α-D-*xylo*-hex-5-enofuranose (XIV) crystallized. The mixture was cooled in ice for 1 hr, and compound XIV was separated by filtration. The filtrate was concentrated and the above process of crystallization was repeated with 50 ml of chloroform and 350 ml of petroleum ether. The filtrate after separation of a second batch of compound XIV was concentrated to a pale yellow syrup (20 g). The syrup was then chromatographed over a neutral alumina (100 g) column prepared in benzene. Elution with benzene gave 3,5-anhydro-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-β-L-idofuranose (XIII, 15 g, 33%) which was chromatographically homogeneous by tlc. Compound XIII was then detritylated by stirring at 25° for 24 hr its solution in 35 ml of ethanol, 75 ml of acetic acid, and 18 ml of water. The reaction mixture was cooled to −15° and filtered after 12 hr to remove triphenylmethanol. The filtrate was concentrated to a syrup which was dissolved in 200 ml of chloroform. The chloroform solution was washed with aqueous sodium bicarbonate followed by water. The chloroform solution was dried over anhydrous sodium sulfate and was filtered, and the filtrate was concentrated to a pale yellow syrup (7 g) which was chromatographed over silica gel using eluent C. The proper effluents were collected and concentrated, whereupon compound VIII spontaneously crystallized, mp 50° (yield 5.6 g, 28% of theory).

5-Azido-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (IX).—To a solution of compound VIII (1 g) in 95 ml of DMF was added a slurry of 5 g of sodium azide in 5 ml of water. The mixture was refluxed gently for 7 days. The reaction mixture was cooled, 300 ml of xylene was added, and the mixture was filtered. The filtrate was then concentrated to dryness. The residue was triturated with 100 ml of xylene, and the mixture was filtered. The filtrate was concentrated to a reddish orange syrup (800 mg) which was chromatographed over silica gel using eluent D. The proper fractions (faster running component) were collected and concentrated to a syrup (670 mg) which was again chromatographed over silica gel using eluent E. The fractions containing the faster running component were collected and concentrated whereupon it crystallized spontaneously (150 mg). After recrystallization from ether–hexane, needles were obtained, mp 56°. It was identified as 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose X (lit.[20] mp 56–57°). The fractions which contained the slower running spots containing the azide (IX) were combined and concentrated to a pale yellow syrup (470 mg, 40% of theory) $[\alpha]^{25}D$ −10.55° (*c* 2.18, $CHCl_3$), which showed a strong absorption at 2150 cm^{-1} (azide) in the infrared spectrum. In a similar reaction, compound VIII was refluxed with sodium azide in 2-methoxyethanol–water (19:1) for 24 hr. On isolation in the same way as above a 50% yield of 6-azido-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (XI), mp 108°, was obtained. No change in melting point occurred in a mixture with an authentic sample.[17]

5-Amino-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (VI) and 5-Acetamido-3,6-di-*O*-acetyl-5-deoxy-α-D-glucofuranose (VII).—Compound IX (470 mg) in 25 ml of absolute ethanol containing about 2 g of Raney nickel was hydrogenated at 25° for 2 hr. The reaction mixture, worked up in the usual way, gave a pale yellow syrupy compound VI which had the same R_f in irrigant B as compound VI prepared by the earlier method. It was recrystallized from ethyl acetate, mp 125–126°. Acetylation of VI by the usual procedure gave 5-acetamido-3,6-di-*O*-acetyl-5-deoxy-α-D-glucofuranose (VII) (450 mg) as needles, mp 145–146°. The infrared and nmr spectra were identical with those of compound VII prepared by the method described above. The mixture melting point was undepressed.

Registry No.—II, 16958-26-2; VI, 16958-27-3; VII, 16958-28-4.

(20) H. Ohle, L. von Vargha, and H. Erlbach, *Chem. Ber.*, **61**, 1211 (1928).

