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TETRAHEDRON

Elongation of the Pentose Chain at the Terminal Carbon Atom with Grignard C_1 Reagents. A Study of the Homologation Reaction

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Abstract: Derivatives of four stereoisomeric pentodialdo-1,4-furanoses were reacted with four Grignard C_1 reagents: methoxymethyl-, allyloxymethyl-, benzyloxymethyl, and dimethylphenylsilylmethyl-magnesium chlorides. Derivatives of the expected stereoisomeric hexoses were accompanied in some cases by C-4 inverted products. The results have been discussed in terms of α- and β-chelated transition states. It has been found that the RX (X=O,Si) grouping of the Grignard reagent strongly influences the stereochemical outcome of the elongation reaction. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: pentofuranoses, hexofuranoses, Grignard C_1 reagents, homologation reaction.

INTRODUCTION

The need for preparative amounts of L-*glycero*-D-*manno*-heptose (**1**), a heptose commonly occurring within the core region of bacterial lipopolysaccharides [1,2], prompted interest in developing a convenient synthetic access to this sugar. As a consequence, in 1986 we developed a practical route to **1** basing on elongation of the D-mannopyranoside chain by a C_1 reagent from the terminal (C-6) position [3]. The method consisted of a reaction between an alkoxymethyl Grignard reagent and a C-6 aldehyde. This approach has found wider application [4-7], and also other Grignard reagents have been succesfully applied [8-11].

It is obvious that this method has a larger potential and can be applied for chain extension reaction in different sugar structures („ascending synthesis", starting from the terminal carbon atom [12]). In view of the simplicity and versatility of the approach we wanted to examine the chain elongation reaction of derivatives of four stereoisomeric pentoses using four C_1 Grignard reagents. We expected that the results of these reactions might shed some light on the extensively studied nucleophilic additions to α-oxy carbonyl compounds [13-20] Only a few chain-elongation reactions according to this protocol have been described in literature.

Dedicated to Professor Henk van der Plas on the occassion of his 70th birthday.

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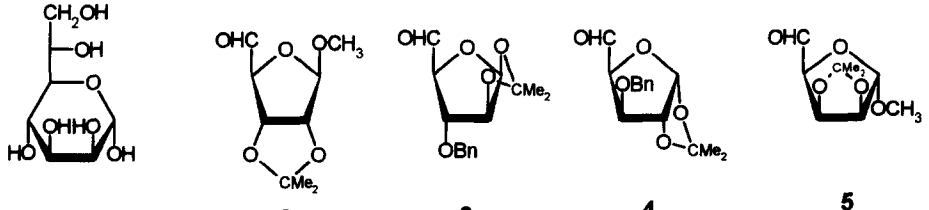
(Phenyldimethylsilyl)methylmagnesium chloride was used by P. Smid *et al.* [21]. for the carbon atom chain extension in 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose and 3-*O*-benzyl-1,2-*O*-isopropylidene-*xylo*-pentodialdo-1,4-furanose. 3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,4-furanose was elongated with methoxymethylmagnesium chloride [22].

Scheme 1



1 2 3 4 5

$BnOCH_2MgCl$ **6**

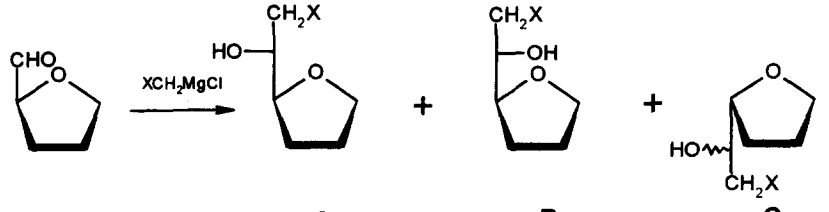
$AllOCH_2MgCl$ **7**

$MeOCH_2MgCl$ **8**

$PhMe_2SiCH_2MgCl$ **9**

RESULTS

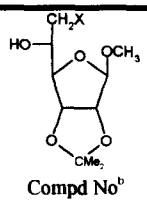
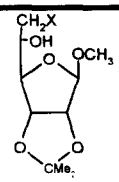
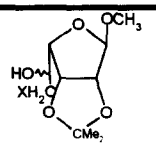
Four stereoisomeric pentose-derived aldehydes (Scheme 1): methyl 2,3-*O*-isopropylidene-β-D-*ribo*-pentodialdo-1,4-furanoside (**2**), 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*arabino*-pentodialdo-1,4-furanose (**3**), 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**4**) and methyl 2,3-*O*-isopropylidene-α-D-*lyxo*-pentodialdo-1,4-furanoside (**5**) were prepared by conventional methods (*cf.* Experimental). The aldehydes were reacted with four freshly prepared Grignard reagents **6-9** as shown schematically in Eq. 1. The products were isolated by column chromatography. The results of reactions are collected in Tables 1-4. The expected C-5 stereoisomeric products A and B were accompanied in some cases (especially in the *ribo* series)



X = RO, R_3Si **A** **B** **C** (Eq 1)

by C-4 inverted products C [*cf.* 6,7]. The identification of products was based on: 1. comparison with authentic derivatives obtained by independent routes (compounds No. **35**, **43**), 2. comparison of the physico-chemical data with literature figures (compounds No. **24**, **36**, **37**), and 3. circular dichroism data [23] (remaining compounds except C-4 inverted; *cf.* Experimental). The configuration of the inverted *ribo* products **15** and **16** could be readily assigned by comparison of their ^{1}H and ^{13}C NMR spectra with those of the *lyxo* compounds **41**and **42**. Both pairs: **15,42** and **16,41** displayed identical spectra which confirmed their enantiomeric

Table 1
Chain elongation reaction between methyl 2,3-O-isopropylidene-β-D-*ribo*-pentodialdo-1,4-furanoside (**2**) and Grignard reagents **6-9**[a]

Entry No.	Reagent	Overall yield (%)	X	 Compd No[b]	 Compd. No.[b]	 Compd. No.[b]
1	**6**	91.6	BnO	**10** (31)	**11** (55)	**12** (14)
2	**7**	83.8	AllO	**13** (27)	**14** (73)	-
3	**7**[c]	89.0	AllO	**13** (11)	**14** (89)	-
4	**8**	54.1	MeO	-	-	**15** (70) **16** (30)
5	**8**[c]	76.2	MeO	-	-	**15** (88) **16** (12)
6	**9**	81.0	$PhMe_2Si$	**17** (66)	**18** (14)	**19** (13) **20** (7)
7	**9**[d]	77.2	$PhMe_2Si$	**17** (20)	**18** (14)	**19** (47) **20** (19)
8	**9**[e]	61.4	$PhMe_2Si$	**17** (22)	**18** (71)	**19** (7) **20** (traces)

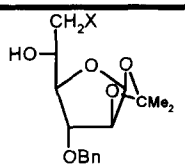
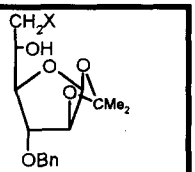
[a] 1 Mol equiv of **2** was reacted with 4 mol equiv of Grignard reagents **6-9** at -30 °C in THF solution (*cf.* Experimental). [b] Proportion of products in %. [c] At -78 °C. [d] At 0 °C. [e] Two mol equiv. of **9** were taken for reaction at -30 °C.

relationship. Specific rotations were of the same magnitude but of opposite sign. The configuration at C-5 of the remaining C-4 inverted compounds was not determined.

High yields of reactions are secured if reaction conditions (*cf.* Experimental) are strictly observed. The formation of Grignard reagents **6-8** is strongly dependent on the quality of the chloromethyl ethers used. In the experiments described here freshly prepared and freshly distilled alkyl chloromethyl ethers were employed. Grignard reagents prepared were stable below -20 °C. These remarks seem to be important as earlier notes [8,24] claimed difficulty in using this type of Grignard for chain elongation reactions despite the clear

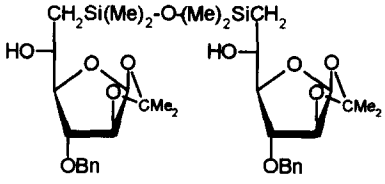
advantage of the method resulting in direct introduction of properly blocked hydroxymethyl groups to the molecule. Silyl reagent **9** is distinctly less sensitive to the reaction conditions and the reactions can be performed without any special precautions. However, the stereochemical outcome of the reactions is different for Grignards **6-8** and for **9**.

Table 2
Chain elongation reaction between methyl 3-*O*-benzyl-1,2-*O*-isopropylidene-β-D-*arabino*-pentodialdo-1,4-furanose (**3**) and Grignard reagents **6-9**[a]

Entry No.	Reagent	Overall yield (%)	X	 Compd. No.[b]	 Compd. No.[b]
1	**6**	71.0	BnO		**21** (>95)[c] -
2	**7**	71.8	AllO	**22** (24)	**23** (75)
3	**8**	89.3	MeO		**24** (90)[d]
4	**9**	89.0	$PhMe_2Si$	**25** (45)[e]	**26** (55)

[a] Reaction conditions as in footnote a (Table 1). [b] Proportion of products in %.
[c] Trace amount of a 5-O-benzyloxymethyl ether was detected. [d] *Ca* 10% of a 5-O-methoxymethyl ether of **25** has been isolated. [e] Oxidation (CH_3CO_3H) of **25** led to **27**.

It is convenient to discuss first the results obtained with the *arabino* and *ribo* aldehydes (**3** and **2**). As shown in Table 2, essentially only one or two stereoisomeric products were formed from each reaction. Compounds of L configuration at C-5 (L-*galacto*, compounds **21**, **23** and **24**) dominated, at least, 9-3:1 over the D-counterparts (D-*altro*, **22**). Silyl Grignard **9** gave both stereoisomeric products **26** (L-*galacto*) and **25** (D-*altro*) with poor diastereoselectivity (55:45).

