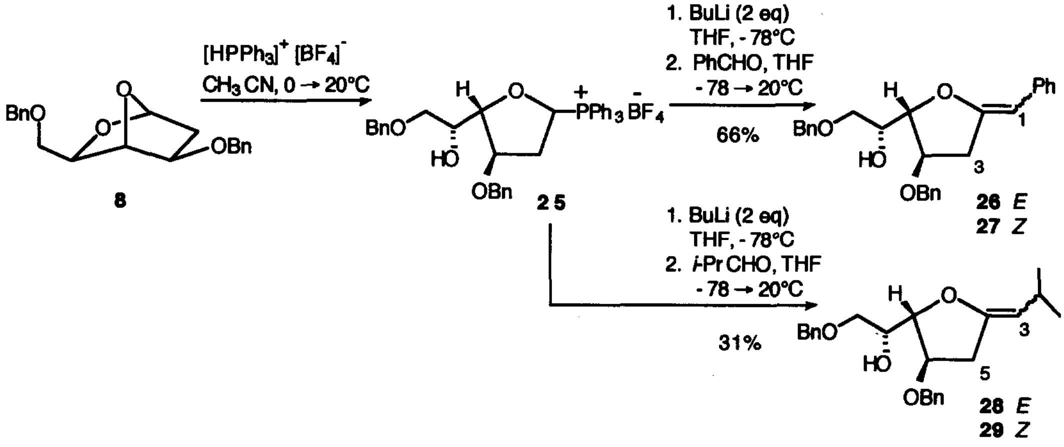
Scheme 4

We were therefore pleased to obtain a 6.5:1 mixture of *C*-allyl β-**21** and α-**22** furanosides (Scheme 4) in 89% yield when acetal **8** was treated with allyltrimethylsilane in acetonitrile in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf). The non-chelating Lewis acid preferentially silylates the *O*-5 oxygen atom delivering tetrahydrofuran compounds with an exocyclic $OSiMe_3$ group (*O*-silylated **21** and **22** were indeed isolated when the reaction mixture was quenched with triethylamine before work-up). Coupling constants between H-4 and H-5a,b gave no information about the configuration at *C*-4 ($J_{4,5a}$ 6.5 and 5.5, $J_{4,5b}$ 7.1 and 3.6 Hz for **21** and **22** respectively). Optical rotations of *C*-glycosides have been shown[36] to follow the same rules as those of *O*-glycosides. The values $[\alpha]_D$ -40 and +31 for **21** and **22** respectively therefore clearly establish their configuration. From what is known[15,17] about cationic polymerisation of [2.2.1] bicyclic acetals a major S_N 2 mechanism cannot be excluded, the nucleophile approaching the acetal from its *exo* face with simultaneous cleavage of the *C*-1–*O*-5 bond. But stabilization of a five membered cyclic oxycarbenium ion by acetonitrile or propionitrile seems more probable; *trans*-2,5-disubstituted tetrahydrofurans would thus be preferentially obtained because of the steric influence of the carbon chain (shorter C–O bonds make *cis*-2,5-disubstituted tetrahydrofurans sterically less favored). S_N2-like displacement of an α-isonitrilium adduct by the allylsilane can be also considered.

Acetal **11** gave similarly the *C*-allyl β-furanoside **23**, $[\alpha]_D$ -14, in 61% yield. The H-4 signal has the same chemical shift (δ 4.14) as in **21** and similar coupling constants ($J_{4,5a}$ 5.7 and $J_{4,5b}$ 7.4 Hz). Loss of both silyl groups at *O*-8 and *O*-9 occurred during the reaction. To this respect we observed that the 6-*O*-TBDMS group can occasionally compete with an external nucleophile (Me_3SiCN) to give 1,6-anhydro-3-*O*-benzyl-2-deoxy-α-D-galactofuranose **24**. Coupling constant $J_{5,6endo}$ 10.2 Hz between two vicinal *trans*-diaxial hydrogens confirms the chair conformation of the dioxane ring in **24**.

Synthesis of furanoid exocyclic enol ethers

Pyranosylphosphonium salts have been prepared by opening of a 1,6-anhydro-2-deoxysugar[37] with $Ph_3P \cdot HBF_4$ or addition of $Ph_3P \cdot HBr$ to a pyranoid glycal.[38] We found that addition of triphenylphosphonium tetrafluoroborate[39] to the bicyclic acetal **8** in acetonitrile at room temperature gave the furanosylphosphonium salt **25** which generated a phosphorane by treatment with *n*-butyllithium (2 eq.) in tetrahydrofuran (Scheme 5).



Scheme 5

Wittig reactions with benzaldehyde and *i*-butyraldehyde gave mixtures of exocyclic enol ethers **26***E*, **27***Z* (2:3) and **28***E*, **29***Z* (2:3) in 66 and 31% overall yields respectively. In both cases *E* and *Z* isomers could be partially separated by flash chromatography. The vinyl hydrogen appears, as expected, at higher field (δ ~ 3.8) in *i*-propyl compounds **28** and **29** than in phenyl ones **26** and **27** ($\delta \sim 4.7$) and shows a small allylic coupling (1.5 Hz) with the hydrogen *cis* to the *O*-benzyl group only in *E* isomers. Attribution of *EZ* geometries is speculative. However, in compound **26***E*, H-3a which is *cis* to the 4-*O*-benzyl group ($J_{3a,4}$ 2.1 Hz) is shifted towards lower fields ($\Delta\delta \sim +0.2$ ppm) being closer to the phenyl group at *C*-1 than it is in **27***Z*. In compound **28***E* H-5b which is *cis* to the 6-*O*-benzyl group ($J_{5b,6}$ 2 Hz) is conversely shifted towards higher fields ($\Delta\delta \sim -0.2$ ppm) being closer to the *i*-propyl group than it is in **29***Z*. Moreover, respective polarities of *EZ* isomers as observed in chromatography are reversed when going from compounds **26** and **27** (with an electron-attracting phenyl group) to compounds **28** and **29** (with an electron-releasing *i*-propyl group). The above interpretation seems more coherent that the one given earlier.[20] Similar furanoid exocyclic enol ethers have been reported in the literature.[40-42]

CONCLUSION

We have demonstrated that [2:2:1] bicyclic acetals easily obtained from 6-*O*-protected D-galactal through oxidative iodocyclisation are excellent electrophilic substrates for regioselective access to furanosyl compounds. Their reactivity towards *C*-nucleophiles in the presence of a Lewis acid could be extended to 2-(trimethylsilyloxy)furan, a butenolide nucleophilic equivalent; tetrahydrofuran fragments of annonaceous acetogenins were thus efficiently constructed[43] from D-galactal in a limited number of steps. Other glycals are under study and, although less readily, iodocyclisation of 6-*O*-*tert*butyldiphenylsilyl-D-glucal has already led in 58% yield to the corresponding D-*manno*-bicyclic acetal with all its substituents *endo*. Ketoses such as D-fructose might, through their *endo* or *exo* glycals[44], afford *C*-2 disubstituted tetrahydrofurans which are commonly found in polyether antibiotics.[1]

EXPERIMENTAL PART

General Procedures:

Melting points were determined using a Kofler hot stage apparatus under a Reichert microscope and are uncorrected. Optical rotations were measured at room temperature on a Perkin-Elmer 341 automatic polarimeter (concentration in g/100 mL). NMR spectra were recorded on a Bruker ARX-400 instrument. ^{1}H NMR were obtained at 400 MHz (s=singlet, d=doublet, t=triplet, m=multiplet, b=broad). Assignments were confirmed by homonuclear 2D COSY correlated experiments. ^{13}C NMR were obtained at 100 MHz in the proton-decoupled mode. Heteronuclear 2D correlated spectra were recorded in order to assist in carbon resonance assignments. Chemical shifts are given in ppm relative to internal TMS (δ scale) and coupling constants (J) in Hz. CI (ammonia) mass spectrum of compound **24** was taken with a Nermag R10-10 spectrometer. Thin layer chromatography (TLC) was performed on Merck DC-Alufolien Kieselgel 60 F_{254} Art. 5554 with detection by UV light and charring with 1:10 H_2SO_4–EtOH. Flash chromatography was performed on Merck Kieselgel 60 (40-63 µm). All solvents were dried and distilled according to standard laboratory procedures. Elemental analyses were performed by the Service de Microanalyse du Centre National de la Recherche Scientifique (Gif-sur-Yvette, France).