Selective Cleavage of the Glycosidic Bond in Acetylated 2-Acetamido-2-deoxy-β-D-glucopyranosides by a Chemical Transglycosylation

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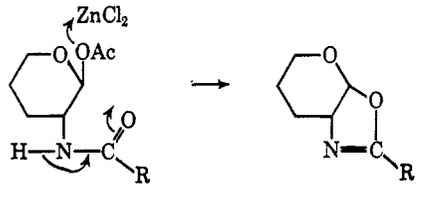
The anchimeric assistance afforded by acylamino groups to nucleophilic displacements on neighboring carbon atoms suggests that derivatives of 2-acylamino-2-deoxyaldoses with a *trans* arrangement of the groups at C-1–C-2 may be more susceptible than other aldose derivatives to the action of certain cleaving reagents. Since it has been shown that acetic anhydride–zinc chloride converts 2-acylamino-2-deoxyaldoses into oxazolines, and, since such oxazolines undergo reaction with alcohols to give glycosides, the behavior of a number of acetylated aldose derivatives with zinc chloride–benzyl alcohol has been investigated. In each case, the reaction has been conducted in butyl acetate solution at 125° for varying times. Under these conditions, 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (1) is rapidly converted into benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**3**) in high yield; its anomer, **4**, reacts much more slowly, giving **3** and a small amount of the anomeric benzyl glycoside **5**. The *trans* glycoside methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**6**) is readily cleaved to a mixture of **3** and **5** but its *cis* anomer **7** is not attacked. Likewise, methyl β-D-glucopyranoside tetraacetate (**8**) is stable under these reaction conditions. The glycosidic bond in the β-linked disaccharide derivative, chitobiose octaacetate (**9**), is slowly attacked by the reagent to give (after reacetylation) **3** and **5** but, under the conditions employed, compounds which appear to be the acetylated derivatives of the anomeric benzyl glycosides of the disaccharide (α and β **11**) were also obtained. The potential utility of this apparently selective solvolysis for the investigation of the structures of oligosaccharides is pointed out.

A recent investigation in this laboratory[2] has shown that the acetylation of 2-acylamino-2-deoxyaldoses with acetic anhydride and anhydrous zinc chloride can give rise to the formation of acetylated oxazolines. This reaction may be construed as a combination of two reactions: in the first, normal acetylation takes place and, in the second, an acetoxy group at C-1 is displaced with the formation of an oxazoline. It seems reasonable to assume that the latter reaction proceeds by the mechanism portrayed in eq 1 and that the marked



(1)

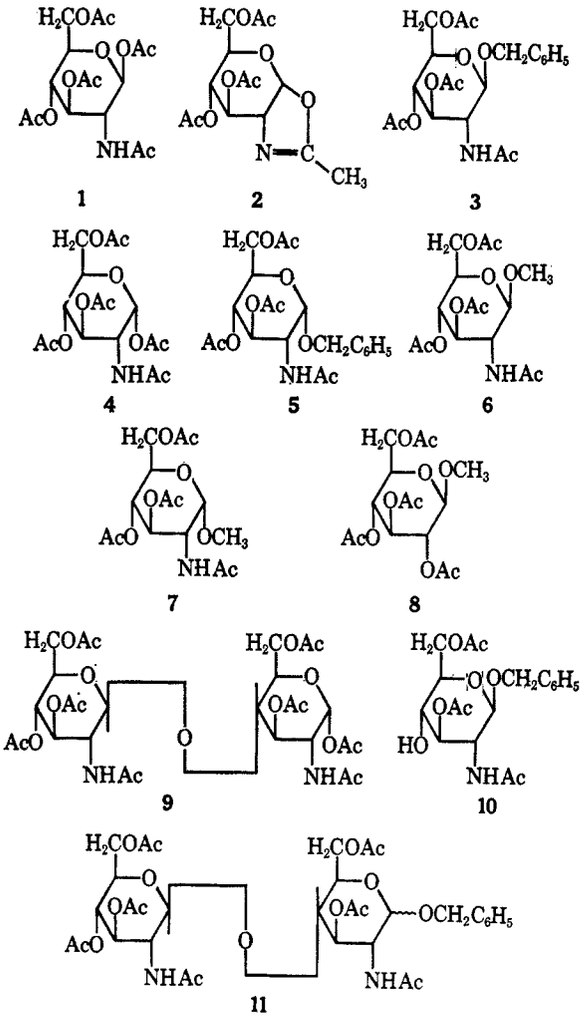
(1) Staff Fellow, National Institutes of Health, 1967–1968.

