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A Facile Synthesis of Per-*O*-alkylated Glycono-δ-lactones from Per-*O*-alkylated Glycopyranosides and a Novel Ring Contraction for Pyranoses

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Abstract: A novel one-pot synthesis of a variety of *O*-peralkylated δ-aldonolactones **9** from their corresponding glycosides **1** is introduced. This facile procedure involves combining glycoside precursor, tin(IV) chloride and trimethylsilyl azide in methylene chloride at room temperature to furnish the title compounds in moderate to high yields. A side reaction involving extrusion of C-1 of the common carbohydrate intermediate leads to D-arabino-furanoside and D-lyxofuranoside derivatives **10a** and **10b** respectively.

INTRODUCTION

Glycono-δ-lactones play an important role as synthetic intermediates in numerous syntheses of antibiotics such as valioloamine, destomycin C, avermectine, milbemycine and nogalamycine.[1] They are furthermore key intermediates for *C*-glycosides[2], spiroketals[3] and a selection of glycosidase inhibitors such as (+)-castanospermine and (-)-swainsonine.[4]

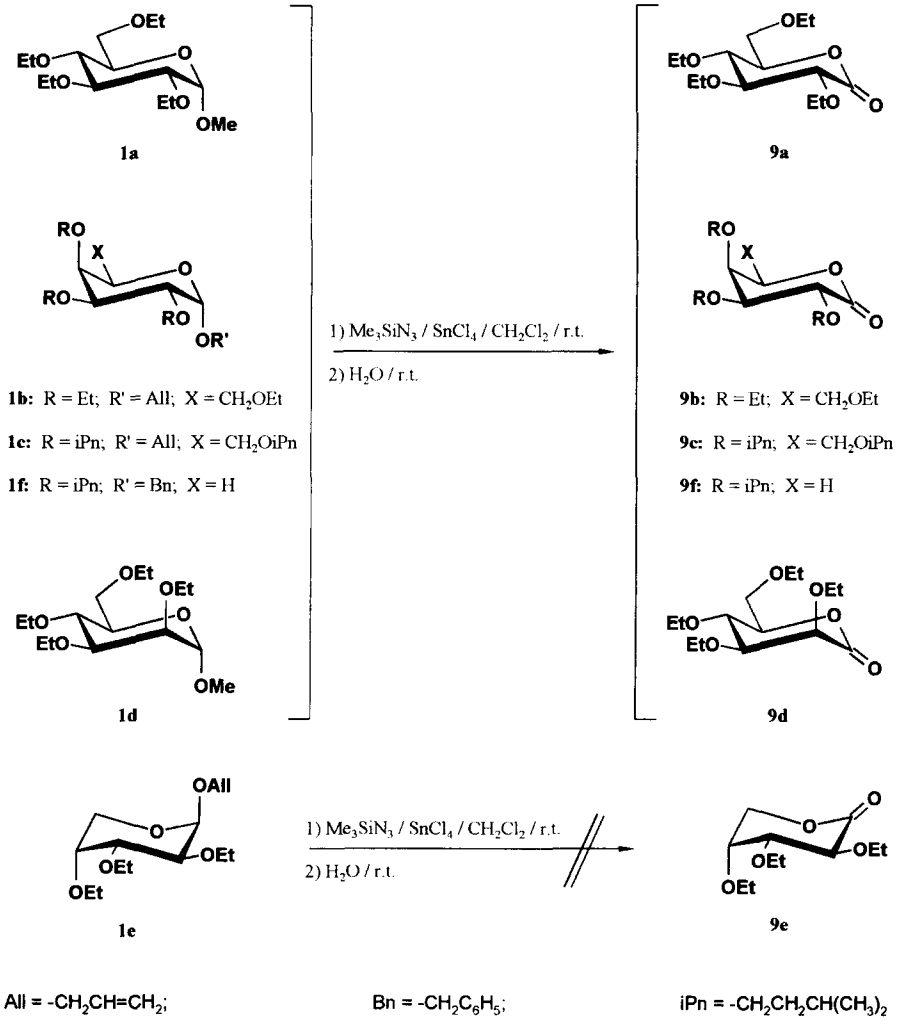
Previous synthetic methods for peracetylated or perbenzylated glycono-δ-lactones involved deprotection at C-1 of the carbohydrate moiety and susequent oxidation, usually via the procedure of Swern *et al.*[5] Alternatively, bromine and silver carbonate on Celite have been employed.[6] Recently, an efficient oxidation of unprotected and partially protected aldohexoses and -pentoses to their corresponding γ-lactones was reported, employing a water-soluble organometallic complex.[7]

To our knowledge, only three syntheses employing direct conversion of an *O*-glycoside to its corresponding δ-lactone have been reported,[8a-c] one of which involves the elegant photochemical cleavage of peracetylated 2-keto-propyl glycosides to yield acetone and the desired δ-lactones in basically quantitative yields.[8a] However, the pre-requisite glycosides must first be prepared in a multi-step procedure with low to moderate yields. Another method utilizes α,β-unsaturated carbohydrates, $BF_3{\cdot}OEt_2$ as Lewis acid and MCPBA as oxidant.[8c] In a series of reaction steps involving organometallic intermediates, α-methylene δ-lactones may be prepared from *S*-glycosides through rearrangement of a cyclic vinyl sulfoxide.[8d] The reverse approach, alkylation of *O*-unprotected aldonolactones under basic conditions is not feasible as it leads to complex product mixtures.[8e]

RESULTS AND DISCUSSION

Initial promising results with methyl-2,3,4,6-tetra-*O*-methyl-D-glucopyranoside[9] prompted us to take a thorough look into the scope and limitations of the title reaction which represents a formal oxidation of an *O*-protected

anomeric center. We subsequently found that the reaction is of quite broad scope regarding the aglycon and carbohydrate frame employed and represents a viable synthesis of the title compounds **9** from the easily accessible peralkylated glycosides **1** (Scheme 1).



Scheme 1: δ-Aldonolactones **9** from per-*O*-alkylated glycopyranosides **1**.

In a typical reaction, glycoside **1**, trimethylsilyl azide and tin(IV) chloride are simply mixed together in methylene chloride and stirred at room temperature under exclusion of moisture to furnish the title compounds **9**. Only in the case of larger batches does the mixture have to be cooled during addition of tin(IV) chloride to dissipate the initial heat of reaction. The pure lactones **9** are obtained after hydrolytic work-up by either distillation or column chromatography. Alternatively, they can be obtained by extraction with aqueous base and subsequent re-extraction with solvent upon acidification.

The furanoside products **10**, arising from a net extrusion of the former C-1 in the glycosides **1** ("C-1 extrusion products"), are formed via a novel ring contraction reaction as valuable side-products. They have been unambiguously identified in the reaction mixtures of **1a**, **1b** and **1d**. In the case of **1b** the resulting D-lyxofuranoside **10b** may be obtained in pure form upon simple distillation, albeit in low yield (Scheme 3).

