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1,6-ANHYDRO-3-*O*-BENZYL-2-DEOXY-2,4-DI-*C*-METHYL-β-D-HEXOPYRANOSES: SYNTHESIS AND PROPERTIES

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ABSTRACT

The synthesis of the isomeric 1,6-anhydro-3-*O*-benzyl-2-deoxy-2,4-di-*C*-methyl-β-D-hexopyranoses and their spectral characterisation are described. 1,6-Anhydro-3-*O*-benzyl-2-deoxy-4-*O*-mesyl-2,4-di-*C*-methyl-β-D-galactopyranose undergoes ring-contraction on solvolysis.

INTRODUCTION

In our work directed towards the synthesis of macrolide antibiotics, it became necessary to obtain certain branched 1,6-anhydrohexopyranoses containing a tertiary hydroxyl group at position 4. The strategy[1,2] for the synthesis of erythronolide A involved the preparation of the C-9/C-13 segment from 1,6-anhydro-β-D-glucopyranose (**1**, levoglucosan) *via* the derivatives **2** and **3**. Conversion of the mesylate (**4**) of **3** would then give the D-*gluco* derivative (**5**). However, difficulties were encountered because of the rearrangement of the 1,6-anhydrohexopyranose derivative **4** into the 1,6-anhydrohexofuranose derivative **7**, and because of the complexity of the n.m.r. spectra which were difficult to interpret. These circumstances prompted a study of the synthesis and some conversions of compounds of type **4**.

RESULTS AND DISCUSSION

*1,6-Anhydro-3-*O*-benzyl-2,4-dideoxy-2-*C*-methyl-4-methylene-β-*D*-xylo- and -ribo-hexopyranoses.* — When a solution of **4** in nitromethane was boiled, a complex mixture of products was formed, from which 30% of **7** was isolated. This compound was erroneously thought[1,2] to be the isomeric mesylate **5**, but has been proved to be a furanose-type derivative formed by rearrangement (*vide infra*). The reaction is accompanied by release of methanesulfonic acid, which then causes extensive destruction of the products. When the reaction was performed in the presence of 4 Å molecular sieves, which bind methanesulfonic acid, the yield of **7** was increased to 59%. The methylene derivative **6** (35%) was also isolated from the

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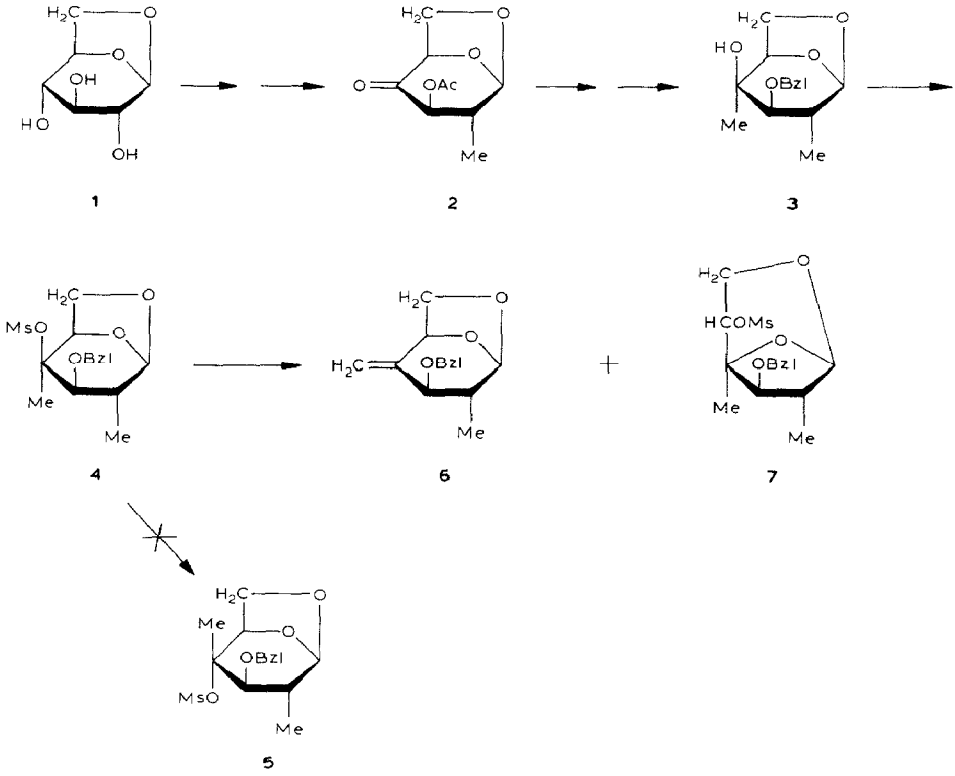
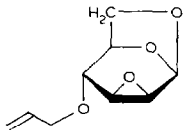
reaction mixture, and was the only product when the reaction was carried out in the presence of ethyldi-isopropylamine.

The structure of **6** follows from a comparison of its ^{1}H- and ^{13}C-n.m.r. spectra with those of the 3-*O*-methyl analogue[3]. The spectra coincide well, taking into account the different nature of the substituents at O-3. The coupling constants ($J_{5,6}$ 5.5, $J_{6,6}$ 7, and $J_{1,2}$ 1 Hz) of **6** are typical of 1,6-anhydrohexopyranoses. In the ^{13}C-n.m.r. spectrum, there were signals in the region expected for the carbon atom of a methylene group (117 p.p.m.) and of C-4 (140.6 p.p.m.), which characterise the conversion **4** → **6**. The chemical shifts of the other signals corresponded with the structure assigned.



The methylene derivative **6** was a convenient starting-material for the synthesis of the D-*gluco* compound **16**, which possesses the correct stereochemistry for the construction of the C-9/C-13 segment of erythronolide A, and a more efficient synthesis of **6** and its 3-epimer was developed.

