Carbohydrate Research, 82 (1980) 237–252

O-BENZYLATED OXAZOLINE DERIVATIVES OF 2-ACETAMIDO-2-DEOXY-D-GLUCOPYRANOSE FROM 1-PROPENYL GLYCOSIDES. SYNTHESIS OF THE PROPENYL GLYCOSIDES AND THEIR DIRECT CYCLIZATION*

MINA A. NASHED†, CHARLES W. SLIFE, MAKOTO KISO‡, AND LAURENS ANDERSON**

Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin, Madison, WI 53706 (U.S.A.)

(Received October 5th, 1979; accepted for publication in revised form, December 15th, 1979)

ABSTRACT

1-Propenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α- and -β-D-glucopyranosides (**3α**, **3β**) were obtained by the successive isomerization and acetylation of the known allyl glycosides **1α** and **1β**. The allyl glycosides were also converted, *via* their benzylidene 4,6-acetals, into the 4,6-di-*O*-benzyl-3-*O*-(2-butenyl) derivatives **9α** and **9β**. The simultaneous decrotylation and isomerization of **9β**, followed by acetylation, gave 1-propenyl 2-acetamido-3-*O*-acetyl-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**11**). The 4-*O*-acetyl-3,6-di-*O*-benzyl isomer (**18**) of **11** was synthesized from **1β** by a route involving selective, partial benzoylation, and then protection of O-4 as the 2-tetrahydropyranyl ether. As previously described, the 1-propenyl β-glycosides **3β**, **11**, and **18**, and the tri-*O*-benzyl analog **5β**, were converted in near-quantitative yield into the corresponding, substituted oxazolines by the action of mercuric chloride and mercuric oxide in boiling acetonitrile. An optimized procedure for this cyclization is given. The ^{1}H-n.m.r. spectra of the tri-*O*-acetyl (**19**) and the 4-*O*-acetyl-3,6-di-*O*-benzyl (**21**) oxazolines indicate a modified $^{O}S_2$ conformation for these compounds.

INTRODUCTION

The *O*-acetyl-di-*O*-benzyl derivatives **20** and **21** (see Scheme IV) of 2-methyl-(1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline are useful as precursors of β-linked, internal 2-acetamido-2-deoxy-D-glucopyranose ("*N*-acetyl-D-glucosamine") residues in synthetic oligosaccharides. As described in a preliminary communication[1], we recently undertook the preparation of these two oxazolines, using either allyl 2-acetamido-2-deoxy-α- or -β-D-glucopyranoside (**1α**, **1β**) as starting materials. In

---

*Dedicated to Professor Stephen J. Angyal on the occasion of his retirement.

†On leave of absence from the Department of Chemistry, Alexandria University, Alexandria, Egypt.

‡Present address: Department of Agricultural Chemistry, Gifu University, Gifu 504, Japan.

**Please address correspondence to this author.

executing the syntheses, we planned in each case to proceed first to the appropriate 1-propenyl *O*-acetyldi-*O*-benzyl-α- or -β-glycoside. We then expected to hydrolyze the 1-propenyl glycosides to liberate the anomeric hydroxy groups, and convert the products into oxazolines *via* either the glycosyl chlorides[2] or the β-1-acetates[3]. However, we found that the 1-propenyl β-glycosides could be cyclized directly to oxazolines by treatment with mercuric chloride–mercuric oxide in acetonitrile[1]. As the yield was essentially quantitative, the reaction was incorporated into our synthetic schemes, and these were fully developed for the β-anomeric series.

Concurrently with our work, the synthesis of *O*-benzylated oxazolines of 2-amino-2-deoxy-D-glucose was accomplished in other laboratories. Warren *et al.*[4] prepared three of these compounds, including **21** and **22**, from the 1-propenyl α-glycosides *via* the glycosyl chlorides. In Sinaÿ's laboratory[5], the β-1-acetate route was used to obtain **20** and **21**.

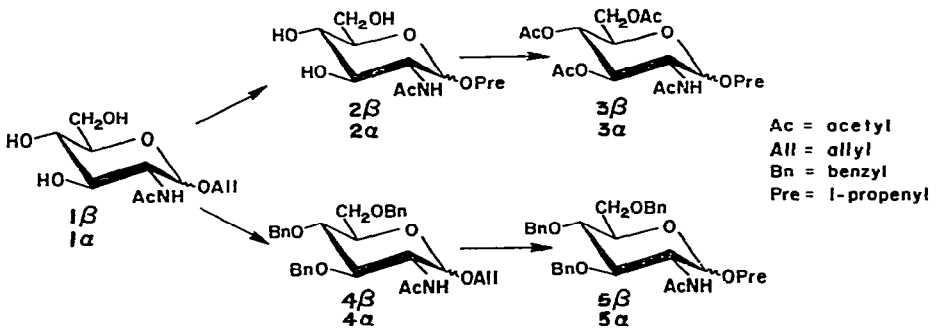
The present paper describes the preparation of the 1-propenyl glycosides used in our investigation, and gives improved directions for conducting the mercuric ion-induced, cyclization reaction. Full details of the propenyl glycoside syntheses are included where these led to new products (**3β**, **3α**), or followed routes different from those employed by Warren *et al.*[4], or by Rollin and Sinaÿ[5] (**11**, **18**). For some intermediates already described by the Boston and Orléans groups, revised or additional data on physical properties are given. The ^{1}H-n.m.r. parameters of the oxazolines are recorded, and the conformational implications of the values are discussed.

RESULTS AND DISCUSSION

Synthesis of the fully protected propenyl glycosides. — Most of the allyl 2-acetamido-2-deoxy-β-D-glucopyranoside (**1β**) used as a starting material was made by the Koenigs–Knorr reaction of allyl alcohol with 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride (procedure of Lee and Lee[6]). *O*-Deacetylation of the coupling-product gave **1β**. To avoid the large-scale use of mercuric cyanide, we also prepared **1β** by first converting the glycosyl chloride into the tri-*O*-acetyl oxazoline **19** (procedure of Lemieux and Driguez[2]) and then treating the oxazoline with allyl alcohol and *p*-toluenesulfonic acid, and *O*-deacetylating the product*. The α anomer (**1α**) was made by the direct glycosidation of allyl alcohol with 2-acetamido-2-deoxy-D-glucopyranose, catalyzed by boron trifluoride etherate[6].

