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SPECIFIC SPECTRAL ASSIGNMENTS FOR ACETOXYL-GROUP RESONANCES IN PROTON MAGNETIC RESONANCE SPECTRA OF METHYL β-D-GLUCOPYRANOSIDE TETRAACETATE AND RELATED DERIVATIVES*

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ABSTRACT

Methyl β-D-glucopyranoside tetraacetates (**1**) having a trideuterioacetyl group at O-2 (**1a**), O-3, (**1b**), O-4 (**1c**), and O-6 (**1d**) were synthesized by unambiguous routes to permit assignment of each individual acetoxyl-group signal in the p.m.r. spectrum of **1**. The 6-acetoxyl resonance appears at lower field than signals of the other acetoxyl groups in carbon tetrachloride, chloroform-*d*, and methyl sulfoxide-d_6, but in pyridine-d_5 and benzene-d_6, the 2-acetoxyl-group signal appears at lower field. The acetoxyl resonances of methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**2**), methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (**3**), methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**5**), methyl 2,3-di-*O*-acetyl-β-D-glucopyranoside (**6**), methyl 2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**7**), and methyl 2,3-di-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**12**) were assigned similarly after synthesis of the 2-(trideuterioacetyl) (**2a**, **3a**, **5a**, **6a**, **7a**, and **12a**), 3-(trideuterioacetyl) (**2b**, **3b**, **5b**, **6b**, **7b**, and **12b**), 4-(trideuterioacetyl) (**2c** and **3c**), and 6-(trideuterioacetyl) (**7c**) analogues. In chloroform-*d* and benzene-d_6, the 4-acetoxyl resonance appeared at about 0.3 p.p.m. to higher field than the other acetoxyl-group signals of **2**. In chloroform-*d* and methyl sulfoxide-d_6, the 3-acetoxyl resonance is observed at highest field in compounds **1**, **3**, and **5**. In all of these instances, the 4-hydroxyl group is substituted by an acetyl or benzylidene group. When no 4-substituent is present (compounds **6**, **7**, and **12**), the 3-acetoxyl group resonates at lower field than the other acetoxyl groups.

INTRODUCTION

In the previous paper in this series[1], it was demonstrated that the extent of acetylation of each hydroxyl group in a partially acetylated carbohydrate or polyol

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may be determined after acetylation to completion with acetic anhydride-d_6. A single, peracetylated product is obtained that is heterogeneous only to the extent of replacement of CH_3 by CD_3 at various positions in the molecule. The n.m.r. spectrum of the product is essentially identical with that of the all-protiated material, except that the signals for the acetate-methyl groups are diminished to the extent of labeling by deuterium. By comparing the signal intensities of the acetoxyl groups with those of the fully protiated peracetate, the fractional degree of substitution at each position may be determined. The method requires: (*a*) suitable spectral dispersion, so that separate resonances are observed for the different acetate groups, (*b*) specific attribution of acetoxyl-group signals, (*c*) conditions of acetylation that do not permit acetyl-group migration, and (*d*) verification that no exchange of protioacetate by deuterioacetate (or *vice versa*) occurs. With methyl α-D-glucopyranoside tetraacetate as the example, all of these four requirements were established[1], and it may reasonably be assumed that the conditions used for acetylation are applicable generally to other polyhydroxy compounds without risk of migration or exchange. However, for each new compound considered, it is necessary to achieve the requisite spectral dispersion of signals and to assign the individual resonances.

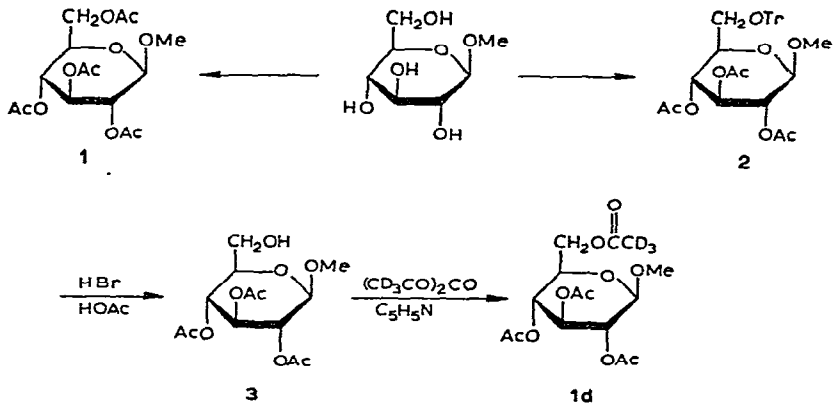
The procedure used[1] for assigning the acetoxyl-group signals in methyl α-D-glucopyranoside tetraacetate involved specific and unequivocal syntheses of the four possible analogues having one of the acetate groups replaced by a deuterioacetate group. Methods of assignment based on supposed analogies between related, but nevertheless different, compounds are considered[2] quite unreliable. This specific deuterioacetylation method was previously applied[2,3] with various amino sugar derivatives, and similar examples of partial or complete assignments of acetate-group signals of monosaccharide[4] and disaccharide[5] derivatives have been recorded, together with related examples in which methoxyl-group resonances in permethylated sugars have been assigned through synthesis of specifically deuteriomethylated derivatives[6].

This paper records the unequivocal synthesis of the specifically mono(deuterioacetyl)ated analogues of methyl β-D-glucopyranoside tetraacetate and a range of related derivatives, and the study of their acetyl-group, n.m.r. resonances in various solvents (see Figs. 1–6). Methyl β-D-glucopyranoside is a useful model compound for cellulose[7,8], and the assignments reported here permit quantitative studies[9] on the relative extents of acetylation at the different hydroxyl groups in this molecule when it is exposed to limited proportions of acetylating reagent.

RESULTS AND DISCUSSION

Synthesis of specifically deuterated derivatives. — Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**1d**) was prepared by detritylation[1] of methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**2**) to give the known[10] methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (**3**), followed by acetylation of **3** with acetic anhydride-d_6 and pyridine to give (**1d**). Although previous[1] and present work

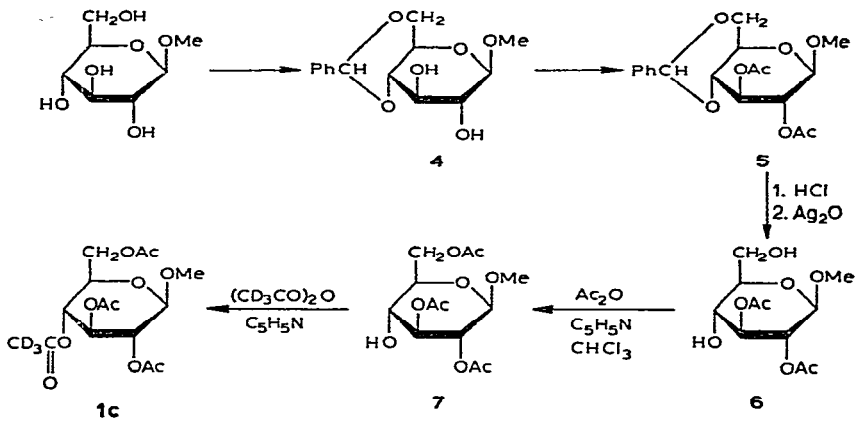
did not indicate the occurrence of any 4→6 acetyl migration under the conditions of acetylation, nevertheless, to exclude any possible base-catalyzed migration during this last step, the triacetate **3** was first dissolved in dry benzene, acetic anhydride-d_6 was then added and, after thorough mixing, pyridine was added. Specific details are recorded in the Experimental section for all hydrolysis and acetylation steps, as the specific deuteration, without migration, achieved by the procedures given are not necessarily reproducible if the experimental conditions are modified.



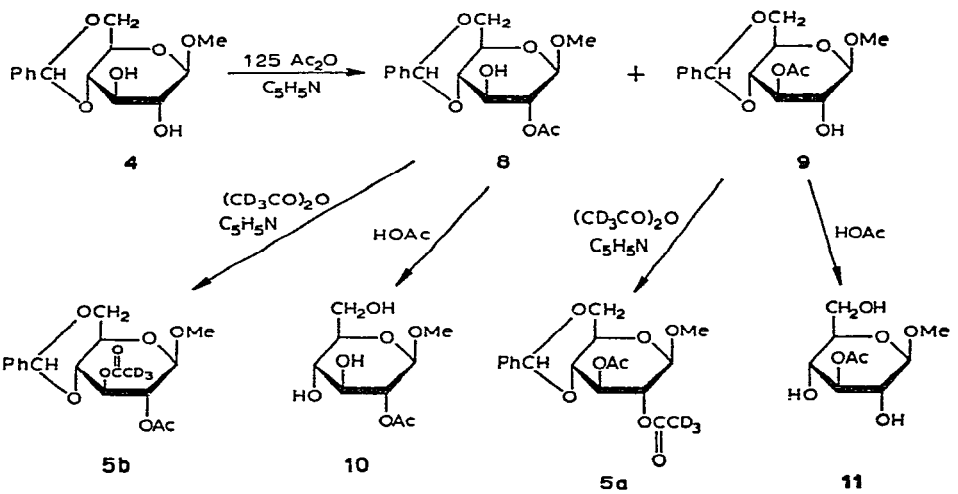
The triacetate mono(trideuterioacetate) **1d** gave a p.m.r. spectrum identical with that of **1**, except that one of the acetoxyl-group signals was absent, and this missing signal could thus be assigned to the 6-acetoxyl group (see Fig. 1 and Table I). All other mono(deuterioacetates) reported here likewise gave p.m.r. spectra identical to those of the protioacetate analogues, except for the complete absence of one acetoxyl-group resonance that could thus be specifically assigned.

Synthesis of the tetraacetates of the glycoside **1**, deuterated specifically in the 4-acetoxyl group (**1c**), 3-acetoxyl group (**1b**), and 2-acetoxyl group (**1a**) was accomplished by way of methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**4**). Acetylation of **4** with acetic anhydride–pyridine gave a 93% yield of the known[11] 2,3-diacetate **5**, which, with refluxing 25mM hydrogen chloride in aqueous acetone[12], underwent cleavage of the benzylidene group with negligible hydrolysis of the acetyl groups, to give the known[12,13], crystalline methyl 2,3-di-*O*-acetyl-β-D-glucopyranoside (**6**). Monoacetylation of **6** by the procedure of Levene and Raymond[12] yielded the known[12], crystalline 2,3,6-triacetate **7**. Acetylation of **7** with acetic anhydride-d_6–pyridine gave methyl 2,3,6-tri-*O*-acetyl-4-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**1c**), whose p.m.r. spectrum was identical with that of **1** except for the absence of one acetoxyl-group signal, which could, therefore, be attributed to the 4-acetoxyl group (see Fig. 1 and Table I).

Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**8**) and its 3-*O*-acetyl isomer (**9**) were prepared according to known methods[14,15] from methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**4**) by treatment with 1.25 molar equivalents



of acetic anhydride in pyridine, followed by separation of the products on a column of silica gel. Acetylation of **8** with acetic anhydride-d_6 in pyridine gave methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**5b**), and similar treatment of **9** gave methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**5a**). The p.m.r. spectra of both **5b** and **5a** showed only one acetate-group signal, but otherwise the spectra were identical with that of methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**5**), and thus the individual acetyl-group signals in **5** could therefore be assigned (see Fig. 2 and Table I).



Compounds **5b** and **5a** were hydrolyzed by the same procedure[12] as that used for **5**, to give methyl 2-*O*-acetyl-3-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**6b**) and methyl 3-*O*-acetyl-2-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**6a**), respectively. The p.m.r. spectra of **6b** and **6a** showed only one acetoxyl-group signal, thus permitting

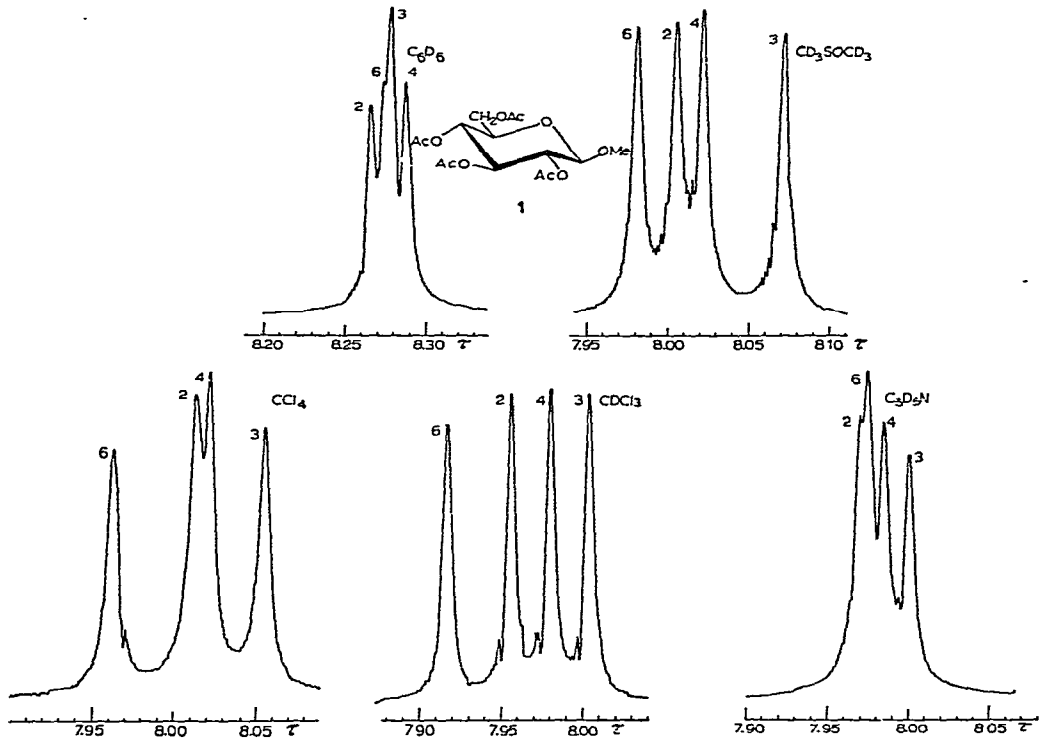


Fig. 1. The acetoxyl-group signals in the p.m.r. spectrum of methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**1**) at 100 MHz in carbon tetrachloride, chloroform-*d*, pyridine-d_5, benzene-d_6, and methyl sulfoxide-d_6.

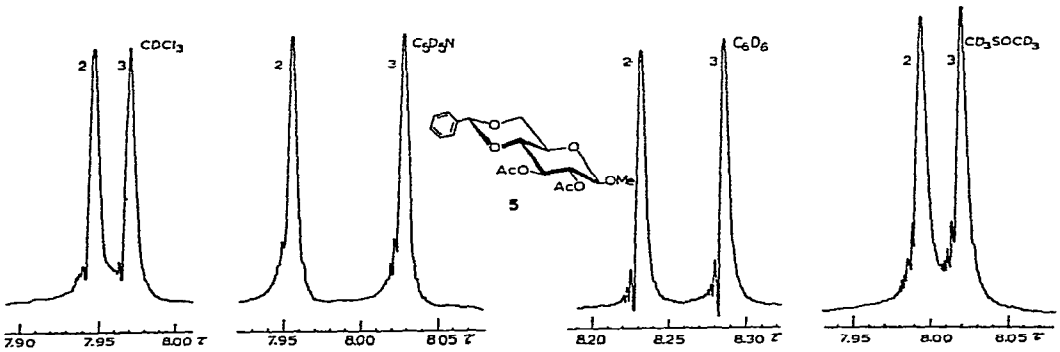
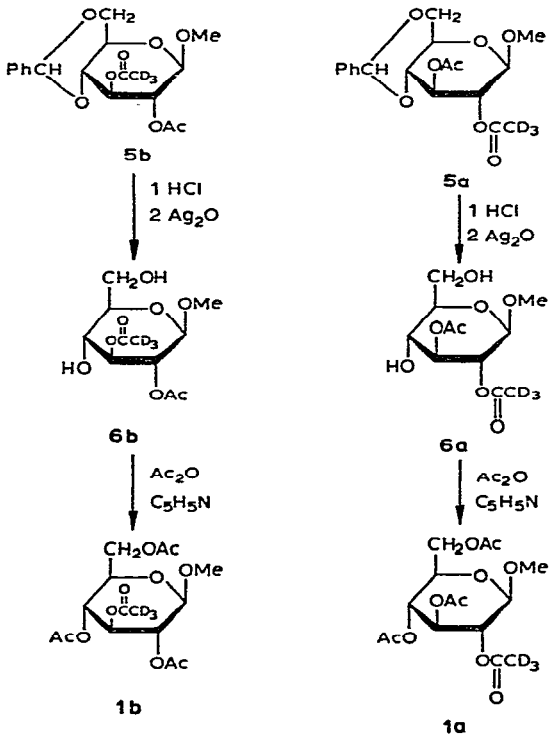


Fig. 2. The acetoxyl-group signals in the p.m.r. spectrum of methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**5**) at 100 MHz in chloroform-*d*, pyridine-d_5, benzene-d_6, and methyl sulfoxide-d_6.



specific differentiation between the acetoxyl-group signals in the parent compound **6** (see Fig. 3 and Table I).

Compounds **6b** and **6a** were acetylated to completion with acetic anhydride in pyridine to give methyl 2,4,6-tri-*O*-acetyl-3-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**1b**) and methyl 3,4,6-tri-*O*-acetyl-2-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**1a**), respectively, whose p.m.r. spectra, showing three acetoxyl-group resonances, allowed the 2- and 3-acetoxyl signals in the spectrum of **1** to be identified (see Fig. 1 and Table I).

An alternative route to compound **1a** was also used. 1,2,3,4,6-Penta-*O*-acetyl-β-D-glucopyranose (**13**) was converted into 3,4,6-tri-*O*-acetyl-2-*O*-(trichloroacetyl)-β-D-glucopyranosyl chloride (Brigl's chloride[16]) (**14**) and the latter was then converted by ethereal ammonia into 3,4,6-tri-*O*-acetyl-D-glucopyranosyl chloride (**15**), obtained as an anomeric mixture[16]. The pure β anomer (**15a**) could be isolated by recrystallization of the anomeric mixture from ethyl acetate, but this step was not found beneficial in the synthetic scheme, as **15a** immediately anomerized on contact with the reagents used in the next step. Furthermore, increased yields of 3,4,6-tri-*O*-acetyl-1,2-anhydro-α-D-glucopyranose (Brigl's anhydride, **16**), which were obtained by passing ammonia gas through a dispersion of the chloride **15** in dry benzene, could be achieved if **15** was not dried before use[17]. Methanolysis of compound **16** by the procedure of Hickinbottom[18] gave crystalline methyl 3,4,6-tri-*O*-acetyl-β-D-gluco-

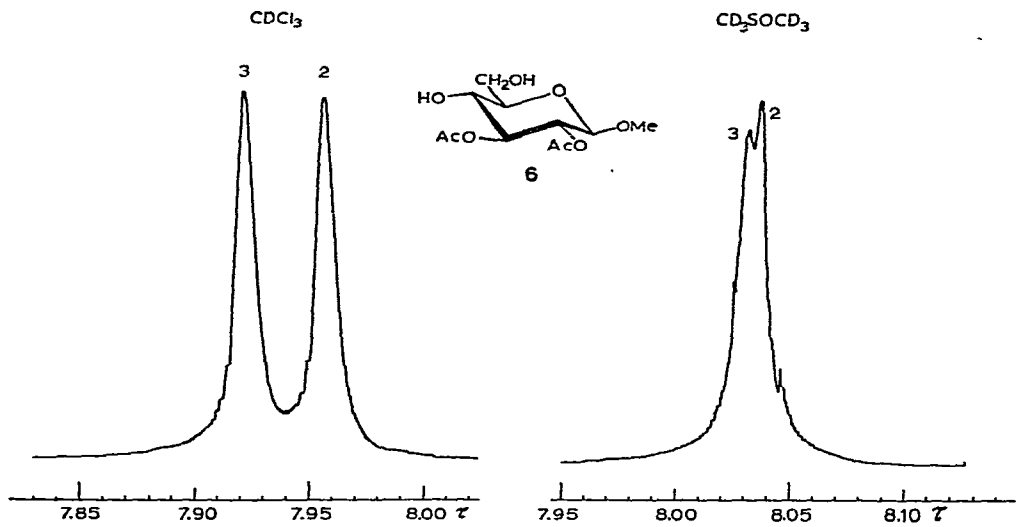
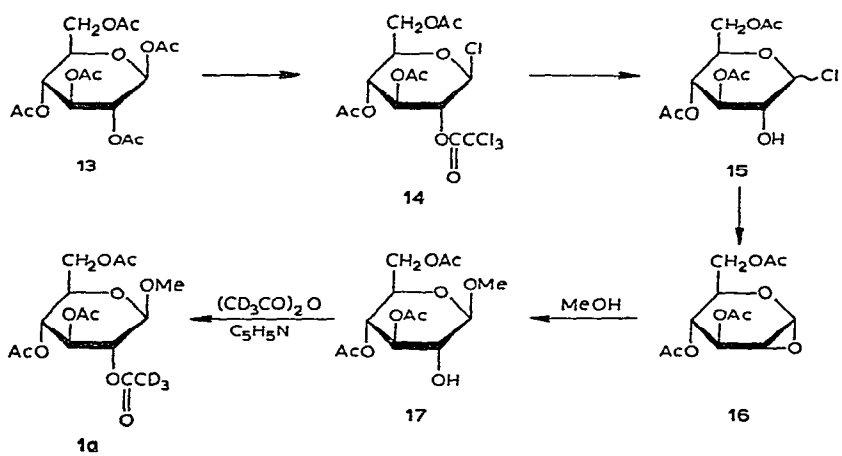


