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Endocyclic Cleavage of Glycosides. VI. Substituent Effects of the Alkylative Endocyclic Cleavage of Glycosides.

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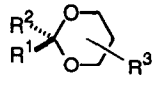
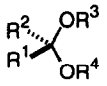
Abstract.: A number of pentopyranoside derivatives were treated with Me_3Al in order to investigate the influence of structural parameters on the methyl group transfer in the endocyclic alkylative cleavage reaction of these substrates. A cyclic CH···O hydrogen bonded model is suggested as an intermediate, which is used to explain the stereoselectivities for different substrates. In several cases the diastereoselectivities were better than 9:1. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

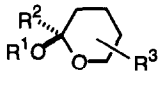
Lewis acid induced alkylative or reductive regio- and steroselective opening of acetals of type I and II has attracted considerable attention by several research groups.[1-7]



I

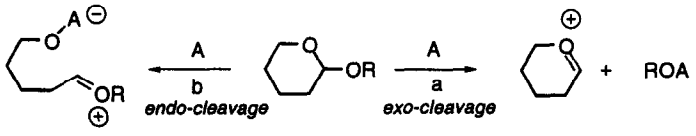


II



III

Glycosides, representing the third group of acetals (type III), have been mainly studied in connection with syntheses of new glycosidic bonds where the *exo*-C-O bond is cleaved selectively and a new aglycon is introduced at C-1, often with high stereoselectivity (Scheme 1, path a). This is the basis of the very successful areas of oligosaccharide[8] and C-glycoside synthesis.[9] The question of whether glycosides are cleaved via the *exo* or *endo* (Scheme 1, path b) routes by glycosidases is under continous debate.[10-13] In protic solvents there seems to be evidence for both modes of reaction.[14-16]



Scheme 1.

For general synthetic purposes it is of interest to introduce a new C-C bond at C-1 of pyranosides and furanosides either via *exo* or *endo* C-O-bond cleavage. While alkylative *exo*-cleavage reactions have been used frequently,[9] only a few alkylative *endo*-cleavage reactions have so far been reported[17-21] in addition to our own work.[22-27] Several other cases of *endo* cleavage of pyranosidic rings have been reported by Guindon

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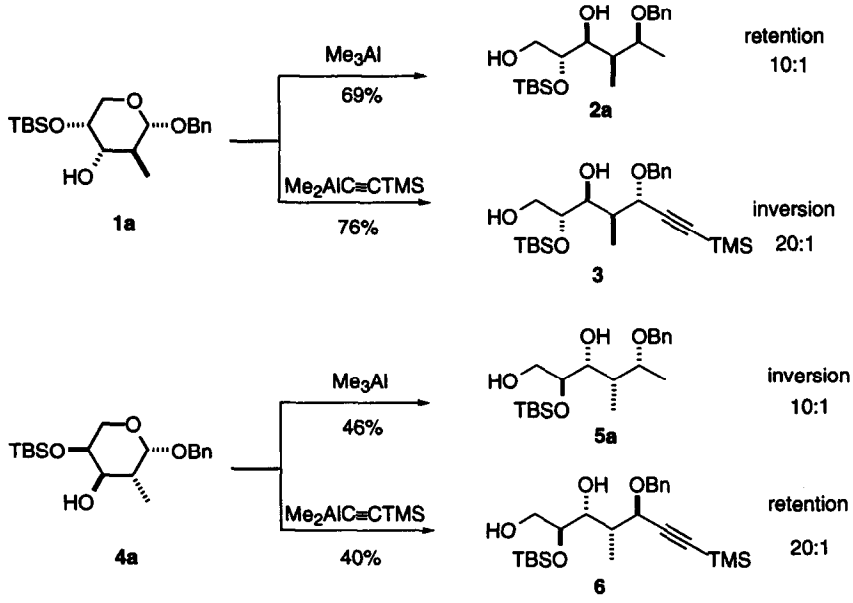
et al. but these examples did not directly result in the formation of new C-C-bonds.[28-30]

We previously found that benzyl pentopyranoside derivatives underwent stereoselective alkylative *endo*-cleavage on treatment with organoaluminium reagents.[22,23] Thus, trimethylaluminum converted compound **1** into the methylated major product **2a** with retention at C-1 (Scheme 2). Surprisingly, the acetylenic aluminum reagents $Me_2AlC{\equiv}CR$ gave *endo*-cleavage with *inversion* at C-1 (**3**). Even more surprising was the fact that the diastereomeric pentopyranoside **4a** gave the opposite result for both reagents i. e. inversion instead of retention in the first case (**5a**) and retention instead of inversion in the second case (**6**). Moreover, it initially seemed important to use derivatives having the 3-OH group unprotected for these ring openings to procede with reasonable yields and rates.[22]



Scheme 2.

This investigation was undertaken in order to gain a better understanding of the substituent effects including the structural requirements of the carbohydrate part using Me_3Al as the reagent.

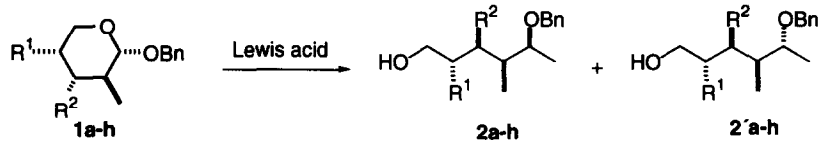
RESULTS

Coordinating solvents such as diethyl ether and THF drastically reduced the reactivity of the alane reagents resulting in very poor yields of ring-opening products.[22] Hexane and toluene were essentially equally good when used at about the same temperature (70 °C, table 1, entry 2 and 4), while the use of refluxing dichloromethane resulted in a significantly lower diastereoselectivity despite the lower reaction temperature (table 1, entry 5). Also the β-L-Ara derivative **4b** gave a lower selectivity in CH_2Cl_2 than in hexane (Scheme 3).

The somewhat lower yield and selectivity for toluene may be due to its capacity as a π-donor, which may alter the reagent by complex formation. Obviously, the temperature of refluxing toluene was too high, which

resulted in considerable degradation (table 1, entry 3). Thus, hexane was judged the best solvent and was used in the further experimentations.

Table 1. Alkylative Endocyclic cleavage of **1a-h**.



1a-h **2a-h** **2'a-h**

Entry	Sub.	R^1	R^2	Lewis acid (equiv..)	solvent/ Temp. (°C)	Time (h)[a]	2:2' (ret:inv)[b]	Isol. yield (%)
1	**1a**	OTBS	OH	Me_3Al(3)	hexane/ 69	1	92:8[c]	69
2	**1b**	OTIPS	OH	Me_3Al(3)	hexane/ 69	5	94:6[c]	62
3	**1b**	OTIPS	OH	Me_3Al(3)	toluene/ 110	5	90:10[c]	35
4	**1b**	OTIPS	OH	Me_3Al(3)	toluene/ 70	5	90:10	58
5	**1b**	OTIPS	OH	Me_3Al(3)	CH_2Cl_2/ 69	5	78:22[c]	62
6	**1b**	OTIPS	OH	Me_3Al(1)/Me_2AlCl(2)[d]	hexane/ 69	0.5	92:8[c]	80
7	**1c**	OH	OH	Me_3Al(3)	hexane/ 69	48	50:50	70[e]
8	**1d**	OH	OTBS	Me_3Al(3)	hexane/ 69	10	95:5	74
9	**1e**	OMe	OMe	Me_3Al(3)	hexane/ 69	24	55:45[f]	70
10	**1f**	H	OH	Me_3Al(3)	hexane/ 69	7	85:15	70
11	**1g**	OTBS	H	Me_3Al(3)	hexane/ 69	36	75:25[f]	52
12	**1h**	OTBS	OMe	Me_3Al(3)	hexane/ 69	10	60:40[f]	80
13	**1i**	OTBS	OTBS	Me_3Al(3)	hexane/ 69	24	—	0
14	**1j**	H	OTBS	Me_3Al(3)	hexane/ 69	60	91:9	37

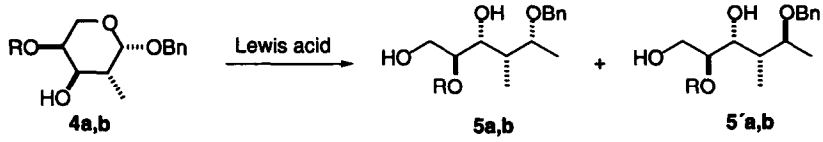
[a] Time at which all of the starting material was consumed. [b] Determined by ^1H NMR spectroscopy and capillary GLC. [c] Determined by ^1H NMR spectroscopy and capillary GLC of acetylated product. [d] 1 equiv. of Me_3Al was first added to the starting material followed by 2 equiv.. of the other noted Lewis acid. [e] Isolated as the triacetate. [f] Tentative assignment of diastereomers.

Previously, we used the *tert*-butyldimethylsilyl group (TBS) as OH-protection at O-4 of the pentopyranoside substrates (Scheme 2 and 3), but due to problems with unintentional cleavage of the TBS group we decided to test the triisopropylsilyl (TIPS) protection as well. The TIPS group is more sterically demanding than TBS and also more resistant towards cleavage.[31] As seen in Table 1, entries 1 and 2 the use of the TIPS group did not alter the diastereoselectivity or yield of the reaction seriously, although the reaction time had to be extended to five instead of one hour in refluxing hexane.

It should be possible to increase the reaction rate by the use of a stronger Lewis acid. Thus, first the free OH was converted into the correspondning dimethylaluminium alcoholate by reaction with one equivalent of Me3Al. Then two equivalents of the stronger Lewis acid Me_2AlCl was applied. Indeed, a much faster reaction was noted and also a better yield (table 1, entry 6). Also for the other diastereomer, the β-L-Ara derivative **4b**, similar results were obtained (Table 2, entry 3). The diastereomeric ratios (dr) were about the

same as when only Me_3Al was used. Thus, the TIPS protection at O-4 can be used in preference to the TBS group. The third equivalent of the Lewis acid was not absolutely necessary since an experiment with only two equivalents on **1a** also worked, although the reaction was slower and a slightly lower yield was obtained; 62% instead of 69%. It is not likely that the coordintion of Me_3Al to the oxygen of the silylether is involved, since Keck et al.[32] and Shambayati et al.[33] has pointed out that the Lewis basicity of such oxygens is quite low. Therefore it seems more likely that the influence of the 4-O-silyl group is mostly of steric origin.

Table 2. Alkylative Opening of **4a,b**.