The synthesis of the 1-propenyl 2-acetamido-3,4,6-tri-*O*-acetyl- (**3β**, **3α**) and 2-acetamido-3,4,6-tri-*O*-benzyl- (**5β**, **5α**) -2-deoxy-D-glucopyranosides is shown in Scheme I. Because of the basic nature of the reagent (potassium *tert*-butoxide) used to isomerize the allyl glycosides[9], isomerization had to be accomplished prior to

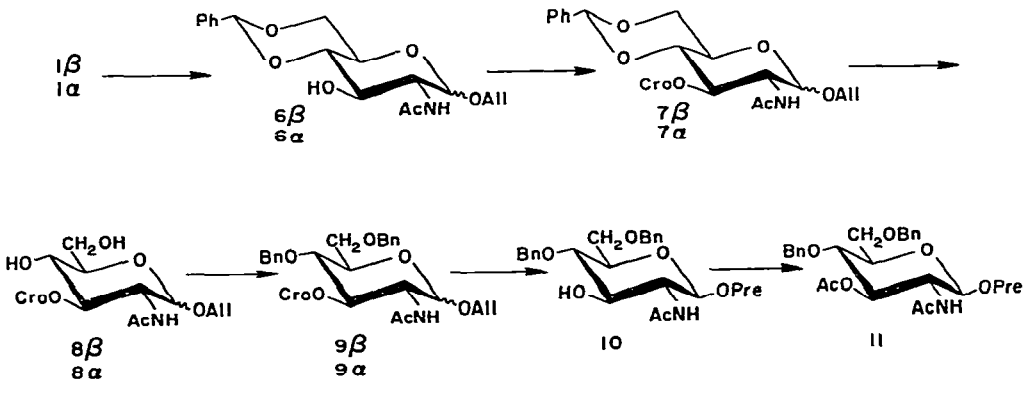
*This method gave variable yields when used on the 25–50-g scale. An equally convenient, though longer, route to **1β** proceeds *via* 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (Bergmann and Zervas[7], four steps), which can be directly coupled with allyl alcohol to provide the *O*-acetylated β-glycoside[8].



Scheme I

O-substitution in the case of the *O*-acetylated derivatives. In preparing the *O*-benzylated compounds it is more convenient, though presumably not necessary, to reverse the sequence of operations. As good yields of the *O*-acetylated glycosides **3β** (crystalline) and **3α** (syrup) were obtained directly from crude **2β** and **2α** respectively, these latter intermediates were not purified. The tri-*O*-benzyl derivatives **4β**, **4α**, **5β**, and **5α** have been described by Gent *et al.*[10] (β series), and by Warren and co-workers[4,11].

To obtain 1-propenyl 2-acetamido-3-*O*-acetyl-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**11**), we followed the route shown in Scheme II. The hydroxy group at C-3 of the allyl 4,6-*O*-benzylidene β-glycoside[5,12] **6β** was temporarily protected as the 2-butenyl (crotyl) ether[13], and the product (**7β**) was hydrolyzed to the 4,6-diol **8β**. Benzylation of the diol yielded the fully substituted glycoside **9β**. Then, the treatment of **9β** with potassium *tert*-butoxide in methyl sulfoxide effected simultaneous removal of the 3-crotyl group and isomerization of the glycosidic allyl group. Acetylation of the decrotylated, isomerized product (**10**) completed the synthesis.

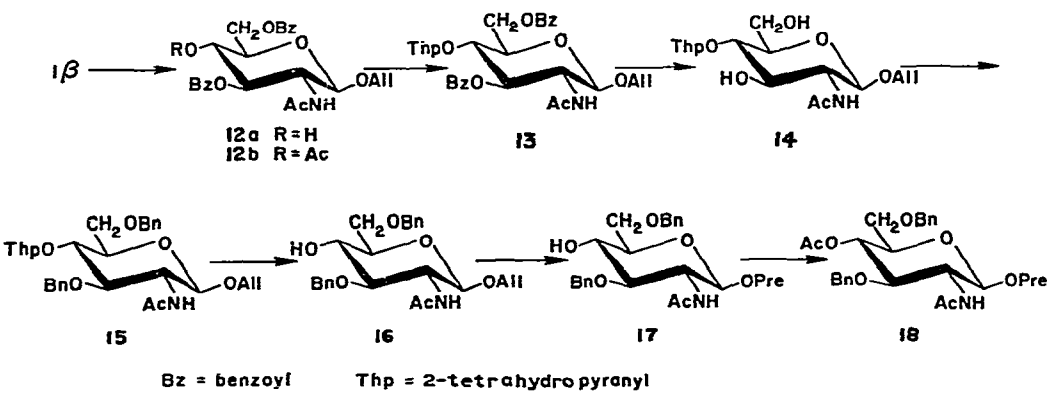


Scheme II

In the α series, the intermediates **7α**, **8α**, and **9α** were obtained by successive crotylation, hydrolysis, and benzylation of the allyl 4,6-*O*-benzylidene α-glycoside **6α**, but the *O*-benzylated allyl glycoside (**9α**) was not carried through the deprotection–rearrangement and acetylation steps. All of the intermediates in both the α and β series, and the final product **11**, were readily isolated crystalline and in good yield. Chromatographic purification was required only after the decrotylation–rearrangement step (**9β**→**10**).

In addition to serving as the precursors of 4,6-dibenzyl ethers, the 4,6-*O*-benzylidene allyl glycosides **6α** and **6β** have been used by Warren and Jeanloz[11] and by Rollin and Sinaÿ[5] as starting materials for the synthesis of 3,6-di-*O*-benzyl derivatives. In these syntheses, **6α** and **6β** were benzylated at position 3, and the 3-*O*-benzyl-4,6-diols were generated by removal of the benzylidene group. Partial benzylation of the 4,6-diols gave the 3,6-dibenzyl ethers as the principal products. However, substantial portions of 3,4-di- and 3,4,6-tri-benzyl ether were formed, and the product mixtures had to be resolved chromatographically*.

