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Syntheses and ^{1}H- and ^{13}C-Nuclear Magnetic Resonance Spectra of All Positional Isomers of Tetra-*O*-acetyl-D-glucopyranoses, and Their Monobenzyl and Monotrityl Derivatives

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All the isomers of the tetra-*O*-acetyl-D-glucopyranoses, and their monobenzyl and monotrityl derivatives were synthesized and systematic ^{1}H- and ^{13}C-nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) studies were carried out. Complete assignments of the ^{1}H- and ^{13}C-NMR signals were achieved by $^{1}H[^{1}H]$- and $^{13}C[^{1}H]$-decoupling techniques and by the use of a shift reagent and changes of solvents. Moreover, when necessary, $^{1}H[^{1}H]$- and $^{13}C[^{1}H]$-shift-correlated 2D NMR spectroscopy at higher frequency (Bruker AM 400) was applied. The shifts on deacetylation, benzylation, and tritylation were estimated on the basis of the ^{1}H- and ^{13}C-chemical shifts of these compounds, and the effects of deacetylation and benzyl- or trityl-substitution are discussed.

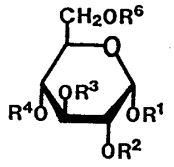
Keywords——tetra-*O*-acetyl-D-glucopyranose; monobenzyl tetra-*O*-acetyl-D-glucopyranose; monotrityl tetra-*O*-acetyl-D-glucopyranose; ^{1}H-NMR; ^{13}C-NMR; deacetylation shift; benzylation shift; tritylation shift

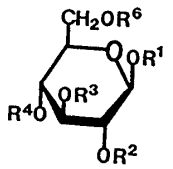
In our previous investigations[1] of syntheses of gluco-oligosaccharide derivatives, it became clear that systematic studies on the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectra of the unit compounds (glucose derivatives) were desirable for the convenient determination of the positions substituted. Furthermore, the utility of ^{1}H-NMR spectroscopy at higher frequency for signal assignment has recently been confirmed in carbohydrate chemistry. Therefore, all the isomers of the tetra-*O*-acetyl-D-glucopyranoses, and corresponding monobenzyl and monotrityl derivatives which may serve as important synthetic intermediates, were unambiguously synthesized (Chart 1). The ^{1}H- and ^{13}C-NMR spectra of these thirty compounds were measured, the deacetylation, benzylation, and tritylation shifts were estimated on the basis of the ^{1}H- and ^{13}C-chemical shifts and the effects of deacetylation and benzyl- or trityl-substitution are discussed.

Results and Discussion

Syntheses of Tetraacetyl-D-glucopyranoses

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranose (H—Iβ)[2] and 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (H-IIα)[3] were prepared according to the procedures previously reported: treatment of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide with freshly prepared active silver carbonate gave H-Iβ (84.0%), which was crystallized from ether–ligroin, mp 113.0—114.0 °C,[4] $[\alpha]_D^{16}$ +14.5° (c=2.00, $CHCl_3$); acetylation of D-glucose with acetic anhydride and perchloric acid, followed by treatment with phosphorus tribromide and water gave H-IIα (22.6%), which was crystallized from ether, mp 97.0—98.0 °C (lit.[3] 98—99 °C). The α-anomer of H-Iβ (H-Iα) was obtained in a small amount as a by-product of the preparation of H-IIα.





B-Iα:	R^1=Bzl, R^2=R^3=R^4=R^6=Ac	B-Iβ:	R^1=Bzl, R^2=R^3=R^4=R^6=Ac
B-IIα:	R^2=Bzl, R^1=R^3=R^4=R^6=Ac	B-IIβ:	R^2=Bzl, R^1=R^3=R^4=R^6=Ac
B-IIIα:	R^3=Bzl, R^1=R^2=R^4=R^6=Ac	B-IIIβ:	R^3=Bzl, R^1=R^2=R^4=R^6=Ac
B-IVα:	R^4=Bzl, R^1=R^2=R^3=R^6=Ac	B-IVβ:	R^4=Bzl, R^1=R^2=R^3=R^6=Ac
B-VIα:	R^6=Bzl, R^1=R^2=R^3=R^4=Ac	B-VIβ:	R^6=Bzl, R^1=R^2=R^3=R^4=Ac
T-Iα:	R^1=Tr, R^2=R^3=R^4=R^6=Ac	T-Iβ:	R^1=Tr, R^2=R^3=R^4=R^6=Ac
T-IIα:	R^2=Tr, R^1=R^3=R^4=R^6=Ac	T-IIβ:	R^2=Tr, R^1=R^3=R^4=R^6=Ac
T-IIIα:	R^3=Tr, R^1=R^2=R^4=R^6=Ac	T-IIIβ:	R^3=Tr, R^1=R^2=R^4=R^6=Ac
T-IVα:	R^4=Tr, R^1=R^2=R^3=R^6=Ac	T-IVβ:	R^4=Tr, R^1=R^2=R^3=R^6=Ac
T-VIα:	R^6=Tr, R^1=R^2=R^3=R^4=Ac	T-VIβ:	R^6=Tr, R^1=R^2=R^3=R^4=Ac
H-Iα:	R^1=H, R^2=R^3=R^4=R^6=Ac	H-Iβ:	R^1=H, R^2=R^3=R^4=R^6=Ac
H-IIα:	R^2=H, R^1=R^3=R^4=R^6=Ac	H-IIβ:	R^2=H, R^1=R^3=R^4=R^6=Ac
H-IIIα:	R^3=H, R^1=R^2=R^4=R^6=Ac	H-IIIβ:	R^3=H, R^1=R^2=R^4=R^6=Ac
H-IVα:	R^4=H, R^1=R^2=R^3=R^6=Ac	H-IVβ:	R^4=H, R^1=R^2=R^3=R^6=Ac
H-VIα:	R^6=H, R^1=R^2=R^3=R^4=Ac	H-VIβ:	R^6=H, R^1=R^2=R^3=R^4=Ac

Bzl=$-CH_2C_6H_5$, Tr=$-C(C_6H_5)_3$, Ac=$-COCH_3$

Chart 1

H-Iα has not been crystallized, but its structure was confirmed by NMR studies and by its chromatographic behavior on thin-layer chromatography (TLC).

1,2,3,6-Tetra-*O*-acetyl derivatives (H-IVα and H-IVβ) and 1,2,3,4-tetra-*O*-acetyl derivatives (H-VIα and H-VIβ) were obtained by detritylation of 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl derivatives (T-VIα and T-VIβ). Trityl ethers are widely used for the selective protection of primary hydroxyl groups and several methods have been suggested for their cleavage.[5] However, detritylation of trityl peracetyl derivatives may be more or less accompanied by acetyl migration. A mild detritylation of 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-α-D-glucopyranose (T-VIα) with 50% acetic acid at 80 °C for 30 min resulted in some acetyl migration from O-4 to O-6, giving a 42.4% yield of 1,2,3,4-tetra-*O*-acetyl-α-D-glucopyranose (H-VIα) and a 19.7% yield of 1,2,3,6-tetra-*O*-acetyl-α-D-glucopyranose (H-IVα). On the other hand, detritylation of the β-anomer, 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-β-D-glucopyranose (T-VIβ) with 50% acetic acid did not cause any acetyl migration even at elevated temperature (such as 100 °C) and gave 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose (H-VIβ) in 72.9% yield. In order to obtain 1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose (H-IVβ) from T-VIβ, the 4-*O*-acetyl group was forced to migrate by the use of a stronger acid. Treatment of T-VIβ with 20% trifluoroacetic acid in acetic acid at 50 °C for 80 min produced H-IVβ (34.8%) together with H-VIβ (29.3%).

