Carbohydrate Research, 224 (1992) 75–87
Elsevier Science Publishers B.V., Amsterdam

Synthesis and conformational analysis of substituted 2,6-dioxabicyclo[3.1.1]heptanes: 1,3-anhydro-2,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranose by ^{1}H-NMR spectroscopy and molecular mechanics calculation*

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(Received May 13th, 1991; accepted in revised form December 9th, 1991)

ABSTRACT

A highly selective ring opening reduction of methyl 3-*O*-allyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside provided the 2,4-di-*O*-benzyl derivative. This was toluenesulfonylated or iodinated and subsequently reduced to give crystalline methyl 3-*O*-allyl-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside in good yield. Acid hydrolysis followed by deallylation and acetylation afforded a 1,3-diacetate which, on treatment with hydrogen chloride in diethyl ether, gave the crystalline key intermediate 3-*O*-acetyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl chloride. Ring closure of the chloride with lithium methoxide afforded 1,3-anhydro-2,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranose (**15**). Vicinal and long-range proton–proton coupling constants suggested that the conformation of the 1,3-anhydro sugar ether is essentially $B_{2,5}$ for the pyranose ring and a chair for the 1,3-dioxane ring. Molecular mechanics calculations using program MMP2 were applied to compound **15** and its analogue, 1,3-anhydro-2,4-di-*O*-benzyl-β-D-rhamnopyranose, and the results were in good agreement with those calculated by a modified Karplus equation and those measured on molecular models.

INTRODUCTION

As a part of our studies on the synthesis and conformational analysis of the 2,6-dioxabicyclo[3.1.1]heptane ring system occurring[1,2] in thromboxane A_2(TXA_2), we have investigated 1,3-anhydro-rhamno-[3,4], -galacto-[5] and -6-azido-6-deoxy-manno-pyranose[6] derivatives. Earlier, 1,3-anhydro-gluco-[7,8] and -mannopyranose[9,10] derivatives had been prepared by Schuerch's group. It was found that ring closure of the intermediate α-glycopyranosyl chlorides with potassium *tert*-butoxide went smoothly in the mannopyranose series[3,4,6,10], while in the glucopyranose

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* Project supported by the National Sciences Foundation of China.

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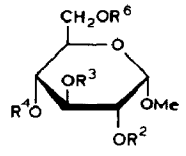
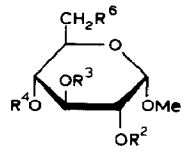
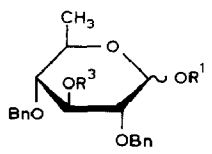


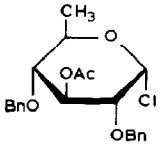
	R^2	R^3	R^4	R^6
1	H	H	-PhCH-	
2	Bn	H	-PhCH-	
3	H	Bn	-PhCH-	
4	Bn	All	-PhCH-	
5	Bn	All	H	H
6	Bn	All	Bn	H
7	Bn	All	H	Ts
8	Bn	All	Bn	Ts



	R^2	R^3	R^4	R^6
9	Bn	All	Bn	I
10	Bn	All	Bn	H



	R^1	R^3
11	H	All
12	H	H
13	Ac	Ac



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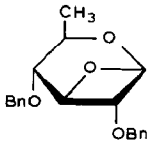

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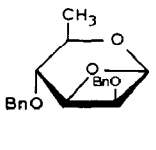

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Scheme 1

series the major product was an unwanted glycal derivative[8]. Nevertheless, treatment of the substituted glucosyl chloride with lithium ethoxide (generated in situ from methyllithium and absolute ethanol) gave a high yield of the 1,3-anhydro-glucopyranose derivative[8]. Thus, it was of interest to investigate further the ring closure of the corresponding 6-deoxy-glucopyranosyl chloride. The expected 1,3-anhydrosugar (**15**) has potential utility for oligosaccharide synthesis, and its stereoregular polymerization may afford an α-(1 → 3)-linked 6-deoxy-D-glucopyranan.

Conformational analysis by molecular mechanics calculation[11] has proved effective for a variety of ring systems[12–14]. Here we report the synthesis of compound **15**, and its conformational analysis by ^{1}H-NMR spectroscopy and by the molecular mechanics method.

RESULTS AND DISCUSSION

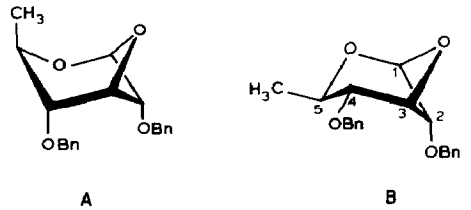
Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranside (**2**) was prepared either by the phase transfer method[15] or via the dibutylstannylene derivative[16] from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**1**). Treatment of the dibutylstannylene derivative with benzyl bromide (4 equiv) and tetrabutylammonium iodide (1 equiv) in toluene gave better selectivity and yield.

Allylation of compound **2** by a conventional method afforded a quantitative

yield of product **4**. Methyl 3-*O*-allyl-2,4-di-*O*-benzyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside (**8**) was then synthesized by either of two methods. Carefully controlled acid-catalyzed debenzylidenation of **4** furnished **5**. Selective tolylsulfonylation of **5** and then benzylation afforded a reasonable yield of **8**. Alternatively, compound **4** was converted into **6** by selective reduction of the benzylidene group with lithium aluminum hydride and aluminum chloride, using a reported procedure[17]. Crystalline **6** was obtained in high yield, and its tolylsulfonylation gave compound **8** quantitatively. The latter route was thus more effective than the former.