To avoid the rather non-specific, partial benzylation step, we made the 4-*O*-acetyl-3,6-di-*O*-benzyl propenyl glycoside (**18**) by the route shown in Scheme III. Allyl 2-acetamido-3,6-di-*O*-benzoyl-2-deoxy-β-D-glucopyranoside (**12a**), prepared in good yield from **1β** by partial benzoylation[14], was treated with 2,3-dihydro(4*H*)pyran to give **13**. On removal of its benzoyl groups, **13** furnished the 2-tetrahydropyranyl ether **14**, and benzylation of the latter gave the fully substituted allyl glycoside **15**. Intermediates **13** and **14** were formed in essentially quantitative yields, and did not require purification before use in their respective steps of the synthesis. The dibenzylated compound **15** was nicely crystalline, even though it was presumably a diastereomeric mixture of (*R*)- and (*S*)-2-tetrahydropyranyl derivatives. The overall yield of **15** from **12a** was 84%. Cleavage of the tetrahydropyranyl group from **15** gave the

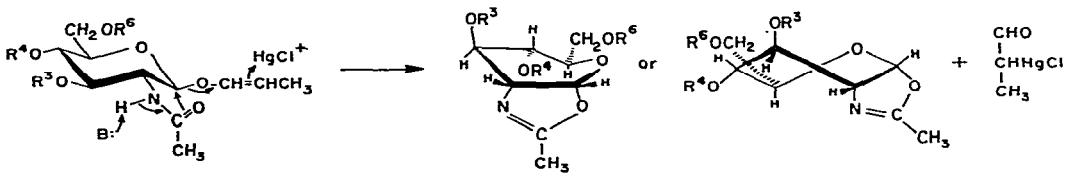


Scheme III

*An efficient, two-step procedure for the selective monobenzylation of position 6 in 4,6-diols has now been described by Sinaÿ *et al.*[13a].

known 3,6-di-*O*-benzyl allyl glycoside[4,5] **16**, which was readily isomerized to the 1-propenyl glycoside[4] **17**. This on acetylation furnished the fully protected glycoside **18**.

Conversion of 1-propenyl glycosides into oxazolines. — As already mentioned, cyclization was accomplished by treating the 1-propenyl glycosides, in acetonitrile solution, with mercuric chloride and mercuric oxide. The conditions are similar to those used for the hydrolytic cleavage of 1-propenyl ethers (including glycosides)[15], except that the cleavage reaction is conducted in media containing water. The two reactions are clearly analogous. For the cyclization, one may therefore postulate the mechanism shown in Scheme IV. The reaction is presumably initiated by the attack of a mercuric species on C-2′ (C-2 of the propenyl group)[15], generating positive charge on C-1′. Delocalization of the charge to the anomeric carbon atom (C-1) of the sugar would render that atom susceptible to back-side attack by the carbonyl oxygen of the *N*-acetyl group. In a nearly anhydrous medium, this process would be favored over the nucleophilic addition of water to C-1′. On formation of the new C-1–O bond, the erstwhile propenyloxy group would be ejected as 2-chloromercuripropanal. We made no effort to detect 2-chloromercuripropanal in the mixtures, but the compound has been identified[15] as a product of the related hydrolytic cleavage-reaction.



Glycosides	R^3	R^4	R^6	Oxazolines
3β	Ac	Ac	Ac	19
11	Ac	Bn	Bn	20
18	Bn	Ac	Bn	21
5β	Bn	Bn	Bn	22

Scheme IV

The possibility was considered that oxazoline formation from 1-propenyl glycosides is a stepwise process. One might imagine the initial, mercurated intermediate undergoing dissociation to 2-chloromercuripropanal and a glycosyl cation, which would later cyclize. Such a mechanism appears to be ruled out, however, by our observation that the 1-propenyl α-glycosides **3α** and **5α** gave no oxazolines under conditions that effected complete conversion of their β anomers. The fact that 1-propenyl β-glycosides are required for successful reaction is strong evidence for a concerted mechanism.

The general features of this mechanism are probably common to the several reactions whereby oxazolines are obtained from derivatives of 2-acylamido-2-deoxy sugars. The individual reactions differ in the nature of the *trans*-disposed anomeric substituent that serves as a leaving-group. That group may be an acetoxyl–iron(III)

complex (in the procedure of Matta and Bahl[3]), a chloride ion[2], or 2-chloromercuripropanal.

Mercuric oxide was initially included as a reagent because hydrogen chloride is a product of the cyclization reaction, and it was supposed that neutralization of the acid would be essential. Moreover, reaction of the oxide with the hydrogen chloride would replenish a part (presumably 50%) of the mercuric chloride consumed in the process. Experimentally, it could be shown that the oxide was not required for cyclization to proceed, but that its addition greatly enhanced the rate of the reaction. It was also found that, to assure reasonable reaction rates, an excess of mercuric chloride must be present, such that the final ratio of the chloride to product oxazoline is not less than 1 : 1. This ratio results when the initial mixture contains 1.5 molar proportions of mercuric chloride, with respect to propenyl glycoside, plus mercuric oxide.

Under the conditions just outlined, the times required for completion of the reaction at the boiling temperature of acetonitrile (82° at 1 atm) ranged from 5 min for the 1-propenyl tri-*O*-benzyl glycoside **5β** to 40 min for the tri-*O*-acetyl analog **3β**. The times for the *O*-acetyldi-*O*-benzyl compounds **11** and **18** were intermediate. These data show that the reactivity of the 1-propenyl glycosides is modulated by the substituents at positions (3,4,6) remote from the anomeric center. The effect is similar to that noted by Ishikawa and Fletcher[16], and later by other workers[17,18], in experiments with glycosyl halides. In both types of compound, the replacement of acyl substituents by alkyl (benzyl) groups enhances activity.

The mercuric chloride-induced cyclization of 1-propenyl β-glycosides provides a simple, rapid, and high-yielding procedure for the preparation of oxazoline derivatives of 2-acetamido-2-deoxy-D-glucose (and 2-acetamido-2-deoxy-D-galactose[14]). It thus merits comparison with another direct synthesis of oxazolines, namely the acetolysis method of Matta and Barlow[19]. The most obvious advantage of the acetolysis reaction is that it is applicable to methyl[19] and allyl[20] α-glycosides of 2-acetamido-2-deoxy-D-glucose, including disaccharide derivatives. In many cases, these α-glycosidic intermediates will be somewhat more readily available than the allyl β-glycosides required by our method. As to disadvantages, the acetolysis procedure may be sensitive to small variations in reaction conditions. In our hands, it gave a substantial proportion of α-1-acetate (2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose), as well as oxazoline (**19**), from methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside. Also, acetolysis gives unsatisfactory results when *O*-benzyl protecting-groups are present[19]. The "propenyl cyclization" method is therefore superior for *O*-benzylated derivatives. It appears to be more dependable than acetolysis, and it should be compatible with a wider variety of protecting-groups.