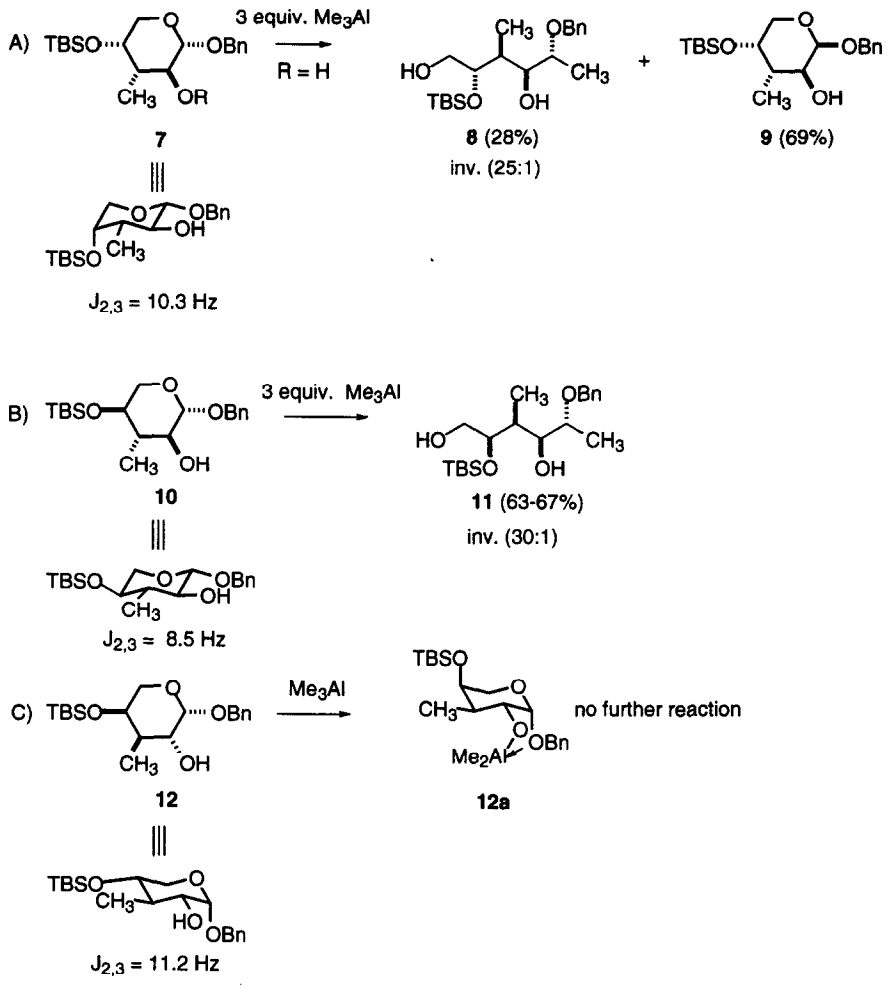
4a,b **5a,b** **5'a,b**

Entry	Sub.	R	Lewis acid (equiv.)	solvent	Temp. (°C)	Time (h)	5:5' (inv:ret)[b]	Isol. yield (%)
1	**4a**	TBS	Me_3Al(3)	hexane	69	22	91:9	46[22]
2	**4b**	TIPS	Me_3Al(3)	CH_2Cl_2	50	30	78:22	60
3	**4b**	TIPS	Me_3Al(1)/Me_2AlCl(2)	hexane	60	4	90:10	69

[a] 1 equivalent of Me_3Al was first added to starting material followed by 2 equiv.. of the other noted Lewis acid. [b] Determined by ^1H NMR spectroscopy.

Our earlier belief that a free 3-OH group was necessary for an efficient reaction could not be substatiated since the 3-OTBS derivative **1d** gave essentially the same selectivity and yield as **1a** (table 1, entry 8). Also the 3-deoxy derivative **1g** ring-opened in a fairly good yield and diastereoselectivity (entry 11). The importance of the protecting groups was, however, clearly manifested by the result of the initially non-protected derivative **1c**. In this case, the C-1 methylation was very slow and completely non-stereoselective, even though the yield was satisfactory (Table 1, Entry 7). Similar results were obtained for the 3-OMe/4-OMe and the 4-OTBS/3-OMe derivatives **1e** and **1h**, respectivley (Table 1, entries 9 and 12). Surprisingly, the 3,4-di-OTBS derivative **1i** was completety unreactive (Table 1, Entry 13). When the bulk at the 4-position was reduced as for the 4-deoxy derivative **1f** both selectivity and yield were quite high (Table 1, entry 10).

Ring opening was also observed for some 2-OH, 3-C-methyl derivatives (Scheme 3). Thus, as we previously reported a 28% yield of the C-1 methylated compound **8** was formed (inversion:retention 30:1) together with the anomerized product **9** (68%) on treatment of **7** with Me_3Al (Equation A).[22] Now, the importance of aluminium alcoholate formation was again manifested since the corresponding 2-OMe or 2-OTBS derivatives **7** (R = Me or TBS, respectively) were completely unreactive. Besides, also the stronger Lewis acid Me_2AlCl was ineffective. However, a good yield of the ring opening product **11** (inversion:retention 30:1) was obtained from the C-4 epimer **10** (Equation B). No reaction at all was noticed for the α-D-xylo derivative **12** (Equation C). It should be noted that for both **7** and **10** the major ring-opening products **8** and **11** were formed *via* inversion.



Scheme 3. Endocleavage experiments with the 2-OH compounds **7**, **10** and **12**. The coupling constants are literature data recorded in $CDCl_3$.[22]

DISCUSSION

The interpretation of the influence of the substitution and protecting group patterns on the reaction is not straight forward, but some aspects are discussed below. First, the most important coordination sites for the Lewis acid are at O5 and O1 even though coordination to other sites may also take place. Hitherto we have not observed that the rather weak Lewis acid Me_3Al caused exocleavage of neither α- nor β-glycosides. This is supported by the findings of both Fraser-Reid et al.[34] and Liras et al.[13] For α-glycosides endo-cleavage does not seem to take place and exo-cleavage requires rather strong Lewis acids. Both endo- and exocleavage may occur for β-glycosides but Liras et al.[13] showed that exocleavage has a higher activation energy than endocleavage for β-glycosides.

Semi-empirical calculations (PM3) of O5-coordinated complexes of **1a** showed that all structures had

elongated O5-C1 bonds (a) and contracted C1-O1 bonds (b) as compared to the corresponding parent conformers (Fig. 1). In this comparison the $^{1}C_4$ equatorially coordinated complex had the longest O5-C1 bond indicating its greater tendency to endocleavage. Shortening of bond length (b) indicates a stereoelectronic assistance from the exocyclic oxygen atom stabilising a partial positive charge at C-1. The axially coordinated complexes were of considerably higher energy and should therefore not be much populated. Similar results concerning the elongation of the O5-C1 bond were obtained for the anomeric derivative **4a** (Fig 2). However, here the lowest energy was obtained for the $^{4}C_1$ Me_3Al eq complex but the $^{1}C_4$ Me_3Al eq had the longest (a)-bond.

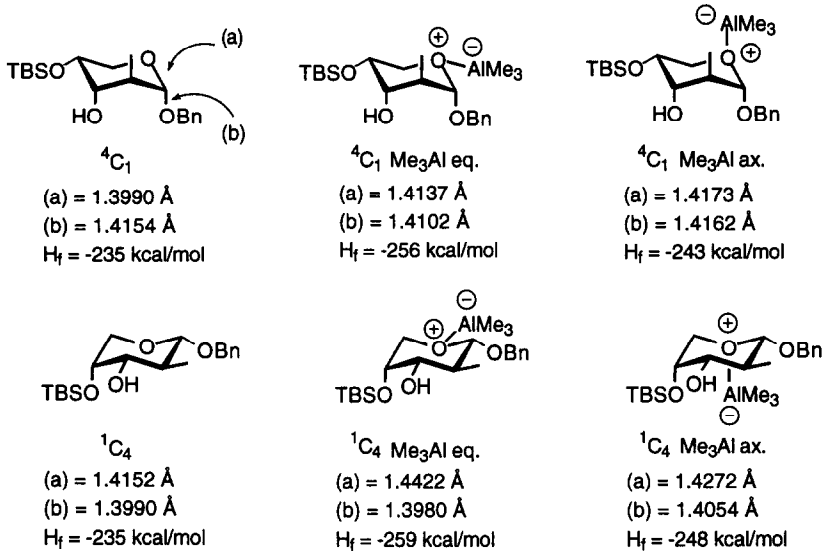


Figure 1. PM3 calculations of bond lengths and heats of formation for Me_3Al associated benzyl pentopyranoside complexes of **1a**.

According to NMR analysis, the major conformer of **4a** had an axial glycosidic bond, while the equilibrium mixture of **1a** had more of the chair conformation adopting an equatorial glycosidic bond. The discussion above indicates that an endocyclic cleavage should be favoured for substrates having an equatorial glycosidic bond. In line with this reasoning is the fact that **1a** reacted 22 times faster than **4a** (table 1 and scheme 4).

Compared to the non-complexed glycoside, the coordination of Me_3Al to **1a** in toluene resulted in downfield ^{1}H NMR chemical shift changes both for H1 ($\Delta\delta$ 0.43 ppm) and for $H5_b$ ($\Delta\delta$ 0.32 ppm), which indicated that at least some of the coordination was at O5 (Table 3). Due to the aluminate formation with O3 also the signal for H3 moved 0.95 ppm downfield.

Transfer of the methyl group most likely occurs intramolecularly from coordinated Me_3Al since the nucleophilicity of a methyl group of the resulting ate-complex is regarded to be higher than for both noncoordinated Me_3Al and a dimethylaluminium alcoxide formed in cases where free hydroxyl groups are available in the starting material.[35] The inertness of **1i** may then be due to steric hindrance by the two large TBS groups thus hindering the approach of the dimeric Me_3Al to O5.