Reaction of the epoxide **8**, prepared[4] from levoglucosan (**1**), with dimethylmagnesium, under conditions described previously[3], afforded, selectively and nearly quantitatively, the alcohol **9**. The ^{1}H-n.m.r. spectrum of **9** contained signals for *C*-methyl (δ 1.14, $J_{2,Me}$ 7.5 Hz) and hydroxyl groups, and the small coupling constants, $J_{1,2} = J_{2,3} = 1$ Hz, were similar to those observed for the 4-*O*-benzyl



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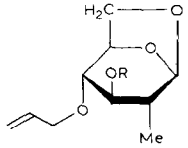

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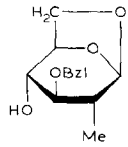

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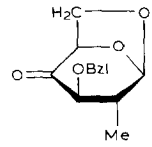

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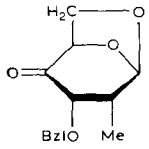

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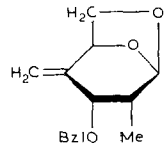

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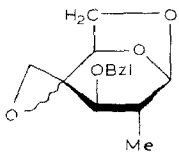
analogue[3] and correspond to a diaxial arrangement of the substituents at C-2,3. Benzylation of **9** proceeded smoothly (→**10**), thus providing suitable protection for HO-3. Subsequent conventional[5] *O*-deallylation of **10**, followed by Swern oxidation[6] of the resulting alcohol **11**, gave the key-intermediate ketone **12**. The ^{1}H- and ^{13}C-n.m.r. spectra of **12** were similar to those of the 3-*O*-methyl analogue[3].

Treatment of **12** with methanolic sodium methoxide caused rapid and almost quantitative isomerisation at C-3, yielding the ketone **13**. Comparison of the ^{1}H-n.m.r. spectra of **12** and **13** indicated a change in the conformation of the pyranose ring. Thus, the coupling constants ($J_{1,2}$ 0.5, $J_{2,3}$ 7.6 Hz) for **12** correspond to $B_{o,3}$ or ^3S_o conformations of the pyranose ring, and those ($J_{1,2}$ 2.1, $J_{2,3}$ 7.6 Hz) for **13** correspond more to a half-chair conformation.

Reaction of the ketone **12** with methylenetriphenylphosphorane afforded the 4-methylene derivative **6**. This route to **6** is more advantageous than that described previously[1,2] (elimination of methanesulfonic acid from the mesylate **4**) in terms of availability of the starting material, simplicity of reagents, and better yields at each stage. Likewise, the reaction of the ketone **13** with methylenetriphenylphosphorane gave the 4-methylene derivative **14**. In the ^{13}C-n.m.r. spectrum of **14**, the signal (143.4 p.p.m.) for C-4 was shifted upfield compared with that for **13** (201.5 p.p.m.), and the signal (110.2 p.p.m.) for the methylene carbon appeared in the expected region but was considerably shifted upfield ($\Delta\delta$ 7 p.p.m.) as compared to that of **6**. The influence of the equatorial benzyloxy group in **14** on the signals for C-5 (upfield shift of 3.3 p.p.m.) and the methyl group at C-2 (upfield shift of 5.6 p.p.m.) is also appreciable as compared with that of the axial group in **6**.

*1,6-Anhydro-3-*O*-benzyl-2-deoxy-2,4-di-*C*-methyl-β-*D*-hexopyranoses.* — The required, isomeric tertiary alcohols were obtained from the ketones **12** and **13**, and the 4-methylene derivatives **6** and **14**. The reaction of **12** with methylmagnesium bromide afforded almost quantitatively the D-*galacto* isomer **3** described previously[3]. Treatment of **6** with *m*-chloroperoxybenzoic acid gave a mixture of epoxides **15**, which was reduced with lithium aluminium hydride.



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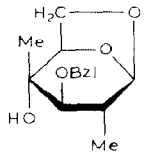

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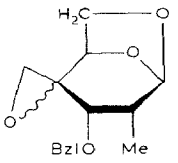

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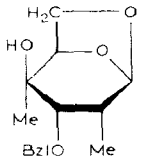

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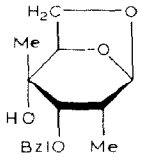

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Chromatography on silica gel then gave the D-*galacto*[3] (**3**) and D-*gluco* (**16**) tertiary alcohols.

Epoxidation of the double bond in **14** also gave a mixture of epoxides **17**, which was reduced with lithium aluminium hydride to afford the alcohols **18** (77.5%) and **19** (14.5%) which were isolated by chromatography. Treatment of the ketone **13** with methylmagnesium bromide yielded 94% of the alcohol **19**.

The direction of attack of the Grignard reagent on the carbonyl groups in **12** and **13** is determined by the orientation of the substituent at C-3. When the benzyloxy group is axial, the attack occurs exclusively from the *endo*-side to give the D-*galacto* isomer **3** in quantitative yield, whereas attack occurs from the *exo*-side in **13**. According to the ^{1}H-n.m.r. data noted above, **13** appears to possess a half-chair conformation, which implies flattening of the C-2,3,4,5 fragment and facilitates approach of the Grignard reagent from the *exo*-side. Epoxidation of the methylene derivatives **6** and **14** was less stereospecific, but one product preponderated.

The structure of the compounds obtained follows from an analysis of the ^{1}H- and ^{13}C-n.m.r. spectra and n.O.e. studies. The structure of the alcohol **16** was confirmed by an X-ray study of its 4-benzyl ether[8]. The n.O.e., which allows[9] spatially close groups of atoms with no direct spin–spin interaction to be identified, was of value in determining the structure of the tertiary alcohols **3, 16, 18,** and **19**. Thus, pre-irradiation of H-6*endo* in **16** resulted in an increase in the intensity of the signal for Me-4 by 5.7%, and pre-irradiation of Me-4 caused changes in the signals for H-6*endo* (2.1%), H-5 (2.6%), and H-3 (1.5%). These data, in conjunction with the synthesis route and the spectral evidence, confirm the structure assigned to **16**.

Pre-irradiation of Me-4 of the *galacto* isomer **3** resulted in an increase in the intensities of the signals for H-3 (1.6%), H-5 (1.3%), and Me-2 (1.8%), which accords with its stereochemistry and confirms previous conclusions based on spectral data and chemical transformations.

The stereochemistry of the C-4 epimers **18** and **19** was established in a similar manner. Thus, pre-irradiation of the H-3 doublet in **19** resulted in a 4.3% increase in the intensity of the H-6*endo* signal, whereas pre-irradiation of Me-4 had a

TABLE I

^{13}C-N M R. DATA FOR THE ALCOHOLS **3**, **16**, **18**, AND **19**

	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Me-2*	*Me-4*	CH_2Ph
3	103.9	38.3	83.9	67.8	79.2	63.7	16.4	26.6	72.2
16	104.2	37.4	83.2	72.0	79.5	63.9	16.8	21.4	72.1
18	104.9	38.7	79.0	72.1	79.7	64.4	9.7	22.7	71.1
19	104.9	37.7	75.2	72.2	80.1	65.1	10.7	23.4	71.0

corresponding effect on the signals for H-3 (1%), H-5 (1.5%), and H-6*endo* (1.1%), in accord with the proposed structure.