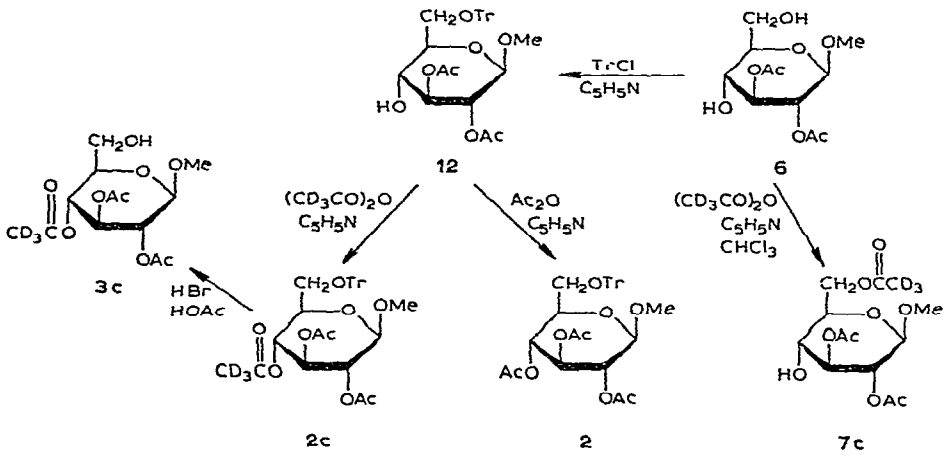
Fig. 3. The acetoxyl-group signals in the p.m.r. spectrum of methyl 2,3-di-*O*-acetyl-β-D-glucopyranoside (**6**) at 100 MHz in chloroform-*d* and methyl sulfoxide-d_6.

pyranoside (**17**). Acetylation of compound **17** with acetic anhydride-d_6 in pyridine gave methyl 3,4,6-tri-*O*-acetyl-2-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**1a**), identical in all respects with **1a** produced from the route **4** → **9** → **5a** → **6a** → **1a**.

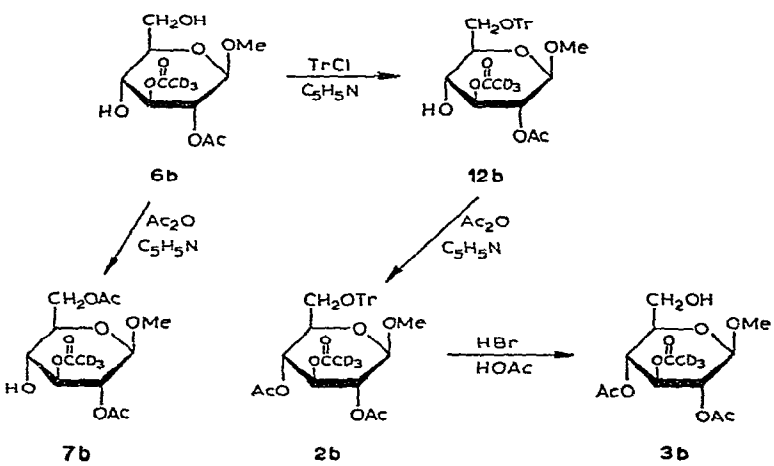


Methyl 2-*O*-acetyl-β-D-glucopyranoside (**10**) was prepared by hydrolysis of the benzylidene acetal **8** with refluxing, 50% aqueous acetic acid. The structure of **10** was verified by spin-decoupling experiments on the ring-proton resonances in its p.m.r. spectrum (see Table II). In a similar way, the known[15] methyl 3-*O*-acetyl-β-D-glucopyranoside (**11**) was prepared, and characterized by p.m.r. spectroscopy (see Tables I–IV).

Methyl 2,3-di-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**12**) was prepared by treating **6** with chlorotriphenylmethane in pyridine by the procedure[19] used for the corresponding compound in the α-series. The structure of **12** was assigned on the basis of (*a*) the procedure used in its synthesis (no acetyl migration anticipated in dry pyridine), and (*b*) the results of spin-decoupling experiments on the ring protons in the p.m.r. spectrum of **12** (see Table III), which verified that the low-field, ring-proton resonances were those of H-3, H-2, and H-1; the H-4 signal resonated at considerably higher field[4], and thus no 3 → 4 acetyl migration had taken place during tritylation.



Treatment of compound **12** with acetic anhydride in pyridine yielded **2**, identical with **2** produced by the previously mentioned procedure, and treatment of **12** with acetic anhydride-d_6 in pyridine yielded methyl 2,3-di-*O*-acetyl-4-*O*-(trideuterioacetyl)-6-*O*-trityl-β-D-glucopyranoside (**2c**). The p.m.r. spectrum of **2c** showed two acetoxyl-



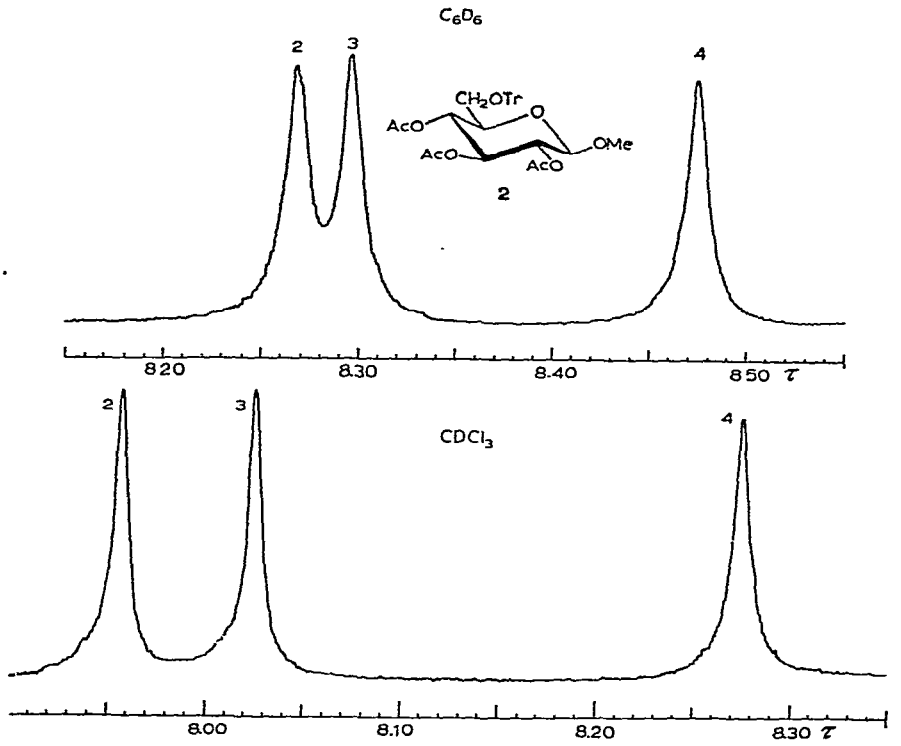


Fig. 4. The acetoxyl-group signals in the p.m.r. spectrum of methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (2) at 100 MHz in chloroform-*d* and benzene-d_6.

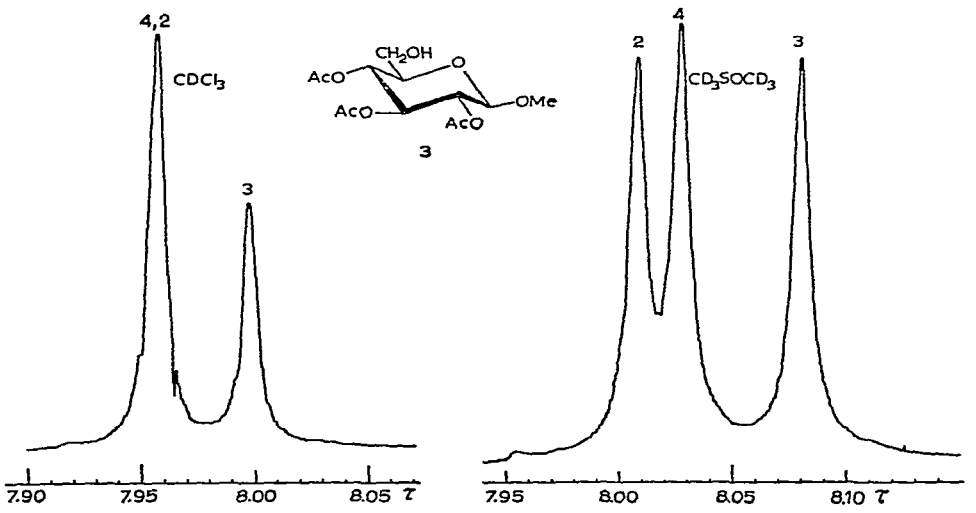


Fig. 5. The acetoxyl-group signals in the p.m.r. spectrum of methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (3) in chloroform-*d* and methyl sulfoxide-d_6.

group signals, and permitted assignment of the 4-acetoxyl group in the spectrum of **2** (see Fig. 4 and Table I).

Detritylation of **2c** by the same procedures used for **2** gave methyl 2,3-di-*O*-acetyl-4-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**3c**). The p.m.r. spectrum of **3c** lacked one of the acetoxyl-group signals observed in the spectrum of **3**, and thus the 4-acetoxyl group signal was assigned (see Fig. 5 and Table I).

When **6** was monoacetylated with acetic anhydride-d_6 in pyridine, in a way similar to that used in the preparation of **7**, methyl 2,3-di-*O*-acetyl-6-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**7c**) was produced. From the p.m.r. spectrum of **7c**, the 6-acetoxyl group signal of **7** was assigned (see Fig. 6 and Table I).