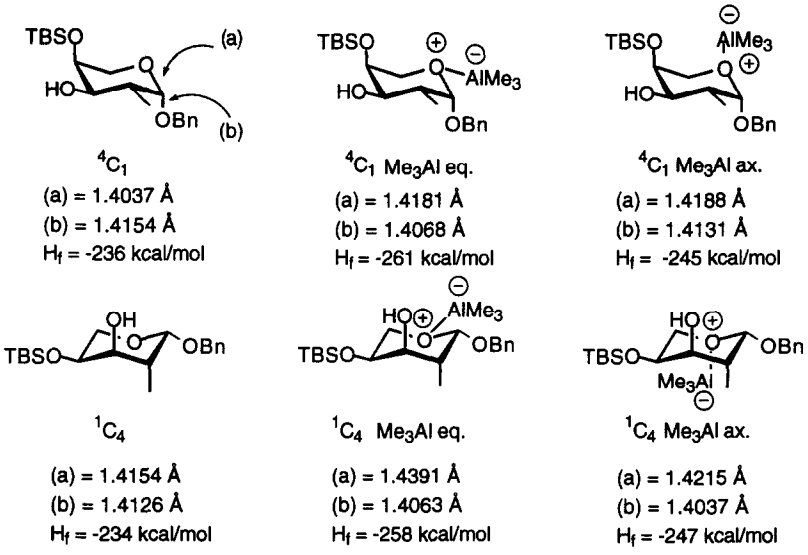


Figure 2. PM3 calculations of bond lengths and heats of formation for Me_3Al associated benzyl pentopyranoside complexes of **4a**.

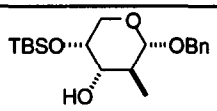
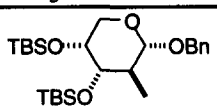
Indeed, the NMR spectrum of **1i** in toluene was only slighty affected by the presence of 1 or 2 equivalents of Me_3Al, which indicated that there was not a strong interaction between these molecules. A further contribution to the inertness of **1i** may be due to an unfavourable ring conformation. Even if the details were not analyzed it is apparent from the ^1H NMR coupling constants, in particular J_{23}, that **1a** and **1i** have different ring conformations.

Computations performed in order to clarify the origin of the selectivity implied that a seven-membered CH···O hydrogen-bonded intermediate **13a-d** was formed prior to the methyl transfer.[25,36] Electrostatic interactions including the CH···O/C···HO hydrogen bonding should contribute to the stabilisation of **13a-d**. Related hydrogen bonds are discussed in recent papers by Corey et al.[37-40]

Since an equatorial glycosidic bond is necessary for endocleavage, **1a** and **ent-4a** must have different ring conformations i. e. $^1C_4$ and $^4C_1$, respectively. But both **1a** and **ent-4a** gave the same products with the same dr, which strongly indicated that the initially formed intermediates of different geometries relax to one and the same intermediate, or at least to a system that allows interconversion of the different conformers such as **13a-d** (Scheme 4).

It seemed reasonable to assume that the bulk of the 2-C methyl group would have a dominating directing effect on the nucleophilic attack at the C-1 reaction center and that the diastereoselectivity would be very similar for all substrates shown in Table 1. Obviously, this was not the case, which may be explained by the shift in the equilibrium between **13a** and **13b** depending on the substitutents in the ring. Whether Me_3Al coordinates equatorially or axially was not possible to detect experimentally, but it seems unlikely that the axial arrangements **13d** and **13c** contribute significantly to the equilibrium due to 1,3-diaxial repulsions. Thus, in **13a** the 2-C methyl group is located close to the plane of the oxocarbenium ion unit and therefore would have only little influence on the face-selectivity of the nucleophile. On the other hand the axial methyl in **13b** would strongly hinder the attack from above the plane.

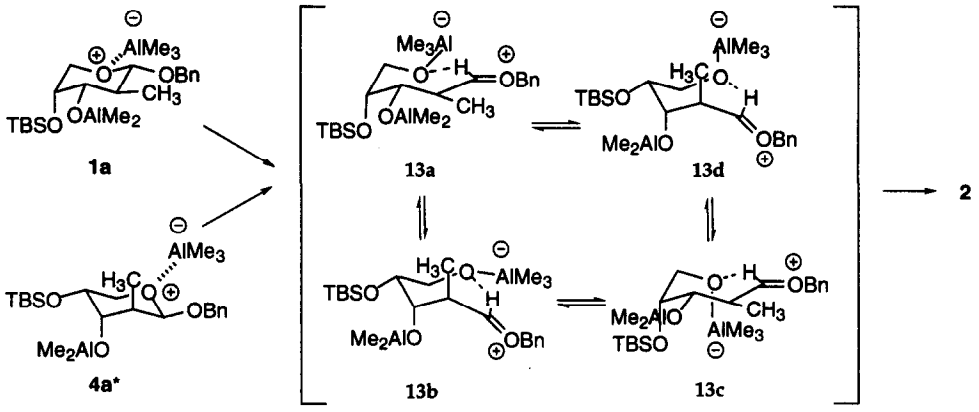
Table 3. Selected ^{1}H NMR data of **1a** and **1i** in the absence and presence of Me_3Al.

	 **1a**			 **1i**	
ppm/Hz		1 eq.Me_3Al	2 eq. Me_3Al		1-2 eq. Me_3Al
δ_{H1}/J_{12}	3.96/6.7	4.19/4.1	4.39/bs	4.06/6.7	4.17/5.8
δ_{H2}/J_{23}	2.05/8.8	-	-	2.35/11.9	2.32/7.9
δ_{H3}/J_{34}	3.14/3.4	4.07/m	4.07/m	3.24/2.7	3.28/2.5
δ_{H4}	3.56	3.80	3.80	3.62	3.65
δ_{H5a}/J_{45a}	3.84/4.2	4.07/-	3.84/-	3.89/4.2	3.95/ 4.9
δ_{H5b}/J_{45b}	3.10/2.3	3.20/-	3.42/-	3.14/1.7	3.21/ ca 1
O-CH_2-Ph	4.77, 4.40	4.74, 4.45	4.78, 4.47	4.83, 4.47	4.81, 4.47

The diol derivative **1c** gave a quite high yield of ring opening products but with no diastereoselectivity at all (Table 1, entry 7), which shows that the influence of the 2-C-methyl group vanishes completely. In this case it could be argued that a cyclic alanate was formed in analogy with other 1,2-diols,[41] which may force the ring to attain a conformation where the methyl group is placed almost in the plane of the oxocarbenium ion. However, NMR spectral evidence of a cyclic alanate could not be obtained due to the formation of insoluble material on mixing Me_3Al and **1c**, indicating the formation of a gel-like polymer.

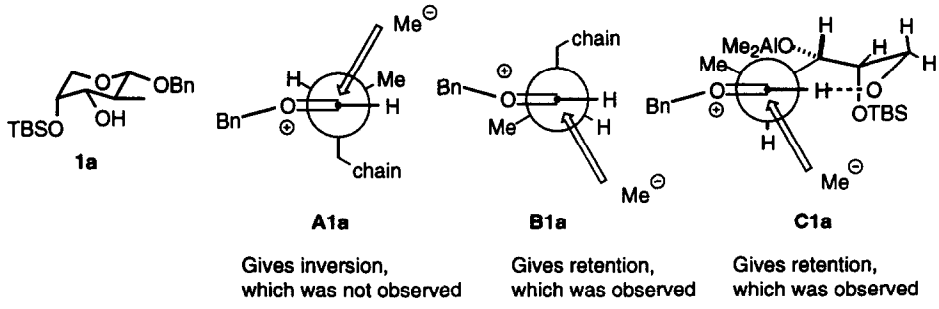
The selectivity was lost or drastically reduced also when the 3-OH group was blocked as a methyl ether as shown for **1e** and **1h** (Table 1, Entry 9 and 12). It is possible that these compounds formed intermediates analogous to **13** and that their geometries are close to that of **13a** i. e. where the 2-C-methyl group has little or no influence on the selectivity. Even if we have not analyzed the situation in detail a further contributing factor for the low stereoselectivity found for **1e** and **1h** may also be due to the presence of an extra coordination site as compared to **1a**, thus making available alternative ring conformations and competing pathways for the methyl group transfer. Despite that the all-equatorial substituent pattern for **1j** should make it an ideal candidate for the endocleavage reaction, its reaction was very slow. Also the rate of the all equatorial 4-epimer of **1a** was about six times slower than for **1a**. This higher energy of activation may originate from a lower ground state energy than for most of the other substrates.

When the substituents of the 2- and 3-positions were reversed i. e. as in the 3-C-methyl derivative **7** (Scheme 3) the ring opening occured to some extent, but the major reaction was anomerisation. Since Me_3Al is a too weak Lewis acid to induce exocleavage we believe that the anomerisation is a result of endocleavage followed by chelate-driven ring closure to give the non-reactive axial anomer **9** ($J_{1,2}$ = 3.7 Hz). Compound **10** would not directly form a favourable chelate and should behave essentially as **7**. But in contrast to **7**, the ring opening of **10** dominated effectively over the anomerisation to give a quite useful yield of **11**. The α-L-xylo derivative **12** was inert towards Me_3Al, which was not unexpected since NMR data indicated that this compound was mainly in the $^4C_1$ conformation having an axial glycosidic bond ($J_{2,3}$ 11.2 Hz and $J_{1,2}$ 3.7 Hz). Moreover, the possibility to form a 1,2-cis tetracoordinated chelate **12a** (Scheme 3)[21,42,43] upon reaction with Me_3Al would prevent ring flip to the more reactive conformer having an equatorial glycosidic bond.



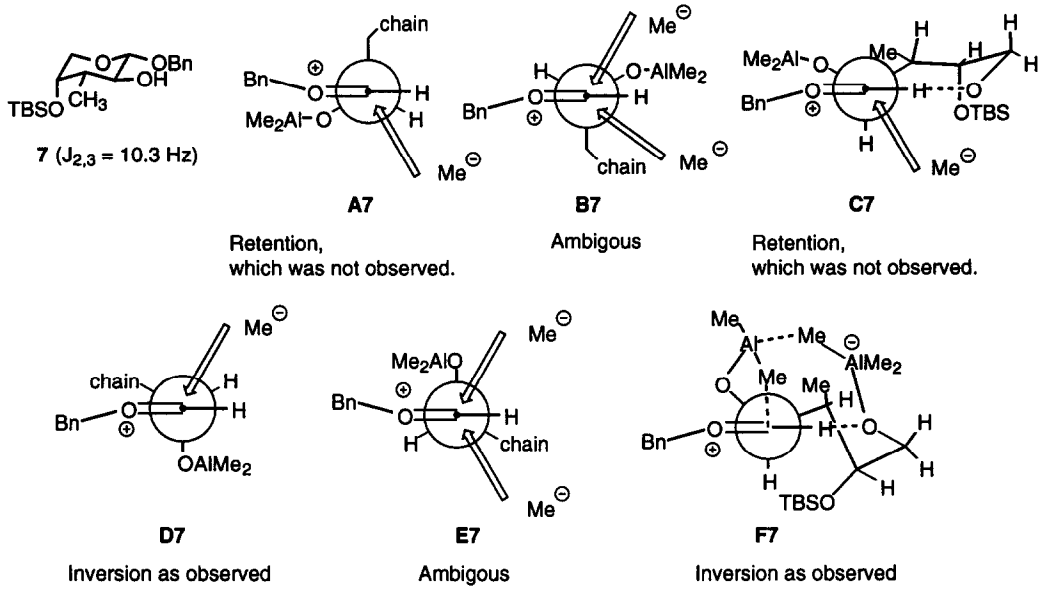
Scheme 4. Prototype mechanism for the alkylative endocyclic ring cleavage.