For the alcohol **18**, pre-irradiation of Me-4 affected the signals for H-5 (1.5%) and Me-2 (1.4%), and characterised the 2,4-diaxial orientation of these methyl groups. Pre-irradiation of H-3 increased the signal intensities for HO-4 (5%) and H-6*endo* (7.5%). The molecular models of the alcohols **3**, **16**, **18**, and **19** accord with the observed n.O.e. data.

The ^{13}C-n.m.r. data for **3**, **16**, **18**, and **19** are presented in Table I. The configuration at C-3 is the determining factor: when the benzyloxy group is axial, the signal for C-3 is considerably shifted downfield (83 p.p.m. for **3** and **16**, *cf.* 79 and 75.2 p.p.m. for **18** and **19**, respectively). The configuration at C-3 also determines the position of the signal for Me-2. Also, **3** and **16** can be readily distinguished by the position of the signal for C-4, and **18** and **19** by the position of the signal for C-3.

The position of the signal of Me-2 is essentially determined by the spatial interactions of its protons with H-3 and the CH_2Ph protons (taking into account the alternant character of the effect due to the number of bonds separating the interacting protons[10]). In the alcohols **3** and **16**, H-2 and the protons of Me-2 (*i.e.*, the protons at 1,3-carbons) are in close proximity, and, as a result, their signals are shifted downfield, compared with those in **18** and **19** where Me-2 and H-3 are well separated. Likewise, the protons of the CH_2Ph group and Me-2 (*i.e.*, the protons at 1,4-carbons) are in close proximity in **18** and **19**, resulting in upfield shifts of the signals of Me-2, C-3, and CH_2Ph compared with those for **3** and **16**.

Analysis of the ^{1}H coupling constants for **3**, **16**, **18**, and **19** (Table II) indicates the pyranoid ring to be slightly flattened in the C-2,3,4,5 region. The magnitude of the $J_{2,3}$ value is diagnostic for the orientation of H-3 (~7 Hz for pseudo-axial, and ~1 Hz for pseudo-equatorial). Small $J_{1,2}$ values for all the compounds can also be explained by this flattening of the ring. Analysis of the data in Table II reveals other discriminative features, including the chemical shifts of H-2, H-3, H-6*endo*, and Me-4.

The above data indicate that none of the isomeric alcohols correspond to the derivative **21** obtained *via* demesylation of **17**.

The D-*gluco* isomer **16** has been used[11,12] in the synthesis of the C-9/C-13 segment of erythronolide A.

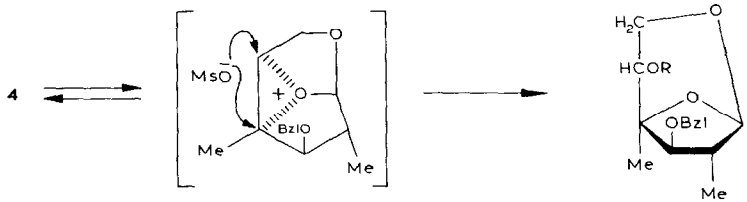
TABLE II

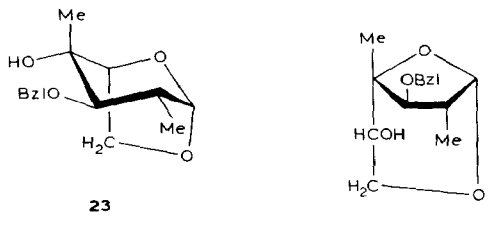
^{1}H-N M R DATA FOR THE TERTIARY ALCOHOLS **3, 16, 18,** AND **19** ($CDCl_3$, δ, J IN Hz)

	H-1	*H-2*	*H-3*	*H-5*	*H-6*exo	*H-6*endo	*Me-2*	*Me-4*	*PhCH$_2$; OH*
3	5.26 (s) $J_{1,2} = J_{1,3} = 1$	2.22 (q)	3.15 (s) $J_{2,3}$ 1	4.03 (d) $J_{5,6exo}$ 5.1; $J_{5,6endo}$ 0.6	3.63 (dd)	4.26 (dd) $J_{6,6'}$ 7	1.08 (d) $J_{2,Me}$ 7.4	1.44 (s)	4.40 and 4.70 (2 d) J_{gem} 11; 3.91 (s)
16	5.32 (s) $J_{1,2} = J_{1,3} = 1$	2.07 (q)	3.13 (s)	4.09 (d) $J_{5,6exo}$ 5.5; $J_{5,6endo}$ 0.9	3.71 (dd)	4.28 (dd) $J_{6,6'}$ 6.8	1.12 (d) $J_{2,Me}$ 7.4	1.23 (s)	4.37 and 4.61 (2 d) J_{gem} 11; 2.97 (s)
18	5.32 (d) $J_{1,2}$ 1.8	2.37 (ddq)	3.77 (d) $J_{2,3}$ 6.7	4.07 (d) $J_{5,6exo}$ 5; $J_{5,6endo}$ 0.5	3.61 (dd)	4.14 (d) $J_{6,6'}$ 7 2	0.97 (d) $J_{2,Me}$ 6.9	1.42 (s)	4.41 and 4.62 (2 d) J_{gem} 11.2; 2.28 (s)
19	5.39 (d) $J_{1,2}$ 2	2.3 (ddq)	3.49 (d) $J_{2,3}$ 6.8	4.24 (d) $J_{5,6exo}$ 5; $J_{5,6endo}$ 0.5	3.68 (dd)	3.75 (d) $J_{6,6'}$ 7.5	1.12 (d) $J_{2,Me}$ 6.8	1.18 (s)	4.40 and 4.67 (2 d) J_{gem} 11; 2.62 (s)

Rearrangement of the mesylate **4** *on solvolysis.* — The mesylate **7**, formed together with **6** on solvolysis of **4** as noted above, was previously[1,2] erroneously assigned the structure **5**. Comparison of the ^{1}H- and ^{13}C-n.m.r. data indicated **4** and **7** to be isomeric and to contain the same functional groups. The spectral data for **4** and **7** were similar (see Experimental). However, the downfield positions of the signals for C-3 of **7** (91.9 p.p.m.), its demesylated derivative **21** (93.5 p.p.m.), and the benzyl ether **23** (92.6 p.p.m.) were not previously observed for the 1,6-anhydrohexopyranose derivatives. Detailed analysis of the ^{1}H-n.m.r. data for **7, 21,** and **22**, and compounds derived therefrom[13], n.O.e. studies, and an X-ray study[8] of **7** unambigously established their structures. Thus, the signals for H-5 and H-6 appear as three separate doublets of doublets with $J_{5,6exo}$ 5.6, $J_{5,6endo}$ 10.1, and $J_{6,6'}$ 10.5 Hz in accord with 1,6-anhydro-β-L-idofuranose structures, and the $J_{2,3}$ and $J_{1,2}$ values of 3.5 and 1 Hz, respectively, correspond to those for the 1,6-anhydrofuranoses of the same relative configuration[14]. The anomalous downfield shift of the signals for C-3 in these compounds has analogies with the 1,3-dimethyl derivatives of cyclohexane and cyclopentane[15,16]. Thus, $\Delta\delta$ for C-2 in 1,3-dimethylcyclohexane is 5–8 p.p.m., depending on the orientation of the methyl groups, and the corresponding value for 1,3-dimethylcyclopentane is 18–20 p.p.m. irrespective of the orientation of the methyl groups. Thus, if the α-effect of benzylation can shift the signal for C-3 down to 80–83 p.p.m., then, taking into account the two-fold β-effect associated with the interaction of Me-2 and Me-4, an additional shift of the signal for C-3 down to 92–93 p.p.m. may be expected.