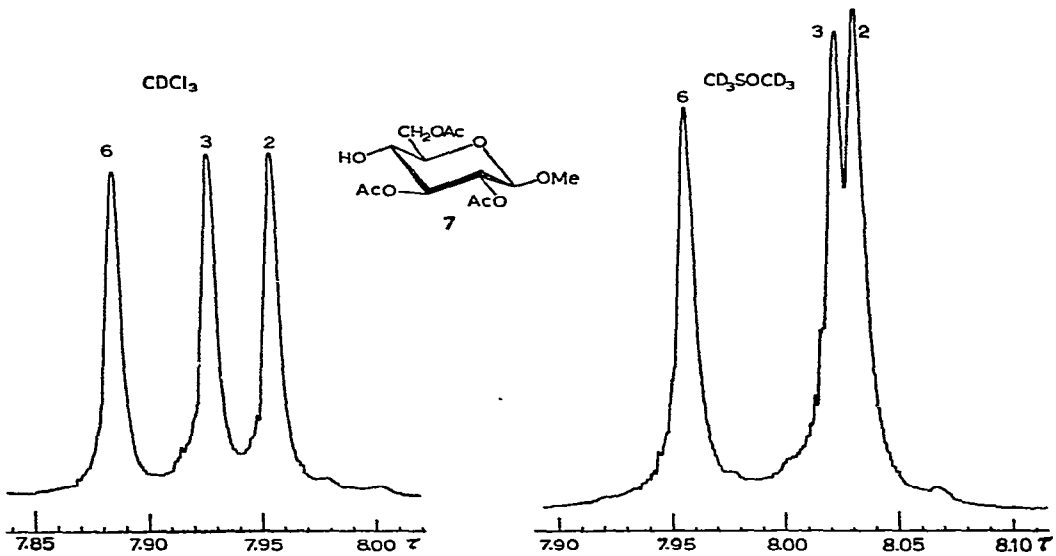
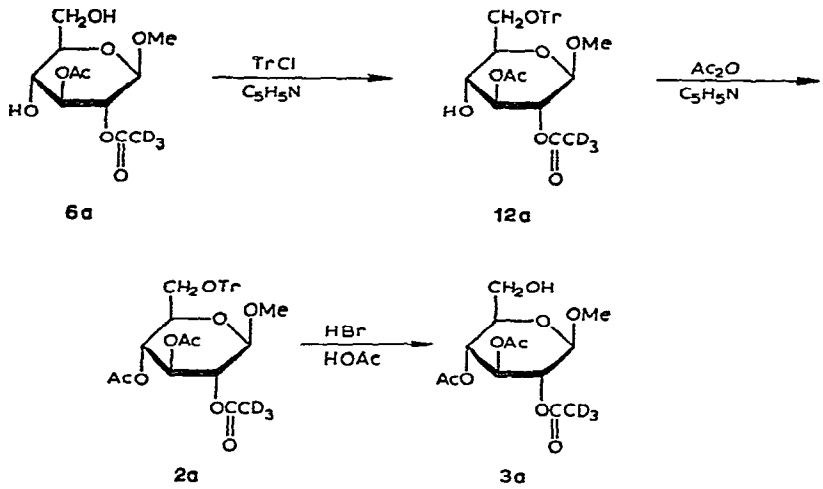


Fig. 6. The acetoxyl-group signals in the p.m.r. spectrum of methyl 2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**7**) at 100 MHz in chloroform-*d* and methyl sulfoxide-d_6.

By procedures analogous to those already mentioned, compound **6b** was tritylated and the ether acetylated to give **2b**, and the latter was then detritylated to give **3b**. Monoacetylation of **6b** yielded **7b**. All of the foregoing compounds had p.m.r. spectra identical tho those of their all-protio analogues, except for the lack of acetoxyl-group signals caused by the presence of deuterioacetyl groups.

Similar procedures were used, and results obtained, by performing the aforementioned steps starting from compound **6a**.

N.m.r. spectrometer instrumentation and operation. — The spectrometer was modified to permit the use of infinitely variable sweep-widths in the HA-modes of operation (see Experimental section). The range of the sweep was controlled by two auxiliary potentiometers. However, there was a slow decrease in the sweep width over relatively short periods of time, because of the increase in the resistance of the



potentiometers caused by heat generated by the current passing through them. Thus, the sweep widths were calibrated before each spectrum was determined. The use of 15-Hz sweep-widths allowed the resolution of acetoxyl-group resonances as close as 0.003 p.p.m. Careful adjustment of homogeneity controls was needed in order to prevent extreme distortion of peak shape with sudden changes in homogeneity. Such distortion is not noticeable at wider sweep-widths. The sweep time used for determination of the acetoxyl-group resonances was 250 sec. The spectra shown in Figs. 1–6 were measured at a sweep width of 50 Hz; the excellent resolution of the instrument still permitted the resolution of all acetoxyl-group resonances, except that the two acetoxyl groups of compound **3** resonating at lower field in chloroform-*d* were not resolved. Thus, careful operation of the spectrometer has allowed resolution and assignment of acetoxyl-group resonances previously unassignable[20] because of their close spacing.

Except for spin-decoupling experiments, all spectra were determined and integrated in the HA field-sweep mode in order to minimize the effect of the phase shift of the frequency-swept oscillator. Spectra were determined with the r.f. fields adjusted at, or just below, saturation.

Solvent and concentration dependence of acetoxyl-group signals. — The appearance of the acetoxyl-group signals of methyl β-D-glucopyranoside tetraacetate (**1**) at 100 MHz in carbon tetrachloride, chloroform-*d*, pyridine-d_5, benzene-d_6, and dimethyl sulfoxide-d_6 are shown in Fig. 1. Although no concentration studies were made on the compounds in this work, previous investigations[1] have shown that there is negligible concentration-dependence of the position of acetoxyl-group resonances in chloroform-*d* solutions for compounds similar to **1**. However, downfield solvent-shifts of up to 0.06 p.p.m. have been reported[21] for solutions in benzene-d_6 when the concentration of sugar acetate was increased from 0.3 to 0.9M. The ranges of the acetoxyl-group resonances of all compounds studied, except for the derivatives **2**, **8**,

and **9**, are typical for those reported for D-glucopyranose acetates in the solvents indicated[1,20,21–24]. In chloroform-*d*, the 2-acetoxyl-group signal of methyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**8**) and the 3-acetoxyl-group signal of methyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**9**) resonate at unusually low field for non-anomeric, secondary acetoxyl groups. The large upfield shift of the 4-acetoxyl-group signal of methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**3**) is typical of molecules in which there is strong interaction between an acetoxyl group and an aromatic nucleus. Shifts of unidentified resonances have been noted previously[1,2,24], and have been specifically identified for compound **2** (this work), its α anomer[25], and 2,3,4,6-tetra-*O*-acetyl-1-*O*-(indol-3-ylacetyl)-β-D-glucopyranose[4(b)] (where the 2-acetoxyl group resonates at τ 8.42 in chloroform-*d*).

The dispersion of the acetoxyl-group resonances of each compound in the various solvents is of interest, as the determination of acetoxyl-group distribution in partially substituted carbohydrates by the methods put forth in this and previous work[1] requires the maximum dispersion of the acetoxyl-group signals to aid in accurate integration of the spectra. In most cases, chloroform-*d* gives the best separation of all signals. The major exceptions to this behavior are methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (**3**), where the 2-OAc and 4-OAc signals are overlapped in chloroform-*d*, but all three resonances are well separated in dimethyl sulfoxide-d_6. The acetoxyl-group signals of compound **5** are better separated in pyridine-d_5 than in chloroform-*d*; this is in direct contrast to the behavior of the corresponding α anomer[1], where the acetoxyl-group signals are barely resolved in pyridine. The preferential, upfield shift (0.1 p.p.m.) shown by the 2-acetoxyl group in the α anomer of compound **1** in pyridine-d_5 and benzene-d_6 is not shown by compound **1** itself.

The ordering in the individual acetoxyl-group signals is also noteworthy. In non-aromatic solvents, all compounds studied in this work that have an acetoxyl group at C-6 show the resonance of this group at lowest field of the set of acetate signals. The acetoxyl-group signal at C-2 is usually at the next highest field, followed by the resonance of the group at C-4 (exception: **3** in chloroform-*d*), and at highest field, the 3-acetoxyl signal. However, when the hydroxyl group at C-4 is unsubstituted (**6**, **7**, and **12**), the 2-acetoxyl group resonates at higher field than the 3-acetoxyl group, in contrast to the corresponding, substituted (acetate or benzylidene) derivatives (**1**, **2**, **3**, and **5**). In chloroform-*d*, the ordering of the resonances for compounds **1** and **5** is the same as that for the corresponding α anomers[1].

The cause of the large, upfield shifts in the resonances of acetoxyl groups exposed to benzene nuclei, either intramolecularly (such as from triphenylmethyl ethers, or aromatic aglycons), or intermolecularly (benzene-d_6 as the solvent), has been studied by Freemantle and Overend[21]. They have postulated a loose, 1:1 complex between the carbonyl group of each acetoxyl group and a suitably oriented benzene ring. The orientation of the benzene ring in such a complex is such that the protons on the acetoxyl group are in the shielding region of the benzene ring[21,26]. This was further demonstrated[22] by studying the acetoxyl-group resonances of 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranose in mixtures of chloroform-*d* and benzene-

d_6. The field position of the 1-acetoxyl resonance was identified by the fact that it is the lowest-field acetoxyl-group signal in pure chloroform-*d*. As the concentration of benzene-d_6 was increased from 0 to 40% (*v/v*) the 1-OAc resonance was shifted upfield by 0.25 p.p.m. As the proportion of benzene-d_6 was further increased, the rate of upfield shift of the resonance decreased: increasing the proportion of benzene-d_6 from 40 to 80% (*v/v*) further increased the field position by only 0.14 p.p.m. A similar effect was noted in the position of the acetoxyl-group resonances for **2**. The presence of the triphenylmethyl group in **2** raises the field position of the 4-acetoxyl group of the corresponding, nontritylated compounds **1** and **3** by ~0.3 p.p.m. in chloroform-*d*. Dissolving **3** in benzene-d_6 raises the field position of 4-acetoxyl-group resonance by only an additional 0.2 p.p.m. However, examination of the spectrum of **1** and **5** in pyridine-d_5 showed that pyridine is only about one-tenth as effective as benzene-d_6 in shifting acetoxyl-group resonances upfield, even though both solvents are aromatic.