Our simple lactonization procedure may advantageously be scaled up into the molar range with virtually no change in yield. Conveniently, the glycosides **11a** and **11d** are commercially available and we can easily obtain the allyl D-*galacto* and D-*arabino* glycosides **11b** and **11e** from the parent sugars by $BF_3{\cdot}OEt_2$-mediated glycosylation of allyl alcohol. Improved yields over other literature procedures[10,11] for **11b** and **11e** are achieved and excessive furanoside by-product formation complicating isolation is avoided. Alkylation of the glycosides **11** to yield **1a - f** proceeds smoothly via a modified protocol by Brimacombe *et al.* (Scheme 2).[12,13]

Table 1. Variation of Reaction Parameters for Lactonization / Ring Contraction Reactions

Run	glycoside	c(**1**) [mol/l]	c($SnCl_4$) [mol/l]	c(Me_3SiN_3) [mol/l]	reaction time [h]	yield **9** [%]	ratio[a] **9** : **10**	crude yield[b] [%]
1	**1a**	0.39	0.46	0.59	18	32[a]	10.3	92
2	**1a**	0.37	0.87	0.56	20	35[c]	3.6	85
3	**1a**	0.37	0.88	0.92	22	45[d]	8.4	84
4	**1b**	0.23	0.33	0.38	20	61[d]	12.7[e]	79
5	**1b**	0.23	0.33	0.38	17	79[a]	19.7	83
6	**1c**	0.23	0.33	0.38	19	88[h]	-[f]	-[f]
7	**1d**	0.40	0.46	0.59	19	15[c]	8.1	73
8	**1d**	0.37	0.87	0.57	20	25[c]	-[f]	50
9	**1d**	0.37	0.63	0.75	17	48[d]	4.4	75
10	**1e**	0.23	0.33	0.38	20	< 1[g]	-[f]	-[f]
11	**1f**	0.23	0.49	0.34	22	15[h]	-[f]	-[f]

[a] determined via ^1H NMR spectroscopy
[b] calculated as lactone
[c] after extraction from crude product mixture
[d] after distillation from crude product mixture
[e] ratio of isolated products
[f] not determined
[g] determined by GC/MS
[h] after chromatography

The results in this novel lactonization will be discussed in the following section and are summarized in Table 1. A mechanistic scheme is presented which best supports the gathered data.

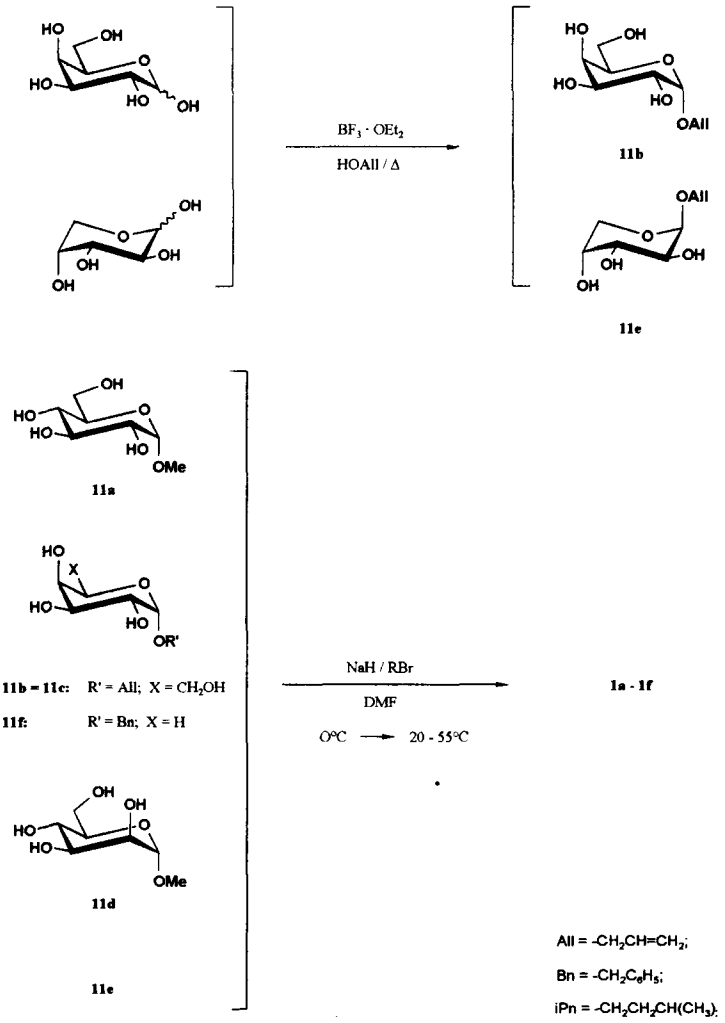
Our results for the employed aglycons in the glycosides **1** show that methyl and allyl glycosides as commonly employed anomeric protecting groups prove useful in our lactonization procedure. As a further example, benzyl glycoside **1f** also leads to the expected lactone **9f**. Allyl glycosides furnish the best results in terms of efficiency, as the yield of lactone as well as the ratio of lactone **9** to C-1 extrusion product **10** are both highest within the investigated aglycons for hexopyranosides. Gratifyingly, the required amounts of Lewis acid and azide are both lowest for these same substrates. On the other hand, benzyl and especially the commercially available methyl glycosides require more vigorous conditions. However, the required conditions and the moderate yield employing benzyl glycoside **9f** are attributed more to the pentopyranoside frame rather than the aglycon (*vide infra*). In the case of methyl glucopyranoside **1a**, only incomplete coversion of starting material is observed, whereas the corresponding methyl mannopyranoside **1d** results in basically quantitative turnover, albeit necessitating high reagent concentrations and leading to increased formation of **10** among other by-products.

The results for the carbohydrate frames employed in glycosides **1** are more complex. All hexopyranosides **1a - 1d** furnish the corresponding lactones **9** in medium to high yields. The D-*galacto* configuration in **1b** and **1c** gives the best results, followed by the D-*manno* and D-*gluco* configurations in **1d** and **1a** as stated above. For the D-*galacto*

configuration little dependence of yield on the steric bulk of the *O*-protecting groups was observed (**1b** vs. **1c**). In stark contrast, D-*arabino* pentopyranoside **1e** as the *quasi*-enantiomer to **1b** gives poor results, the only structural difference being the absence of a side chain at C-5. The reaction mixture (Table 1, run 10) contains a plethora of products apart from large amounts of unreacted starting material with only trace amounts assignable to **9e**, as determined by GC/MS. Arabinopyranosides may nonetheless be converted to the corresponding δ-lactones by moving to bulkier alkyl groups and switching to benzyl as the anomeric protecting group. Thus, L-*arabino* pyranoside **1f** was converted to the corresponding lactone **9f**, albeit in moderate yield.