The formation of **7** can be accounted for by the participation of the pyranose ring oxygen, which generates the oxonium ion **20** which, when attacked by the





mesylate anion at C-5, produces **7**. A two-fold inversion of configuration at C-4 and C-5 in **4** confirms the suggested mechanism for the formation of **7**.

On the basis of a 1,6-anhydro-β-L-hexofuranose structure for **7**, the formation of the pyranose derivative **23** (94%) on methanolysis of **21** is readily explained, and the methyl glycoside is not formed. The $J_{2,3}$ value of 10 Hz for **23** is evidence in favour of the antiperiplanar arrangement of H-2 and H-3, and the position and multiplicity of signals for H-5 and H-6 ($J_{5,6endo}$ 0.9, $J_{5,6exo}$ 5.5, and $J_{6,6'}$ 10.0 Hz) are characteristic of 1,6-anhydrohexopyranoses.

It is also of interest to compare the spectral data for **21** and **24**. The latter compound is formed in 22% yield on treatment of the D-*galacto* isomer **3** with methanolic 3% hydrogen chloride, and is the 4,5-epimer of **21**. The Me-2*exo* group in **21** is deshielded by 8.8 p.p.m., as compared to Me-2*endo* in **24** (**21**, 19.6 p.p.m.; **24**, 10.8 p.p.m.). However, the positions of the signal for C-6 are not greatly different (**21**, 65.6 p.p.m.; **24**, 63.9 p.p.m.) A similar picture has been observed[17] for the analogous derivatives of bicyclo[3.2.1]octane.

The n.O.e. study of the dibenzyl derivative **22** revealed the close proximity of H-2 and H-6*endo*. Thus, pre-irradiation of H-2 increased the intensity of the signal for H-6*endo* by 5%, and, conversely, pre-irradiation of H-6*endo* caused a similar effect at H-2 (6%). Pre-irradiation of Me-4 of **23** increased the intensity of the multiplets for H-2 (1%) and H-5 (<0.5%), whereas pre-irradiation of H-3 caused corresponding changes in the signals of H-6*endo* (6%) and the benzyl methylene group (<0.5%). These results, together with ^{1}H-n.m.r. data, are consistent with the structure assigned to **23**, and, consequently, with that for **21** and its mesylate **7**.

Compound **7** has been used[13] in the synthesis of the C-9/C-13 segment of 13-epi-erythronolide A.

EXPERIMENTAL

Specific rotations were measured on solutions in chloroform with a Perkin–Elmer 141 polarimeter; ^{1}H- and ^{13}C-n.m.r. spectra (internal Me_4Si) were recorded with a Bruker WM-250 instrument. N.O.e. studies, for solutions degassed with argon, were performed according to the TOE procedure (the difference version)[9]. Reactions were monitored, and the purity of products was assessed, by t.l.c. on silica gel (Merck), and by g.l.c. with a Biochrom-21 instrument (50-m glass capillary columns, OV-101, XE-60). H.p.l.c. was performed with Silpearl silica gel (25–40 μm) and linear or optimum exponential gradients of solvents, or with Silosorb-600 (10 μm) in an isocratic regime. Reactions sensitive toward oxygen and moisture were carried out under argon. All operations to prepare dry solvents were performed under argon and over a suitable dehydrating agent.

1,6-Anhydro-3-O-benzyl-2-deoxy-2,4-di-C-methyl-4-O-mesyl-β-D-galacto-pyranose (**4**). — A mixture of 1,6-anhydro-3-*O*-benzyl-2-deoxy-2,4-di-*C*-methyl-β-D-galactopyranose[7] (**3**; 0.66 g, 2.5 mmol), dry pyridine (0.635 mL, 8 mmol), and

trifluoromethanesulfonic anhydride[18] (0.87 g, 5 mmol) in dichloromethane (9 mL) was stirred for 60–100 h at room temperature, poured into water, and extracted with chloroform. The extract was washed successively with M hydrochloric acid, saturated aqueous sodium hydrogencarbonate, and saturated aqueous sodium chloride, dried, and concentrated. Column chromatography of the residue with a benzene–ether gradient (0→25%) yielded **4** (0.74 g, 82%), m.p. 63–63.5° (from ether), $[\alpha]_D$ −55° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.27 (s, 1 H, H-1), 2.30 (bq, 1 H, H-2), 3.72 (s, 1 H, H-3), 4.18 (bd, 1 H, $J_{5,6exo}$ 5.5 Hz, H-5), 4.56 (bd, 1 H, $J_{5,6endo}$ 1 Hz, H-6*endo*), 3.68 (dd, 1 H, $J_{6,6'}$ 7.5 Hz, H-6*exo*), 1.06 (d, 3 H, $J_{2,Me-2}$ 7.5 Hz, Me-2), 1.90 (s, 3 H, Me-4), 2.74 (s, 3 H, Ms), 4.42 and 4.62 (2d, 2 H, J_{gem} 11 Hz, AB system of PhCH_2O-3); ^{13}C, δ 104.6 (C-1), 38.8 (C-2), 82.6 (C-3), 85.7 (C-4), 77.1 (C-5), 64.6 (C-6), 16.1 (Me-2), 25.6 (Me-4), 40.1 (Ms), and 71.8 (Ph*C*H_2O-3).

Anal. Calc. for $C_{16}H_{22}O_6S$: C, 56.00; H, 6.48. Found: C, 55.82; H, 6.15.