TABLE I

CHEMICAL SHIFTS OF ACETOXYL GROUPS AS ASSIGNED FROM SPECIFIC SYNTHESIS[a]

Compound	*Solvent*	*2-OAc*	*3-OAc*	*4-OAc*	*6-OAc*
Methyl 2,3,4-tetra-*O*-acetyl-β-D-glucopyranoside (**1**)	CCl_4	8.011	8.054	8.019	7.962
	$CDCl_3$	7.954	8.001	7.978	7.915
	C_5D_5N	7.970	7.994	7.986	7.974
	C_6D_6	8.262	8.275	8.285	8.272
	CD_3SOCD_3	8.002	8.066	8.018	7.978
Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**2**)	$CDCl_3$	7.956	8.024	8.274	
	C_6D_6	8.267	8.295	8.473	
Methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (**3**)	$CDCl_3$	7.958	7.998	7.955	
	CD_3SOCD_3	8.006	8.079	8.026	
Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**5**)	$CDCl_3$	7.947	7.970		
	C_5D_5N	7.962	8.033		
	C_6D_6	8.222	8.279		
	CD_3SOCD_3	7.992	8.019		
Methyl 2,3-di-*O*-acetyl-β-D-glucopyranoside (**6**)	$CDCl_3$	7.954	7.919		
	CD_3SOCD_3	8.036	8.030		
Methyl 2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**7**)	$CDCl_3$	7.953	7.924		7.886
	CD_3SOCD_3	8.032	8.022		7.959
Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**8**)	$CDCl_3$	7.899			
	CD_3SOCD_3	7.962			
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**9**)	$CDCl_3$		7.890		
	CD_3SOCD_3		7.974		
Methyl 2-*O*-acetyl-β-D-glucopyranoside (**10**)	CD_3SOCD_3	7.986			
Methyl 3-*O*-acetyl-β-D-glucopyranoside (**11**)	CD_3SOCD_3		7.988		
Methyl 2,3-di-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**12**)	$CDCl_3$	7.969	7.957		

[a]Chemical shifts are on the τ scale, for 10% solutions.

TABLE II

CHEMICAL SHIFTS OF PHENYL, BENZYLIC, METHOXYL, HYDROXYL, AND ACETOXYL GROUPS[a]

Compound	*Solvent*	*Phenyl*	*Benzylic*	*Methoxyl*	*Hydroxyl*[b]	*Acetoxyl*
Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (1)	$CDCl_3$			6.48		[c]
	C_5D_5N			6.52		[c]
	C_6D_6			6.78		[c]
	CD_3SOCD_3			6.62		[c]
Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (2)	$CDCl_3$	2.4–2.9		6.42		[c]
	C_6D_6	2.5–2.9		6.68		[c]
Methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (3)	$CDCl_3$			6.51	7.53(6)	[c]
	CD_3SOCD_3			6.58		[c]
Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (5)	$CDCl_3$	2.3–2.7	4.49	6.49		[c]
	C_5D_5N	2.6–2.7	4.24	6.50		[c]
	C_6D_6	2.4–2.9	4.82	6.78		[c]
	CD_3SOCD_3	2.6	4.35	6.59		[c]
Methyl 2,3-di-*O*-acetyl-β-D-glucopyranoside (6)	$CDCl_3$			6.52	7.02(6)	[c]
	CD_3SOCD_3			6.63	4.58(4)	[c]
Methyl 2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (7)	$CDCl_3$			6.52	6.67(4)	[c]
	CD_3SOCD_3			6.63	4.37(4)	[c]
Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (8)	$CDCl_3$	2.4–2.6	4.48	6.54	7.18(3)	[c]
	CD_3SOCD_3	2.4–2.7	4.39	6.62	4.46(3)	[c]
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (9)	$CDCl_3$	2.4–2.7	4.50	6.46	7.10(2)	[c]
	CD_3SOCD_3	2.6	4.41	6.55	4.39(2)	[c]
Methyl 2-*O*-acetyl-β-D-glucopyranoside (10)	CD_3SOCD_3			6.66	4.82 4.92 5.46(6)	[c]
Methyl 3-*O*-acetyl-β-D-glucopyranoside (11)	CD_3SOCD_3			6.60	4.76 4.88 5.46(6)	[c]
Methyl 2,3-di-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (12)	$CDCl_3$	2.4–2.8		6.50	6.96(4)	[c]
3,4,6-Tri-*O*-acetyl-2-*O*-(trichloroacetyl)-β-D-glucopyranosyl chloride (14)	CD_3SOCD_3					7.96 8.00 8.04

(*Table continued on p. 23*)

TABLE II (continued)

Compound	*Solvent*	*Phenyl*	*Benzylic*	*Methoxyl*	*Hydroxyl*[b]	*Acetoxyl*
3,4,6-Tri-*O*-acetyl-D-glucopyranosyl chloride (**15**)	CD_3SOCD_3					8.00 8.02 8.03
1,2-Anhydro-3,4,6-tri-*O*-acetyl-α-D-glucopyranose (**16**)	$CDCl_3$					7.91 7.92 7.97
Methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (**17**)	$CDCl_3$			6.44	7.07(2)	7.92 7.93 7.98

[a]Chemical shifts are on the τ scale, for 10% solutions. [b]The number in parentheses refers to the position of the hydroxyl group. [c]See Table I.

TABLE III

CHEMICAL SHIFTS OF RING PROTONS AND SIDE-CHAIN METHYLENE PROTONS[a]

Compound	*Solvent*	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*
Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**1**)	$CDCl_3$	5.54	4.66	———	5.13	6.28	5.69	5.87
	C_5D_5N	5.21	4.61	4.31	4.56	5.94	5.45	5.65
	C_6D_6	5.82	4.41	———	4.90	6.70	5.73	5.95
	CD_3SOCD_3	4.63	———	———	4.85	5.20	———	5.63
Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**2**)	$CDCl_3$	5.52	4.68	———	5.06	6.42	6.70	6.88
	C_6D_6	5.78	3.94	———	4.21	6.54	———	6.99
Methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (**3**)	$CDCl_3$	5.52	[b]	4.70	[b]	6.15	———	6.77
	CD_3SOCD_3	4.75	———	———	5.43	6.45	———	6.70
Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**5**)	$CDCl_3$	5.49	5.01	4.67	6.29	6.50	5.62	6.20
	C_5D_5N	5.20	4.59	4.23	6.03	6.47	5.55	6.09
	C_6D_6	5.83	4.56	4.76	6.53	6.85	5.94	6.55
	CD_3SOCD_3	5.07–5.33		4.68	[b]	[b]	5.73	[b]
Methyl 2,3-di-*O*-acetyl-β-D-glucopyranoside (**6**)	$CDCl_3$	5.55	5.13	4.93	6.40	———	———	6.70
	CD_3SOCD_3	4.97	———	5.57	6.20	———	———	6.70
Methyl 2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**7**)	$CDCl_3$	5.59	4.84–5.20		6.27–6.57		5.44–5.75	
	CD_3SOCD_3	4.90	———	5.50	6.25–6.70		5.71	5.80
Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**8**)	$CDCl_3$	5.63	5.11	6.17	6.47	6.63	5.67	6.24
	CD_3SOCD_3	5.25–5.55		6.15	———	6.75	5.77	[b]
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**9**)	$CDCl_3$	5.65	[b]	4.77	6.24	[b]	5.66	6.24
	CD_3SOCD_3	5.59	[b]	4.94	6.15–6.75		5.77	[b]
Methyl 2-*O*-acetyl-β-D-glucopyranoside (**10**)	CD_3SOCD_3	5.72	5.50	6.20	———	———	———	6.90
Methyl 3-*O*-acetyl-β-D-glucopyranoside (**11**)	CD_3SOCD_3	5.84	[b]	5.25	6.20	———	———	7.05

(*Table continued on p. 24*)

TABLE III (continued)

Compound	*Solvent*	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*
Methyl 2,3-di-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (12)	$CDCl_3$	5.58	5.05	4.93	6.00	———		6.67
3,4,6-Tri-*O*-acetyl-2-*O*-(trichloroacetyl)-β-D-glucopyranosyl chloride (14)	CD_3SOCD_3	3.90	4.72	4.38	4.83	5.65	———	6.00
3,4,6-Tri-*O*-acetyl-D-glucopyranosyl chloride (15)	CD_3SOCD_3	[b]	[b]	[b]	[b]	[b]	[b]	[b]
1,2-Anhydro-3,4,6-tri-*O*-acetyl-α-D-glucopyranose (16)	$CDCl_3$	4.98	6.99	5.03	4.82	6.03	5.62	5.96
Methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (17)	$CDCl_3$	5.72	6.45	4.78–5.08		6.32	5.70	5.91

[a]Chemical shifts are on the τ scale, for 10% solutions. [b]Chemical shifts not measured, because of second-order effects.

TABLE IV

FIRST-ORDER COUPLING-CONSTANTS FOR THE RING PROTONS[a]

Compound	*Solvent*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{H,OH}$[c]
Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-gluco-pyranoside (1)	$CDCl_3$	7.5	[b]	[b]	9.2	4.5	2.7	12.4	
	C_5D_5N	7.6	9.4	9.4	9.7	4.6	2.5	12.3	
	C_6D_6	7.8	[b]	[b]	9.5	4.5	2.5	12.2	
	CD_3SOCD_3	[b]	[b]	[b]	[b]	[b]	[b]	[b]	
Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-gluco-pyranoside (2)	$CDCl_3$	7.5	[b]	[b]	[b]	2.5	4.5	10.5	
	C_6D_6	[b]	[b]	[b]	[b]	[b]	[b]	[b]	
Methyl 2,3,4-tri-*O*-acetyl-β-D-gluco-pyranoside (3)	$CDCl_3$	7.8	9.5	9.5	[b]	[b]	[b]	[b]	8(6), 5.5(6')
	CD_3SOCD_3	[b]	[b]	[b]	[b]	[b]	[b]	[b]	
Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-gluco-pyranoside (5)	$CDCl_3$	7.6	9.4	9.4	9.4	4.5	10.3	10.3	
	C_5D_5N	7.8	9.5	9.5	9.5	4.2	10.0	10.0	
	C_6D_6	7.5	9.2	9.2	9.2	4.5	10.1	10.1	
	CD_3SOCD_3	[b]	9.5	9.5	[b]	[b]	[b]	[b]	
Methyl 2,3-di-*O*-acetyl-β-D-gluco-pyranoside (6)	$CDCl_3$	7.5	9.5	9.5	[b]	[b]	[b]	[b]	6.5(6,6')
	CD_3SOCD_3	[b]	[b]	[b]	[b]	[b]	[b]	[b]	5.5(4), 8.5(6,6')
Methyl 2,3,6-tri-*O*-acetyl-β-D-gluco-pyranoside (7)	$CDCl_3$	[b]	[b]	[b]	[b]	[b]	[b]	[b]	4.0(4)
	CD_3SOCD_3	[b]	8.5	8.5	[b]	2.5	5.2	12.0	5.5(4)
Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-gluco-pyranoside (8)	$CDCl_3$	7.8	9.3	9.1	8.5	4.7	9.0	11.0	3.3(3)
	CD_3SOCD_3	7.8	8.1	[b]	[b]	3.7	[b]	10.0	5.2(3)