(2) N. Pravdić, T. D. Inch, and H. G. Fletcher, Jr., *J. Org. Chem.*, **32**, 1815 (1967).

ability of a benzamido or acetamido group to participate in the nucleophilic displacements of *trans* substituents on neighboring carbon atoms is an essential feature of the process. This aspect of the reaction suggests that, with 2-acylamino-2-deoxyaldose derivatives which are not readily anomerized by zinc chloride, the acylamino group may facilitate the departure of a *trans*-oriented substituent at C-1 while a *cis* substituent is unaffected. Furthermore, since an acyloxy group provides less anchimeric assistance than an acylamino group, one might expect that acylated derivatives of ordinary aldoses would be stable under the conditions required for the formation of oxazolines from 2-acylamino-2-deoxyaldoses and that one might thereby have in hand a reagent which would selectively attack *trans* derivatives of 2-acylamino-2-deoxyaldoses in complex molecules containing a variety of types of aldose moieties. In order to explore this possibility, we have carried out a number of experiments with comparatively simple aldose derivatives and these experiments will now be described.

At the outset, it was deemed desirable to ascertain whether zinc chloride alone would suffice for the formation of an oxazoline from an acetylated 2-acylamino-2-deoxyaldose. 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (**1**)[3] was heated with anhydrous zinc chloride in butyl acetate solution at 125° for 75 min. Extensive decomposition took place but 4,5-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyrano)-2-methyl-Δ^2-oxazoline (**2**) could be detected on tlc and was isolated by column chromatography. No effort was made to obtain the substance in pure form as its infrared spectrum clearly identified it. Similar experiments with other 2-acetamido-2-deoxy-D-glucose derivatives showed that oxazolines were readily obtainable by this simple procedure. However, oxazoline formation was always accompanied by decomposition and, in any case, oxazolines such as **2** are comparatively unstable substances. They react, for instance, with alcohols[4] to give glycosides in which the aglycon is *trans* to the acylamino group at C-2. With this reaction in mind, we endeavored to "trap" the oxazoline as formed by deliberately adding an alcohol in excess to the reaction mixture. The alcohol chosen was benzyl alcohol since benzyl glycosides are readily cleaved by catalytic hydrogenolysis, a property of potential utility in their identification.

Treatment of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (**1**) with zinc chloride and 112 mol equiv of benzyl alcohol in butyl acetate at 125° for 75 min caused no visible decomposition and subsequent chromatography led to the isolation of the known benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**3**)[5] in 89% yield. The conditions used for this and subsequent reactions were arrived at after performing a large number of small-scale experiments which were monitored by tlc. It may be noted, in passing, that the conditions are of critical importance. The yield of **3** from **1**, for instance, dropped to 60% when the concentration of zinc chloride was increased by a factor of 2.88 even though the ratio of zinc chloride to **1** was unchanged.



Attention was now turned to the anomeric ester **4**.[3] With zinc chloride and benzyl alcohol in butyl acetate at 125° this substance was much more slowly attacked than **1**. After a reaction time of 5 hr, unchanged **4** was still present although **3** was isolated in 42% yield and its anomer, benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (**5**)[6] (8.9% yield) was also obtained. We conclude from this experiment that, under these conditions, anomerization of **4** is comparatively slow—so slow, in fact, that some of the β glycoside (**3**) also suffered anomerization.

Since the main objective in undertaking this investigation concerned the cleavage of glycosidic bonds, we next studied the behavior of methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**6**)[7] with zinc chloride and benzyl alcohol. After a reaction period of 3 hr, this glycoside gave **3** in 46% yield and **5** in 9.6% yield. The anomeric (*cis*) glycoside, methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (**7**),[8] on the other hand, proved resistant to cleavage; after 6 hr, the unchanged glycoside was recovered in 79% yield although it was accompanied by 12% of **6**. The sharp contrast between the lability of the *trans* glycoside **6** and the stability of the *cis* glycoside **7** under these reaction conditions is given further emphasis by the difference in exposure times used.

Methyl β-D-glucopyranoside tetraacetate (**8**) was

(3) C. S. Hudson and J. K. Dale, *J. Amer. Chem. Soc.*, **38**, 1431 (1916).
(4) F. Micheel and H. Köchling, *Chem. Ber.*, **90**, 1597 (1957).
(5) R. Kuhn and W. Kirschenlohr, *ibid.*, **86**, 1331 (1953).
(6) P. H. Gross and R. W. Jeanloz, *J. Org. Chem.*, **32**, 2759 (1967).
(7) D. H. Leaback and P. G. Walker, *J. Chem. Soc.*, 4754 (1957).
(8) R. Kuhn, F. Zilliken, and A. Gauhe, *Chem. Ber.*, **86**, 466 (1953).

chosen as a representative *trans* glycoside with an acyloxy, rather than an acylamino, group at C-2. After treatment with zinc chloride and benzyl alcohol in butyl acetate solution for 6 hr at 125°, **8** was recovered in 92% yield.