In an open chain situation the methyl transfer by nucleophilic attack on the oxocarbenium center would be governed by the Felkin-Ahn model[44] in the 2-C-Me compounds, and the Heathcock model[44] in the 2-OH compounds. In both cases the free OH-groups are converted into the corresponding O-$AlMe_2$ derivatives under the reaction conditions. The aluminate group has no possibility to form a chelate with the benzyloxocarbenium center, thus the Cram chelate model should not apply. For the 2-C-Me compound **1a** the Felkin-Ahn model **B1a** (Scheme 5) predicts the same major stereoisomer as the cyclic hydrogen bonded model **C1a** as shown in Scheme 5. However, the selectivity effects of the groups at C3 and C4 are not directly accounted for by **B1a**. Thus, while **1a** gave a better than 10:1 diastereoselectivity the C4-epimer gave only 3:2,[22] the 4-deoxy compound **1f** 8:1, and the diol **1c**, having the same configuration as **1a**, was completely unselective (1:1, entry 7). Even though we have not made rigorous analysis of the ring puckering of the cyclic hydrogen bonded model, it seems better suited for explaining the "remote-group" effect. In a linear outstreched conformation of the carbon chain the C3 and C4 substituents are rather distant form the reaction center, while the cyclic hydrogen bonded model not only brings them closer but would also rigidify the whole system.



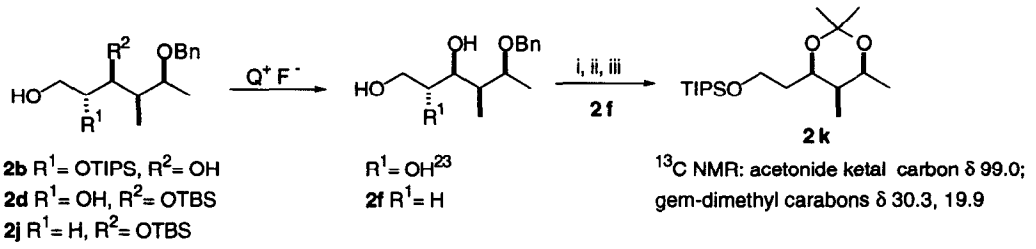
Scheme 5. The Felkin-Ahn and cyclic model analysis of **1a**. For simplicity the methyl nucleophile is depicted as a methyl anion instead of an ate-complex of Me_3Al.

The cyclic hydrogen bonded model did not give the right stereochemical prediction when applied to the 2-OH cases **7** and **10** (Scheme 6). Here, inversion was observed but both the hydrogen bonded model **C7** and the best FA-arrangement **A7** would lead to retention. The other FA-arragement **B7** should force the nucleophile to attack from the less favourable direction and is therefore ambigous. On the other hand, the open chain Heathcock methoxy model **D7** does explain the results but the other alternative **E7** allows an ambigous interpretation as seen in Scheme 6. However, introduction of a methyl-bridged hydrogen bonded model **F7** (Scheme 6) would help to better explain the very high diastereoselectivities obtained for **7** and **10**. This model was found by PM3 calculations of an initial geometry of the hydrogen bonded intermediate originating from **7**, in which the bridging methyl group between the aluminium atoms was already present. The calculations resulted in the positioning of one of the methyl groups of the 2-$OAlMe_2$ group directly above C1; an ideal location for a high selectivity in the methyl transfer step.



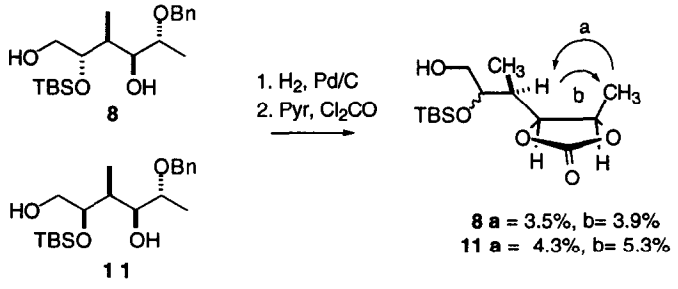
Scheme 6. The Felkin-Ahn analysis (**A7-C7**), the Heathcock methoxy model (**D7, E7**) and the hydrogen bonded methyl-bridged model **F7** of the 2-OH system **7**. Inversion was observed. A similar analysis would hold for **10**.

Structure determination of compounds **2b, 2d, 2f, 2j, 8** *and* **11**. The stereochemical outcome of the methyl-addition reactions of the 3-OH derivative was determined by chemical correlation or by ^{13}C NMR spectroscopy of the corresponding 1,3-acetonides (Scheme 7).[45-47] The conformational differences between the syn (chair) and anti (twist boat) 1,3-diol acetonides result in significantly different ^{13}C NMR chemical shifts of the ketal carbon and the associated methyl substituents. In general, the *syn* isomers display carbon resonances for the acetonide methyl groups at 30 and 19 ppm and for the ketal carbon below 100 ppm, while the *anti* isomers have methyl resonances in the range 24-26 ppm and the ketal carbon above 100 ppm.



Scheme 7. Synthesis of cyclic acetonides for structure determination of the major product in Table 1. i) TIPSCl, imidazole; ii)H_2, Pd/C; iii) 2,2-dimethoxypropane, H^+.

The stereochemical outcome of the methyl-addition reactions on the 2-OH derivative **8** and **11** was determined by ^1H NMR NOE difference spectroscopy of the corresponding 4,5-cyclic carbonate derivatives as shown in Scheme 8.[48] The cis realationship between the chain and the C-5 methyl group was clearly shown by the NOE enhancements as indicated by the arrows in **8a** ans **11a**.



Scheme 8. Cyclic carbonate formation and structure determination by NOE-difference spectroscopy.

EXPERIMENTAL

Column chromatography separations were performed by using Merck SiO_2 60Å (0.035-0.070 mm) silica gel with ethyl acetate/heptane (E/H) mixtures as eluents. TLC analyses were made on Merck SiO_2 60 F254 precoated glass plates and the spots were visualized by charring with a solution of phosphomolybdic acid (25g), $Ce(SO_4)_2.4\ H_2O$ (10g), conc. H_2SO_4 (60 ml) in H_2O (940 ml). NMR spectra were recorded in $CDCl_3$ at 21 °C (^1H) 400 MHz, $CHCl_3$ δ 7.27 and (^{13}C) 100 MHz, $CHCl_3$ δ 77.2). GLC analyses were performed with DBwax (J&W Scientific) capillary column (30 m, 0.25 mm i.d., 0.25 μm stationary phase). Melting points are given uncorrected. All reactions were carried out in oven-dried glassware equipped with rubber septa and under an argon atmosphere. The organometallic reagents were transferred by dried, argon-flushed syringes. Heptane was distilled from sodium and hexane was distilled from CaH_2 and stored over 4Å molecular sieves. Ethyl acetate was distilled immediately before use. Me_3Al (2.0M in hexane; Aldrich) and Me_2AlCl (1.0M in hexane; Aldrich) were used as delivered. Substrates **1a**, **4a**, **7**, **8**[22] and **10** were prepared according to the litterature procedures.[49] Na_2SO_4 was used as drying agent throughout unless otherwise

stated.

General Method for the pyranosidic ring-opening reactions (Table 1 and 2). The Lewis acid was added to the substrate (0.2 M in hexane) at room temperature. After 10 min, the reaction mixtures were treated as indicated below for each experiment, cooled to 0 °C, and worked up as follows: the reaction mixture was added with vigorous stirring into cold aqueous ≈2 M solution of NH_4Cl (adjusted to pH ≈8 with 2 M NH_4OH). The solid was filtered off and thoroughly washed with ethyl acetate, and the combined organic phases were washed with water and brine followed by drying, and removal of the solvent under reduced pressure.

Reaction conditions for Table 1 (entry 6) and Table 2 (entry 3): The substrate (0.2 M in hexane) was treated with Me_3Al (1.0 equiv., 2.0 M in hexane) at room temperature. After 5 min Me_2AlCl (1 M in hexane) was added, and after another 10 min, the reaction mixture was heated and stirred for the time indicated in each experiment, cooled to 0 °C, and worked up as described above.

Standard work-up procedure: The reaction mixture was poured into ice-water and extracted with ethyl acetate. The collected organic extracts were washed sequentially with aqueous saturated NH_4Cl, water and brine followed by drying and removal of the solvent under reduced pressure. The residue was then treated as described for the actual case.

Acetylation: The alcohol was added to a mixture of acetic anhydride (2 equiv.), pyridine (2 equiv.) and 4-pyrrolidinopyridine (0.1 equiv.) in dry CH_2Cl_2 at room temperature (rt) under an argon atmosphere. The resulting mixture was stirred at rt for 24 h and then worked up as follows: sequential washing with HCl (0.1 M), aqueous sat $NaHCO_3$, water, and brine followed by drying ($MgSO_4$), and removal of the solvent under reduced pressure. The diastereomeric purity was determined from ^1H NMR integrals and/or from GLC analyses. The NMR data refer to the major diastereomers unless otherwise indicated.

Benzyl 2,3-anhydro-4-*O*-(triisopropylsilyl)-α-D-ribopyranoside. Benzyl 2,3-anhydro-α-D-ribopyranoside[49] (5.00 g, 22.5 mmol) was added in portions to a mixture of triisopropyl chlorosilane (5.73 ml, 27.0 mmol) and imidazole (3.80 g, 56.0 mmol) in DMF (15 ml, dried over 4-Å moleculare sieves) at 40 °C. The mixture was stirred for 4h and then cooled to ambient temperature, whereafter dichloromethane was added and the solution was washed with aqueous HCl (1M), saturated aqueous $NaHCO_3$, and water, dried and concentrated under reduced pressure. Column chromatography (E/H, 1:15) of the residue gave the title compound (oil, 8.10 g, 95 %): (E/H 1:3, R_f 0.76); $[\alpha]_D^{20}$= +90 (c 2.22, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.93 (d, 1H, J =3.0 Hz), 4.81, 4.59 (AB q, each 1H, $J_{A,B}$ = 12.3 Hz), 4.22 (m, 1H), 3.71 3.37 (d AB q, each 1H, $J_{A,B}$ = 10.3 Hz, J = 10.2, 4.2 Hz), 3.44 (m, 2H), 1.09 (bs, 21H); ^{13}C NMR ($CDCl_3$) δ 137.7, 128.6, 128.3, 128.0, 91.7, 69.3, 66.5, 59.9, 54.7, 53.7, 18.2, 12.5; HRMS (CI-CH_4) Calc. for $C_{21}H_{35}O_4Si$ (M+1): 379.2305, found 379.2306.