1,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranose (H-IIβ), 1,2,4,6-tetra-*O*-acetyl-α-D-glucopyranose (H-IIIα), and the latter's β-anomer (H-IIIβ) were synthesized from the corresponding monobenzyl tetraacetyl derivatives (B-IIβ, B-IIIα, and B-IIIβ) by debenzylation with 10% formic acid in methanol and 10% palladium-on-charcoal.[6]

Syntheses of Monobenzyl Tetraacetyl-D-glucopyranoses

For the unambiguous syntheses of the ten isomeric monobenzyl tetraacetyl-D-glucopyranoses, four hydroxyl groups other than the desired one of D-glucose were protected with appropriate protecting groups and then the free hydroxyl group was benzylated by one of the following methods: (A) is a general method, using benzyl chloride and sodium hydride in dimethylsulfoxide[7]; (B) is a mild method with a weak base such as silver oxide and benzyl bromide,[8] for compounds containing base-labile protecting groups; (C) and (D) are methods

using more reactive alkylating reagents such as benzyl trifluoromethanesulfonate (triflate)[9-11] and benzyl trichloroacetimidate,[12] respectively.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranose (B-IIIβ) was prepared by benzylation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[13] using method A, followed by deisopropylidenation and acetylation. The corresponding α-anomer (B-IIIα) was obtained from B-IIIβ by anomerization with zinc chloride in acetic anhydride.

1,3,4,6-Tetra-*O*-acetyl-2-*O*-benzyl-β-D-glucopyranose (B-IIβ) was synthesized according to the procedure of Brenner and Finan,[14] that is, benzylation of 3,4,6-tri-*O*-acetyl-1-deoxy-1-piperidino-β-D-glucopyranose by method B gave 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-1-deoxy-1-piperidino-D-glucopyranose,[15] and subsequent depiperidination with dilute acetic acid and acetylation gave B-IIβ.

All the other benzyl derivatives were prepared by benzylation of the corresponding tetraacetyl-D-glucopyranoses. Benzylation of H-Iβ in benzene by method B gave benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (B-Iβ) as the major product (67.3%) together with a small amount (10.7%) of its α-anomer (B-Iα). Both 1,2,3,4-tetra-*O*-acetyl-6-*O*-benzyl-α-D-glucopyranose (B-VIα) and the corresponding β-anomer (B-VIβ) were also readily prepared in the same way and obtained in 71.5% and 84.2% yields, respectively.

On the other hand, benzylation of H-IIα under similar conditions resulted in partial migration of an acetyl group from O-1 to O-2. It has been reported[9-11] that the application of benzyl triflate as an alkylating agent in carbohydrate chemistry prevented acetyl group migration and gave the benzylated products in high yields. Thus, H-IIα was treated with benzyl triflate, prepared *in situ*,[10] using 2,6-di-*tert*-benzylpyridine as a base at *ca.* −60 °C (method C). The reaction afforded 1,3,4,6-tetra-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranose (B-IIα) in 56.0% yield.

The reaction of H-IV with benzyl bromide (method B) was difficult and required a large excess of the reagent. 1,2,3,6-Tetra-*O*-acetyl-4-*O*-benzyl-α-D-glucopyranose (B-IVα) and its β-anomer (B-IVβ) were obtained in only 18.8% and 15.9% yields by this method. Since the reactivity of the hydroxyl group on C-4 of H-IVα and H-IVβ was markedly low, a more reactive alkylating reagent such as benzyl trichloroacetimidate[12] was tried (method D). With this reagent, benzylation of H-IVα and H-IVβ in cyclohexane–methylene dichloride in the presence of catalytic amounts of triflic acid gave good yields of the corresponding monobenzyl ethers: B-IVα (83.4%) and B-IVβ (87.1%). Neither deacetylation nor acetyl migration was observed during this benzylation.

Syntheses of Monotrityl Tetraacetyl-D-glucopyranoses

Tritylation of the primary hydroxyl group of glucose with 1.2 mol of trityl chloride in pyridine and subsequent acetylation yielded an anomeric mixture of 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-D-glucopyranoses (T-VIα and T-VIβ). These products were isolated by column chromatography and centrifugal chromatography.

The compounds having a trityl substituent on a secondary or hemiacetal hydroxyl group of glucose (T-Iα, T-IIα, T-IIIα, T-IVα, T-Iβ, T-IIβ, T-IIIβ, and T-IVβ) were prepared in higher yields (from 52.7% to 88.3%) by reactions of the corresponding tetraacetyl-D-glucopyranoses (H-Iα, H-IIα, H-IIIα, H-IVα, H-Iβ, H-IIβ, H-IIIβ, and H-IVβ) with triphenylmethyl perchlorate[16] in the presence of 2,6-di-*tert*-butyl-4-methylpyridine.

Assignments of ^{1}H- and ^{13}C-NMR Signals

Complete assignments of the signals in the ^{1}H- and ^{13}C-NMR spectra (taken on a JNM FX200 NMR spectrometer in chloroform-*d*) of these thirty compounds (Chart 1) were accomplished in the following manner. Since a doublet peak of an anomeric proton is very characteristic, all methine and methylene protons could be fully assigned by the ^{1}H[^{1}H]-decoupling technique. On the basis of this result, the ^{13}C-signals were assigned by the

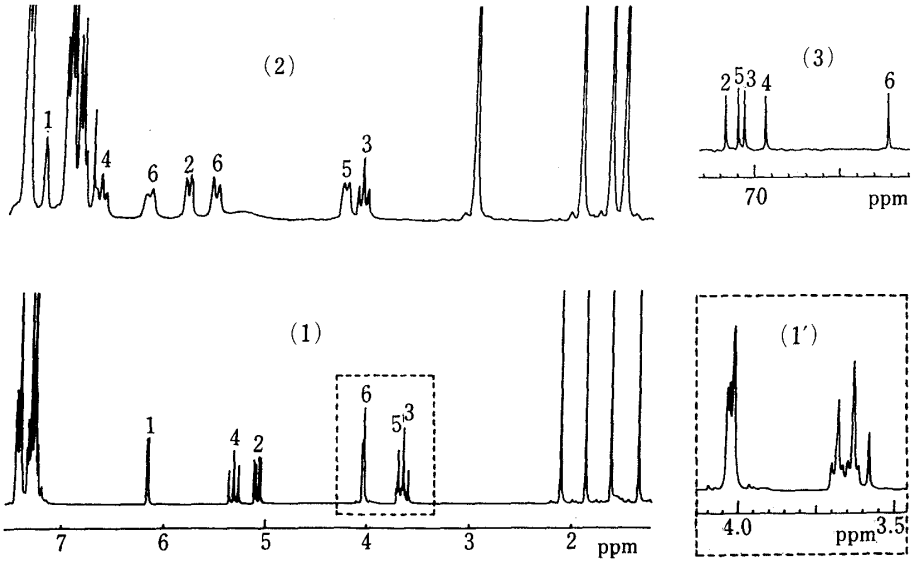


Fig. 1. (1) ^{1}H-NMR Spectrum of 1,2,4,6-Tetra-*O*-acetyl-3-*O*-trityl-α-D-glucopyranose (T-IIIα), (1′) an Expansion of the H-3, H-5 and H-6 Region, (2) ^{1}H-NMR Spectrum of T-IIIα, Shifted by Addition of Eu(FOD)$_3$, (3) ^{13}C-NMR Spectrum of T-IIIα