*1,6-Anhydro-3-*O*-benzyl-2-deoxy-5-*O*-mesyl-2,4-di-*C*-methyl-α-*L*-idofuranose* (**7**) *and 1,6-anhydro-3-*O*-benzyl-2,4-dideoxy-2-*C*-methyl-4-methylene-β-*D*-xylo-hexopyranose* (**6**). — A solution of **4** (6.5 g, 19 mmol) in anhydrous nitromethane (60 mL) was boiled for 20 h in the presence of molecular sieves (4 Å), filtered, and concentrated. Column chromatography of the residue with a light petroleum–ether gradient (10→50%) yielded, first, **7** (3.79 g, 58.5%), m.p. 63.5–64° (from ether–pentane), $[\alpha]_D$ +5° (*c* 8.4, chloroform), R_F 0.19 (ether–hexane, 1:1). N.m.r. data ($CDCl_3$): ^1H, δ 4.85 (s, 1 H, H-1), 2.46 (dq, 1 H, H-2), 3.48 (d, 1 H, $J_{2,3}$ 3.3 Hz, H-3), 4.69 (dd, 1 H, $J_{5,6endo}$ 9.9 Hz, H-5), 4.32 (dd, 1 H, H-6*endo*), 4.14 (dd, 1 H, $J_{6,6'}$ 10 Hz, H-6*exo*), 1.19 (d, 3 H, $J_{2,Me-2}$ 7 Hz, Me-2), 1.53 (s, 3 H, Me-4), 2.92 (s, 3 H, Ms), 4.58 and 4.64 (2 d, 2 H, J_{gem} 11 Hz, AB system of PhCH_2O-3); ^{13}C, δ 104.7 (C-1), 44.9 (C-2), 91.9 (C-3), 82.1 (C-4), 75.4 (C-5), 62.1 (C-6), 19.2 (Me-2), 22.6 (Me-4), 38.3 (Ms), and 72.9 (Ph*C*H_2O-3).

Anal. Calc. for $C_{16}H_{22}O_6S$: C, 56.00; H, 6.48. Found: C, 55.91; H, 6.25.

Eluted second was syrupy **6** (1.62 g, 35%), $[\alpha]_D$ −5° (*c* 10, chloroform), R_F 0.39. N.m.r. data ($CDCl_3$): ^1H, δ 5.00 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 2.20 (ddq, 1 H, H-2), 3.53 (dd, 1 H, $J_{2,3}$ 1.3 Hz, H-3), 4.66 (d, 1 H, H-5), 4.14 (dd, 1 H, $J_{5,6endo}$ 0.8 Hz, H-6*endo*), 3.75 (dd, 1 H, $J_{5,6exo}$ 5.2, $J_{6,6'}$ 6.7 Hz, H-6*exo*), 0.91 (d, 3 H, $J_{2,Me-2}$ 7.2 Hz, Me-2), 4.28 and 4.57 (d, 2 H, J_{gem} 12 Hz, AB system of PhCH_2O-3), 5.24 (d, 1 H, J_{gem} 1.8 Hz, =CH), and 5.29 (dd, 1 H, $J_{3,4'}$ 1.3 Hz, =CH); ^{13}C, δ 104.1 (C-1), 42.2 (C-2), 79.9 (C-3), 140.6 (C-4), 77.1 (C-5), 67.5 (C-6), 14.8 (Me-2), 69.6 (Ph*C*H_2O-3), and 117.1 (CH_2=).

A solution of **4** (0.32 g, 0.94 mmol) and ethyldi-isopropylamine (0.35 g, 2.7 mmol) in anhydrous nitromethane (5 mL) was boiled for 32 h, and then concentrated. Column chromatography of the residue with a light petroleum–ether gradient (10→25%) yielded **6** (0.204 g, 92%).

1.8M Butyl-lithium in hexane (10.6 mL) was added to a suspension of methyl triphenylphosphonium bromide (6.82 g, 19.1 mmol) in dry benzene (95 mL). The mixture was stirred for 15 min and heated to boiling, and a solution of ketone **12**

(3.165 g, 12.75 mmol) in benzene (15 mL) was added. The mixture was boiled for 10 min, excess of phosphorane was decomposed with acetone, the precipitate was removed, the filtrate was concentrated, and the residue was chromatographed, to give **6** (2.625 g, 84%).

4-O-Allyl-1,6-anhydro-2-deoxy-2-C-methyl-β-D-glucopyranose (**9**). — A solution of 4-*O*-allyl-1,6;2,3-dianhydro-β-D-mannopyranose[15] (**8**; 54.2 g, 294 mmol) in dry ether (200 mL) was added to M dimethylmagnesium in ether (350 mL) and boiled for 12 h. The mixture was treated with saturated aqueous ammonium chloride (35 mL), the precipitate was collected and washed with ether, and the combined filtrate and washings were concentrated, to yield syrupy **9** (59 g, 100%), which was homogeneous in t.l.c. and g.l.c., and had $[\alpha]_D$ −45° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.37 (s, 1 H, $J_{1,2}$ 1 Hz, H-1), 1.87 (d, 1 H, $J_{2,3}$ 1.5 Hz, H-2), 3.58 (d, 1 H, $J_{3,OH}$ 6 Hz, H-3), 3.37 (s, 1 H, H-4), 5.59 (d, 1 H, $J_{5,6endo}$ 1 Hz, H-5), 4.10 (d, 1 H, H-6*endo*), 3.73 (dd, 1 H, $J_{5,6exo}$ 5.4, $J_{6,6'}$ 7.3 Hz, H-6*exo*), 1.13 (d, 3 H, $J_{2,Me\text{-}2}$ 7.3 Hz, Me-2), 2.72 (d, 1 H, OH), 4.12 (dt), 5.21 (dq), and 5.93 (ddt, 5 H, CH_2=$CHCH_2$O-4); ^{13}C, δ 104.6 (C-1), 41.3 (C-2), 71.7 (C-3), 79.6 (C-4), 74.7 (C-5), 65.4 (C-6), 14.9 (Me-2), 70.5 (CH_2=$CHCH_2$O-4), 117.1 (CH_2=$CHCH_2$O-4), and 134.7 (CH_2=$CHCH_2$O-4).