*1,5-Anhydro-2-deoxy-6-O-pivaloyl-*D-lyxo-*hex-1-enitol* (**2**).

Sodium hydride (60% suspension in oil, 215 mg, 5.4 mmol) was added to a mixture of D-galactal **1** (731 mg, 5 mmol) and 3-pivaloylthiazolidine-2-thione (1.12 g, 5.5 mmol) in dry tetrahydrofuran (20 mL) at 0°C under nitrogen. The mixture was stirred for 1 h at 0°C, then quenched with saturated aqueous NH_4Cl (2.5 mL) and extracted with dichloromethane. The extract was dried ($MgSO_4$), then concentrated. The residue was purified by flash chromatography (dichloromethane–ethyl acetate, 7:3) to give **2** (863 mg, 75%); mp 47-48°C; $[\alpha]_D$ -10 (*c* 0.99, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 6.38 (dd, 1 H, $J_{1,2}$ 6.1, $J_{1,3}$ 1.5 Hz, H-1), 4.74 (ddd, 1 H, $J_{1,2}$ 6.1, $J_{2,3} \sim J_{2,4} \sim$ 2 Hz, H-2), 4.44-4.40 (m, 2 H, H-3,6a), 4.29 (dd, 1 H, $J_{5,6b}$ 6.6, $J_{6a,6b}$ 11.7 Hz, H-6b), 4.08 (m, 1 H, H-5), 3.89 (m, 1 H, H-4), 2.67 and 2.53 (2 d, 2 H, *J* 6.1 and 8.1 Hz, OH-3,4) and 1.22 (s, 9 H, CMe_3); ^{13}C NMR ($CDCl_3$): δ 178.74 (C=O), 144.21 (C-1), 103.19 (C-2), 74.56, 65.23 and 64.03 (C-3,4,5), 62.89 (C-6), 38.88 (*C*Me_3) and 27.27 (C*Me*$_3$). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.25; H, 8.04.

1,4-Anhydro-2-deoxy-2-iodo-6-O-pivaloyl-β-D-galactopyranose (**3**).

A mixture of **2** (2.17 g, 9.42 mmol), bis(tributyltin) oxide (3.85 mL, 7.56 mmol) and powdered 3Å molecular sieves (3 g) in dry acetonitrile (60 mL) was heated at reflux for 2 h under vigorous stirring, then cooled to 0°C under a stream of nitrogen. *N*-Iodosuccinimide (4.24 g, 18.85 mmol) was rapidly added and the mixture was stirred for 30 min at 0°C, then filtered over Celite. The filtrate was concentrated and the residue was taken up with dichloromethane. The extract was washed with saturated aqueous $Na_2S_2O_3$ until colourless, dried ($MgSO_4$) and concentrated. The residue was taken up with a small volume of dichloromethane and deposited at the top of a silica gel column equilibrated in petroleum ether. Elution was performed first with petroleum ether to get rid of the tin by-products, then with 7:3 petroleum ether–ethyl acetate to give **3** (2.85g, 85%); mp 91°C (petroleum ether); $[\alpha]_D$ +94 (*c* 0.99, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 5.54 (d, 1 H, $J_{1,2}$ 2.6 Hz, H-1), 4.47 (d, 1 H, $J_{2,4}$ 1.5 Hz, H-4), 4.19 (dd, 1 H, $J_{2,3}$ 1.5, $J_{3,OH}$ 8.1 Hz, H-3), 4.07 (dd, 1 H, $J_{5,6a}$ 4.6, $J_{6a,6b}$ 11.2 Hz, H-6a), 3.91 (dd, 1 H, $J_{5,6b}$ 7.1, $J_{6a,6b}$ 11.2 Hz, H-6b), 3.83 (dd, 1 H, $J_{5,6a}$ 4.6, $J_{5,6b}$ 7.1 Hz, H-5), 3.66 (ddd, 1 H, $J_{1,2}$ 2.6, $J_{2,3}$ 1.5, $J_{2,4}$ 1.5 Hz, H-2), 2.33 (d, 1 H, $J_{3,OH}$ 8.1 Hz, OH-3) and 1.22 (s, 9 H, CMe_3); ^{13}C NMR ($CDCl_3$): δ 178.20 (C=O), 101.06 (C-1), 83.37, 81.32 and 72.26 (C-3,4,5), 62.96 (C-6), 38.79 (*C*Me_3), 30.62 (C-2) and 27.14 (C*Me*$_3$). Anal. Calcd for $C_{11}H_{17}IO_5$: C, 37.10; H, 4.81. Found: C, 37.17; H, 4.96.

3-O-Acetyl-1,4-anhydro-2-deoxy-2-iodo-6-O-pivaloyl-β-D-galactopyranose (**4**).

Acetic anhydride (0.5 mL, 5.3 mmol) was added to a solution of **3** (420 mg, 1.18 mmol) and *N,N*-dimethylaminopyridine (a few mg) in 20:1 dichloromethane–pyridine (10.5 mL). The mixture was stirred at room temperature for 2 h, then cooled to 0°C, quenched with methanol (5 mL) and concentrated. The residue was taken up with dichloromethane and the extract was washed with aqueous 0.1 M HCl, then saturated aqueous $NaHCO_3$, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 4:1) to give **4** (446 mg, 95%) as a colourless syrup; $[\alpha]_D$ +100 (*c* 0.96, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 5.55 (d, 1 H, $J_{1,2}$ 2.6 Hz, H-1), 4.88 (d, 1 H, $J_{2,3}$ 2 Hz, H-3), 4.59 (d, 1 H, $J_{2,4}$ 1 Hz, H-4), 4.09 (dd, 1 H, $J_{5,6a}$ 8.1, $J_{6a,6b}$ 14.8 Hz, H-6a), 3.94-3.89 (m, 2 H, H-5,6b), 3.78 (ddd, 1 H, $J_{1,2}$ 2.6, $J_{2,3}$ 2, $J_{2,4}$ 1 Hz, H-2), 2.12 (s, 3 H, OAc) and 1.21 (s, 9 H, CMe_3). Anal. Calcd for $C_{13}H_{19}IO_6$: C, 39.21; H, 4.81. Found: C, 39.23; H, 4.91.

*1,4-Anhydro-2-deoxy-6-O-pivaloyl-β-D-*lyxo*-hexopyranose* (**6**).

A solution of **3** (3.56 g, 10 mmol) in benzene (310 mL) was deoxygenated for 10 min by a stream of nitrogen, then brought to reflux. Tributyltin hydride (4.03 mL, 15 mmol) and azobis(isobutyronitrile) (a few mg) were rapidly added and the mixture was heated at reflux for 1 h, then cooled and concentrated. The residue was purified by flash chromatography (petroleum ether, then petroleum ether–ethyl acetate, 1:1) to give **6** (2.12 g, 92%) as a syrup; $[\alpha]_D$ +31 (*c* 0.74, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 5.72 (d, 1 H, $J_{1,2exo}$ 2.6 Hz, H-1), 4.51 (d, 1 H, $J_{2exo,4}$ ~ 1 Hz, H-4), 4.10 (ddd, 1 H, $J_{2endo,3}$ 6.6, $J_{2exo,3}$ 1.5, $J_{3,OH}$ 8.7 Hz, H-3), 4.01 (dd, 1 H, $J_{5,6a}$ 5.6, $J_{6a,6b}$ 11.2 Hz, H-6a), 3.91 (dd, 1 H, $J_{5,6b}$ 7.1, $J_{6a,6b}$ 11.2 Hz, H-6b), 3.63 (dd, 1 H, $J_{5,6a}$ 5.6, $J_{5,6b}$ 7.1 Hz, H-5), 2.31 (dd, 1 H, $J_{2endo,2exo}$ 13.7, $J_{2endo,3}$ 6.6 Hz, H-2endo), 1.88 (d, 1 H, $J_{3,OH}$ 8.7 Hz, OH-3), 1.63 (dddd, 1 H, $J_{1,2exo}$ 2.6, $J_{2endo,2exo}$ 13.7, $J_{2exo,3}$ 1.5, $J_{2exo,4}$ ~ 1 Hz, H-2exo) and 1.21 (s, 9 H, CMe_3); ^{13}C NMR ($CDCl_3$): δ 178.27 (C=O), 100.29 (C-1), 82.88 (C-4), 72.09 (C-5), 70.75 (C-3), 63.81 (C-6), 44.92 (C-2), 38.76 ($\mathit{C}Me_3$) and 27.14 ($C\mathit{Me}_3$). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.08; H, 8.07.

