815. *Nitrogen-containing Carbohydrate Derivatives. Part I. Methyl 4,6-O-Benzylidene-3-deoxy-3-phenylazo-α-D-glucoside.**

By R. D. GUTHRIE and (in part) LEROY F. JOHNSON.

The product obtained on reaction of aqueous phenylhydrazine with periodate-oxidised methyl 4,6-*O*-benzylidene-α-D-glucoside has been shown to be that named in the title. Its proton magnetic resonance spectrum has been studied in some detail. This reaction, whose mechanism is discussed, provides a new route to derivatives of 3-amino-3-deoxy-D-glucose (kanosamine).

REACTION of aqueous phenylhydrazine with periodate-oxidised methyl 4,6-*O*-benzylidene-α-D-glucoside [in whose aqueous solutions an equilibrium exists between the dialdehyde (III) and the hemialdal (IV) [1,2]] gave a yellow product (*A*) which, on limited evidence, was assigned structure (I) or (II).[1] These structures were based on elementary analysis ($C_{20}H_{22}O_5N_2$) and formation of a monobenzoate; neither substance (*A*) nor its benzoate gave a formazan (showing the absence of the CH=N·NHPh group [3]). The benzoate had no NH absorption in its infrared spectrum. It was difficult to account for the colour of substance (*A*).

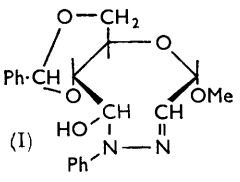
Preparation of mono-*O*-acetyl and mono-*O*-methyl derivatives of substance (*A*) has now confirmed the presence of one hydroxyl group; neither derivative gave a formazan, or had NH absorption in its infrared spectrum. Molecular-weight determinations showed that substance (*A*) was a monomer.

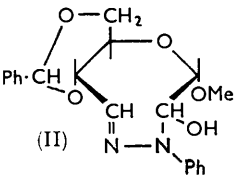
Reduction of substance (*A*) in ethanol in the presence of Raney nickel gave aniline and a colourless substance (*B*); the latter on complete acetylation yielded methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside 2-acetate (X). Substance (*B*) therefore has structure (VIII), and this was confirmed by the following evidence: (i) oxidation with aqueous sodium metaperiodate gave a crystalline product identical with periodate-oxidised methyl 4,6-*O*-benzylidene-α-D-glucoside (IV), one molecular proportion of periodate being reduced; (ii) acetylation with acetic anhydride–pyridine for 5 minutes gave methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside (IX); this was converted into its toluene-*p*-sulphonyl ester (XI) which gave only a trace of sodium toluene-*p*-sulphonate when heated with sodium iodide in acetone at 100°; (iii) hydrolysis of compound (IX) gave

* This work has been briefly reported: Guthrie, *Proc. Chem. Soc.*, 1960, 387.

[1] Guthrie and Honeyman, *J.*, 1959, 2441.
[2] Guthrie, Honeyman, and Parsons, *J.*, 1959, 2449.
[3] Mester, *Adv. Carbohydrate Chem.*, 1958, **13**, 105.

an amorphous product, presumably methyl 3-acetamido-3-deoxy-α-D-glucoside, which did not reduce sodium metaperiodate and on acetylation gave methyl 3-acetamido-3-deoxy-α-D-glucoside 2,4,6-triacetate (XII).


(I)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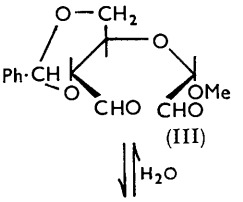
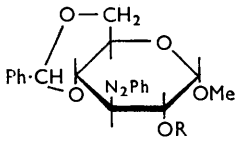
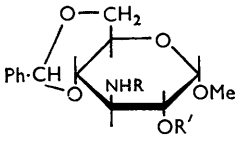
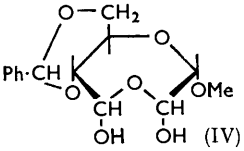
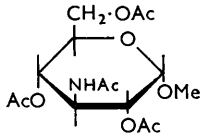
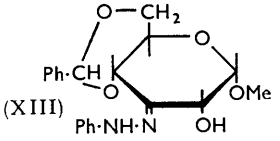

(III)


(V) R = H
(VI) R = Me
(VII) R = Ac


(VIII) R = R′ = H
(IX) R = Ac; R′ = H
(X) R = R′ = Ac
(XI) R = Ac; R′ = p-Me·C$_6$H$_4$·SO$_2$


(IV)


(XII)


(XIII)

These reactions show that cyclisation occurs during the formation of substance (*A*), and in conjunction with the facts previously obtained enable its structure to be assigned as methyl 4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucoside (V) or the corresponding alloside.