Benzyl 2-deoxy-2-*C*-methyl-4-*O*-(triisopropylsilyl)-α-D-arabinopyranoside (1b) and Benzyl 3-Deoxy-3-*C*-methyl-4-*O*-(triisopropylsilyl)-α-D-xylopyranoside. Ethereal MeLi (1.60 M, 29.1 ml, 46.5 mmol) was slowly added to Me_3Al (11.6 ml, 23.2 mmol) at room temperature. After 10 min, hexane (100 ml) followed by benzyl 2,3-anhydro-4-*O*-(triisopropylsilyl)-α-D-ribopyranoside (8.0 g, 21.2 mmol) dissolved in hexane (100 ml) were added. The resulting solution was refluxed for 4 h, cooled (0 °C), diluted with diethyl ether, injected into a rapidly stirred cold (0 °C) aqueous solution of NH_4Cl (~2 M, 450 ml, adjusted to ~pH 8 with 2 M NH_4OH), and then worked up as described under General Methods. Column chromatographic separation

(E/H 1:20) yielded the two title compounds: **1b** (oil, 4.0 g, 48 %), E/H 1:3, Rf 0.52; $[\alpha]_D^{20}$= +52 (c 2.26, $CHCl_3$); IR(neat) 3500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.83, 4.54 (AB q, each 1H, $J_{A,B}$ = 12.2 Hz), 4.31 (d, 1H, *J* = 4.4 Hz), 3.98 (m, 2H), 3.50 (m, 2H), 2.66 (d, 1H, *J* = 8.3 Hz), 2.12 (m, 1H), 1.10 (bs, 21H), 1.06 (d, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 137.8, 128.6, 128.1, 127.9, 101.8, 73.5, 69.7, 67.3, 62.8, 39.4, 18.2, 14.1, 12.6; HRMS (CI-CH_4) Calc. for $C_{22}H_{39}O_4Si$ (M+1): 395.2617, found 395.2619; and **benzyl 3-deoxy-3-*C*-methyl-4-*O*-(triisopropylsilyl)-α-D-xylopyranoside** (oil, 1.5 g, 18%): (E/H, 1:3, Rf 0.50); $[\alpha]_D^{20}$= +71 (c 1.69, $CHCl_3$); IR(neat) 3430 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.82 (d, 1H, *J* =3.8 Hz), 4.81, 4.52 (AB q, each 1H, $J_{A,B}$ = 11.7 Hz), 3.65-3.50 (m, 3H), 3.25 (m, 1H), 1.82 (d, 1H, *J* =8.5 Hz), 1.79 (m, 1H), 1.17 (d, 3H, *J* = 6.5 Hz), 1.07 (bs 21H); ^{13}C NMR ($CDCl_3$) δ 137.6, 128.7, 128.2, 128.1, 96.9, 72.9, 71.8, 69.6, 64.1, 42.2, 18.3, 14.3, 12.9; HRMS (CI-CH_4) Calc. for $C_{22}H_{39}O_4Si$ (M+1): 395.2617, found 395.2607.

Benzyl 2-deoxy-2-*C*-methyl-α-D-arabinopyranoside (1c). Tetrabutylammoniumfluoride (1.1 g, 3.4 mmol) was added to a solution of compound **1a** (1.0 g, 2.8 mmol) in THF (25 ml) at room temperature under an argon atmosphere. The resulting solution was stirred at rt for 4 h followed by standard work-up. The residue was column chromatographed (E/H 2:1) to give **1c** (648 mg, 95%) as a white solid: (E/H 2:1, Rf 0.14); mp 137 °C; $[\alpha]_D^{20}$= +51 (c 0.88, EtOH); ^1H NMR (CD_3OD) δ 7.35 (m, 5H), 4.83, 4.55 (AB q, each 1H, $J_{A,B}$ = 11.8 Hz), 4.15 (d, 1H, *J* = 8.0 Hz), 3.94, 3.55 (d AB q, each 1H, $J_{A,B}$ = 12.5 Hz, *J* = 3.3 , 1.6 Hz), 3.66 (m, 1H), 3.29 (m, 1H), 1.90 (m, 1H), 1.03 (d, 3H, *J* = 6.7 Hz); ^{13}C NMR (CD_3OD) δ 139.9, 129.5, 129.2, 128.6, 105.4, 74.9, 71.6, 68.7, 67.5, 39.8, 13.0; HRMS (CI-CH_4) Calc. for $C_{13}H_{19}O_4$ (M+1): 239.1283, found 239.1281.

Benzyl 2-deoxy-2-*C*-methyl-3-*O*-(*tert*-butyldimethylsilyl)-α-D-arabinopyranoside (1d). NaH (60% in oil, 250 mg, 6.25 mmol) and a catalytic amount of imidazole was added to a solution of compound **1a** (1.0 g, 2.8 mmol) in THF (35 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred ar rt for 2h and then cooled to 0 °C, whereafter water (5 ml) was slowly added in order to destroy remaining NaH. Following standard work-up the residue was column chromatographed (E/H 1:10) to give **1a** (450 mg, 45%) as a syrup and **1d** (550 mg, 55%) as a syrup. **1a**: (H/E 3:1, Rf 0.52); **1d**: (H/E 3:1, Rf 0.43); $[\alpha]_D^{20}$= +38 (c 2.19, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.89, 4.57 (AB q, each 1H, $J_{A,B}$ = 12.0 Hz), 4.12, 3.48 (d AB q, each 1H, $J_{A,B}$ = 12.7 Hz, *J*= 1.6, 2.7 Hz), 4.09 (d, 1H, *J* = 7.9 Hz), 3.65 (m, 1H), 3.43 (dd, 1H, *J* = 9.8; 3.5 Hz), 2.50 (bs, 1H), 2.00 (m, 1H), 1.01 (d, 3H, *J* = 6.7 Hz), 0.93 (bs, 9H), 0.12, 0.11 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 138.1, 128.5, 128.1, 127.8, 103.2, 75.2, 70.1, 68.0, 65.2, 38.9, 25.9, 18.2, 13.1, -4.2, -4.5; HRMS (CI-CH_4) Calc. for $C_{19}H_{33}O_4Si$ (M+1): 353.2148, found 353.2140.

Benzyl 2-deoxy-2-*C*-methyl-3,4-di-*O*-methyl-α-D-arabinopyranoside (1e). Iodomethane (0.28 ml, 4.5 mmol) was added to a mixture of **1c** (350 mg, 1.47 mmol) and NaH (80% i oil, 130 mg, 4.33 mmol) in THF (10 ml) at 0 °C. The resulting mixture was stirred at rt for 15 h and then cooled to 0 °C, whereafter water (2 ml) was slowly added in order to destroy remaining NaH. Standard work-up gave a residue, which was column chromatographed (E/H 2:1) to give **1e** (320 mg, 80%) as an oil: (E/H 2.1, Rf 0.38); $[\alpha]_D^{20}$= +22 (c 5.00, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.90, 4.57 (AB q, each 1H, $J_{A,B}$ = 12.1 Hz), 4.23, 3.30 (d

AB q, each 1H, $J_{A,B}$ = 12.9 Hz, J = 2.7 , 1.3 Hz), 4.08 (d, 1H, J = 8.1 Hz), 3.50 (m, 1H), 3.49, 3.41 (s, each 3H), 2.91 (dd, 1H, J = 3.1, 10.5 Hz), 2.11 (m, 1H), 1.04 (d, 3H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 137.9, 128.4, 128.0, 127.7, 103.8, 83.0, 72.6, 70.2, 62.4, 57.4, 56.9, 37.6, 12.7; MS (FAB-K) 305 (M^+ +39). MS (FAB-Na) 289 (M^++23); HRMS (CI-CH_4) Calc. for $C_{15}H_{21}O_4$ (M-1): 265.1439, found 265.1448.

Benzyl 2,4-di-deoxy-2-*C*-methyl-α-D-arabinopyranoside (1f). Tetrabutylammoniumfluoride (0.61 g, 1.9 mmol) was added to a solution of compound **1j** (0.50 g, 1.5 mmol) in THF (10 ml) at room temperature under an argon atmosphere. The resulting solution was srirred at rt for 3 h, whereafter the mixture was poured into ice-water (10 ml) and subjected to standard work-up. The residue was column chromatographed (E/H 1:1) to give **1f** (290 mg, 89%) as a white solid: (E/H 1:1, R_f 0.18); mp 81 °C; $[\alpha]_D^{20}$ = +115 (c 0.76, $CHCl_3$); IR(KBr) 3370 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.82, 4.52 (AB q, each 1H, $J_{A,B}$ = 11.8 Hz), 4.44 (d, 1H, J = 3.9 Hz), 4.07 (m, 1H), 3.55 (m, 2H), 3.11 (d, 1H, J = 8.3 Hz), 2.00 (m, 1H), 1.85 (m, 1H), 1.58 (m, 1H) 1.06 (d, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 137.6, 128.7, 128.1, 128.0, 102.3, 70.3, 69.9, 57.6, 40.8, 30.6, 14.3; HRMS (FAB-Na) Calc. for $C_{13}H_{18}O_3Na$ (M^++23): 245.1154, found 245.1152; HRMS (CI-CH_4) Calc. for $C_{13}H_{17}O_3$ (M-1): 221.1178, found 221.1195.