*1,4-Anhydro-3-O-benzoyl-2-deoxy-6-O-pivaloyl-*β-D-lyxo-*hexopyranose* (**7**).

A solution of benzoyl chloride (0.46 mL, 4 mmol) in dichloromethane (2 mL) was added dropwise to a solution of **3** (1.2 g, 3.37 mmol) in dichloromethane (5 mL) and pyridine (1.2 mL, 15 mmol) at 0°C. The mixture was stirred at room temperature for 1 h, cooled to 0°C, quenched with methanol (1 mL) and diluted with dichloromethane (100 mL). The solution was washed with aqueous 0.1 M HCl (30 mL), then saturated aqueous $NaHCO_3$ (30 mL) and water (30 mL), dried ($MgSO_4$) and concentrated. The residue (1.3 g, 84%) was pure **5** as checked by TLC (petroleum ether–ethyl acetate, 4:1). ^1H NMR (C_6D_6): δ 7.99 (m, 2 H, C_6H_3*H-oH-o'*), 7.13 (m, 1 H, C_6H_4*H-p*), 7.03 (m, 2 H, C_6H_3*H-mH-m'*), 5.09 (bd, 1 H, $J_{1,2}$ 2.2 Hz, H-1), 5.00 (d, 1 H, $J_{2,3}$ 1.9 Hz, H-3), 4.39 (bs, 1 H, H-4), 3.97 (dd, 1 H, $J_{5,6a}$ 5.4, $J_{6a,6b}$ 11.4 Hz, H-6a), 3.86 (dd, 1 H, $J_{5,6b}$ 6.2, $J_{6a,6b}$ 11.4 Hz, H-6b), 3.64 (dd, 1 H, $J_{5,6a}$ 5.4, $J_{5,6b}$ 6.2 Hz, H-5), 3.46 (m, 1H, H-2) and 1.14 (s, 9 H, CMe_3).

A solution of **5** (1.22 g, 2.65 mmol) in benzene (100 mL) was treated with tributyltin hydride (1.07 mL, 4 mmol) and azobis(isobutyronitrile) (a few mg) as described for the preparation of **6**. The crude product was purified by flash chromatography (petroleum ether, then petroleum ether–ethyl acetate, 9:1) to give **7** (860 mg, 97%) as a syrup; $[\alpha]_D$ +34 (*c* 1.18, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.04 (m, 2 H, C_6H_3*H-oH-o'*), 7.57 (m, 1 H, C_6H_4*H-p*), 7.44 (m, 2 H, C_6H_3*H-mH-m'*), 5.79 (dd, 1 H, $J_{1,2endo}$ 0.5, $J_{1,2exo}$ 2.6 Hz, H-1), 5.15 (dd, 1 H, $J_{2endo,3}$ 7, $J_{2exo,3}$ 2.2 Hz, H-3), 4.79 (bs, 1 H, H-4), 4.05 (dd, 1 H, $J_{5,6a}$ 5.7, $J_{6a,6b}$ 11.2 Hz, H-6a), 3.95 (dd, 1 H, $J_{5,6b}$ 6.8, $J_{6a,6b}$ 11.2 Hz, H-6b), 3.83 (dd, 1 H, $J_{5,6a}$ 5.7, $J_{5,6b}$ 6.8 Hz, H-5), 2.44 (ddd, 1 H, $J_{1,2endo}$ 0.5, $J_{2endo,2exo}$ 13.6, $J_{2endo,3}$ 7 Hz, H-2endo), 1.95 (dddd, 1 H, $J_{1,2exo}$ 2.6, $J_{2endo,2exo}$ 13.6, $J_{2exo,3}$ 2.2, $J_{2exo,4}$ 1.4 Hz, H-2exo) and 1.23 (s, 9 H, CMe_3); ^{13}C NMR ($CDCl_3$): δ 178.12 and 166.24 (2 C=O), 133.36, 129.71 and 128.42 (5 C arom.), 129.52 (C quat. arom.), 100.27 (C-1), 80.47, 73.02 and 72.56 (C-3,4,5), 63.51 (C-6), 41.75 (C-2), 38.77 ($\mathit{C}Me_3$) and 27.16 ($C\mathit{Me}_3$). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.46; H, 6.89.

*1,4-Anhydro-3,6-di-O-benzyl-2-deoxy-*β-D-lyxo-*hexopyranose* (**8**).

Sodium (230 mg, 10 mmol) was added to a solution of **6** (2.3 g, 10 mmol) in dry methanol (100 mL). The mixture was stirred for 18 h at room temperature, then concentrated at 45°C under vacuum. The residue was thoroughly dried under good vacuum, then dissolved into *N*,*N*-dimethylformamide (50 mL). Benzyl bromide (4 mL, 33.6 mmol) was added and the solution was cooled to 0°C. Sodium hydride (60% suspension in oil, 1.6 g, 40 mmol) was added portionwise under stirring. When evolution of hydrogen has almost ceased, the mixture was stirred for 1 h at room temperature, then quenched at 0°C with methanol (20 mL), diluted with dichloromethane (400 mL), washed with saturated aqueous NaCl, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 4:1) to give **8** (2.85 g, 87%) as a syrup; $[\alpha]_D$ +33 (*c* 1.05, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.38-7.27 (m, 10 H, 2 Ph), 5.67 (d, 1 H, $J_{1,2exo}$ 2.5 Hz, H-1), 4.69 (bs, 1 H, H-4), 4.54-4.51 (m, 4 H, 2 CH_2Ph), 3.84 (dd, 1 H, $J_{2endo,3}$ 6.6, $J_{2exo,3}$ 2 Hz, H-3), 3.57 (dd, 1 H, $J_{5,6a}$ 5.6, $J_{5,6b}$ 7.6 Hz, H-5), 3.37 (dd, 1 H, $J_{5,6a}$ 5.6, $J_{6a,6b}$ 9.2 Hz, H-6a), 3.32 (dd, 1 H, $J_{5,6b}$ 7.6, $J_{6a,6b}$ 9.2 Hz, H-6b), 2.17 (dd, 1 H, $J_{2endo,2exo}$ 13.2, $J_{2endo,3}$ 6.6 Hz, H-2endo) and 1.78 (ddd, 1 H, $J_{1,2exo}$ 2.5, $J_{2endo,2exo}$ 13.2, $J_{2exo,3}$ 2 Hz, H-2exo); ^{13}C NMR ($CDCl_3$): δ 137.82 and 137.62 (2 C quat. arom.), 128.44-127.73 (10 C arom.), 99.97 (C-1), 79.93, 77.45 and 73.32 (C-3,4,5), 73.51, 70.96 and 70.12 (2 CH_2Ph, C-6) and 41.91 (C-2). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.54; H, 6.87.

*1,4-Anhydro-6-O-*tert*-butyldimethylsilyl-2-deoxy-β-D-*lyxo*-hexopyranose* (**10**).