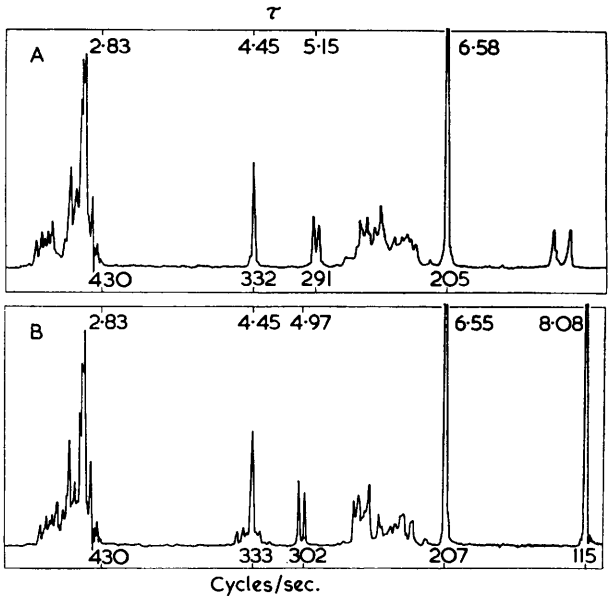
High-resolution proton magnetic resonance studies (with L. F. J.) support this structure and show that substance (*A*) has the *gluco*-configuration. The spectrum of substance (*A*), shown in Fig. 1A, is at first sight consistent with structure (I). However, integration of the spectrum showed that the group of signals above τ ~2·75 due to aromatic and other protons on doubly bound carbon atoms [4] corresponded to ten protons. Since there were two phenyl groups in the molecule there could be no other double bonds present, as in (I) and (II). The signals at τ 4·45 and 5·15 were assigned to the acetal-protons (that is –O–C**H**–O–) of the benzylidene group and at $C_{(1)}$, respectively. These signals occurred on the low-field side of the group of signals between τ 5·40 and 6·50, assigned to protons on aliphatic carbon atoms also bearing oxygen atoms.[4] The acetal-carbon atom is bonded to two oxygen atoms, and hence the acetal-proton should be less shielded and the signals should be at lower field. The signal at 4·45 is not split because there is no adjacent proton-bearing atom. The signal at 5·15 is a doublet because of spin–spin coupling with the proton on $C_{(2)}$; the splitting of about 4 cycles/sec. is characteristic of the equatorial-axial relation of the two protons.[4,5] That this splitting was not due to spin–spin coupling with a proton on a doubly bound carbon atom, as in (I), was shown by using the double-resonance technique; this showed that the proton splitting the signal from the anomeric proton was one resonating at τ ~5·50, whose own signal was buried in the cluster between τ 5·40 and 6·50, due to aliphatic protons (excluding the acetal protons and those of the methoxyl group [4] which gave the signal at τ 6·58). The signal from the hydroxyl proton

[4] Jackman, " Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, London, 1959.
[5] Lemieux, Kullnig, Bernstein, and Schneider, *J. Amer. Chem. Soc.*, 1958, **80**, 6098.

was to the right of the methoxyl signal; this assignment was verified by the addition of a trace of hydrochloric acid to the solution, which caused proton exchange and eliminated the splitting due to spin–spin coupling.

Fig. 1B shows the spectrum of the acetate of substance (*A*). This had similar features to the previous one, including the signal from ten aromatic protons; the signal from the CH_3 protons of the acetate group [4] was at τ 8·08. The feature of interest in this spectrum was the quadruplet splitting of the signal due to the proton on $C_{(2)}$, which bears the acetate group. This signal, originally at τ about 5·50, has been characteristically shifted [4] by ~1·05 p.p.m. downfield to τ 4·45, but unfortunately one of the four peaks lay under the signal from the benzylidene acetal-proton. The smaller splitting of about 4 cycles/sec. was characteristic [4,5] of an equatorial-axial arrangement of protons, which in fact occurs on $C_{(1)}$ and $C_{(2)}$; this splitting is also seen in the signal from the anomeric proton at τ 4·97,

FIG. 1. *Proton magnetic resonance spectra of* (A) *methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-*phenylazo*-α-D-*glucoside* (V), *and* (B) *the acetate of* (V) [*compound* (VII)].



and was the same splitting as occurred in the spectrum of the unacetylated compound (*A*). The larger splitting of about 10 cycles/sec., therefore due to the coupling of the protons on $C_{(2)}$ and $C_{(3)}$, was characteristic [4,5] of two axial protons, showing that the 3-phenylazo-group occupied the equatorial position. Hence substance (*A*) and its acetate had the *gluco*-configuration [compounds (V) and (VII)].