Benzyl 2,3-di-deoxy-2-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-α-D-arabinopyranoside (1g). 1,1′-Thiocarbonyldiimidazole (1.0 g, 5.7 mmol) was added to a mixture of compound **1a** (1.0 g, 2.8 mmol) in benzene (30 ml) at room temperature under an argon atmosphere. The resulting mixture was stirred at reflux for 4h and then concentrated under reduced pressure. The residue was filtered through a short plug of silica to give an pale yellow oil. $HSnBu_3$ (1.5 ml, 5.7 mmol) was added droppwise to a mixture of this yellow oil and a catalytic amount of azobis(isobutyronitrile) in toluene (70 ml) at reflux under an argon atmosphere. The resulting solution was stirred at reflux temperature for 6h and then cooled to ambient temperature, whereafter it was concentrated under reduced pressure. The residue was column chromatographed (H/E 1:0 → 10:1) to give **1g** (770 mg, 82%) as a syrup: (H/E 3:1, R_f 0.49); $[\alpha]_D^{20}$ = +78(c 8.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.81, 4.52 (AB q, each 1H, $J_{A,B}$ = 12.1 Hz), 4.32 (d, 1H, J =3.8 Hz), 3.89 (m, 1H) 3.66, 3.55 (d AB q, each 1H, $J_{A,B}$ = 11.0 Hz, J = 7.2 , 4.1 Hz), 2.09 (m, 1H), 1.89 (m, 1H), 1.53 (m, 1H), 1.03 (d, 3H, J = 7.1 Hz), 0.91 (bs, 9H), 0.08 (bs, 6H); ^{13}C NMR ($CDCl_3$) δ 138.4, 128.5, 128.0, 127.7, 101.9, 69.2, 67.1, 64.0, 36.4, 32.4, 26.1, 18.4, 17.2, -4.5, -4.5; HRMS (CI-CH_4) Calc. for $C_{19}H_{33}O_3Si$ (M+1): 337.2199, found 337.2196.

Benzyl 2-deoxy-2-*C*-methyl-3-*O*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-α-D-arabinopyranoside (1h). Iodomethane (0.27 ml, 4.3 mmol) was added to a mixture of compound **1a** (0.50 g, 1.4 mmol) and NaH (80% in oil, 0.13 g, 4.3 mmol) in THF (7 ml) at 0 °C. The resulting mixture was stirred at rt for 24 h and then worked up as described for **1e**. Column chromatography (E/H 1:10) gave **1h** (450 mg, 86%) as an oil: (E/H, 1:3, R_f 0.62); $[\alpha]_D^{20}$ = +35 (c 2.26, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.89, 4.57 (AB q, each 1H, $J_{A,B}$ = 12.2 Hz), 4.14, 3.33 (d AB q, each 1H, $J_{A,B}$ = 12.6 Hz, J = 2.6, 1.2 Hz), 4.08 (d, 1H, J = 8.1 Hz), 3.49 (s, 3H), 3.40 (dd, 1H, J = 10.3 , 3.0 Hz), 3.23 (bs, 1H) 2.12 (m, 1H), 1.00 (d, 3H, J = 6.7 Hz), 0.93 (bs, 9H), 0.10, 0.08 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 138.2, 128.4, 128.1, 127.7, 103.8, 77.8, 75.5, 70.1, 63.0, 58.0, 39.2, 26.1, 18.4, 13.1; MS (FAB-Na) 389 (M^++23); HRMS (CI-CH_4) Calc. for $C_{20}H_{35}O_4Si$ (M+1): 367.2305, found 367.2282; HRMS (CI-CH_4) Calc. for $C_{20}H_{33}O_4Si$ (M-1): 365.2148, found 365.2158.

Benzyl 2,4-di-deoxy-2-*C*-methyl-3-*O*-(*tert*-butyldimethylsilyl)-α-D-arabinopyranoside (1j). NaH (60%

in oil, 0.25 g, 6.2 mmol) and a catalytic amount of imidazole was added to a solution of compound **1a** (1.0 g, 2.8 mmol) in THF (35 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred at rt for 1 h, whereafter CS_2 (1.3 ml, 22.7 mmol) was added. Stirring was continued for 2h before iodomethane (0.35 ml, 5.7 mmol) was added. The resulting mixture was stirred at rt for 2h and then cooled to 0 °C, whereafter water (5 ml) was slowly added in order to destroy remaining NaH. Standard work-up gave a residue, which was filtered through a short plug of silica to give an pale yellow oil. $HSnBu_3$ (1.5 ml, 5.7 mmol) was added droppwise to a mixture of the yellow oil and a catalytic amount of azobis(isobutyronitrile) in toluene at reflux under an argon atmosphere. Stirring was continued at this temperature for 12h and then the mixture was cooled to ambient temperature and concentrated under reduced pressure. The residue was column chromatographed (H/E 20:1) to give **1j** (610 mg, 64%) as a syrup: (H/E 3:1, Rf 0.69); $[\alpha]_D^{20}$ = +49 (c 0.86, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.36 (m, 5H), 4.88, 4.58 (AB q, each 1H, $J_{A,B}$ = 12.2 Hz), 4.05 (d, 1H, J = 8.4 Hz), 4.01 (m, 1H), 3.35 (m, 2H), 1.80-1.53 (m, 3H), 1.01 (d, 3H, J = 6.6 Hz), 0.89 (bs, 9H), 0.06, 0.05 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 138.2, 128.5, 128.1, 127.8, 104.2, 73.5, 70.4, 62.0, 45.1, 35.6, 26.0, 18.2, 13.1, -3.9, -4.5; MS (FAB-Na) 359 (M^++23); HRMS (CI-CH_4) Calc. for $C_{19}H_{31}O_3Si$ (M-1): 335.2042, found 335.2041.

Benzyl 2,3-anhydro-4-*O*-(triisopropylsilyl)-β-L-ribopyranoside. Benzyl 2,3-Anhydro-β-L-ribopyranoside[49] (10.0 g, 45.0 mmol) was silylated as described for benzyl 2,3-anhydro-4-*O*-(triisopropylsilyl)-α-D-ribopyranoside. Column chromatography (H/E 15:1) gave (14.2 g, 83%) as a syrup: (H/E 3:1, Rf 0.78); $[\alpha]_D^{20}$ = +13 (c 1.60, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 5H), 4.94 (s, 1H), 4.82, 4.57 (AB q, each 1H, $J_{A,B}$ = 11.6 Hz), 4.24 (m, 1H), 3.74, 3.34 (d AB q, each 1H, $J_{A,B}$ = 11.7 Hz, J = 5.3, 6.0 Hz), 3.39 (t, 1H, J = 3.5 Hz), 3.27 (d, 1H, J = 4.1 Hz), 1.07 (bs, 21H); ^{13}C NMR ($CDCl_3$) δ 137.2, 128.7, 128.3, 128.2, 95.2, 69.3, 70.8, 65.0, 62.0, 54.7, 53.5, 18.1, 12.4; HRMS (CI-CH_4) Calc. for $C_{21}H_{35}O_4Si$ (M+1): 379.2305, found 379.2308.

Benzyl 2-deoxy-2-*C*-methyl-4-*O*-(triisopropylsilyl)-β-L-arabinopyranoside (4b). Me_3Al (7.90 ml, 15.8 mmol) was rapidly added to a solution of benzyl 2,3-anhydro-4-*O*-(triisopropylsilyl)-β-L-ribopyranoside (5.00 g, 13.2 mmol) in hexane (125 ml) at room temperature. The solution was refluxed for 48h, cooled (0 °C), and then worked up as described under General Methods. Column chromatography (H/E 25:1) gave **4b** (700 mg, 14%) as a syrup: (H/E 3:1 R_f 0.75); $[\alpha]_D^{20}$ = +101 (c 1.37, $CHCl_3$); IR(neat) 3540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.34 (m, 5H), 4.80 (d, 1H, J = 3.2 Hz), 4.74, 4.52 (AB q, each 1H, $J_{A,B}$ = 12.2 Hz), 4.04 (m, 1H), 3.88 (dd, 1H, J = 12.2, 2.1 Hz), 3.70 (m, 2H), 2.10 (m, 1H), 2.07 (d, 1H, J = 9.4 Hz), 1.10 (bs 21H), 1.07 (d, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 138.4, 128.5, 127.7, 127.7, 100.5, 71.3, 69.5, 69.5, 64.1, 37.7, 18.3, 18.2, 12.7, 12.2; MS (FAB-Na) 417 (M^++23); HRMS (CI-CH_4) Calc. for $C_{22}H_{37}O_4Si$ (M-1): 393.2461, found 393.2462.

Benzyl 3-deoxy-2-*O*-methyl-3-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-α-D-arabinopyranoside. Benzyl 3-deoxy-3-*C*-methyl-4-*O*-(*tert*-butyldimethylsilyl)-α-D-arabinopyranoside (**7**) (0.25 g, 0.71 mmol) was methylated as described for **1h**. The residue was column chromatographed (H/E 20:1) to give the title compound (189 mg, 74%) as a syrup: (H/E 3:1, Rf 0.71); $[\alpha]_D^{20}$ = +21 (c 0.96, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.91, 4.60 (AB q, each 1H, $J_{A,B}$ = 12.1 Hz), 4.43 (d, 1H, J = 5.7 Hz), 3.79 (m, 2H), 3.51 (s,

3H), 3.40 (m, 1H), 3.15 (m, 1H), 1.80 (m, 1H), 1.09 (d, 3H, J = 6.9 Hz), 0.93 (bs, 9H), 0.08, 0.07 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 138.2, 128.5, 127.8, 127.7, 102.8, 81.4, 70.3, 69.2, 67.1, 60.0, 39.5, 26.1, 18.4, 13.0, -4.2, -4.7; MS (FAB-Na) 389 (M^++23); HRMS (CI-CH_4) Calc. for $C_{20}H_{33}O_4Si$ (M-1): 365.2148, found 365.2143.