Treatment of **8** with lithium aluminum hydride in dry oxolane afforded methyl 3-*O*-allyl-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (**10**) in high yield. Alternatively, treatment of **6** with triphenylphosphine and iodine in the presence of imidazole afforded a quantitative yield of **9**, which was treated with sodium borohydride or sodium cyanoborohydride to furnish **10** in 80% yield (from **6**). Hydrolysis of **10** under acidic conditions gave 3-*O*-allyl-2,4-di-*O*-benzyl-6-deoxy-D-glucopyranose (**11**). Next, rearrangement of the allyl to a 1-propenyl group with tris(triphenylphosphine)rhodium(I) chloride and subsequent treatment with M hydrochloric acid gave crystalline 2,4-di-*O*-benzyl-6-deoxy-D-glucopyranose (**12**). Acetylation of **12** with acetic anhydride in pyridine gave the 1,3-diacetate **13** quantitatively, and this was reacted with hydrogen chloride in diethyl ether to furnish the crystalline key intermediate 3-*O*-acetyl-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranosyl chloride (**14**). On treatment of **14** with potassium *tert*-butoxide or sodium methoxide in oxolane the main product was a glycal derivative, identified by ^{1}H-NMR spectroscopy and TLC. The formation of this compound, by *trans* diaxial elimination of hydrogen chloride from C-1 and C-2, is similar to the result obtained with 2,4,6-tri-*O*-benzyl-α-D-glucopyranosyl chloride[8]. However, treatment of **14** in boiling oxolane with lithium methoxide (generated in situ from lithium hydride and absolute methanol) afforded 1,3-anhydro-2,4-di-*O*-benzyl-6-deoxy-β-D-glucopyranose (**15**) in a good yield.

The finding that the treatment of **14** with lithium methoxide afforded the target anhydro sugar derivative while potassium *tert*-butoxide gave only the glycal derivative could not be attributed to the basicity difference between *tert*-butoxide and methoxide, because the smaller steric bulk of the latter should offset this difference, and make the methoxide more effective in the abstraction of H-2. This assumption was supported by the fact that treatment of **14** with sodium methoxide gave a result similar to that obtained with potassium *tert*-butoxide. Thus, we postulate that lithium methoxide together with excess lithium hydride exists in oxolane as an associated form rather than as single molecules, and this associated lithium methoxide may be further solvated by oxolane. Consequently, large steric bulk and decreased reactivity might be expected for the associated methoxide, and this is in agreement with the result that the lithium methoxide attacked the equatorial 3-*O*-acetyl group rather than the more sterically hindered, axial H-2. Further support for this hypothesis is the fact that excess lithium methoxide (> 8 equiv with respect to glucosyl chloride) was necessary for the ring closure.



A B

Fig. 1. Two possible conformations for the 1,3-anhydro sugar ether **15**.

Compound **15** was acid labile, decomposing on silica gel plates, but relatively stable under basic conditions. Its structure required confirmation, and this was accomplished by mass and ^{1}H-NMR spectroscopy. The mass spectrum showed a parent peak having low intensity at m/z 326, and a relatively strong peak at m/z 253, characteristic for 1,3-anhydro glycopyranoses and attributable to the ion (BnOCH=CHCH=O$^+$Bn)[18]. The ^{1}H-NMR spectrum included a triplet at δ 5.5, characteristic for H-1 of 1,3-anhydro sugar derivatives. Further assignment of the ^{1}H-NMR spectrum was carried out by single frequency decoupling, and a conformational analysis of **15** in solution was based on the observed vicinal proton–proton coupling constants.

As shown in Fig. 1, two conformations, A and B, may be considered for the 1,3-anhydro sugar ether **15**, and these conformations differ in dihedral angles $\phi_{3,4}$ and $\phi_{4,5}$. The dihedral angles for **15**, calculated from the modified Karplus equation[19] and measured from molecular models, are listed in Table IV. It may be seen that the calculated dihedral angles are in good agreement with those measured from model B with some flattening at C-5. Thus the pyranose ring in **15** assumes essentially a $B_{2,5}$ conformation with some flattening of the boathead at C-5, and the 1,3-dioxane ring has a chair conformation.

Similar treatment of 1,3-anhydro-2,4-di-*O*-benzyl-β-D-rhamnopyranose (**16**) indicated the same conformation as for **15**; the results are shown in Table V.

We used the MMP2 program[20] to calculate the favored conformations of molecules **15** and **16**. The total energies at different conformations were calculated based on the stretching, bending, stretch–bending, torsional, and dipolar contributions, and Van der Waals interactions. The magnitude of the dielectric constant used for calculation was 1.50. The starting atomic coordinates for the energy minimization were obtained from a structure having essentially conformation B.

Some important bond lengths, bond angles, and torsion angles in molecules **15** and **16**, calculated from the final atomic coordinates of the minimal energy structure, are summarized in Tables I, II, and III. It may be seen from the values presented that compounds **15** and **16** have basically the same conformation. For both **15** and **16** the van der Waals distance between C-1 and C-3 is shorter than that between C-2 and O-1, and shorter than the averaged 1,3 van der Waals distance in the pyranose ring.

From the bond angles of **15**, O-5–C-1–C-2 (117.0°), C-2–C-3–C-4 (113.8°), O-5–C-1–O-1 (109.5°), and O-1–C-3–C-4 (105.9°), it can be seen clearly that the

TABLE I

Calculated values of some important interatomic distances in compounds **15** and **16**

Atoms	Distances (Å)	
	15	**16**
O-5–C-1	1.424	1.431
C-1–C-2	1.552	1.554
C-2–C-3	1.552	1.553
C-3–C-4	1.538	1.539
C-4–C-5	1.552	1.555
C-5–O-5	1.430	1.436
C-5–C-6	1.538	
C-1–O-1	1.430	1.425
O-1–C-3	1.434	1.435
C-2–O-2	1.412	
C-1–C-3	1.971	1.968
C-2–O-1	2.111	2.142
C-2–C-5	2.856	2.735
C-5–O-1	2.800	2.823
C-1–C-4	2.660	
O-1–O-5	2.331	2.310
C-3–O-5	2.668	

ring is flattened at C-2 compared to the normal boat conformation. The bond angles of **16**, O-5–C-1–C-2 (113.0°), C-2–C-3–C-4 (111.6°), O-5–C-1–O-1 (107.9°), and O-1–C-3–C-4 (105.4°), evidence less flattening at C-2 than in the case of **15**. This may be attributed to the interaction of the endo, axial benzyloxy group with C-5 in **15**, leading to flattening at both boatheads (C-2 and C-5) and puckering of