The spectrum of methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside 2-acetate (X) was also studied for comparison. This showed the same main features as the above spectra, and the following assignments were made: τ 4·47, 5·09, 6·56, 7·90, and 8·05 to the benzylidene proton, the anomeric proton, methoxyl, the *N*-acetyl, and the *O*-acetyl, respectively. The signals from the $C_{(2)}$ proton appeared as an unmasked quadruplet at τ 4·90 with ~4 and 10 cycles/sec. The anomeric proton's signal again showed a splitting of ~3 cycles/sec. These results for this compound of known structure bear out the assignments made for compounds (I) and (IV) above. It is believed that this is the first use of high-resolution proton magnetic resonance techniques for a structural study of comparatively complex carbohydrate molecules, other than the polyacetates.[5] The spin–spin splitting of the signal from the anomeric proton in methyl glycosides (at τ ~5·10) appears to be of potential use in assigning their configuration and conformation.

The phenylazo-group in compound (V) and its derivatives is further supported by comparison of the ultraviolet spectra of these compounds with that reported for phenylazomethane [6] (see Table). Infrared spectral studies on phenylhydrazones and methylphenylhydrazones showed that these compounds had a very strong absorption at about 1600 cm.$^{-1}$; no such band was present in the spectra of compound (V) or its derivatives.

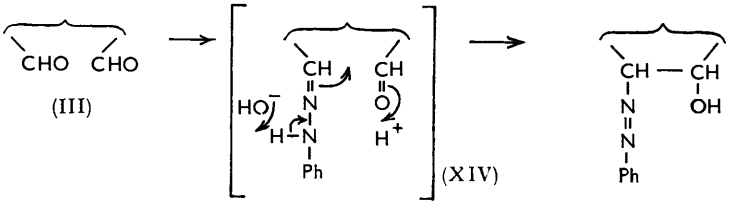
TABLE 1. *Ultraviolet maxima (for ethanol solutions).*

	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
Me 4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucoside (V)[a]	266	10,280	390	257
Me 4,6,-*O*-benzylidene-3-deoxy-2-*O*-methyl-3-phenylazo-α-D-glucoside (VI)	266	10,930	393	227
Me 4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucoside 2-acetate (VII)	267	10,590	392	248
Phenylazomethane [6, b]	265	9950	392	145

[a] These values are thought to be more accurate than those previously reported.[1] Values estimated from graph.

It was not possible to use the configuration of the reduced product (VIII) as evidence for the *gluco*-configuration in (*A*) because phenylazoalkanes can rearrange to the corresponding phenylhydrazones: [7] $R_2CH{\cdot}N{=}NPh \longrightarrow R_2C{=}N{\cdot}NHPh$. As yet, the non-occurrence of this rearrangement under the reduction conditions has not been proved. If it did occur, the 3-oxophenylhydrazone (XIII) would be an intermediate from both glucoside and alloside phenylazo-derivatives and would also give rise to 3-amino-3-deoxy-derivatives of both glycosides. Paper chromatography of the crude reduction mixture showed two faint ninhydrin-positive spots in addition to the main one due to compound (VIII); one of these may be methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-alloside. The main component (VIII) was isolated in 90% yield from this reduction mixture.

Cyclisation to the phenylazo-compound (V) is believed to occur by the mechanism shown, in which the initially formed dialdehyde monophenylhydrazone (XIV) rearranges. This mechanism is supported by the non-formation of a similar arylazo-derivative from the dialdehyde (III) and *p*-nitrophenylhydrazine, even when one molecular proportion of



base is used.[8] Here, the *p*-nitro-group will lessen the availability of electrons necessary for the rearrangement. The configuration of compound (V) is the conformationally expected one, both phenylazo- and hydroxy- groups assuming equatorial positions. The mechanism as postulated does not preclude the formation of both 2- and 3-phenylazo-derivatives of allose, altrose, glucose, or mannose. Chromatography of the crude product has detected, in addition to the 3-phenylazoglucose derivative (V), about 10% of a yellow compound which is being further investigated. Comparison of the reduction products from crude (*A*) and from compound (V) by paper chromatography show the presence of an additional faint ninhydrin-positive spot in the former; the amount of 2-phenylazo-compounds formed in the initial reaction must therefore be very small, if any. No reason is yet proposed for the preferential attack on what appears from molecular models to be the more sterically hindered aldehyde group.