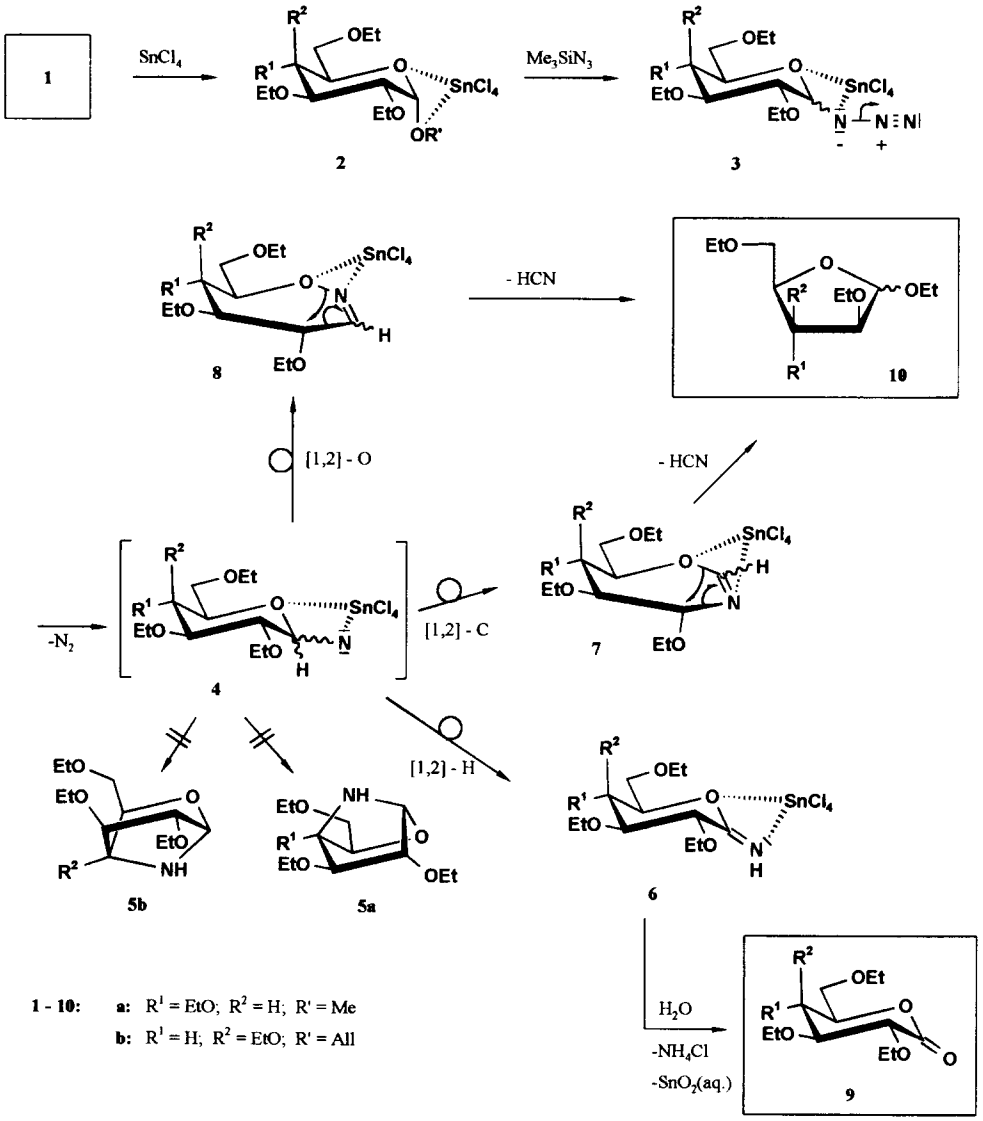
The proposed mechanism for the lactonization sequence is shown in Scheme 3, exemplified by the D-*gluco* and D-*galacto* compounds **1a** and **1b** respectively. It involves the $SnCl_4$-complexed pyranosyl azides **3** as intermediates.

Initially, complexation of tin by the carbohydrate ring is thought to occur, which is in agreement with an observed characteristic high field shift in ^{119}Sn NMR (δ = - 460 ppm against Me_4Sn as external standard) for six-coordinate tin(IV) alkoxy complexes[14]. Concomitant labilization of the glycosidic bond in **2** leads to substitution of the alkoxy



Scheme 2: Preparation of per-*O*-alkylated glycopyranosides **1**.

group by nucleophilic TMS-azide. The present data shows glucose being less reactive than the 1,2-*trans*-diaxial arranged mannose frame. As opposed to the former, the latter arrangement favors cleavage of the glycosidic bond, conceivably via anchimeric assistance of O-2. A similar assistance may be effective in the D-*galacto* system involving



Scheme 3: Proposed mechanistic scheme for the formation of δ-lactones **9** and alkyl pentofuranosides **10**.

interaction between O-4 and the anomeric center, however requiring an energetically disfavored boat conformational intermediate.

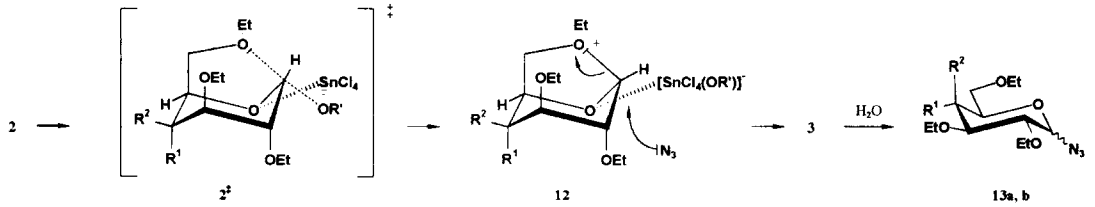
Of greater and more general importance for the labilization of the glycosidic bond in **2** is the presence or absence of a side chain at C-5 in the carbohydrate moiety of **1**. A pronounced dependence of successful lactonization on this

structural feature in **1** is observed, exemplified by the poor reactivity of arabinoside **1e**. This striking difference in reactivities of the D-*arabino* vs. the D-*galacto* frame points to a reactive intermediate $\mathbf{2}^{\ddagger}$ which can only be formed by glycosides **1** with a side chain at C-5. This proposed pathway stabilizes the formal carbenium ion at C-1 in addition to stabilization provided by the pyranose ring oxygen, as compared to only stabilization by the pyranose ring oxygen for glycosides **1** lacking a side chain at C-5. A bicyclic 1,6-*O*-bridged species **12** would result from this internal S_N2-type reaction and attack by the nucleophilic TMS-azide would be greatly facilitated for steric and electronic reasons, leading to the complexed azides **3** (Scheme 4). Precedents for this interpretation are to be seen in reports on the mechanism of hydrolysis of glycosidic bonds[15] and in results by Kishi *et al.*[16] concerning *C*-glycosylations. Our experimental data supports this stated stabilization via $\mathbf{2}^{\ddagger}$ and **12** for all performed reactions with hexopyranosides **1a - d**. The conjunction of this stabilization with the easily cleavable anomeric protecting groups of **1b** and **1c** should therefore account for the observed high yields in lactonizations leading to **9b** and **9c**.

