Functionalised Monocyclic Five- to Seven-Membered *exo*-Glycals by Alkynol Cycloisomerisation of Hydroxy Buta-1,3-diynes and 1-Haloalkynols

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Dedicated to *András Lipták* on the occasion of his 70th birthday

Base-promoted (KOH or MeONa in MeOH, or NaH in THF) cycloisomerisation of partially benzylated, 1-substituted (R = Ph–C≡C, pyridin-2-yl, or Br) ald-1-ynitols leads to (*Z*)-configured five-, six-, and seven-membered *exo*-glycals. The reactivity of the ald-1-ynitols depends upon their configuration. The ald-1-ynitols were derived from 2,3,5-tri-*O*-benzyl-D-ribofuranose **1**, and the corresponding, partially *O*-benzylated galactose, glucose, and mannose hemiacetals by ethynylation. The hex-1-ynitol **2** derived from **1** (61%) was transformed *via* the 1-phenylbuta-1,3-diyne **3** and the 1-(pyridin-2-yl)acetylene **5** into the five-membered *exo*-glycals **4** and **6** (in 66 and 72% yields, resp., from **2**). The analoguous ethynylation of 2,3,4,6-tetra-*O*-benzyl-D-galactose **8** was accompanied by elimination of one benzyloxy (BnO) group to the hept-3-en-1-ynitol **9** (71%), which was transformed into the non-5-ene-1,3-diynitol **10** and further into the six-membered *exo*-glycal **11** (50% from **9**). Addition of $Me_3SiC{\equiv}CH$ to the galactose **8** and to the *gluco*- and *manno*-analogues **16** and **24** gave epimeric mixtures of the silylated oct-1-ynitols (86% of **12L**/**12D** 45 : 55, 94% of **17L**/**17D** 7 : 3, and 86% of **25L**/**25D** 55 : 45), which were separated by flash chromatography, and individually transformed into the corresponding 1-bromooct-1-ynitols. Upon treatment with NaH in THF, only the minor epimers **13L**, **18D**, and **26D** cyclised readily to form the seven-membered hydroxy *exo*-glycals. They were acetylated to the more stable monoacetates **14L**, **23D**, and **28D** (82–89% overall yield). Under the same conditions, the epimers **13D**, **18L**, and **26L** decomposed within 12 h mostly to polar products. The difference of reactivity was rationalised by analysing the consequences of an intramolecular C(3)O–H···$^-$OC(7) H-bond of the intermediate alkoxides on the orientation of $^-$O–C(7) of **13L**, **18D**, and **26D** and its proximity to the ethynyl group.

Introduction. – We have recently reported our investigations on the base-promoted alkynol cycloisomerisation of buta-1,3-diynlated and haloethynylated glycopyranosyl and -furanosyl alcohols to bicyclic *exo*-glycals [1]. In this paper, we describe the results of the alkynol cycloisomerisation of buta-1,3-diynlated, bromo-, and (pyridin-2-yl)ethynylated alditols to monocyclic *exo*-glycals of different ring size.

In the course of the structure elucidation of naturally occurring oligoacetylenes, *Jones et al.* [2] and *Bohlmann et al.* [3] discovered the base-catalysed 5-*exo-dig* cyclisation of hydroxylated oligoacetylenes to 2-methylidene-oxolanes. This alkynol cycloisomerisation is favoured when the alkynyl group is activated, as in cumulated triple bonds, or by substitution with a 1-bromo, 1-chloro, 1-phenylchalcogeno (S or Se), or 1-(het)aryl group, and also by the proximity of the reacting groups, as in cyclic starting materials [1][4–6]. Activation of an isolated alkynyl group by coordination with a *Lewis* acid also promotes the cycloisomerisation [7]. In most cases, cyclosiomerisation resulted in (*Z*)-configured 2-methylidene-oxolanes, but (*Z*)/(*E*)-mixtures were also obtained.

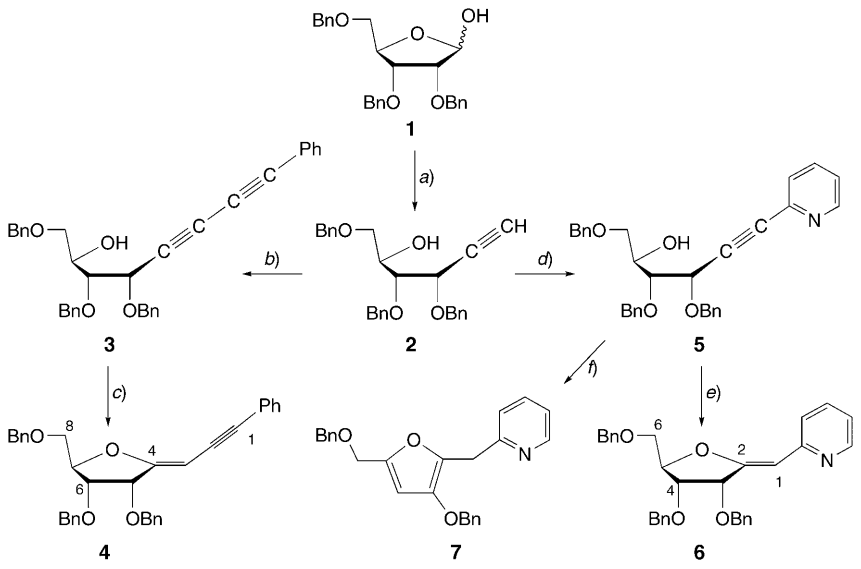
With the exception of the 6-alkylidene-1,5-dioxabicyclo[2.2.2]octanes that we described [1], only five-membered *exo*-glycals were prepared by base-catalysed alkynol cycloisomerisation. We were interested in the limitation of the ring size of *exo*-glycals

resulting from the cyclosiomerisation of acyclic partially protected ald-1-ynitols, and the effect of the relative configuration of the hydroxyalkynes on the reactivity, and now report the results of the base-promoted cyclisation of ald-1-ynitols to five- to seven-membered *exo*-glycals. The ald-1-ynitols should be easily available from partially protected aldoses (ribose, galactose, glucose, and mannose) by transforming the aldehyde group to an ethynyl moiety, or by addition of acetylides.

Results and Discussion. – 1. *Synthesis of Five-Membered* exo-*Glycals.* Although the *Corey–Fuchs* reaction [8], as a rule, allows for a ready transformation of aldehydes into alkynes *via* intermediate dibromoethenes (see [9] and refs. cit. therein), its application to the ribofuranose **1** gave **2** in a very poor yield (*Scheme 1*).

The desired alkynol **2** was, however, obtained in 61% yield by treating **1** with dimethyl 1-diazo-2-oxopropyl phosphonate (*Ohira*'s reagent [10]) with K_2CO_3 in MeOH [11][12] (compare [13][14]). It was transformed, by *Sonogashira* coupling with (bromoethynyl)benzene and 2-bromopyridine under the conditions described by *Siebeneicher* and *Doye* [15], into the diynol **3** and the (pyridin-2-yl)alkynol **5** in 83% and 78% yield, respectively. Cycloisomerisation of **3** with KOH in MeOH at 25° yielded 80% of the *exo*-glycal **4**. Similarly, treating **5** with MeONa in boiling MeOH provided the (pyridin-2-yl)-enol ether **6** (92%), while NaH in THF transformed **5** into the trisubstituted furan **7** (89%). It is most probably formed *via* **6** by β-elimination and isomerisation, possibly by 1,5-sigmatropic rearrangement. Under similar conditions, **3** gave exclusively the enol ether **4**.

Scheme 1



a) Dimethyl 1-diazo-2-oxopropyl phosphonate, K_2CO_3, THF/MeOH; 61%. *b*) (Bromoethynyl)benzene, $[Pd(PPh_3)_2Cl_2]$, CuI, PPh_3, Et_3N; 83%. *c*) KOH, MeOH; 80%. *d*) 2-Bromopyridine, $[Pd(PPh_3)_2Cl_2]$, CuI, PPh_3, Et_3N; 78%. *e*) MeONa, MeOH; 92%. *f*) NaH, THF; 89%.

The furanose ring of **4** and **6** is evidenced by the vicinal coupling constants (**4**: $J(5,6)=4.8$, $J(6,7)=6.0$, **6**: $J(3,4)=4.8$, $J(4,5)=7.2$ Hz). They agree well with the calculated values (MM3* force field [16]) of 5.0 and 7.9, as compared to 3.2 and 9.3 Hz for the corresponding allals. H–C(3) of **4** resonates at 4.92 ppm and shows a small allylic coupling of 0.6 Hz with H–C(5). The *s* for H–C(1) of **6** is shifted downfield to 5.78 ppm. The enol-ether moiety of **4** and **6** gives rise to a *s* at 163.0 and 156.7, and to a *d* at 83.9 and 104.1 ppm. The same configuration of the C=C bond of **4** and **6** is revealed by similar chemical shifts for H–C(5), H–C(6), C(5), and C(6) of **4** and the corresponding ^{1}H- ($\Delta\delta \leq 0.06$ ppm) and ^{13}C-NMR ($\Delta\delta \leq 0.6$ ppm) signals of **6**. The (*Z*)-configuration of **4** is suggested by similar δ values for the enol ether ^{13}C *s* of **4** and of a closely related bicyclic (*Z*)-configured analogue [1] (163.0 *vs.* 164.2 ppm) differing clearly from that of the corresponding (*E*)-isomer (168.8 ppm)[1]).

2. *Synthesis of a Six-Membered* exo-*Glycal.* Ethynylation of the galactopyranose **8** (*Scheme 2*) under the same conditions as used for preparation of the *ribo*-analogue **2** was accompanied by β-elimination of BnOH, and led to the (*Z*)-yn-enol ether **9** (71%). *Sonogashira* coupling of **9** with (bromoethynyl)benzene gave the diynenol ether **10** (71%), which cyclised upon treatment with MeONa in refluxing MeOH to the crystalline (*Z*)-yne-dienol diether **11** (83%).

The crystal structure of **11** was established by X-ray analysis (*Fig. 1*)[2]). Two molecules differing mainly in the orientation of the primary BnO group were found in the unit cell, conceivably as the result of the opposite effect of crystal-packing forces and the interaction of two Ph groups. The crystal structure confirms the (*Z*)-configuration of the exocyclic C=C bond, and reveals the E_8 conformation of the pyranose ring, an axial BnO–C(7), and an equatorial $BnOCH_2$ group in the *gt*-conformation.

The IR spectrum of the yne-dienol ether **11** shows bands at 2193 and 1643 cm^{-1}. The dienol-ether moiety gives rise to two *s*s at 152.4 and 148.4, and two *d*s at 86.7 for C(3) and 97.4 ppm for C(6). The *s* for H–C(3) appears at 5.64 ppm, and the *d* for H–C(6) upfield at 5.16 ppm ($J(6,7)=4.2$ Hz).

3. *Synthesis of Seven-Membered* exo-*Glycals.* Only a few oxygenated seven-membered *exo*-glycals are known. They were prepared either by methylenation of ε-lactones or by elimination reactions [20][21], and used as intermediates in the synthesis of marine polycyclic ethers [21]. Base-promoted alkynol cyclisation would provide a short access to seven-membered *exo*-glycals[3]), and the precursors should be readily prepared by addition of acetylides to 2,3,4,6-*O*-protected hexopyranoses. To learn about the dependence of the alkynylation and cycloisomerisation on the configuration of the starting materials, we planned to study the transformations of *galacto*-, *gluco*-, and *manno*-isomers.

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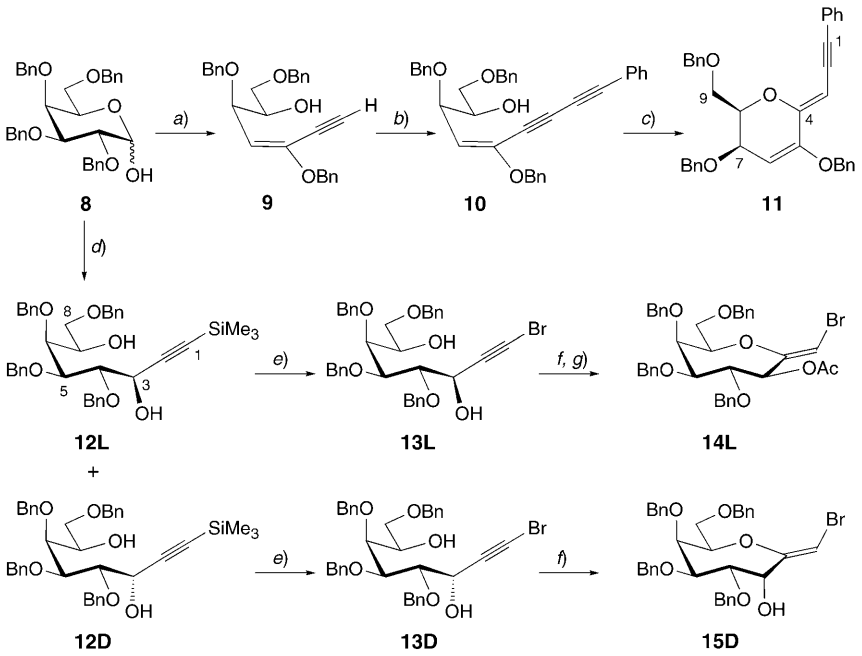
[1]) C(2) of (*Z*)- and (*E*)-2-methyleneoxolanes shows the same relative chemical shift as C(1) of (*Z*)- and (*E*)-lactone oximes and hydrazones [17–19].

[2]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-248023. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

[3]) Seven-membered *endo*-glycals were prepared by a transition-metal catalysed cyclisation of isopropylidenated hex-5-ynitols [22].

Scheme 2



a) Dimethyl 1-diazo-2-oxopropylphosphonate, K_2CO_3, MeOH; 71%. *b*) (Bromoethynyl)benzene, [Pd_2(dba)$_3$], CuI, P(fur)$_3$, Et_3N, DMF; 71%. *c*) MeONa, MeOH; 83%. *d*) Lithium (trimethylsilyl)acetylide, THF; 47% of **12D** and 39% of **12L**. *e*) NBS, $AgNO_3$, acetone; 71% of **13D**; 76% of **13L**. *f*) NaH, THF; *ca.* 10% of 2,3,4,6-tetra-*O*-benzyl-D-galactonolactone/**15D** 3:1. *g*) Ac_2O, pyridine; 82% of **14L**.