A special case is the tri-*O*-benzyl oxazoline **22**, which we first prepared by the deacetylation–benzylation (benzyl chloride, potassium hydroxide) of the tri-*O*-acetyl oxazoline **19**. Because the yields were poor, we preferred to make **22** from the propenyl glycoside **5β**. However, Rollin and Sinaÿ[5] achieved a practical yield (50%) of **22**

TABLE I

THE EFFECT OF CYCLIZATION TO OXAZOLINES ON THE ^{1}H-N.M.R. PARAMETERS OF (1-PROPENYL) β-GLYCOSIDES OF 2-ACETAMIDO-2-DEOXY-D-GLUCOPYRANOSE

Compd. no. (Type)	*Solvent*	*Chemical shifts (δ) and first-order couplings (Hz) at 270 MHz*						
		H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6,6'*	*C-CH$_3$*
3β (Glycoside)	$CDCl_3$	4.87d	4.03ddd	5.33dd	5.11dd	3.79ddd	4.27 (AB of 4.14 ABX)	
		$J_{1,2}$ 8.1	$J_{2,3}$ 10.3 $J_{2,NH}$ 8.8	$J_{3,4}$ 9.6	$J_{4,5}$ 9.6	$J_{5,6}$ 4.8; $J_{5,6'}$ 2.6		
19 (Oxazoline)	$CDCl_3$	5.97d $J_{1,2}$ 7.3	4.14m $J_{2,3}$ 2.6 $J_{2,4}$ 1.5	5.27dd $J_{3,4}$ 2.2	4.94dq $J_{4,5}$ 9.2	3.61dt $(J_{5,6} + J_{5,6'})/2 = 4.0$	4.18d	2.09d $J_{2\,CH_3}$ 1.8
	$(CD_3)_2SO$	6.03d $J_{1,2}$ 7.3	4.18–4.02[a] $J_{2,3}$ 2.2 $J_{2,4}$ 1.1	5.05t $J_{3,4}$ 2.2	4.79dq $J_{4,5}$ 8.8	3.58m	4.18–4.02[a]	2.00d J_{2,CH_3} 1.8
18 (Glycoside)	$CDCl_3$	5.15d $J_{1,2}$ 7.7	3.41m $J_{2,3}$ 9.2 $J_{2,NH}$ 8.0	4.32t $J_{3,4}$ 9.2	5.04t $J_{4,5}$ 9.2	3.71m	3.65m	
21 (Oxazoline)	$CDCl_3$	6.01d $J_{1,2}$ 7.4	4.13m $J_{2,3}$ 2.9 $J_{2,4}$ <1	3.87m $J_{3,4}$ 1.5	5.09m $J_{4,5}$ 7.0	← 3.62–3.50m →		2.05d J_{2,CH_3} 1.5

[a]Overlapping signals.

from **19** by separating the deacylation and alkylation steps, and using benzyl bromide and sodium hydride as the reagents for the benzylation.

Conformation of the oxazolines. — The chemical shifts and vicinal coupling-constants of the ring protons of the oxazolines **19** and **21** were readily determined from the ^{1}H-n.m.r. spectra. These were fully resolved at 270 MHz. The values are given in Table I, together with the corresponding values for the precursors, propenyl glycosides **3β** and **18**. A detailed analysis of the n.m.r. spectra of oxazolines **20** and **22** was not possible.

It may be noted that the J values of the vicinal couplings of H-1–H-4 in the propenyl glycosides are all in the normal range (~8–10 Hz) for protons in the anti-periplanar arrangement. From this, it can be inferred that the glycosides have the $^4C_1$ conformation, with H-1–H-4 axially disposed. On conversion of the glycosides into oxazolines, the signal for H-1 is shifted ~1 p.p.m. to lower field. The values of the coupling constants $J_{2,3}$ and $J_{3,4}$ decrease dramatically, and $J_{1,2}$ and $J_{4,5}$ are decreased by small amounts. Additional characteristic features of the spectra are the long-range couplings between H-2 and H-4 (^4J), and between H-2 and the protons of the methyl group at position 2 of the oxazoline ring (^5J)*. It is evident, primarily from the large decreases shown by $J_{2,3}$ and $J_{3,4}$, that a major conformational change accompanies the closing of the oxazoline ring.

The vicinal coupling-constants of the tri-*O*-acetyloxazoline **19** in the polar solvent methyl sulfoxide did not differ significantly from those found in chloroform solution (Table I). Moreover, except for a slight increase in $J_{3,4}$ with increasing temperature, the values in chloroform solution were constant, within experimental error, over the range −30 to +55° (data not shown). It may therefore be postulated that **19** in solution exists preponderantly as a single conformer. From the J values, it may be estimated that, in **19** and **21**, the proton dihedral angle $\phi_{2,3}$ is in the range 50–60°, and $\phi_{3,4}$ is in the range 110–120°. The angle $\phi_{4,5}$ appears to be >160° in **19**, but somewhat smaller in **21**. For $\phi_{1,2}$, values of 20–30° are suggested because $J_{1,2}$ is smaller than would be expected for H-1 and H-2 in the eclipsed arrangement.

If the oxazoline rings of **19** and **21** were completely planar, the available conformations would be the half-chairs $^4H_5$ or $^5H_4$, and the boat forms $^{O,3}B$ or $B_{O,3}$. However, the oxazoline ring appears to be slightly puckered ($\phi_{1,2} \neq 0$). This puckering must necessarily shift the conformation of the pyranose ring toward a distorted half-chair (four possibilities), or toward one of the skew forms adjacent to the $^{O,3}B$ or $B_{O,3}$ forms in the "flexible cycle" (four possibilities). Examination of a model shows that, of all these possible conformations, a modified $^OS_2$ form (Scheme IV) is the only one in which the magnitudes of all vicinal H–H dihedral angles correspond to the estimates of the preceding paragraph. We therefore conclude that the conformations of **19** and **21** are best designated as modified $^OS_2$ having $\phi_{1,2}$ smaller than in the "theoretical" skew form.

*Some of the ^{1}H-n.m.r. parameters of compounds **19**, **20**, and **22** have been recorded by other workers. Our values are in good agreement with these published figures.

EXPERIMENTAL

Instrumental and chromatographic procedures. — Melting points, which are uncorrected, were determined in Pyrex capillaries in a Hershberg-type (heated oil-bath) apparatus. Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter. Proton magnetic resonance spectra "for the record" were taken on a Bruker WH-270 spectrometer. Chemical shifts are referenced to tetramethylsilane as the internal standard. Elemental analyses were performed by the Micro-Tech Laboratories, Skokie, IL.