[6] Grammaticakis, *Compt. rend.*, 1947, **225**, 684.
[7] Rodd, " Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1954, Vol. IIIA, p. 371.
[8] Colbran, Guthrie, and Parsons, *J.*, 1960, 3532.

The cyclisation of the dialdehyde monophenylhydrazone (XIV) must be reversible since compound (V) was hydrolysed in the presence of phenylhydrazine to glyoxal bisphenylhydrazone;[1] this reaction presumably has (XIV) as an intermediate. Compound (V) also reduced Fehling's solution.[1]

There are several examples[9] of reactions of aqueous phenylhydrazine with periodate-oxidised carbohydrates in which one molecule of base has reacted with each " dialdehyde unit " to give yellow or orange products; some of these may well contain the –CH(OH)·CH(N:N·Ph)– group.

The above reaction, whose general applicability is being examined, provides a new route to derivatives of 3-amino-3-deoxy-D-glucose (kanosamine), a component of the antibiotic kanamycin.[10] It is the second synthesis of amino-sugars by ring-closure of a periodate-oxidised carbohydrate derivative, the first being the Fischer cyclisation with nitromethane.[11]

Experimental

Alumina was of type H, 100—200 mesh, supplied by Peter Spence Ltd. The identity of compounds was proved where necessary by mixed m. p. and by infrared spectrometry. All new compounds had infrared spectra consistent with the assigned structures. Rotations are for chloroform solution, unless otherwise stated.

Reaction of Phenylhydrazine with 7,9-*dihydroxy*-6α-*methoxy*-2-*phenyl*-trans-m-*dioxano*[5,4-*e*][1,4]*dioxepan* (IV) *Hydrate*.—This reaction was carried out as described previously,[1] except that the crude product (85%) was purified by recrystallisation from a small volume of butan-1-ol, to give *methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-*phenylazo*-α-D-*glucoside* (V) (60%), m. p. 182—183°, $[\alpha]_D^{20}$ +8·6° (*c* 1·81) [Found: C, 64·8; H, 6·0; N, 7·1%; *M*, 343 (ebullioscopic in benzene), 367 (*X*-ray method). $C_{20}H_{22}N_2O_5$ requires C, 64·9; H, 6·0; N, 7·6%; *M*, 370]. It reduced Fehling's solution and did not form a formazan; ultraviolet maxima are shown in Table 1.

Chromatography of the crude product (440 mg.) on alumina gave, with benzene–chloroform (5 : 1) as eluent, a yellow oil (2 mg.) and the 3-phenylazo-3-deoxyglucose derivative (V) (310 mg.); chloroform eluted a yellow-orange solid (43 mg.).

Hydrolysis of the product, as described previously[1] but with a reaction time of 6 hr., gave glyoxal bisphenylhydrazone (74%), m. p. 162—164° (it is regretted that an incorrect reaction time was given in ref. 1).

Benzoylation of compound (V), as described previously,[1] gave *methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-*phenylazo*-α-D-*glucoside* 2-*benzoate*, m. p. 123—124°, $[\alpha]_D^{21}$ +158° (*c* 1·2) (Found: C, 68·8; H, 5·7; N, 5·6; Bz, 23·3, 22·1. $C_{27}H_{26}N_2O_6$ requires C, 68·3; H, 5·5; N, 5·9; Bz, 22·2%). The compound did not yield a formazan.

Methylation of compound (V) with Purdie's reagents gave *methyl* 4,6-O-*benzylidene*-3-*deoxy*-2-O-*methyl*-3-*phenylazo*-α-D-*glucoside* (VI), m. p. 123—124°, $[\alpha]_D^{16}$ +72·8° (*c* 1·2) (Found: C, 66·1; H, 6·3; N, 7·2; OMe, 15·9. $C_{21}H_{24}N_2O_5$ requires C, 65·6; H, 6·3; N, 7·3; OMe, 16·1%). The product did not form a formazan; ultraviolet maxima are shown in Table 1.