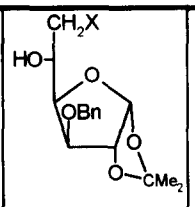
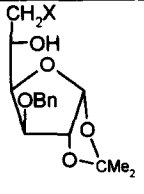
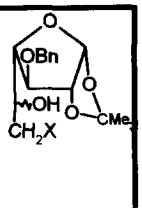


27

The predominance of C-5 L-configured products is also noted in Table 1, where the results obtained with the *ribo* aldehyde **2** are collected: L-*talo* compounds **11** and **14** dominated over D-*allo* products **10** and **13** 1.8:1 and 8:1, respectively. Substantial amounts of the C-4 inverted products were noted for reactions with Grignards **6** and **9**, becoming the exclusive products when aldehyde **2** was reacted with methoxymethylmagnesium chloride (**8**) at -30 °C and also at -78 °C (entries 4 and 5). The stereochemistry of the reaction between **2** and silyl reagent **9** at -30 °C was dependent on the proportion of both reagents taken. When the ratio **2**:**9** was 1:4 (entry 6) the D-*allo* stereoisomer **17** was the main product. When this ratio was reduced to 1:2 (entry 8), the L-*talo* compound was

the main product with the „inverted" products formed in low yield. In contrast, when the reaction was performed at 0 °C, the „inverted" sugars were the main products of the reaction.

Table 3
Chain elongation reaction between methyl 3-O-benzyl-1,2-O-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**4**) and Grignard reagents **6-9**[a]

Entry No.	Reagent	Overall yield (%)	X	 Compd No.[b]	 Compd. No.[b]	 Compd. No.[b]
1	**6**	80.6	BnO	**28** (>95)[c]	-	-
2	**7**	79.8	AllO	**29** (81)	**30** (11)	**31** (8)
3	**8**	82.4	MeO	**32** (82)	**33** (13)	**34** (5)
4	**9**	95.0	$PhMe_2Si$	**35** (7)	**36** (93)	-

[a] Reaction conditions as in footnote a (Table 1). [b] Proportion of products in %.
[c] Only traces (TLC) of the L-*ido* stereoisomer.

A different stereochemistry of the main products was noted for both the other aldehydes of D-*xylo* (**4**) and D-*lyxo* (**5**) configuration. From the reactions of **5** with Grignard reagents **6-9** only two products were formed. Alkoxy Grignards **6-8** led to D-*manno* products **37**, **39** and **41** in predominance over the L-*gulo* stereoisomers **38**, **40** and **42** (Table 4, entries 1-4). Silyl reagent **9**, as in previous cases (Tables 1 and 2), led to L-*gulo* product **44** in 1.4:1 prevalence over the D-*manno* stereoisomer **43**.

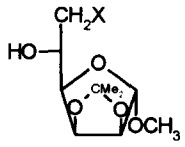
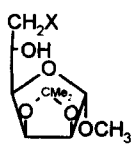
The dominating D-stereoselectivity was even more distinct for the D-*xylo* aldehyde **4** (Table 3). Hexose products of D-*gluco* configuration **28**, **29**, and **32** were obtained in 9-6:1 predomination over the L-*ido* stereoisomers **30** and **33** (entries 1-3). Small amounts of the „inverted" products **31** and **34** were also noted (entries 2 and 3). Here again, silyl Grignard **9** afforded L-*ido* product **36** in a distinct preference (13:1) over the D-*gluco* partner **35** (entry 4).

DISCUSSION

The reactions described above - besides affording access to less common hexose structures (e.g. D-allose, L-talose, L-galactose, L-gulose) - present also a contribution to the field of nucleophilic additions to chiral oxy aldehydes. All four aldehydes **2-5** contain an α-oxygen atom (furanose ring oxygen) and a β-oxygen atom in a sterically defined position: *trans* (**2** and **3**) or *cis* (**4** and **5**) in relation to the formyl group. These atoms should influence the sterical course of addition of nucleophiles depending on the importance of α- or β-chelation [18].

Table 4

Chain elongation reaction between methyl 2,3-O-isopropylidene-α-D-*lyxo*-pentodialdo-1,4-furanoside (**5**) and Grignard reagents **6-9**[a]

Entry No.	Reagent	Overall yield (%)	X	 Compd No [b]	 Compd. No.[b]
1	**6**	75.2	BnO	**37** (57)	**38** (43)
2	**6**[c]	69.1	BnO	**37** (89)	**38** (11)
3	**7**	81.3	AllO	**39** (86)	**40** (14)
4	**8**	69.2	MeO	**41** (60)	**42** (40)
5	**9**	78.7[d]	$PhMe_2Si$	**43** (42)	**44** (58)

[a] Reaction conditions as in footnote a (Table 1). [b] Proportion of products in %.[c] At -78 °C.
[d] The mixture of **43** and **44** was not separated. Configuration (and proportion) of both products was deduced from the ^1H and ^{13}C NMR spectra.

The problem of α- and β-chelation in α- and β-alkoxy-aldehydes and -ketones has been studied experimentally [13-17] and theoretically [26,27]. Most relevant experimental investigations have been performed by E.L. Eliel [20,28,29] and theoretical calculations by E. Nakamura and K. Morokuma [30]. From the experiments it is known that α-chelation has a profound impact on the stereochemical outcome of reactions [20]. β-Chelation seems not to provide a sufficient bias to achieve high stereoselectivities in nucleophilic additions [20,25]. However, *ab initio* calculations indicate that both types of chelation facilitate product formation through low-energy transition states (TS)[30].

The interpretation of the results presented in Tables 1-4 rests on the assumption that both types of chelation play an essential role in determining the stereochemical outcome of reactions, not excluding the participation a of non-chelated reaction pathway. Thus, the main, normal (not „inverted") products of addition of alkoxymethyl Grignards **6-8** to *ribo* and *arabino* aldehydes (**2** and **3**, Tables 1 and 2) are formed by intermediation of α-chelated transition states. In this case α-chelation forces the approach of the nucleophile from „below the ring" (Fig. 1A) this leading to L-configuration of the new CHOH grouping. Products of the D configuration at C-5 are formed probably *via* the non-chelated TS.

For the *xylo* and *lyxo* aldehydes (**4** and **5**, Tables 3 and 4), having β-oxygens in *cis* disposition towards the formyl group, β-chelation becomes more important and the major products formed have D-configuration of the new CHOH grouping (Fig. 1B).

Incidentally, the attack of nucleophiles on β-chelated aldehydes **4** and **5** follows also the Felkin-Anh model: the *anti* approach towards the ring oxygen atom.

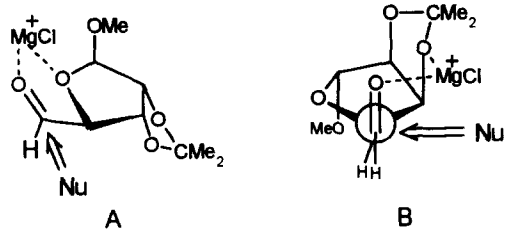


Fig. 1

The dimethylphenylsilyl Grignard reagent **9** displays a marked preference for the formation of hexose derivatives having L-configuration at C-5. This must be again interpreted with a preferred α-chelated TS in all four aldehydes, the possibility of forming β-chelates (in case of **4** or **5**) being neglected. This indicates that besides the metal, reaction conditions, and proportion of reagents [17,31], the kind of substitution on the alkyl of the organomagnesium compound ($PhMe_2Si$ instead of RO) also influences the course of addition to the carbonyl group. However, as the data in Table 1 show, the steric course of reaction between **9** and aldehyde **2** strongly depends also on the proportion of reagents and the temperature of reaction.

A comment on the formation of the so-called „inverted" products is necessary. Their formation, first noted in the synthesis of L-*glycero*-D-*manno*-heptose derivatives [6], played a substantial role in carbon atom chain extension of the *ribo* system (Table 1). Reaction of **2** with methoxymethylmagnesium chloride led exclusively to two inverted products **15** and **16** in spite of lowering the reaction temperature. The interpretation is based on the assumption that aldehyde **2** is particularly sensitive to the basic medium of the Grignard reaction and readily undergoes epimerization [31] at C-4 before reacting with nucleophiles. This is apparently true also for other aldehydes although to a lesser extent. We are checking presently the behaviour of the aldehydes **2**, **4** and **5** in the presence of strong bases and the results will be reported.

CONCLUSION

Chain-extension reactions of pentodialdo-1,4-furanoses **2-5** with C_1 Grignard reagents **6-9** opens a facile access to higher sugar homologs. Hexoses which are otherwise difficult to obtain may be obtained in this way. A variety of 6-O etherified hexoses become readily available. The reaction also adds to the wealth of nucleophilic additions to aldehydes having α- and β-oxygen atoms in sterically defined positions. Our results indicate that when formation of a β-chelate is sterically facile, the reaction goes through this transition state in preference to an α-chelated form. It seems that β-chelation to acetonide oxygen atoms (aldehyde **5**) is almost as effective as to ether oxygen atom (aldehyde **4**). The stereochemical preference of the silyl Grignard **9** is for α-chelated forms in the transition state, thus leading to a preferred L-configuration at the new CHOH grouping.

We continue our studies on this homologation reaction applied to hexose systems.