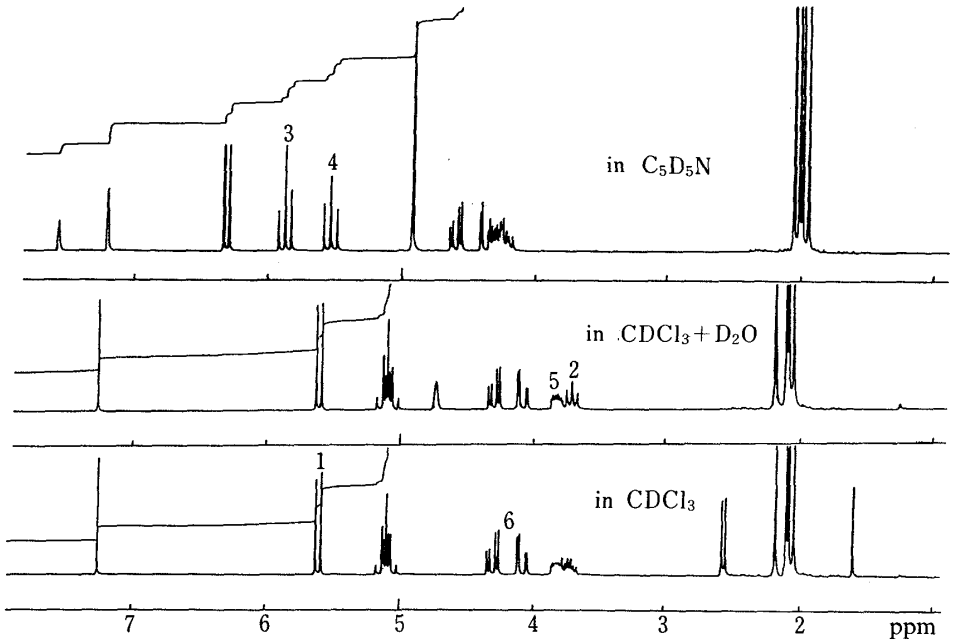


Fig. 2. ^{1}H-NMR Spectra of 1,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranose (H-IIβ) in Three Kinds of Solvents

selective ^{13}C[^{1}H]-decoupling technique. In several cases, the use of Eu(FOD)$_3$ as a shift reagent or replacement of the solvent by benzene-d_6 or pyridine-d_5 was done to confirm the assignments. As an example of the former, NMR spectra of 1,2,4,6-tetra-*O*-acetyl-3-*O*-trityl-α-D-glucopyranose (T-IIIα) are shown in Fig. 1. The H-5 and H-3 signals in the ^{1}H-NMR spectrum [Fig. 1 (1)] are overlapping. Fig. 1 (1′) shows an expansion of this signal region. By the use of Eu(FOD)$_3$ as a shift reagent, the H-5 and H-3 signals were isolated [Fig. 1 (2)], and then C-5 and C-3 signals in the ^{13}C-NMR spectrum [Fig. 1 (3)] could be assigned by selective ^{13}C[^{1}H]-decoupling. Figure 2 shows an example of a solvent effect. The H-2 signal in the ^{1}H-

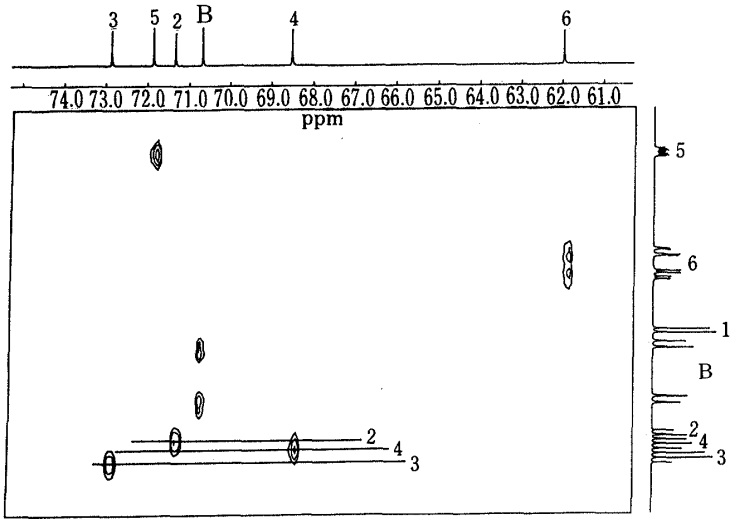


Fig. 3. C–H COSY NMR Spectrum of Benzyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (B-Iβ)

TABLE I. Assignments for ^{1}H-NMR Signals of D-Glucopyranose Tetraacetates

Compound	H-1	H-2	H-3	H-4	H-5	H-6$_a$	H-6$_b$
α-Glucose pentaacetate	6.33 (d)	5.10 (q)	5.48 (t)	5.14 (t)	4.12 (o)	4.28 (q)	4.09 (q)
H-Iα	5.47 (d)	4.91 (q)	5.54 (q)	5.09 (t)	4.32 — 4.09 (m)		
H-IIα	6.24 (d)	3.89 (o)	5.27 (t)	5.10 (t)	4.09—3.99 (m)	4.28 (q)	4.09—3.99 (m)
H-IIIα	6.30 (d)	4.97 (q)	4.12—3.99 (m)	5.01 (t)	4.09—3.99 (m)	4.29 (q)	4.11 (q)
H-IVα	6.30 (d)	5.04 (q)	5.33 (q)	3.59 (t)	3.95 (o)	4.54 (q)	4.24 (q)
H-VIα	6.34 (d)	5.07 (q)	5.53 (q)	5.11 (t)	3.93 (o)	3.72 (q)	3.57 (q)
β-Glucose pentaacetate	5.72 (d)	5.14 (t)	5.26 (t)	5.13 (t)	3.84 (o)	4.30 (q)	4.11 (q)
H-Iβ	4.74 (q)	4.88 (q)	5.27 (t)	5.08 (t)	3.76 (o)	4.27 (q)	4.15 (q)
H-IIβ	5.61 (d)	3.72 (t)	5.18—5.02 (m)		3.83 (o)	4.31 (q)	4.09 (q)
H-IIIβ	5.67 (d)	4.99 (q)	3.85—3.72 (m)	4.98 (t)	3.85—3.72 (m)	4.31 (q)	4.13 (q)
H-IVβ	5.72—5.68 (m)	5.16—5.02 (m)		3.70—3.53 (m)		4.54 (q)	4.28 (q)
H-VIβ	5.73 (d)	5.11 (q)	5.31 (t)	5.09 (t)	3.84 — 3.52 (m)		

δ, ppm from TMS in $CDCl_3$. Signal multiplicities are symbolized by d (doublet), t (triplet), q (quartet), o (octet), and m (complex multiplet).

NMR spectrum of 1,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (H-IIβ) was coupled with the 2-hydroxyl group, and was simplified by addition of deuterium oxide. The H-3 and H-4 signals which were overlapping to a considerable extent in chloroform-*d* were completely resolved in pyridine-d_5.