TABLE II

Calculated values of some important bond angles in compounds **15** and **16**

Angle	Magnitudes (deg)	
	15	**16**
O-5–C-1–C-2	117.0	113.0
C-1–C-2–C-3	78.8	78.5
C-2–C-3–C-4	113.8	111.6
C-3–C-4–C-5	109.5	107.8
C-4–C-5–O-5	113.2	111.5
C-5–O-5–C-1	114.1	113.1
O-5–C-1–O-1	109.5	107.9
C-1–O-1–C-3	87.0	87.0
O-1–C-3–C-4	105.9	105.4
O-1–C-1–C-2	90.0	91.7
O-1–C-3–C-2	89.9	91.4
O-2–C-2–C-1	116.9	
O-2–C-2–C-3	115.5	
C-4–C-5–C-6	112.0	
O-5–C-5–C-6	108.8	

TABLE III

Calculated values of some important torsion angles in compounds **15** and **16**

Angle	Magnitude (deg)	
	15	**16**
Pyranose ring		
O-5–C-1–C-2–C-3	−84.7	−85.9
C-1–C-2–C-3–C-4	80.5	83.0
C-2–C-3–C-4–C-5	−40.0	−35.2
C-3–C-4–C-5–O-5	−18.5	−29.0
C-4–C-5–O-5–C-1	18.6	30.0
C-5–O-5–C-1–C-2	41.8	35.3
C-5–O-5–C-1–O-1	−58.2	−64.6
O-5–C-1–O-1–C-3	88.7	88.7
C-1–O-1–C-3–C-4	−85.7	−86.8
O-1–C-3–C-4–C-5	57.1	62.7
Oxetane ring		
O-1–C-1–C-2–C-3	27.2	24.4
C-1–C-2–C-3–O-1	−27.1	−24.3
C-2–C-3–O-1–C-1	29.1	26.1
C-3–O-1–C-1–C-2	−29.1	−26.1
Other		
C-6–C-5–C-4–C-3	−141.9	−151.3
C-6–C-5–O-5–C-1	143.7	154.1
O-2–C-2–C-3–C-4	−34.4	−158.1
O-2–C-2–C-3–O-1	140.3	94.7
O-2–C-2–C-1–O-5		163.4
O-2–C-2–C-1–O-1		−86.3

O-1. The difference between the van der Waals distances C-2–C-5 and O-1–C-5 is 0.056 Å for **15** and −0.088 Å for **16**, verifying a deviation of the one conformation from the other. Inspection of the ring torsion angles of **15** and **16** confirms the conformations described above. The values of the asymmetry parameter[21] ΔC_2(C-3–C-4) for the 1,3-dioxane chair-form ring of **15** (68.7°) and for the corresponding ring of **16** (58.5°) indicate that C-5 in **15** is more flattened than in **16**. The values of the asymmetry parameter[21] ΔC_s(C-3–C-4) for the original pyranose boat-form ring of **15** (64.0°)° and for that of **16** (55.0°) also confirmed the different degrees of flattening at C-5 and C-2 in molecules **15** and **16**. The values calculated for the torsion angles (Table III) are consistent with the conclusion drawn here.

The dihedral angles between H-1 and H-2, H-2 and H-3, H-3 and H-4, and H-4 and H-5 found for **15** and **16** by theoretical calculation are shown in Tables IV and V, respectively. The values are in good agreement with those calculated by the modified Karplus equation from coupling constants, and those measured from model B. Although there was no certainty that the structure deduced by energy minimization is that of the lowest energy, because of the problem of "false minima", or that the conformation deduced from NMR spectroscopy is an "aver-

TABLE IV

H–H Torsion angles in **15**

Method of estimation	Magnitudes (deg)			
	$\Phi_{1,2}$	$\Phi_{2,3}$	$\Phi_{3,4}$	$\Phi_{4,5}$
Measured from model A	35	325	35	285
Measured from model B	35	325	80	200
Measured from model B with some flattening at C-5	35	325	65	220
Calculated from the coupling constants by the modified Karplus equation	51	308	68	215
Calculated by MMP2	31	333	61	220

age" one, the good agreement of the two methods suggests that compounds **15** and **16** have minimal-energy conformations in solution in chloroform.

EXPERIMENTAL

General methods.—These were as given in a previous paper[3]. ^{1}H- And ^{13}C-NMR spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a JEOL GX-400 MHz NMR spectrometer. The working frequencies were 399.78 MHz for ^{1}H, and 100.4 MHz for ^{13}C.

Methyl 3-O-allyl-2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**4**) *and its O-debenzylidenation.*—Compound **1** (14.0 g, 50 mmol) and dibutyltin oxide (7.45 g, 50 mmol) were suspended in MeOH (100 mL), the mixture was boiled under reflux for 4–5 h until the suspension became clear, and this was cooled and evaporated to give a white, foamy residue. To the residue was added toluene (100 mL), tetrabutylammonium iodide (18.5 g, 50 mmol), and benzyl bromide (24 mL, 0.2 mmol), and the mixture was refluxed for 8 h, when TLC showed the disappearance of the starting material. Sodium hydrogen carbonate (5 g) was added, and the reaction mixture was steam distilled to remove excess benzyl bromide. The residue syrup was chromatographed over silica gel to give **2** as a solid, yield 9 g (48%); mp

TABLE V

H–H Torsion angles in **16**

Method of estimation	Magnitudes (deg)			
	$\Phi_{1,2}$	$\Phi_{2,3}$	$\Phi_{3,4}$	$\Phi_{4,5}$
Measured from model A	265	95	35	285
Measured from model B	265	95	80	200
Measured from model B with some flattening at C-5	265	95	65	220
Calculated from the coupling constants by the modified Karplus equation	266	87	64	215
Calculated by MMP2	256	112	68	204

128° (from methylene chloride–petroleum ether) (lit.[22] mp 129.5°), and methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**3**) as crystals, yield 6 g (32%); mp 180° (lit.[22] mp 185°).