EXPERIMENTAL

General methods. Melting points were determined with a Kofler apparatus and are uncorrected. Solvents were purified and distilled under argon. ^{1}H NMR spectra were recorded with a Varian AC-200 (200 MHz) or Bruker AM-500 (500 MHz) spectrometers using $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded in the DEPT mode. Signals of the phenyl, benzyl and allyl groups have been omitted in the description of spectra. The assignments of signals for compounds **16**, **17**, **18**, **31**, **32**, and **33** was based on ^{1}H - ^{13}C COSY spectra. High resolution mass spectra (HR-MS) were measured in the FAB^+ ion mode with an AMD-604 mass spectrometer. Infra red spectra were recorded with a Perkin-Elmer 1640 FT-IR spectrophotometer as films. IR spectra of compounds synthesized contained bands 3400-3500 cm^{-1} (OH) and 1090-1110 cm^{-1} (C-O-C). Optical rotation were measured with a JASCO DIP-360 automatic polarimeter at 24 ± 2 °C. CD spectra were recorded between 280-750 nm at room temperature with a JASCO J715 spectropolarimeter using DMSO or $CHCl_3$ solution in cells of 0.1 or 2.0 path lenght (spectral band width 1 nm, sensitivity $10x10^{-6}$ ΔA unit/nm). CD. spectra of hexose derivatives having free C-5 hydroxyl group (6-8 mg) with $(CF_3COO)_4Rh_2$ complex (3-4 mg) were measured in chloroform (10 ml, Spectrograde)[23] Positive E band at 342-358 nm indicated D configuration. For column chromatography silica gel 70-230 mesh (Merck) was used.

Substrates were obtained according to published methods: methyl 2,3-*O*-isopropylidene-β-D-*ribo*-pentodialdo-1,4-furanoside (**2**) was prepared in two steps from D-ribose: methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside [32] was oxidized according to the procedure of D.Horton *et al* [33]. The same procedure was used for oxidation of 3-*O*-benzyl-1,2-*O*-isopropylidene-β-D-arabinofuranose [34] to **3**. Methyl 2,3-*O*-isopropylidene-α-D-*lyxo*-pentodialdo-1,4-furanoside (**5**) was prepared by periodate cleavage ($NaIO_4$) of methyl 2,3-O-isopropylidene-α-D-mannofuranoside [35]. 3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**4**) was prepared analogously from 3-O-benzyl-1,2-O-isopropylidene-α-D-glucofuranose.

The reaction of pentodialdo-1,4-furanoside with an alkoxymethyl Grignard reagents is exemplified below:

Methyl 6-*O*-allyl-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranoside (29), -β-L-idofuranoside (30) and (31)

Dry magnesium turnings (0,432g, 18.4 mmol) were covered with abs. tetrahydrofuran (1 mL) and sublimed mercuric(II) chloride (30 mg) was added. The mixture was stirred *ca* 2 min, cooled to -30 °C, and a few drops of neat, freshly prepared allyloxymethyl chloride were added. When formation of the Grignard reagent started, a solution of the remaining allyloxymethyl chloride (1.95g, 18.4 mmol) in abs. THF (4 mL) was slowly added.

After completion of the Grignard reagent formation (about 2 h) a soln of **4** (1.27 g, 4.5 mmol) in abs. THF (10mL) was added dropwise and stirring at -30 °C was continued for 2 h. Afterwards the reaction mixture was allowed to attain room temperature and additionally stirred for 12 h. The mixture was cooled to 0 °C, poured to cold aq ammonium chloride (50 mL) and extracted with diethyl ether. The ether extract was dried over $MgSO_4$ and concentrated *in vacuo* to dryness. The residue was separated on a silicagel column with hexane-ethyl acetate 8:3 as eluent. First eluted was **29** (1.03 g, 65%). Next eluted was **30** (0.14 g, 9.0%). As the third fraction was eluted **31** (0.08 g, 6%) as a mixture of diastereoisomers.

In a similar manner were synthesized all 6-*O*-alkyl (Bn, All, Me) substituted derivatives of D and L hexofuranoses (Tables 2 and 3) and methyl hexofuranosides (Tables 1 and 4).

Grignard reagent **9**, containing phenyldimethylsilylmethyl group, was obtained according to Fleming *et al* [36] using the procedure of van Boom *et al* [10]. The reactions of **9** with pentodialdo-1,4-furanoses (**2-5**) were performed in typical manner at -30°C. Unmasking of the silyl group from the mixture of **35** and **36** was accomplished with AcOOH/NaBr/AcONa [21] to furnish a mixture of 3-O-benzyl-1,2-O-isopropylidene-α-D-gluco and β-L-ido-hexofuranoses, which were separated by column chromatography with hexane-ethyl acetate 3:2 to 1:1 as eluent.

In the same way were isolated derivatives **17, 18, 19** and **25**. The separation of the mixture of products **43** and **44** as free 5,6-diols (after oxidation as above) of α-D-*manno* and β-L-*gulo* configuration failed. Nevertheless methyl 2,3-O-isopropylidene-α-D-mannofuranoside could be identified by comparison of its ^1H ^{13}C NMR data with the data of an authentic sample.

Oxidation of **25** under unmasking conditions with 15% peroxyacetic acid, led to „dimer" **27.**

Specific rotation data of compounds **28, 32, 36**, and **37** are in agreement with the literature values (see below).

Methyl 6-*O*-benzyl-2,3-*O*-isopropylidene-β-D-allofuranoside (10)

Yield: 28%, colourless oil; ν_{max} (film) 3489, 1604, 1496, 1374, 1210, 1109 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.37-7.33 (5 H, m, Ph), 4.91 (1 H, s, H-1), 4.84 (1 H, d, *J* 5.9 Hz, H-3), 4.69, 4.61 (2 H, ABq, C<u>H</u>$_2$Ph), 4.55 (1 H, d, *J* 5.9 Hz, H-2), 4.06 (1 H, d, *J* 5.7 Hz, H-4), 3.73 (1 H, ddd, *J* 1.9, 5.7, 7.9 Hz, H-5), 3.60 (1 H, dd, *J* 1.9, 10.0 Hz, H-6a), 3.48 (1 H, dd, *J* 7.9, 10.0 Hz, H-6b), 3.41 (3 H, s, OCH_3), 1.47, 1.31 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 128.4-127.5 (Ph), 110.3 (C-1), 88.0, 85.5, 82.3 (C-2, 3, 4), 73.2 (<u>C</u>H$_2$Ph), 70.4 (C-5), 71.9 (C-6), 55.8 (OCH_3), 26.3, 24.7 [(<u>C</u>H$_3$)$_2$C].

Methyl 6-*O*-benzyl-2,3-*O*-isopropylidene-α-L-talofuranoside (11)

Yield: 50%, colourless oil; [Found: C. 62.7; H, 7.5. $C_{17}H_{24}O_6$ requires C, 62.95; H, 7.46%]; $[\alpha]_D$ -11.8 (*c* 0.74, $CHCl_3$). ν_{max} (film) 3482, 1602, 1458, 1376, 1209, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.36-7.29 (5 H, m Ph),4.96 (1 H, s, H-1), 4.93 (1 H, d, *J* 5.8 Hz, H-3), 4.72, 4.68 (2 H, ABq, $C\underline{H}_2Ph$), 4.58 (1 H, d, *J* 5.8 Hz, H-2), 4.35 (1 H, d, *J* 4.9 Hz, H-4), 3.81 (1 H, ddd, *J* 2.6, 4.9, 8.7 Hz, H-5), 3.60 (1 H, dd, *J* 2.6, 10.2 Hz, H-6a), 3.40 (1 H, dd, *J* 8.7, 10.2 Hz, H-6b), 3.38 (3 H, s, OCH_3), 1.48, 1.32 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 129.7-126.8 (Ph), 110.4 (C-1), 88.1, 85.5, 82.4 (C-2, 3, 4), 70.5 (C-5) 73.4 ($\underline{C}H_2Ph$), 71.1 (C-6), 56.0 (OCH_3), 26.4, 24.8 [$(\underline{C}H_3)_2C$].

Methyl 6-*O*-allyl-2,3-*O*-isopropylidene-β-D-allofuranoside (13)

Yield: 10%, colourless oil, $[\alpha]_D$ -51.1 (*c* 1.4, $CHCl_3$); ν_{max} (film) 3493, 1645, 1454, 1376, 1217, 1075, 1023 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.92 (1 H, m, =C$\underline{H}$), 5.33, 5.27 (2 H, 2 q, =C$\underline{H}_2$), 4.97 (1 H, s, H-1), 4.86 (1 H, d, *J* 6.0 Hz, H-3), 4.56 (1 H, d, *J* 6.0 Hz, H-2), 4.04 (1 H, d, *J* 5.6 Hz, H-4), 4.03 (2 H, m, OCH_2), 3.74 (1 H, ddd, *J* 1.8, 5.6, 8.2 Hz, H-5), 3.50 (1 H, dd, *J* 1.8, 9.9 Hz, H-6a), 3.40 (1 H, dd, *J* 8.2, 9.9 Hz, H-6b), 3.44 (3 H, s, OCH_3), 1.48, 1.32 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 134.5, 117.1, 72.4 (allyl C), 110.3 (C-1), 88.0, 85.4, 82.3 (C-2, 3, 4), 70.3 (C-5), 70.9 (C-6), 55.9 (OCH_3), 26.3, 24.7 [$(\underline{C}H_3)_2C$]. HRMS (EI): $(M\text{-}CH_3)^+$, found 259.1172. $C_{12}H_{19}O_6$ requires 259.1181; *m/z* (EI) 259 (45, M-CH_3), 227 (33), 173 (61), 156 (28), 127 (41), 126 (25), 115 (42), 113 (42), 101 (22), 99 (26), 85 (100).