4-O-Allyl-1,6-anhydro-3-O-benzyl-2-deoxy-2-C-methyl-β-D-glucopyranose (**10**). — A solution of **9** (6.58 g, 32.9 mmol) in dry *N,N*-dimethylformamide (20 mL) was stirred at 20° with sodium hydride (1.4 g, 58.5 mmol) for 1 h, benzyl bromide (10.0 g, 58.5 mmol) was then added, and stirring was continued for 0.5 h. The excess of sodium hydride was decomposed with methanol, and the mixture was poured into water and extracted with ether. The extract was washed with water and saturated aqueous sodium chloride, and concentrated. Column chromatography of the residue with a benzene–ethyl acetate gradient (0→20%) yielded **10** (9.15 g, 96%) as a syrup, $[\alpha]_D$ −33° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.31 (s, 1 H, $J_{1,2}$ 1 Hz, H-1), 2.00 (q, 1 H, H-2), 3.30 (m, 1 H, $J_{2,3} \simeq J_{3,4} \simeq J_{3,5} \simeq 1.5$ Hz, H-3), 3.36 (s, 1 H, H-4), 5.56 (d, 1 H, H-5), 4.14 (dd, 1 H, $J_{5,6endo}$ 1.3 Hz, $J_{6,6'}$ 6.9 Hz, H-6*endo*), 3.74 (dd, 1 H, $J_{5,6exo}$ 5.8 Hz, H-6*exo*), 4.53 and 4.60 (2 d, 2 H, AB system of PhCH_2O-3), 4.02 (dt), 5.27 (dq), and 5.50 (ddt, 5 H, CH_2=$CHCH_2$O-4); ^{13}C, δ 104.1 (C-1), 78.2 (C-2), 37.9 (C-3), 77.6 (C-4), 74.2 (C-5), 64.9 (C-6), 15.7 (Me-2), 70.2 (CH_2=$CHCH_2$O-4), 117.1 (CH_2=$CHCH_2$O-4), 134.7 (CH_2=$CHCH_2$O-4), and 71.5 (PhCH_2O-3).

1,6-Anhydro-3-O-benzyl-2-deoxy-2-C-methyl-β-D-glucopyranose (**11**). — A solution of **10** (8.83 g, 30.4 mmol) and potassium *tert*-butoxide (8.33 g, 74.5 mmol) in dry methyl sulfoxide (45 mL) was heated at 100° for 1 h, poured into water, and extracted with chloroform. The extract was washed with water and saturated aqueous sodium chloride, and concentrated. A solution of the residue in acetone–water (10:1, 300 mL) was stirred with mercury(II) oxide (6.6 g, 30.5 mmol) for 5 min, and a solution of mercury(II) chloride (8.27 g, 30.5 mmol) in acetone–water (10:1, 100 mL) was then aded. The precipitate was removed, and the filtrate was diluted with water and extracted with chloroform. The extract was washed with

aqueous 10% potassium iodide, water, and saturated aqueous sodium chloride, dried, and concentrated. Column chromatography of the residue yielded **11** (6.12 g, 80%) as a syrup, $[\alpha]_D$ −41° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.32 (s, 1 H, H-1), 2.02 (q, 1 H, H-2), 3.31 (s, 1 H, H-3), 3.70 (d, 1 H, $J_{4,OH}$ 8.5 Hz, H-4), 4.48 (d, 1 H, $J_{5,6exo}$ 6 Hz, H-5), 4.23 (d, 1 H, $J_{5,6endo}$ 1, $J_{6,6'}$ 7 Hz, H-6*endo*), 3.75 (dd, 1 H, H-6*exo*), 1.10 (d, 3 H, $J_{2,Mc\text{-}2}$ 7.5 Hz, Me-2), 4.57 (s, 1 H, OH), 4.52 and 4.59 (2 d, 2 H, J_{gem} 11 Hz, AB system of $PhCH_2O$-3); ^{13}C, δ 104.4 (C-1), 37.7 (C-2), 80.6 (C-3), 70.5 (C-4), 76.3 (C-5), 64.7 (C-6), 16.4 (Me-2), and 71.6 ($PhCH_2O$-3).

*1,6-Anhydro-3-*O*-benzyl-2-deoxy-2-*C*-methyl-β-*D*-xylopyranos-4-ulose* (**12**). — 2.4M Methyl sulfoxide in dichloromethane (17.3 mL, 41.5 mmol) was added at −60° during 5 min to 0.6M oxalyl chloride in dichloromethane (34.5 mL, 20.7 mmol). The mixture was stirred for 10 min, a solution of **11** (4.34 g, 17.3 mmol) in dry dichloromethane (15 mL) was added, and stirring at −60° was continued for 15 min. Triethylamine (7 mL, 50.4 mmol) was added, cooling was stopped, and the temperature of the reaction mixture was rapidly (3–5 min) elevated to 0°, water (30 mL) was added, and the aqueous layer was extracted with dichloromethane. The extract was washed with M hydrochloric acid, saturated aqueous sodium hydrogencarbonate, and saturated aqueous sodium chloride, dried, and concentrated to yield **12** (4.24 g, 98.5%), m.p. 66–66.5° (from ether–pentane), $[\alpha]_D$ +72° (*c* 1.3, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.36 (s, 1 H, H-1), 1.89 (dq, 1 H, H-2), 3.83 (d, 1 H, $J_{2,3}$ 7.6 Hz, H-3), 4.64 (d, 1 H, H-5), 3.96 (dd, 1 H, $J_{5,6endo}$ 0.7, $J_{6,6'}$ 7.2 Hz, H-6*endo*), 3.71 (dd, 1 H, $J_{5,6exo}$ 5.2 Hz, H-6*exo*), 1.21 (d, 3 H, $J_{2,Me\text{-}2}$ 7.2 Hz, Me-2), 4.48 and 4.92 (2 d, 2 H, J_{gem} 11.2 Hz, AB system of $PhCH_2O$-3); ^{13}C, δ 106.2 (C-1), 42.1 (C-2), 82.4 (C-3), 210.0 (C-4), 78.7 (C-5), 67.6 (C-6), 16.9 (Me-2), and 73.8 ($PhCH_2O$-3).

Anal. Calc. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.68; H, 6.29.

*1,6-Anhydro-3-*O*-benzyl-2-deoxy-2-*C*-methyl-β-*D*-ribo-hexopyranos-4-ulose* (**13**). — A solution of **12** (0.63 g, 2.54 mmol) in methanolic M sodium methoxide (10 mL) was kept at 20° for 1 h, neutralised with carbon dioxide, diluted with water, and extracted with chloroform. The extract was washed with water and saturated aqueous sodium chloride, dried, and concentrated, and the residue was recrystallised from ether–pentane to yield **13** (0.56 g, 89%), m.p. 67–67.5°, $[\alpha]_D$ −56° (*c* 1.3, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.43 (d, 1 H, $J_{1,2}$ 2.3 Hz, H-1), 2.85 (ddq, 1 H, $J_{2,Me\text{-}2} = J_{2,3} = 7$ Hz, H-2), 4.23 (d, 1 H, H-3), 4.50 (bd, 1 H, $J_{5,6exo}$ 5 Hz, H-5), 3.91 (dd, 1 H, $J_{5,6endo}$ 0.7, $J_{6,6'}$ 8.5 Hz, H-6*endo*), 3.83 (dd, 1 H, H-6*exo*), 0.99 (d, 3 H, Me-2), 4.57 and 4.80 (2 d, 2 H, J_{gem} 12 Hz, AB system of $PhCH_2O$-3); ^{13}C, δ 105.3 (C-1), 46.6 (C-2), 79.5 (C-3), 201.5 (C-4), 77.5 (C-5), 66.5 (C-6), 10.4 (Me-2), and 72.5 ($PhCH_2O$-3).