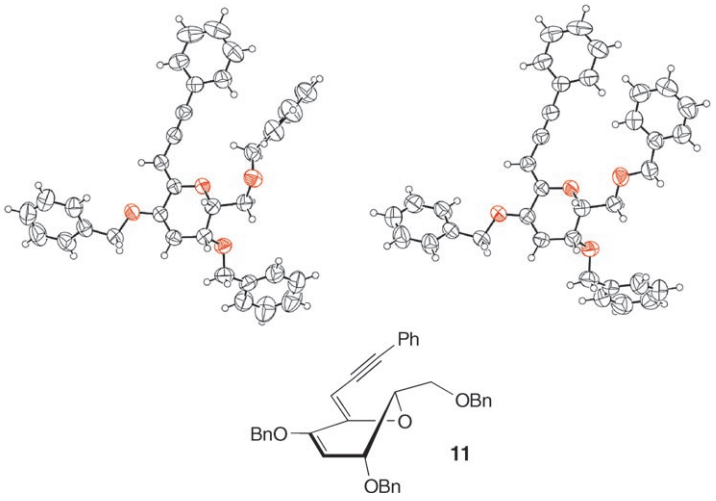


Fig. 1. *Crystal structure of the dienynol ether* **11**

Treatment of the galactopyranose **8** with lithium (trimethylsilyl)acetylide [23] gave 86% of a 55:45 mixture of the propargyl alcohols **12D** and **12L**[4]) that were separated by flash chromatography into the more polar **12D** and the less polar **12L** (*Scheme 2*). Individual bromination of **12D** and **12L** with *N*-bromosuccinimide (NBS) in the presence of catalytic amounts of $AgNO_3$ in acetone gave 71–76% of the propargyl bromides **13D** and **13L**. Treatment of **13L** with 2.3 equiv. of NaH in THF for 1.5 h at room temperature, followed by acetylation, afforded the (*Z*)-*exo*-glycal **14L** (82%). These cyclisation conditions hardly affected the epimer **13D**. Upon prolonging the reaction to 12 h, **13D** mostly decomposed to polar compounds (base line on TLC (AcOEt/hexane 1:2)). Small amounts of a 3:1 mixture of two apolar compounds were isolated by flash chromatography (R_f 0.65 and 0.63; *ca.* 10%), and identified by IR and NMR spectroscopy, and mass spectrometry, as 2,3,4,6-tetra-*O*-benzyl-D-galactonolactone [24] and the desired cyclisation product **15D**. The cyclisation product was identified on the basis of the characteristic peaks for $[M+Na]^+$ and $[M+K]^+$ in the mass spectrum, and by the *s* for H–C(1) at 5.30 and the *d* for H–C(3) at 4.09 ppm (*Table 1* in the *Exper. Part*). Less than 3% of **13D** underwent cyclisation to the *exo*-glycal.

Similarly as the galactopyranose **8**, the benzylated glucopyranose **16** was treated with lithium (trimethylsilyl)acetylide. Flash chromatography of the crude gave 94% of a 7:3 mixture of the more polar diol **17L** and its less polar isomer **17D**[5]) (*Scheme 3*). Addition of HC≡CMgBr to **16** led to the same product ratio. Pure fractions of **17L** and **17D** were obtained by a second flash chromatography. Bromination of the minor **17D** yielded 70% of the bromo-alkynediol **18D** which readily cyclised to the *exo*-glycal **22D** (89%). Although **22D** was stable under the conditions of its formation, it slowly decomposed when kept in substance at room temperature. Its acetate **23D** proved stable. Bromination of the major diol **17L** gave 62% of the desired bromo-alkynediol **18L** and 15% of the 2-(dibromomethylene)oxolane **19**[6]). The alcohol **19** decomposed slowly at room temperature, and was acetylated to the thermally stable acetate **20**. The base-catalysed cyclisation of the major diol **18L** was sluggish, and its reaction with 2.3 equiv. of NaH in THF led to a complete conversion to a mixture consisting mainly of polar (R_f (AcOEt/hexane 1:1) 0.00) and some less polar products (R_f 0.62 and 0.59). The major apolar component was isolated by flash chromatography (R_f 0.62) in a yield of 14% and assigned the structure of the 1-*C*-acetylglucopyranose **21**. The minor apolar component, presumably **22L**, was not isolated. Treatment of **18L**/**18D** with ^{t}BuOK in ^{t}BuOH for 12 h at 23° followed by acetylation led to a 1:9 mixture of **23L** and **23D**. Isolation of this mixture in addition to pure **23D** allowed to assign the NMR data of **23L**.

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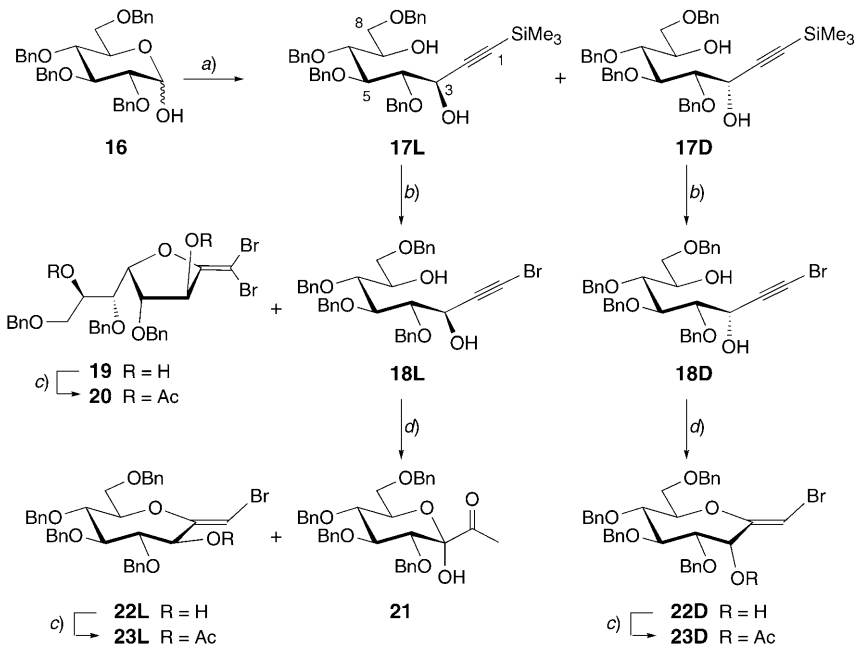
[4]) The systematic numbering of heptynitols and heptenitols (see *Exper. Part*) depends on the alphabetic order of the configurational prefixes (Recommendations of Nomenclature of Carbohydrates, 1996). For convenience, in the *Theoretical Part* and in the *Tables*, the numbering of the heptynitols and heptenitols starts always at the unsaturated end. The orientation of HO–C(3) is indicated by **L** and **D**.

[5]) A *ca.* 5:95 mixture of **17L** and **17D** was obtained by the addition of lithium (trimethylsilyl)acetylide to 2,3,4,6-tetra-*O*-benzyl-D-gluconolactone, followed by $NaBH_3CN$ reduction [25].

[6]) Such debenzylating nucleophilic ring closures are well known; see *e.g.* [26–31]. Similarly, monomesylation of both **17L** and **17D** led in high yields (*ca.* 82%) to the 3,6-anhydro-oct-1-ynitols and not to the desired 3,7-anhydrooct-1-ynitols [25].

Scheme 3

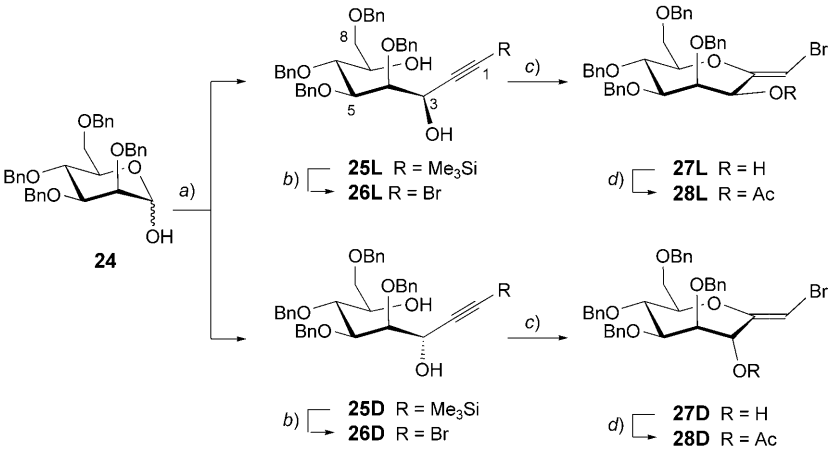


a) Lithium (trimethylsilyl)acetylide, THF; 66% of **17L** and 28% of **17D**. *b*) NBS, $AgNO_3$, acetone; 62% of **18L** and 15% of **19**; 70% of **18D**. *c*) Ac_2O, pyridine; 98% of **20**; 89% of **23D** from **18D**. *d*) NaH, THF; 14% of **21**.

The mass spectra of the dibromides **19** and **20** show characteristic $[M+Na]^+$ peaks at *m*/*z* 659/657/655 and 743/741/739. The tetrasubstituted ethylene moiety of **19** and **20** is evidenced by IR bands at 1635 and 1643 cm^{-1}, a C(1) *s* at 66.06 and 68.41 ppm, and a C(2) *s* at 157.49 and 153.88 ppm, respectively (*Table 2* in the *Exper. Part*). HO–C(3) and HO–C(7) of **19** are evidenced by the strong downfield shift of H–C(3) and H–C(7) upon acetylation to the diacetate **20**. A small $J(3,4)$ (**19**: 2.4, **20**: 1.1 Hz) and a larger $J(4,5)$ (**19**: 5.1, **20**: 3.9 Hz) agree well with the *trans-cis*-orientation of H–C(3), H–C(4), and H–C(5), and evidence that the configuration of the stereogenic C-atoms of **17L** is not affected by cyclisation to **19**. The Ac group of **21** gives rise to a ^1H *s* at 1.91 ppm, and to a ^{13}C *s* at 203.7 and *q* at 22.31 ppm. The δ and *J* values for H–C(4) to H–C(8) of **21** (see *Exper. Part*) agree well with those of a tetrabenzylated α-D-glucopyranosyl unit. The downfield shift of HO–C(3) at 4.56 ppm is characteristic for anomeric OH groups, and C(3) resonates at 96.8 ppm, typical for a hemiacetal C-atom.

Addition of HC≡CMgBr to the benzylated mannopyranose **24** (*Scheme 4*) gave a 55:45 mixture of the diols **25L** and **25D** (91%). They were separated by flash chromatography and individually brominated to the bromo-alkynediols **26L** (76%) and **26D** (72%). Upon treatment with NaH in THF, the bromo compound **26D** cyclised readily to the *exo*-glycal **27D** (85% yield). Acetylation led to the thermally stable acetate **28D** (85% from **26D**). The isomeric bromo compound **26L** mostly decomposed to polar

Scheme 4



a) Lithium (trimethylsilyl)acetylide, THF; 50% of **25L** and 41% of **25D**. *b*) NBS, $AgNO_3$, acetone; 76% of **26L**; 72% of **26D**. *c*) NaH, THF. *d*) Ac_2O, pyridine; 33% of **28L**/**28D** 1:4 from **26L**/**26D** 55:45; 85% of **28D** from **26D**.

products upon similar treatment with NaH. A 4:1 mixture **28D**/**28L** (33%) was obtained from NaH-promoted ring closure of a 3.2-g batch of **26D**/**26L** 45:55, followed by acetylation.

The bromomethylidene group of **14L**, **22D**, **23D**, **23L**, **27D**, **28D**, and **28L** was evidenced by the downfield shift of the C(2) *s* at 150.0–156.1 ppm and the upfield shift of the C(1) *d* at 88.9–95.9 ppm (*Tables 1–3* in the *Exper. Part*). These values exclude the formation of an eight-membered *endo*-glycal, as the *s* of the brominated C(1) of such an *endo*-glycal is expected at *ca*. 130 ppm and the *d* of C(2) at *ca*. 100 ppm (compare [32][33]). H–C(1) of **15D**, **22D**, **23D**, **27D**, and **28D** resonates as a *s* at 5.30–5.61 ppm and is only weakly influenced by the axial HO–C(3) or AcO–C(3). H–C(1) of **28L** resonates at 5.58 ppm, whereas the H–C(1) signals of **14L** and **23L** are shifted downfield to 5.97–6.01 ppm, evidencing the dependence of the orientation of the equatorial AcO–C(3) upon the configuration at C(4). This shift difference suggests the (*Z*)-configuration of the seven-membered *exo*-glycals. This configuration is confirmed by NOEs of 9.6–13% between H–C(1) and H–C(3) of **23D** and **28D** (see *Exper. Part*). Only H–C(1) of **23L** shows a weak allylic coupling of 0.5 Hz with H–C(3).

Large $J(3,4)$ values of 8.2–8.6 Hz of the *galacto*-configured **14L** and the minor *gluco*-configured isomer **23L** reveal an equatorial AcO–C(3); the major *gluco*-isomers **22D** and **23D**, and the *galacto*-isomers **15D** show the expected small $J(3,4)$ values (1.7–2.3 Hz) (*Tables 1* and *2* in the *Exper. Part*). MM3* Modeling predicts $J(3,4) = 6.2$ Hz between the *trans*-oriented H–C(3) and H–C(4) of the *manno*-configured **28D**, and 1.3 Hz between the *cis*-oriented H–C(3) and H–C(4) of **28L**. In keeping with the modeling, the isomers **27D** and **28D** ($J(3,4) = 6.4–6.9$ Hz) possess an axial HO–C(3) or AcO–C(3), and the isomer **28L** ($J(3,4) = 1.5$ Hz) an equatorial AcO–C(3) substituent.

The structure determination of the seven-membered *exo*-glycals allows to unambiguously assign the configuration at C(3) of the hept-1-ynitol precursors, confirming the

tentative assignment of a closely related pair of *gluco*-hept-1-ynitols [23]. According to the vicinal coupling constants in *Table 3* (*Exper. Part*), the *manno*-hept-1-ynitols **25D** and **26D** adopt a straight *zig-zag* conformation. $J(7,OH) = 5.9-6.6$ Hz agrees well with an intramolecular C(7)OH ··· OC(8) H-bond, whereas the large $J(3,OH) = 10.0$ Hz suggests a bifurcated H-bond of HO–C(3) to BnO–C(2) and the acetyleno group [34]. The vicinal coupling constants of the epimers **25L** and **26L**, especially $J(3,4) = 5.5$ Hz and $J(3,OH) = 7.0-7.2$ Hz, may be rationalised by assuming a *ca.* 2:1 equilibrium mixture of the straight *zig-zag* conformer possessing an intramolecular C(3)OH ··· OC(5) H-bond and the bent conformer possessing the bifurcated H-bond of HO–C(3) to BnO–C(2) and to the ethynyl group. Persistence of this bifurcated H-bond in the *galacto*- and *gluco*-hept-1-ynitols **17L**/**17D**, **18L**/**18D**, **25L**/**25D**, and **26L**/**26D** is evidenced by $J(3,OH) = 6.8-8.7$ Hz (*Tables 1* and *2* in the *Exper. Part*). However, the straight *zig-zag* conformer is at best a minor component of the conformational equilibrium evidenced by $J(4,5) = 4.1-7.2$ Hz that clearly differs from the calculated value (MM3*: $J(4,5) = 0.5-1.6$ Hz).