Methyl 6-*O*-allyl-2,3-*O*-isopropylidene-α-L-talofuranoside (14)

Yield 79%; colourless oil; $[\alpha]_D$ -74.2 (*c* 0.82, $CHCl_3$); ν_{max} (film) 3495, 1643, 1458, 1379, 1210, 1068, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 5.97 (1 H, m, =CH), 5.34, 5.21 (2 H, 2 q, =CH_2), 4.96 (1 H, s, H-1), 4.93 (1 H, d, *J* 5.9 Hz, H-3), 4.60 (1 H, d, *J* 5.9 Hz, H-2), 4.32 (1 H, d, *J* 4.7 Hz, H-4), 4.07-4.01 (2 H, m, OCH_2), 3.80 (1 H, ddd, *J* 1.7, 4.7, 3.6 Hz, H-5), 3.57 (2 H, bd, H-6a, H-6b), 3.39 (3 H, s, OCH_3), 1.48, 1.32 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 134.4, 117.3, 72.3 (allyl C), 109.8 (C-1), 88.3, 85.5, 80.7 (C-2, 3, 4), 71.1 (C-5) 70.6 (C-6), 55.5 (OCH_3), 26.4, 24.7 [$(\underline{C}H_3)_2C$]. HRMS (EI): $(M\text{-}CH_3)^+$, found 259.1165. $C_{12}H_{19}O_6$ requires 259.1172; *m/z* (EI) 259 (48, M-CH_3), 227 (35), 173 (65), 171 (27), 156 (21), 127 (38), 113 (46), 101 (21), 99 (27), 85 (100).

Methyl 2,3-*O*-isopropylidene-6-*O*-methyl-β-D-gulofuranoside (15)

Yield 67%; colourless oil; $[\alpha]_D$ -62.1 (*c* 0.95, $CHCl_3$); ν_{max} (film) 3481, 1457, 1373, 1210, 1110, 1026 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 4.95 (1 H, s, H-1), 4.72 (1 H, dd, *J* 3.6, 6.0 Hz, H-3), 4.62 (1 H, d, *J* 6.0 Hz, H-2), 4.16 (1

H, dddd, *J* 2.4, 5.9, 7.9 Hz, H-5), 3.99 (1 H, dd, *J* 3.4, 5.9 Hz, H-4), 3.60 (1 H, dd, *J* 2.4, 9.8 Hz, H-6a), 3.53 (1 H, dd, *J* 7.9, 9.8 Hz, H-6b), 3.42 (3 H, s, OCH_3), 3.33 (3 H, s, OCH_3), 1.47, 1.31 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 106.7 (C-1), 85.3, 80.3, 79.0 (C-2, 3, 4), 73.2 (C-6), 69.5 (C-5), 59.3, 54.6 (2xOCH_3), 25.9, 24.6 [$(\underline{C}H_3)_2C$]. HRMS (EI): $(M-CH_3)^+$, found 233.1016. $C_{10}H_{17}O_6$ requires 233.1025; *m/z* (EI) 233 (22, M-CH_3), 171 (12), 159 (11), 130 (26), 113 (19), 85 (32), 45 (100).

Methyl 2,3-*O*-isopropylidene-6-*O*-methyl-α-L-mannofuranoside (16)

Yield 9%; colourless oil; $[\alpha]_D$ -72.4 (*c* 1.9, $CHCl_3$); ν_{max} (film) 3483, 1451, 1374, 1272, 1195, 1098, 1023 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 4.90 (1 H, s, H-1), 4.85 (1 H, dd, *J* 3.6, 5.9 Hz, H-3), 4.58 (1 H, d, *J* 5.9 Hz, H-2), 4.12 (1 H, ddd, *J* 3.2, 6.1, 8.3 Hz, H-5), 3.90 (1 H, dd, *J* 3.6, 8.3, H-4), 3.60 (1 H, dd, *J* 3.2, 9.9 Hz, H-6a), 3.56 (1 H, dd, *J* 6.1, 9.9 Hz, H-6b), 3.42 (3 H, s, OCH_3) 3.30 (3 H, s, OCH_3), 1.47, 1.33 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 107.0 (C-1), 84.7, 79.9, 78.8 (C-2, 3, 4), 74.2 (C-6), 68.7 (C-5), 59.2, 54.4 (2xOCH_3), 26.0, 24.6 [$(\underline{C}H_3)_2C$]. HRMS (EI): $(M-CH_3)^+$, found 233.1026. $C_{10}H_{17}O_6$ requires 233.1025; *m/z* (EI) 233 (24, M-CH_3), 171 (15), 159 (15), 130 (31), 113 (17), 87 (26), 85 (32), 71 (29), 59 (42), 45 (100).

Methyl 6-deoxy-2,3-*O*-isopropylidene-6-(phenyldimethylsilyl)-β-D-allofuranoside (17)

Yield 54%; white foam; $[\alpha]_D$ -32.4 (*c* 0.9, $CHCl_3$); [Found C, 61.47; H, 8.05. $C_{18}H_{28}O_5Si$ requires C, 61.33; H, 8.01%]; ν_{max} (film) 3498, 1427, 1381, 1247, 1210, 1112 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 7.55-7.32 (5 H, m, Ph), 4.94 (1 H, s, H-1), 4.88 (1 H, d, *J* 6.0 Hz, H-3), 4.56 (1 H, d, *J* 6.0, H-2), 4.14 (1 H, d, *J* 4.4, H-4), 3.86 (1 H, ddd, *J* 2.7, 4.4, 6.1 Hz, H-5), 3.38 (3 H, s, OCH_3), 1.46, 1.31 (6 H, 2 s, $(CH_3)_2C$), 1.10 (1 H, dd, *J* 2.7, 10.1 Hz, H-6a), 0.98 (1 H, dd, *J* 6.1, 10.1 Hz, H-6b), 0.37, 0.35 (6 H, 2 s, $(CH_3)_2Si$). ^{13}C NMR ($CDCl_3$) δ: 133.6-127.6 (Ph), 110.1 (C-1), 93.9 (C-4), 85.8 (C-2), 79.5 (C-3), 69.8 (C-5), 55.6 (OCH_3), 26.3, 24.7 [$(\underline{C}H_3)_2C$], 20.1 (C-6), -1.9, -1.7 [$(CH_3)_2Si$].

Methyl 6-deoxy-2,3-*O*-isopropylidene-6-(phenydimethylsilyl)-α-L-talofuranoside (18)

Yield 11%; white foam; $[\alpha]_D$ -41.0 (*c* 1.8, $CHCl_3$); ν_{max} (film) 3500, 1432, 1374, 1241, 1206, 1092 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.56-7.33 (5 H, m, Ph), 4.94 (1 H, s, H-1), 4.67 (1 H, dd, *J* 3.6, 5.9 Hz, H-3), 4.52 (1 H, d, *J* 5.9 Hz, H-2), 4.19 (1 H, dd, *J* 3.6, 3.1 Hz, H-4), 3.69 (1 H, ddd, *J* 3.1, 5.2, 7.1 Hz, H-5), 3.41 (3 H, s, OCH_3), 1.46, 1.31 (6 H, 2 s, $(CH_3)_2C$), 1.15 (1 H, dd, *J* 5.2, 9.6 Hz, H-6a), 0.97 (1 H, dd, *J* 7.1, 9.6 Hz, H-6b), 0.37, 0.35 (6 H, 2 s, $(CH_3)_2Si$). ^{13}C NMR ($CDCl_3$) δ: 133.6-127.7 (Ph), 110.3 (C-1), 93.9 (C-4), 85.5 (C-2), 82.5 (C-3), 69.8 (C-4), 55.7 (OCH_3), 26.3, 24.7 [$(\underline{C}H_3)_2C$], 21.6 (C-6), -2.22, -2.31 [$(CH_3)_2Si$]. HRMS (EI): $(M-CH_3)^+$, found 337.1472. $C_{17}H_{25}O_5Si$ requires 337.1471; *m/z* (EI) 337 (12, M-CH_3), 292 (22), 262 (24), 218 (21), 137 (30), 135 (100), 116 (49), 101 (34), 87 (20).

Methyl 6-deoxy-2,3-*O*-isopropylidene-6-(phenyldimethylsilyl)-β-D-gulofuranoside (19)

Yield 10%; white foam; [Found: C, 61.2; H, 8.1. $C_{18}H_{28}O_5Si$ requires C, 61.33; H, 8.01%]; $[\alpha]_D$ -28.3 (*c* 0.85, $CHCl_3$); ν_{max} (film) 3506, 1427, 1381, 1248, 1210, 1112 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.55-7.33 (5 H, m, Ph), 4.90 (1 H, s, H-1), 4.66 (1 H, dd, *J* 3.6, 5.9 Hz, H-3), 4.56 (1 H, d, *J* 5.9 Hz, H-2), 4.13 (1 H, ddd, *J* 1.5, 6.0, 6.2 Hz, H-5), 3.72 (1 H, dd, *J* 3.6, 6.0 Hz, H-4), 3.29 (OCH_3), 1.41, 1.27 (6 H, 2 s, $(CH_3)_2C$), 1.35 (1 H, dd, *J* 1.5, 9.8 Hz, H-6a), 1.21 (1 H, dd, *J* 6.2, 9.8 Hz, H-6b), 0.39, 0.36 $(CH_3)_2Si$). ^{13}C NMR ($CDCl_3$) δ: 133.7-127.7 (Ph), 106.7 (C-1), 85.3, 84.4, 80.1 (C-2, 3, 4), 68.3 (C-5), 54.5 (OCH_3), 25.9, 24.5 [($\underline{C}H_3)_2C$], 20.3 (C-6), -1.56, -2.59 [$(CH_3)_2Si$].