From these experiments on comparatively simple aldopyranosides it appears that the *trans* glycosides of 2-acylamino-2-deoxyaldoses may indeed be more susceptible to cleavage by zinc chloride–benzyl alcohol than their *cis* anomers or their 2-acyloxy analogs. It now became of interest to test this combination of reagents on somewhat more complex molecules and the most accessible substrate of appropriate structure and configuration appeared to be the so-called "α-chitobiose octaacetate" (**9**). In the Experimental Section we describe a modernized version of the procedure which Barker and his coworkers[9] developed for the preparation of this substance from chitin. When **9** was heated with 212 mol equiv of benzyl alcohol and 14.9 mol equiv of anhydrous zinc chloride in butyl acetate at 125°, no **3** was detected after 5 hr. However, with 9.9 mol equiv of zinc chloride and an initial 9.8 mol equiv of benzyl alcohol, followed at intervals by two further additions of 9.8 mol equiv of benzyl alcohol, cleavage occurred at 125° although some decomposition was evident.[10] While the nonreducing moiety of **9** would be expected to yield **3**, the reducing portion of **9** should give benzyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**10**). With the intention of converting **10** into **3**, the partially purified reaction mixture was acetylated. Examination by tlc then showed but a trace of **9** remaining; in addition, there were four products which were subsequently separated by column chromatography. One of these, isolated in 7.2% yield, proved to be **5** while a second (11% yield) was its anomer **3**. A third substance, obtained in 12% yield, was evidently a benzyl glycoside. The crystalline material was dextrorotatory {$[\alpha]^{20}D$ +29.4° (*c* 0.43, chloroform)} and, after hydrogenolysis over palladium and subsequent acetylation, was found to have been converted, in part, into a product which was chromatographically indistinguishable from **9**; on the basis of this evidence, it is likely that the third substance isolated is α **11**, the acetylated benzyl glycoside derived from **9**. The fourth product, also a crystalline substance, was obtained in 35% yield. It melted at 273–274° and had a rotation of $[\alpha]^{20}D$ −66.5° (*c* 0.93, chloroform); Zehavi and Jeanloz[11] have recently synthesized β **11** from **9** in 19% yield and have reported mp 281–282° and $[\alpha]^{26}D$ −61° (*c* 0.34, chloroform) for this substance.

It will be recalled that **6** was effectively converted into a mixture of **3** and **5** on treatment for only 3 hr. With **9**, even 6 hr of reaction time failed to effect complete scission of the intersaccharidic linkage, the anomeric forms of **11** being obtained in substantial yield. While the optimum conditions for the cleavage of **9** may not have been attained, it appears that the glycosidic linkage in this disaccharide is more resistant to cleavage than that in simple glycosides such as **6**.

In conclusion, it is obvious that the method reported here may be adaptable to work on a very small scale through the use of gas–liquid partition chromatography. Further investigation of its utility in the investigation of the structure of oligosaccharides is under way in this laboratory. In addition, we wish to point out that the transglycosylation reported here may offer a relatively simple means for stereospecifically transferring 2-acylamino-2-deoxyaldopyranosyl moieties (from **1**) to molecules more complex than benzyl alcohol and thus be suitable for the synthesis of oligosaccharides, etc.

(9) S. A. Barker, A. B. Foster, M. Stacey, and J. M. Webber, *J. Chem. Soc.*, 2218 (1958).

(10) A similar stepwise addition of benzyl alcohol was tried in the solvolysis of simple glycosides but appeared to offer no advantage in these cases.

(11) U. Zehavi and R. W. Jeanloz, *Carbohyd. Res.*, **6**, 129 (1968).

Experimental Section

Melting points are equivalent to corrected values.