Anal. Calc. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.64; H, 6.32.

*1,6-Anhydro-3-*O*-benzyl-2-deoxy-2-*C*-methyl-4-methylene-β-*D*-ribo-hexopyranose* (**14**). — 1.8M Butyl-lithium in hexane (0.95 mL, 1.71 mmol) was added to a suspension of methyltriphenylphosphonium bromide (0.61 g, 1.71 mmol) in dry

benzene (3.5 mL). The mixture was stirred for 15 min and heated to boiling, and a solution of ketone **13** (0.324 g, 1.3 mmol) in dry benzene (2 mL) was added. The mixture was boiled for 10 min, the excess of phosphorane was decomposed with acetone, the precipitate was removed, and the filtrate was concentrated. Column chromatography of the residue yielded **14** (0.32 g, 100%) as a syrup, $[\alpha]_D$ +12° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.07 (t, 1 H, $J_{1,2} = J_{1,3} = 2$ Hz, H-1), 2.47 (ddq, 1 H, H-2), 4.34 (dt, 1 H, $J_{3,CH=}$ 2 Hz, H-3), 4.72 (d, 1 H, H-5), 4.72 (m, 2 H, $J_{5,6endo}$ 1, $J_{6,6'}$ 7, $J_{5,6exo}$ 4.5 Hz, H-6,6'), 3.38 (d, 1 H, J_{gem} 2.5 Hz, CH=), 5.25 (dd, 1 H, CH=), 4.63 and 4.50 (2 d, 2 H, J_{gem} 11.5 Hz, AB system of PhCH_2O-3), and 0.88 (d, 3 H, $J_{2,Me-2}$ 7 Hz, Me-2); ^{13}C, δ 105.2 (C-1), 41.6 (C-2), 78.3 (C-3), 143.4 (C-4), 73.8 (C-5), 67.8 (C-6), 9.2 (Me-2), 110.2 (CH_2=), and 70.7 (PhCH_2O-3).

*1,6-Anhydro-3-O-benzyl-2-deoxy-2,4-di-C-methyl-β-*D*-gluco-* (**16**) *and -galacto-pyranose* (**3**). — A solution of **6** (1.05 g, 4.26 mmol) and *m*-chloroperoxybenzoic acid (0.96 g, 5.02 mmol) in chloroform (5 mL) was boiled for 12 h, treated with saturated aqueous sodium sulfite, and extracted with chloroform. The extract was washed with water and saturated aqueous sodium chloride, dried, and concentrated. To a solution of the residue in dry tetrahydrofuran (2 mL) was added 1.18M lithium aluminium hydride in tetrahydrofuran (2 mL), and, after 10 min, the excess of hydride was decomposed with water. The mixture was diluted with chloroform, filtered, washed with water and saturated aqueous sodium chloride, and concentrated. Column chromatography of the residue with a benzene–ether gradient (0→25%) yielded, first, **3** (0.23 g, 21%), m.p. 57–58° (from pentane), $[\alpha]_D$ −89° (*c* 1, chloroform), R_F 0.33 (benzene–ether, 3:1). See Tables I and II for the ^1H- and ^{13}C-n.m.r. data. N.O.e.: [Me-4] Me-2, 1.8%; [Me-4] H-5, 1.3%; [Me-4] H-3, 1.6%.

Anal. Calc. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.91; H, 7.59.

Eluted second was **16** (0.63 g, 56%) as a syrup, $[\alpha]_D$ −87° (*c* 1.35, chloroform), R_F 0.22. See Tables I and II for the ^1H- and ^{13}C-n.m.r. data. N.O.e.: [Me-4] H-6*endo*, 2.1%; [Me-4] H-5, 2.6%; [Me-4] H-3, 1.5%; [H-6*endo*] Me-4, 5.7%.

*1,6-Anhydro-3-O-benzyl-2-deoxy-2,4-di-C-methyl-β-*D*-gluco-* (**18**) *and -allo-pyranose* (**19**). — (*a*). A solution of **14** (0.292 g, 1.19 mmol) and *m*-chloroperoxybenzoic acid (0.274 g, 1.43 mmol) in chloroform (1.5 mL) was boiled for 5 h, treated with saturated aqueous sodium sulfite, and extracted with chloroform. The extract was washed with water and saturated aqueous sodium chloride, and concentrated. Column chromatography of the residue with a benzene–ether gradient (0→25%) gave the oxiranes, which were then treated with excess of lithium aluminium hydride in tetrahydrofuran, as described above for **3**, to yield, first, **18** (0.241 g, 77.5%), m.p. 68.5–69° (from ether–pentane), $[\alpha]_D$ +32° (*c* 1, chloroform). See Tables I and II for the ^1H- and ^{13}C-n.m.r. data. N.O.e.: [H-3] H-6*endo*, 7.5%; [H-3] OH, 5%; [Me-4] Me-2, 1.4%; [Me-4] H-5, 1.5%.

Anal. Calc. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.03; H, 7.54.

Eluted second was **19** (0.045 g, 14.5%), m.p. 85.5–86° (from ether–pentane),

$[\alpha]_D$ +34° (*c* 0.97, chloroform). See Tables I and II for the ^1H- and ^{13}C-n.m.r. data. N.O.e.: [H-3] H-6*endo*, 4.3%; [Me-4] H-6*endo*, 1.1%; [Me-4] H-5, 1.4%.

Anal. Calc. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.00; H, 7.56.

(*b*) To a solution of **13** (0.135 g, 0.545 mmol) in dry ether (2 mL) was added 1.2M methylmagnesium bromide in tetrahydrofuran (0.5 mL, 0.6 mmol). The mixture was stirred at 20° for 30 min and then treated with saturated aqueous ammonium chloride (0.5 mL), the residue was collected and washed with ether, and the combined filtrate and washings were concentrated to yield **19** (0.143 g, 98%). Recrystallisation from ether–pentane (1:5) gave **19** (0.135 g, 94%), m.p. 85.5–86°.