Methyl 6-deoxy-2,3-*O*-isopropylidene-6-(phenyldimethylsilyl)-α-L-mannofuranoside (20)

Compound **20** was not isolated in a pure state. Its NMR data could be, however, found from the spectra of a mixture of both stereoisomers **19** and **20** in a proportion of 2.7:1. Proportion was taken from the integration of H-1 signals. Yield 5%; white foam; ^1H NMR ($CDCl_3$) δ: 7.57-7.48 (5 H, m, Ph), 4.89 (1 H, s, H-1), 4.77 (1 H, dd, *J* 3.8, 6.0 Hz, H-3), 4.52 (1 H, d, H-2), 4.07 (1 H, ddd, *J* 2.7, 5.9, 6.4 Hz, H-5), 3.66 (1 H, dd, H-4), 3.27 (3 H, s, OCH_3), 1.43, 1.29 [6 H, 2 s, $(CH_3)_2C$], 1.27 (1 H, dd, 2.7, 9.9 Hz, H-6a), 1.15 (1 H, dd, 5.9 Hz, H-6b), 0.38, 0.34 [6 H, 2 s, ($\underline{C}H_3)_2C$]. ^{13}C NMR ($CDCl_3$) δ: 133.7-127.6 (Ph), 106.8 (C-1), 84.8, 83.9, 80.0 (C-2, 3, 4), 68.4 (C-5), 54.5 (OCH_3), 25.7, 24.4 [($\underline{C}H_3)_2C$], 20.3 (C-6), -1.54, -2.61 [$(CH_3)_2Si$].

3,6-di-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-galactofuranose (21)

Yield 67%, colourless oil; [Found: C, 69.2; H, 7.1 $C_{23}H_{28}O_6$ requires C, 68.98; H, 7.05%]; $[\alpha]_D$ +4.3 (*c* 1.8, $CHCl_3$); ν_{max} (film) 3483, 1455, 1376, 1215, 1074, 1026 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.32-7.29 (10 H, m, 2 Ph), 5.90 (1 H, d, *J* 3.9 Hz, H-1), 4.64 (1 H, d, *J* 3.9 Hz, H-2), 4.59-4.53 (4 H, 2 ABq, 2 $C\underline{H}_2Ph$), 4.27 (1 H, d, *J* 1.9 Hz), 3.98 (1 H, ddd, *J* 3.2, 5.2, 8.4, Hz, H-5), 4.10 (1 H, dd, *J* 1.9, 8.4 Hz, H-4), 3.70 (1 H, dd, *J* 3.2, 9.7 Hz, H-6a), 3.59 (1 H, dd, *J* 5.2, 9.7 Hz, H-6b), 2.63 (1 H, d, *J* 5.0, OH), 1.48, 1.30 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 128.4-127.6 (Ph), 105.9 (c-1), 85.6, 84.8, 82.9 (C-2, 3, 4), 73.4 (C-6), 71.5 ($\underline{C}H_2Ph$, C-6), 70.8 ($\underline{C}H_2Ph$, C-3), 69.9 (C-5), 26.9, 25.9 [($\underline{C}H_3)_2C$].

6-*O*-Allyl-3-*O*-benzyl-1,2-*O*-isopropylidene β-D-altrofuranose (22)

Compound **22** was not isolated in a pure state. Its NMR data could be, however, found from the spectra of a mixture of both stereoisomers **22** and **23** in a proportion of 4:1. Proportion was taken from the integration of H-1signal. Yield 17%; ^1H NMR ($CDCl_3$) δ: 7.36-7.28 (5 H, m, Ph), 5.92 (1 H, m, =CH), 5.90 (1 H, d, *J* 4.4 Hz, H-1), 5.32, 5.14 (2 H, 2 q, $=CH_2$), 4.62 (1 H, d, *J* 4.4 Hz, H-2), 4.58, 4.52 (2 H, ABq, CH_2Ph), 4.02-3.99

(2 H, m, OCH_2), 4.15 (1 H, d, *J* 3.2 Hz, H-3), 4.17 (1 H, dd, *J* 3.2, 6.2 Hz, H-4), 3.97 (1 H, ddd, *J* 3.2, 6.2, 8.6 Hz, H-5), 4.0 (1 H, dd, *J* 3.2, 9.9 Hz, H-6a), 3.56 (1 H, dd, *J* 8.6, 9.9 Hz, H-6b), 1.53, 1.34 (6 H. 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 134.5, 117.4, 72.5 (Allyl C), 128.6-127.7 (Ph), 105.5 (C-1), 85.7, 85.3, 83.1 (C-2, 3, 4), 73.1 (C-6), 71.3 ($\underline{C}H_2Ph$), 69.7 (C-5), 27.1, 26.4 [$(\underline{C}H_3)_2C$].

6-*O*-Allyl-3-*O*-benzyl-1,2-*O*-isopropylidene α-L-galactofuranose (23)

Yield 54%, colourless oil, $[\alpha]_D$ +7.9 (*c* 1.1, $CHCl_3$); ν_{max} (film) 3445, 1646, 1454, 1376, 1217, 1077, 1026cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.34-7.28 (5 H, m, Ph), 5.91 (1 H, d, *J* 3.9 Hz, H-1), 5.89 (1 H, m, =CH), 5.34-5.16 (2 H, 2 q, $=CH_2$), 4.64 (1 H, d, *J* 3.9 Hz, H-2), 4.60-4.58 (2 H, ABq, CH_2Ph), 4.26 (1 H, d, *J* 2.0 Hz, H-3), 4.10 (1 H, dd, *J* 2.0, 6.1 Hz, H-4), 3.96 (1 H, ddd, *J* 3.3, 5.6, 6.1 Hz, H-5), 3.66 (1 H, dd, *J* 3.3, 9.7 Hz, H-6a), 3.54 (1 H, dd, *J* 5.6, 9.7 Hz, H-6b), 1.49, 1.31 (6 H. 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 134.4, 117.3, 70.7 (Allyl C), 128.4-127.6 (Ph), 105.9 (C-1), 85.6, 84.9, 82.9 (C-2, 3, 4), 72.2 (C-6) 70.7 ($\underline{C}H_2Ph$), 69.9 (C-5), 26.9, 25.9 [$(\underline{C}H_3)_2C$]. HRMS (EI): $(M\text{-}CH_3)^+$, found 335.1499. $C_{18}H_{23}O_6$ requires 335.1494; *m/z* (EI) 335 (10, $M\text{-}CH_3$), 292 (12), 251 (20), 245 (57), 203 (40), 189 (41), 105 (34), 91 (100).

3-*O*-Benzyl-1,2-*O*-isopropylidene-6-*O*-methyl-α-L-galactofuranose (24)

Yield 80%, colourless oil; [Found:C, 62.7; H, 7.3. $C_{17}H_{24}O_6$ requires C, 62.95; H, 7.46%]; $[\alpha]_D$ +6.8 (*c* 1.4, $CHCl_3$); ν_{max} (film) 3442, 1454, 1376, 1217, 1077, 1026 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.35-7.28 (5 H, m Ph), 5.90 (1 H, d, *J* 4.0 Hz, H-1), 4.65 (1 H, d, *J* 4.0 Hz, H-2), 4.60 (2 H, s, CH_2Ph), 4.26 (1 H, d, *J* 1.9 Hz, H-3), 4.07 (1 H. dd, *J* 1.9, 8.7 Hz, H-4), 3.94 (1 H, ddd, *J* 3.0, 5.6, 8.7 Hz, H-5) 3.60 (1 H, dd, *J* 3.0, 9.7 Hz, H-6a), 3.48 (1 H, dd, *J* 5.6, 9.7 Hz, H-6b), 3.38 (3 H, s, OCH_3), 2.63 (1 H, d, *J* 4.9, OH), 1.50, 1.32 (6 H, 2 s, $(C\underline{H}_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 128.6-127.8 (Ph), 106.0 (C-1), 85.7, 85.0, 82.9 (C-2, 3, 4), 73.2 (C-6), 71.6 ($\underline{C}H_2Ph$), 69.9 (C-5), 59.2 (OCH_3), 27.0, 26.0 [$(\underline{C}H_3)_2C$].

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-6-(phenyldimethylsilyl)-β-D-altrofuranose (25)

Yield 40%, white solid, mp. 78-79 °C [Found: C, 67.27; H, 7.56. $C_{24}H_{32}O_5Si$ requires C, 67.26; H, 7.53%]; $[\alpha]_D$ +41.1 (*c* 1.7, $CHCl_3$); ν_{max} (film) 3485, 1427, 1378, 1245, 1076, 1021 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.36-7.31 (10 H, m, 2 Ph), 5.83 (1 H, d, *J* 4.2 Hz, H-1), 4.64 (1 H, dd, *J* 4.2, 1.1 Hz, H-2), 4.58, 4.52 (2 H, ABq, CH_2Ph), 3.84 (1 H, dd, *J* 3.8, 5.0 Hz, H-4), 3.15 (1 H, dd, *J* 1.1, 3.8 Hz, H-3), 4.01 (1 H, ddd, *J* 5.0, 3.6 Hz, H-5), 1.45, 1.32 (6 H, 2 s, $(CH_3)_2C$), 1.10 (1 H, dd, *J* 3.6, 14.7 Hz, H-6a), 0.89 (1 H, dd, *J* 10.2, 14.7 Hz, H-6b) ^{13}C NMR ($CDCl_3$) δ: 133.4-127.8 (Ph), 105.2 (C-1), 90.2, 85.6, 81.8 (C-2, 3, 4), 71.7 ($\underline{C}H_2Ph$) 68.6 (C-5), 27.2, 26.4 [$(\underline{C}H_3)_2C$], 20.16 (C-6), -2.1, -2.3 [$(\underline{C}H_3)_2Si$].