A solution of **9** (7.03 g, 18.2 mmol) in benzene (400 mL) was treated with tributyltin hydride (7.34 mL, 27.3 mmol) and azobis(isobutyronitrile) (a few mg) as described for the preparation of **6**. The crude product was purified by flash chromatography (petroleum ether, then petroleum ether–ethyl acetate, 7:3) to give **10** (4.71 g, 98%) as a syrup; $[\alpha]_D$ +14 (*c* 0.51, $CHCl_3$). ^1H NMR (C_6D_6): δ 5.34 (d, 1 H, $J_{1,2exo}$ 3.1 Hz, H-1), 4.45 (d, 1 H, $J_{2exo,4}$ 1 Hz, H-4), 3.59 (m, 1 H, H-3), 3.55 (dd, 1 H, $J_{5,6a}$ 5.1, $J_{6a,6b}$ 10.2 Hz, H-6a), 3.47 (dd, 1 H, $J_{5,6b}$ 8.1, $J_{6a,6b}$ 10.2 Hz, H-6b), 3.31 (dd, 1 H, $J_{5,6a}$ 5.1, $J_{5,6b}$ 8.1 Hz, H-5), 1.82 (dd, 1 H, $J_{2endo,2exo}$ 13.2, $J_{2endo,3}$ 7.1 Hz, H-2endo), 1.40 (d, 1 H, $J_{3,OH}$ 7.1 Hz, OH-3), 1.18 (dddd, 1 H, $J_{1,2exo}$ 3.1, $J_{2endo,2exo}$ 13.2, $J_{2exo,3}$ 1.5, $J_{2exo,4}$ 1 Hz, H-2exo), 0.90 (s, 9 H, CMe_3) and 0.04 (s, 6 H, 2 Me). Anal. Calcd for $C_{12}H_{24}O_4Si$: C, 55.35; H, 9.29. Found: C, 55.26; H, 9.44.

*1,4-Anhydro-3-O-benzyl-2-deoxy-6-O-*tert*-butyldimethylsilyl-β-D-*lyxo*-hexopyranose* (**11**).

A solution of **10** (4.71g, 18.1 mmol) in dry tetrahydrofuran (40 mL) was added dropwise to a suspension of sodium hydride (60% suspension in oil, 1.45 g, 36.2 mmol) in dry tetrahydrofuran (140 mL) at 0°C. A solution of benzyl bromide (2.6 mL, 27.7 mmol) in *N,N*-dimethylformamide (18 mL) was then added dropwise and the mixture was stirred at 0°C for 2 h, then quenched with methanol (20 mL), diluted with dichloromethane (350 mL), washed with saturated aqueous NaCl, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 23:2) to give **11** (5.32 g, 84%) as a syrup; $[\alpha]_D$ +23 (*c* 1, $CHCl_3$). ^1H NMR (C_6D_6): δ 7.25-7.08 (m, 5 H, Ph), 5.46 (d, 1 H, $J_{1,2exo}$ 2.6 Hz, H-1), 4.74 (bd, 1 H, H-4), 4.22 (m, 2 H, CH_2Ph), 3.56 (dd, 1 H, $J_{5,6a}$ 5.1, $J_{6a,6b}$ 9.9 Hz, H-6a), 3.51 (dd, 1 H, $J_{2endo,3}$ 6.7, $J_{2exo,3}$ 2.1 Hz, H-3), 3.49 (dd, 1 H, $J_{5,6b}$ 8.4, $J_{6a,6b}$ 9.9 Hz, H-6b), 3.36 (dd, 1 H, $J_{5,6a}$ 5.1, $J_{5,6b}$ 8.4 Hz, H-5), 1.86 (dd, 1 H, $J_{2endo,3}$ 6.7, $J_{2endo,2exo}$ 12.9 Hz, H-2endo), 1.58 (dddd, 1 H, $J_{1,2exo}$ 2.6, $J_{2endo,2exo}$ 12.9, $J_{2exo,3}$ 2.1, $J_{2exo,4}$ ~ 1 Hz, H-2exo), 0.92 (s, 9 H, CMe_3) and 0.04 (s, 6 H, 2 Me). Anal. Calcd for $C_{19}H_{30}O_4Si$: C, 65.10; H, 8.63. Found: C, 64.93; H, 8.46.

*Methyl 2-Deoxy-6-O-pivaloyl-α-D-*lyxo*-hexofuranoside* (**12**) *and methyl 3,5-di-O-acetyl-2-deoxy-6-O-pivaloyl-β-D-*lyxo*-hexofuranoside* (**14**).

Acetyl chloride (23 μL, 0.32 mmol) was added to a solution of **6** (230 mg, 1 mmol) in dry methanol (23 mL) at 0°C under nitrogen. The solution was left for 4 h at room temperature, then neutralized with solid $NaHCO_3$, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 1:1) to give first **12** (34 mg, 13%) as a syrup; $[\alpha]_D$ +30 (*c* 1.03, $CHCl_3$). ^1H NMR (CD_3OD): δ 5.11 (dd, 1 H, $J_{1,2a}$ 2, $J_{1,2b}$ 5.6 Hz, H-1), 4.46 (ddd, 1 H, $J_{2a,3}$ 7.1, $J_{2b,3}$ 6.6, $J_{3,4}$ 5.1 Hz, H-3), 4.19 (dd, 1 H,

$J_{5,6a}$ 5.1, $J_{6a,6b}$ 10.9 Hz, H-6a), 4.14 (dd, 1 H, $J_{5,6b}$ 6.6, $J_{6a,6b}$ 10.9 Hz, H-6b), 3.88 (dd, 1 H, $J_{3,4}$ 5.1, $J_{4,5}$ 4.6 Hz, H-4), 3.82 (ddd, 1 H, $J_{4,5}$ 4.6, $J_{5,6a}$ 5.1, $J_{5,6b}$ 6.6 Hz, H-5), 3.41 (s, 3 H, OMe), 2.22 (ddd, 1 H, $J_{1,2a}$ 2, $J_{2a,2b}$ 13.2, $J_{2a,3}$ 7.1 Hz, H-2a), 2.06 (ddd, 1 H, $J_{1,2b}$ 5.6, $J_{2a,2b}$ 13.2, $J_{2b,3}$ 6.6 Hz, H-2b) and 1.26 (s, 9 H, CMe_3). Anal. Calcd for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45. Found: C, 54.58; H, 8.58.

Then was eluted **13** (214 mg, 82%) as a slightly impure syrup. ^{1}H NMR (CD_3OD): δ 5.08 (dd, 1 H, $J_{1,2a}$ 5.1, $J_{1,2b}$ 1.5 Hz, H-1), 4.31 (ddd, 1 H, $J_{2a,3}$ 8.1, $J_{2b,3}$ 3.6, $J_{3,4}$ 4.1 Hz, H-3), 4.19-4.14 and 3.96-3.91 (2 m, 4 H, H-4,5,6a,6b), 3.38 (s, 3 H, OMe), 2.35 (ddd, 1 H, $J_{1,2a}$ 5.1, $J_{2a,2b}$ 13.7, $J_{2a,3}$ 8.1 Hz, H-2a), 1.87 (ddd, 1 H, $J_{1,2b}$ 1.5, $J_{2a,2b}$ 13.7, $J_{2b,3}$ 3.6 Hz, H-2b) and 1.26 (s, 9 H, CMe_3). Conventional acetylation of **13** (214 mg) with acetic anhydride (0.69 mL) and *N*, *N*-dimethylaminopyridine (a few mg) in dichloromethane (6 mL) and pyridine (0.34 mL) for 90 min at room temperature gave after flash chromatography (petroleum ether–ethyl acetate, 4:1) syrupy **14** (240 mg, 85%); $[\alpha]_D$ -88 (*c* 1.06, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 5.39 (ddd, 1 H, $J_{4,5}$ ~ $J_{5,6a}$ ~ 4.1, $J_{5,6b}$ 7.6 Hz, H-5), 5.10 (dd, 1 H, $J_{1,2a}$ 5.6, $J_{1,2b}$ 1 Hz, H-1), 4.97 (ddd, 1 H, $J_{2a,3}$ 8.6, $J_{2b,3}$ 2.5, $J_{3,4}$ 4.1 Hz, H-3), 4.31 (dd, 1 H, $J_{5,6a}$ ~ 4.1, $J_{6a,6b}$ 11.7 Hz, H-6a), 4.23 (dd, 1 H, $J_{3,4}$ 4.1, $J_{4,5}$ ~ 4.1 Hz, H-4), 4.19 (dd, 1 H, $J_{5,6b}$ 7.6, $J_{6a,6b}$ 11.7 Hz, H-6b), 3.38 (s, 3 H, OMe), 2.39 (ddd, 1 H, $J_{1,2a}$ 5.6, $J_{2a,2b}$ 14.7, $J_{2a,3}$ 8.6 Hz, H-2a), 2.10 and 2.08 (2 s, 6 H, 2 OAc), 1.96 (ddd, 1 H, $J_{1,2b}$ 1, $J_{2a,2b}$ 14.7, $J_{2b,3}$ 2.5 Hz, H-2b) and 1.19 (s, 9 H, CMe_3). Anal. Calcd for $C_{16}H_{26}O_8$: C, 55.48; H, 7.57. Found: C, 55.45; H, 7.67.