Thin-layer chromatography (t.l.c.) was performed on glass plates coated with Silica Gel G (Merck). Spots were detected by charring with sulfuric acid. For column chromatography, Silica Gel 60, particle size 0.063–0.200 mm (Merck), was used. In both procedures, the solvents employed were mixtures of ethyl acetate and chloroform, for compounds of low polarity, or methanol and chloroform, for the more-polar compounds.

General chemical methods. — For benzylation, compounds were dissolved in *N*,*N*-dimethylformamide and treated with benzyl bromide in the presence of barium oxide and barium hydroxide, according to the directions of Harrison and Fletcher[21]. The benzylated products were isolated as described by the original authors. Isomerization of allyl to propenyl glycosides was accomplished by the method of Gigg and Gigg[9], in which a solution of the allyl derivative and potassium *tert*-butoxide in methyl sulfoxide is heated at 100° under nitrogen. (Warren *et al.*[4] reported that *N*,*N*-dimethylformamide is equally suitable as a solvent.) Acetylations were performed conventionally, with mixtures of acetic anhydride and pyridine.

The progress of reactions was routinely monitored by t.l.c. In the isomerizations, aliquots of the mixtures were treated with acid[9], or aqueous mercuric salts[1], prior to spotting. Conversion to the propenyl glycoside was judged complete when only the hydrolysis product appeared in t.l.c. Conversely, the loss of susceptibility to hydrolysis[11] was used to verify the cyclization of propenyl glycosides to oxazolines.

Starting materials. — 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride was prepared from 2-acetamido-2-deoxy-α-D-glucopyranose by treatment with neat acetyl chloride, as directed by Horton[22]. Confirming the observation of Pravdić *et al.*[23], we found that glycosyl chloride made by this method always contained several per cent of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose ("α-acetate"). The use of acetic anhydride–hydrogen chloride for the acylation (McLaren *et al.*[24]) did not fully remedy the situation. However, a product nearly free of α-acetate was obtained by the acetyl chloride procedure when titanium tetrachloride was used to accelerate the final, slow phase[23] of the reaction. Our procedure (not optimized) was to conduct the reaction normally for 16–24 h, then add a 25% (v/v) solution of titanium tetrachloride in dichloromethane (40 mL per 100 mL of acetyl chloride originally taken), keep the mixture again overnight, and isolate the glycosyl chloride in the usual way.

Glycosyl chloride containing α-acetate was coupled with allyl alcohol by the

procedure of Lee and Lee[6]. After crystallization from ethanol, the product, allyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, had m.p. 167–168.5° (lit.[6,25] 162–163°, 160°), $[\alpha]_D^{25}$ −17.4° (lit.[25] −15.1°), $[\alpha]_{436}^{25}$ −33.5° (*c* 0.78, chloroform). *O*-Deacetylation gave allyl 2-acetamido-2-deoxy-β-D-glucopyranoside[6] (**1β**); ^{1}H-n.m.r. [$(CD_3)_2SO$ plus 2 drops D_2O]: δ 7.85 (d, 1 H, $J_{NH,2}$ 9.5 Hz, N*H*), 5.92–5.77 (m, 1 H, =C*H*–), 5.27–5.10 (m, 2 H, CH_2=), 4.31 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.26–3.94 (m, 2 H, –OCH_2CH=), 3.73–3.07 (m, 6 H, C*H* of sugar), and 1.85 (s, 3 H, CH_3CO).

The reaction of allyl alcohol with 2-acetamido-2-deoxy-D-glucopyranose, carried out as described by Lee and Lee[6], gave allyl 2-acetamido-2-deoxy-α-D-glucopyranoside (**1α**). The product contained traces of the β anomer, but was suitable for use in further synthetic steps. A sample purified by column chromatography had m.p. 175–176° (lit.[6] 172–174°), $[\alpha]_D^{25}$ +154.8° (lit.[6] +148.8°), $[\alpha]_{436}^{25}$ +306° (*c* 1.43, water); ^{1}H-n.m.r. [$(CD_3)_2SO$ plus D_2O]: δ 5.97–5.75 (m, 1 H, =C*H*–), 5.29–5.14 (m, 2 H, CH_2=), 4.69 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.57–3.50 (3 m, total 8 H, –OCH_2CH= and C*H* of sugar), and 1.84 (s, 3 H, CH_3CO).

*1-Propenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside* (**3β**). — Pure **1β** (3.0 g, 11.4 mmol) was heated with potassium *tert*-butoxide in methyl sulfoxide according to the general procedure for isomerizations. When conversion to the propenyl glycoside **2β** was complete, the reaction mixture was cooled, and pyridine and acetic anhydride were added. On conclusion of the acetylation the reaction mixture was poured into ice–water. Isolation by conventional extraction with chloroform and purification by column chromatography gave 3.27 g (73.5%) of the title compound. Crystallization from abs. ethanol provided needles, m.p. 180.5–181.5°, $[\alpha]_D^{25}$ −11.3°, $[\alpha]_{436}^{25}$ −23.0° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): see Table I; in addition, the spectrum showed δ 6.18–6.15 (dq, 1 H, *J* 6.3 and 1.5 Hz, –OC*H*=), 6.03 (d, 1 H, $J_{2,NH}$ 8.8 Hz, N*H*), 4.61 [quintet (degenerate dq), 1 H, *J* 6.3 and 6.3 Hz, =C*H*–], 2.08, 2.05, 2.03, and 1.96 (4 s, 3 H ea., CH_3CO), and 1.57 (dd, 3 H, *J* 1.5 and 6.3 Hz, CH_3CH=).

Anal. Calc. for $C_{17}H_{25}NO_9$ (387.39): C, 52.71; H, 6.51; N, 3.62. Found: C, 52.69; H, 6.50; N, 3.69.

Isomerization and acetylation of allyl 2-acetamido-2-deoxy-α-D-glucopyranoside. — Compound **1α** was treated as just described for the β anomer. Column chromatography gave syrupy material characterized as *1-propenyl 2-acetamido-2,3,4-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside* (**3α**) from t.l.c. and n.m.r. data. The preparation showed $[\alpha]_D^{25}$ +88.4°, $[\alpha]_{436}^{25}$ +173.6° (*c* 0.5, chloroform); the ^{1}H-n.m.r. spectrum ($CDCl_3$) was very similar to that of **3β**, except that the signal for H-1 appeared at δ 5.09 (d, $J_{1,2}$ 3.7 Hz).