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-6-(phenyldimethylsilyl)-α-L-galactofuranose (26)

Compound **26** was not isolated in a pure state. Its NMR data could be, however, found from the spectra of a mixture of both stereoisomers **25** and **26** in a proportion of 3.5:1. Proportion was taken from the integration of H-1signal. Yield 49%, white foam; ^{1}H NMR ($CDCl_3$) δ: 7.39-7.32 (10 H, m, 2 Ph), 5.84 (1 H, d, *J* 4.0 Hz, H-1), 4.65, 4.48 (2 H, ABq, CH_2Ph), 4.64 (1 H, dd, *J* 4.0 Hz, H-2), 4.13 (1 H, dd, *J* 1.3, 3.8 Hz, H-3), 3.86 (1 H, dd, *J* 1.3, 8.3 Hz, H-4), 3.94 (1 H, ddd, *J* 5.0, 8.3 10.3 Hz, H-5), 1.38, 1.28 (6 H, 2 s, $(CH_3)_2C$), 1.12 (1 H, dd, *J* 8.3, 10.3 Hz, H-6a), 0.92 (1 H, dd, *J* 5.0, 10.3 Hz, H-6b). ^{13}C NMR ($CDCl_3$) δ: 133.6-128.4 (Ph), 105.6 (C-1), 91.2, 85.0, 82.8 (C-2, 3, 4), 71.5 ($\underline{C}H_2Ph$), 68.7 (C-5), 26.6, 26.1 [$(\underline{C}H_3)_2C$], 20.5 (C-6), -1.7, -2.5 [$(\underline{C}H_3)_2Si$].

1,3-Di-[3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-β-D-altrofuranos-6-yl]-1,1,3,3-tetramethyl-disiloxane (27)

Yield 71%; white solid, m.p. 124-126 °C; $[\alpha]_D$ 15.4 (*c* 2.6, $CHCl_3$). ν_{max} (KBr) 3493, 1497, 1454, 1376, 1255, 1071, 1026 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 5.87 (1 H, d, *J* 4.1 Hz, H-1), 4.65 (1 H, dd, *J* 4.1, 3.2 Hz, H-2), 4.18 (1 H, d, *J* 3.2, Hz, H-3), 4.05 (1 H, ddd, *J* 3.4, 5.8, 9.9 Hz, H-5), 3.88 (1 H, dd, *J* 3.2, 5.8 Hz, H-4), 1.51, 1.31 (6 H, 2 s, $(CH_3)_2C$), 0.98 (1 H, dd, *J* 3.4, 14.9 Hz, H-6a), 0.86 (1 H, dd, *J* 9.9, 14.9 Hz, H-6b). ^{13}C NMR ($CDCl_3$) δ: 105.4 (C-1), 90.5 (C-4), 85.6 (C-2), 82.3 (C-3), 68.4 (C-5), 27.3, 26.4 [$(CH_3)_2C$], 1.5, 1.1 [$(CH_3)_2Si$]. HRMS (LSIMS):$(M+Na)^+$ 741.3129. $C_{36}H_{54}O_{11}Si_2Na$ requires 741.3102.

3,6-Di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (28)

Yield 77%; colourless oil, $[\alpha]_D$ -18.6 (*c* 1.6, $CHCl_3$); Lit.[36]: $[\alpha]_D$ -20.6 (*c* 1.1, $CHCl_3$). ν_{max} (film) 3487, 1454, 1374, 1216, 1075, 1026 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.35-7.28 (10 H, m, 2 Ph), 5.92 (1 H, d, *J* 3.7 Hz, H-1), 4.64, 4.50 (2 H, ABq, CH_2Ph), 4.62 (1 H, d, *J* 3.7 Hz, H-2), 4.24 (1 H, dd, *J* 3.6, 5.6 Hz, H-4), 4.01 (1 H, d, *J* 3.6 Hz, H-3), 4.09 (1 H, ddd, *J* 3.2, 5.6, 10.2 Hz, H-5), 3.74 (1 H, dd, *J* 3.2, 12.6 Hz, H-6a), 3.60 (1 H, dd, *J* 10.2, 12.6 Hz, H-6b), 1.46, 1.31 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 128.5-127.7 (Ph), 105.1 (C-1), 82.3, 82.1, 79.8 (C-2,3,4), 73.4, 72.3 (2 $\underline{C}H_2Ph$), 72.1 (C-6), 68.0 (C-5), 26.7, 26.3 [$(\underline{C}H_3)_2C$]. HRMS (EI):M^+ 400.1887. $C_{23}H_{28}O_6Na$ requires 400.1886; *m/z* (EI) 400 (8, M), 385 (18), 309 (30), 251 (12), 145 (11), 113 (12), 91 (100).

6-*O*-Allyl-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (29)

Yield 65%; colourless oil, $[\alpha]_D$ 28.2 (*c* 4, $CHCl_3$). ν_{max} (film) 3454, 1646, 1454, 1376, 1217, 1075, 1023 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.35-7.30 (5 H, m, Ph), 5.92 (1 H, d, *J* 2.8 Hz, H-1), 5.90 (1 H, m, =CH), 5.32, 5.15 (2 H, 2 q, $=CH_2$), 4.68, 4.59 (2 H, ABq, CH_2Ph), 4.60 (1 H, d, *J* 3.8 Hz, H-2), 4.14 (1 H, ddd, *J* 5.6, 1.3 Hz, H-

5), 4.10 (2 H, dt, OCH_2), 4.08 (1 H, d, *J* 3.5 Hz, H-3), 4.11 (1 H, dt, *J* 5.6 Hz, H-4), 3.66 (1 H, dd, *J* 2.4, 11.3 Hz, H-6a), 3.56 (1 H, dd, *J* 5.8, 11.3 Hz, H-6b), 1.48, 1.31 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 134.4, 117.2, 72.2 (Allyl C), 128.5-127.7 (Ph), 105.0 (C-1), 82.2 (C-3), 81.9 (C-2), 79.7 (C-4), 72.2 ($\underline{C}H_2Ph$), 71.8 (C-6), 67.8 (C-5), 26.6, 26.2 [$(\underline{C}H_3)_2C$]. HRMS (LSIMS):$(M+Na)^+$ 373.1638. $C_{19}H_{26}O_6Na$ requires 373.1627.

6-*O*-Allyl-3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-idofuranose (30)

Yield 9%; colourless oil; $[\alpha]_D$ -44.3 (*c* 2.9, $CHCl_3$); ν_{max} (film) 3458, 1645, 1454, 1376, 1216, 1074, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.33-7.29 (5 H, m, Ph), 6.00 (1 H, d, *J* 3.8 Hz, H-1), 5.85 (1 H, m, =CH), 5.28, 5.12 (2 H, 2 q, $=CH_2$), 4.72, 4.48 (2 H, ABq, CH_2Ph), 4.65 (1 H, d, *J* 3.8 Hz, H-2), 4.24 (1 H, dd, *J* 3.5, 5.1 Hz, H-4), 4.15 (1 H, ddd, *J* 5.1, 1.92, 6.3, H-5), 4.01 (1 H, d, *J* 3.5 Hz, H-3), 3.96 (2 H, dt, OCH_2), 3.48 (2 H, bd, H-6a, H-6b), 1.48, 1.33 (6 H, 2s, $(CH_3)_2C$). ^{13}C ($CDCl_3$) δ: 134.4, 117.1, 71.8 (Allyl C), 128.6-127.9 (Ph), 104.8 (C-1), 82.9 (C-3), 82.2 (C-2), 79.6 (C-4), 72.3 ($\underline{C}H_2Ph$), 70.7 (C-6), 69.3 (C-5), 26.7, 26.3 [$(\underline{C}H_3)_2C$]. HRMS (EI): $(M-CH_3)^+$ 335.1491. $C_{18}H_{23}O_6$ requires 335.1494; *m/z* (EI) 335 (10, $M-CH_3$), 245 (20), 173 (19), 159 (38), 127 (32), 113 (20), 91 (100).

31, mixture of two products in unequal amounts. ^{13}C NMR ($CDCl_3$) of the major component: δ: 104.8 (C-1), 85.0, 79.6, 75.7, 69.4 (C-2,3,4,5), 71.0 (C-6), 26.7, 26.0 [$(\underline{C}H_3)_2C$]. Minor: 105.0 (C-1), 82.0, 81.9, 79.9, 69.2 (C-2,3,4,5), 70.8 (C-6), 26.7, 26.0 [$(\underline{C}H_3)_2C$].