Methyl 3-O-Benzoyl-2-deoxy-6-O-pivaloyl-α (**15**) *and* -β-(**16**)-D-lyxo-*hexofuranosides.*

Acetyl chloride (15 μL, 0.21 mmol) was added to a solution of **7** (150 mg, 0.45 mmol) in dry methanol (15 mL). The solution was left for 9 h at room temperature, then neutralized with solid $NaHCO_3$, filtered and concentrated. The residue was purified by flash chromatography (toluene–ethyl acetate, 17:3) to give first **15** (30 mg, 18%) as a syrup; $[\alpha]_D$ +30.5 (*c* 1.13, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.02 (m, 2 H, C_6H_3*H-oH-o'*), 7.58 (m, 1 H, C_6H_4*H-p*), 7.45 (m, 2 H, C_6H_3*H-mH-m'*), 5.63 (ddd, 1 H, $J_{2a,3}$ 7.4, $J_{2b,3}$ 3.5, $J_{3,4}$ 2.1 Hz, H-3), 5.28 (dd, 1 H, $J_{1,2a}$ 2.6, $J_{1,2b}$ 6 Hz, H-1), 4.41 (dd, 1 H, $J_{3,4}$ 2.1, $J_{4,5}$ 2.3 Hz, H-4), 4.24 (dd, 1 H, $J_{5,6a}$ 6.7, $J_{6a,6b}$ 10.9 Hz, H-6a), 4.11-4.00 (m, 2 H, H-5,6b), 3.49 (s, 3 H, OMe), 2.52 (ddd, 1 H, $J_{1,2a}$ 2.6, $J_{2a,2b}$ 15, $J_{2a,3}$ 7.4 Hz, H-2a), 2.42 (ddd, 1 H, $J_{1,2b}$ 6, $J_{2a,2b}$ 15, $J_{2b,3}$ 3.5 Hz, H-2b) and 1.21 (s, 9 H, CMe_3); ^{13}C NMR ($CDCl_3$): δ 178.39 and 166.18 (2 C=O), 133.33, 129.64 and 128.45 (5 C arom.), 129.60 (C quat. arom.), 106.22 (C-1), 85.88, 76.60 and 69.51 (C-3,4,5), 65.09 (C-6), 56.06 (OMe), 39.74 (C-2), 38.79 (CMe_3) and 27.19 (C*Me*$_3$). Anal. Calcd for $C_{19}H_{26}O_7$: C, 62.28; H, 7.15. Found: C, 62.52; H, 7.38.

Then was eluted syrupy **16** (110 mg, 67%); $[\alpha]_D$ -98.5 (*c* 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.04 (m, 2 H, C_6H_3*H-oH-o'*), 7.57 (m, 1 H, C_6H_4*H-p*), 7.45 (m, 2 H, C_6H_3*H-mH-m'*), 5.44 (ddd, 1 H, $J_{2a,3}$ 8.3, $J_{2b,3}$ 2.1, $J_{3,4}$ 3.7 Hz, H-3), 5.18 (dd, 1 H, $J_{1,2a}$ 5.3, $J_{1,2b}$ 0.9 Hz, H-1), 4.35-4.28 and 4.23-4.14 (2 m, 4 H, H-4,5,6a,6b), 3.40 (s, 3 H, OMe), 2.48 (ddd, 1 H, $J_{1,2a}$ 5.3, $J_{2a,2b}$ 14.6, $J_{2a,3}$ 8.3 Hz, H-2a), 2.17 (ddd, 1 H, $J_{1,2b}$ 0.9, $J_{2a,2b}$ 14.6, $J_{2b,3}$ 2.1 Hz, H-2b) and 1.22 (s, 9 H, CMe_3); ^{13}C NMR ($CDCl_3$): δ 178.62 and 166.66 (2 C=O), 133.25, 129.76 and 128.41 (5 C arom.), 129.60 (C quat. arom.), 105.31 (C-1), 83.15, 75.31 and 69.63 (C-3,4,5), 65.75 (C-6), 55.09 (OMe), 39.08 (C-2), 38.83 (CMe_3) and 27.17 (C*Me*$_3$). Anal. Calcd for $C_{19}H_{26}O_7$: C, 62.28; H, 7.15. Found: C, 62.64; H, 7.38.

n-*Octyl 3-O-Benzoyl-2-deoxy-6-O-pivaloyl-α* (**17**) *and* -β (**18**) -D-lyxo-*hexofuranosides.*

(±)-10-Camphorsulfonic acid (696 mg, 3 mmol) was added to a solution of **7** (403 mg, 1.2 mmol) and 1-octanol (0.94 mL, 6 mmol) in dichloromethane (30 mL). The mixture was stirred for 210 min at room temperature, then washed with saturated aqueous $NaHCO_3$ until neutral, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 19:1) to give first **17** (215 mg, 38%) as a syrup; $[\alpha]_D$ +23 (*c* 1.12, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.02 (m, 2 H, C_6H_3*H-oH-o'*), 7.58 (m, 1 H, C_6H_4*H-p*), 7.45 (m, 2 H, C_6H_3*H-mH-m'*), 5.63 (ddd, 1 H, $J_{2a,3}$ 7.3, $J_{2b,3}$ 3.4, $J_{3,4}$ 2.1 Hz, H-3), 5.37 (dd, 1 H, $J_{1,2a}$ 2.5, $J_{1,2b}$ 6 Hz, H-1), 4.40 (dd, 1 H, $J_{3,4}$ 2.1, $J_{4,5}$ 2.4 Hz, H-4), 4.20 (m, 1 H, H-6a), 4.08-3.99 (m, 2 H, H-5,6b), 3.82 and 3.49 (2 dt, 2 H, *J* 6.6, 6.8 and 9.4 Hz, CH_2O), 3.44 (d, 1 H, $J_{5,OH}$ 8 Hz, OH-5), 2.52 (ddd, 1 H, $J_{1,2a}$ 2.5, $J_{2a,2b}$ 14.9, $J_{2a,3}$ 7.3 Hz, H-2a), 2.42 (ddd, 1 H, $J_{1,2b}$ 6, $J_{2a,2b}$ 14.9, $J_{2b,3}$ 3.4 Hz, H-2b), 1.58 (m, 2 H, CH_2CH_2O), 1.28 (m, 10 H, 5 CH_2), 1.21 (s, 9 H, CMe_3) and 0.89 (t, 3 H, *J* 7 Hz, Me); ^{13}C NMR ($CDCl_3$): δ 178.24 and 166.17 (2 C=O), 133.29, 129.63 and 128.44 (5 C arom.), 129.67 (C quat. arom.), 104.95 (C-1), 85.79, 76.74 and 69.46 (C-3,4,5), 69.22 and 64.99 (C-6, CH_2O), 39.85 (C-2), 38.76 (CMe_3), 31.81, 29.47, 29.36, 29.20, 26.11 and 22.65 (6 CH_2), 27.17 (CMe_3) and 14.10 (Me). Anal. Calcd for $C_{26}H_{40}O_7$: C, 67.22; H, 8.68. Found: C, 67.23; H, 8.88.