Thin layer chromatography was conducted on silica gel G_{254} (E. Merck AG, Darmstadt), compounds being detected by spraying with 10% sulfuric acid and heating at *ca.* 100°. Column chromatography was carried out with silica gel no. 7734 (0.05–0.2 mm) of E. Merck AG. The following solvent systems were employed (v/v): A, benzene–ether–methanol (14:14:1); B, benzene–ether–methanol (14:14:3); C, dichloromethane–ether–methanol (20:10:1); D, chloroform–methanol (15:1). Silica gel columns were packed in the least polar component of each solvent system. Reagent grade zinc chloride was fused, powdered, and then stored over phosphorus pentoxide prior to use. Butyl acetate was redistilled and then stored over Molecular Sieve, Type 4A (Fisher Scientific Co.); benzyl alcohol was also stored over this desiccant. Nmr spectra were obtained using a Varian A-60 spectrometer and tetramethylsilane as an internal standard.

2-Acetamido-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-1,3,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose (9, "α-Chitobiose Octaacetate").—The procedure of Barker, *et al.*,[9] was modified and column chromatography employed to obtain an enhanced yield of **9**. Chitin (Mann Research Laboratories, Inc., New York, N. Y.) was powdered in a ball mill and a sample of it (20 g) was added to cooled acetic anhydride (200 ml) containing concentrated sulfuric acid (26.0 ml). The reaction mixture was stirred at 40° for 3 days and then at 45° for 1 day. It was then cooled and poured into a solution of sodium acetate (160 g) in water (1 l.) and the crude product was extracted with four 100-ml portions of chloroform. The combined extracts were washed with water (100 ml), with saturated aqueous sodium bicarbonate solution (100 ml), and again with water (100 ml). Moisture was removed with sodium sulfate and the solution was concentrated *in vacuo* to a yellow syrup (26 g) which was chromatographed on a column (6 × 26 cm) of silica gel using system C and collecting 23-ml fractions of eluate. Fractions 150 to 250 contained **9** (tlc, system C) and were pooled and concentrated *in vacuo* to yield 3.6 g (11%) of product which was crystallized from methanol: 1.8 g; mp 294–296° dec; $[\alpha]^{20}D$ +54.5° (*c* 1.27, acetic acid) {lit. mp 308–309° dec,[9] 296.5°;[12] $[\alpha]^{18}D$ +55.0° (*c* 0.5, acetic acid),[9] $[\alpha]^{25}D$ +55.5° (*c* 1.0, acetic acid)[11]}.

Behavior of 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (1). A. With Zinc Chloride.—The compound (**1**, 202 mg) was dissolved in butyl acetate (32 ml) and zinc chloride (400 mg, 12.5 mg/ml) was added. The reaction mixture was stirred and heated at 125° (bath) for 75 min, becoming dark amber in color and, eventually, depositing a small amount of brown precipitate. After cooling, the reaction mixture was diluted with dichloromethane and the solution was washed thrice with water. Moisture was removed with sodium sulfate and the solution was concentrated *in vacuo* to give a dark brown syrup. Tlc in system A revealed degradation products (R_f = 0), unchanged **1** and a faster moving component. The latter was separated by chromatography on a column of silica gel using system A and obtained as a pale yellow syrup which had infrared absorption (neat) at 1750 (OAc) and 1672 cm^{-1} (C=N) as would be expected for **4,5-(3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyrano)-2-methyl-Δ²-oxazoline (2)**.

B. With Zinc Chloride and Benzyl Alcohol.—Compound **1** (100 mg) was dissolved in butyl acetate (16 ml) and zinc chloride (200 mg, 12.5 mg/ml) and benzyl alcohol (3 ml, 112 mol/mol of **1**) were added. The reaction mixture was stirred and heated

(12) J. D. Distler and S. Roseman, *Methods Carbohyd. Chem.*, **1**, 305 (1962).

at 125° (bath) for 75 min; it remained clear and colorless during this treatment. It was cooled and diluted with dichloromethane and the solution was washed thrice with water. Moisture was removed with sodium sulfate and the solution was concentrated *in vacuo* to a syrup which was examined by tlc using system A. A trace of **1** remained but the major component migrated more rapidly than **1** and (in contrast to **1**) was visible as a dark spot when viewed under a uv source of 254 nm. Using system A, the material was chromatographed on a column of silica gel (2.7 × 27 cm), 4-ml fractions of eluate being collected. Fractions 153 to 201 contained the faster moving component and were pooled and concentrated *in vacuo* to give 99.7 mg (89%). From its solution in ethanol, the **benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (3)** crystallized: mp 166–167°; $[\alpha]^{20}D$ −43.3° (*c* 0.89, methanol) {lit. mp 165–167°[5] and 170°;[6] $[\alpha]^{20}D$ −43.4° (methanol)[5] and $[\alpha]^{26}D$ −43° (*c* 1, methanol)[6]}.