*Allyl and 1-propenyl 3,4,6-tri-*O*-benzyl glycosides.* — Benzylation of **1β** by the general procedure gave allyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**4β**), analytically pure after recrystallization from methanol; $[\alpha]_D^{25}$ +11.1°, $[\alpha]_{436}^{25}$ +22.2° (*c* 1.3, chloroform). A reproducible m.p. of 146.5–149° was observed when the melting-point bath was preheated to 130° before insertion of the

sample, and the rate of increase in temperature was controlled at ~2° per min. Compound **4β** was initially reported[10] to have m.p. 133–135°, $[\alpha]_D$ +7°; more-recent figures are[4] m.p. 150–151°, $[\alpha]_D^{22}$ +21°; and[5] m.p. 150–151°, $[\alpha]_D$ +8.3°.

Allyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside (**4α**), similarly prepared from **1α**, was purified by column chromatography, and then recrystallized from methanol–ether. The pure compound had m.p. 136–137°, and $[\alpha]_D^{25}$ +112.8°, $[\alpha]_{436}^{25}$ +201° (*c* 0.5, chloroform). The previously reported values[11] are m.p. 128–130° and $[\alpha]_D^{25}$ +92°.

1-Propenyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranoside[4] (**5β**) and its α anomer[4] (**5α**) were obtained from **4β** and **4α**, respectively, by the general procedure for isomerization. The physical constants were as given by the referenced authors.

*Allyl 2-acetamido-4,6-*O*-benzylidene-3-*O*-(2-butenyl)-2-deoxy-β-*D*-glucopyranoside* (**7β**). — In a slight modification of the general procedure for benzylations, allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside[5,12] (**6β**; 9.15 g, 26.2 mmol) was treated with 1-bromo-2-butene (9 mL, 87 mmol), barium oxide (18 g), and barium hydroxide octahydrate (6.3 g). The reaction was conducted at room temperature, and it was complete after 1.5 h. Crystallization of the crude product from methanol gave 10.25 g (97%) of **7β** as fine needles. The compound melted with decomposition over the range 230–245°; $[\alpha]_D^{25}$ −16.6°, $[\alpha]_{436}^{25}$ −29.3° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$; signals diagnostic of groups added to the precursor **1β**): δ 7.50–7.35 (m, 5 H, Ph-H), 5.81–5.48 (m, 2 H, –C*H*=C*H*–), 5.54 (s, 1 H, PhC*H*), 5.15 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), and 1.70–1.58 (m, 3 H, CH_3–CH=).

Anal. Calc. for $C_{22}H_{29}NO_6$ (403.48): C, 65.49; H, 7.24; N, 3.47. Found: C, 65.74; H, 6.96; N, 3.32.

*Allyl 2-acetamido-4,6-*O*-benzylidene-3-*O*-(2-butenyl)-2-deoxy-α-*D*-glucopyranoside* (**7α**) was prepared in the same way as its β anomer, from allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside[11] (**6α**). Compound **7α** had m.p. 203–204°, $[\alpha]_D^{25}$ +162.2°, $[\alpha]_{436}^{25}$ +302° (*c* 0.6, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.47–7.35 (m, 5 H, Ph-H), 6.00–5.82 (m, 2 H, –C*H*=C*H*–), 5.57 (s, 1 H, PhC*H*), 4.90 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), and 1.73–1.58 (m, 3 H, CH_3CH=).

Anal. Calc. for $C_{22}H_{29}NO_6$ (403.48): C, 65.49; H, 7.24; N, 3.47. Found: C, 65.44; H, 7.28; N, 3.26.

*Allyl 2-acetamido-3-*O*-(2-butenyl)-2-deoxy-β-*D*-glucopyranoside* (**8β**). — Pure **7β** (8.7 g, 21.6 mmol) was dissolved in 175 mL of 3:2 (v/v) acetic acid–water, the solution was heated at 70°, and the reaction was monitored by t.l.c. Heating was discontinued as soon as hydrolysis was complete (~1 h), because prolongation of the reaction time was found to reduce the yield of product. The mixture was evaporated to dryness under diminished pressure, and then several portions of water were successively added and evaporated off. Crystallization of the residue from ethyl acetate and recrystallization from ethanol gave 6.38 g (94%) of **8β** as fine needles, m.p. 168–169.5°, $[\alpha]_D^{25}$ −33.3°, $[\alpha]_{436}^{25}$ −67.7° (*c* 0.88, ethanol); ^{1}H-n.m.r.

[$(CD_3)_2SO$ plus 2 drops D_2O]: signals for Ph-H and PhC*H* (compare **7β**) were absent; δ 4.35 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1).

Anal. Calc. for $C_{15}H_{25}NO_6$ (315.37): C, 57.13; H, 7.99; N, 4.44. Found: C, 57.07; H, 7.95; N, 4.36.

*Allyl 2-acetamido-3-*O*-(2-butenyl)-2-deoxy-α-*D*-glucopyranoside* (**8α**) was obtained from **7α**, in 90% yield, by the procedure just described for the β anomer. The m.p. was 136–137°, $[\alpha]_D^{25}$ +108.6°, $[\alpha]_{436}^{25}$ +209° (*c* 0.84, chloroform); ^{1}H-n.m.r. [$(CD_3)_2SO$ plus 2 drops D_2O]: signals for Ph-H and PhC*H* (compare **7α**) were absent; δ 4.65 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1).

Anal. Calc. for $C_{15}H_{25}NO_6$ (315.37): C, 57.13; H, 7.99; N, 4.44. Found: C, 56.97; H, 8.07; N, 4.54.

*Allyl 2-acetamido-4,6-di-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-*D*-glucopyranoside* (**9β**). — Application of the general procedure for benzylations to compound **8β** (4.60 g, 14.6 mmol) gave a residue containing some high-boiling, aromatic impurities. These were removed by suspending the material in hexane (Skellysolve B), collecting it on a filter, and washing with additional hexane. After drying, the washed, crude product weighed 6.74 g (93%). It crystallized from methanol as very long needles, m.p. 149–151°, $[\alpha]_D^{25}$ +9.9°, $[\alpha]_{436}^{25}$ +20.3° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.34–7.20 (m, 10 H, Ph-H), 4.91 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.79 and 4.55 (q_{AB}, 2 H, *J* 11.0 Hz, PhCH_2), 4.61 and 4.54 (q_{AB}, 2 H, *J* 12.5 Hz, PhCH_2).

Anal. Calc. for $C_{29}H_{37}NO_6$ (495.62): C, 70.28; H, 7.53; N, 2.83. Found: C, 70.28; H, 7.39; N, 2.47.