*1,6-Anhydro-3-*O*-benzyl-2-deoxy-2,4-di-*C*-methyl-α-*L*-idofuranose* (**21**). — A mixture of mesylate **7** (3.95 g, 11.6 mmol), dry ether (25 mL), and lithium aluminium hydride (2 g, 26 mmol) was boiled for 30 h. The excess of hydride was decomposed with water, the sediment was removed, and the filtrate was concentrated. Column chromatography of the residue with a benzene–ether gradient (0→25%) yielded **21** (3.0 g, 98.5%) as a syrup, $[\alpha]_D$ −22° (*c* 1.35, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 4.82 (s, 1 H, H-1), 2.47 (dq, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 3.50 (d, 1 H, H-3), 3.00–4.10 (m, 4 H, H-5,6,6′ and OH), 4.48 and 4.61 (2 d, 2 H, J_{gem} 11.5 Hz, AB system of PhCH_2O-3), 1.13 (d, 3 H, $J_{2,Me\text{-}2}$ 7.5 Hz, Me-2), and 1.47 (s, 3 H, Me-4); ^{13}C, δ 104.8 (C-1), 43.7 (C-2), 93.5 (C-3), 81.8 (C-4), 73.6 (C-5), 65.5 (C-6), 19.6 (Me-2), 21.7 (Me-4), and 70.6 (PhCH_2O-3).

*1,6-Anhydro-3,5-di-*O*-benzyl-2-deoxy-2,4-di-*C*-methyl-α-*L*-idofuranose* (**22**). — A solution of **21** (1.02 g, 3.86 mmol) in dry *N,N*-dimethylformamide (3 mL) was stirred with sodium hydride (0.1 g) for 1 h, benzyl bromide (0.5 mL) was then added, and stirring was continued for 2 h. The excess of sodium hydride was decomposed with methanol, and the mixture was poured into water and extracted with chloroform. The extract was washed with water and saturated aqueous sodium chloride, and concentrated. Column chromatography of the residue yielded **22** (1.36 g, 100%) as a syrup, $[\alpha]_D$ +23° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 4.79 (s, 1 H, H-1), 2.43 (dq, 1 H, $J_{2,3}$ 3.6 Hz, H-2), 3.42 (dd, 1 H, $J_{3,5}$ 1.2 Hz, H-3), 3.61 (ddd, 1 H, $J_{5,6endo}$ 10.1, $J_{5,6exo}$ 5.6 Hz, H-5), 4.14 (dd, 1 H, H-6*endo*), 3.98 (dd, 1 H, $J_{6,6'}$ 10.5 Hz, H-6*exo*), 1.15 (d, 3 H, $J_{2,Me\text{-}2}$ 7.3 Hz, Me-2), 1.50 (s, 3 H, Me-4), 4.47 and 4.73 (2 d, 2 H, J_{gem} 11.2 Hz, AB system of PhCH_2O-4), 4.58 and 4.61 (2 d, 2 H, J_{gem} 12 Hz, AB system of PhCH_2O-3); ^{13}C, δ 104.4 (C-1), 45.5 (C-2), 92.6 (C-3), 83.4 (C-4), 78.0 (C-5), 62.8 (C-6), 19.4 (Me-2), 23.3 (Me-4), 72.7 and 73.3 (PhCH_2O-3 and PhCH_2O-4). N.O.e.: [H-2] H-6*endo*, 5.3%; [H-6*endo*] H-2, 6.2%.

*1,6-Anhydro-3-*O*-benzyl-2-deoxy-2-*C*-methyl-β-*L*-idopyranose* (**23**). — A solution of **21** (2.86 g, 18.3 mmol) in methanolic 20% hydrogen chloride (20 mL) was kept at 0° for 24 h, diluted with ether, neutralised with gaseous ammonia, filtered, and concentrated. Column chromatography of the residue yielded **23** (2.69 g, 94%), m.p. 83–84° (from ether–pentane), $[\alpha]_D$ +108° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.15 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 1.72 (ddq, 1 H, H-2), 3.30 (d,

1 H, $J_{2,3}$ 10.0 Hz, H-3), 4.01 (d, 1 H, $J_{5,6exo}$ 5.5 Hz, H-5), 4.09 (dd, 1 H, $J_{5,6endo}$ 0.9, $J_{6,6'}$ 7.8 Hz, H-6*endo*), 3.62 (dd, 1 H, H-6*exo*), 1.04 (d, 3 H, $J_{2,Me\text{-}2}$ 7.1 Hz, Me-2), 1.40 (s, 3 H, Me-4), 4.7 and 4.78 (d, 2 H, J_{gem} 12 Hz, AB system of PhCH_2O-3); ^{13}C, δ 104.4 (C-1), 42.6 (C-2), 84.1 (C-3), 73.5 (C-4), 80.6 (C-5), 64.7 (C-6), 13.4 (Me-2), 21.4 (Me-4), and 75.9 (PhCH_2O-3), N.O.e.: [Me-4] H-2, 0.9%; [H-3] H-6*endo*, 6%.

Anal. Calc. for $C_{15}H_{20}O_4$: C, 68.18; H, 7.50. Found: C, 67.93; H, 7.27.

1,6-Anhydro-3-O-benzyl-2-deoxy-2,4-di-C-methyl-α-D-galactofuranose (**24**). — A solution of **3** (9.8 g, 37.1 mmol) in methanolic 3% hydrogen chloride was boiled for 3 h, neutralised with Amberlite IRA-400 (CO_3^{2-}) resin, and concentrated. Column chromatography of the residue with a chloroform–acetone gradient (0→40%) yielded **24** (2.21 g, 22%) as a syrup, $[\alpha]_D$ +36° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 5.10 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 3.39 (ddq, 1 H, $J_{2,3}$ 4.5, $J_{2,Me\text{-}2}$ 7.5 Hz, H-2), 3.75 (d, 1 H, H-3), 3.90 (dd, 1 H, $J_{5,6endo}$ 11.3, $J_{5,6exo}$ 6.6 Hz, H-5), 3.75 (dd, 1 H, H-6*exo*), 3.20 (dd, 1 H, $J_{6,6'}$ 10.5 Hz, H-6*endo*), 1.15 (d, 3 H, Me-2), 1.42 (s, 3 H, Me-4), 4.57 (s, 2 H, PhCH_2O-3), and 2.62 (s, 1 H, OH); ^{13}C, δ 99.7 (C-1), 47.3 (C-2), 82.7 (C-3), 85.7 (C-4), 67.8 (C-5), 64.0 (C-6), 10.8 (Me-2), 17.0 (Me-4), and 71.6 (PhCH_2O-3).

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