The reactive species of the bromoacetylenes leading to the *exo*-glycals must adopt a U-shape conformation (as depicted in the *Schemes*). Ideally, the reactive conformer will be similar to the preferred ground-state conformer, *i.e.*, to the one of the corresponding alditol; it would then be characterised by similar vicinal coupling constants as the corresponding pyranoside. According to the *J* values in *Schemes 1–3*, however, the reactive conformers hardly participate in the conformational equilibrium of the hept-1-ynitols in $CHCl_3$ solution. Monodeprotonation of the 3,7-unprotected 1-bromohept-1-ynitols by NaH in THF leads to alcoholates. They are expected to form a strong, intramolecular flip-flop C(3)O ··· H ··· OC(7) H-bond. The ease of cyclisation will depend on the conformation imposed by this intramolecular H-bond that defines the distance between attacking OH group and ethynyl moiety, and, to a minor extent, on electronic and other steric factors. Surprisingly at first sight, the **L** isomer of both the *gluco*- and *manno*-hept-1-ynitols is the more reactive one, in contradistinction to the *galacto*-analogues. This difference evidences a dominant influence upon the reactivity of the relative configuration of C(3) and C(6) and a neglible influence of the relative configuration at C(3) and C(4); the interaction of HO–C(3) and BnO–C(4) is thus of minor importance at best.

To obtain a deeper insight into intramolecular H-bonds of hydroxyalkoxides we searched the *Cambridge* database for such H-bonds, and modeled the reactive species using the semiempirical programme AM1 implemented in the Ampac 6.0 package [35]. In the solid state, a seven-membered, intramolecular H-bond C(5′)O^- ··· H–OC(2) was observed in a β-D-arabinofuranosylpyrimidine [36]; it is the only example of such an intramolecular H-bond in the database. The H-bond is slightly asymmetric (C(2′)O–H distance: 1.239 Å, C(5′)O^- ··· H distance: 1.409 Å) and linear (bond angle O–H ··· O: 177°). For a more convenient modeling, we replaced the BnO–C(8) group of the bromo compounds **13**, **18**, and **26** by a H-atom, and the remaining BnO by MeO groups. The modeled alkoxides were numbered in the same way as the benzylated diols, but numbers are marked with an asterisk. The linearity of the H-bond and the formation of an eight-membered ring leads to a stronger puckering of **13L***/**13D***, **18L***/**18D***, and **26L***/**26D***. Each analogue can adopt a chair-like conformation (H-bond below the hypothetical pyranose ring) and a boat-like conformation (H-bond above the hypo-

thetical pyranose ring). AM1 does not model H-bonds between alkoxides and OH groups correctly; although the H-bond is linear, the $O^- \cdots O$ distance is slightly larger (2.80–2.85 instead of 2.65 Å), the O–H bond is short (< 1 Å), and the $O^- \cdots H$ distance large (> 1.8 Å), *i.e.*, the OH H-atom is not correctly localised. Nevertheless, the calculations allow a qualitative interpretation of the observed reactivity.

The boat-like conformer of **13L*** is more stable by 3 kcal/mol than the chair-like conformer. $C(7)O^-$ is located directly below HO–C(3), as evidenced by the torsion angle H–C(3)–O–H of −169° (*Fig. 2*). In contradistinction, the chair-like conformer of **18D*** is more stable by 1 kcal/mol than the boat-like conformer. $C(7)O^-$ is located above HO–C(3), slightly further away from the ethynyl group (torsion angle H–C(3)–O–H of 155°), but in the plane going through C≡C–C–H. In both cases, a slight rotation about the C(3)–C(4) bond moves $C(7)O^-$ into a favourable position to attack the C≡C bond (ideally at an $O \cdots C{\equiv}C$ angle of 125–127°, as modeled for the attack of MeO^- at 1-bromoprop-1-yne). The favoured chair-like conformer of **13D*** (0.8 kcal/mol more stable than the boat-like conformer) adopts a similar conformation as **18D*** (torsion angle H–C(3)–O–H of −155°) also suggesting a facile cyclisation of **18D**. However, shortening the $C(7)O^- \cdots OC(3)$ distance to 2.65 Å and lengthening the H–O bond to 1.24 Å may allow the formation of a bifurcated H-bond of HO–C(3) to O^-–C(7) and BnO–C(6); this conformer would not cyclise readily (estimated torsion angle H–C(3)–O–H of 130°), in agreement with observation. In the favoured chair-like conformers of **18L*** and **26L*** (0.8 and 3 kcal/mol more stable than the corresponding boat-like conformers), $C(7)O^-$ is not in a favourable position (torsion angle H–C(3)–O–H of −139° and −22°) to attack the ethynyl group. The chair-like conformer of **26D*** is not a minimum; upon minimisation, it was transformed into the favoured boat-like conformer where $C(7)O^-$ is in a position (torsion angle H–C(3)–O–H of 29°) preventing an attack on the C≡C bond. However, shortening of the $C(7)O^- \cdots OC(3)$ distance to 2.65 Å and lengthening of the H–O bond to 1.24 Å may allow the formation of a bifurcated H-bond of HO–C(3) to O^-–C(7) and

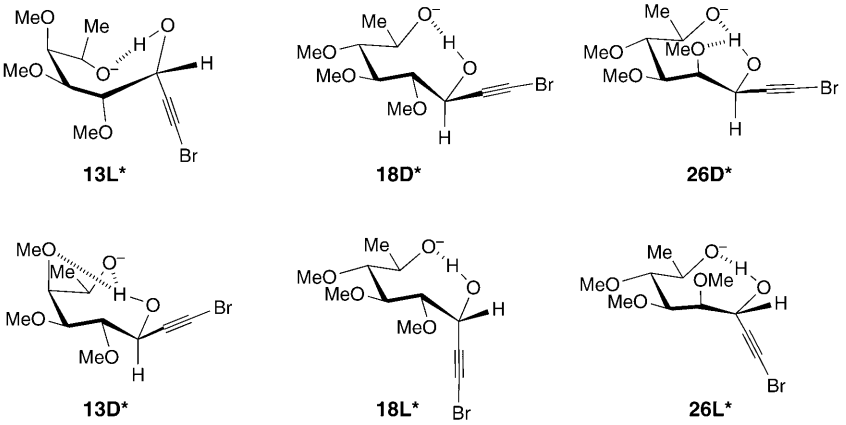


Fig. 2. *Preferred H-bonded conformers favouring alkynol cyclisation of* **13L***, **18D***, *and* **26D***, *and preventing alkynol cyclisation of* **13D***, **18L***, *and* **26L***

BnO–C(4); this chair-like conformer of **26D*** is similar to the favoured conformer of **18D*** and should readily cyclise, as observed.

According to this rationalisation, cyclisation takes only place when the intramolecular C(3)O–H ··· OC(7) H-bond locates C(7)O^- in a position that favours addition to the C≡C bond. One expects that 3-*O*-alkylated derivatives of **13**, **18**, and **26** (both the **L** and the **D** isomers), where there is no such intramolecular H-bond, will undergo at best a slow base-catalysed cyclisation on account of to the very low population of the reactive U-shaped conformation, as suggested by the failure to form 3,7-anhydro-oct-1-ynitols by monosulfonylation of **17L** and **17D**[6]).

We thank Dr. *B. Schweizer* for the crystal-structure determination and the *Swiss National Science Foundation* for generous support.

Experimental Part

General. See [37]. Commercial 65% NaH in oil was washed with hexane and dried.

3,4,6-Tri-O-*benzyl-1,2-dideoxy*-D-ribo-*hex-1-ynitol* (**2**). A soln. of dimethyl 2-oxopropylphosphonate (2.0 g, 12 mmol) in THF (30 ml) was cooled to 0°, treated with K_2CO_3 (1.84 g, 13.2 mmol) and 4-acetamidobenzenesulfonyl azide (2.9 g, 12 mmol), stirred for 2 days, and allowed to gradually warm to 25°. The soln. was treated with a soln. of **1** (1.26 g, 3.0 mmol) in MeOH (30 ml) and K_2CO_3 (0.66 g, 4.8 mmol), stirred for 2 days, poured into cold (0°) sat. aq. NH_4Cl soln. (50 ml), and extracted with $CHCl_3$ (3×30 ml). The combined org. layers were washed with brine (2×20 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/cyclohexane 1:10) gave **2** (0.76 g, 61%). Colourless oil. R_f (AcOEt/cyclohexane 1:2) 0.54. $[\alpha]_D^{25} = +83.2$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3456*w* (br.), 3284*w*, 3063*w*, 3030*w*, 2865*w*, 2108*w*, 1605*w*, 1584*w*, 1496*w*, 1453*m*, 1392*w*, 1349*w*, 1208*w*, 1086*s*, 1066*s*, 1026*s*, 819*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.28 (*m*, 15 arom. H); 4.94, 4.64 (2*d*, *J* = 11.4, PhCH_2); 4.93, 4.54 (2*d*, *J* = 11.7, PhCH_2); 4.60 (*dd*, *J* = 3.6, 2.1, H–C(3)); 4.53, 4.47 (2*d*, *J* = 12.0. PhCH_2); 3.98 (*dtd*, *J* ≈ 7.8, 5.5, 3.0, H–C(5)); 3.82 (*dd*, *J* = 7.8, 3.6, H–C(4)); 3.67 (*dd*, *J* = 9.6, 3.0, H–C(6)); 3.60 (*dd*, *J* = 9.6, 5.4, H′–C(6)); 2.63 (*d*, *J* = 5.7, OH); 2.59 (*d*, *J* = 2.1, H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.13, 137.82, 137.49 (3*s*); 128.36 (4*d*); 128.24 (2*d*); 128.22 (2*d*); 127.85 (2*d*); 127.81 (2*d*); 127.72 (2*d*); 127.62 (*d*); 80.12 (*d*, C(4)); 79.87 (*s*, C(2)); 76.02 (*s*, C(1)); 74.22, 73.40 (2*t*, 2 PhCH_2); 71.32, 70.56 (2*d*, C(3), C(5)); 71.17 (*t*, PhCH_2); 70.73 (*t*, C(6)). HR-MALDI-MS: 440.1913 (30), 439.1884 (100, $[M+Na]^+$, $C_{27}H_{28}NaO_4^+$; calc. 439.1880).

5,6,8-Tri-O-*benzyl-1,2,3,4-tetradeoxy-1-phenyl*-D-ribo-*octa-1,3-diynitol* (**3**). A suspension of $[PdCl_2(PPh_3)_2]$ (6.7 mg, 9.6 μmol), CuI (3.6 mg, 19 μmol), and PPh_3 (5 mg, 19 μmol) and (bromoethynyl)benzene (87 mg, 0.48 mmol) in Et_3N (5 ml) was degassed, stirred for 30 min, treated with **2** (200 mg, 0.48 mmol), stirred at 25° for 12 h, diluted with AcOEt (20 ml), and washed with cold (0°) aq. NH_4Cl soln. (2×15 ml). The aq. phase was extracted with AcOEt (2×10 ml). The combined org. layers were washed with brine (2×10 ml), dried ($NaSO_4$), and evaporated. FC (AcOEt/cyclohexane 1:10) gave **3** (206 mg, 83%). Colourless oil. R_f (AcOEt/cyclohexane 1:2) 0.62. $[\alpha]_D^{25} = +52.5$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3458*w* (br.), 3063*w*, 3030*w*, 2909*w*, 2865*w*, 2237*w*, 1605*w*, 1495*w*, 1453*m*, 1393*w*, 1350*m*, 1208*w*, 1097*s*, 1067*s*, 1027*s*, 913*w*, 844*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.53–7.50 (*m*, 2 arom. H); 7.41–7.27 (*m*, 18 arom. H); 4.94, 4.55 (2*d*, *J* = 12.0, PhCH_2); 4.93, 4.63 (2*d*, *J* = 11.4, PhCH_2); 4.72 (*d*, *J* = 3.6, H–C(5)); 4.53, 4.47 (2*d*, *J* = 12.0, PhCH_2); 3.97 (*dtd*, *J* ≈ 7.8, 5.4, 3.0, H–C(7)); 3.83 (*dd*, *J* = 7.8, 3.6, H–C(6)); 3.67 (*dd*, *J* = 9.9, 3.0, H–C(8)); 3.60 (*dd*, *J* = 9.9, 5.4, H′–C(8)); 2.60 (*d*, *J* = 5.1, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.03, 137.79, 137.32 (3*s*); 132.54 (2*d*); 129.22 (*d*); 128.36 (6*d*); 128.27 (2*d*); 128.24 (2*d*); 127.90 (2*d*); 127.81 (3*d*); 127.73, 127.64 (2*d*); 121.45 (*s*); 80.44 (*d*, C(6)); 79.07, 78.16 (2*s*, C(1), C(4)); 74.26, 73.43 (2*t*, 2 PhCH_2); 73.66, 72.43 (2*s*, C(2), C(3)); 72.12, 70.70 (2*d*, C(5), C(7)); 71.47 (*t*, PhCH_2); 70.58 (*t*, C(8)). HR-MALDI-MS: 555.1928 (13, $[M+K]^+$, $C_{35}H_{32}KO_4^+$; calc. 555.1938), 540.2223 (39), 539.2190 (100, $[M+Na]^+$, $C_{35}H_{32}NaO_4^+$; calc. 539.2193).