3-*O*-Benzyl-6-*O*-methyl-1,2-*O*-isopropylidene-α-D-glucofuranose (32)

Yield 68%; colourless oil; $[\alpha]_D$ -39.7 (*c* 1.8, $CHCl_3$) {Lit. [37]: $[\alpha]_D$ -40.4 (*c* 2.0, $CHCl_3$)}. ν_{max} (film) 3452, 1455, 1376, 1217, 1077, 1026 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.36-7.31 (5 H, m, Ph), 5.92 (1 H, d, *J* 3.8 Hz, H-1), 4.69, 4.59 (2 H, ABq, CH_2Ph), 4.60 (1 H, d, *J* 3.8 Hz, H-2), 4.21 (1 H, dd, *J* 3.6, 5.2 Hz, H-4), 4.12 (1 H, ddd, *J* 5.2, 5.8, 3.4 Hz, H-5), 3.99 (1 H, d, *J* 3.6 Hz, H-3), 3.41 (1 H, dd, *J* 3.4, 9.7 Hz, H-6a), 3.39 (1 H, dd, *J* 5.8, 9.7 Hz, H-6b), 3.40 (3 H, s, OCH_3), 1.48, 1.33 (6 H, 2s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 128.5-127.8 (Ph), 105.1 (C-1), 82.2 (C-2), 81.9 (C-4), 79.8 (C-3), 74.3 (C-6), 72.3 ($\underline{C}H_2Ph$), 67.8 (C-5), 59.2 (OCH_3), 26.3 [$(\underline{C}H_3)_2C$]. HRMS (LSIMS):$(M+Na)^+$ 347.1488. $C_{17}H_{24}O_6Na$ requires 347.1471

3-*O*-Benzyl-6-*O*-methyl-1,2-*O*-isopropylidene-β-L-idofuranose (33)

Yield 11%; colourless oil; [Found C, 62.7; H,7.7; $C_{17}H_{24}O_6$ requires C, 62.95; H, 7.46%]; $[\alpha]_D$-19.3 (*c* 1.0, $CHCl_3$); ν_{max} (film) 3450, 1454, 1375, 1216, 1074, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.35-7.31 (5 H, m, Ph), 5.97 (1 H, d, *J* 3.9 Hz, H-1), 4.71, 4.47 (2 H, ABq, CH_2Ph), 4.62 (1 H, d, *J* 3.9 Hz, H-2), 4.18 (1 H, dd, *J* 3.6, 5.2 Hz, H-4), 4.10 (1 H, ddd, *J* 5.2, 2.3, 9.7 Hz, H-5), 3.97 (1 H, d, *J* 3.6 Hz, H-3), 3.41 (1 H, dd, *J* 2.3, 10.5

Hz, H-6a), 3.38 (1 H, dd, *J* 9.7, 10.5 Hz, H-6b), 3.30 (3 H, s, OCH_3), 1.46, 1.31 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 128.6-127.9 (Ph), 104.8 (C-1), 82.8 (C-3), 82.2 (C-2), 79.7 (C-4), 73.3 (C-6), 71.8 ($\underline{C}H_2Ph$), 69.2 (C-5), 59.1 (OCH_3), 26.7, 26.3 [$(\underline{C}H_3)_2C$].

3-*O*-Benzyl-6-*O*-methyl-1,2-*O*-isopropylidene-α-D-galactofuranose (34)

Yield 4%; colourless oil; [Found C, 62.8; H, 7.5. $C_{17}H_{24}O_6$ requires C, 62.95; H, 7.46%]; $[\alpha]_D$ -20.1 (*c* 0.8, $CHCl_3$). ν_{max} (film) 3448, 1453, 1375, 1218, 1075, 1027 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.38-7.32 (5 H, m, Ph), 5.96 (1 H, d, *J* 3.6 Hz, H-1), 4.59 (1 H, s, CH_2Ph), 4.53 (1 H, d, *J* 3.6 Hz, H-2), 4.35 (1 H,, d, *J* 2.7 Hz, H-3), 4.21 (1 H, ddd, *J* 3.5, 5.9, 6.1 Hz, H-5), 4.11 (1 H, dd, *J* 2.8, 6.1 Hz, H-4), 3.7 (1 H, dd, *J* 3.5, 9.9 Hz, H-6a), 3.64 (1 H, dd, *J* 5.9, 9.9 Hz, H-6b), 3.39 (3 H, s, OCH_3), 1.48, 1.31 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 128.7-127.6 (Ph), 104.8 (C-1), 85.1 (C-2), 79.7 (C-4), 75.8 (C-3), 73.6 ($\underline{C}H_2Ph$), 71.0 (C-6), 69.5 (C-5), 59.1 (OCH_3), 26.7, 26.3 [$(\underline{C}H_3)_2C$].

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-6-(phenyldimethylsilyl)-α-D-glucofuranose (35)

Compound **35** was not isolated in a pure state. Its NMR data could be, however, found from the spectra of a mixture of both stereoisomers **35** and **36** in a proportion of 1:10. Proportion was taken from the integration of H-1signal. Yield 7%; white foam; ^1H NMR ($CDCl_3$) δ: 7.53-7.46 (5 H, m, Ph), 5.92 (1 H, d, *J* 3.8 Hz, H-1), 4.58, 4.32 (2 H, ABq, CH_2Ph), 4.52 (1 H, d, *J* 3.8 Hz, H-2), 4.18 (1 H, ddd, *J* 3.6, 5.9, 7.2 Hz, H-5), 4.02 (1 H, dd, *J* 3.6, 5.9 Hz, H-4), 3.86 (1 H, d, *J* 3.8 Hz, H-3), 1.48, 1.30 (6 H, 2 s, $(CH_3)_2C$), 1.12 (1 H, dd, *J* 3.6, 10.8 Hz, H-6a), 0.98 (1 H, dd, *J* 7.2, 10.8 Hz, H-6b), 0.41, 0.32 (6 H, 2 s, $(CH_3)_2Si$). ^{13}C NMR ($CDCl_3$) δ: 133.7-127.6 (Ph), 105.1 (C-1), 84.2 82.7, 82.5 (C-2,3,4), 72.2 ($\underline{C}H_2Ph$), 69.6 (C-5), 26.8, 26.4 [$(\underline{C}H_3)_2C$], 20.2 (C-6), -2.2, -2.4 [$(CH_3)_2Si$].

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-6-(phenyldimethylsilyl)-β-L-idofuranose (36)

Yield 88%; white foam; [Found: C, 67.3; H,7.6. $C_{24}H_{35}O_5Si$ requires C, 67.26; H, 7.53%]; $[\alpha]_D$ -53.8 (*c* 1.8, $CHCl_3$). Lit. [21]: $[\alpha]_D$ -48.9 (*c* 5.0, $CHCl_3$). ν_{max} (film) 3437, 1455, 1427, 1249, 1114, 1077 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.54-7.32 (10 H, m, 2 Ph), 5.94 (1 H, d, *J* 2.8 Hz, H-1), 4.66, 4.34 (2 H, ABq, CH_2Ph), 4.61 (1 H, d, *J* 2.8 Hz, H-2), 4.10 (1 H, ddd, *J* 3.2, 3.7, 6.4 Hz, H-5), 3.96 (1 H, dd, *J* 3.3, 6.4 Hz, H-4), 3.89 (1 H, d, *J* 3.3 Hz, H-3), 1.03 (1 H, dd, *J* 3.7, 14.4 Hz, H-6a), 0.80 (1 H, dd, *J* 3.2, 14.4 Hz, H-6b), 0.34, 0.32 (6 H, 2 s, $(CH_3)_2Si$). ^{13}C NMR ($CDCl_3$) δ: 133.8-127.6 (Ph), 104.8 (C-1), 85.4 (C-3), 82.1 (C-2, C-4), 71.6 ($\underline{C}H_2Ph$), 67.8 (C-5), 26.6, 26.2 [$(\underline{C}H_3)_2C$], 19.8 (C-6), -1.6, -2.5 [$(CH_3)_2Si$].

Methyl 6-*O*-benzyl-2,3-*O*-isopropylidene-α-D-mannofuranoside (37)

Yield 62%; colourless oil; $[\alpha]_D$ +54.9 (*c* 2.7, $CHCl_3$); Lit.[38]: $[\alpha]_D$ +59.5 (*c* 0.4, $CHCl_3$). ν_{max} (film) 3473, 1495, 1453, 1375, 1275, 1111, 1024 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.35-7.30 (5 H, m, Ph), 4.88 (1 H, s, H-1), 4.83 (1 H, dd, *J* 3.6, 5 9 Hz, H-3), 4.62, 4.58 (2 H, ABq, CH_2Ph), 4.55 (1 H, d, *J* 5.9 Hz, H-2), 4.15 (1 H, ddd, *J* 3.4, 5.7, 8.2 Hz, H-5), 3.96 (1 H, dd, *J* 3.6, 8.2 Hz, H-4), 3.76 (1 H, dd, *J* 3.4, 9.8 Hz, H-6a), 3.64 (1 H, dd, *J* 5.7, 9.8 Hz, H-6b), 3.26 (3 H, s, OCH_3), 1.46, 1.32 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 128.4-127.6 (Ph), 107.1 (C-1), 84.7, 80.0, 78.8 (C-2, 3, 4), 73.5 ($\underline{C}H_2Ph$), 71.8 (C-6), 68.9 (C-5), 54.4 (OCH_3), 25.9, 24.6 [$(\underline{C}H_3)_2C$]. HRMS (EI):$(M-CH_3)^+$ 309.1328. $C_{16}H_{21}O_6$ requires 309.1338; *m/z* (EI) 309 (8, $M-CH_3$), 234 (11), 171 (6), 105 (9), 91 (100).

Methyl 6-*O*-benzyl-2,3-*O*-isopropylidene-β-L-gulofuranoside (38)

Yield 8%; colourless oil; [Found C, 62.8; H, 7.41. $C_{17}H_{24}O_6$ requires C, 62.95; H, 7.46%]; $[\alpha]_D$ +35.4 (*c* 2.3, $CHCl_3$); ν_{max} (film) 3472, 1495, 1453, 1375, 1279, 1095, 1049 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.34-7.31 (5 H, m, Ph), 4.94 (1 H, s, H-1), 4.67 (1 H, dd, *J* 6.0, 3.5 Hz, H-3), 4.60, 4.56 (2 H, ABq, CH_2Ph), 4.56 (1 H, d, *J* 6.0 Hz, H-2), 4.20 (1 H, ddd, *J* 5.8, 1.8, 5.1 Hz, H-5), 4.04 (1 H, dd, *J* 3.5, 5.8 Hz, H-4), 3.76 (1 H, dd, *J* 1.8, 9.8 Hz, H-6a), 3.60 (1 H, dd, *J* 5.1, 9.8 Hz, H-6b), 3.31 (OCH_3), 1.45, 1.28 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 128.4-127.6 (Ph), 106.7 (C-1), 85.3, 80.3, 78.9 (C-2, 3, 4), 73.2 ($\underline{C}H_2Ph$), 70.7 (C-6), 69.6 (C-5), 54.6 (OCH_3), 25.9, 24.5 [$(\underline{C}H_3)_2C$].