Inferring the complexed azides **3** as intermediates is supported by the fact that the analogous *acylated* hexoses and pentoses do not react beyond the stage of the glycosyl azides, under similar reaction conditions[17]. In the aforementioned compounds, tin would be complexed by the far more electron rich carbonyl oxygens versus the azide group, impeding or preventing reaction of the azide group in agreement with the results of the above authors. However, in the present case of *alkylated* sugars, the azide group exhibits the greater electron density versus the ether oxygens. Therefore, complexation of tin should indeed occur at the azide group, activating this group for the second stage in the proposed two stage mechanism of lactonization.

This striking difference between alkylated and acylated glycosyl azides can be fittingly termed as the former being "armed" towards transformations of the azide group (and ultimately C-1 of the glycosyl moiety), whereas the acylated glycosyl azides are "disarmed" in this respect[18].

Also in accord with the presence of the complexed azides **3** in our proposed mechanism of lactonization is the fact that the corresponding decomplexed azides **13** can be detected (along with unreacted starting material) in the final product mixture in most cases. Furthermore, lowering the concentration of $SnCl_4$ relative to TMS-azide under otherwise identical reaction conditions leads to increased and ultimately sole formation of pyranosyl azides **13** as determined after hydrolytic work-up[9], in agreement with a two stage mechanism and **3** as a key intermediate.



Scheme 4: Reactive 1,6-*O*-bridged species $\mathbf{2}^{\ddagger}$ and **12**, shown for D-*gluco* and D-*galacto* compounds (R^1, R^2 viz. Scheme 3).

The second stage of the proposed mechanism is initiated by tin-mediated cleavage of the N-N bond in the aglycon with a subsequent 1,2 shift of either H-1, C-2 or O-5 leading to the rearrangement products **6 - 8**. The relative ease of migration of these groups ultimately determines the ratio of products **9** : **10**. Intermediates **7** and **8** both lead to the same C-1 extrusion product **10** via an unprecedented sigmatropic ring contraction in pyranoside rings. As may be anticipated, the 1,2 hydride shift leading to **6** is by far the most facile, mirrored by the predominance of lactones **9** in the product mixtures (Table 1). All data gathered so far suggests a concerted elimination-migration step, rendering the presence of free or complexed nitrene **4** highly improbable. Thus, typical products stemming from nitrenes[19], such as the bicyclic species **5a** or **5b** arising from intramolecular insertion of the nitrene group into the C-4 - H-4 bond or polymers, are not observed. Final hydrolysis of the iminolactones **6** leads to the title compounds **9**.

The discussed roles of $SnCl_4$ and TMS-azide in the modification of the carbohydrate frame leading to lactones **9** are also transferable to suitable aglycons with the result of inverse product functionalities, i.e. aglycon oxidation to an aldehyde and *O*-silylation by TMS-azide at the anomeric center. Thus, in the reaction with benzyl glycoside **1f**, benz-

aldehyde and benzoic acid are detectable as by-products after work-up amid other, unidentified aromatic products. This is ascribed to similar stabilities of the benzyl versus the glycopyranosyl cation, thus leading to a similar reaction sequence for the former, ultimately resulting in benzaldehyde. The enhanced reactivity of **1f** vs. **1e** (Table 1), both lacking side chains at C-5, can be ascribed to the greater stability of the benzyl vs. the allyl cation in a similar fashion. Conceivably, **1f** can undergo silylation by TMS-azide at the glycosidic oxygen after liberation of the benzyl group as benzyl azide. The resulting TMS glycoside is extremely labile under the employed Lewis-acid conditions and should lead to a complexed azide of the type **3** with the aid of a second equivalent of TMS-azide, ultimately resulting in **9f**. Conversely, a similar pathway for the less stable allyl group in **1e** is disfavored and degradation reactions dominate.

The above outlined transglycosidation approach with *in situ* formed TMS glycosides is promising for opening up the field of pentopyranosides for high yielding syntheses of *O*-peralkylated δ-aldonolactones.

CONCLUSION

We have presented a viable new one-pot synthesis of *O*-peralkylated δ-aldonolactones **9** from their corresponding *O*-glycosides **1**. This procedure employs inexpensive and commercially available starting materials. The synthesis has been shown to consist of two consecutive reactions with the *O*-peralkylated glycosyl azides **13** as intermediate products. An unprecedented side reaction was found to lead to furanoside products **10** with a net extrusion of the former C-1. Contrary to results of other authors with *acylated* glycosyl azides under similar reaction conditions, our *alkylated* analogues **13** react via tin(IV) complexation to **3** and subsequent rearrangement to furnish the title compounds. In this respect, we refer to them as "armed" glycopyranosyl azides. Allyl, benzyl and methyl have all been shown to work as aglycons in the starting materials. Yields are moderate to high; hexopyranosides and allyl aglycons giving the best yields so far. Pentopyranosides suffer from lack of reactivity and low yields. A mechanistic scheme compatible with these results and offering solutions is presented. A scale-up of the lactonization procedure into the molar range is possible without experimental modifications and with virtually no change in yield. Bulk preparations for the carbohydrate substrates have also been presented. Our future research will extend into the synthetically more widespread per-*O*-benzylated sugars, probing their scope and limitations in our lactonization procedure. Furthermore, modifications of our procedure to suit the field of pentopyranosides will also be studied.

EXPERIMENTAL SECTION

All chemicals used were commercially available and used without further purification except when stated otherwise. CH_2Cl_2 was distilled from $CaCl_2$ and stored under nitrogen prior to use. Allyl alcohol was distilled and dried over molecular sieves prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 360 spectrometer at 360 and 90 MHz respectively in $CDCl_3$ as solvent, unless stated otherwise. All shifts are given in δ-values and coupling constants are in Hz. TOCSY and HMQC NMR spectra were obtained for representative compounds and recorded on a Bruker AC 200 spectrometer at 200 MHz. GC coupled mass spectra were recorded on a Varian MAT 1125 (70 eV) with a Carlo Erba 4160 capilliary gas chromatograph (30 m, OV-1), chemical ionizations with isobutane. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer, all values given in cm^{-1}. Optical rotations were measured with a Perkin-Elmer 241 MC polarimeter and are given in $CHCl_3$ unless stated otherwise. Melting points were determined on a Büchi SMP-20 apparatus in open tubes and are uncorrected. Analytical and preparative chromatography was performed with Merck Kieselgel 60_{F254} plates and Merck Kieselgel 60 (40-63 μ) respectively.