(Z)-*4,7-Anhydro-5,6,8-tri*-O-*benzyl-1,2,3-trideoxy-1-phenyl*-D-ribo-*oct-3-en-1-ynitol* (**4**). A soln. of **3** (30 mg, 0.06 mmol) in MeOH (5 ml) was treated with KOH (8.4 mg, 0.15 mmol), stirred at 25° for 3 h, and evaporated. The residue was treated with cold (0°) aq. NH_4Cl soln. (10 ml), and extracted with AcOEt (3×5 ml). The combined org. layers were washed with brine (2×5 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/cyclohexane 1:30) gave **4** (24 mg, 80%). Colourless oil. R_f (AcOEt/cyclohexane 1:2) 0.76. $[\alpha]_D^{25} = +74.7$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3061*w*, 3030*w*, 2919*w*, 2863*w*, 2196*w*, 1660*m*, 1594*w*, 1489*m*, 1453*m*, 1365*m*, 1312*w*, 1285*m*, 1257*m*,

1207*w*, 1090*s* (br.), 1071*s*, 1025*s*, 957*m*, 912*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47–7.43 (*m*, 2 arom. H); 7.38–7.25 (*m*, 18 arom. H); 4.92 (*d*, *J* = 0.6, H–C(3)); 4.73, 4.58 (2*d*, *J* = 12.0, PhCH_2); 4.68 (*dt*, *J* ≈ 6.0, 3.3, H–C(7)); 4.623, 4.54 (2*d*, *J* = 12.0, PhCH_2); 4.618, 4.53 (2*d*, *J* = 12.0, PhCH_2); 4.33 (br. *d*, *J* ≈ 4.8, H–C(5)); 4.07 (*dd*, *J* = 6.0, 4.8, H–C(6)); 3.78 (*dd*, *J* = 11.7, 3.0, H–C(8)); 3.64 (*dd*, *J* = 11.7, 3.6, H′–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 162.99 (*s*, C(4)); 137.83, 137.30, 137.23 (3*s*); 131.29 (2*d*); 128.44 (2*d*); 128.38 (3*d*); 128.33 (2*d*); 128.06 (5*d*); 128.01 (2*d*); 127.94, 127.88 (2*d*); 127.61 (2*d*); 123.97 (*s*); 93.00 (*s*, C(1)); 84.22 (*s*, C(2)); 83.86 (*d*, C(3)); 81.81 (*d*, C(7)); 76.35, 75.55 (2*d*, C(5), C(6)); 73.47, 72.06, 70.64 (3*t*, 3 PhCH_2); 68.48 (*t*, C(8)). HR-MALDI-MS: 540.2230 (40), 539.2195 (100, $[M+Na]^+$, $C_{35}H_{32}NaO_4^+$; calc. 539.2193).

*3,4,6-Tri-*O*-benzyl-1,2-dideoxy-1-(pyridin-2-yl)-*D-ribo*-hex-1-ynitol* (**5**). A suspension of $[PdCl_2(PPh_3)_2]$ (4 mg, 5.8 μmol), CuI (2.2 mg, 11.6 μmol), PPh_3 (3 mg, 11.6 μmol), and 2-bromopyridine (45.5 mg, 0.29 mmol) in Et_3N (3 ml) was degassed, stirred for 30 min, treated with **2** (120 mg, 0.29 mmol), stirred at 25° for 12 h, diluted with AcOEt (20 ml), and washed with cold (0°) aq. NH_4Cl soln. (2 × 10 ml). The aq. phase was extracted with AcOEt (2 × 10 ml). The combined org. layers were washed with brine (2 × 10 ml), dried ($NaSO_4$), and evaporated. FC (AcOEt/cyclohexane 1:2) gave **5** (112 mg, 78%). Colourless oil. R_f (AcOEt/cyclohexane 1:1) 0.35. $[\alpha]_D^{25} = +106.6$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3390*w* (br.), 3059*w*, 3030*w*, 2905*w*, 2864*w*, 2227*w*, 1735*w*, 1582*m*, 1562*w*, 1496*w*, 1463*m*, 1453*m*, 1428*m*, 1393*w*, 1350*m*, 1264*w*, 1208*w*, 1087*s*, 1068*s*, 1027*s*, 999*m*, 909*m*, 821*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.60 (*ddd*, *J* = 5.1, 1.8, 0.9, H–C(6′)); 7.65 (*td*, *J* = 7.8, 1.8, H–C(4′)); 7.44–7.27 (*m*, 15 arom. H, H–C(3′)); 7.22 (*ddd*, *J* = 7.8, 5.1, 1.2, H–C(5′)); 4.98, 4.65 (2*d*, *J* = 11.4, PhCH_2); 4.95, 4.60 (2*d*, *J* = 11.7, PhCH_2); 4.82 (*d*, *J* = 3.6, H–C(3)); 4.53, 4.47 (2*d*, *J* = 12.0, PhCH_2); 4.06 (*ddd*, *J* = 7.5, 5.7, 3.0, H–C(5)); 3.91 (*dd*, *J* = 7.5, 3.6, H–C(4)); 3.69 (*dd*, *J* = 9.6, 3.0, H–C(6)); 3.62 (*dd*, *J* = 9.6, 5.7, H′–C(6)); 2.55 (br. *s*, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.77 (*d*, C(6′)); 142.66 (*s*, C(2′)); 138.26, 137.95, 137.55 (3*s*); 136.12 (*d*, C(4′)); 128.34 (4*d*); 128.19 (2*d*); 128.15 (2*d*); 127.87 (2*d*); 127.80 (2*d*); 127.69, 127.66, 127.55 (3*d*); 127.43 (*d*, C(3′)); 123.02 (*d*, C(5′)); 86.95, 85.86 (2*s*, C(1), C(2)); 80.61 (*d*, C(4)); 74.20, 73.43 (2*t*, 2 PhCH_2); 71.79, 70.73 (2*d*, C(3), C(5)); 71.47 (*t*, PhCH_2); 70.97 (*t*, C(6)). HR-MALDI-MS: 517.2188 (37), 516.2151 (100, $[M+Na]^+$, $C_{32}H_{31}NNaO_4^+$; calc. 516.2145), 494.2330 (21, $[M+H]^+$, $C_{32}H_{32}NO_4^+$; calc. 494.2331). Anal. calc. for $C_{32}H_{31}NO_4$ (493.59): C 77.87, H 6.33, N 2.84; found: C 77.95, H 6.48, N 3.02.

(Z)-*2,5-Anhydro-3,4,6-tri-*O*-benzyl-1-deoxy-1-(pyridin-2-yl)-*D-ribo*-hex-1-enitol* (**6**). A soln. of **5** (100 mg, 0.2 mmol) in MeOH (15 ml) was treated with MeONa (16.5 mg, 0.3 mmol), kept at reflux for 12 h, and evaporated. The residue was treated with cold (0°) aq. NH_4Cl soln. (30 ml), and extracted with AcOEt (3 × 15 ml). The combined org. layers were washed with brine (2 × 10 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/cyclohexane 1:3) gave **6** (92 mg, 92%). Colourless oil. R_f (AcOEt/cyclohexane 1:1) 0.43. $[\alpha]_D^{25} = +121.3$ (*c* = 1.0, $CHCl_3$). IR (ATR): 3059*w*, 3030*w*, 2925*w*, 2863*w*, 1672*m*, 1584*m*, 1561*w*, 1496*w*, 1465*m*, 1453*m*, 1432*m*, 1365*m*, 1300*w*, 1258*w*, 1208*m*, 1142*s*, 1110*s*, 1087*s*, 1072*s*, 1025*s*, 959*s*, 902*m*, 837*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.52 (*ddd*, *J* = 5.1, 1.8, 1.2, H–C(6′)); 7.99 (*dt*, *J* ≈ 7.5, 1.2, H–C(3′)); 7.62 (*td*, *J* ≈ 7.5, 1.5, H–C(4′)); 7.44–7.24 (*m*, 15 arom. H); 7.03 (*ddd*, *J* = 7.5, 5.1, 1.5, H–C(5′)); 5.78 (*s*, H–C(1)); 4.82, 4.64 (2*d*, *J* = 12.0, PhCH_2); 4.78 (*ddd*, *J* = 7.2, 4.2, 2.7, H–C(5)); 4.65, 4.51 (2*d*, *J* = 11.7, PhCH_2); 4.59, 4.54 (2*d*, *J* = 12.0, PhCH_2); 4.39 (*d*, *J* = 4.8, H–C(3)); 4.09 (*dd*, *J* = 7.2, 4.8, H–C(4)); 3.82 (*dd*, *J* = 11.1, 2.7, H–C(6)); 3.66 (*dd*, *J* = 11.1, 4.2, H′–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.66 (*s*, C(2)); 154.76 (*s*, C(2′)); 148.89 (*d*, C(6′)); 137.82, 137.44, 137.26 (3*s*); 135.92 (*d*, C(4′)); 128.41 (2*d*); 128.38 (2*d*); 128.33 (2*d*); 128.10 (2*d*); 128.02 (2*d*); 127.94, 127.80, 127.63 (3*d*); 127.50 (2*d*); 123.26 (*d*, C(5′)); 120.33 (*d*, C(3′)); 104.14 (*d*, C(1)); 83.63 (*d*, C(5)); 76.66, 76.11 (2*d*, C(3), C(4)); 73.36, 72.09, 70.31 (3*t*, 3 PhCH_2); 68.88 (*t*, C(6)). HR-MALDI-MS: 516.2144 (100, $[M+Na]^+$, $C_{32}H_{31}NNaO_4^+$; calc. 516.2151), 495.2349 (35), 494.2320 (100, $[M+H]^+$, $C_{32}H_{32}NO_4^+$; calc. 494.2326). Anal. calc. for $C_{32}H_{31}NO_4$ (493.59): C 77.87, H 6.33, N 2.84; found: C 77.71, H 6.33, N 2.81.

3-(Benzyloxy)-5-[(benzyloxy)methyl]-2-[(pyridin-2-yl)methyl]furan (**7**). A soln. of **5** (100 mg, 0.2 mmol) in THF (15 ml) was treated with NaH (washed with hexane and THF, 9.6 mg, 0.4 mmol), stirred at 25° for 3 h, cooled to 0°, treated with aq. NH_4Cl soln. (30 ml), and extracted with AcOEt (3 × 15 ml). The combined org. layers were washed with brine (2 × 10 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/cyclohexane 1:10) gave **7** (69 mg, 89%). Colourless oil. R_f (AcOEt/cyclohexane 1:1) 0.65. IR (ATR): 3064*w*, 3030*w*, 2919*w*, 2855*w*, 1642*m*, 1590*m*, 1568*w*, 1496*w*, 1473*m*, 1454*m*, 1434*m*, 1420*m*, 1407*m*, 1369*w*, 1357*m*, 1300*m*, 1252*w*, 1210*w*, 1146*w*, 1105*s*, 1084*s*, 1066*s*, 1026*m*, 993*m*, 971*m*, 908*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.52 (br. *d*, *J* ≈ 5.1, H–C(6′)); 7.54 (*td*, *J* = 7.5, 1.5, H–C(4′)); 7.35–7.29 (*m*, 10 arom. H); 7.10 (br. *dd*, *J* = 7.5, 5.1, H–C(5′)); 7.04 (br. *d*, *J* = 7.5, H–C(3′)); 6.26 (*s*, H–C(4)); 4.95, 4.50 (2*s*, 2 PhCH_2); 4.35 (*s*, CH_2–C(5)); 4.14 (*s*, CH_2–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): 158.41 (*s*, C(2′)); 149.08 (*d*, C(6′)); 148.70, 143.35 (2*s*, C(2), C(5)); 137.85, 137.74 (2*s*); 137.07 (*s*, C(3)); 136.41 (*d*, C(4′)); 128.39 (2*d*); 128.32 (2*d*); 127.59 (*d*); 127.88 (2*d*); 127.68 (3*d*);

122.59, 121.32 (2*d*, C(3′), C(5′)); 103.99 (*d*, C(4)); 74.22, 71.88 (2*t*, 2 Ph*C*H$_2$); 64.45 (*t*, *C*H$_2$–C(5)); 34.29 (*t*, *C*H$_2$–C(2)). HR-MALDI-MS: 408.1574 (72, $[M+Na]^+$, $C_{25}H_{23}NNaO_3^+$; calc. 408.1576), 386.1752 (87, $[M+H]^+$, $C_{25}H_{24}NO_3^+$; calc. 386.1756), 278.1175 (100, $[M-BnO]^+$, $C_{18}H_{16}NO_2^+$; calc. 278.1181).

(E)-*3,5,7-Tri*-O-*benzyl-1,2,4-trideoxy*-D-threo-*hept-3-en-1-ynitol* (**9**). A mixture of **8** (213 mg, 0.384 mmol), K_2CO_3 (159 mg, 1.15 mmol), and MeOH (3 ml) was heated under Ar to reflux. Dimethyl 1-diazo-2-oxopropylphosphonate (221 mg, 1.15 mmol) was added over 6 h (syringe pump), cooled to r.t., and filtered through a glass-frit. After evaporation of the filtrate, the residue was distributed between AcOEt and H_2O. The combined org. layers were dried (Na_2SO_4) and evaporated. FC (hexane/AcOEt 5:1) gave a mixture of **8** and an unknown product (42 mg), and **9** (120 mg, 71%).

Data of **9**. Colourless oil. R_f (hexane/AcOEt 2:1) 0.45. $[\alpha]_D^{25} = +25.5$ ($c = 0.96$ $CHCl_3$). IR ($CHCl_3$): 3580*w* (br.), 3303*w*, 3090*w*, 3067*w*, 3032*m*, 3012*m*, 2917*w*, 2868*m*, 2104*w*, 1952*w*, 1875*w*, 1810*w*, 1669*w*, 1638*w*, 1600*w*, 1497*m*, 1454*m*, 1341*m*, 1162*m*, 1085*s*, 1070*s*, 1028*s*, 912*w*, 814*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.22 (*m*, 15 arom. H); 5.21 (*d*, $J = 9.9$, H–C(4)); 4.86 (br. *s*, Ph*CH*$_2$); 4.55, 4.37 (2*d*, $J = 11.6$, Ph*CH*$_2$); 4.52 (br. *s*, Ph*CH*$_2$); 4.40 (*dd*, $J = 9.6, 6.9$, H–C(5)); 3.78 (*ddt*, $J \approx 6.9, 6.0, 3.9$, H–C(6)); 3.55 (*dd*, $J = 9.9, 3.6$, H–C(7)); 3.46 (*dd*, $J = 9.9, 6.0$, H–C(7′)); 3.18 (*s*, H–C(1)); 2.75 (*d*, $J = 3.9$, HO–C(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.52 (*s*, C(3)); 138.17, 138.04, 135.96 (3*s*); 128.49 (2*d*); 128.23 (4*d*); 128.10 (*d*); 127.95 (2*d*); 127.72 (2*d*); 127.70 (2*d*); 127.58 (*d*); 127.52 (*d*); 110.83 (*d*, C(4)); 82.45 (*s*, C(2)); 77.37 (*d*, C(5)); 73.44 (*t* of Ph*CH*$_2$, *d* of C(6), *s* of C(1)); 70.74, 70.56, 70.24 (3*t*, C(7), 2 Ph*CH*$_2$). HR-MALDI-MS: 451.1876 ($[M+Na]^+$, $C_{28}H_{28}NaO_4^+$; calc. 451.1880). Anal. calc. for $C_{28}H_{28}O_4$ (428.52): C 78.33, H 6.76; found: C 78.12, H 6.82.