(*Table continued on p. 25*)

TABLE IV (continued)

Compound	*Solvent*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{H,OH}$[c]
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (9)	$CDCl_3$	7.8	9.1	9.1	9.1	4.0	9.4	10.5	3.0(2)
	CD_3SOCD_3	7.8	9.1	9.1	[b]	3.7	[b]	9.0	5.7(2)
Methyl 2-*O*-acetyl-β-D-glucopyranoside (10)	CD_3SOCD_3	8.0	8.0	[b]	[b]	[b]	[b]	[b]	6.5(6,6')
Methyl 3-*O*-acetyl-β-D-glucopyranoside (11)	CD_3SOCD_3	7.5	9.0	9.0	[b]	[b]	[b]	[b]	6.1(6,6')
Methyl 2,3-di-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (12)	$CDCl_3$	7.2	10.2	10.2	[b]	[b]	[b]	[b]	4.5(4)
3,4,6-Tri-*O*-acetyl-2-*O*-(trichloroacetyl)-β-D-glucopyranosyl chloride (14)	CD_3SOCD_3	8.5	9.5	9.5	[b]	[b]	[b]	[b]	
3,4,6-Tri-*O*-acetyl-D-glucopyranosyl chloride (15)	CD_3SOCD_3	[b]	[b]	[b]	[b]	[b]	[b]	[b]	
1,2-Anhydro-3,4,6-tri-*O*-acetyl-α-D-glucopyranose (16)	$CDCl_3$	2.4	0	8.5	8.7	4.2	2.5	12.7	
Methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (17)	$CDCl_3$	8.0	[b]	[b]	[b]	4.5	3.0	12.0	3.5(2)

[a]Coupling constants are given in Hz. [b]Coupling constant not measured, because of second-order effects. [c]The number in parentheses refers to the position of the hydroxyl group.

EXPERIMENTAL

General methods. — Unless otherwise noted, solutions were evaporated below 50° under diminished pressure. Melting points were determined with a Thomas–Hoover "Unimelt" apparatus (Arthur H. Thomas Co., Philadelphia, Pa.) and are corrected. Infrared spectra were recorded with a Perkin–Elmer Model 457 infrared spectrophotometer. Optical rotations were determined in a 1-dm cell with a Perkin–Elmer Model 141 photoelectric polarimeter. N.m.r. spectra were recorded with a Varian HA-100 n.m.r. spectrometer operating at 100 MHz in the HA field-sweep mode. The spectrometer was modified by incorporating a Wavetek Model 114 voltage-controlled oscillator (Wavetek, 9045 Balboa Ave., San Diego, California 92123), driven by an RCA Model WP-700A constant-voltage DC power supply, whose output was attenuated by the recorder-sweep potentiometer in place of the

sweep-frequency oscillator in the Varian V-4354A internal-reference, n.m.r. stabilized controller (see Publication No. 87-140-404, Varian Associates, Palo Alto, California). This modification allows the use of infinitely variable sweep-widths in the HA modes of operation. Spin-decoupling experiments were performed with the HA-100 instrument operating in the frequency-sweep mode. Unless otherwise specified, spectra were recorded at a sample concentration of 10% (w/v). The solutions also contained 5% (w/v) of tetramethylsilane ($\tau = 10.000$) as the internal standard and to provide a lock signal [spectra recorded in dimethyl sulfoxide-d_6 contained only enough tetramethylsilane (~2%, w/v) to saturate the solution]. Chemical shifts are given on the τ scale, and were taken from the chart recording and/or were measured electronically by using the "Diff 1" position of the previously mentioned V-4354A unit in conjunction with a Varian V-4315 Frequency Counter. Chemical shifts of the acetoxyl resonances were determined at a sweep width of 15.0 Hz. The values reported are an average of at least three scans, and are considered to be accurate to within ± 0.003 p.p.m. Unless otherwise specified, the temperature in the probe was approximately 25°. The recorded pseudo-first-order coupling-constants are the measured peak-spacings. P.m.r. data are recorded in Tables I–IV. Elemental analyses were performed by W. N. Rond. X-Ray powder diffraction data give interplanar spacings, Å, for CuKα radiation. The camera diameter was 114.59 mm. Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities. T.l.c. was performed with Silica Gel G (E. Merck, Darmstadt, Germany), activated at 120°, as the adsorbent, and sulfuric acid as the indicator. Column chromatography was performed with Silica Gel No. 7734 (Merck) as the adsorbent, with 1 g of the mixture to be separated per 30 g of adsorbent. The components were eluted with the solvent mixtures (v/v) indicated. Petroleum ether refers to the fraction boiling from 30–60°. Pyridine was distilled from barium oxide before use.

Acetylation reaction-mixtures were processed by evaporation of the solvent, and then toluene and carbon tetrachloride were added to, and evaporated from, the residue.

Specifically trideuterioacetylated products all gave X-ray powder diffraction patterns indistinguishable from those of the parent protioacetates; i.r. spectra (CCl_4 or $CHCl_3$) were likewise identical, except for very minor differences attributable to the CD_3 groups.

*Preparation of methyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside* (**1**). — Methyl β-D-glucopyranoside (5.0 g, 26 mmoles) in dry pyridine (30 ml) was treated with acetic anhydride (20 ml, 210 mmoles). The mixture was shaken until all of the solids had dissolved; the solution was kept for 15 h at room temperature, and then evaporated. The crystalline residue was recrystallized from ethanol–water to give 8.23 g (90%) of **1**; m.p. 104.5° (lit.[27] m.p. 104–105°); $\nu_{max}^{CCl_4}$ 1762, 1450, 1430, 1270, 1250, 1225, 1170, 1080, 1045, and 905 cm^{-1}; X-ray powder diffraction data: 10.04 s (2,2), 8.75 m, 7.25 m, 6.41 s (2,2), 5.90 s (3), 5.40 vw, 5.12 w, 4.41 m, 3.86 vs (1), 3.53 m, 3.72 vw, 3.08 vw, and 2.88 w.

Preparation of methyl 2,3,4-tri-O-acetyl-6-O-trityl-β-D-glucopyranoside (**2**). — The standard method for preparing this compound[28] yielded a product that was grossly impure in each of numerous attempts at its preparation. Therefore, two alternative procedures were devised.

A. Methyl β-D-glucopyranoside (5.00 g, 26 mmoles) and chlorotriphenylmethane (7.18 g, 26 mmoles) were dissolved in pyridine (40 ml). The system was protected from atmospheric moisture with a Drierite trap, and the mixture was heated for 2 h on a steam bath. After brief cooling, acetic anhydride (11 ml, 0.12 mole) was added with stirring, and the solution was kept for 18 h, and then evaporated to dryness. The residue was dissolved in carbon tetrachloride, the suspension filtered, and the filtrate passed through a column of silica gel for purification. Elution with 3:2 petroleum ether–ether gave 5.72 g (40%) of **2**, m.p. 123–126° (lit.[28] m.p. 126°); $\nu_{max}^{CCl_4}$ 1760, 1448, 1350, 1245, 1218, 1055, 1032, 704, 695, and 632 cm^{-1}.

B. Methyl 2,3-di-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**12**; 2.00 g, 3.84 mmoles) was dissolved in pyridine (10 ml), and acetic anhydride (0.57 ml, 6.0 mmoles) was added. After 18 h, the mixture was treated with ice–water, and the solid product filtered off. Recrystallization from methanol yielded 1.92 g (89%) of **2**, m.p. 123–126°.

Preparation of methyl 2,3,4-tri-O-acetyl-β-D-glucopyranoside (**3**). — Compound **2** (10.0 g, 18 mmoles) was detritylated, according to the procedure[1] used for the corresponding α anomer, to give 3.99 g (73%) of **3**, m.p. 134–136° (lit.[10] m.p. 134°); $\nu_{max}^{CCl_4}$ 1778, 1375, 1285, 1260, 1235, 1212, 1102, 1052, 998, and 820 cm^{-1}; X-ray powder diffraction data: 9.11 vs (1), 7.82 vw, 6.55 m (3), 5.82 vw, 5.15 vw, 4.67 vw, 4.46 s (2), 4.11 vw, 3.75 w, 3.63 w, 3.39 vw, 3.25 w, 3.06 w, 2.92 vw, and 2.79 m.

Methyl 2,3,4-tri-O-acetyl-6-O-(trideuterioacetyl)-β-D-glucopyranoside (**1d**). — Compound **3** (1.00 g, 3.12 mmoles) was dissolved in benzene (7 ml), and acetic anhydride-d_6 (0.37 ml, 4.68 mmoles) was added. After thorough mixing, pyridine (5 ml) was added, and the mixture was kept for 15 h at ~25°, and then evaporated. The crystalline residue was recrystallized from ethanol–water to yield 0.96 g (84%) of **1d**, m.p. 103–104.5°. The p.m.r. spectra of **1d** in carbon tetrachloride, chloroform-*d*, pyridine-d_5, benzene-d_6, and dimethyl sulfoxide-d_6 were identical with those of **1**, except for the lack of 3-proton singlets at τ 7.962, 7.915, 7.974, 8.272, and 7.978, respectively.

Preparation of methyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranoside[11] (**5**). — Methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**4**; 10.0 g, 36 mmoles) was dissolved in pyridine (70 ml), and acetic anhydride (10 ml, 0.11 mole) was added. After 18 h at ~25°, the mixture was poured into ice–water, and the solid product was filtered off, washed with water, and recrystallized from ethanol–water; yield 11.7 g (93%); m.p. 170.5–172° (lit.[11] m.p. 171–172°); $\nu_{max}^{CCl_4}$ 1758, 1368, 1238, 1221, 1103, 1065, 1044, 1031, 995, and 695 cm^{-1}; X-ray powder diffraction data: 12.80 vw, 11.04 m, 10.60 s (3), 7.76 w, 6.41 vw, 6.02 vw, 5.57 w, 5.27 w, 4.98 s (2,2), 4.77 s (2,2), 4.62 m, 4.23 vs (1), 3.95 w, 3.85 w, 3.72 w, and 3.54 w.