General procedure for allyl pyranosides: A suspension of the respective carbohydrate (330 mmol) in dry allyl alcohol (700 ml) is vigorously stirred at r.t. with exclusion of moisture. $BF_3{\cdot}OEt_2$ (0.067 molar eq.) is carefully added to the suspension which is heated to reflux under continued stirring. Dissolution of the carbohydrate proceeds typically within 10 min. After refluxing for 3 h, the solution is cooled and then concentrated to approx. half its volume at low temperature. Toluene (100 ml) is added and the solution concentrated again to its previous volume. Subsequent

codistillation of the resulting oil with toluene (3 x 150 ml) at low temperature and removal of remaining solvent *in vacuo* furnishes the crude title compounds as waxy to brittle solids which are recrystallized from *i*-propanol or ethanol.

Allyl-α-D-*galactopyranoside* **11b**: Yield 61% after recrystallization from ethanol. Mp.: 143-143.5°C (colourless matted needles). $[\alpha]_D^{20}$: + 181.4 (c = 5.8, H_2O). Lit.[10]: Yield 24% (crude). Mp.: 145-46°C (corr.), $[\alpha]_D^{20}$: + 185.0 (c = 5.8, H_2O). ^{1}H NMR (DMSO-d_6): 3.47 (*pseudo*-okt, 2H, $^2J_{6,6'}$ = 11.0, $^3J_{5,6}$ = 5.7, H-6, H-6'), 3.57 (m, 3H, H-2, H-3, H-5), 3.69 (s (broad), 1H, H-4), 3.91 (ddd, 1H, ^2J = 13.6, ^3J = 5.6, $^4J_{allyl}$ = 1.2, $OCH_2CH{=}CH_2$), 4.10 (ddt, 1H, ^3J = 4.8, $^4J_{allyl}$ = 1.5, $OCH_2CH{=}CH_2$), 4.34 (d, 1H, ^3J = 4.0, OH), 4.50 (d, 1H, ^3J = 6.0, OH), 4.53 (d, 1H, ^3J = 5.5, OH), 4.55 (d, 1H, ^3J = 5.7, OH), 4.67 (d, 1H, $^3J_{1,2}$ = 3.3, H-1), 5.12 (d, 1H, $^3J_{cis}$ = 10.5, $OCH_2CH{=}CH_2$), 5.30 (d (broad), 1H, $^3J_{trans}$ = 17.3, $OCH_2CH{=}CH_2$), 5.90 (m, 1H, $OCH_2CH{=}CH_2$). ^{13}C NMR (DMSO-d_6): 60.38 (C-6), 66.94 ($OCH_2CH{=}CH_2$), 68.13, 68.62, 69.35, 71.07 (C-2 - C-5), 98.02 (C-1), 115.97 ($OCH_2CH{=}CH_2$), 134.73 ($OCH_2CH{=}CH_2$). $C_9H_{16}O_6$ (220.2).

Allyl-β-D-*arabinopyranoside* **11e**: Yield 67% after recrystallization from ethanol. Mp.: 117-119°C (colourless crystalline mass). $[\alpha]_D^{20}$: - 203.0 (c = 1.1, H_2O). Lit.[11]: Yield 41%. Mp.: 121-123°C, $[\alpha]_D^{20}$: - 216.0 (c = 1.1, H_2O). ^{13}C NMR (DMSO-d_6): 63.07 (C-5), 67.49 ($OCH_2CH{=}CH_2$), 68.17, 68.52, 68.96 (C-2 - C-4), 98.68 (C-1), 116.17 ($OCH_2CH{=}CH_2$), 134.82 ($OCH_2CH{=}CH_2$). $C_8H_{14}O_5$ (190.2).

General alkylation procedure: A solution of the starting pyranoside **11** (260 mmol) in dry DMF (1200 ml) is vigorously stirred at r.t. under an inert gas blanket. Powdered NaH (~ 1.5 eq. per -OH group) is carefully added and the suspension cooled to 0°C. After the evolution of gas ceases (usually 20 min), the corresponding alkylating agent RX (2.0 eq. per -OH group) is added dropwise at the same temperature with occasional shaking of the now pasty suspension. On addition of all the alkylating agent (usually 20-30 min), the paste is slowly allowed to warm to room temperature, leading to a stirrable, usually clear solution after approx. 22 h. Bulky alkyl groups require longer reaction times (≥ 72 h). The reaction is stopped by careful addition of MeOH (150 ml) and the solvent removed *in vacuo*. The remainig syrup is diluted with water (500 ml) and extracted with $CHCl_3$ (4 x 400 ml; R = Et) or hexanes (3 x 500 ml). The combined extracts are washed with water (2 x 200 ml) and dried over Na_2SO_4. After removal of the solvent, the oily residue is distilled over glass wool (R = Et) or used as obtained.

Allyl-2,3,4,6-tetra-O-ethyl-α-D-*galactopyranoside* **1b**: Yield 80% from glycoside **11b** after distillation. $Bp._{0.45}$: 156-57°C (colourless oil). $[\alpha]_D^{20}$: + 104.5 (c = 1.8). ^{1}H NMR: 1.21 (m, 12H, 4 x CH_3), 3.47 - 3.77 (m, 12H, H-2 - H-6', 3 x OCH_2CH_3), 3.90 (m, 1H, OCH_2CH_3), 3.94 (ABX_3-dq, 1H, $^2J_{A,B}$ = 9.5, $^3J_{A,X}$ = 7.0, OCH_2CH_3), 4.07 (ddt, 1H, ^2J = 13.1, ^3J = 6.6, $^4J_{allyl}$ = 1.1, $OCH_2CH{=}CH_2$), 4.18 (ddt, 1H, ^3J = 5.1, $^4J_{allyl}$ = 1.4, $OCH_2CH{=}CH_2$), 4.98 (d, 1H, $^3J_{1,2}$ = 3.7, H-1), 5.19 (ddd, 1H, ^2J = 1.6, $^3J_{cis}$ = 10.2, $OCH_2CH{=}CH_2$), 5.31 (ddd, 1H, $^3J_{trans}$ = 17.3, $OCH_2CH{=}CH_2$), 5.94 (m, 1H, $OCH_2CH{=}CH_2$). ^{13}C NMR: 15.13 - 15.76 (4 x CH_3), 66.19, 66.65, 66.82, 68.08, 68.76, 68.98 (C-6, $OCH_2CH{=}CH_2$, 4 x OCH_2CH_3), 69.13 (C-5), 75.52, 76.47, 78.51 (C-2 - C-4), 96.26 (C-1), 117.75 ($OCH_2CH{=}CH_2$), 134.14 ($OCH_2CH{=}CH_2$). MS (EI): m/z = 229 (1.1), 116 (100). MS (CI): m/z = 333 (0.9, $(M+H)^+$), 229 (100). $C_{17}H_{32}O_6$ (332.5): calcd. C: 61.41, H: 9.72; found C: 61.20, H: 9.65.