(E)-*5,7,9-Tri*-O-*benzyl-1,2,3,4,6-pentadeoxy-1*-C-*phenyl*-D-threo-*non-5-ene-1,3-diynitol* (**10**). A suspension of $[Pd_2(dba)_3]$ (6 mg, 0.0125 mmol), CuI (2 mg, 0.01 mmol), P(fur)$_3$ (6 mg, 12.5 μmol), **9** (214 mg, 0.5 mmol), and (bromoethynyl)benzene (91 mg, 0.5 mmol) in DMF (3 ml) was degassed twice and stirred at 22° for 5 min. The mixture was treated with Et_3N (0.3 ml) and stirred for 12 h at 22°. The soln. was diluted with Et_2O (10 ml), treated with H_2O (10 ml) and 0.1 M aq. HCl (3 ml). The Et_2O layer was washed with H_2O (2×15 ml). The aq. layer was extracted with Et_2O (4×10 ml). The combined org. fractions were dried ($MgSO_4$) and evaporated. FC (hexane/AcOEt 4:1) gave **10** (187 mg, 71%). Colourless oil. R_f (hexane/AcOEt 2:1) 0.58. $[\alpha]_D^{25} = +23.9$ ($c = 0.88$, $CHCl_3$). IR ($CHCl_3$): 3579*w* (br.), 3350*w* (sh), 3089*w*, 3067*w*, 3033*m*, 3013*s*, 2916*w*, 2868*m*, 2213*w*, 1952*w*, 1882*w*, 1809*w*, 1625*m*, 1496*m*, 1454*m*, 1384*m*, 1336*m*, 1268*m*, 1170*m*, 1085*s*, 1067*s*, 1027*s*, 915*w*, 821*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.54–7.24 (*m*, 20 arom. H); 5.33 (*d*, $J = 9.9$, H–C(6)); 4.89 (*s*, Ph*CH*$_2$); 4.56, 4.39 (2*d*, $J = 11.7$, Ph*CH*$_2$); 4.54, 4.52 (2*d*, $J = 12.0$, Ph*CH*$_2$); 4.41 (*dd*, $J = 9.9, 6.6$, H–C(7)); 3.78 (*ddt*, $J = 6.6, 5.4, 3.9$, H–C(8)); 3.55 (*dd*, $J = 10.2, 3.9$, H–C(9)); 3.46 (*dd*, $J = 10.2, 5.4$, H′–C(9)); 2.76 (*d*, $J = 3.9$, HO–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 139.97 (*s*, C(5)); 138.52, 138.35, 136.85 (3*s*); 132.87 (2*d*); 129.92 (*d*); 128.77–127.76 (several *d*); 121.36 (*s*); 118.81 (*d*, C(6)); 83.52 (*s*, C(4)); 77.37 (*s*, C(1)); 75.00 (*s*, C(2)); 73.60 (*t*, Ph*CH*$_2$); 73.53 (*d*, C(7)); 73.24 (*s*, C(3)); 72.76 (*d*, C(8)); 71.77, 71.11, 70.76 (3*t*, C(9), 2 Ph*CH*$_2$). HR-MALDI-MS: 551.2195 ($[M+Na]^+$, $C_{36}H_{32}NaO_4^+$; calc. 551.2193).

(Z)-*4,8-Anhydro-5,7,9-tri*-O-*benzyl-1,2,3,6-tetradeoxy-1*-C-*phenyl*-D-threo-*nona-3,5-dien-1-ynitol* (**11**). A suspension of **10** (53 mg, 0.1 mmol) in dry MeOH (3 ml) was treated with one batch of MeONa (20 mg, 0.37 mmol), kept at reflux for 10 h, and evaporated. The residue was treated with a soln. of 0.1 M HCl (0.5 ml) in H_2O (10 ml) and extracted with AcOEt (3×15 ml). The combined org. fractions were washed with brine (10 ml), dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 8:1) gave **11** (44 mg, 83%). Colourless crystals. R_f (hexane/AcOEt 4:1) 0.46. M.p. 92–93°. $[\alpha]_D^{25} = -117.8$ ($c = 0.96$ $CHCl_3$). IR ($CHCl_3$): 3067*w*, 3033*m*, 3013*s*, 2916*w*, 2868*m*, 2193*w*, 1951*w*, 1878*w*, 1809*w*, 1729*w*, 1643*w*, 1607*m*, 1590*m*, 1490*m*, 1454*m*, 1443*w*, 1404*m*, 1365*m*, 1305*s*, 1141*s*, 1093*s*, 1071*s*, 1028*s*, 913*w*, 810*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47–7.18 (*m*, 20 arom. H); 5.64 (*s*, H–C(3)); 5.16 (*d*, $J = 4.2$, H–C(6)); 4.88, 4.84 (2*d*, $J = 11.4$, Ph*CH*$_2$); 4.68, 4.63 (2*d*, $J = 12.3$, Ph*CH*$_2$); 4.62, 4.56 (2*d*, $J = 11.7$, Ph*CH*$_2$); 4.40–4.32 (*m*, H–C(7), H–C(8)); 3.79–3.68 (*m*, 2 H–C(9)). ^{13}C-NMR (75 MHz, $CDCl_3$): 152.41, 148.37 (2*s*, C(4), C(5)); 137.99, 137.90, 136.00 (3*s*); 131.33 (2*d*); 128.46–127.22 (several *d*); 123.96 (*s*); 97.39 (*d*, C(6)); 96.37 (*s*, C(1)); 86.72 (*d*, C(3)); 85.38 (*s*, C(2)); 77.80 (*d*, C(7)); 73.51, 70.55 (2*t*, 2 Ph*CH*$_2$); 70.21 (*d*, C(8)); 69.62, 69.00 (2*t*, C(9), Ph*CH*$_2$). HR-MALDI-MS: 551.2200 ($[M+Na]^+$, $C_{36}H_{32}NaO_4^+$; calc. 551.2193). Anal. calc. for $C_{36}H_{32}O_4$ (528.65): C 81.79, H 6.10; found: C 81.62, H 6.05.

X-Ray Analysis of **11**[2]). Recrystallisation of **11** in Et_2O/hexane 4:1 gave crystals suitable for X-ray analysis: $C_{36}H_{32}O_4$ (528.648); orthorhombic $P2_12_12_1$; $a = 10.24630(10)$, $b = 19.2972(3)$, $c = 29.1235(5)$ Å. $V = 5758.44$ Å^3; $Z = 8$; $D_{calc.} = 1.220$ Mg/m^3. Intensities were measured on an *Enraf-Nonius CAD-4* diffractometer with MoK_α radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 298 K, Θ range 0.998–24.407°. Of the 9417 total collected reflections, 9393 independent reflections were observed. $R = 0.0524$, $R_w = 0.1413$.

Addition of Me$_3$SiC≡CH to **8**. A soln. of $Me_3SiC{\equiv}CH$ (6.3 ml, 45 mmol) in THF (20 ml) at −78° was treated with 1.6 M BuLi in hexane (28 ml, 45 mmol), stirred for 30 min, treated with **8** (3.0 g, 5.5 mmol), allowed

Table 1. *Selected ^1H- and ^{13}C-NMR Chemical Shifts* [ppm], *and Coupling Constants [*Hz] *of the Galactose-Derived Oct-1-ynitol and Oct-1-enitols* **12**–**14** *in $CDCl_3$*[4])

	12L	**13L**	**14L**	**12D**	**13D**	**15D**[a])
H–C(1)	–	–	6.01	–	–	5.30
H–C(3)	4.62	4.665	5.51	4.715	4.72	4.09
H–C(4)	3.844	3.81	4.27	3.78	3.77	3.80
H–C(5)	4.00	3.98	3.65	4.32	4.22	3.89
H–C(6)	3.852	3.895	4.11	3.87	3.87	4.57
H–C(7)	4.05	4.065	4.04	4.13	4.12	4.49–4.44
H–C(8)	3.555	3.585	3.82	3.56	3.585	3.68
H′–C(8)	3.49	3.52	3.74	3.49	3.51	3.54
HO–C(3)	2.92	3.17	–	3.16	3.25	[b])
HO–C(7)	3.20	3.20	–	2.85	2.91	–
J(1,3)	–	–	0	–	–	0
J(3,4)	3.1	3.3	8.2	5.3	5.0	2.3
J(4,5)	5.9	5.8	9.3	4.1	4.7	9.1
J(5,6)	4.6	4.5	1.5	6.2	5.6	2.6
J(6,7)	2.2	2.5	1.0	1.9	2.1	2.2
J(7,8)	5.6	5.6	5.4	6.2	5.9	5.8
J(7,8′)	6.5	6.5	8.4	6.2	6.5	8.3
J(8,8′)	9.3	9.3	9.3	9.3	9.3	9.3
J(3,OH)	6.8	6.8	–	7.9	8.1	[b])
J(7,OH)	4.7	4.7	–	6.5	6.2	–
C(1)	90.75	46.21	96.14	91.92	47.11	
C(2)	104.87	79.50	153.08	104.63	79.01	
C(3)	62.72	63.17	73.56	62.62	63.21	
C(4)	81.75	81.37	79.83[c])	79.76[c])	79.79[c])	
C(5)	80.22	79.95	83.56	79.67[c])	80.04[c])	
C(6)	77.55	77.85	76.91	77.48	77.49	
C(7)	69.88	69.89	79.35[c])	69.56	69.60	
C(8)	70.84	70.83	68.80	71.19	71.06	

[a]) From 2,3,4,6-tetra-*O*-benzyl-D-galactonolactone/**15D** 3:1. [b]) Not assigned. [c]) Assignments may be interchanged.

to warm to 23°, stirred for 24 h, and poured into cold (0°) aq. NH_4Cl soln. (200 ml). After extraction with AcOEt (3×60 ml), the combined org. phases were washed with brine (2×60 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/hexane 1:10) gave **12L**/**12D** 45:55 (3.02 g, 86%). An additional FC (AcOEt/hexane 1:20 → 1:15 → 1:10 → 1:8) afforded pure fractions of **12L** (560 mg) and **12D** (630 mg).

Data of 1,3,4,5-Tetra-O-*benzyl-7,8-dideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-galacto-*oct-7-ynitol* (**12L**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.48. $[\alpha]_D^{25} = -10.0$ ($c = 0.8$, $CHCl_3$). IR (ATR): 3413*w* (br.), 3087*w*, 3062*w*, 3030*w*, 2953*w*, 2895*w*, 2866*w*, 2170*w*, 1603*w*, 1583*w*, 1496*w*, 1454*m*, 1396*w*, 1360*w*, 1328*w*, 1306*w*, 1249*m*, 1208*w*, 1085*s*, 1064*s*, 1027*s*, 910*w*, 841*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 7.37–7.24 (*m*, 20 arom. H); 4.92, 4.78 (2*d*, $J = 11.0$, PhCH_2); 4.71 (br. *s*, PhCH_2); 4.65, 4.48 (2*d*, $J = 11.5$, PhCH_2); 4.475, 4.42 (2*d*, $J = 11.8$, PhCH_2); 0.19 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 1*; additionally, 137.83 (3*s*); 137.55 (*s*); 128.31 (8*d*); 128.04 (6*d*); 127.86 (2*d*); 127.77 (4*d*); 127.69, 127.61 (2*d*); 74.90, 74.81, 73.51, 73.33 (4*t*, 4 PhCH_2); −0.09 (*q*, Me_3Si).

Data of 1,3,4,5-Tetra-O-*benzyl-7,8-dideoxy-8*-C-*(trimethylsilyl)*-L-glycero-L-galacto-*oct-7-ynitol* (**12D**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.42. $[\alpha]_D^{25} = -1.6$ ($c = 0.9$, $CHCl_3$). IR (ATR): 3413*w* (br.), 3087*w*, 3062*w*, 3030*w*, 2953*w*, 2895*w*, 2866*w*, 2170*w*, 1603*w*, 1583*w*, 1496*w*, 1454*m*, 1396*w*, 1360*w*, 1328*w*, 1306*w*, 1249*m*, 1208*w*, 1085*s*, 1064*s*, 1027*s*, 910*w*, 841*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 7.39–7.19 (*m*, 20 arom. H); 4.88, 4.81 (2*d*, $J = 10.8$, PhCH_2); 4.80, 4.60 (2*d*, $J = 11.5$, PhCH_2); 4.56, 4.43 (2*d*, $J = 11.5$, PhCH_2); 4.50, 4.44 (2*d*, $J = 11.8$, PhCH_2); 0.19 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 1*; additionally, 137.87,

137.75, 137.69, 137.62 (4*s*); 128.43–127.65 (several *d*); 74.78, 73.54, 73.33, 72.79 (4*t*, 4 PhCH$_2$); 0.00 (*q*, Me$_3$Si). HR-MALDI-MS: 677.2716 (6, $[M+K]^+$), 662.2977 (47), 661.2949 (100, $[M+Na]^+$, $C_{39}H_{46}NaO_6Si^+$; calc. 661.2956).

1,3,4,5-Tetra-O-*benzyl-8-bromo-7,8-dideoxy*-D-glycero-L-galacto-*oct-7-ynitol* (**13L**). A soln. of **12L** (256 mg, 0.4 mmol) was treated with NBS (142 mg, 0.8 mmol) and $AgNO_3$ (8 mg, 0.047 mmol), and stirred in the dark for 8 h. The grey precipitate was filtered off, and the filtrate was evaporated. A soln. of the residue in Et_2O (100 ml) was washed with cold (0°) sat. aq. $NaHCO_3$ soln. (2×20 ml) and brine (2×20 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/hexane 1:8) gave **13L** (194 mg, 76%). Colourless oil. R_f (AcOEt/hexane 1:2) 0.36. $[\alpha]_D^{25} = -12.0$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3415*w* (br.), 3087*w*, 3062*w*, 3030*w*, 2908*w*, 2866*w*, 2210*w*, 1605*w*, 1585*w*, 1496*w*, 1453*m*, 1395*w*, 1363*w*, 1209*w*, 1085*s*, 1062*s*, 1026*s*, 910*m*, 820*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 7.39–7.24 (*m*, 20 arom. H); 4.86, 4.78 (2*d*, $J = 11.1$, PhCH_2); 4.745, 4.70 (2*d*, $J = 11.2$, PhCH_2); 4.65, 4.515 (2*d*, $J = 11.5$, PhCH_2); 4.50, 4.445 (2*d*, $J = 11.9$, PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 1*; additionally, 137.78 (2*s*); 137.57, 137.51 (2*s*); 128.41–127.71 (several *d*); 74.76, 74.71, 73.83, 73.41 (4*t*, 4 PhCH$_2$). HR-MALDI-MS: 670.1674 (43), 669.1647 (98, $[M+Na]^+$, $C_{36}H_{37}{}^{81}BrNaO_6^+$; calc. 669.1651), 668.1698 (41), 667.1659 (100, $[M+Na]^+$, $C_{36}H_{37}{}^{79}BrNaO_6^+$; calc. 667.1666).