Methylene carbons of monobenzyl derivatives were identified by the insensitive nuclei enhanced by polarization transfer (INEPT) technique. Moreover, if necessary, ^{1}H[^{1}H]-shift-correlated 2D NMR spectroscopy (COSY) and ^{13}C[^{1}H]-shift-correlation (C–H COSY) at higher frequency (Bruker AM 400) were applied. An example is shown in Fig. 3. Though it was difficult to resolve the H-2, H-3, and H-4 signals in the ^{1}H-NMR spectrum of benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (B-Iβ) by 200 MHz NMR, they could be assigned by C–H COSY (400 MHz NMR) measurement.

TABLE II. Assignments for ^{1}H-NMR Signals of Monobenzyl-D-glucopyranose Tetraacetates

Compound	H-1	H-2	H-3	H-4	H-5	H-6_a	H-6_b	$C_6H_5CH_2$
B-Iα	5.13 (d)	4.88 (q)	5.53 (q)	5.08 (t)	4.08—3.97 (m)	4.29—4.20 (m)	4.08—3.97 (m)	4.65 (q)
B-IIα	6.35 (d)	3.68 (q)	5.40 (t)	5.03 (t)	4.11—4.00 (m)	4.28 (q)	4.11—4.00 (m)	4.58 (q)
B-IIIα	6.31 (d)	5.07 (q)	3.96 (t)	5.16 (t)	4.01 (o)	4.21 (q)	4.07 (q)	4.66 (q)
B-IVα	6.26 (d)	5.02 (q)	5.56 (q)	3.70 (t)	4.09—3.99 (m)	4.31 (q)	4.25 (q)	4.59 (d)
B-VIα	6.35 (d)	5.09 (q)	5.46 (q)	5.21 (q)	4.10—4.02 (m)	3.54 (q)	3.52 (q)	4.52 (q)
B-Iβ	4.55 (d)	5.04 (q)	5.15 (t)	5.08 (t)	3.66 (o)	4.28 (q)	4.16 (q)	4.76 (q)
B-IIβ	5.66 (d)	3.61 (q)	5.23 (t)	5.01 (t)	3.81 (o)	4.30 (q)	4.07 (q)	4.66 (q)
B-IIIβ	5.65 (d)	5.17 (q)	3.75 (t)	5.16 (t)	3.73 (o)	4.23 (q)	4.09 (q)	4.61 (sx)
B-IVβ	5.70 (d)	5.03 (q)	5.30 (q)	3.73—3.65 (m)		4.34 (q)	4.22 (q)	4.58 (q)
B-VIβ	5.71 (d)	5.14 (t)	5.26—5.18 (m)		3.82—3.74 (m)	3.60 (q)	3.52 (q)	4.51 (q)

δ, ppm from TMS in $CDCl_3$. Signal multiplicities are symbolized by d (doublet), t (triplet), q (quartet), sx (sextet), o (octet), and m (complex multiplet).

TABLE III. Assignments for ^{1}H-NMR Signals of Monotrityl-D-glucopyranose Tetraacetates

Compound	H-1	H-2	H-3	H-4	H-5	H-6_a	H-6_b
T-Iα	5.41 (d)	4.97 (q)	5.79 (q)	5.04 (q)	3.72 (sx)	3.88 (q)	2.92 (q)
T-IIα	5.25 (d)	3.72 (q)	5.65 (t)	4.80 (q)	4.19 — 3.87 (m)		
T-IIIα	6.16 (d)	5.08 (q)	3.64 (t)	5.31 (t)	3.67 (sx)	4.04 (d)	4.02 (d)
T-IVα	6.12 (d)	4.71 (q)	5.58 (q)	3.54 (t)	4.26—4.18 (m)	4.27 (q)	3.68 (q)
T-VIα	6.43 (d)	5.16 (q)	5.42 (t)	5.30 (t)	4.05—3.98 (m)	3.32 (q)	3.02 (q)
T-Iβ	4.19 (d)	5.39—5.27 (m)	5.01 (t)	4.97 (t)	2.97 (o)	3.92 (q)	3.63 (q)
T-IIβ	5.75 (d)	3.41 (q)	5.43 (t)	4.72 (q)	3.85 (o)	4.24 (q)	3.99 (q)
T-IIIβ	5.27 (d)	5.21 (q)	3.48 (t)	5.19 (t)	3.34 (o)	4.06 (q)	4.01 (q)
T-IVβ	5.77 (d)	4.73 (t)	5.30 (t)	3.53 (q)	3.99 (sp)	4.26 (q)	3.62 (q)
T-VIβ	5.72 (d)	5.31 — 5.12 (overlap)			3.69 (o)	3.33 (q)	3.07 (q)

δ, ppm from TMS in $CDCl_3$. Signal multiplicities are symbolized by d (doublet), t (triplet), q (quartet), sx (sextet), sp (septet), o (octet), and m (complex multiplet).

^{1}H-NMR Spectra

The chemical shifts of signals in the 200 MHz spectra of tetra-*O*-acetyl-D-glucopyranoses, and their monobenzyl and monotrityl derivatives are shown in Table I, II, and III, respectively. Included in Table I for comparison are data for α- and β-D-glucopyranose pentaacetates.

A large upfield shift (underlined δ-values, Table I) is observed at each deacetylated position. The deacetylation shifts of three kinds of hydroxyl groups, the anomeric hydroxyl group at C-1, the secondary hydroxyl groups at C-2, C-3, and C-4 and the primary hydroxyl group at C-6 are −0.9——1.0, −1.2——1.6, and −0.5——0.6 ppm, respectively. The shift values of the α- and β-anomers are approximately the same. Regarding the proton signals of neighboring positions, the shifts were extremely small.

When one acetyl group is replaced by a benzyl or trityl group, a large upfield shift is also observed at each replaced position (underlined in Tables II and III). The shift values of monobenzyl or monotrityl derivatives were −1.2——1.5 and −0.9——1.8 ppm, respectively. The shift values on 6-*O*-substitution are a little smaller than those on substitution at the other positions.

These shift values should be very useful to determine the deacetylated positions, and positions substituted by benzyl or trityl groups, since the upfield shifts of the proton signals of interest are significant, whereas the signals of adjacent protons remain practically unchanged.

^{13}C-NMR Spectra

(1) ^{13}C-NMR Spectra of Tetra-*O*-acetyl-D-glucopyranoses——The ^{13}C-chemical shifts of signals in the 50.10 MHz spectra of tetraacetyl-D-glucopyranoses are shown in Table IV together with data for the reference compounds, glucose pentaacetates. The deacetylation shifts ($\Delta\delta^{DeAc}$) were calculated as $\Delta\delta^{DeAc} = \delta$ (glucose tetraacetate) $- \delta$ (glucose pentaacetate), and are given in Table V. Regular downfield shifts ($\Delta\delta^{DeAc} = +2$ to $+3$ ppm) are observed at β-carbons adjacent to the deacetylated position (α-carbon). However, typical shifts are not

Table IV. ^{13}C-Chemical Shifts of D-Glucopyranose Tetraacetates

Compound	C-1	C-2	C-3	C-4	C-5	C-6
α-Glucose pentaacetate	89.20	69.38	69.99	68.15	69.99	61.64
H-Iα	90.20	71.25	70.02	68.71	67.30	62.11
H-IIα	91.42	69.99	73.32	67.65	69.79	61.76
H-IIIα	89.44	71.98	70.08	70.52	70.08	61.87
H-IVα	89.41	69.26	72.36	68.79	72.50	62.54
H-VIα	89.20	69.49	69.76	68.41	72.18	60.97
β-Glucose pentaacetate	91.80	70.40	72.85	67.98	72.85	61.58
H-Iβ	95.63	73.41	72.36	68.65	72.21	62.11
H-IIβ	93.90	71.51	75.36	67.95	72.76	61.79
H-IIIβ	91.74	73.06	73.87	70.55	72.91	61.84
H-IVβ	91.95	70.43	75.33	68.65	75.07	62.60
H-VIβ	91.86	70.57	72.76	68.36	75.07	61.00

δ, ppm from TMS in $CDCl_3$.