Preparation of methyl 2,3-di-O-acetyl-β-D-glucopyranoside (**6**). — This com-

pound was prepared according to the procedure of Levene and Raymond[12], and crystallized according to the procedure of Bredereck[13]. Compound **5** (50 g) yielded 28 g (73%) of **6**, m.p. 109–111° (lit.[13] m.p. 109–111°). T.l.c. (1:1 ether–acetone) showed two spots moving more slowly than the product. Column chromatography on silica gel, with 1:1 ether–acetone as the eluant, gave 24 g of pure **6**, m.p. 113–113.5°; $\nu_{max}^{CHCl_3}$ 3600, 3470, 2935, 1755, 1449, 1428, 1377, 1248, 1225, 1192, 1082, 1053, 1037, 1002, and 903 cm^{-1}; X-ray powder diffraction data: 10.52 s (2,2), 8.26 s (3,3), 7.19 m, 6.70 m, 6.15 vs (1), 5.64 m, 5.34 vw, 4.98 w, 4.77 w, 4.39 s (2,2), 4.17 w, 3.95 m, 3.81 s (3,3), and 3.57 vw.

*Preparation of methyl 2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**7**). — This compound was prepared in 41% yield from the 2,3-diacetate **6** according to the procedure of Levene and Raymond[12]. Column chromatography on silica gel with 3:2 petroleum ether–ether as the eluant yielded **7**; m.p. 113–114° (lit.[12] m.p. 113–114°); R_F 0.4 (3:2 petroleum ether–ether); $\nu_{max}^{CHCl_3}$ 1745, 1448, 1374, 1232, 1168, 1090, 1048, and 990 cm^{-1}; X-ray powder diffraction data: 13.18 vw, 7.75 w, 7.08 s (3,3), 6.60 m, 5.82 s (3,3), 5.18 w, 4.92 w, 4.48 s (1), 4.21 w, 3.98 s (2), 3.67 vw, 3.53 m, and 3.30 w.

*Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(trideuterioacetyl)-β-*D*-glucopyranoside* (**1c**). — Compound **7** (1.00 g, 3.12 mmoles) was dissolved in pyridine (5 ml), and treated with acetic anhydride-d_6 (0.37 ml, 4.65 mmoles). After 18 h, the mixture was evaporated, and the crystalline residue was recrystallized from ethanol–water to yield 0.71 g (62%) of product, m.p. 104–104.5°. The p.m.r. spectra of **1c** in carbon tetrachloride, chloroform-*d*, pyridine-d_5, benzene-d_6, and dimethyl sulfoxide-d_6 were identical with those of **1**, except for the lack of 3-proton singlets at τ 8.019, 7.978, 7.986, 8.285, and 8.018, respectively.

*Monoacetylation of methyl 4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**4**). — Compound **4** (10.0 g, 34.4 mmoles) was acetylated with 1.25 molar equivalents of acetic anhydride according to the procedure of Jeanloz and Jeanloz[14]. After 24 h, the mixture was evaporated, the crystalline residue was dissolved in chloroform, and the solution applied to a column of silica gel. Elution with 7:3 petroleum ether–ether yielded 4.90 g of methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**5**), m.p. 170–171°. Elution with 1:1 petroleum ether–ether yielded 2.75 g of methyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**8**), m.p. 174.5–175° (lit.[15] m.p. 174–177°). Elution with 7:3 ether–petroleum ether yielded 2.40 g of methyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**9**), m.p. 154–156° (lit.[15] m.p. 162–163°); elution with methanol yielded 4.40 g of methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**4**), m.p. 200–201°.

*Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(trideuterioacetyl)-β-*D*-glucopyranoside* (**5b**). — Compound **8** (1.00 g, 3.08 mmoles) was dissolved in pyridine (7 ml), and acetic anhydride-d_6 (0.36 ml, 4.63 mmoles) was added. After 18 h, the mixture was treated with ice–water until precipitation of the product was complete, the suspension was filtered, and the solid was recrystallized from ethanol–water, to give **5b**; yield 1.00 g (89%), m.p. 171–172°. The p.m.r. spectra of **5b** in chloroform-*d*, pyridine-d_5,

benzene-d_6, and dimethyl sulfoxide-d_6 were identical with those of **5**, except for the lack of 3-proton singlets at τ 7.970, 8.033, 8.279, and 8.019, respectively.

Methyl 3-O-acetyl-4,6-O-benzylidene-2-O-(trideuterioacetyl)-β-D-glucopyranoside (**5a**). — This compound was prepared by the same method as that used for **5b**. From methyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**9**; 1.00 g, 3.08 mmoles), acetic anhydride-d_6 (0.36 ml, 4.63 mmoles), and pyridine (7 ml), there was obtained 1.00 g (89%) of compound **5a**, m.p. 171–172°. The n.m.r. spectra of **5a** in chloroform-*d*, pyridine-d_5, benzene-d_6, and dimethyl sulfoxide-d_6 were identical with those of **5**, except for the lack of 3-proton singlets at τ 7.947, 7.962, 8.222, and 7.992, respectively. The i.r. spectrum (CCl_4) was indistinguishable from that of **5**.

Methyl 2-O-acetyl-β-D-glucopyranoside (**10**). — Compound **8** (1.82 g, 5.61 mmoles) was hydrolyzed for 10 min in boiling 50% acetic acid under reflux. The solution was evaporated to a syrup at 60°, and then toluene was added to, and evaporated from, the residue; this was chromatographed on silica gel with 1:1 acetone–ether as the eluant, to yield 0.62 g (47%) of **10**, m.p. 141–143°, $[\alpha]_D^{25}$ −34.1° (*c* 1, 95% ethanol); R_F 0.3 (acetone–ether); ν_{max}^{KBr} 3508, 3440, 3260, 1728, 1405, 1395, 1378, 1265, 1139, 1092, 1066, 1035, 1004, and 640 cm^{-1}; X-ray powder diffraction data: 9.60 vs (1), 6.32 w, 6.04 vw, 5.21 vw, 4.37 s (2,2), 4.22 w, 3.81 vw, 3.70 s (2,2), 3.47 w, 3.33 w, 3.17 vw, 3.03 vw, 2.62 vw, and 2.54 vw.

Anal. Calc. for $C_9H_{16}O_7$: C, 45.75; H, 6.81. Found: C, 46.04; H, 6.77.

Preparation of methyl 3-O-acetyl-β-D-glucopyranoside (**11**). — Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**9**; 1.00 g, 3.08 mmoles) was hydrolyzed in boiling, aqueous acetic acid under reflux according to the procedure of Tulloch and Hill[15], to give **11**; yield 0.291 g (40%), m.p. 134–136° (lit.[15] m.p. 137–139°).

Methyl 2-O-acetyl-3-O-(trideuterioacetyl)-β-D-glucopyranoside (**6b**). — Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**5b**; 1.64 g, 4.44 mmoles) was hydrolyzed, by the same procedure as that used for **6**, to give **6b**; yield 0.851 g (67%), m.p. 110–111°. The p.m.r. spectra of **6b** in chloroform-*d* and dimethyl sulfoxide-d_6 were identical to those of **6**, except for the lack of 3-proton singlets at τ 7.919 and 8.030, respectively.

Methyl 3-O-acetyl-2-O-(trideuterioacetyl)-β-D-glucopyranoside (**6a**). — Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**5a**; 0.500 g, 1.36 mmoles) was hydrolyzed by the same procedure as for **6**, to give **6a**; yield 0.202 g (53%), m.p. 107–109°. The p.m.r. spectra of **6a** in chloroform-*d* and dimethyl sulfoxide-d_6 were identical to those of **6**, except for the lack of 3-proton singlets at τ 7.955 and 8.036, respectively.

Methyl 2,3-di-O-acetyl-6-O-trityl-β-D-glucopyranoside (**12**). — Methyl 2,3-di-*O*-acetyl-β-D-glucopyranoside (**6**; 4.00 g, 14.4 mmoles) and chlorotriphenylmethane (4.00 g, 14.4 mmoles) were dissolved in pyridine (40 ml). The mixture was protected from atmospheric moisture with a Drierite trap, kept for 4 days at room temperature, and then poured into ice–water, and the product extracted into dichloromethane; the extract was evaporated to dryness, and toluene and then carbon tetrachloride

were added to, and evaporated from, the residue. T.l.c. of the residue (3:1 ether–petroleum ether) indicated the presence of four components. Column chromatography of the mixture with the t.l.c. solvent-sytem yielded 5.70 g (76%) of an amorphous solid, $[\alpha]_D^{25}$ −35.6° (*c* 1, chloroform); R_F 0.6 (3:1 ether–petroleum ether); $\nu_{max}^{CHCl_3}$ 1753, 1490, 1449, 1374, 1245, 1165, 1058, 703, and 631 cm^{-1}.

Anal. Calc. for $C_{30}H_{32}O_8$: C, 69.21; H, 6.20. Found: C, 69.22; H, 6.40.

*Methyl 2,3-di-*O*-acetyl-4-*O*-(trideuterioacetyl)-6-*O*-trityl-β-*D*-glucopyranoside* (**2c**). — Compound **12** (2.00 g, 3.84 mmoles) was dissolved in pyridine (10 ml), acetic anhydride-d_6 (0.45 ml, 5.76 mmoles) was added, and the mixture was kept for 18 h and then poured into ice–water. The solid product was filtered off, and recrystallized from methanol, to give **2c**; yield 1.92 g (87%) m.p. 123–126°. The p.m.r. spectra of **2c** in chloroform-*d* and benzene-d_6 were identical with those of **2**, except for the lack of 3-proton singlets at τ 8.28 and 8.473, respectively.

*Methyl 2,3-di-*O*-acetyl-4-*O*-(trideuterioacetyl)-β-*D*-glucopyranoside* (**3c**). — Compound **2c** (3.00 g, 5.29 mmoles) was detritylated, by the procedure used to detritylate compound **3**, to give **3c**; yield 0.71 g (41%), m.p. 134–136°. The p.m.r. spectra of **3c** in chloroform-*d* and dimethyl sulfoxide-d_6 were identical with those of **3**, except for the lack of 3-proton singlets at τ 7.955 and 8.026, respectively.

*Methyl 2,3-di-*O*-acetyl-6-*O*-(trideuterioacetyl)-β-*D*-glucopyranoside* (**7c**). — Methyl 2,3-di-*O*-acetyl-β-D-glucopyranoside (**6**; 1.00 g, 3.60 mmoles) was dissolved in pyridine (3 ml), the solution was cooled to 0°, and a solution of acetic anhydride-d_6 (0.31 ml, 4.0 mmoles) in dichloromethane was added dropwise during 30 min. After 24 h, the solution was evaporated, and the residue was chromatographed on a column of silica gel with 3:2 petroleum ether–ether as the eluant; yield 0.510 g (44%), m.p. 112–113.5°. The p.m.r. spectra of **7c** in chloroform-*d* and dimethyl sulfoxide-d_6 were identical with those of **7**, except for the lack of 3-proton singlets at τ 7.886 and 7.959, respectively.

*Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(trideuterioacetyl)-β-*D*-glucopyranoside* (**1b**). — Methyl 2-*O*-acetyl-3-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**6b**; 0.165 g, 0.6 mmole) was dissolved in pyridine (2 ml), acetic anhydride (0.18 ml, 1.8 mmoles) was added, and the solution was kept for 18 h and then evaporated. The crystalline residue was recrystallized from ethanol–water to yield 0.210 g (96%) of **1b**, m.p. 103–104°. The p.m.r. spectra of **1b** in carbon tetrachloride, chloroform-*d*, pyridine-d_5, benzene-d_6, and dimethyl sulfoxide-d_6, were identical with those of **1**, except for the lack of 3-proton singlets at τ 8.054, 8.001, 7.994, 8.275, and 8.066, respectively.

*Methyl 2,4-di-*O*-acetyl-3-*O*-(trideuterioacetyl)-6-*O*-trityl-β-*D*-glucopyrano: ide* (**2b**). — Methyl 2-*O*-acetyl-3-*O*-(trideuterioacetyl)-6-*O*-trityl-β-D-glucopyranoside (**12b**; 1.00 g, 1.94 mmoles) was dissolved in pyridine (12 ml), acetic anhydride (0.28 ml, 3.0 mmoles) was added, the solution was kept for 18 h, and ice–water was added. The precipitate was filtered off, dried under vacuum, and recrystallized from methanol, yielding 0.84 g (77%) of **2b**, m.p. 126–127°. The p.m.r. spectra of **2b** in chloroform-*d* and benzene-d_6 were identical with those of **2**, except for the lack of 3-proton singlets at τ 8.024 and 8.295, respectively.

Methyl 2,4-di-O-acetyl-3-O-(trideuterioacetyl)-β-D-glucopyranoside (**3b**). — To a solution of compound **2b** (0.395 g, 0.7 mmole) in acetic acid (2.24 ml), cooled in an ice bath, was added acetic acid saturated with hydrogen bromide at 0° (0.25 ml), and the mixture was shaken for 1 min. The precipitated bromotriphenylmethane was filtered off, and washed with acetic acid and water. The filtrate and washings were combined, extracted with chloroform, the extract evaporated, and toluene was repeatedly added to, and evaporated from, the residue, which was crystallized from ether; yield 0.137 g (60%), m.p. 134–135°. The p.m.r. spectra of **3b** in chloroform-*d* and dimethyl sulfoxide-d_6 were identical with those of **3**, except for the lack of 3-proton singlets at τ 7.998 and 8.079, respectively. The i.r. spectrum (CCl_4) and the X-ray powder diffraction pattern were indistinguishable from those of **3**.

Methyl 2,6-di-O-acetyl-3-O-(trideuterioacetyl)-β-D-glucopyranoside (**7b**). — To a solution of methyl 2-*O*-acetyl-3-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**6b**; 0.109 g, 0.38 mmole) in pyridine (0.3 ml), cooled in an ice bath, was added, dropwise, a solution of acetic anhydride (0.040 ml, 0.42 mmole) in dichloromethane (0.3 ml), and the resulting solution was kept for 24 h, and then evaporated. The residue was chromatographed on silica gel with 3:2 petroleum ether–ether as the eluant, to yield 0.055 g (45%) of **7b**, m.p. 107–109°. Recrystallization from ether–petroleum ether yielded pure **7b**, m.p. 113–114°. The p.m.r. spectra of **7b** in chloroform-*d* and dimethyl sulfoxide-d_6 were identical with those of **7**, except for the lack of 3-proton singlets at τ 7.924 and 8.022.

Methyl 2-O-acetyl-3-O-(trideuterioacetyl)-6-O-trityl-β-D-glucopyranoside (**12b**). — To a solution of methyl 2-*O*-acetyl-3-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**6b**; 1.00 g, 3.55 mmoles) in pyridine (10 ml) was added chlorotriphenylmethane (1.00 g, 3.55 mmoles); the mixture was kept for 4 days at ~25°, poured into ice–water, and the product extracted into chloroform. The extract was evaporated, and the residue was chromatographed on silica gel with 3:2 petroleum ether–ether as the eluant, to yield 1.34 g (71%) of **12b**.

Methyl 3,4,6-tri-O-acetyl-2-O-(trideuterioacetyl)-β-D-glucopyranoside (**1a**). — To a solution of methyl 3-*O*-acetyl-2-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**6a**; 0.130 g, 464 μmoles) in pyridine (3 ml) was added acetic anhydride (0.18 ml, 1.8 mmole); the mixture was kept for 18 h, and evaporated to a crystalline residue, which was recrystallized from ethanol–water, to yield 0.065 g (41%) of **1a**, m.p. 103–104°. This material was identical with **1a** synthesized from methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (**17**).

Methyl 3,4-di-O-acetyl-2-O-(trideuterioacetyl)-6-O-trityl-β-D-glucopyranoside (**2a**). — To a solution of methyl 3-*O*-acetyl-2-*O*-(trideuterioacetyl)-6-*O*-trityl-β-D-glucopyranoside (**12a**; 0.200 g, 0.39 mmole) in pyridine (3 ml) was added acetic anhydride (0.06 ml, 0.6 mmole), the solution was kept for 18 h, ice–water was added, and the precipitated product was filtered off, and dried *in vacuo*, affording 0.158 g (73%) of **2a**, m.p. 123–125°. The p.m.r. spectra of **2a** in chloroform-*d* and benzene-d_6 were identical with those of **2**, except for the lack of 3-proton singlets at τ 7.956 and 8.267, respectively.

Methyl 3,4-di-O-acetyl-2-O-(trideuterioacetyl)-β-D-glucopyranoside (**3a**). — To a solution of compound **2a** (0.100 g, 175 μmoles) in acetic acid (0.32 ml), cooled in an ice bath, was added acetic acid saturated with hydrogen bromide at 0° (32 μl), and the mixture was shaken for 1 min. The precipitated bromotriphenylmethane was filtered off, and washed with acetic acid and water. The filtrate and washings were combined, extracted with chloroform, and the extract evaporated; toluene was repeatedly added to, and evaporated from, the residue. The resulting syrup was dissolved in a little chloroform, and purified by passage through a column of silica gel with 1:1 petroleum ether–ether as the eluant. The product (**3a**; yield 28 mg, 52%) still contained a small proportion of **7a** [the 3,6-diacetate 2-(trideuterioacetate) arising from 4→6 migration]. However, after making allowances for the peaks due to **7a**, the p.m.r. spectra of **3a** in chloroform-*d* and dimethyl sulfoxide-d_6 were identical with those of **3**, except for the lack of 3-proton singlets at τ 7.958 and 8.006, respectively.

Methyl 3,6-di-O-acetyl-2-O-(trideuterioacetyl)-β-D-glucopyranoside (**7a**). — To a solution of methyl 3-*O*-acetyl-2-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**6a**; 0.885 g, 3.14 mmoles) in pyridine (2.5 ml) was added, dropwise, a solution of acetic anhydride (0.33 ml, 3.5 mmoles) in dichloromethane (1.5 ml), and the resulting solution was kept for 18 h; the mixture was then processed in the same way as for compound **7b**; yield 0.47 g (47%) of **7a**, m.p. 111–113°. The p.m.r. spectra of **7a** in chloroform-*d* and dimethyl sulfoxide-d_6 were identical with those of **7**, except for the lack of 3-proton singlets at τ 7.953 and 8.032, respectively.

Methyl 3-O-acetyl-2-O-(trideuterioacetyl)-6-O-trityl-β-D-glucopyranoside (**12a**). — To a solution of methyl 3-*O*-acetyl-2-*O*-(trideuterioacetyl)-β-D-glucopyranoside (**6a**; 0.200 g, 0.71 mmole) in pyridine (2 ml) was added chlorotriphenylmethane (0.200 g, 0.71 mmole), and the mixture was kept for 4 days, and then processed in the same way as for compound **12b**, to yield 0.257 g (70%) of **12a**. The p.m.r. spectrum of **12a** was identical with that of **12**, except for the lack of a 3-proton singlet at τ 7.969.

Preparation of 3,4,6-tri-O-acetyl-2-O-(trichloroacetyl)-β-D-glucopyranosyl chloride (Brigl's chloride) (**14**). — 1,2,3,4,6-Penta-*O*-acetyl-β-D-glucopyranose (**13**) was fused with phosphorus pentachloride according to the method of Brigl[16]. Recrystallization of the product from ether–petroleum ether gave **14**, m.p. 139–140° (lit.[16] m.p. 138–142°) in 6–30% yields. The higher yields were obtained when the phosphorus pentachloride was resublimed immediately before use.

Preparation of 3,4,6-tri-O-acetyl-D-glucopyranosyl chloride (**15**). — Compound **14** was treated with ammoniacal ether at 0° according to the procedure of Brigl[16], to give a 90% yield of **15** as an anomeric mixture, dec. 137–139° (lit.[16] dec. 137–139°). Recrystallization from 10 parts of ethyl acetate gave a 50% overall yield of the pure β anomer (**15a**), dec. 152° (lit.[16] dec. 158°).

Preparation of 3,4,6-tri-O-acetyl-1,2-anhydro-α-D-glucopyranose (Brigl's anhydride) (**16**). — The anomeric mixture of 3,4,6-tri-*O*-acetyl-D-glucopyranosyl chlorides (**15**) was suspended in dry benzene, and ammonia gas was bubbled through slowly, by the Purves and Gladding modification[17] of the original procedure of

Brigl[29]. Yields of product, recrystallized from ether–petroleum ether, ranged from 0–55% for **16** having m.p. 54–56° (lit.[29] m.p. 57–58°).

*Preparation of methyl 3,4,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**17**). — This compound was prepared in 23% yield by methanolysis of the anhydride **16** according to the procedure of Hickinbottom[18]; m.p. 95–97° (lit.[18] m.p. 96–98°).

*Methyl 3,4,6-tri-*O*-acetyl-2-*O*-(trideuterioacetyl)-β-*D*-glucopyranoside* (**1a**). — To a solution of compound **17** (0.150 g, 0.47 mmole) in pyridine (2 ml) was added acetic anhydride-d_6 (0.06 ml, 0.71 mmole); after 18 h, the mixture was evaporated, and the crystalline residue was recrystallized from ethanol–water, to yield 0.101 g (59%) of **1a**, m.p. 103–104.5°. The p.m.r. spectra of **1a** in carbon tetrachloride, chloroform-*d*, pyridine-d_5, benzene-d_6, and dimethyl sulfoxide-d_6 were identical with those of **1**, except for the lack of 3-proton singlets at τ 8.011, 7.954, 7.970, 8.262, and 8.002, respectively.

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