1,3,4,5-Tetra-O-*benzyl-8-bromo-7,8-dideoxy*-D-glycero-L-galacto-*oct-7-ynitol* (**13D**). Similarly to the preparation of **13L**, **12D** (367 mg, 0.57 mmol) was transformed into **13D** (260 mg, 71%). Colourless oil. R_f (AcOEt/hexane 1:2) 0.34. $[\alpha]_D^{25} = -2.8$ ($c = 1.2$, $CHCl_3$). IR (ATR): 3415*w* (br.), 3087*w*, 3062*w*, 3030*w*, 2908*w*, 2866*w*, 2210*w*, 1605*w*, 1585*w*, 1496*w*, 1453*m*, 1395*w*, 1363*w*, 1209*w*, 1085*s*, 1062*s*, 1026*s*, 910*m*, 820*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 7.39–7.21 (*m*, 20 arom. H); 4.85, 4.81 (2*d*, $J = 11.2$, PhCH_2); 4.75, 4.63 (2*d*, $J = 11.2$, PhCH_2); 4.575, 4.46 (2*d*, $J = 11.2$, PhCH_2); 4.515, 4.45 (2*d*, $J = 11.8$, PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 1*; additionally, 137.81, 137.67, 137.53, 137.49 (4*s*); 128.45 (4*d*); 128.40, 128.36, 128.28, 127.99 (4×2*d*); 127.90 (4*d*); 127.85 (3*d*); 127.71 (*d*); 74.87, 73.69, 73.37, 73.21 (4*t*, 4 PhCH$_2$).

(Z)-*6*-O-*Acetyl-2,7-anhydro-1,3,4,5-tetra*-O-*benzyl-8-bromo-8-deoxy*-D-glycero-L-galacto-*oct-7-enitol* (**14L**). A soln. of **13L** (100 mg, 0.15 mmol) in THF (10 ml) was treated with NaH (8.4 mg, 0.35 mmol), stirred at 23° for 1.5 h, poured into cold (0°) aq. NH_4Cl soln. (30 ml), and extracted with AcOEt (3×10 ml). The combined org. layers were washed with brine (2×20 ml), dried (Na_2SO_4), and evaporated. A soln. of the dried residue in Ac_2O/pyridine 1:1 (2 ml) was stirred for 12 h at r.t. Evaporation and FC (AcOEt/hexane 1:15) gave **14L** (85 mg, 82%). Colourless oil. R_f (AcOEt/hexane 1:2) 0.60. $[\alpha]_D^{25} = -33.5$ ($c = 4.7$, $CHCl_3$). IR (ATR): 3091*w*, 3066*w*, 3029*w*, 2912*w*, 2868*w*, 1740*m*, 1636*w*, 1605*w*, 1585*w*, 1496*w*, 1453*m*, 1369*m*, 1273*w*, 1226*s*, 1138*m*, 1095*s*, 1050*s*, 1026*s*, 910*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 7.40–7.21 (*m*, 20 arom. H); 5.03, 4.680 (2*d*, $J = 11.4$, PhCH_2); 4.865, 4.66 (2*d*, $J = 11.5$, PhCH_2); 4.855, 4.685 (2*d*, $J = 11.8$, PhCH_2); 4.55, 4.495 (2*d*, $J = 12.0$, PhCH_2); 1.94 (*s*, AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 1*; additionally, 169.56 (*s*, C=O); 138.53, 138.32, 138.23, 137.77 (4*s*); 128.38–127.43 (several *d*); 75.57, 74.94, 74.20, 74.00 (4*t*, 4 PhCH$_2$); 21.13 (*q*, Me). HR-MALDI-MS: 727.1453 (20, $[M+K]^+$, $C_{38}H_{39}{}^{81}BrKO_7^+$), 725.1493 (17, $[M+K]^+$, $C_{38}H_{39}{}^{79}BrKO_7^+$), 711.1757 (32, $[M+Na]^+$, $C_{38}H_{39}{}^{81}BrNaO_7^+$; calc. 711.1757), 710.1774 (15), 709.1774 (31, $[M+Na]^+$, $C_{38}H_{39}{}^{79}BrNaO_7^+$; calc. 709.1777), 588.2430 (38), 587.2402 (100, $[M-AcBr+Na]^+$, $C_{36}H_{36}NaO_6^+$; calc. 587.2410).

Cyclisation of **13D**. A soln. of **13D** (100 mg, 0.15 mmol) in THF (10 ml) was treated with NaH (8.4 mg, 0.35 mmol), stirred at 23° for 12 h, poured into cold (0°) aq. NH_4Cl soln. (30 ml), and extracted with Et_2O (3×10 ml). The combined org. layers were washed with brine (2×20 ml), dried (Na_2SO_4), and evaporated. FC (Et_2O/pentane 1:10) gave a 3:1 mixture (8 mg, *ca.* 10%) of 2,3,4,6-tetra-*O*-benzyl-D-galactonolactone [24] and **15D**. Colourless oil. R_f (AcOEt/hexane 1:2) 0.65 (lactone) and 0.63 (**15D**). ^{1}H-NMR (400 MHz, $CDCl_3$; 3:1 mixture of lactone and **15D**): data of **15D**: see *Table 1*; additionally, 4.93 (*d*, $J = 12.1$, PhC*H*); 4.615 (*d*, $J = 11.3$, PhC*H*). HR-MALDI-MS: data of **15**: 578.2023 (22), 577.1979 (58, $[M+K]^+$), 562.2277 (37), 561.2243 (58, $[M+Na]^+$, $C_{34}H_{34}NaO_6^+$); data of cyclisation product: 685.1373 (13, $[M+K]^+$, $C_{36}H_{37}{}^{81}BrKO_6^+$), 683.1398 (13, $[M+K]^+$, $C_{36}H_{37}{}^{79}BrKO_6^+$), 670.1678 (11), 669.1649 (31, $[M+Na]^+$, $C_{36}H_{37}{}^{81}BrNaO_6^+$; calc. 669.1651), 668.1700 (11), 667.1654 (30, $[M+Na]^+$, $C_{36}H_{37}{}^{79}BrNaO_6^+$; calc. 667.1666).

Addition of Me$_3$SiC≡CH to **16**. A soln. of Me$_3$SiC≡CH (3.5 ml, 25 mmol) in THF (20 ml) was cooled to −78°, treated with 1.6M BuLi in hexane (16 ml, 25 mmol), stirred for 30 min, treated with **16** (1.66 g, 3.07 mmol), allowed to warm to 23°, stirred for 48 h, and poured into cold (0°) aq. NH_4Cl soln. (100 ml). After extraction with AcOEt (3×30 ml), the combined org. phases were washed with brine (2×30 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/hexane 1:10) gave **17L**/**17D** 7:3 (1.84 g, 94%). An additional FC (AcOEt/hexane 1:20 → 1:15 → 1:10 → 1:8) afforded pure **17D** (296 mg) and **17L** (689 mg).

Data of 1,3,4,5-Tetra-O-*benzyl-7,8-dideoxy-8*-C-*(trimethylsilyl)*-D-glycero-L-gulo-*oct-7-ynitol* (**17L**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.44. $[\alpha]_D^{25} = +1.3$ ($c = 0.9$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 7.41–7.23 (*m*, 20 arom. H); 4.94, 4.85 (2*d*, $J = 11.1$, PhCH_2); 4.78, 4.66 (2*d*, $J = 11.2$, PhCH_2);

Table 2. *Selected ^{1}H- and ^{13}C-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Glucose-Derived Oct-1-ynitols* **17** *and* **18**, *and the Oct-1-enitols* **19**, **20**, **22**, *and* **23** *in $CDCl_3$*[4])

	17L	**18L**	**19**	**20**[a])	**23L**[a]) [b])	**17D**	**18D**	**22D**	**23D**[a])
H–C(1)	–	–	–	–	5.975	–	–	5.44	5.61
H–C(3)	4.48	4.43	4.802	5.83	5.59	4.67	4.63	4.45	5.89
H–C(4)	4.07–4.00	3.95	4.68	4.02	[c])	3.863	3.86	3.69	3.72
H–C(5)	4.07–4.00	4.01	4.798	4.68	[c])	4.24	4.16	4.05	3.983
H–C(6)	3.77	3.75	4.03	4.17	[c])	3.876	3.85	3.80	3.80
H–C(7)	4.07–4.00	4.03	3.80	5.09	[c])	3.98	3.98	4.53	4.29
H–C(8)	3.67	3.665	3.64	3.87	3.90	3.635	3.65	3.94	3.975
H′–C(8)	3.62	3.625	3.59	3.50	3.90	3.595	3.61	3.88	3.86
HO–C(3)	2.96	3.08	2.30	–	–	3.23	3.23	2.53	–
HO–C(7)	3.06	3.03	2.30	–	–	2.86	2.89	–	–
J(1,3)	–	–	–	–	0.5	–	–	0	0
J(3,4)	2.7	3.1	2.4	1.1	8.6	4.6	5.3	2.1	1.7
J(4,5)	[c])	7.2	5.1	3.9	[c])	5.0	4.7	8.7	9.3
J(5,6)	3.0	3.4	6.6	8.2	[c])	4.7	4.3	8.1	8.7
J(6,7)	7.2	7.5	6.6	3.0	[c])	6.8	7.6	9.3	9.7
J(7,8)	3.9	3.4	4.2	7.3	2.2	3.7	3.3	3.6	3.5
J(7,8′)	5.1	4.7	5.4	4.5	2.2	5.0	5.0	2.4	2.2
J(8,8′)	9.9	10.0	9.6	9.7	[c])	10.0	9.9	10.8	11.0
J(3,OH)	8.4	8.7	[c])	–	–	7.2	7.5	4.0	–
J(7,OH)	5.1	5.0	[c])	–	–	4.7	4.7	–	–
C(1)	90.39	45.93	66.06	68.41	95.94	91.45	46.59	88.91	91.00
C(2)	105.10	79.81	157.49	153.88	153.22	104.99	79.35	154.50	151.11
C(3)	63.18	63.74	74.26	74.82	73.02	63.21	63.84	72.51	71.16
C(4)	78.92	78.83	83.60	80.93	81.07	79.21[d])	79.29[d])	82.24	80.26
C(5)	81.96	81.57	85.80	86.90	84.28	79.44[d])	79.41[d])	83.09	83.74
C(6)	77.18	77.07	77.26	78.13	80.41	77.32	76.90	79.94	79.88
C(7)	70.90	71.03	70.62	71.75	79.28	71.50	71.37	78.75	78.05
C(8)	71.20	71.25	70.39	67.40	69.58	71.22	71.14	69.95	69.72

[a]) Assignment based on a HSQC spectrum. [b]) From **23D**/**23L** 9:1. [c]) Not assigned. [d]) Assignments may be interchanged.

4.59, 4.58 (2*d*, *J* = 11.4), 4.51 (*d*, *J* = 11.4, 2 H) (2 PhCH_2); 0.20 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 138.09, 137.93, 137.80, 137.48 (4*s*); 128.41–127.69 (several *d*); 75.58, 75.12, 73.50, 73.13 (4*t*, 4 PhCH_2); 0.01 (*q*, Me_3Si).

Data of 4,5,6,8-Tetra-O-*benzyl-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-gulo-*oct-1-ynitol* (**17D**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.48. $[\alpha]_D^{25} = +18.9$ (*c* = 1.2, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.20 (*m*, 20 arom. H); 4.81, 4.675 (2*d*, *J* = 11.5, PhCH_2); 4.745 (br. *s*, PhCH_2); 4.64, 4.52 (2*d*, *J* = 11.4, PhCH_2); 4.565, 4.495 (2*d*, *J* = 11.9 PhCH_2); 0.18 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 138.25, 138.08, 137.89, 137.64 (4*s*); 128.91 (2*d*); 128.71 (2*d*); 128.61 (6*d*); 128.29 (2*d*); 128.23 (2*d*); 128.07 (*d*); 128.03 (3*d*); 127.99, 127.93 (2*d*); 74.58, 73.74, 73.61, 73.42 (4*t*, 4 PhCH_2); 0.02 (*q*, Me_3Si).

Data of **17L**/**17D** 2:1. IR (ATR): 3420*w* (br.), 3062*w*, 3030*w*, 2953*w*, 2900*w*, 2867*w*, 2171*w*, 1603*w*, 1585*w*, 1496*w*, 1454*m*, 1397*w*, 1357*w*, 1308*w*, 1249*m*, 1208*w*, 1085*s*, 1064*s*, 1026*s*, 911*w*, 840*s*. HR-MALDI-MS: 662.2994 (49), 661.2964 (100, $[M+Na]^+$, $C_{39}H_{46}NaO_6Si^+$; calc. 661.2956). Anal. calc. for $C_{39}H_{46}O_6Si$ (638.87): C 73.32, H 7.26; found: C 73.14, H 7.16.

Bromination of **17**. A soln. of **17L** (250 mg, 0.39 mmol) was treated with NBS (139 mg, 0.78 mmol) and $AgNO_3$ (7 mg, 0.042 mmol), and stirred in the dark for 9 h. The grey precipitate was filtered off, and the filtrate was evaporated. A soln. of the residue in Et_2O (100 ml) was washed with cold (0°) sat. aq. $NaHCO_3$ soln. (2 × 20 ml) and brine (2 × 20 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/cyclohexane 1:8) gave **18L** (156 mg, 62%) and **19** (37 mg, 15%).

Data of 1,3,4,5-Tetra-O-*benzyl-8-bromo-7,8-dideoxy*-D-glycero-L-gulo-*oct-7-ynitol* (**18L**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.34. $[\alpha]_D^{25} = -3.1$ ($c = 0.6$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 7.40–7.28 (*m*, 18 arom. H); 7.24 (*dd*, *J* = 7.2, 2.4, 2 arom. H); 4.64 (br. *s*, PhCH_2); 4.755, 4.635 (2*d*, *J* = 11.4, PhCH_2); 4.58, 4.512 (2*d*, *J* = 11.8, PhCH_2); 4.553, 4.512 (2*d*, *J* = 11.8, PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 138.19, 138.09, 137.92, 137.57 (4*s*); 128.72 (2*d*); 128.64 (10*d*); 128.57 (2*d*); 128.24 (*d*); 128.11 (4*d*); 127.99 (*d*); 75.61, 75.22, 73.68, 73.29 (4*t*, 4 PhCH_2).