Benzyl 3-deoxy-3-*C*-methyl-2,4-*O*-bis(*tert*-butyldimethylsilyl)-α-D-arabinopyranoside. Compound 7 (0.25 g, 0.71 mmol) was silylated as described for benzyl 2,3-anhydro-4-*O*-(triisopropylsilyl)-β-L-ribopyranoside except that triisopropylsilylchloride was replaced by tert-butyldimethylsilylchloride. The residue was column chromatographed (H/E 20:1) to give the title compound (250 mg, 77%) as a syrup: (H/E 6:1, R_f 0.57); $[\alpha]_D^{20}$ = +25 (c 2.40, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.85, 4.53 (AB q, each 1H, $J_{A,B}$ = 12.0 Hz), 4.35 (d, 1H, J = 4.7 Hz), 3.94 (m, 1H), 3.77, 3.45 (d AB q, each 1H, $J_{A,B}$ = 11.5 Hz, J = 5.7, 2.9 Hz), 3.67 (dd, 1H, J = 7.0, 4.8 Hz), 1.80 (m, 1H), 1.08 (d, 3H, J = 7.1 Hz), 0.93, 0.88 (bs, each 9H), 0.08, 0.07, 0.05, 0.02 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 138.1, 128.4, 128.1, 127.6, 102.6, 77.5, 77.2, 76.9, 73.1, 69.8, 68.8, 65.8, 41.7, 26.1, 26.1, 18.4, 18.4, 12.9, -4.1, -4.3, -4.6, -4.7; MS (FAB-Na) 489 (M^++23); HRMS (CI-CH_4) Calc. for $C_{25}H_{46}O_4Si_2$ (M-1): 465.2856, found 465.2845;

(2*R*,3*S*,4*S*,5*S*)- and (2*R*,3*S*,4*S*,5*R*)-5-*O*-Benzyl-4-methyl-2-*O*-(triisopropylsilyl)-1,2,3,5-hexantetrol (2b and 2b'). Compound **1b** (100 mg, 0.260 mmol) was subjected to the General Method for ring-opening reaction condition. The residue was column chromatographed (E/H 1:5) to give **2b/ 2b'** (oil, see Table 1, entries 2-6.): IR (neat) 3410 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 5H), 4.66, 4.40 (AB q, each 1H, $J_{A,B}$ = 11.4 Hz), 3.90-3.65 (m, 5H), 3.59 (bs, 1H), 2.92 (m, 1H), 2.00 (m, 1H), 1.23 (d, 3H, J = 6.3 Hz), 1.07 (bs 21H), 1.00 (d, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 138.3, 128.8, 128.0, 127.9, 80.7, 80.1, 72.0, 70.6, 66.4, 38.7, 18.4, 17.0, 13.0, 6.4; HRMS (CI-CH_4) Calc. for $C_{23}H_{43}O_4Si$ (M+1): 411.2930, found 411.2926. For GLC analysis, a fraction was acetylated to yield the 1,3-di-acetates of **2b/2b'**: IR (neat) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 5H), 5.20 (t, 1H, J = 4.9 Hz), 4.57, 4.43 (AB q, each 1H, $J_{A,B}$ = 11.4 Hz), 4.28 (m, 1H), 4.13 (m, 2H), 3.55 (m, 1H), 2.09 (m, 1H), 2.01, 1.96 (s, each 3H), 1.26 (d, 3H, J = 6.3 Hz), 1.07 (bs 21H), 1.01 (d, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.2, 170.5, 139.1, 128.4, 127.5, 127.4, 77.2, 75.7, 71.3, 70.6, 66.0, 38.9, 21.2, 21.0, 18.2, 16.4, 12.9, 10.9; HRMS (CI-CH_4) Calc. for $C_{27}H_{47}O_6Si$ (M+1): 495.3142, found 495.3143.

(2*R*,3*S*,4*S*,5*S*)- and (2*R*,3*S*,4*S*,5*R*)-1,2,3-Tri-*O*-acetyl-5-*O*-benzyl-4-methyl-1,2,3,5-hexantetrol (2c and 2c'). Compound **1c** (100 mg, 0.418 mmol) was subjected to the General Method for ring-opening. The crude triol was acetylated following the procedure described above. Column chromatography (E/H 1:3) gave **2c/2c'** (syrup, 111 mg, 70%, ret:inv = 50:50): IR (neat) 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 10H), 5.50 (dd, 1H, J = 6.7, 4.1 Hz), 5.39 (m, 1H), 5.30 (dd, 1H, J = 5.1, 6.5 Hz), 5.21 (m, 1H), 4.55, 4.40 (AB q, each 2H, $J_{A,B}$ = 10.9 Hz), 4.29 (m, 2H), 4.14 (m, 2H), 3.55 (m, 1H), 3.37 (m, 1H), 2.06, 2.05, 2.04, 2.02, 2.01, 1.97 (s, each 3H), 1.26 (d, 3H, J = 6.4 Hz), 1.21 (d, 3H, J = 6.2 Hz), 0.96 (d, 3H, J = 6.9 Hz), 0.92 (d, 3H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 171.0, 170.9, 170.4, 170.4, 170.3, 170.3, 138.8, 138.7, 128.5, 128.4, 127.7, 127.5, 76.9, 76.0, 72.9, 71.5, 71.1, 71.1, 70.9, 70.7, 62.5, 62.4, 39.4, 39.3, 21.1, 21.0, 20.9,16.6, 15.8, 11.5, 10.3; HRMS (CI-CH_4) Calc. for $C_{20}H_{29}O_7$ (M+1): 381.1913, found 381.1913.

(2*R*,3*S*, 4*R* , 5 *S*)- and (2*R*,3*S*,4*R*,5*R*)-5-*O*-Benzyl-4-methyl-3-*O*-(*tert*-butyldimethylsilyl)-1,2,3,5-hexantetrol (2d and 2d'). Compound **1d** (100 mg, 0.280 mmol) was subjected to the General Method for ring-opening. The residue was column chromatgraphed (E/H 1:5) to give **2d/2d'** (syrup, 77mg, 74%, ret:inv = 95:5): ^{1}H NMR ($CDCl_3$) δ 7.34 (m, 5H), 4.65, 4.40 (AB q, each 1H, $J_{A,B}$ = 11.1 Hz), 3.95 (m, 1H), 3.77-

3.45 (m, 4H), 2.23 (m, 1H), 1.76 (m, 1H), 1.27 (d, 3H, *J*= 6.3 Hz), 1.08 (d, 3H, *J* = 7.6 Hz), 0.89 (bs, 9H), 0.09, 0.05 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 138.1, 128.7, 128.2, 128.1, 75.3, 74.1, 74.0, 70.8, 64.6, 45.3, 26.0, 18.2, 17.6, 11.8, -4.2, -4.3; HRMS (CI-CH_4) Calc. for $C_{37}H_{43}O_4Si$ (M+1): 369.2461, found 369.2456.

(2*R*,3*S*,4*S*,5*S*)- and (2*R*,3*S*,4*S*,5*R*)-5-*O*-Benzyl-4-methyl-2,3-di-*O*-methyl-1,2,3,5-hexantetrol (2e and 2e′). Compound **1e** (100 mg, 0.380 mmol) was subjected to the General Method for ring-opening. The residue was column chromatographed (E/H 1:1) to give **2e/2e′** (syrup, 78 mg, 70%, ratio ret:inv = 55:45): IR (neat) 3480 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 10H), 4.62, 4.42 (AB q, each 2H, $J_{A,B}$ = 11.7 Hz), 3.85-3.65 (m, 5H), 3.55-3.20 (m, 5H), 3.46, 3.41, 3.39, 3.37 (s, each 3H), 2.44 (t, 1H, *J*=6.1 Hz), 2.26 (dd, 1H, *J*=4.9 Hz, 7.8 Hz) 1.89 (m, 1H), 1.25 (d, 3H, *J* = 6.3 Hz), 1.24 (d, 3H, *J* =6.1 Hz), 1.03 (d, 3H, *J* = 7.0 Hz), 0.92 (d, 3H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 139.0, 138.9, 129.4, 128.6, 128.4, 127.9, 127.8, 127.7, 82.1, 81.7, 81.6, 80.0, 77.4, 76.8, 70.7, 70.3, 61.0, 60.7, 60.6, 60.4, 57.8, 57.8, 40.5, 40.4, 17.1, 16.7, 10.8; HRMS (CI-CH_4) Calc. for $C_{16}H_{27}O_4$ (M+1): 283.1909, found 283.1907.

(3*R*,4*S*,5*S*)- and (3*R*,4*S*,5*R*)-5-*O*-Benzyl-4-methyl-1,3,5-hexantriol (2f and 2f′). Compound **1f** (169 mg, 0.760 mmol) was subjected to the General Method for ring-opening. The residue was column chromatographed (E/H 2:1) to give **2f/2f′** (syrup, 140 mg, 77%, ratio ret:inv = 85:15): ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 5H), 4.65, 4.38 (AB q, each 1H, $J_{A,B}$ = 11.3 Hz), 4.06 (d, 1H, *J* =10.2 Hz), 3.82 (m, 3H), 3.64 (bs, 1H), 2.74 (m, 1H), 1.87 (m, 1H), 1.48 (m, 2H), 1.24 (d, 3H, *J* = 6.3 Hz), 1.00 (d, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 138.0, 128.5, 127.8, 127.6, 79.9, 76.4, 71.1, 70.3, 62.2, 43.2, 36.6, 16.8, 5.7; HRMS (CI-CH_4) Calc. for $C_{14}H_{23}O_3$ (M+1): 239.1647, found 239.1648.

(2*S*,4*S*,5*S*)- and (2*S*,4*S*,5*R*)-5-*O*-Benzyl-4-methyl-2-*O*-(*tert*-butyldimethylsilyl)-1,2,5-hexantriol (2g and 2g′). Compound **1g** (100 mg, 0.297 mmol) was subjected to the General Method for ring-opening. The residue was column chromatgraphed (E/H 1:5) to give **2g/2g′** (syrup, 56mg, 52%, ret:inv = 75:25); IR (neat) 3480 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5H), 4.57, 4.47 (AB q, each 1H, $J_{A,B}$ = 11.8 Hz), 3.89 (m, 1H), 3.59 (m, 1H), 3.45 (m, 2H), 1.90 (m, 1H), 1.78 (m, 1H), 1.27 (m, 1H), 1.15 (d, 3H, *J* = 6.2 Hz), 0.93 (d, 3H, *J* = 6.9 Hz), 0.91 (bs, 9H), 0.09 (bs, 6H); ^{13}C NMR ($CDCl_3$) δ 139.4, 139.4, 128.5, 128.5, 127.8, 127.7, 127.6, 127.5, 79.0, 79.0, 77.5, 77.2, 76.9, 71.3, 71.2, 70.7, 70.6, 67.1, 67.1, 66.9, 37.5, 36.4, 33.6, 33.3, 26.1, 18.3, 16.1, 15.8, 15.6, 15.2, -4.1, -4.1, -4.3, -4.3; HRMS (CI-CH_4) Calc. for $C_{20}H_{36}O_3Si$ (M+1): 353.2512, found 353.2512.