*Allyl 2-acetamido-4,6-di-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-α-*D*-glucopyranoside* (**9α**). — Benzylation of **8α** (0.29 g, 0.92 mmol) gave the title compound, which was purified as just described for **9β**. The yield of recrystallized **9α** was 0.35 g (77%); m.p. 130–131°, $[\alpha]_D^{25}$ +77.6°, $[\alpha]_{436}^{25}$ +162.4° (*c* 0.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.29–6.98 (m, 10 H, Ph-H), 4.84 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), and 4.81–4.26 (2 q_{AB}, 4 H, PhCH_2).

Anal. Calc. for $C_{29}H_{37}NO_6$ (495.62): C, 70.28; H, 7.53; N, 2.83. Found: C, 70.24; H, 7.71; N, 2.77.

*1-Propenyl 2-acetamido-4,6-di-*O*-benzyl-2-deoxy-β-*D*-glucopyranoside* (**10**). — Allyl glycoside **9β** (7.29 g, 14.7 mmol) was subjected to the general procedure for isomerizations. On dilution of the mixture with water, the crude title compound (5.7 g, 88%) crystallized. Recrystallization from ethyl acetate–hexane yielded a portion of the compound in pure form, and the remainder was recovered by column chromatography (9:1 dichloromethane–methanol). The pure substance melted at 139.5–140.5°, and had $[\alpha]_D^{25}$ 0.0°, $[\alpha]_{436}^{25}$ +1.6° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): signals for the butenyl group were absent; δ 6.20–6.17 (m, 1 H, –OC*H*=), 4.67 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.69–4.51 (m, 1 H, =C*H*–), 1.64 (broad s, 1 H, O*H*), and 1.59 (dd, 3 H, *J* 1.5 and 7.0 Hz, =CHCH_3).

Anal. Calc. for $C_{25}H_{31}NO_6$ (441.52): C, 68.01; H, 7.08; N, 3.17. Found: C, 67.93; H, 7.12; N, 2.89.

*1-Propenyl 2-acetamido-3-*O*-acetyl-4,6-di-*O*-benzyl-β-*D*-glucopyranoside* (**11**). —

The acetylation of **10** (1.75 g, 3.97 mmol) (see General Methods) gave 1.83 g (95%) of the crude title-compound. It crystallized from dichloromethane–hexane as very fine needles, m.p. 160.5–161.5°, $[\alpha]_D^{25}$ −30.2°, $[\alpha]_{436}^{25}$ −63.2° (*c* 1.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.97 (s, 3 H, CH_3CO).

Anal. Calc. for $C_{27}H_{33}NO_7$ (483.56): C, 67.07; H, 6.88; N, 2.90. Found: C, 67.06; H, 6.92; N, 2.59.

*Crude allyl 2-acetamido-2-deoxy-4-*O*-(2-tetrahydropyranyl)-β-*D*-glucopyranoside* (**14**). — Allyl 2-acetamido-3,6-di-*O*-benzoyl-2-deoxy-β-D-glucopyranoside[14] (**12**; 5 g, 10.6 mmol) in chloroform (50 mL) was treated with 2,3-dihydro-4*H*-pyran (4 mL) and *p*-toluenesulfonic acid (60 mg), and kept at room temperature. When the reaction was complete (30 min), the solution was washed with aqueous sodium hydrogencarbonate and water, and dried. Evaporation of the chloroform under diminished pressure left a residue of crude *allyl 2-acetamido-3,6-di-*O*-benzoyl-2-deoxy-4-*O*-(2-tetrahydropyranyl)-β-*D*-glucopyranoside* (**13**).

The syrupy **13** was dissolved in 50 mL of methanol, 30 mL of 0.2M methanolic sodium methoxide was added, and the mixture was boiled for 3 h under reflux. The methanol was evaporated off under diminished pressure, the residue was taken up in a small volume of chloroform, and the solution was extracted thrice with water. The product was recovered by evaporation of the aqueous extract. It was then dissolved in methanol for deionization by Amberlite IRC-50 (pyridinium form). (Direct deionization of the aqueous solution should be feasible.) Evaporation of the filtrate from the resin-treatment gave 3.7 g (100%) of **14** as a white solid; ^{1}H-n.m.r. (D_2O) was essentially that of **1β**, with the addition of signals for the tetrahydropyranyl group from δ 2.0–1.0.

*Allyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2-tetrahydropyranyl)-β-*D*-glucopyranoside* (**15**). — The solid material obtained by benzylation of 3.7 g of **14** was chromatographed on a column of silica gel. This afforded a major fraction, consisting of the title compound **15**, and a minor fraction of lower mobility. The yield of **15** was 4.7 g (83%). After recrystallization from ethyl acetate–hexane, the compound had m.p. 156–157°, $[\alpha]_D^{25}$ +28.6°, $[\alpha]_{436}^{25}$ +60° (*c* 0.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.43–7.20 (m, 10 H, Ph-H), 4.68 and 4.59 (2 q_{AB}, 2 H ea., $PhCH_2$).

Anal. Calc. for $C_{30}H_{39}NO_7$ (525.64): C, 68.55; H, 7.48; N, 2.66. Found: C, 68.71; H, 7.43; N, 2.32.

The substance of the minor fraction (440 mg) was recrystallized from ethyl acetate–hexane. It melted at 165–165.5° and had $[\alpha]_D^{25}$ +53.4°, $[\alpha]_{436}^{25}$ +110° (*c* 0.5, chloroform). The ^{1}H-n.m.r. spectrum and elemental analysis of the compound showed it to be a monobenzyl derivative of **14**. It could be either the 6-benzyl or the 3-benzyl ether, most probably the former.

*1-Propenyl 2-acetamido-4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-β-*D*-glucopyranoside* (**18**). — Compound **15** (4.7 g) was dissolved in a mixture of methanol (40 mL) and 3:2 (v/v) acetic acid–water (80 mL). The solution was kept for 2 h at 50°, then evaporated under diminished pressure to give 3.5 g (89%) of allyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**16**). After recrystallization from ethyl

acetate–hexane, the preparation showed m.p. 140.5–141° (lit.[4] 145–146°), $[\alpha]_D^{25}$ −10.6°, $[\alpha]_{436}^{25}$ −16.4° (*c* 0.5, chloroform) (lit.[4] $[\alpha]_D$ −10°).

Isomerization of the allyl group of **16** gave 1-propenyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**17**). This likewise was recrystallized from ethyl acetate–hexane; m.p. 153.5–154.5° (lit.[4] 150–152°), $[\alpha]_D^{25}$ −4.0°, $[\alpha]_{436}^{25}$ −5.6° (*c* 0.5, chloroform) (lit.[4] $[\alpha]_D$ −6°).