Data of **18L**/**18D** 2:1. IR (ATR): 3420*w* (br.), 3063*w*, 3030*w*, 2924*w*, 2848*w*, 2210*w*, 1604*w*, 1583*w*, 1496*w*, 1453*m*, 1396*w*, 1355*w*, 1208*w*, 1085*s*, 1065*s* (br.), 1026*s*, 911*m*, 819*w*. HR-MALDI-MS: 670.1692 (40), 669.1665 (100, $[M+Na]^+$, $C_{36}H_{37}{}^{79}BrNaO_6^+$; calc. 669.1651), 668.1709 (37), 667.1673 (86, $[M+Na]^+$, $C_{36}H_{37}{}^{79}BrNaO_6^+$; calc. 667.1666). Anal. calc. for $C_{36}H_{37}BrO_6$ (645.59): C 66.98, H 5.78, Br 12.38; found: C 67.00, H 5.91, Br 12.48.

4,7-Anhydro-1,3,5-tri-O-*benzyl-8,8-dibromo-8-deoxy*-D-glycero-L-gulo-*oct-7-enitol* (**19**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.25. IR (ATR): 3551*w*, 3413*w* (br.), 3030*w*, 2924*w*, 2850*w*, 1635*w*, 1496*w*, 1453*m*, 1362*w*, 1213*m*, 1192*m*, 1086*s*, 1058*s*, 1026*s*, 971*s*, 939*m*, 911*m*, 865*w*, 829*m*, 801*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 7.43–7.24 (*m*, 15 arom. H); 4.90 (*d*, *J* = 11.4), 4.68 (*d*, *J* = 11.7), 4.52 (br. *d*, *J* = 11.4, 3 H), 4.46 (*d*, *J* = 12.0) (3 PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 138.32, 137.66, 137.00 (3*s*); 128.51 (2*d*); 128.40 (2*d*); 128.29 (2*d*); 128.06 (*d*); 127.89 (2*d*); 127.81 (3*d*); 127.59 (2*d*); 127.47 (*d*); 75.44, 73.42 72.30 (3*t*, 3 PhCH_2). MALDI-MS: 659 (51, $[M+Na]^+$), 657 (100, $[M+Na]^+$), 655 (52, $[M+Na]^+$).

2,6-Di-O-*acetyl-4,7-anhydro-1,3,5-tri*-O-*benzyl-8,8-dibromo-8-deoxy*-D-glycero-L-gulo-*oct-7-enitol* (**20**). A soln. of **19** (37 mg, 0.058 mmol) in Ac_2O/pyridine 1:1 (2 ml) was kept for 12 h at r.t. Evaporation and FC (AcOEt/hexane 1:15) gave **20** (41 mg, 98%). Colourless oil. R_f (AcOEt/hexane 1:2) 0.62. $[\alpha]_D^{25} = -22.2$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3063*w*, 3034*w*, 2875*w*, 1743*s*, 1643*w*, 1496*w*, 1454*w*, 1400*w*, 1370*w*, 1220*s*, 1202*m*, 1101*s*, 1026*s*, 999*s*, 913*m*, 834*m*, 801*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Table 2*; additionally, 7.42–7.26 (*m*, 13 arom. H); 7.16 (*dd*, *J* = 7.9, 1.4, 2 arom. H); 4.88, 4.68 (2*d*, *J* = 11.3, PhCH_2); 4.78, 4.60 (2*d*, *J* = 11.5, PhCH_2); 4.40, 4.36 (2*d*, *J* = 11.7, PhCH_2); 2.01, 1.87 (2*s*, 2 AcO). ^{13}C-NMR (125 MHz, $CDCl_3$; assignment based on HSQC spectrum): see *Table 2*; additionally, 169.90, 169.82 (2*s*, 2 C=O); 138.71, 138.03, 136.72 (3*s*); 129.04–127.64 (several *d*); 75.21, 73.40, 72.18 (3*t*, 3 PhCH_2); 21.30, 20.63 (2*q*, 2 Me). HR-MALDI-MS: 744.0585 (19), 743.0555 (55, $[M+Na]^+$, $C_{33}H_{34}{}^{81}Br_2NaO_8^+$; calc. 743.0477), 742.0601 (36), 741.0560 (100, $[M+Na]^+$, $C_{33}H_{34}{}^{81}Br^{79}BrNaO_8^+$; calc. 741.0498), 740.0614 (17), 739.0574 (48, $[M+Na]^+$, $C_{33}H_{34}{}^{79}Br_2NaO_8^+$; calc. 739.0518). Anal. calc. for $C_{33}H_{34}Br_2O_8$ (718.43): C 55.17, H 4.77, Br 22.24; found: C 55.23, H 4.93, Br 22.22.

1-Deoxy-4,5,6,8-tetra-O-*benzyl*-α-D-gluco-*octo-2,3-diulo-3,7-pyranose* (**21**). A soln. of **18L** (100 mg, 0.15 mmol) in THF (10 ml) was treated with NaH (8.4 mg, 0.35 mmol), stirred at 23° for 12 h, poured into cold (0°) aq. NH_4Cl soln. (30 ml), and extracted with Et_2O (3 × 10 ml). The combined org. layers were washed with brine (2 × 20 ml), dried (Na_2SO_4), and evaporated. FC (Et_2O/pentane 1:10) gave **21** (12 mg, 14%; traces of **22L** not isolated). Colourless oil. R_f (AcOEt/hexane 1:2) 0.61. IR (ATR): 3448*w* (br.), 3085*w*, 3064*w*, 3030*w*, 2923*w*, 2863*w*, 1729*m*, 1605*w*, 1595*w*, 1497*w*, 1454*m*, 1383*w*, 1359*m*, 1243*w*, 1209*w*, 1152*m*, 1070*s*, 1028*m*, 1000*m*, 910*w*, 846*w*, 813*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.36–7.18 (*m*, 20 arom. H); 4.94, 4.90 (2*d*, *J* = 11.0, PhCH_2); 4.86, 4.635 (2*d*, *J* = 10.8, PhCH_2); 4.80, 4.60 (2*d*, *J* = 11.6, PhCH_2); 4.57, 4.49 (2*d*, *J* = 12.3, PhCH_2); 4.56 (*s*, HO–C(3)); 4.08 (*t*, *J* = 9.2, H–C(5)); 4.01 (*ddd*, *J* = 10.0, 3.8, 1.9, H–C(7)); 3.782 (*t*, *J* ≈ 9.6, H–C(6)); 3.780 (*d*, *J* = 9.1, H–C(4)); 3.770 (*dd*, *J* = 11.1, 3.7, H–C(8)); 3.61 (*dd*, *J* = 11.1, 1.8, H′–C(8)); 1.91 (*s*, Me). ^{13}C-NMR (100 MHz, $CDCl_3$): 203.73 (*s*, C=O); 138.41, 138.20, 138.12, 137.54 (4*s*); 128.63, 128.49, 128.48, 128.41, 128.35 (5 × 2*d*); 128.14 (*d*); 127.81 (2*d*); 127.75 (3*d*); 127.71, 127.60 (2*d*); 127.56 (2*d*); 96.80 (*s*, C(3)); 83.75 (*d*, C(5)); 78.33 (*d*, C(4)); 78.04 (*d*, C(6)); 75.76, 75.05, 74.15, 73.25 (4*t*, 4 PhCH_2); 72.83 (*d*, C(7)); 68.45 (*t*, C(8)); 22.31 (*q*, Me). HR-MALDI-MS: 622.2294 (13), 621.2229 (37, $[M+K]^+$, $C_{36}H_{38}KO_7^+$; calc. 621.2255), 606.2520 (42), 605.2498 (100, $[M+Na]^+$, $C_{36}H_{38}NaO_7^+$; calc. 605.2512).

4,5,6,8-Tetra-O-*benzyl-1-bromo-1,2-dideoxy*-D-glycero-D-gulo-*oct-1-ynitol* (**18D**). Similarly to the preparation of **18L**, **17D** (240 mg, 0.37 mmol) was transformed into **18D** (168 mg, 70%). Colourless oil. R_f (AcOEt/hexane 1:2) 0.35. $[\alpha]_D^{25} = +15.9$ ($c = 0.9$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 7.40–7.26 (*m*, 18 arom. H); 7.23 (*dd*, *J* = 7.2, 2.4, 2 arom. H); 4.747, 4.68 (2*d*, *J* = 11.5, PhCH_2); 4.745, 4.69 (2*d*, *J* = 10.9, PhCH_2); 4.58 (br. *d*, *J* ≈ 11.8, 2 H), 4.53 (*d*, *J* = 11.2), 4.51 (*d*, *J* = 11.8) (2 PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 138.21, 137.89, 137.69, 137.43 (4*s*); 128.92 (2*d*); 128.75 (4*d*); 128.64 (4*d*); 128.44 (2*d*); 128.38 (2*d*); 128.35, 128.22 (2*d*); 128.08 (3*d*); 127.98 (*d*); 74.52, 73.76, 73.71, 73.67 (4*t*, 4 PhCH_2).

(Z)-*2,7-Anhydro-4,5,6,8-tetra*-O-*benzyl-1-bromo-1-deoxy*-D-glycero-D-gulo-*oct-1-enitol* (**22D**). A soln. of **18D** (100 mg, 0.15 mmol) in THF (10 ml) was treated with NaH (8.4 mg, 0.35 mmol), stirred at 23° for 1.5 h, poured into cold (0°) aq. NH_4Cl soln. (30 ml), and extracted with AcOEt (3 × 10 ml). The combined org. layers were washed with brine (2 × 20 ml), dried (Na_2SO_4), and evaporated to afford crude **22D** (93 mg). FC (AcOEt/

cyclohexane 1:15) of a sample from a similar reaction gave pure **22D**. Colourless oil. R_f (AcOEt/cyclohexane 1:2) 0.57. IR (ATR): 3438*s* (br.), 3095*w*, 3064*w*, 3031*w*, 2924*w*, 2872*w*, 1628*w*, 1496*w*, 1453*m*, 1398*w*, 1362*m*, 1330*w*, 1315*m*, 1284*m*, 1250*m*, 1210*w*, 1172*m*, 1137*m*, 1098*s*, 1072*s*, 1062*s*, 1035*s*, 1025*s*, 912*m*, 839*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 2*; additionally, 7.42–7.18 (*m*, 20 arom. H); 4.87, 4.815 (2*d*, *J* = 10.8, PhCH_2); 4.805, 4.72 (2*d*, *J* = 10.5, PhCH_2); 4.785, 4.59 (2*d*, *J* = 11.1, PhCH_2); 4.745, 4.675 (2*d*, *J* = 12.3, PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 138.83, 138.70, 138.44, 137.82 (4*s*); 128.74–127.64 (several *d*); 75.80, 75.33, 74.12, 73.93 (4*t*, 4 PhCH_2). HR-MALDI-MS: 670.1691 (38), 669.1659 (100, $[M+Na]^+$, $C_{36}H_{37}{}^{81}BrNaO_6^+$; calc. 669.1651), 668.1705 (37), 667.1671 (88, $[M+Na]^+$, $C_{36}H_{37}{}^{79}BrNaO_6^+$; calc. 667.1651).

(Z)-*3*-O-*Acetyl-2,7-anhydro-4,5,6,8-tetra*-O-*benzyl-1-bromo-1-deoxy*-D-glycero-D-gulo-*oct-1-enitol* (**23D**). A soln. of crude **22D** (93 mg) in Ac_2O/pyridine 1:1 (2 ml) was kept for 12 h at r.t. Evaporation and FC (AcOEt/hexane 1:15) gave **23D** (92 mg, 89% from **18D**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.63. $[\alpha]_D^{25} = +57.2$ (*c* = 1.8, $CHCl_3$). IR (ATR): 3091*w*, 3062*w*, 3030*w*, 2920*w*, 2867*w*, 1747*m*, 1701*w*, 1635*w*, 1601*w*, 1583*w*, 1496*w*, 1453*m*, 1369*m*, 1312*m*, 1215*s*, 1169*m*, 1068*s* (br.), 1026*s*, 936*m*, 912*m*, 827*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): see *Table 2*; additionally, 7.41–7.18 (*m*, 20 arom. H); 4.92, 4.80 (2*d*, *J* = 10.6, PhCH_2); 4.85, 4.765 (2*d*, *J* = 10.2, PhCH_2); 4.75, 4.72 (2*d*, *J* = 12.7, PhCH_2); 4.67, 4.62 (2*d*, *J* = 11.2, PhCH_2); 2.11 (*s*, AcO); irrad. at 5.61 (H–C(1)) → NOE of 13% for H–C(3) at 5.89; irrad. at 5.89 (H–C(3)) → NOE of 10.7% for H–C(1) at 5.61 and of 1% for H–C(4) at 3.72. ^{13}C-NMR (125 MHz, $CDCl_3$): see *Table 2*; additionally, 169.34 (*s*, C=O); 138.74, 138.37, 138.16, 137.27 (4*s*); 128.49–127.48 (several *d*); 76.05, 75.74, 73.91, 73.39 (4*t*, 4 PhCH_2); 21.25 (*q*, Me). HR-MALDI-MS: 712.1773 (39), 711.1749 (100, $[M+Na]^+$, $C_{38}H_{39}{}^{81}BrNaO_7^+$; calc. 711.1757), 710.1795 (40), 709.1762 (99, $[M+Na]^+$, $C_{38}H_{39}{}^{79}BrNaO_7^+$; calc. 709.1777), 588.2411 (11), 587.2383 (29, $[M-AcBr+Na]^+$, $C_{36}H_{36}NaO_6^+$; calc. 587.2410). Anal. calc. for $C_{38}H_{39}BrO_7$ (687.63): C 66.38, H 5.72, Br 11.62; found: C 66.29, H 5.65, Br 11.80.

Addition of Me$_3$SiC≡CH to **24**. A soln. of $Me_3SiC{\equiv}CH$ (2.1 ml, 15 mmol) in THF (10 ml) at −78° was treated with 1.6 M BuLi in hexane (9.4 ml, 15 mmol), stirred for 30 min, treated with **24** (1.0 g, 1.8 mmol), allowed to gradually warm to 23°, stirred for 12 h, and poured into cold (0°) aq. NH_4Cl soln. (100 ml). After extraction with AcOEt (3×20 ml), the combined org. phases were washed with brine (2×20 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/hexane 1:10) gave **25L**/**25D** 55:45 (1.08 g, 91%). An additional FC (AcOEt/hexane 1:20 → 1:15 → 1:10 → 1:8) gave pure **25D** (212 mg) and **25L** (312 mg).