Compound **4** was obtained by allylation of compound **2** (2.5 g, 6.5 mmol) with allyl bromide and sodium hydride in oxolane, yield 2.5 g (90%); mp 93–94° (from diethyl ether–petroleum ether) (lit.[22] mp 96–98°); $[\alpha]_D^{20}$ + 40.5° (*c* 0.8, $CHCl_3$) (lit.[22] + 40.5°); ^{1}H-NMR ($CDCl_3$): δ 7.50–7.30 (m, 10 H, aromatic H), 6.00–5.93 (m, 1 H, CH_2=C*H*), 5.51 (s, 1 H, PhC*H*), 5.30, 5.15 (2 br. d, *J* 18.8, 10.3 Hz, CH_2=CH), 4.84, 4.69 (q_{AB}, 2 H, *J* 12.3, Hz, PhCH_2), 4.57 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.39, 4.30 (2 dd, 2 H, ^2J 12.3, ^3J 5.6 Hz, CH_2=CHCH_2), 4.24 (dd, 1 H, $J_{5,6}$ 4.7, $J_{6,6'}$ 9.5 Hz, H-6), 3.91 (t, 1 H, $J_{2,3}$ and $J_{3,4}$ 10.0 Hz, H-3), 3.82–3.76 (m, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 4.7 Hz, H-5), 3.68 (t, 1 H, $J_{5,6'}$ and $J_{6,6'}$ 9.5 Hz, H-6'), 3.52 (t, 1 H, $J_{3,4}$ and $J_{4,5}$ 10.0 Hz, H-4), 3.49 (dd, $J_{2,3}$ 10.0, $J_{1,2}$ 3.5 Hz, H-2), and 3.38 (s, 3 H, OCH_3); ^{13}C-NMR ($CDCl_3$): δ 138.2, 137.3 (aromatic C-1), 135.2 (CH_2=*C*H), 128.9, 128.7, 128.4, 128.2, 127.9, 126.0 (aromatic C), 116.8 (*C*H_2=CH), 101.3 (Ph*C*H), 99.3 (C-1), 82.1, 78.8, 78.0 (C-2, 3, 4), 74.03, 73.86 (PhCH_2, CH_2=CH-*C*H_2), 69.1 (C-6), 62.3 (C-5), and 55.3 (O*C*H_3).

A suspension of compound **4** (2.5 g, 6.1 mmol) in 80% acetic acid (20 mL) was heated on a steam bath for 3–4 h, after which time the acid was removed by sequential additions and evaporations of water and EtOH. To remove part of the byproducts, the syrupy residue was treated on a steam bath for 30 min with 12:5:3 MeOH–water–triethylamine (4 mL) according to a reported procedure[23]. After evaporation of the solvents the residue was washed with petroleum ether several times to remove unchanged starting material and byproducts. The aqueous phase was continuously extracted with methylene chloride to give crude methyl 3-*O*-allyl-2-*O*-benzyl-α-D-glucopyranoside (**5**, 2.1 g), which was purified by column chromatography. The final yield was 1.6 g (82%), ^{1}H-NMR ($CDCl_3$): δ 7.37–7.29 (m, 5 H, aromatic H), 5.98–5.94 (m, 1 H, CH_2=C*H*), 5.31–5.20 (2 br. d, 2 H, *J* 17.1, 10.4 Hz, CH_2=CH), 4.75, 4.62 (q_{AB}, 2 H, ^2J 12.2 Hz, PhCH_2), 4.58 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.49, 4.27 (2 dd, 2 H, ^2J 12.8, ^3J 5.8 Hz, CH_2=CHCH_2), 3.83 (dd, 1 H, $J_{6,6'}$ 11.6, $J_{5,6}$ 3.8 Hz, H-6), 3.78 (dd, 1 H, $J_{5,6'}$ 4.5 Hz, H-6'), 3.68 (t, $J_{2,3}$ and $J_{3,4}$ 9.6 Hz, H-3), 3.65–3.61 (m, 1 H, H-5), 3.50 (t, $J_{4,5}$ 9.6 Hz, H-4), 3.43 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$ 9.6 Hz, H-2), 3.38 (s, 3 H, OCH_3), and 2.10–2.05 (br. s, 2 H, 2 O*H*); ^{13}C-NMR: δ 138.0 (aromatic C-1), 135.1 (CH_2=*C*H), 128.5, 128.0 (aromatic C), 117.1 (*C*H_2=CH), 98.21 (C-1), 80.90, 79.58 (C-2, C-3), 74.19, 73.11 (PhCH_2, CH_2=CH*C*H_2), 70.75, 70.17 (C-4, C-5), 62.19 (C-6), and 55.23 (O*C*H_3).

Methyl 3-O-allyl-2,4-di-O-benzyl-α-D-glucopyranoside (**6**).—Lithium aluminum hydride (480 mg, 12 mmol) was suspended in anhydrous diethyl ether (25 mL) and the mixture was cooled to −15°. A solution of anhydrous aluminum chloride (1.6 g, 12 mmol) in dry diethyl ether (25 mL) was slowly added from a dropping funnel, and then a solution of compound **4** (2.5 g, 6.1 mmol) in dry methylene chloride (35 mL) added while the temperature was maintained at −5°. The mixture was allowed to warm to 25° during 4 h and then boiled under reflux for 12 h. Excess