Table V. Deacetylation Shifts[a] for the D-Glucopyranose Acetates

Compound	C-1	C-2	C-3	C-4	C-5	C-6
H-Iα	+1.00	+1.87	+0.03	+0.56	−2.69	+0.47
H-IIα	+2.22	+0.61	+3.33	−0.50	−0.20	+0.12
H-IIIα	+0.24	+2.60	+0.09	+2.37	+0.09	+0.23
H-IVα	+0.21	−0.12	+2.37	+0.64	+2.51	+0.90
H-VIα	0.00	+0.11	−0.23	+0.26	+2.19	−0.67
H-Iβ	+3.83	+3.01	−0.49	+0.67	−0.64	+0.53
H-IIβ	+2.10	+1.11	+2.51	−0.03	−0.09	+0.21
H-IIIβ	−0.06	+2.66	+1.02	+2.57	+0.06	+0.26
H-IVβ	+0.15	+0.03	+2.48	+0.67	+2.22	+1.02
H-VIβ	+0.06	+0.17	−0.09	+0.38	+2.22	−0.58

$\Delta\delta^{DeAc}$, ppm. *a*) $\Delta\delta^{DeAc} = \delta$ (glucose tetraacetate) $- \delta$ (glucose pentaacetate); a downfield shift is indicated by a positive value.

observed at α-carbons.

H-Iα and H-Iβ show significant shift values: $\Delta\delta^{DeAc} = -2.69$ ppm for C-5 of H-Iα and $\Delta\delta^{DeAc} = +3.83$ ppm for C-1 of H-Iβ. Komura *et al.*[17] have already reported similar results. They suggested that the larger downfield shift observed at C-1 of H-Iβ may be attributed to larger changes in the interaction between the C-1 equatorial substituent and the lone-pair electron lobes of the pyranoid ring-oxygen atom in a *gauche* relationship, but they could not find any positive effect at C-5 for H-Iα. On the other hand, Yoshimoto *et al.*[18] studied the acylation (myristoylation) shifts of glucose, and found significant shifts of 1-*O*-acyl-D-glucopyranoses at C-1 (upfield shift, −0.4 and −2.9 ppm for α- and β-anomers, respectively) and at C-5 (downfield shift, +3.3 and +1.0 ppm for α- and β-anomers, respectively). They interpreted the result at C-1 in terms of *exo*-anomeric effect,[19] and that at C-5 in terms of anomeric effect.[19] Glucose pentaacetates are 1-*O*-acetyl derivatives and should show similar abnormal acylation shifts. On the basis of the chemical shift values of glucose pentaacetates, we calculated the deacetylation shift values of tetraacetyl derivatives. The shift values of C-5 of H-Iα and C-I of H-Iβ were abnormally large, having opposite sign to the acylation shift, as was expected.

(2) ^{13}C-NMR Spectra of Monobenzyl Tetraacetyl-D-glucopyranoses——The ^{13}C-chemical shifts of monobenzyl tetraacetyl-D-glucopyranoses in the 50.10 MHz spectra (Table VI) were compared with those of tetraacetyl-D-glucopyranoses (Table IV) to obtain the benzylation

TABLE VI. ^{13}C-Chemical Shifts of Monobenzyl-D-glucopyranose Tetraacetates

Compound	C-1	C-2	C-3	C-4	C-5	C-6	$C_6H_5\underline{C}H_2$
B-Iα	95.16	70.87	70.19	68.76	67.63	61.93	70.34
B-IIα	89.32	75.60	71.68	68.21	69.76	61.76	73.06
B-IIIα	89.61	71.60	77.12	69.32	70.40	61.96	74.78
B-IVα	89.29	69.76	71.98	75.45	71.13	62.25	74.95
B-VIα	89.26	69.44	70.17	68.91	71.25	68.30	73.73
B-Iβ	99.32	71.35	72.87	68.53	71.86	61.98	70.70
B-IIβ	93.79	78.11	74.20	68.30	72.59	61.73	74.69
B-IIIβ	92.09	71.68	80.06	69.23	73.14	61.93	74.17
B-IVβ	91.95	71.25	75.13	75.71	74.11	62.52	74.75
B-VIβ	91.92	70.55	73.14	68.79	74.08	68.15	73.61

δ, ppm from TMS in $CDCl_3$.

TABLE VII. Benzylation Shifts[a] of Monobenzyl-D-glucopyranose Tetraacetates

Compound	C-1	C-2	C-3	C-4	C-5	C-6
B-Iα	+4.96	−0.38	+0.17	+0.05	+0.33	−0.18
B-IIα	−2.10	+5.61	−1.64	+0.56	−0.03	0.00
B-IIIα	+0.17	−0.38	+7.04	−1.20	+0.32	+0.09
B-IVα	−0.12	+0.50	−0.38	+6.66	−1.37	−0.29
B-VIα	+0.06	−0.05	+0.41	+0.50	−0.93	+7.33
B-Iβ	+3.69	−2.06	+0.51	−0.12	−0.35	−0.13
B-IIβ	−0.11	+6.60	−1.16	+0.35	−0.17	−0.06
B-IIIβ	+0.35	−1.38	+6.19	−1.32	+0.23	+0.09
B-IVβ	0.00	+0.82	−0.20	+7.06	−0.96	−0.08
B-VIβ	+0.06	−0.02	+0.38	+0.43	−0.99	+7.15

$\Delta\delta^{Bzl}$, ppm. *a*) $\Delta\delta^{Bzl} = \delta$ (monobenzylglucose tetraacetate) − δ (glucose tetraacetate); a downfield shift is indicated by a positive value.

TABLE VIII. ^{13}C-Chemical Shifts of Monotrityl-D-glucopyranose Tetraacetates

Compound	C-1	C-2	C-3	C-4	C-5	C-6	$(C_6H_5)_3\underline{C}O$
T-Iα	92.15	71.04	70.84	68.65	67.45	61.14	88.27
T-IIα	90.58	71.04	71.71	69.06	68.76	61.99	88.30
T-IIIα	89.85	71.68	70.60	69.38	70.98	62.19	89.00
T-IVα	89.12	70.52	72.18	70.28	71.74	62.84	89.12
T-VIα	89.47	69.64	70.52	68.56	71.39	61.58	86.72
T-Iβ	95.98	71.51	73.26	69.03	71.13	61.93	89.15
T-IIβ	93.58	72.59	74.66	68.94	72.36	61.90	88.94
T-IIIβ	92.42	71.95	73.64	69.79	73.32	62.37	89.32
T-IVβ	91.34	71.71	75.04	70.31	74.81	63.16	89.09
T-VIβ	92.07	70.75	73.29	68.56	74.20	61.99	86.81

δ, ppm from TMS in $CDCl_3$.