Data of 1,3,4,5-Tetra-O-*benzyl-7,8-dideoxy-8*-C-*(trimethylsilyl)*-D-glycero-D-manno-*oct-7-ynitol* (**25L**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.48. $[\alpha]_D^{25} = +15.6$ (*c* = 1.1, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.39–7.26 (*m*, 18 arom. H); 7.20 (*dd*, *J* = 7.2, 2.1, 2 arom. H); 4.86, 4.63 (2*d*, *J* = 11.7, PhCH_2); 4.67 (br. *s*, PhCH_2); 4.61, 4.46 (2*d*, *J* = 11.2, PhCH_2); 4.54, 4.48 (2*d*, *J* = 11.9, PhCH_2); 0.17 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 137.94, 137.87, 137.78, 137.45 (4*s*); 128.36 (8*d*); 128.09, 127.99, 127.84 (3×2*d*); 127.81 (3*d*); 127.78, 127.68, 127.66 (3*d*); 73.80 (*t*, 2 PhCH_2); 73.44 (*t*, 2 PhCH_2); 0.00 (*q*, Me_3Si).

Data of 4,5,6,8-Tetra-O-*benzyl-1,2-dideoxy-1*-C-*(trimethylsilyl)*-D-glycero-D-galacto-*oct-1-ynitol* (**25D**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.44. $[\alpha]_D^{25} = +8.4$ (*c* = 0.7, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.38–7.21 (*m*, 20 arom. H); 4.95, 4.510 (2*d*, *J* = 11.5, PhCH_2); 4.78 (br. *s*, PhCH_2); 4.551, 4.501 (2*d*, *J* ≈ 11.5, PhCH_2); 4.529 (br. *s*, PhCH_2); 0.19 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 138.21 (*s*); 137.77 (2*s*); 137.74 (*s*); 128.37 (8*d*); 128.28, 128.15, 127.84 (3×2*d*); 127.78 (4*d*); 127.55 (2*d*); 74.69, 73.73, 73.43, 73.11 (4*t*, 4 PhCH_2); −0.03 (*q*, Me_3Si).

Data of **25L**/**25D** 55:45. IR (ATR): 3430*w* (br.), 3091*w*, 3062*w*, 3030*w*, 2953*w*, 2893*w*, 2866*w*, 2171*w*, 1603*w*, 1585*w*, 1496*w*, 1454*m*, 1394*w*, 1360*w*, 1330*w*, 1249*m*, 1209*w*, 1082*s*, 1065*s*, 1027*s*, 911*m*, 840*s*. HR-MALDI-MS: 663.2995 (13), 662.2980 (46), 661.2948 (100, $[M+Na]^+$, $C_{39}H_{46}NaO_6Si^+$; calc. 661.2956).

1,3,4,5-Tetra-O-*benzyl-8-bromo-7,8-dideoxy*-D-glycero-D-manno-*oct-7-ynitol* (**26L**). A soln. of **25L** (256 mg, 0.4 mmol) was treated with NBS (142 mg, 0.8 mmol) and $AgNO_3$ (8 mg, 0.047 mmol), and stirred in the dark for 8 h. The grey precipitate was filtered off, and the filtrate was evaporated. A soln. of the residue in Et_2O (100 ml) was washed with cold (0°) sat. aq. $NaHCO_3$ soln. (2×20 ml) and brine (2×20 ml), dried (Na_2SO_4), and evaporated. FC (AcOEt/cyclohexane 1:8) gave **26L** (196 mg, 76%). Colourless oil. R_f (AcOEt/hexane 1:2) 0.39. $[\alpha]_D^{25} = +23.0$ (*c* = 2.0, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.38–7.26 (*m*, 18 arom. H); 7.21 (*dd*, *J* = 7.2, 2.2, 2 arom. H); 4.80, 4.62 (2*d*, *J* = 11.5, PhCH_2); 4.695, 4.64 (2*d*, *J* = 11.5, PhCH_2); 4.58, 4.503 (2*d*, *J* = 11.2, PhCH_2); 4.56, 4.501 (2*d*, *J* = 12.1, PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 138.15 (*s*); 137.93 (2*s*); 137.73 (*s*); 128.66 (2*d*); 128.63 (8*d*); 128.37 (4*d*); 128.28 (2*d*); 128.11 (3*d*); 127.99 (*d*); 74.15, 73.97 (2*t*, 2 PhCH_2); 73.63 (*t*, 2 PhCH_2).

4,5,6,8-Tetra-O-*benzyl-1-bromo-1,2-dideoxy*-D-glycero-D-galacto-*oct-1-ynitol* (**26D**). Similarly to the preparation of **26L**, **25D** (132 mg, 0.20 mmol) was transformed into **26D** (95 mg, 72%). Colourless oil. R_f (AcOEt/hexane 1:2) 0.38. $[\alpha]_D^{25} = +20.5$ (*c* = 0.7, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.38–7.27

Table 3. *Selected ^{1}H- and ^{13}C-NMR Chemical Shifts* [ppm], *and Coupling Constants* [Hz] *of the Mannose-Derived Oct-1-ynitol and Oct-1-enitols* **25**–**28**[4])

	25L	**26L**	**28L**[a])	**25D**	**26D**	**27D**	**28D**	
	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
H–C(1)	–	–	5.58	–	–	5.48	5.55	5.57
H–C(3)	4.745	4.745	5.49	4.71	4.738	4.20	5.56	5.82
H–C(4)	3.93	3.895	[b])	3.92	3.895	3.85	3.89	4.01
H–C(5)	4.11	4.062	3.63	4.075	4.087	4.06	3.81	3.85
H–C(6)	3.87	3.87	[b])	3.835	3.825	4.15	4.06	4.25
H–C(7)	4.10	4.105	4.01	4.082	4.07	4.49	4.16	4.37
H–C(8)	3.67	3.685	[b])	3.705	3.715	3.925	3.93	3.97
H′–C(8)	3.58	3.60	[b])	3.65	3.66	3.885	3.88	3.89
HO–C(3)	3.48	3.45	–	3.09	3.23	2.06	–	–
HO–C(7)	3.06	3.01	–	2.65	2.64	–	–	–
J(1,3)	–	–	0	–	–	0	0	0
J(3,4)	5.5	5.5	1.5	2.2	2.3	6.9	6.6	6.4
J(4,5)	4.6	4.7	2.4	8.3	8.2	2.1	2.4	2.2
J(5,6)	3.5	3.7	7.8	2.7	2.5	6.9	7.8	7.8
J(6,7)	8.0	8.1	9.0	7.6	7.8	8.1	9.1	9.0
J(7,8)	3.2	3.2	4.0	3.4	3.4	3.3	4.0	4.5
J(7,8′)	5.3	5.3	2.7	5.3	5.0	4.2	2.7	2.4
J(8,8′)	9.6	9.7	[b])	9.6	9.65	10.8	10.8	11.0
J(3,OH)	7.0	7.2	–	10.0	10.0	3.0	–	–
J(7,OH)	5.3	5.3	–	6.6	5.9	–	–	–
C(1)	91.00	46.38	94.6	90.78	46.20	88.87	91.58	91.08
C(2)	104.70	79.37	150.06	105.88	80.36	156.13	151.66	152.47
C(3)	63.42	64.18	71.85	61.93	62.80	72.03	71.17	71.53
C(4)	81.95	82.05	84.21	80.29	80.23	80.04	79.19	79.96
C(5)	79.16	79.23	85.33	78.36	78.89	81.00	81.03	81.28
C(6)	77.96	78.06	[b])	78.19	78.37	77.79	75.57	76.32
C(7)	70.82	70.83	78.92	70.14	70.25	78.95	77.23	77.83
C(8)	71.13	71.24	70.05	71.20	71.27	70.82	70.05	70.41

[a]) From **28D**/**28L** 4:1. [b]) Not assigned.

(*m*, 18 arom. H); 7.245 (*dd*, *J* = 7.2, 2.2, 2 arom. H); 4.84, 4.516 (2*d*, *J* = 11.2, PhCH_2); 4.82, 4.741 (2*d*, *J* = 10.9, PhCH_2); 4.561, 4.502 (2*d*, *J* = 12.1, PhCH_2); 4.532 (br. *s*, PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 138.37, 138.02, 137.90, 137.72 (4*s*); 128.69 (8*d*); 128.58, 128.42, 128.23 (3 × 2*d*); 128.20, 128.10 (2*d*); 128.07 (2*d*); 127.83 (2*d*); 75.07, 73.84, 73.60, 73.35 (4*t*, 4 PhCH_2).

Data of **26L**/**26D** 55:45. IR (ATR): 3430*w* (br.), 3087*w*, 3062*w*, 3030*w*, 2908*w*, 2866*w*, 2209*w*, 1604*w*, 1585*w*, 1496*w*, 1453*m*, 1394*w*, 1328*w*, 1305*w*, 1248*w*, 1209*w*, 1085*s*, 1065*s*, 1027*s*, 908*m*. HR-MALDI-MS: 670.1691 (39), 669.1660 (100, $[M+Na]^+$, $C_{36}H_{37}{}^{81}BrNaO_6^+$; calc. 669.1651), 668.1705 (37), 667.1674 (93, $[M+Na]^+$, $C_{36}H_{37}{}^{79}BrNaO_6^+$; calc. 667.1666).

(Z)-*2,7-Anhydro-4,5,6,8-tetra*-O-*benzyl-1-bromo-1-deoxy*-D-glycero-D-galacto-*oct-1-enitol* (**27D**). A soln. of **26D** (65 mg, 0.1 mmol) in THF (10 ml) was treated with NaH (5 mg, 0.2 mmol), stirred at 23° for 1.5 h, poured into cold (0°) aq. NH_4Cl soln. (20 ml), and extracted with AcOEt (3 × 10 ml). The combined org. layers were washed with brine (2 × 20 ml), dried (Na_2SO_4), and evaporated to afford crude **27D** (61 mg) which was directly acetylated. A pure sample of **27D** was obtained from a similar reaction by FC (AcOEt/hexane 1:10). R_f (AcOEt/hexane 1:2) 0.51. ^{1}H-NMR (300 MHz, C_6D_6): see *Table 3*; additionally, 7.38 (br. *d*, *J* = 7.2, 2 arom. H); 7.29–7.24 (*m*, 4 arom. H); 7.20–7.04 (*m*, 14 arom. H); 4.62, 4.56 (2*d*, *J* = 12.0, PhCH_2); 4.60, 4.48 (2*d*, *J* = 11.1, PhCH_2); 4.58, 4.495 (2*d*, *J* = 12.3, PhCH_2); 4.51, 4.455 (2*d*, *J* = 12.3, PhCH_2). ^{13}C-NMR (75 MHz, C_6D_6): see *Table 3*; additionally, 139.09, 139.05, 138.89, 138.67 (4*s*); 128.50–127.59 (several *d*); 74.23, 73.88, 73.61, 73.05 (4*t*, 4 PhCH_2).

(Z)-*3*-O-*Acetyl-2,7-anhydro-4,5,6,8-tetra*-O-*benzyl-1-bromo-1-deoxy*-D-glycero-D-galacto-*oct-1-enitol* (**28D**). A soln. of crude **27D** (61 mg) in Ac_2O/pyridine 1:1 (2 ml) was stirred for 12 h at r.t. Evaporation and FC (AcOEt/hexane 1:15) gave **28D** (59 mg, 85% from **26D**). Colourless oil. R_f (AcOEt/hexane 1:2) 0.58. $[\alpha]_D^{25} = +57.6$ ($c = 2.8$, $CHCl_3$). IR (ATR): 3088*w*, 3062*w*, 3029*w*, 2924*w*, 2867*w*, 1746*m*, 1636*w*, 1605*w*, 1585*w*, 1496*w*, 1453*m*, 1368*m*, 1316*m*, 1216*s*, 1152*m*, 1095*s*, 1072*s*, 1025*s*, 911*m*, 819*w*. ^{1}H-NMR (300 MHz, C_6D_6): see *Table 3*; additionally, 7.39 (br. *d*, $J = 6.9$, 2 arom. H); 7.30 (br. *d*, $J = 6.6$, 2 arom. H); 7.24–7.03 (*m*, 16 arom. H); 4.72, 4.58 (2*d*, $J = 10.8$, PhCH_2); 4.68, 4.605 (2*d*, $J = 12.0$, PhCH_2); 4.545, 4.50 (2*d*, $J = 11.4$, PhCH_2); 4.535, 4.50 (2*d*, $J = 11.4$, PhCH_2); 1.41 (*s*, AcO); irrad. at 5.57 (H–C(1)) → NOE of 9.6% for H–C(3) at 5.82; irrad. at 5.82 (H–C(3)) → NOE of 12% for H–C(1) at 5.57, of 3% for PhCH_2O–C(4) at 4.54–4.52, and of 6.9% for H–C(4) at 4.01. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.41 (*dd*, $J = 7.4$, 1.8, 2 arom. H); 7.36–7.20 (*m*, 18 arom. H); 4.78, 4.68 (2*d*, $J = 10.5$, PhCH_2); 4.765, 4.72 (2*d*, $J = 12.3$, PhCH_2); 4.72, 4.635 (2*d*, $J = 12.3$, PhCH_2); 4.70, 4.61 (2*d*, $J = 11.8$, PhCH_2); 1.97 (*s*, AcO). ^{13}C-NMR (75 MHz, C_6D_6): see *Table 1*; additionally, 168.15 (*s*, C=O); 139.09, 138.96, 138.60, 138.28 (4*s*); 128.49–127.15 (several *d*); 74.85, 74.04, 73.57, 73.23 (4*t*, 4PhCH_2); 20.23 (*q*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 3*; additionally, 168.73 (*s*, C=O); 138.42, 137.73 (2*s*); 138.01 (2*s*); 128.38–127.37 (several *d*); 75.06, 73.87, 73.58, 73.28 (4*t*, 4PhCH_2); 21.15 (*q*, Me). HR-MALDI-MS: 712.1774 (9), 711.1750 (22, $[M+Na]^+$, $C_{38}H_{39}{}^{81}BrNaO_7^+$; calc. 711.1757), 710.1800 (9), 709.1763 (21, $[M+Na]^+$, $C_{38}H_{39}{}^{79}BrNaO_7^+$; calc. 709.1777), 588.2411 (39), 587.2380 (100, $[M-AcBr+Na]^+$, $C_{36}H_{36}NaO_6^+$; calc. 587.2410). Anal. calc. for $C_{38}H_{39}BrO_7$ (687.63): C 66.38, H 5.72; found: C 66.41, H 5.69.

Cyclisation of **26L**. *a*) Pure **26L** (100 mg, 0.15 mmol) was exposed for 12 h to the same conditions as **26D**. TLC evidenced complete conversion of **26L**, mainly to polar products (R_f (AcOEt/hexane 1:2) 0.00) and to traces of **27L** (R_f 0.52; not isolated).

b) Similarly, **26D**/**26L** 55:45 (3.2 g, 5.0 mmol) was exposed for 12 h to the same conditions as **26D**. A soln. of the residue in Ac_2O/pyridine 1:1 (30 ml) was stirred for 12 h at r.t. Evaporation and FC (AcOEt/hexane 1:10) gave **28D**/**28L** 4:1 (1.08 g, 33%).

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