reagent was decomposed by the careful dropwise addition of water-saturated EtOAc while the flask was cooled in an ice bath. The solid was filtered off and the filtrate evaporated to dryness. The residue was dissolved in methylene chloride, and the solution was washed with satd aq $NaHCO_3$, then dried over Na_2SO_4. Purification by column chromatography furnished compound **6** (2.05 g, 81%) as a solid. Recrystallization from diethyl ether–petroleum ether gave pure **6** as white needles, mp 85–86° (lit.[22] mp 84–85°); ^{1}H-NMR ($CDCl_3$); δ 7.40–7.20 (m, 10 H, aromatic H), 6.03–5.96 (m, 1 H, CH_2=C*H*), 5.30, 5.17 (2 br. d, *J* 16.9, 10.3 Hz, C*H*$_2$=CHCH$_2$), 4.88, 4.77, 4.64, 4.63 (4 d as 2 q_{AB}, 4 H, ^2J 11.7, 12.3 Hz, 2 PhC*H*$_2$), 4.54 (d, 1 H, $J_{1,2}$ 3.1 Hz, H-1), 4.45, 4.31 (2 dd, 2 H, ^2J 12.1, ^3J 5.7 Hz, CH$_2$=CHC*H*$_2$), 3.84 (t, 1 H, $J_{2,3}$ and $J_{3,4}$ 9.5 Hz, H-3), 3.73 (dd, 1 H, $J_{5,6}$ 2.9, $J_{6,6'}$ 12.3 Hz, H-6), 3.66 (dd, 1 H, $J_{5,6'}$ Hz, H-6′), 3.59 (m, 1 H, H-5), 3.46 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.42 (dd, 1 H, $J_{1,2}$ 3.1, $J_{2,3}$ 9.5 Hz, H-2), 3.32 (s, 3 H, OC*H*$_3$), and 1.82 (br. s, 1 H, O*H*); ^{13}C-NMR ($CDCl_3$): δ 138.2 (aromatic C-1), 135.2 (CH$_2$=*C*H), 128.4, 128.0, 127.7, 127.4, 127.2, 127.1 (aromatic C), 116.6 (*C*H$_2$=CH), 98.08 (C-1), 81.51 (C-3), 79.62 (C-2), 77.26 (C-4), 75.00, 74.33, 73.38 (2 PhC*H*$_2$, CH$_2$=CH*C*H$_2$), 70.53 (C-5), 61.84 (C-6), and 55.12 (O*C*H$_3$).

*Methyl 3-O-allyl-2-O-benzyl-6-O-p-tolylsulfonyl-α-*D*-glucopyranoside* (**7**).—To a cold (−15°) solution of **5** (1.5 g, 4.6 mmol) in pyridine (1.5 mL) was added *p*-toluenesulfonyl chloride (960 mg, 5.0 mmol) and the mixture was allowed to gradually warm to ambient temperature overnight. After conventional processing the crude product was purified by column chromatography on silica gel to afford syrupy compound **7**, yield 2.0 g (91%), $[\alpha]_D^{20}$ +35.5° (*c* 1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 7.79–7.26 (m, 9 H, aromatic H), 5.98–5.91 (m, 1 H, CH_2=C*H*), 5.28, 5.18 (2 br. d, 2 H, *J* 16.8, 10.4 Hz, C*H*$_2$=CH), 4.72, 4.60 (q_{AB}, 2 H, ^2J 12.1 Hz, PhC*H*$_2$), 4.52 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.44, 4.21 (m, 2 H, ^2J 13.0, ^3J 5.5 Hz, CH$_2$=CHC*H*$_2$), 4.14 (d, 2 H, $J_{5,6}$ 3.9 Hz, 2 H-6), 3.71 (dt, 1 H, $J_{4,5}$ 9.6, $J_{5,6}$ 3.9 Hz, H-5), 3.62 (t, 1 H, $J_{2,3}$, $J_{3,4}$ 9.6 Hz, H-3), 3.42 (t, 1 H, H-4), 3.38 (dd, H-2), 3.31 (s, 3 H, C*H*$_3$O), and 2.43 (s, 3 H, PhC*H*$_3$); ^{13}C-NMR ($CDCl_3$): δ 144.8, 137.9 (aromatic C-1), 134.9 (CH$_2$=*C*H), 132.9 (aromatic C-4), 129.8, 128.0, 127.6 (aromatic C), 117.3 (*C*H$_2$=CH), 98.17 (C-1), 80.69 (C-3), 79.26 (C-2), 74.18, (PhC*H*$_2$, CH$_2$=CH*C*H$_2$), 69.44, 68.91 (C-4, 5, 6), 55.36 (O*C*H$_3$), and 21.63 (PhC*H*$_3$).

Anal. Calcd for $C_{24}H_{30}O_8S$ (478.54): C, 60.23; H, 6.31. Found: C, 60.42; H, 6.31.

*Methyl 3-O-allyl-2,4-di-O-benzyl-6-O-p-tolylsulfonyl-α-*D*-glucopyranoside* (**8**).—(*a*) Compound **7** (1.5 g, 3.1 mmol) was dissolved in dry oxolane (50 mL), the solution was stirred and cooled in an ice bath, and sodium hydride (186 mg of 80% dispersion in oil, 6.2 mmol) and benzyl bromide (0.45 mL, 3.71 mmol) were added. The mixture was refluxed for 3–4 h, after which time the reaction was complete as indicated by TLC. The solid was filtered off and the filtrate concentrated. The residue was dissolved in methylene chloride and the solution was washed with satd $NaHCO_3$, dried (Na_2SO_4), and concentrated. Column chromatography of the residue gave **8** as white crystals, yield 1.6 g (90%); mp 53–54° after recrystallization as needles from diethyl ether–petroleum ether; ^{1}H-NMR ($CDCl_3$): δ 7.76–7.20