Allyl-2,3,4,6-tetra-O-(3-methylbutyl)-α-D-*galactopyranoside* **1c**: Yield 76% from glycoside **11b** of an amber coloured oil after 10 d at +48°C. Small amounts of lower alkylated products remain as impurities (GC). ^{1}H NMR: 0.90 (m, 24H, 8 x CH_3), 1.47 (m, 8H, 4 x $OCH_2CH_2CH(CH_3)_2$), 1.72 (m, 4H, 4 x $OCH_2CH_2CH(CH_3)_2$), 3.40 - 3.76 (m, 12H, H-2 - H-6', 6H of 4 x $OCH_2CH_2CH(CH_3)_2$), 3.90 (m, 2H, 2H of 4 x $OCH_2CH_2CH(CH_3)_2$), 4.06 (ddt, 1H, ^2J = 13.0, ^3J = 6.8, $^4J_{allyl}$ = 0.9, $OCH_2CH{=}CH_2$), 4.17 (ddt, 1H, ^3J = 5.1, $^4J_{allyl}$ = 1.3, $OCH_2CH{=}CH_2$), 4.97 (d, 1H, $^3J_{1,2}$ = 3.7, H-1), 5.17 (dd (broad), 1H, ^2J = 1.6, $^3J_{cis}$ = 10.2, $OCH_2CH{=}CH_2$), 5.29 (dd (broad), 1H, $^3J_{trans}$ = 17.2, $OCH_2CH{=}CH_2$), 5.92 (m, 1H, $OCH_2CH{=}CH_2$). ^{13}C NMR:

22.43 - 22.71 (8 x CH_3), 24.78 -25.09 (4 x $OCH_2CH_2CH(CH_3)_2$), 38.62 - 39.24 (4 x $OCH_2CH_2CH(CH_3)_2$), 68.01, 69.35 (C-6, $OCH_2CH=CH_2$), 69.35 (C-5), 69.69, 69.96, 70.00, 71.66 (4 x $OCH_2CH_2CH(CH_3)_2$), 75.56, 76.77, 78.90 (C-2 - C-4), 96.05 (C-1), 117.84 ($OCH_2CH=CH_2$), 134.13 ($OCH_2CH=CH_2$). MS (EI): m/z = 355 (0.5), 71 (100), 43 (99). MS (CI): m/z = 443 (60, $[(M+H)-HOAll]^+$), 267 (100). $C_{29}H_{56}O_6$ (500.8).

Methyl-2,3,4,6-tetra-O-ethyl-α-D-*mannopyranoside* **1d**: Yield 78% from methyl-α-D-mannopyranoside. $Bp._{0.25}$: 118-19°C (colourless oil). $[\alpha]_D^{20}$: + 50.5 (c = 2.2). ^1H NMR: 1.20 (m, 12H, 4 x CH_3), 3.34 (s, 3H, OCH_3), 3.49 (ABX_3-dq, 1H, $^2J_{A,B}$ = 9.3, $^3J_{A,X}$ = 7.0, OCH_2CH_3), 3.55 - 3.74 (m, 12H, H-2 - H-6', 6H of 4 x OCH_2CH_3), 3.87 (ABX_3-dq, 1H, $^2J_{A,B}$ = 9.2, $^3J_{A,X}$ = 7.1, OCH_2CH_3), 4.72 (d, 1H, $^3J_{1,2}$ = 1.6, H-1). ^{13}C NMR: 15.23 - 15.82 (4 x CH_3), 54.73 (OCH_3), 65.49, 66.58, 66.78, 67.17 (4 x OCH_2CH_3), 69.88 (C-6), 71.68, 74.74, 75.70, 79.89 (C-2 - C-5), 99.23 (C-1). MS (EI): m/z = 275 (0.3, $(M-MeO^{\cdot})^+$), 116 (100). $C_{15}H_{30}O_6$ (306.5): calcd. C: 58.79, H: 9.89; found C: 58.51, H: 9.71.

Allyl-2,3,4-tri-O-ethyl β-D-*arabinopyranoside* **1e**: Yield 85% from glycoside **11e**. $Bp._{0.10}$: 106-7°C (colourless oil). $[\alpha]_D^{20}$: - 158.4 (c = 2.0). IR (film): 1646 (m, ν-C=C). ^1H NMR: 1.21 (m, 9H, 3 x CH_3), 3.64 - 3.75 (m, 11H, H-2 - H-5', 3 x OCH_2CH_3), 4.07 (ddt, 1H, ^2J = 13.3, ^3J = 6.6, $^4J_{allyl}$ = 1.3, $OCH_2CH=CH_2$), 4.20 (ddt, 1H, ^3J = 5.3, $^4J_{allyl}$ = 1.5, $OCH_2CH=CH_2$), 4.96 (d, 1H, $^3J_{1,2}$ = 3.1, H-1), 5.20 (ddt, 1H, ^2J = 1.3, $^3J_{cis}$ = 10.2, $OCH_2CH=CH_2$), 5.32 (ddt, 1H, $^3J_{trans}$ = 17.3, $OCH_2CH=CH_2$), 5.91 (m, 1H, $OCH_2CH=CH_2$). ^{13}C NMR: 15.53 - 15.71 (3 x CH_3), 60.72 (C-5) 65.72, 66.00, 66.89, 68.16 ($OCH_2CH=CH_2$, 3 x OCH_2CH_3), 75.03, 76.29, 77.07 (C-2 - C-4), 96.70 (C-1), 117.65 ($OCH_2CH=CH_2$), 134.15 ($OCH_2CH=CH_2$). MS (EI): m/z = 217 (1.0, $(M-AllO^{\cdot})^+$), 129 (100). MS (CI): m/z = 275 (0.3, $(M+H)^+$), 217 (100). $C_{14}H_{26}O_5$ (274.4): calcd. C: 61.29, H: 9.55; found C: 61.08, H: 9.44.