Then was eluted syrupy **18** (222 mg, 40%); $[\alpha]_D$ -75 (*c* 1.07, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.04 (m, 2 H, C_6H_3*H-oH-o'*), 7.57 (m, 1 H, C_6H_4*H-p*), 7.43 (m, 2 H, C_6H_3*H-mH-m'*), 5.44 (ddd, 1 H, $J_{2a,3}$ 8.1, $J_{2b,3}$ 2, $J_{3,4}$ 3.5 Hz, H-3), 5.28 (dd, 1 H, $J_{1,2a}$ 5.2, $J_{1,2b}$ 0.9 Hz, H-1), 4.32-4.26 and 4.20-4.13 (2 m, 4 H, H-4,5,6a,6b), 3.70 and 3.43 (2 dt, 2 H, *J* 6.3, 6.8 and 9.5 Hz, CH_2O), 2.42 (ddd, 1 H, $J_{1,2a}$ 5.2, $J_{2a,2b}$ 14.4, $J_{2a,3}$ 8.1 Hz, H-2a), 2.38 (d, 1 H, $J_{5,OH}$ 7.6 Hz, OH-5), 2.18 (ddd, 1 H, $J_{1,2b}$ 0.9, $J_{2a,2b}$ 14.4, $J_{2b,3}$ 2 Hz, H-2b), 1.58 (m, 2 H, CH_2CH_2O), 1.26 (m, 10 H, 5 CH_2), 1.21 (s, 9 H, CMe_3) and 0.86 (t, 3 H, *J* 7 Hz, Me); ^{13}C NMR ($CDCl_3$): δ 178.57 and 166.61 (2 C=O), 133.20, 129.74 and 128.37 (5 C arom.), 129.86 (C quat. arom.), 104.00 (C-1), 83.12, 75.43 and 69.66 (C-3,4,5), 67.55 and 65.70 (C-6, CH_2O), 39.13 (C-2), 38.81 (CMe_3), 31.84, 29.77, 29.45, 29.30, 26.30 and 22.66 (6 CH_2), 27.17 (CMe_3) and 14.09 (Me). Anal. Calcd for $C_{26}H_{40}O_7$: C, 67.22; H, 8.68. Found: C, 67.03; H, 8.84.

Pent-4-enyl 3-O-Benzoyl-2-deoxy-6-O-pivaloyl-α (**19**) *and -β* (**20**) *-*D*-*lyxo*-hexofuranosides.*

A solution of **7** (362 mg, 1.08 mmol) and 4-pentenol (0.56 mL, 5.42 mmol) in dichloromethane (30 mL) was treated for 1 h at room temperature with (±)-10-camphorsulfonic acid (696 mg, 3 mmol), then worked up as described for the preparation of **17** and **18**. Flash chromatography (petroleum ether–ethyl acetate, 83:17) gave first **19** (138 mg, 30%) as a syrup; $[\alpha]_D$ +30 (*c* 0.92, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.01 (m, 2 H, C_6H_3*H-oH-o'*), 7.58 (m, 1 H, C_6H_4*H-p*), 7.44 (m, 2 H, C_6H_3*H-mH-m'*), 5.81 (m, 1 H, $CH=CH_2$), 5.63 (ddd, 1 H, $J_{2a,3}$ 7.3, $J_{2b,3}$ 3.5, $J_{3,4}$ 2.1 Hz, H-3), 5.36 (dd, 1 H, $J_{1,2a}$ 2.6, $J_{1,2b}$ 6.1 Hz, H-1), 5.08-4.97 (m, 2 H, $CH_2=$), 4.39 (dd, 1 H, $J_{3,4}$ 2.1, $J_{4,5}$ ~ 2.1 Hz, H-4), 4.20 (dd, 1 H, $J_{5,6a}$ 6.4, $J_{6a,6b}$ 10.7 Hz, H-6a), 4.10-3.99 (m, 2 H, H-5,6b), 3.84 and 3.51 (2 dt, 2 H, *J* 6.5, 6.7 and 9.6 Hz, CH_2O), 3.38 (d, 1 H, $J_{5,OH}$ 10 Hz, OH-5), 2.53 (ddd, 1 H, $J_{1,2a}$ 2.6, $J_{2a,2b}$ 14.9, $J_{2a,3}$ 7.3 Hz, H-2a), 2.41 (ddd, 1 H, $J_{1,2b}$ 6.1, $J_{2a,2b}$ 14.9, $J_{2b,3}$ 3.5 Hz, H-2b), 2.13 and 1.72 (2 m, 4 H, 2 CH_2) and 1.21 (s, 9 H, CMe_3); ^{13}C NMR ($CDCl_3$): δ 178.29 and 166.17 (2 C=O), 137.66 ($CH=CH_2$), 133.31, 129.63 and 128.45 (6 C arom.), 115.24 ($CH_2=$), 105.05 (C-1), 85.79, 76.68 and 69.47 (C-3,4,5), 68.41 and 64.99 (C-6, CH_2O), 39.82 (C-2), 38.77 (CMe_3), 30.12 and 28.56 (2 CH_2) and 27.17 (CMe_3). Anal. Calcd for $C_{23}H_{32}O_7$: C, 65.70; H, 7.67. Found: C, 65.59; H, 7.74.

Then was eluted syrupy **20** (191 mg, 42%); $[\alpha]_D$ -99 (*c* 0.78, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.05 (m, 2 H, C_6H_3*H-oH-o'*), 7.57 (m, 1 H, C_6H_4*H-p*), 7.44 (m, 2 H, C_6H_3*H-mH-m'*), 5.81 (m, 1 H, $CH=CH_2$), 5.45 (ddd, 1 H, $J_{2a,3}$ 8.1, $J_{2b,3}$ 2, $J_{3,4}$ 3.6 Hz, H-3), 5.28 (dd, 1 H, $J_{1,2a}$ 5.2, $J_{1,2b}$ 0.8 Hz, H-1), 5.01-4.92 (m, 2 H, $CH_2=$), 4.29 (dd, 1 H, $J_{5,6a}$ 8.5, $J_{6a,6b}$ 12.9 Hz, H-6a), 4.20 (dd, 1 H, $J_{3,4}$ 3.6, $J_{4,5}$ 2.4 Hz, H-4), 4.18-

4.13 (m, 2 H, H-5,6b), 3.72 and 3.45 (2 dt, 2 H, *J* 6.2, 6.6 and 9.5 Hz, CH_2O), 2.43 (ddd, 1 H, $J_{1,2a}$ 5.2, $J_{2a,2b}$ 14.4, $J_{2a,3}$ 8.1 Hz, H-2a), 2.39 (bs, 1 H, OH-5), 2.18 (ddd, 1 H, $J_{1,2b}$ 0.8, $J_{2a,2b}$ 14.4, $J_{2b,3}$ 2 Hz, H-2b), 2.14 and 1.69 (2 m, 4 H, 2 CH_2) and 1.21 (s, 9 H, CMe_3); ^{13}C NMR ($CDCl_3$): δ 178.60 and 166.59 (2 C=O), 138.20 ($CH=CH_2$), 133.23 (2 C arom.), 129.83 (C quat. arom.), 129.72 and 128.41 (3 C arom.), 114.78 ($CH_2=$), 104.07 (C-1), 83.17, 75.40 and 69.69 (C-3,4,5), 66.83 and 65.72 (C-6, CH_2O), 39.14 (C-2), 38.82 (CMe_3), 30.39 and 28.94 (2 CH_2) and 27.17 (CMe_3). Anal. Calcd for $C_{23}H_{32}O_7$: C, 65.70; H, 7.67. Found: C, 65.55; H, 7.78