(m, 14 H, aromatic H), 6.10–5.90 (m, 1 H, CH_2=C*H*), 5.30, 5.16 (2 br. d, 2 H, *J* 16.9, 10.3 Hz, CH_2=CH), 4.84, 4.74, 4.62, 4.45 (4 d as 2 q_{AB}, 4 H, ^2J 10.2, 12.5 Hz, 2 PhCH_2), 4.50 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.44, 4.28 (2 dd, 2 H, ^2J 11.3, ^3J 5.6 Hz, CH_2=CHCH_2), 4.21–4.14 (m, 2 H, 2 H-6), 3.80 (t, 1 H, $J_{2,3}$, $J_{3,4}$ 9.5 Hz, H-3), 3.72 (m, 1 H, $J_{4,5}$ 9.5 Hz, H-5), 3.40 (dd, 1 H, H-2), 3.39 (t, 1 H, H-4), 3.28 (s, 3 H, OCH_3), and 2.36 (s, 3 H, PhCH_3); ^{13}C-NMR ($CDCl_3$): δ 144.8, 137.7, 138.0 (aromatic C-1), 135.0 (CH_2=*C*H), 132.8 (aromatic C-4), 129.7, 129.3, 128.4, 128.0, 127.4 (aromatic C), 116.6 (*C*H_2=CH), 98.03 (C-1), 81.34 (C-3), 79.28 (C-2), 76.76 (C-4), 72.90, 74.25, 73.35 (2 Ph*C*H_2, CH_2=CH*C*H_2), 68.55, 68.34 (C-5, C-6), 55.21 (O*C*H_3), and 21.55 (Ph*C*H_3).

Anal. Calcd for $C_{31}H_{36}O_8S$ (568.66): C, 65.47; H, 6.38. Found: C, 65.49; H, 6.34.

(*b*) To a cold (−15°) solution of **6** (570 mg, 1.38 mmol) in pyridine (1.0 mL) was added *p*-toluenesulfonyl chloride (420 mg, 2.07 mmol), and the solution was stirred at room temperature for 12 h. After conventional processing, the crude product was purified by column chromatography on silica gel to furnish compound **8** in quantitative yield.

*Methyl 3-O-allyl-2,4-di-O-benzyl-6-deoxy-α-*D*-glucopyranoside* (**10**).— (*a*) To a solution of compound **8** (500 mg, 0.88 mmol) in oxolane (10 mL) was added lithium aluminum hydride (50 mg, 1.3 mmol). The mixture was refluxed for 4 h, when TLC indicated the reaction to be complete. Ethyl acetate was carefully added, to decompose excess lithium aluminum hydride, while the flask was cooled in an ice bath. The solid was filtered off, the filtrate was evaporated to dryness, and the syrup thus obtained was subjected to column chromatography to afford compound **10** (250 mg, 70%), mp 109–110° (after crystallization from diethyl ether–petroleum ether); $[\alpha]_D^{20}$ +84.1° (*c* 1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 7.50–7.20 (m, 10 H, aromatic H), 6.04–5.95 (m, 1 H, CH_2=C*H*), 5.30–5.16 (2 br. d, 2 H, *J* 18.8, 8.4 Hz, CH_2=CH), 4.89, 4.77, 4.65, 4.62 (4 d as 2 q_{AB}, 4 H, ^2J 11.7, 10.5 Hz, 2 PhCH_2), 4.51 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1), 4.45, 4.31 (2 dd, 2 H, ^2J 13.2, ^3J 5.6 Hz, CH_2=CHCH_2), 3.80 (t, 1 H, $J_{2,3}$, $J_{3,4}$ 9.5 Hz, H-3), 3.70-3.65 (m, 1 H, H-5), 3.45 (dd, 1 H, H-2), 3.34 (s, 3 H, OCH_3), 3.06 (t, $J_{4,5}$ 9.5 Hz, H-4), and 1.22 (d, 3 H, $J_{5,6}$ 6.8 Hz, 3 H-6); ^{13}C-NMR ($CDCl_3$): δ 138.1 (aromatic C-1), 135.1 (CH_2=*C*H), 128.2 127.9, 127.3 (aromatic C), 116.5 (*C*H_2=CH), 97.82 (C-1), 83.52 (C-4), 81.29 (C-3), 79.73 (C-2), 75.13, 74.18, 73.13 (2 Ph*C*H_2, CH_2=CH*C*H_2), 66.26 (C-5), 54.83 (O*C*H_3), and 17.67 (C-6).

Anal. Calcd for $C_{24}H_{30}O_5$ (398.48): C, 72.33; H, 7.58. Found: C, 72.35; H, 7.64.

(*b*) To a solution of **6** (2.44 g, 5.89 mmol) in toluene (100 mL) were added triphenylphosphine (3.10 g, 11.8 mmol), imidazole (2.0 g, 29.4 mmol), and iodine (2.6 g, 20.5 mmol). The reaction mixture was boiled under reflux with vigorous stirring until the color disappeared (15 min). A solution of $NaHCO_3$ (5%, 50 mL) was then added and, after stirring for 10 min, iodine was added until the color of the mixture remained purple. Aqueous sodium thiosulfate (10%) was added dropwise with stirring until the purple colour was removed. The mixture was then diluted with EtOAc (100 mL), washed with water, and concentrated. A solution of

the residue in ether (80 mL) was cooled to −15°, filtered after 2 h, and concentrated. Purification of the residue by column chromatography gave methyl 3-*O*-allyl-2,4-di-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside (**9**) as a syrup in a quantitative yield.

A solution of compound **9** (1.5 g, 2.06 mmol) in *N*,*N*-dimethylformamide (5 mL, dried over molecular sieves 4A) was treated with hexamethylphosphoric triamide (15 mL) and sodium cyanoborohydride (380 mg, 95%, 5.74 mmol). The reaction was carried out with stirring for 12 h at 75°. The mixture was then poured into ice–water and extracted with ether, and the extract was washed with satd aq $NaHCO_3$, dried over Na_2SO_4, and concentrated. Purification by column chromatography afforded compound **10** as crystals (910 mg, 80%).