In another experiment, a mixture of **1** (178 mg), butyl acetate (12.8 ml), zinc chloride (356 mg, 36 mg/ml), and benzyl alcohol (5.0 ml, 105 mol/mol of **1**) was heated and stirred at 125° (bath) for 75 min. The light amber mixture was worked up as described above to give a syrup which contained **3** (tlc, system A) along with what were presumably degradation products. After chromatography on a column of silica gel, **3** (120.3 mg, 60%) was isolated: mp 165.6–166°; $[\alpha]^{20}D$ −46° (*c* 0.73, methanol).

Behavior of 2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (4) with Zinc Chloride and Benzyl Alcohol.—A mixture of **4** (150 mg), butyl acetate (24 ml), zinc chloride (300 mg, 5.71 mol/mol of **4**), and benzyl alcohol (0.45 ml, 11 mol/mol of **4**) was heated and stirred at 125° for 5 hr. The mixture was worked up as described earlier to give a syrup in which tlc (system A) showed the presence of two products as well as unchanged **4**. Chromatography of the mixture on a column of silica gel (2 × 22 cm) using system A gave 15 mg (8.9%) of **benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (5)** which was crystallized from ether–pentane: mp and mmp 112–114° (lit.[13] 111°). A second component (71 mg, 42%) was found to be benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**3**): mp 165–166°; $[\alpha]^{20}D$ −42.0° (*c* 0.56, methanol).

Behavior of Methyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (6) with Zinc Chloride and Benzyl Alcohol.—A mixture of **6**[7] (300 mg), butyl acetate (30 ml), zinc chloride (600 mg), and benzyl alcohol (0.45 ml) was heated and stirred at 125° (bath) for 6 hr, more benzyl alcohol (0.45 ml) being added after 1 hr and, again, after 3 hr. The cooled mixture was worked up in the usual fashion to yield a syrup which was chromatographed on a column of silica gel using system A, **5** (35 mg, 9.6%; mp 112–114°) and **3** {168 mg, 46%; mp 165–166°; $[\alpha]^{20}D$ −42.5° (*c* 0.5, methanol)} being isolated.

Behavior of Methyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (7) with Zinc Chloride and Benzyl Alcohol.—A mixture of **7** (200 mg), butyl acetate (15 ml), zinc chloride (400 mg), and benzyl alcohol (0.3 ml) was heated and stirred at 125° (bath) for 6 hr, 0.3-ml portions of benzyl alcohol being added at 1 hr and at 3 hr. The faintly yellow mixture was cooled and worked up as described earlier to yield 157 mg (79% recovery) of **7** and 24 mg (12%) of **6**.

Behavior of Methyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (8) with Zinc Chloride and Benzyl Alcohol.—A mixture of **8** (200 mg), butyl acetate (15 ml), zinc chloride (400 mg), and benzyl alcohol (0.3 ml) was heated and stirred at 125° (bath) for 6 hr, 0.3-ml portions of benzyl alcohol being added at 1 hr and at 3 hr. After removal of the zinc chloride and solvent, the syrupy residue was examined by tlc using system A; **8** was the main component although there were traces of slower moving contaminants, none of which, however, absorbed uv light of 254 mm. Using system A, the mixture was chromatographed on a column of silica gel to give 168 mg (84% recovery) of **8**, mp and mmp 104–105°.

In a similar experiment in which all of the benzyl alcohol was added at the outset, the recovery of **8** was 92%.