Benzyl-2,3,4-tri-O-(3-methylbutyl)-β-L-*arabinopyranoside* **1f**: Yield 97% from benzyl-β-L-arabinopyranoside[20] of an amber-coloured oil after 12 d at +55°C, pure by GC. $[\alpha]_D^{20}$: + 120.9 (c = 2.1). IR (film): 1650, 1495 (2 x w, ν-C=C). ^1H NMR: 0.88 (m, 18H, 6 x CH_3), 1.47 (m, 6H, 3 x $OCH_2CH_2CH(CH_3)_2$), 1.73 (m, 3H, 3 x $OCH_2CH_2CH(CH_3)_2$), 3.45 - 3.66 (m, 8H, H-5, H-5', 3 x $OCH_2CH_2CH(CH_3)_2$), 3.68 (s (broad), 3H, H-2, H-3, H-4), 4.66 (AB-dd, 2H, Δν = 61.2, ^2J = 12.5, CH_2Ph), 4.92 (d, 1H, $^3J_{1,2}$ = 2.2, H-1), 7.25 (t, 1H, ^3J = 7.0, p-H(Ph)), 7.31 (t, 2H, ^3J = 7.5, m-H(Ph)), 7.39 (d, 2H, ^3J = 6.9, o-H(Ph)). ^{13}C NMR: 22.42 - 22.68 (6 x CH_3), 24.63 -24.99 (3 x $OCH_2CH_2CH(CH_3)_2$), 38.63 - 39.11 (3 x $OCH_2CH_2CH(CH_3)_2$), 58.91 (2 x $OCH_2CH_2CH(CH_3)_2$), 60.90 (C-5), 69.00, 69.78 (CH_2Ph, $OCH_2CH_2CH(CH_3)_2$), 75.26, 76.62, 77.51 (C-2 - C-4), 96.48 (C-1), 127.59 (p-C(Ph)), 128.11, 128.21 (m-, o-C(Ph)), 137.58 (i-C(Ph)). MS (EI): m/z = 342 (0.1, $(M-BnOH)^{+\cdot}$), 71 (100). MS (CI): m/z = 451 (0.1, $(M+H)^+$), 343 (100). $C_{27}H_{46}O_5$ (450.7): calcd. C: 71.95, H: 10.31; found C: 71.72, H: 10.38.

General lactonization procedure: With exclusion of moisture, a solution of $SnCl_4$ (A molar eq.) in dry CH_2Cl_2 (B ml) is carefully added dropwise and with cooling to a stirred solution of glycoside **1** (110 mmol) and trimethylsilyl azide (C molar eq.) in dry CH_2Cl_2 (D ml). Upon addition, evolution of nitrogen is observed which generally tapers off after ~ 30 min. Cooling is discontinued after addition of all $SnCl_4$, the yellow solution being allowed to warm to r.t.. Stirring is continued another 20-22 h at ambient temperature whereupon H_2O (300 ml) is carefully added and the mixture stirred vigorously. After dissipation of evolving gases (**caution: HN_3!**), ~ 15 min, hexanes (300 ml) is added and the organic layer separated, washed with H_2O (2 x 250 ml) and dried (Na_2SO_4). Removal of solvent *in vacuo* results in amber coloured oils which are purified by distillation or column chromatography (SiO_2, hexanes - ethyl acetate). Alternatively, the oil may be taken up in Et_2O or hexanes (~ 10 ml/g), extracted with NaOH (1N, 3 x, ~ 20 ml/g), acidified with the minimum amount of HCl (conc.) and reex-

tracted with the above solvent (2 x, ~ 20 ml/g). All lactones **9** may be purified in this extractive fashion with little compromise of product quality. All purified lactones **9** are colourless oily liquids.

2,3,4,6-Tetra-O-ethyl-D-gluconolactone **9a**: A = 2.40, B = 30, C = 2.50, D = 160. Yield 45% from glycoside **1a**[12] after distillation. $Bp._{0.25}$: 132-34°C. $[\alpha]_D^{20}$: + 93.2 (c = 1.9). IR (film): 1758 (s, ν-CO). ^{1}H NMR: 1.16 - 1.33 (m, 12H, 4 x CH_3), 3.45 - 3.89 (m, 12H, H-2, H-3, H-4, H-6, H-6', 7H of 4 x OCH_2CH_3), 3.93 (ABX_3-dq, 1H, $^2J_{A,B}$ = 9.3, $^3J_{A,X}$ = 7.1, OCH_2CH_3), 4.32 (dt, 1H, $^3J_{5,4}$ = 8.4, $^3J_{5,6}$ = 3.1, $^3J_{5,6'}$ = 2.7, H-5). ^{13}C NMR: 15.10 - 15.57 (4 x CH_3), 67.07, 67.22, 67.40, 67.74 (4 x OCH_2CH_3), 68.74 (C-6), 76.25, 78.19, 78.49, 81.64 (C-2 - C-5), 169.81 (C-1). MS (EI): m/z = 290 (5, M^+), 85 (100). $C_{14}H_{26}O_6$ (290.4): calcd. C: 57.91, H: 9.03; found C: 57.71, H: 8.98.

2,3,4,6-Tetra-O-ethyl-D-galactonolactone **9b**: A = 1.42, B = 70, C = 1.67, D = 330. Yield 61% from glycoside **1b** after distillation. $Bp._{0.3}$: 127-28°C. $[\alpha]_D^{20}$: + 90.9 (c = 2.0). IR (film): 1740 (s, ν-CO). ^{1}H NMR: 1.20, 1.21, 1.24, 1.25 (4 x t, 12H, ^3J = 7.1, 4 x CH_3), 3.47 - 3.77 (m, 9H, H-3, H-6, H-6', 6H of 3 x OCH_2CH_3), 3.98 (t, 1H, $^3J_{4,5}$ = 2.0, H-4), 4.03 (ABX_3-ddq, 2H, Δν = 62.0, $^2J_{A,B}$ = 9.1, $^3J_{A,X}$ = 7.0, 1 x OCH_2CH_3), 4.15 (d, 1H, $^3J_{2,3}$ = 9.4, H-2), 4.28 (ddd, 1H, $^3J_{5,6}$ = 5.5, $^3J_{5,6'}$ = 8.1, H-5). ^{13}C NMR: 15.12 - 15.56 (4 x CH_3), 66.29, 66.96, 67.79, 68.80, 69.02 (C-6, 4 x OCH_2CH_3), 72.96, 77.43, 77.78, 80.40 (C-2 - C-5), 170.52 (C-1). MS (EI): m/z = 290 (24, M^+), 85 (100). $C_{14}H_{26}O_6$ (290.4): calcd. C: 57.91, H: 9.03; found C: 57.85, H: 9.01.

2,3,4,6-Tetra-O-(3-methylbutyl)-D-galactonolactone **9c**: A = 1.42, B = 55, C = 1.67, D = 330. Yield 88% from glycoside **1c** after chromatography. $[\alpha]_D^{20}$: + 54.1 (c = 0.9). IR (film): 1740 (vs, ν-CO). ^{1}H NMR: 0.91 (m, 24H, 8 x CH_3), 1.48 (m, 8H, 4 x $OCH_2CH_2CH(CH_3)_2$), 1.71 (m, 4H, 4 x $OCH_2CH_2CH(CH_3)_2$), 3.40 - 3.70 (m, 9H, H-3, H-6, H-6', 6H of 4 x $OCH_2CH_2CH(CH_3)_2$), 3.91 (ABX_3-dq, 1H, $^2J_{A,B}$ = 9.0, $^3J_{A,X}$ = 6.7, $OCH_2CH_2CH(CH_3)_2$), 3.95 (dd, 1H, $^3J_{3,4}$ = 4.7, $^3J_{4,5}$ = 1.8, H-4), 4.10 (m, 2H, H-2, $OCH_2CH_2CH(CH_3)_2$), 4.27 (m, 1H, H-5). ^{13}C NMR: 22.46 - 22.68 (8 x CH_3), 24.79 -25.09 (4 x $OCH_2CH_2CH(CH_3)_2$), 38.45 - 38.97 (4 x $OCH_2CH_2CH(CH_3)_2$), 67.92, 69.32, 70.20, 71.64, 72.20 (C-6, 4 x $OCH_2CH_2CH(CH_3)_2$), 72.82, 77.29, 78.05, 80.84 (C-2 - C-5), 170.57 (C-1). MS (EI): m/z = 458 (1, M^+), 71 (100), 43 (99). $C_{26}H_{50}O_6$ (458.7): calcd. C: 68.07, H: 11.01; found C: 67.95, H: 11.05.