Acetylation of compound (V) with acetic anhydride–pyridine gave, after two recrystallisations from ethanol, *methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-*phenylazo*-α-D-*glucoside* 2-*acetate* (VII), m. p. 165—166°, $[\alpha]_D^{20}$ +80° (*c* 1·8) (Found: C, 64·5; H, 6·0; N, 6·6; Ac, 11·0. $C_{22}H_{24}N_2O_6$ requires C, 64·1; H, 5·9; N, 6·8; Ac, 10·4%). The product did not give a formazan; ultraviolet maxima are shown in Table 1.

Reduction and Derivatives of the Reduction Product.—Hydrogenation of methyl 4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucoside (V) was carried out in ethanol solution, in the presence of Raney nickel, for 8 hr. at 80—100°/40—60 atm. The colourless solution was evaporated to a gel, which when recrystallised from light petroleum–ethanol or –chloroform, gave *methyl* 3-*amino*-4,6-O-*benzylidene*-3-*deoxy*-α-D-*glucoside* (VIII) (70%), m. p. 184·5—186° (decomp.; sublimed), $[\alpha]_D^{20}$ +102° (*c* 1·5) (Found: C, 59·6; H, 7·0; N, 4·8. $C_{14}H_{19}NO_5$ requires C, 59·8; H, 6·8; N, 5·0%).

[9] Barry and Mitchell, *J.*, 1954, 4020; Mester, *J. Amer. Chem. Soc.*, 1955, **77**, 5452; Mester and Moczar, *Chem. and Ind.*, 1957, 761, 764.

[10] Cron, Evans, Palermiti, Whitehead, Hooper, Chu, and Lemieux, *J. Amer. Chem. Soc.*, 1958, **80**, 4741; Ogawa, Ito, Inoue, and Kondo, *J. Antibiotics*, 1958, **11**, *A*, 166.

[11] Baer and Fischer, *Proc. Nat. Acad. Sci. U.S.A.*, 1958, **44**, 991, and subsequent papers.

The initial gel was washed with benzene, and the washings were combined with the ethanol distillate; this solution was boiled under reflux with 1-chloro-2,4-dinitrobenzene and sodium acetate for 30 min. The yellow solution was concentrated to a small volume, poured into water, and extracted with ether, and the dried extract evaporated. The resulting red solid was recrystallised from ethanol and then from acetic acid, to give 2,4-dinitrodiphenylamine, m. p. 155—157°.

Preliminary experiments have shown that the same reduction can be carried out in 30 min., with platinum oxide as catalyst at 1 atm. and room temperature.

Paper chromatography of the reduction solution on Whatman No. 1 paper with butan-1-ol–ethanol–water (40 : 19 : 11) followed by spraying with ninhydrin gave an intense spot of R_F 0·60, with faint spots of R_F 0·13 and 0·44. Similar chromatography of the solution from reduction of crude compound (*A*) showed the above spots plus an additional faint spot of R_F 0·24.

Methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside (VIII) reduced one mol. of sodium periodate and gave the hemialdal (IV) hydrate [1] (76%), m. p. 136—139°, further characterised as its dibenzoate.[1]

The 3-amino-3-deoxyglucoside (VIII) (1·15 g.) with 1-chloro-2,4-dinitrobenzene (0·95 g.) and sodium acetate (2·0 g.) in ethanol (20 ml.) were boiled under reflux for 1 hr. The mixture was poured into water (*ca.* 100 ml.), the yellow suspension extracted with chloroform, and the extract dried (Na_2SO_4). Evaporation gave a yellow solid which, after two recrystallisations from aqueous ethanol, was *methyl* 4,6-O-*benzylidene*-3-(2,4-*dinitrophenylamino*)-3-*deoxy*-α-D-*glucoside* (0·58 g.), m. p. 188—190°, $[\alpha]_D^{16}$ +89·6° (*c* 1·0) (Found: C, 53·9; H, 4·8; N, 9·3. $C_{20}H_{21}N_3O_9$ requires C, 53·7; H, 4·7; N, 9·4%).