(2*R*,3*S*,4*S*,5*S*)- and (2*R*,3*S*,4*S*,5*R*)-5-*O*-Benzyl-4-methyl-3-*O*-methyl-2-*O*-(*tert*-butyldimethylsilyl)-1,2,3,5-hexantetrol (2h and 2h′). Compound **1h** (96 mg, 0.27 mmol) was subjected to the General Method for ring-opening. The residue was column chromatographed (E/H 1:8) to give **2h/2h′** (syrup, 79 mg, 80%, ret:inv = 60:40): IR (neat) 3490 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 10H), 4.62, 4.40 (AB q, each 2H, $J_{A,B}$ = 12.2 Hz), 4.15 (t, 1H, *J* = 3.46 Hz) 3.93 (dd, 1H, *J* = 3.3, 6.2 Hz), 3.70 (m, 5H), 3.60-3.20 (m, 3H), 3.41, 3.32 (s, each 3H), 2.33 (t, 1H, *J* = 5.8 Hz), 2.27 (t, 1H, *J* = 6.1 Hz) 1.80 (m, 2H), 1.23 (d, 3H, *J* = 6.2 Hz), 1.20 (d, 3H, *J* =6.1 Hz),1.03 (d, 3H, *J* = 7.1 Hz), 0.95 (d, 3H, *J* = 7.1 Hz), 0.94 (bs, 9H), 0.12, 0.09, 0.07, 0.03 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 139.0, 138.9, 128.6, 128.5, 127.8, 127.8, 127.7, 127.6, 82.1, 84.7, 83.4, 77.4, 77.1, 75.6, 73.2, 72.1, 70.6, 70.3, 61.4, 61.3, 58.2, 57.5, 42.3, 26.3, 26.2, 18.6, 17.0, 16.7, 11.5, 11.4, -3.8, -3.9, -4.4, -4.4; HRMS (CI-CH_4) Calc. for $C_{21}H_{39}O_4Si$ (M+1): 383.2617, found 383.2621.

(3*R*,4*R*,5*S*)- and (3*R*,4*R*,5*R*)-5-*O*-Benzyl-4-methyl-3-*O*-(*tert*-butyldimethylsilyl)-1,3,5-hexantriol (2j and 2j′). Compound **1j** (56 mg, 0.17 mmol) was subjected to the General Method for ring-opening. The residue was column chromatgraphed (E/H 1:5) to give **2j/2j′** (syrup, 23 mg, 37%, ret:inv = 91:9); IR (neat) 3460 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.34 (m, 5H), 4.61, 4.38 (AB q, each 1H, $J_{A,B}$ = 11.7 Hz), 3.89 (m, 1H),

3.78-3.60 (m, 3H), 1.85-1.65 (m, 3H), 1.22 (d, 3H, J = 6.2 Hz), 0.99 (d, 3H, J = 7.0 Hz), 0.90 (bs, 9H), 0.09, 0.06 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 139.2, 128.5, 127.8, 127.6, 74.9, 73.3, 70.6, 60.7, 44.2, 35.8, 26.1, 18.2, 17.7, 11.0, -4.1, -4.2; HRMS (CI-CH_4) Calc. for $C_{20}H_{36}O_3Si$ (M+1): 353.2512, found 353.2508.

(3*R*,4*R*,5*S*)- and (3*R*,4*R*,5*R*)-1-*O*-(Triisopropylsilyl)-3,5-di-*O*-isopropylidene-4-methyl-1,3,5-hexantriol (2k and 2k´). Compound **2f/2f´**(100 mg, 0.420 mmol) was partially silylated (as described for **5c** except that 1.1 equiv. of triisopropylchloride was used). Column chromatography (E/H 1:10) gave the 1-*O*-silylated compounds of **2f/2f´**, which were hydrogenolyzed (H_2, Pd/C) in ethanol (3 ml) at room temperature for 24h. The 3,5-diols thus obtained were dissolved in 2,2-dimethoxypropane (5 ml), and a small amount of camphorsulfonic acid was added. After 30 min, the mixture was diluted with ethyl acetate (5 ml), washed with saturated aqueous $NaHCO_3$ (3 ml) and water (3 ml), dried , and the solvent was removed under reduced pressure. The residue was column chromatographed (H/E 10:1) to give **2k/2k´** (syrup, 94 mg, 68%, ret:inv= 88:12): ^{1}H NMR ($CDCl_3$) δ 4.18 (m, 1H), 4.12 (m, 1H), 3.75 (m, 2H), 1.74 (m, 1H), 1.58 (m, 1H), 1.45 (s, 3H), 1.43 (s, 3H), 1.29 (m, 1H), 1.13 (d, 3H, J= 6.4 Hz), 1.07 (bs, 21H), 0.86 (d, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 99.0, 69.8, 69.3, 59.8, 36.5, 30.3, 19.9, 19.2, 18.2, 12.2, 4.8; HRMS (CI-CH_4) Calc. for $C_{19}H_{41}O_3Si$ (M+1): 345.2825, found 345.2826.

(2*R*,3*S*,4*S*, 5*R*)-5-O-Benzyl-4-methyl-1,2,3,5-hexanetetrol. Compounds **2b/2b´** and **2d/2d´** were subjected to the reaction conditions as described for the preparation of **1c.** Column chromatography (SiO_2 deactivated with 5% water, E/H 8:1) gave title compound as a colourless oil. Spectral data were as reported in the litterature.[23]

(3*S*, 4*S*, 5*S*)- and (3*S*, 4*S*, 5*R*)-5-*O*-Benzyl-4-methyl-1,3,5-hexantriol (2f and 2f´). The mixture of **2j/2j´** was subjected to the reaction conditions described for the preparation of **1c.** Column chromatography (E/H 2:1) gave title compound as a colourless oil. The ^{1}H NMR and ^{13}C NMR spectra were identical with those of **2f/2f´** described above.

(2*S*,3*R*,4*R*,5*R*)- and (2*S*,3*R*,4*R*,5*S*)-5-*O*-Benzyl-4-methyl-2-*O*-(triisopropylsilyl)-1,2,3,5-hexantetrol (5b and 5b´). Compound **4b** (100 mg, 0.260 mmol) was subjected to the General Method for ring-opening reaction conditions. The residue was column chromatographed (E/H 1:4) to give **5b/5b´**: The IR, ^{1}H NMR and ^{13}C NMR spectra were identical with those of compounds **2b/2b´**.

Cyclic 4,5-carbonate of (2S,3S,4S,5S)- and (2S,3S,4S,5R)-3-methyl-2-*O*-(*tert*-butyldimethylsilyl)-1,2,4,5-hexanetetrol (8a´/8a). (2S,3S,4S,5S)- and (2S,3S,4S,5R)-5-*O*-Benzyl-3-methyl-2-*O*-(*tert*-butyldimethylsilyl)-1,2,4,5-hexanetetrol **8´/8** (100 mg, 0.272 mmol) were subjected to the reaction conditions described for the preparation of **11a´/11a**. The residue was column chromatographed (H:E 1:1 → 1:4) to give **8a´/8a** (51 mg, 66%, ret:inv = 0:100) as a syrup: IR (neat) 3500, 1790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.91 (m, 1H), 4.82 (dd, 1H, J= 7.5 Hz, 4.3 Hz), 3.66 (m, 2H), 3.60 (m, 1H), 2.20 (m, 1H), 1.71 (m, 1H), 1.47 (d, 3H, J = 6.6 Hz), 1.05 (d, 3H, J = 6.8 Hz), 0.92 (bs, 9H), 0.14 (bs, 6H); ^{13}C NMR ($CDCl_3$) δ 155.1, 79.9, 77.0, 74.5, 63.6, 35.3, 26.0, 18.2, 14.8, 10.6, -4.2, -4.5; HRMS (CI-CH_4) Calc. for $C_{14}H_{29}O_5Si$ (M+1): 305.1784, found 305.1783.

(2R,3S,4S,5S)- and (2R,3S,4S,5R)-5-O-Benzyl-3-methyl-2-O-(*tert*-butyldimethylsilyl)-1,2,4,5-hexantetrol (11´ and 11). Benzyl 3-deoxy-3-*C*-methyl-4-O-(tert-butyldimethylsilyl)-β-L-xylopyranoside (**10**) (100 mg, 0.283 mmol) was subjected to the general conditions for ring opening. The residue was column chromatographed (E/H 1:5) to give **11´/11** (syrup, 64 mg, 67%, ret:inv = < 3:97): $[\alpha]_D^{20}$=-30 (c 0.67, $CHCl_3$); IR (neat) 3400 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 5H), 4.65, 4.42 (AB q, each 1H, $J_{A,B}$ = 11.7 Hz), 3.82

(dd, 1H, J = 7.2 Hz, 1.8 Hz), 3.70 (m, 2H), 3.55 (m, 2H), 2.20 (m, 1H), 1.60 (s, 1H), 1.25 (d, 3H, J = 6.1 Hz), 0.90 (s, 9H), 0.85 (d, 3H, J = 7.2 Hz), 0.08, 0.08 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 138.8, 128.2, 127.6, 127.4, 75.6, 75.0, 71.9, 70.6, 62.6, 37.5, 25.8, 18.1, 16.3, 9.3, -4.7. HRMS (CI-CH_4) Calc. for $C_{20}H_{37}O_4Si$ (M+1): 369.2460, found 369.2461.

Cyclic-4,5 carbonate of (2R,3S,4S,5R)-3-methyl-2-O-(*tert*-butyldimethylsilyl)-1,2,4,5-hexanetetrol (11a). Compound mixture **11′/11** (200 mg, 0.543 mmol) was hydrogenolyzed (H_2, Pd/C) in ethanol (5 ml) at room temperature for 24 h. The 1,4,5-triol mixture thus obtained was dissolved in THF (10 ml) and pyridine (0.26 ml, 3.2 mmol). The reaction mixture was cooled on ice whereafter phosgene (1.0 ml, 2 M in toluene, 2.0 mmol) was added dropwise. After 30 min the reaction was quenched by addition of water and diethyl ether. The phases were separated and the aqueous phase extracted with diethyl ether. The combined organic phases were dried and the solvent was removed under reduced pressure. The residue was column chromatographed (H:E 1:1 →1:4) to give **11a** (111 mg, 72%, ratio ret:inv = 0:100) as a syrup: IR (neat) 3500, 1805 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.85 (m, 2H), 3.70-3.60 (m, 3H), 2.13 (m, 1H), 1.77 (m, 1H), 1.43 (d, 3H, J = 6.4 Hz), 1.08 (d, 3H, J = 7.0 Hz), 0.91 (bs, 9H), 0.12, 0.09 (s, each 3H); ^{13}C NMR ($CDCl_3$) δ 154.9, 79.6, 76.6, 73.4, 63.7, 36.4, 26.0, 18.2, 14.8, 10.5, -4.1, -4.6; HRMS (CI-CH_4) Calc. for $C_{14}H_{29}O_5Si$ (M+1): 305.1784, found 305.1786.

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