2,3,4,6-Tetra-O-ethyl-D-mannonolactone **9d**: A = 1.70, B = 30, C = 2.00, D = 160. Yield 48% from glycoside **1d** after distillation. $Bp_{0.25}$: 132-33°C. $[\alpha]_D^{20}$: + 45.8 (c = 2.3). IR (film): 1774 (vs, ν-CO). ^{1}H NMR: 1.18, 1.21, 1.23, 1.28 (4 x t, 12H, ^3J = 7.1, 4 x CH_3), 3.50 - 3.64 (m, 6H, H-4, 5H of 4 x OCH_2CH_3), 3.67 (*pseudo*-d, 2H, Δν = 4.4, H-6, H-6'), 3.72, 3.81 (2 x ABX_3-dq, 2H, $^2J_{A,B}$ = 9.7, $^3J_{A,X}$ = 7.1, 2H of 4 x OCH_2CH_3), 3.92 (dd, 1H, $^3J_{3,4}$ = 1.8, H-3), 3.96 (ABX_3-dq, 1H, $^2J_{A,B}$ = 8.9, $^3J_{A,X}$ = 7.1, OCH_2CH_3), 4.18 (m, 1H, H-5), 4.20 (d, 1H, $^3J_{2,3}$ = 2.7, H-2). ^{13}C NMR: 15.10 - 15.33 (4 x CH_3), 65.59, 66.79, 66.98, 67.08 (4 x OCH_2CH_3), 70.15 (C-6), 76.38, 76.54, 78.19, 78.68 (C-2 - C-5), 169.71 (C-1). MS (EI): m/z = 290 (6, M^+), 85 (100). $C_{14}H_{26}O_6$ (290.4): calcd. C: 57.91, H: 9.03; found C: 57.79, H: 8.99.

2,3,4-Tri-O-(3-methylbutyl)-L-arabinonolactone **9f**: A = 2.16, B = 65, C = 1.50, D = 320. Yield 15% from glycoside **1f** after chromatography, containing small amounts of carbohydrate impurities. IR (film): 1745 (s, ν-CO). ^{1}H NMR: 0.91 (m, 18H, 6 x CH_3), 1.51 (m, 6H, 3 x $OCH_2CH_2CH(CH_3)_2$), 1.73 (m, 3H, 3 x $OCH_2CH_2CH(CH_3)_2$), 3.30 - 3.80 (m, 6H, 3 x $OCH_2CH_2CH(CH_3)_2$), 3.89 (m, 1H, H-4), 4.02 (m, 1H, H-3), 4.07 (d, 1H, $^3J_{2,3}$ = 8.0, H-2), 4.13 (dd, 1H, $^2J_{5,5'}$ = 11.8, $^3J_{4,5'}$ = 2.4, H-5'), 4.37 (dd, 1H, $^3J_{4,5}$ = 4.3, H-5). ^{13}C NMR: 22.33 - 22.73 (6 x CH_3), 24.74 -25.06 (3 x $OCH_2CH_2CH(CH_3)_2$), 38.46 - 39.08 (3 x $OCH_2CH_2CH(CH_3)_2$), 67.46 (C-5), 68.87, 69.30, 71.64 (3 x $OCH_2CH_2CH(CH_3)_2$), 72.51, 76.71, 77.59 (C-2 - C-4), 170.14 (C-1). MS (EI): m/z = 358 (0.5, M^+), 71 (100), 43 (99). MS (CI): m/z = 359 (100, $(M+H)^+$). $C_{20}H_{38}O_5$ (358.6).

Ethyl-2,3,5-tri-O-ethyl-α-D-arabinofuranoside **10a**: This ring-contraction product present in the reaction mixtures of lactonizations involving **1a** and **1d** was formed in variable yields, depending on reaction conditions, typically less than 10%. It was not isolated and is characterized as its mixture with unreacted **1a** after extraction of **9a** from the lactonization mixture. ^{1}H NMR (only characteristic peaks): 4.08 (m, 1H, H-4), 4.97 (s (broad), 1H, H-1). ^{13}C NMR: 15.12 - 15.89 (4 x CH_3), 62.93, 65.47, 65.86, 66.90 (4 x OCH_2CH_3), 70.59 (C-5), 80.17, 84.32, 89.11 (C-2 - C-4), 105.98 (C-1). MS (EI): m/z = 217 (0.5, $(M\text{-}EtO^{\cdot})^+$), 129 (100). MS (CI): m/z = 263 (1, $(M+H)^+$), 217 (100). $C_{13}H_{26}O_5$ (262.4).

Ethyl-2,3,5-tri-O-ethyl-α-D-lyxofuranoside **10b**: Yield 5% from glycoside **1b** after distillation. $Bp_{.0.2}$: 110°C. $[\alpha]_D^{20}$: + 50.3 (c = 3.1). ^{1}H NMR: 1.22 (m, 12H, 4 x CH_3), 3.43 - 3.74 (m, 7H, 7H of 4 x OCH_2CH_3), 3.65 (*pseudo*-d, 2H, Δν = 1.0, H-5, H-5'), 3.78 (dd, 1H, $^3J_{2,3}$ = 4.7, H-2), 3.79 (ABX_3-dq, 1H, ^2J = 9.6, ^3J = 7.1, OCH_2CH_3), 4.09 (t, 1H, $^3J_{3,4}$ = 5.3, H-3), 4.29 (dt, 1H, $^3J_{4,5}$ = 6.9, $^3J_{4,5'}$ = 5.3, H-4), 5.04 (d, 1H, $^3J_{1,2}$ = 2.4, H-1). ^{13}C NMR: 15.20 - 15.43 (4 x CH_3), 63.63, 66.20, 66.74, 67.22 (4 x OCH_2CH_3), 69.97 (C-5), 78.17, 78.56, 83.21 (C-2 - C-4), 105.13 (C-1). MS (EI): m/z = 217 (1, $(M\text{-}EtO^{\cdot})^+$), 129 (100). MS (CI): m/z = 263 (24, $(M+H)^+$), 217 (100). $C_{13}H_{26}O_5$ (262.4): calcd. C: 59.52, H: 9.99; found C: 59.41, H: 9.93.

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