TABLE IX. Tritylation Shifts[a] of Monotrityl-D-glucopyranose Tetraacetates

Compound	C-1	C-2	C-3	C-4	C-5	C-6
T-Iα	+1.95	−0.21	+0.82	−0.06	+0.15	−0.97
T-IIα	−0.84	+1.05	−1.61	+1.41	−1.03	+0.23
T-IIIα	+0.41	−0.30	+0.52	−1.14	+0.90	+0.32
T-IVα	−0.29	+1.26	−0.18	+1.49	−0.76	+0.30
T-VIα	+0.27	+0.15	+0.76	+0.15	−0.79	+0.61
T-Iβ	+0.35	−1.90	+0.90	+0.38	−1.08	−0.18
T-IIβ	−0.32	+1.08	−0.70	+0.99	−0.40	+0.11
T-IIIβ	+0.68	−1.14	−0.23	−0.76	+0.41	+0.53
T-IVβ	−0.61	+1.28	−0.29	+1.66	−0.26	+0.56
T-VIβ	+0.21	−0.18	+0.63	+0.20	−0.87	+0.99

$\Delta\delta^{Tr}$, ppm. *a*) $\Delta\delta^{Tr} = \delta$ (monotritylglucose tetraacetate) $- \delta$ (glucose tetraacetate); a downfield shift is indicated by a positive value.

shift ($\Delta\delta^{Bzl}$) values (Table VII). The methylene carbons in benzyl groups of B-II, B-III, B-IV, and B-VI resonate at 73—74 ppm. Those of B-I showed a downfield shift of about +3 to +4 ppm (Table VI), and B-I may therefore be distinguishable from the other derivatives. Extremely large downfield shifts are regularly observed at the benzylated positions (α-carbon: $\Delta\delta^{Bzl} = +4.96$ to +7.33 ppm, except for +3.69 of B-Iβ), whereas smaller upfield shifts are seen at the β-carbons ($\Delta\delta^{Bzl} = -0.2$ to −2.1 ppm, except for −0.11 ppm at C-1 of B-IIβ). Those noteworthy benzylation shifts are very favorable for determination of the benzylated position of acetylated gluco-oligosaccharide derivatives.

(3) ^{13}C-NMR Spectra of Monotrityl Tetraacetyl-D-glucopyranoses——The chemical shifts of signals in the 50.10 MHz spectra of monotrityl tetraacetyl-D-glucopyranoses are given in Table VIII. Signals of the quaternary carbon of the trityl groups of all trityl derivatives except T-VI resonated at 88.3 to 89.3 ppm. Since those of the 6-trityl derivative (T-VI) appear at 86.72 and 86.81 ppm (upfield shift about −2 ppm), tritylation at C-6 is easily distinguishable. The tritylation shifts ($\Delta\delta^{Tr}$) were calculated as $\Delta\delta^{Tr} = \delta$ (monotritylglucose tetraacetate) $- \delta$ (glucose tetraacetate), and are summarized in Table IX. Though there is some consistency at the α-carbon ($\Delta\delta^{Tr} = +0.4$ to +2.0 ppm, except for −0.23 of T-IIIβ) and β-carbon ($\Delta\delta^{Tr} = -0.2$ to −1.9 ppm), typical shifts such as seen in the case of benzylation are not observed. We consider that the very bulky trityl group might significantly disturb the stereochemical relationship with neighboring substituents.

TABLE X. Conditions for FT NMR Measurements

Instrument	JEOL JNM-FX200		Bruker AM 400	
	^{1}H (200 MHz)	^{13}C (50.10 MHz)	^{1}H (400 MHz)	^{13}C (100.61 MHz)
Sampling tube (i.d. mm)	5	10	5	5
Concentration (M)	0.02—0.05	0.05—0.09	0.02—0.04	0.13—0.34
Temperature (°C)	23	27—30	24	27—30
Spectral width (Hz)	2000	12004	4000	20000
Acquisition time (s)	4.096	0.682	4.096	1.638
Pulse flipping angle (°)	45	45	30	45
Number of data points (K)	16	16	32	64

Experimental

Optical rotations were determined with a Jasco DIP-4 automatic polarimeter. Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. In several cases, the measured values differed considerably from literature values. Although it is not clear whether these discrepancies resulted from either polymorphism or differences in purity, our compounds were confirmed to be pure by elemental analyses, TLC, and NMR studies. Column chromatography (Col C) was performed on a Lobar prepacked column packed with LiChroprep Si 60 (40—63 μm), size B or C (E. Merck). Centrifugal chromatography (Cen C) was carried out on a Harrison centrifugal Thin Layer Chromatotron, model 7924. TLC was performed on TLC plates, Silica gel 60 (0.25 mm, E. Merck). The following solvent systems (v/v) were used for chromatography: (a) 2 : 3, (b) 1 : 1, (c) 2 : 1, (d) 5 : 1, (e) 7 : 1, (f) 9 : 1, (g) 10 : 1 benzene–ethyl acetate.

Measurements of NMR Spectra——The conditions for FT NMR measurement are shown in Table X. ^{1}H[^{1}H]-Shift-correlated 2D NMR spectra (COSY) and ^{13}C[^{1}H]-shift-correlated 2D NMR spectra (C–H COSY) were recorded with a Bruker AM 400 instrument and the matrix sizes of COSY and C–H COSY spectra were 512 × 512 and 1K × 512, respectively.

1,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranose (H-IIβ)——Compound B-IIβ (1.5 g) was dissolved in MeOH containing 10% HCOOH (150 ml). This solution was added to a stirred suspension of 10% palladium-on-charcoal (7.5 g) in the same solvent mixture (150 ml) and stirring was continued in a nitrogen atmosphere for 2 h. The catalyst was filtered off, and washed with MeOH and H_2O. The filtrate and washings were evaporated, and the residue was crystallized from ether, yield 758 mg (63.6%), mp 136.0—137.0 °C, $[\alpha]_D^{28}$ +35.5° (c=2.00, $CHCl_3$) (lit.[14] mp 136—137 °C, $[\alpha]_D$ +37.5° (c=1, $CHCl_3$).

1,2,4,6-Tetra-*O*-acetyl-α- and -β-D-glucopyranoses (H-IIIα and H-IIIβ)——Debenzylation of B-IIIα (1.275 g) and B-IIIβ (400 mg) was individually carried out as described for the preparation of H-IIβ. Each product was crystallized from CH_2Cl_2–ether. H-IIIα: yield 449 mg (44.3%), mp 162.0—163.0 °C, $[\alpha]_D^{21}$ +87.0° (c=2.00, $CHCl_3$) (lit.[20] mp 161—163 °C, $[\alpha]_D^{21}$ +87.9° (c=2.0, $CHCl_3$). H-IIIβ: yield 264 mg (83.1%), mp 124.0—126.0 °C, $[\alpha]_D^{16}$ −13.0° (c=2.00, $CHCl_3$) (lit.[20] mp 126—127 °C, $[\alpha]_D^{18}$ −13.6° (c=2.5, $CHCl_3$).