Behavior of 2-Acetamido-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-1,3,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose (9, "α-Chitobiose Octaacetate") with Zinc Chloride and Benzyl Alcohol.—A mixture of α-chitobiose octaacetate (**9**, 300 mg), butyl acetate (30 ml), and zinc chloride (600 mg, 9.9 mol/mol of **9**) was heated and stirred at 125° (bath) for 6 hr; extra portions of benzyl alcohol (0.45 ml each) were added at 1 hr and at 3 hr. The **9** and the zinc chloride dissolved in a short time and the solution developed a brownish orange color and gave a small quantity of a brown precipitate. After cooling, the reaction mixture was diluted with dichloromethane and the solution was washed thrice with water. Moisture was removed with sodium sulfate and the solution was concentrated *in vacuo* to yield a syrup which was finally held at 40° (bath) and <0.1 mm of pressure to remove remaining butyl acetate and benzyl alcohol. The syrup was then dissolved in a mixture of pyridine (5 ml) and acetic anhydride (5 ml) and the solution was left at room temperature overnight. It was then concentrated *in vacuo* (<0.1 mm) and 40° (bath) and the viscous orange syrup thus obtained was examined by tlc using system B. The presence of four products, together with a barely detectable trace of **9**, was evident. The syrup was chromatographed on a column of silica gel (2.7 × 46 cm) with system C, 3-ml portions of eluate being collected. Fractions 56 to 70 contained a mixture of two products (CH-1 and CH-2). Fractions 178 to 246 contained a single product (CH-3) and fractions 262 to 350 contained a fourth product (CH-4). The mixture of CH-1 and CH-2 was rechromatographed on a column of silica gel (2.7 × 22 cm), using system A, to yield CH-1 (14 mg, 7.2%) and CH-2 (22 mg, 11%). The product CH-1 was chromatographically indistinguishable from benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (**5**) in systems A and C and appeared as a dark spot when viewed under uv light of 254 nm. Crystallized from ether–pentane, it had mp and mmp 112–114°.

Product CH-2 migrated at the same rate as benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (**3**) in systems A and C. Crystallized from ethanol, it had mp 165–166°.

The fractions containing CH-3 were pooled and concentrated to give 38 mg (12%) of a product which crystallized from its solution in ethyl acetate: mp 273–275°; $[\alpha]^{20}D$ +29.4° (*c* 0.043, chloroform). From its solution in either ethyl acetate or chloroform–ether the substance shows a strong tendency to form gels and considerable care must be exercised on order to obtain proper crystallization. On tlc, the material appeared as a dark spot when viewed under uv light of 254 nm. Although chromatographically homogeneous in systems B, C, and D, the substance failed to give satisfactory elemental analyses. A portion of it (5 mg) was dissolved in methanol, palladium on charcoal was added, and the suspension was shaken with hydrogen overnight. Examination by tlc using system C showed that *ca.* one-third of the material had been debenzylated. Catalyst and solvent were removed and the residue was acetylated in conventional fashion with acetic anhydride–pyridine to yield a crude product with a component which was chromatographically indistinguishable from **9** in systems B, C, and D. On the basis of this evidence and in view of its optical rotation, CH-3 is tentatively designated as **benzyl 2-acetamido-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-3,6-di-*O*-acetyl-2-deoxy-α-D-glucopyranoside (α 11)**.

The fractions containing CH-4 were pooled and concentrated to yield a residue (111 mg, 35%) which readily crystallized from its solution in ethanol. It was twice recrystallized from ethanol and then from chloroform–ethyl acetate: mp 273–274°; $[\alpha]^{20}D$ −66.5° (*c* 0.93, chloroform); nmr (dimethyl sulfoxide-d_6), signals at τ 2.68 (5 H, aromatic protons) and *ca.* 8.1 (21 H, multiplet with five discernible peaks, OAc and NHAc). Zehavi and Jeanloz[11] reported mp 281–282° and $[\alpha]^{26}D$ −61° (*c* 0.34, chloroform) for **benzyl 2-acetamido-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (β 11)**. For analysis, the material was dried *in vacuo* at 100°.

Anal. Calcd for $C_{38}H_{44}N_2O_{16}$ (724.73): C, 54.69; H, 6.12; N, 3.87. Found: C, 53.75; H, 6.15; N, 3.80.

Registry No.—**1**, 7772-79-4; **2**, 17188-75-9; **4**, 7784-54-5; **6**, 2771-48-4; **7**, 2595-39-3; **9**, 7284-18-6; α **11**, 17182-63-7; β **11**, 17188-78-2; zinc chloride, 7646-85-7; benzyl alcohol, 100-51-6.

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(13) Gross and Jeanloz[6] reported mp 111° for **5**. In a personal communication (Feb 16, 1968) Dr. Jeanloz informed us that **5** exists in two readily distinguishable crystalline forms of mp 112.5–114.5 and 111–114°. In the present work we used seed crystals of the higher melting form kindly provided by Dr. Jeanloz.