4,7-Anhydro-6,9-di-O-benzyl-1,2,3,5-tetradeoxy-D-galacto (**21**) *and* -D-talo (**22**) *non-1-enitols.*

Trimethylsilyl trifluoromethanesulfonate (88 µL, 0.46 mmol) was added to a solution of **8** (150 mg, 0.46 mmol) and allyltrimethylsilane (0.36 mL, 2.3 mmol) in dry acetonitrile (10 mL) at -40°C under nitrogen. The mixture was slowly warmed to -10°C, then poured into saturated aqueous $NaHCO_3$. The solution was extracted with dichloromethane and the extract was dried ($MgSO_4$), then concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 4:1) to give first **21** (131 mg, 77%) as a syrup; $[\alpha]_D$ -40 (*c* 0.8, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.36-7.26 (m, 10 H, 2 Ph), 5.79 (m, 1 H, H-2), 5.12-5.04 (m, 2 H, H-1a,1b), 4.58 and 4.53 (2 d, 2 H, *J* 12 Hz, CH_2Ph), 4.53 and 4.45 (2 d, 2 H, *J* 11.7 Hz, CH_2Ph), 4.19 (ddd, 1 H, $J_{5a,6}$ 7, $J_{5b,6}$ 5.6, $J_{6,7}$ 4.8 Hz, H-6), 4.14 (dddd, 1 H, $J_{3a,4}$ ~ $J_{3b,4}$ ~ 6.6, $J_{4,5a}$ 6.5, $J_{4,5b}$ 7.1 Hz, H-4), 3.95 (dd, 1 H, $J_{6,7}$ 4.8, $J_{7,8}$ 4 Hz, H-7), 3.82 (m, 1 H, H-8), 3.55 (m, 2 H, H-9a,9b), 2.47 (m, 1 H, H-3a), 2.42 (d, 1 H, $J_{8,OH}$ 5 Hz, OH-8), 2.32 (m, 1 H, H-3b), 2.27 (ddd, 1 H, $J_{4,5a}$ 6.5, $J_{5a,5b}$ 12.7, $J_{5a,6}$ 7 Hz, H-5a) and 1.77 (ddd, 1 H, $J_{4,5b}$ 7.1, $J_{5a,5b}$ 12.7, $J_{5b,6}$ 5.6 Hz, H-5b); ^{13}C NMR ($CDCl_3$): δ 138.00 and 137.96 (2 C quat. arom.), 134.54 (C-2), 128.40, 128.39, 127.75, 127.70 and 127.61 (10 C arom.), 117.14 (C-1), 82.95 (C-7), 80.41 (C-6), 78.63 (C-4), 73.43 and 71.72 (2 CH_2Ph), 71.96 (C-9), 70.86 (C-8), 40.29 (C-3) and 37.24 (C-5). Anal. Calcd for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 75.18; H, 7.81.

Then was eluted syrupy **22** (20 mg, 12%); $[\alpha]_D$ +31 (*c* 0.73, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.38-7.26 (m, 10 H, 2 Ph), 5.76 (m, 1 H, H-2), 5.08-5.01 (m, 2 H, H-1a,1b), 4.58 (m, 4 H, 2 CH_2Ph), 4.07 (ddd, 1 H, $J_{5a,6}$ 10.5, $J_{5b,6}$ 4.1, $J_{6,7}$ 9 Hz, H-6), 4.00 (m, 1 H, H-7), 3.84-3.68 (m, 4 H, H-4,8,9a,9b), 2.46 (d, 1 H, $J_{8,OH}$ 4.2 Hz, OH-8), 2.44 (m, 1 H, H-3a), 2.20 (m, 1 H, H-3b), 2.07 (ddd, 1 H, $J_{4,5a}$ 5.5, $J_{5a,5b}$ 13.3, $J_{5a,6}$ 10.5 Hz, H-5a) and 1.67 (ddd, 1 H, $J_{4,5b}$ 3.6, $J_{5a,5b}$ 13.3, $J_{5b,6}$ 4.1 Hz, H-5b).

4,7-Anhydro-6-O-benzyl-1,2,3,5-tetradeoxy-D-galacto-*non-1-enitol* (**23**).

Trimethylsilyl trifluoromethanesulfonate (128 µL, 0.71 mmol) was added to a solution of **11** (250 mg, 0.71 mmol) and allyltrimethylsilane (467 µL, 2.94 mmol) in dry propionitrile (5 mL) at -93°C under nitrogen. The mixture was slowly warmed to -10°C, then poured into saturated aqueous $NaHCO_3$. The solution was extracted with dichloromethane and the extract was dried ($MgSO_4$), then concentrated. The residue was purified by flash chromatography (dichloromethane–ethyl acetate, 1:1) to give **23** (120 mg, 61%); $[\alpha]_D$ -14 (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.37-7.27 (m, 5 H, Ph), 5.82-5.73 (m, 1 H, H-2), 5.13-5.05 (m, 2 H, H-1a,1b), 4.52 (m, 2 H, CH_2Ph), 4.16 (ddd, 1 H, $J_{5a,6}$ 7.9, $J_{5b,6}$ 6.1, $J_{6,7}$ 5.2 Hz, H-6), 4.14 (dddd, 1 H, $J_{3a,4}$ 6.7, $J_{3b,4}$ 6.9, $J_{4,5a}$ 5.7, $J_{4,5b}$ 7.4 Hz, H-4), 3.97 (dd, 1 H, $J_{6,7}$ 5.2, $J_{7,8}$ 3.9 Hz, H-7), 3.70 (m, 2 H, H-9a,9b), 3.66 (m, 1 H, H-8), 2.78 (d, 1 H, $J_{8,OH}$ 6.7 Hz, OH-8), 2.68 (dd, 1 H, $J_{9a,OH}$ 5.2, $J_{9b,OH}$ 7.1 Hz, OH-9), 2.45 (m, 1 H, H-3a), 2.34 (m, 1 H, H-3b), 2.28 (ddd, 1 H, $J_{4,5a}$ 5.7, $J_{5a,5b}$ 12.6, $J_{5a,6}$ 7.9 Hz, H-5a) and 1.76 (ddd, 1 H, $J_{4,5b}$ 7.4, $J_{5a,5b}$ 12.6, $J_{5b,6}$ 6.1 Hz, H-5b). Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.16; H, 8.12.

*1,6-Anhydro-3-O-benzyl-2-deoxy-*α-D-lyxo-*hexofuranose* (**24**).

Trimethylsilyl trifluoromethanesulfonate (49 µL, 0.29 mmol) was added to a solution of **11** (100 mg, 0.29 mmol) and cyanotrimethylsilane (114 µL, 0.86 mmol) in dry propionitrile (1 mL) at -93°C under nitrogen. The mixture was treated as described for the preparation of **23**. Flash chromatography (petroleum ether–ethyl acetate, 1:1) gave **24** (14 mg, 21%). ^{1}H NMR (CDCl$_3$): δ 7.29-7.27 (m, 5 H, Ph), 5.48 (d, 1 H, $J_{1,2exo}$ 5.2 Hz, H-1), 4.46 (bs, 2 H, C*H*$_2$Ph), 4.32 (bd, 1 H, H-4), 4.27 (dd, 1 H, $J_{2endo,3}$ 7.2, $J_{2exo,3}$ 2.8 Hz, H-3), 3.93 (ddd, 1 H, $J_{4,5}$ 4.6, $J_{5,6endo}$ 10.2, $J_{5,6exo}$ 6.1 Hz, H-5), 3.83 (ddd, 1 H, $J_{4,6exo}$ 1.5, $J_{5,6exo}$ 6.1, $J_{6endo,6exo}$ 11.2 Hz, H-6exo), 3.13 (dd, 1 H, $J_{5,6endo}$ 10.2, $J_{6endo,6exo}$ 11.2 Hz, H-6endo), 2.28 (dd, 1 H, $J_{2endo,2exo}$ 14.2, $J_{2endo,3}$ 7.2 Hz, H-2endo) and 2.05 (dddd, 1 H, $J_{1,2exo}$ 5.2, $J_{2endo,2exo}$ 14.2, $J_{2exo,3}$ 2.8, $J_{2exo,4}$ 0.8 Hz, H-2exo); ^{13}C NMR (CDCl$_3$): δ 138.13 (C quat. arom.), 128.99, 128.86, 128.21 and 128.20 (C arom.), 99.76 (C-1), 82.59 (C-4), 75.91 (C-3), 71.64 (*C*H$_2$Ph), 64.20 (C-6), 63.01 (C-5) and 38.75 (C-2); MS (CI; NH$_4^+$): m/z 254 (M+18).