1,2,3,4-Tetra-*O*-acetyl-α-D-glucopyranose (H-VIα) and 1,2,3,6-Tetra-*O*-acetyl-α-D-glucopyranose (H-IVα)——Detritylation of T-VIα (6 g) with 50% (v/v) AcOH (300 ml) at 80 °C for 30 min gave two products, H-VIα and H-IVα, in the ratio of 2 : 1 on TLC with solvent (a). The mixture was chromatographed with solvent (c). From the faster-eluting fractions, H-IVα (698 mg, 19.7%) was isolated as a pure syrup, $[\alpha]_D^{24}$ +56.8° (c=0.88, $CHCl_3$) (lit.[21] syrup, $[\alpha]_D^{20}$ +78.3° (c=1.66, $CHCl_3$). From the subsequent fractions, H-VIα (1.5 g, 42.4%) was isolated. The product was crystallized from ether, mp 99.0—101.0 °C, $[\alpha]_D^{16}$ +119° (c=2.00, $CHCl_3$), *Anal.* Calcd for $C_{14}H_{20}O_{10}$: C, 48.28; H, 5.79. Found: C, 48.05; H, 5.79. (lit.[22] mp 102—103 °C, $[\alpha]_D^{16}$ +119° ($CHCl_3$).

1,2,3,4-Tetra-*O*-acetyl-β-D-glucopyranose (H-VIβ)——A suspension of T-VIβ (5 g) in 50% (v/v) AcOH (250 ml) was heated at 100 °C for 15 min to carry out detritylation. The mixture was neutralized, extracted with $CHCl_3$, and isolated by Col C with solvent (b) to give H-VIβ (2.15 g, 72.9%) which was crystallized from ether, mp 126.0—127.0 °C, $[\alpha]_D^{16.5}$ +9.6° (c=2.00, $CHCl_3$) (lit.[22] mp 128—129 °C, $[\alpha]_D^{25}$ +12° (c=6, $CHCl_3$).

1,2,3,6-Tetra-*O*-acetyl-β-D-glucopyranose (H-IVβ)——Detritylation of T-VIβ (1 g) with 20% (v/v) CF_3COOH–AcOH (100 ml) at 50 °C for 80 min gave two products, H-IVβ and H-VIβ, in the ratio of 1 : 1 on TLC with solvent (a). The mixture was chromatographed with solvent (c). From the faster-eluting fractions, H-IVβ (205 mg, 34.8%) was isolated and crystallized from benzene, mp 127.0—127.5 °C, $[\alpha]_D^{21.5}$ −33.5° (c=2.00, $CHCl_3$), *Anal.* Calcd for $C_{14}H_{20}O_{10}$: C, 48.28; H, 5.79. Found: C, 48.06; H, 5.73 (lit.[20] mp 131—133 °C, $[\alpha]_D^{23}$ −32.2° (c=3.07, $CHCl_3$).

Benzyl 2,3,4,6-Tetra-*O*-acetyl-α- and -β-D-glucopyranosides (B-Iα and B-Iβ)——Benzylation of H-Iβ (200 mg, 0.57 mmol) with benzyl bromide (0.28 ml, 2.35 mmol) and freshly prepared Ag_2O (533 mg, 2.30 mmol) in dry benzene

(3 ml) was carried out to give B-Iβ (105 mg), which was crystallized from EtOH. The mother liquor was evaporated and the residue (301 mg) was fractionated by Cen C with solvent (e) to give B-Iα (27 mg) and additional B-Iβ (66 mg). Both products were crystallized from EtOH. B-Iα: mp 111.0—112.0 °C, $[\alpha]_D^{25}$ +144.1° (c=2.01, $CHCl_3$). *Anal.* Calcd for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.35; H, 6.01 (lit.[23] mp 109—110 °C, $[\alpha]_D$ +143.5° (c=1, $CHCl_3$). B-Iβ: mp 97.0—97.5 °C, $[\alpha]_D^{26.5}$ −50.1° (c=2.00, $CHCl_3$), *Anal.* Found: C, 57.42; H, 6.08 (lit.[24] mp 99—100 °C, $[\alpha]_D$ −48° (c=2.5, $CHCl_3$).

1,3,4,6-Tetra-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranose (B-IIα)——Trifluoromethanesulfonic anhydride (0.72 ml, 4.31 mmol) was added under a dry nitrogen atmosphere to dry CH_2Cl_2 at *ca.* −60 °C, then a solution of benzyl alcohol (0.45 ml, 4.31 mmol) and 2,6-di-*tert*-butylpyridine (0.97 ml, 4.31 mmol) in dry CH_2Cl_2 (5 ml) was added dropwise during 5 min. A solution of H-IIα (500 mg, 1.44 mmol) and 2,6-di-*tert*-butylpyridine (0.97 ml, 4.31 mmol) in CH_2Cl_2 (5 ml) was then added over 45 min with stirring. After stirring for 3 d, the solution was allowed to warm to ambient temperature. Pyridine (1 ml) was added with stirring, and B-IIα was extracted with $CHCl_3$, isolated by Col C with solvent (e) and crystallized from EtOH–ligroin, yield 353 mg (56.0%), mp 73.0—73.5 °C, $[\alpha]_D^{22}$ +97.0° (c=2.00, $CHCl_3$), *Anal.* Calcd for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.46; H, 6.00 (lit.[14] mp 75 °C, $[\alpha]_D$ +82° (c=1, $CHCl_3$).

1,3,4,6-Tetra-*O*-acetyl-2-*O*-benzyl-β-D-glucopyranose (B-IIβ)——According to the procedure of Brenner and Finan,[14] B-IIβ was synthesized from penta-*O*-acetyl-β-D-glucopyranose through three intermediates, 3,4,6-tri-*O*-acetyl-1-deoxy-1-piperidino-β-D-glucopyranose (mp 126.0 °C (dec.), 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-1-deoxy-1-piperidino-β-D-glucopyranose (mp 99.0—100.0 °C), and 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranose (mp 141.0—143.0 °C), and crystallized from EtOH: mp 94.0—94.5 °C, $[\alpha]_D^{28}$ +41.5° (c=2.00, $CHCl_3$), *Anal.* Calcd for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.70; H, 6.04 (lit.[14] mp 88 °C, $[\alpha]_D$ +44° (c=1, $CHCl_3$).

1,2,4,6-Tetra-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranose (B-IIIβ)——1,2 : 5,6-Di-*O*-isopropylidene-α-D-glucofuranose[13] was benzylated with benzyl chloride and NaH in DMSO to give 3-*O*-benzyl-1,2 : 5,6-di-*O*-isopropyridene-α-D-glucofuranose,[7] which was deisopropylidenated with Amberlite IR-120 (H^+) cation-exchange resin and acetylated with Ac_2O in dry pyridine. Crystallization of the resulting syrup from EtOH gave B-IIIβ, mp 103.5—104.0 °C, $[\alpha]_D^{18}$ −2.5° (c=2.00, $CHCl_3$), *Anal.* Calcd for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.53; H, 6.08 (lit.[25] mp 107 °C, $[\alpha]_D$ −1.2° ($CHCl_3$).

1,2,4,6-Tetra-*O*-acetyl-3-*O*-benzyl-α-D-glucopyranose (B-IIIα)——Compound B-IIIβ (5.3 g) was anomerized with $ZnCl_2$ (0.53 g) and Ac_2O (26 ml) at 90±1 °C for 30 min. The mixture was poured into ice-water, extracted with $CHCl_3$ and purified by Col C with solvent (e), giving B-IIIα as a pure syrup (1.3 g, 24.1%), $[\alpha]_D^{22}$ +43.3° (c=2.36, $CHCl_3$) (lit.[20] syrup).