3-O-Allyl-2,4-O-benzyl-6-deoxy-α,β-D-glucopyranose (**11**).—A mixture of methyl 3-*O*-allyl-2,4-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside **10** (1.0 g, 2.5 mmol), acetic acid (80%, 4 mL) and HCl (M, 1 mL) was boiled under reflux. After 7 h the reaction was complete as indicated by TLC (1:3 ethyl acetate–petroleum ether). The mixture was evaporated under reduced pressure to remove most of the acids, and the residue was washed with satd $NaHCO_3$ and extracted with diethyl ether. The extracts were dried and evaporated to a syrup. Purification by column chromatography gave compound **11** as a solid, yield 720 mg (75%); mp 89–90°; $[\alpha]_D^{20}$ +33.2° (*c* 0.6, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 7.40–7.20 (m, 10 H, aromatic H), 6.03–5.94 (m, 1 H, CH_2=C*H*), 5.32–5.15 (m, 2 H, CH_2=CH), 5.12 (d, $J_{1,2}$ 2.9 Hz, H-1α), 4.92–4.62 (m, 4 H, 2 PhCH_2), 4.65 (d, $J_{1,2}$ 7.8 Hz, H-1β), 4.43–4.27 (m, 2 H, CH_2=CHCH_2), 3.95 (m, $J_{5,6}$ 5.5, $J_{4,5}$ 9.7 Hz, H-5α), 3.77 (t, $J_{2,3}$, $J_{3,4}$ 9.7 Hz, H-3α), 3.49 (dd, H-2α), 3.48 (br. t, $J_{2,3}$ 7.8, $J_{3,4}$ 9.7 Hz, H-3β), 3.41 (m, $J_{5,6}$ 5.7, $J_{4,5}$ 9.7 Hz, H-5β), 3.32 (t, H-2β), 3.15 (t, H-4β), 3.08 (t, H-4α), 1.29 (d, H-6β), and 1.23 (d, H-6α); ^{13}C-NMR ($CDCl_3$): δ 138.2, 138.1, 138.0, 137.9 (2 aromatic C-1), 128.4, 128.0 (2 aromatic C), 135.1 (CH_2=*C*H), 116.8 (*C*H_2=CH), 97.04 (C-1β), 91.10 (C-1α), 84.08 (C-4β), 88.44, 83.31, 83.17 (C-4α, C-2β, C-3β), 81.15 (C-3α), 80.15 (C-2α), 74.78, 75.29, 74.36, 73.24 (2 Ph*C*H_2, CH_2=CH*C*H_2), 71.26 (C-5β), 66.85 (C-5α), and 17.85 (C-6).

Anal. Calcd for $C_{23}H_{28}O_5$ (384.43): C, 71.80; H, 7.34. Found: C, 72.03; H, 7.18.

2,4-Di-O-benzyl-6-deoxy-α,β-D-glucopyranose (**12**).—To a solution of compound **11** (700 mg, 1.82 mmol) in EtOH (90%, 5 mL) was added tris(triphenylphosphine)chlororhodium (30 mg, 0.03 mmol), and the reaction mixture was heated under reflux for 12 h. TLC (1:3 EtOAc–petroleum ether) indicated the disappearance of the starting material. Hydrochloric acid (M, 2 mL) was added to the reaction mixture and refluxing was continued for a further 2 h. The solution was concentrated, the residue was dissolved in methylene chloride, and the solution washed with aq $NaHCO_3$ and dried over Na_2SO_4. Column chromatorgraphy (1:1 EtOAc–petroleum ether) of the product gave **12** as a solid, yield 550 mg (88%); mp 128–129°; $[\alpha]_D^{20}$ +67.6° (*c* 0.5, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 7.40–7.20 (m, 10 H, aromatic H), 5.16 (d, $J_{1,2}$ 3.9 Hz, H-1α), 4.99–4.65 (m, 5 H, 2 PhCH_2, and H-1β), 4.01 (t, $J_{2,3}$, $J_{3,4}$ 9.2 Hz, H-3α), 3.97 (m, H-5α), 3.69 (t, $J_{2,3}$, $J_{3,4}$ 9.0 Hz,

H-3β), 3.49 (br. s, 1 H, O*H*), 3.43 (m, H-5β), 3.39 (dd, H-2α), 3.20 (dd, $J_{1,2}$ 7.3 Hz, H-2β), 3.12 (t, $J_{4,5}$ 9.0 Hz, H-4β), 3.06 (t, $J_{4,5}$ 9.2 Hz, H-4α), 2.99 (br. s, 1 H, O*H*), 1.31 (d, $J_{5,6}$ 7.1 Hz, H-6β), and 1.26 (d, $J_{5,6}$ 5.6 Hz, H-6α); ^{13}C-NMR ($CDCl_3$): δ 138.3, 137.4 (aromatic C-1), 129.0, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9 (aromatic C), 96.89 (C-1β), 90.60 (C-1α), 83.43, 82.86, 82.63 (C-4, C-2β), 79.97 (C-2α), 74.86, 74.36, 73.09, 72.95 (C-3, 2 Ph*C*H$_2$), 71.31 (C-5β), 66.50 (C-5α), 18.03, and 17.99 (C-6).

Anal. Calcd for $C_{20}H_{24}O_5$ (344.39): C, 69.74; H, 7.02. Found: C, 69.92; H, 6.76.