*2,5-Anhydro-4,7-di-O-benzyl-1,3-dideoxy-1-C-phenyl-*D-lyxo-*hept-1-enitol* (E **26** and Z **27**).

A mixture of triphenylphosphonium tetrafluoroborate (385 mg, 1.1 mmol) and **8** (326 mg, 1 mmol) in dry acetonitrile (20 mL) was stirred under nitrogen for 2 h at 0°C, then overnight at room temperature. The solution was concentrated and the residue was thoroughly dried under good vacuum to give the crude phosphonium salt **25**. ^{1}H NMR (CD$_3$OD): δ 6.08 (m, 1 H, Σ*J* ~ 27 Hz, H-1), 3.12 and 2.35 (2 m, 2 H, H-2a,2b).

n-Butyllithium (1.6 M in hexane, 1.48 mL, 2.4 mmol) was added to a solution of **25** (711 mg) in dry tetrahydrofuran (10 mL) at -78°C under nitrogen. The red solution was stirred for 30 min at -78°C. A solution of benzaldehyde (0.12 mL, 1.18 mmol) in dry tetrahydrofuran (5 mL) was then added and the resulting yellow mixture was slowly warmed to room temperature within 270 min. 25% Aqueous ammonium acetate (10 mL) was added and the mixture was extracted with ether. The extract was dried (MgSO$_4$) and concentrated. The residue was purified by flash chromatography (petroleum ether–ethyl acetate, 4:1 with 1% triethylamine) to give a 42:58 mixture of **26** and **27** (275 mg, 66%). Further chromatography gave first syrupy **26**; *R*$_f$ 0.35 (petroleum ether–ethyl acetate, 7:3). ^{1}H NMR (C$_6$D$_6$): δ 7.69 (d, 2 H, *J* 7 Hz, C$_6$H$_3$*H-oH-o'*C=H), 7.28-7.09 (m, 13 H, Ph), 5.13 (s, 1 H, H-5), 4.74 (bs, 1 H, H-1), 4.28 and 4.11 (2 m, 4 H, 2 C*H*$_2$Ph), 3.57 (dd, 1 H, $J_{6,7a}$ 5.2, $J_{6,7b}$ 7.9 Hz, H-6), 3.51 (dd, 1 H, $J_{3a,4}$ 2.1, $J_{3b,4}$ 6.7 Hz, H-4), 3.34 (dd, 1 H, $J_{6,7a}$ 5.2, $J_{7a,7b}$ 9.2 Hz, H-7a), 3.30 (dd, 1 H, $J_{6,7b}$ 7.9, $J_{7a,7b}$ 9.2 Hz, H-7b), 2.06 (ddd, 1 H, $J_{1,3a}$ 1.5, $J_{3a,3b}$ 12.8, $J_{3a,4}$ 2.1 Hz, H-3a) and 1.82 (dd, 1 H, $J_{3a,3b}$ 12.8, $J_{3b,4}$ 6.7 Hz, H-3b).

The last fractions gave syrupy **27**; *R*$_f$ 0.29 (petroleum ether–ethyl acetate, 7:3). ^{1}H NMR (C$_6$D$_6$): δ 7.56 (d, 2 H, *J* 7 Hz, C$_6$H$_3$*H-oH-o'*C=H), 7.28-7.09 (m, 13 H, Ph), 5.11 (s, 1 H, H-5), 4.71 (s, 1 H, H-1), 4.27 and 4.08 (2 m, 4 H, 2 C*H*$_2$Ph), 3.51 (dd, 1 H, $J_{6,7a}$ 5.1, $J_{6,7b}$ 7.9 Hz, H-6), 3.49 (dd, 1 H, $J_{3a,4}$ 3, $J_{3b,4}$ 5.9 Hz, H-4), 3.32 (dd, 1 H, $J_{6,7a}$ 5.1, $J_{7a,7b}$ 9.3 Hz, H-7a), 3.27 (dd, 1 H, $J_{6,7b}$ 7.9, $J_{7a,7b}$ 9.3 Hz, H-7b) and 1.80 (m, 2 H, H-3a,3b).

*4,7-Anhydro-6,9-di-O-benzyl-1,2,3,5-tetradeoxy-2-C-methyl-*D-lyxo-*non-3-enitol* (E **28** and Z **29**).

A solution of crude **25** (711 mg) in dry tetrahydrofuran (10 mL) was treated with n-butyllithium (1.6 M in hexane, 1.48 mL, 2.4 mmol), then isobutyraldehyde (0.46 mL, 5 mmol) in dry tetrahydrofuran (10 mL) as described for the preparation of **26** and **27**. Flash chromatography (petroleum ether–ethyl acetate, 4:1) gave a 43:57 mixture of **28** and **29** (118 mg, 31%). Further chromatography gave first syrupy **29**; *R*$_f$ 0.46 (petroleum ether–ethyl acetate, 7:3). ^{1}H NMR (C_6D_6): δ 7.25-7.06 (m, 10 H, 2 Ph), 4.68 (s, 1 H, H-7), 4.24 and 4.15 (2 m, 4 H, 2 CH_2Ph), 3.77 (d, 1 H, $J_{2,3}$ 5.1 Hz, H-3), 3.57-3.52 (m, 2 H, H-6,8), 3.31 (dd, 1 H, $J_{8,9a}$ 5.1, $J_{9a,9b}$ 9.2 Hz, H-9a), 3.27 (dd, 1 H, $J_{8,9b}$ 8.6, $J_{9a,9b}$ 9.2 Hz, H-9b), 2.06-1.97 (m, 2 H, H-2,5a), 1.95 (dd, 1 H, $J_{5a,5b}$ 13.2, $J_{5b,6}$ 6.6 Hz, H-5b) and 1.16 and 1.10 (2 d, 6 H, J 6.6 Hz, 2 Me).

The last fractions gave syrupy **28**; R_f 0.40 (petroleum ether–ethyl acetate, 7:3). ^{1}H NMR (C_6D_6): δ 7.26-7.06 (m, 10 H, 2 Ph), 4.67 (s, 1 H, H-7), 4.26 and 4.20 (2 d, 2 H, J 11.7 Hz, CH_2Ph), 4.17 and 4.12 (2 d, 2 H, J 11.7 Hz, CH_2Ph), 3.83 (dd, 1 H, $J_{2,3}$ 4.6, $J_{3,5b}$ 1.5 Hz, H-3), 3.53 (dd, 1 H, $J_{5a,6}$ 6.6, $J_{5b,6}$ 2 Hz, H-6), 3.50 (dd, 1 H, $J_{8,9a}$ 5.1, $J_{8,9b}$ 8.1 Hz, H-8), 3.28 (dd, 1 H, $J_{8,9a}$ 5.1, $J_{9a,9b}$ 9.2 Hz, H-9a), 3.24 (dd, 1 H, $J_{8,9b}$ 8.1, $J_{9a,9b}$ 9.2 Hz, H-9b), 1.96 (dd, 1 H, $J_{5a,5b}$ 12.7, $J_{5a,6}$ 6.6 Hz, H-5a), 1.88 (dsept, 1 H, $J_{2,3}$ 4.6, J 6.6 Hz, H-2), 1.79 (ddd, 1 H, $J_{3,5b}$ 1.5, $J_{5a,5b}$ 12.7, $J_{5b,6}$ 2 Hz, H-5b) and 1.11 and 1.07 (2 d, 6 H, J 6.6 Hz, 2 Me).

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