1,2,3,6-Tetra-*O*-acetyl-4-*O*-benzyl-α-D-glucopyranose (B-IVα)——i) Compound H-IVα (152 mg, 0.44 mmol) was benzylated with benzyl bromide (0.78 ml, 6.56 mmol) and Ag_2O (3.0 g, 12.9 mmol) in benzene (2 ml) for 80 min. The product was purified by Cen C with solvent (f) to give B-IVα as a pure syrup (36.0 mg, 18.8%), $[\alpha]_D^{23}$ +61.0° (c=1.10, $CHCl_3$) (lit.[26] syrup, $[\alpha]_D^{21}$ +58.0° (c=1.2, $CHCl_3$). ii) To a stirred solution of H-IVα (63 mg, 0.18 mmol) and benzyl trichloroacetimidate (0.2 ml, 1.08 mmol) in cyclohexane–CH_2Cl_2 (1 : 1, 1.0 ml) was added CF_3SO_3H (0.01 ml). The mixture was stirred for 3 d, and extracted with $CHCl_3$. The product was purified by Cen C with solvents (g) and (e) to give a pure syrup (66.1 mg, 83.4%).

1,2,3,6-Tetra-*O*-acetyl-4-*O*-benzyl-β-D-glucopyranose (B-IVβ)——i) Compound H-IVβ (200 mg, 0.57 mmol) was benzylated with benzyl bromide (1.02 ml, 8.58 mmol) and Ag_2O (4.0 g, 17.3 mmol) in benzene (3 ml). The reaction product was purified by Cen C with solvent (f), and crystallized from EtOH to give B-IVβ (40 mg, 15.9%), mp 103.0—105.0 °C, $[\alpha]_D^{23}$ −1.56° (c=1.34, $CHCl_3$) (lit.[27] mp 108—109 °C, $[\alpha]_D^{22}$ 0±1° (c=0.9, $CHCl_3$). ii) To a stirred solution of H-IVβ (50 mg, 0.144 mmol) and benzyl trichloroacetimidate (0.1 ml, 0.54 mmol) in cyclohexane–CH_2Cl_2 (1 : 2, 1.5 ml) was added CF_3SO_3H (0.01 ml). The mixture was stirred for 3 d, and extracted with $CHCl_3$. The product was purified by Cen C with solvents (g) and (e) to give pure B-IVβ (54.8 mg, 87.1%).

1,2,3,4-Tetra-*O*-acetyl-6-*O*-benzyl-α- and -β-D-glucopyranoses (B-VIα and B-VIβ)——H-VIα and H-VIβ (100 mg, 0.26 mmol) were each benzylated with benzyl bromide (0.15 ml, 1.26 mmol) and Ag_2O (300 mg, 1.29 mmol) in benzene (2 ml) for 80 min. The products were purified by Cen C with solvent (e) to give B-VIα (90 mg, 71.5%) and B-VIβ (106 mg, 84.2%), respectively. Both products were crystallized from EtOH. B-VIα: mp 119.0—120.0 °C, $[\alpha]_D^{22}$ +124° (c=2.00, $CHCl_3$), *Anal.* Calcd for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.26; H, 6.09. B-VIβ: mp 113.0—114.0 °C, $[\alpha]_D^{18}$ +39.5° (c=2.00, $CHCl_3$), *Anal.* Found: C, 57.25; H, 6.07.

1,2,3,4-Tetra-*O*-acetyl-6-*O*-trityl-α- and -β-D-glucopyranoses (T-VIα and T-VIβ)——Glucose (10 g) was dissolved in dry pyridine (75 ml), trityl chloride (19 g) was added, and the mixture was stirred at 40 °C for 50 min. A further 25 ml of dry pyridine and 30 ml of Ac_2O were added to perform acetylation. The solvent was evaporated off and the residue was poured into ice-water. The precipitate was collected by filtration and crystallized from EtOH–acetone to give T-VIβ (13.0 g). From the mother liquor, T-VIα and additional T-VIβ were isolated by fractional crystallization: T-VIα (3.9 g), mp 124.0—127.0 °C, $[\alpha]_D^{28}$ +96.0° (c=2.00, $CHCl_3$) (lit.[23] mp 129—131 °C, $[\alpha]_D^{27}$ +97.8° (C_5H_5N); T-VIβ (12.0 g), mp 169.0—170.7 °C, $[\alpha]_D^{20}$ +45.0° (c=2.00, $CHCl_3$) (lit.[23] mp 163—164 °C, $[\alpha]_D^{28}$ +45.3° (C_5H_5N). These products exhibit identical chromatographic behavior on TLC.

Trityl 2,3,4,6-Tetra-*O*-acetyl-α- and -β-D-glucopyranosides (T-Iα and T-Iβ), 1,3,4,6-Tetra-*O*-acetyl-2-*O*-trityl-α-

TABLE XI. Yields and Physical and Analytical Data for Monotrityl-D-glucopyranose Tetraacetates

Compound	Yield		mp (°C)	$[\alpha]_D$ in $CHCl_3$			Elemental analysis[a] Found	
	mg	%		(°)	c	Temp. (°C)	C	H
T-Iα	65.0	76.0	78.5—79.5	+115.0	2.00	21	66.70	5.97
T-Iβ	189.0	80.2	149.0[b]	−21.0[b]	2.00	19	67.14	5.86
T-IIα	360.0	70.8	162.0—163.0[c]	+57.5[c]	2.00	23	66.96	5.74
T-IIβ	74.8	88.3	136.5—137.0	+29.5	2.00	28	67.23	5.82
T-IIIα	179.0	52.7	142.0—143.0	+17.5	2.00	18	66.81	5.81
T-IIIβ	133.0	68.2	140.8—141.5	−2.6	2.66	18	66.87	5.81
T-IVα	308.0	65.0	184.0—185.0	+65.0	2.00	22	66.88	5.74
T-IVβ	395.0	77.6	106.0—107.5	+6.5	2.00	21	66.94	5.77

a) *Anal.* Calcd for $C_{33}H_{34}O_{11}$: C, 67.11; H, 5.80. *b*) Lit.[16] mp 145 °C, $[\alpha]_D$ −21°. *c*) Lit.[1c] mp 162.0 °C, $[\alpha]_D^{23}$ +57.5° (c=2.00, $CHCl_3$).

and -β-D-glucopyranoses (T-IIα and T-IIβ), 1,2,4,6-Tetra-*O*-acetyl-3-*O*-trityl-α- and -β-D-glucopyranoses (T-IIIα and T-IIIβ), and 1,2,3,6-Tetra-*O*-acetyl-4-*O*-trityl-α- and -β-D-glucopyranoses (T-IVα and T-IVβ)——Compounds H-Iα (51 mg), H-Iβ (139 mg), H-IIα (300 mg), H-IIβ (50 mg), H-IIIα (200 mg), H-IIIβ (115 mg), H-IVα (279 mg), and H-IVβ (300 mg) were each tritylated with triphenylmethylium perchlorate (74—600 mg) and 2,6-di-*tert*-butyl-4-methylpyridine (45—354 mg) in CH_2Cl_2 (2—10 ml) under stirring at 40 °C for 0.5—4 h. Pyridine (0.05 ml) and MeOH (0.05 ml) were added, and the mixture was concentrated, then extracted with $CHCl_3$. The chloroform layer was concentrated to a syrup, which was purified by Cen C with solvent (d), (e) or (g). Compound T-Iα was crystallized from acetone–ligroin and all the other compounds were crystallized from EtOH. The yields and physical and analytical data of these compounds are listed in Table XI.

References and Notes

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