Methyl 6-*O*-allyl-2,3-*O*-isopropylidene-α-D-mannofuranoside (39)

Yield 70%; colourless oil; $[\alpha]_D$ +59.1 (*c* 1.1, $CHCl_3$); ν_{max} (film) 3455, 1639, 1455, 1375, 1271, 1092 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 6.02 (1 H, m, =CH), 5.34, 5.18 (2 H, 2 q, $=CH_2$), 4.90 (1 H, s, H-1), 4.86 (1 H, dd, *J* 5.9, 3.6 Hz, H-3), 4.57 (1 H, d, *J* 5.9 Hz, H-2), 4.07 (2 H, m, OCH_2), 4.06 (1 H, ddd, *J* 8.3, 2.9, 5.6 Hz, H-5), 3.94 (1 H, dd, *J* 3.6, 8.3 Hz, H-4), 3.78 (1 H, dd, *J* 2.9, 10.0 Hz, H-6a), 3.54 (1 H, dd, *J* 5.6, 10.0 Hz, H-6b), 3.3 (OCH_3), 1.4, 1.3 (6 H, 2 s, $(CH_3)_2C$).^{13}C NMR ($CDCl_3$) δ: 134.4, 117.2, 72.3 (Allyl), 107.1 (C-1), 84.7, 79.9, 78.8 (C-2, 3, 4), 71.7 (C-6), 68.8 (C-5), 54.5 (OCH_3), 25.9, 24.6 [$(\underline{C}H_3)_2C$]. HRMS (EI):$(M-CH_3)^+$ 259.1181. $C_{12}H_{19}O_6$ requires 259.1172; *m/z* (EI) 259 (26, $M-CH_3$), 171 (19), 127 (20), 116 (23), 114 (28), 113 (33), 99 (28), 85 (89), 59 (100).

Methyl 6-*O*-allyl-2,3-*O*-isopropylidene-β-L-gulofuranoside (40)

Yield 11%; colourless oil; ^1H NMR ($CDCl_3$) δ: 6.00 (1 H, m, =CH), 5.34, 5.16 (2 H, 2 q, $=CH_2$), 4.94 (1 H, s, H-1), 4.74 (1 H, dd, *J* 3.6, 5.9 Hz, H-3), 4.60 (1 H, d, *J* 5.9 Hz, H-2), 4.05 (2 H, m, OCH_2), 3.96 (1 H, ddd, *J* 3.4, 5.7, 9.6 Hz, H-5), 4.24 (1 H, dd, *J* 3.6, 5.7 Hz, H-4), 3.78 (1 H, dd, *J* 3.4, 11.5 Hz, H-6a), 3.66 (1 H, dd, *J* 9.6, 11.5 Hz, H-6b), 3.1 (OCH_3), 1.47, 1.33 (6 H, 2 s, $(CH_3)_2C$).^{13}C NMR ($CDCl_3$) δ: 134.6, 117.4, 72.5

(Allyl), 106.8 (C-1), 85.5, 80.5, 79.0 (C-2, 3, 4), 72.5 (C-6), 69.7 (C-5), 54.4 (OCH_3), 25.7, 24.8 [($\underline{C}H_3)_2C$]. (NMR data taken from the spectra of a 1.5:1 mixture of **40** and **41**).

Methyl 2,3-*O*-isopropylidene-6-*O*-methyl-α-D-mannofuranoside (41)

Yield 58%; colourless oil; $[\alpha]_D$ +82.4 (*c* 0.95, $CHCl_3$); ν_{max} (film) 3491, 1456, 1374, 1211, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 4.90 (1 H, s, H-1), 4.85 (1 H, dd, *J* 5.9, 3.6 Hz, H-3), 4.57 (1 H, d, *J* 5.9 Hz, H-2), 4.13 (1 H, ddd, *J* 3.2, 6.1, 8.3 Hz, H-5), 3.91 (1 H, dd, *J* 3.6, 8.3 Hz, H-4), 3.66 (1 H, dd, *J* 3.2, 9.9 Hz, H-6a), 3.56 (1 H, dd, *J* 6.1, 9.9 Hz, H-6b), 3.42 (3 H, s, OCH_3), 3.3 (OCH_3), 1.47, 1.33 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 107.0 (C-1), 84.7, 80.0, 78.7 (C-2, 3, 4), 74.2 (C-6), 68.8 (C-5), 59.2, 54.4 (2xOCH_3), 26.0, 24.6 [($\underline{C}H_3)_2C$]. HRMS (EI):$(M-CH_3)^+$ 233.1035. $C_{10}H_{17}O_6$ requires 233.1025; *m/z* (EI) 233 (100, M-CH_3), 203 (23), 173 (16), 159 (17), 141 (28), 130 (57), 113 (24), 87 (24), 85 (28), 59 (29), 45 (100).

Methyl 2,3-*O*-isopropylidene-6-*O*-methyl-β-L-gulofuranoside (42)

Yield 42%; colourless oil; $[\alpha]_D$ +55.4 (*c* 1.2, $CHCl_3$); ν_{max} (film) 3456, 1458, 1382, 1212, 1094 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 4.95 (1 H, s, H-1), 4.72 (1 H, dd, *J* 3.6, 6.0 Hz, H-3), 4.62 (1 H, d, *J* 6.0 Hz, H-2), 4.18 (1 H, ddd, *J* 2.4, 5.9 7.9 Hz, H-5), 3.99 (1 H, m, *J* 3.4, 5.9 Hz, H-4), 3.60 (1 H, dd, *J* 2.4, 9.8 Hz, H-6a), 3.53 (1 H, dd, *J* 7.9, 9.8 Hz, H-6b), 3.42 (3 H, s, OCH_3), 3.30 (3 H, s OCH_3) 1.47, 1.31 (6 H, 2 s, $(CH_3)_2C$). ^{13}C NMR ($CDCl_3$) δ: 106.7 (C-1), 85.4, 80.3, 79.0 (C-2, 3, 4), 73.2 (C-6). 69.5 (C-5), 59.3, 54.6 (2xOCH_3), 25.9, 24.6 [($\underline{C}H_3)_2C$]. HRMS (EI):$(M-CH_3)^+$ 233.1034. $C_{10}H_{17}O_6$ requires 233.1025; *m/z* (EI) 233 (21, M-CH_3) , 203 (7), 171 (12), 159 (12), 130 (27), 113 (14), 87 (23), 85 (26), 71 (28), 59 (38), 45 (100).

Methyl 6-deoxy-2,3-*O*-isopropylidene-6-(phenyldimethylsilyl)-α-D-mannofuranoside (43)

Yield 33%; white foam; ^1H NMR ($CDCl_3$) δ: 7.38-7.32 (5 H, m, Ph), 4.62 (1 H, s, H-1), 4.38 (1 H, dd, *J* 3.6, 5.9 Hz, H-3), 4.26 (1 H, d, *J* 5.9 Hz, H-2), 3.38 (1 H, dd, *J* 3.6, 7.1 Hz, H-4), 3.75 (1 H, ddd, *J* 2.9, 4.6, 7.1 Hz, H-5), 3.00 (3 H, s, OCH_3), 1.16, 1.02 (6 H, 2 s, $(CH_3)_2C$), 1.02 (1 H, dd, *J* 2.9, 10.2 Hz, H-6a), 0.86 (1 H, dd, *J* 7.9, 10.2 Hz, H-6b), 0.13, 0.09 (6 H, 2 s, $(CH_3)_2Si$), ^{13}C NMR ($CDCl_3$) δ: 128.9-128.1 (Ph), 106 8 (C-1), 84.9, 84.1, 80.0 (C-2, 3, 4), 68.4 (C-5), 54.7 (OCH_3), 26.0, 24.6 [($\underline{C}H_3)_2C$], 26.2, 24.8 [$(CH_3)_2C$], 22.3 (C-6), -1.8, -2.2 [$(CH_3)_2Si$]. (NMR data taken from the spectra of a 1:2.8 mixture of **43** and **44**).

Methyl 6-deoxy-2,3-*O*-isopropylidene-6-(phenyldimethylsilyl)-β-L-gulofuranoside (44)

Yield 46%; white foam; ^1H NMR ($CDCl_3$) δ: 7.38-7.32 (5 H, m, Ph), 4.65 (1 H, s, H-1), 4.50 (1 H, dd, *J* 3.8, 5.9 Hz, H-3), 4.28 (1 H, d, *J* 5.9 Hz, H-2), 3.45 (1 H, dd, *J* 3.8, 6.4 Hz, H-4), 3.85 (1 H, ddd, *J* 1.8, 4.5, 6.4 Hz, H-5), 3.10 (3 H, s, OCH_3), 1.14, 1.00 (6 H, 2 s, $(CH_3)_2C$), 1.12 (1 H, dd, *J* 1.8, 9.8 Hz, H-6a), 1.04 (1 H,

dd, *J* 4.5, 9.8 Hz, H-6b), 0.11, 0.09 (6 H, 2 s, $(CH_3)_2Si$). ^{13}C NMR ($CDCl_3$) δ: 128.9-128.1 (Ph), 106.7 (C-1), 85.4, 84.6, 80.2 (C-2, 3, 4), 68.3 (C-5), 54.6 (OCH_3), 25.9, 24.6 [$(CH_3)_2C$] 20.3 (C-6), -1.5, -2.5 [$(CH_3)_2Si$]. (NMR data taken from the spectra of a 1:2.8 mixture of **43** and **44**).

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