1,3-Di-O-acetyl-2,4-di-O-benzyl-6-deoxy-α,β-D-glucopyranose (**13**).—Compound **12** (550 mg, 1.60 mmol) was acetylated with acetic anhydride in pyridine at room temperature and **13** was obtained in quantitative yield (680 mg); $[\alpha]_D^{20}$ +40.9° (*c* 0.2, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 7.45–7.26 (m, 10 H, aromatic H), 6.27 (d, $J_{1,2}$ 3.5 Hz, H-1α), 5.64 (d, $J_{1,2}$ 8.1 Hz, H-1β), 5.46 (t, $J_{2,3}$, $J_{3,4}$ 9.8 Hz, H-3α), 5.28 (t, $J_{2,3}$, $J_{3,4}$ 9.5 Hz, H-3β), 4.72–4.47 (m, 4 H, 2 PhC*H*$_2$), 3.92 (m, H-5α), 3.63 (m, H-5β), 3.55 (dd, H-2α), 3.49 (dd, H-2β), 3.22 (t, $J_{4,5}$ 9.5 Hz, H-4β), 3.19 (t, $J_{4,5}$ 9.8 Hz, H-4α), 2.15, 1.98 (2 s, C*H*$_3$COα), 2.08, 1.89 (2 s, C*H*$_3$COβ), 1.32 (d, $J_{5,6}$ 6.3 Hz, 3 H-6β), and 1.28 (d, $J_{5,6}$ 6.3 Hz, 3 H-6α); ^{13}C-NMR ($CDCl_3$): δ 173.7, 169.3, 169.0, 164.6 (*C*=O), 137.9 (aromatic C-1), 128.1, 127.5 (aromatic C), 98.59 (C-1β), 92.97 (C-1α), 88.88 (C-4β), 80.86 (C-4α), 78.46 (C-2β), 75.83 (C-2α), 74.60, 73.94, 73.55, 73.43, 72.50, 71.68, (2 Ph*C*H$_2$, C-3), 70.97 (C-5β), 68.52 (C-5α), 20.60 (*C*H$_3$CO), 17.50, and 17.39 (C-6).

Anal. Calcd for $C_{24}H_{28}O_7$ (428.46): C, 67.27; H, 6.58. Found: C, 66.91; 6.60.

3-O-Acetyl-2,4-di-O-benzyl-6-deoxy-α-D-glucopyranosyl chloride (**14**).—Compound **13** (600 mg, 1.4 mmol) was dissolved in dry diethyl ether (10 mL), and HCl was bubbled in to saturation at 0° while the neck of the flask was flushed with nitrogen. The reaction mixture was kept in the sealed flask overnight in a refrigerator at 0° and then for 2 h at room temperature. Nitrogen was bubbled into the solution to remove excess HCl. The yellowish solution was evaporated under diminished pressure to a syrup, this was dissolved in methylene chloride (2 mL), and the solution was evaporated. This procedure was repeated 7 or 8 times to remove as much HCl as possible. The product was purified by analytical LC (1:3 EtOAc–petroleum ether), and crystallized from diethyl ether–petroleum ether, yield 390 mg (70%); mp 94–95°; $[\alpha]_D^{20}$ +116.6° (*c* 0.2, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 7.52–7.26, (m, 10 H, aromatic H), 5.98 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.54 (t, 1 H, $J_{2,3}$, $J_{3,4}$ 9.6 Hz, H-3), 4.66, 4.56 (2 d as q_{AB}, 2 H, ^2J 12.3 Hz, PhC*H*$_2$), 4.60 (s, 2 H, PhC*H*$_2$), 4.14 (m, 1 H, $J_{4,5}$ 9.6, $J_{5,6}$ 6.3 Hz, H-5), 3.61 (dd, 1 H, H-2), 3.21 (t, 1 H, H-4), 1.98 (s, 3 H, C*H*$_3$CO), and 1.30 (d, 3 H, 3 H-6); ^{13}C-NMR ($CDCl_3$): δ 159.6 (C=O), 137.5, 137.1 (aromatic C-1), 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.8 (aromatic C), 92.05 (C-1), 81.10 (C-4), 78.15 (C-2), 74.63 (C-3), 72.62, 73.37 (2 Ph*C*H$_2$), 69.86 (C-5), 21.07 (*C*H$_3$CO), and 17.68 (C-6).

Anal. Calcd for $C_{22}H_{25}ClO_5$ (404.87): C, 65.26; H, 6.22. Found: C, 65.27; H, 6.05.

1,3-Anhydro-2,4-di-O-benzyl-β-D-glucopyranose (**15**).—To a solution of com-

pound **14** (300 mg, 0.74 mmol) in dry oxolane (30 mL) was added lithium hydride (54 mg, 6 mmol) and anhyd MeOH (90 μL, 2.2 mmol), and the reaction mixture was boiled under reflux with nitrogen protection for 3 h. TLC (1:3 EtOAc–petroleum ether) indicated that about half of the starting material was converted into **15**. Further portions of lithium hydride and MeOH were added, and the mixture was continuously boiled until reaction was complete and no starting material was detected on TLC. The mixture was cooled and the solution evaporated under reduced pressure. Methylene chloride was added to dissolve the product and the insoluble salts were removed by centrifuging. Compound **15** was obtained by concentration of the supernatant as a syrup. Purification by analytical LC (1:4 EtOAc–petroleum ether) on a column packed with Lichrosorb-NH_2 yielded syrupy **15** of high purity (130 mg, 54%), $[\alpha]_D^{20}$ +35.5° (*c* 1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 7.42–7.31 (m, 10 H, aromatic H), 5.51 (t, 1 H, $J_{1,2}$, $J_{1,3}$, 3.7 Hz, H-1), 4.80 (m, 1 H, $J_{2,3}$ 5.1, $J_{1,3}$ 3.7, $J_{3,4}$ 2.8 Hz, H-3), 4.78 (m, $J_{4,5}$ 7.0, $J_{5,6}$ 6.5 Hz, H-5), 4.74, 4.73, 4.69, 4.65 (4 d as 2 q_{AB}, 4 H, *J* 12.0, 11.6 Hz, 2 PhCH_2), 4.50 (m, $J_{1,2}$ 3.7, $J_{2,3}$ 5.1, $J_{2,4}$ 1.4 Hz, H-2), 3.82 (ddd, $J_{2,4}$ 1.4, $J_{3,4}$ 2.8, $J_{4,5}$ 7.0 Hz, H-4), and 1.40 (d, 3 H, $J_{5,6}$ 6.5 Hz, 3 H-6).

Anal. Calcd for $C_{20}H_{22}O_4$ (326.38): C, 73.59; H, 6.79. Found: C, 73.69; H, 6.90.

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