When the 3-amino-3-deoxyglucoside (VIII) was treated with acetic anhydride–pyridine for 5 min. at room temperature, the mixture solidified; mixing it with water gave a white solid which, after two recrystallisations from a large volume of ethanol, gave *methyl* 3-*acetamido*-4,6-O-*benzylidene*-3-*deoxy*-α-D-*glucoside* (IX) (70%), m. p. 286—288° (decomp.; sublimed) (Found: C, 59·3; H, 6·4; N, 4·5. $C_{16}H_{21}NO_6$ requires C, 59·4; H, 6·6; N, 4·3%). Fractional crystallisation of the solid obtained on acetylation of the reduction product obtained from crude phenylazo-compound (*A*) gave 90% of the 3-acetamido-3-deoxy-compound (IX).

Acetylation of either compound (VIII) or the above compound (IX) with the above reagent containing 5% of dimethylformamide for 48 hr. at room temperature and with stirring gave, after the usual working up and two recrystallisations from ethanol, methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside 2-acetate (X) (62%), m. p. 274—276° (decomp.; sublimed), $[\alpha]_D^{20}$ +42° (*c* 1·0) (Found: C, 59·2; H, 6·5; N, 3·7. Calc. for $C_{18}H_{23}NO_7$: C, 59·2; H, 6·3; N, 3·8%). Peat and Wiggins [12] report m. p. 270°, $[\alpha]_D$ +44·6°; Foster *et al.*[13], with whose sample the above compound was compared, report m. p. 271°, $[\alpha]_D$ +44°.

Toluene-*p*-sulphonyl chloride (0·5 g.) in pyridine (2·5 ml.) was added to a suspension of the 3-acetamido-3-deoxy-derivative (IX) (0·75 g.) in pyridine (20 ml.), and the whole stirred at room temperature until dissolution was complete (*ca.* 36 hr.). A few drops of water were added to destroy the excess of acid chloride and after 15 min. the mixture was poured into ice-water. The resulting white solid was collected and recrystallised from aqueous ethanol (0·47 g.). Two further recrystallisations gave *methyl* 3-*acetamido*-4,6-O-*benzylidene*-3-*deoxy*-α-D-*glucoside* 2-*toluene*-p-*sulphonate* (XI), m. p. 202—203° (Found: C, 57·9; H, 5·7; N, 3·0. $C_{23}H_{27}NO_8S$ requires C, 57·9; H, 5·7; N, 2·9%).

The toluene-*p*-sulphonate (XI) (0·2 g.) was heated in a sealed tube for 14 hr. at 100° with acetone (3 ml.) containing sodium iodide (0·25 g.). Only a trace of sodium toluene-*p*-sulphonate was formed.

Methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside (IX) (1·5 g.) was hydrolysed with 50% acetic acid (75 ml.) for 30 min. at 100°. The solution was evaporated *in vacuo*, the last traces being evaporated by co-distillation, first with water and then with ethanol, leaving a colourless amorphous solid which was presumed to be methyl 3-acetamido-3-deoxy-α-D-glucoside [Ogawa *et al.*[14] report m. p. 176—178°, $[\alpha]_D^{15}$ +158° (in water) for this compound]. An excess of sodium metaperiodate was added to an aqueous solution of the amorphous solid; no rotational changes occurred during 27 hr. Reaction of the amorphous solid with acetic

[12] Peat and Wiggins, *J.*, 1938, 1810.
[13] Foster, Stacey, and Vardheim, *Acta Chem. Scand.*, 1958, **12**, 1605.
[14] Ogawa, Ito, Kondo, and Inoue, *Bull. Agric. Chem. Soc. Japan*, 1959, **23**, 289.

anhydride–pyridine gave, after two recrystallisations from a small volume of ethanol, colourless prisms of methyl 3-acetamido-3-deoxy-α-D-glucoside 2,4,6-triacetate (XII), m. p. 176—178°, $[\alpha]_D^{20}$ +109 (*c* 1·0). Peat and Wiggins report [12] m. p. 178°, $[\alpha]_D^{15}$ +102°; Ogawa *et al.*[14] report $[\alpha]_D^{28}$ +107° and +109°.

Proton Magnetic Resonance Spectra.—These were measured with a Varian HR-60 spectrometer, operating at 60 megacycles per second, with tetramethylsilane as internal reference. The frequency separations were measured by the audio sideband superposition technique; the precision of measurement was 1 cycle/sec. The spectra were for ~10% solutions in deuterochloroform at 33°. The intensities of the signals were measured by means of a Varian V3521 NMR integrator. The ratio-frequency power was not varied since its amount was far below any level which would produce saturation effects.

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