Acetylation of **17** (700 mg) by the procedure previously outlined yielded 686 mg (89%) of the title compound **18**. Recrystallization from ethyl acetate–hexane gave pure material having m.p. 160–161°, $[\alpha]_D^{25}$ +20.4°, $[\alpha]_{436}^{25}$ +46.6° (*c* 0.5, chloroform); ν_{max}^{Nujol} 3270 (N–H), 1740 (ester C=O), 1650 and 1540 cm^{-1} (amide); ^{1}H-n.m.r. ($CDCl_3$): see Table I; in addition, the spectrum showed δ 7.38–7.21 (m, 10 H, Ph-H), 6.15 (m, 1 H, OC*H*=), 5.77 (d, 1 H, $J_{2,NH}$ 8.0 Hz, N*H*), 4.66–4.48 (m, 5 H, PhCH_2 and =C*H*–), 1.89 and 1.88 (2 s, 3 H ea., CH_3CO), and 1.57 (dd, 3 H, *J* 1.8 and 6.6 Hz, CH_3CH=).

Anal. Calc. for $C_{27}H_{33}NO_7$ (483.56): C, 67.07; H, 6.88; N, 2.90. Found: C, 66.97; H, 6.65; N, 2.48.

Procedure for generation of the oxazolines. — The propenyl glycoside was dissolved in acetonitrile (dried over molecular sieves) to give a 0.15M solution. One molar portion of yellow mercuric oxide and 1.5 molar portions of mercuric chloride were added, and the mixture was stirred and heated under reflux, with protection from atmospheric moisture. To monitor the reaction, a sample for t.l.c. was withdrawn from time to time, and discharged into 2:1 acetone–water. This treatment causes hydrolysis of propenyl glycosides, but does not affect oxazolines. Consequently, t.l.c. plates of the early samples showed two spots, the faster-moving one due to oxazoline, and the slower-moving one due to the hydrolysis product of the propenyl glycoside. When the latter was absent, or present only in traces, the reaction was considered complete.

The mixture was filtered through Celite, and the filter cake washed with acetonitrile. Evaporation of the filtrate gave a residue, which was dissolved in dichloromethane. The dichloromethane solution was washed twice with saturated aqueous potassium iodide and twice with water, dried, and evaporated to dryness. The syrupy oxazoline so obtained was pure enough for use in synthetic work.

The oxazolines listed below were prepared by the procedure outlined here. All were sufficiently stable to withstand chromatography on columns of silica gel, and analytical samples were obtained in that way.

*2-Methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-*D*-glucopyrano)-[2,1-*d*]-2-oxazoline* (**19**), from propenyl glycoside **3β** (reaction time 40 min), had $[\alpha]_D^{25}$ +7.2°, $[\alpha]_{436}^{25}$ +10.3° (*c* 2.3, chloroform), as compared with lit.[26] $[\alpha]_D^{20}$ +10 ±2°, and lit.[2] $[\alpha]_D^{27}$ +16.3°. A sample prepared by the method of Matta and Bahl[3] had $[\alpha]_D^{25}$ +7.5 and $[\alpha]_{436}^{25}$ +9.6° (chloroform). The ^{1}H-n.m.r. data are given in Table I; in addition, the spectrum showed δ 2.12, 2.10, and 2.08 (3 s, 3 H ea., CH_3CO); ν_{max}^{KBr} no absorption at 1510 or 3420 cm^{-1}.

*2-Methyl-(3-*O*-acetyl-4,6-di-*O*-benzyl-1,2-dideoxy-α-*D*-glucopyrano)-[2,1-*d*]-2-*

oxazoline (**20**), from propenyl glycoside **11** (reaction time 15 min), had $[\alpha]_D^{25}$ +52.3°, $[\alpha]_{436}^{25}$ +99.5° (*c* 1.0, chloroform) (lit.[5] $[\alpha]_D^{23}$ +59°); ν_{max}^{KBr} no absorption at 1510 or 3420 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 7.37–7.20 (m, 10 H, Ph-H), 5.99 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1), 5.44 (m, 1 H, H-3), 4.79 and 4.51 (q_{AB}, 2 H, PhCH_2), 4.42 and 4.36 (q_{AB}, 2 H, PhCH_2), 4.16–3.32 (m, 5 H, C*H* of sugar), 2.06 (s, 3 H, CH_3CO), and 2.06 (d, 3 H, J_{2,CH_3} 1.8 Hz, CCH_3).

Anal. Calc. for $C_{24}H_{27}NO_6$ (425.48): C, 67.75; H, 6.40; N, 3.29. Found: C, 67.43; H, 6.57; N, 3.24.

*2-Methyl-(4-*O*-acetyl-3,6-di-*O*-benzyl-1,2-dideoxy-α-*D*-glucopyrano)-[2,1-*d*]-2-oxazoline* (**21**), from propenyl glycoside **18** (reaction time 25 min), had $[\alpha]_D^{25}$ +17.1°, $[\alpha]_{436}^{25}$ +27.1° (*c* 0.7, chloroform) (lit.[5] $[\alpha]_D$ −4.9°, lit.[4] $[\alpha]_D^{22}$ +9°; the latter value was obtained with a sample of doubtful purity); ν_{max}^{film} 1730 (C=O) and 1665 cm^{-1} (C=N), no absorption at 1510 or 3420 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): see Table I; in addition, the spectrum showed δ 7.39–7.23 (m, 10 H, Ph-H), 4.85–4.53 (2 q_{AB}, 2 H ea., PhCH_2), and 1.98 (s, 3 H, CH_3CO).

Anal. Calc. for $C_{24}H_{27}NO_6$ (425.48): C, 67.75; H, 6.40; N, 3.29. Found: C, 67.43; H, 6.32; N, 3.05.

*2-Methyl-(3,4,6-tri-*O*-benzyl-1,2-dideoxy-α-*D*-glucopyrano)-[2,1-*d*]-2-oxazoline* (**22**), from propenyl glycoside **5β** (reaction time 5 min), had $[\alpha]_D^{25}$ +29.7°, $[\alpha]_{436}^{25}$ +57.9° (*c* 1.9, chloroform) (lit.[5] $[\alpha]_D$ +33.5°); ν_{max}^{KBr} no absorption at 1510 or 3420 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 6.01 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1) and 2.03 (d, 3 H, J_{2,CH_3} 1.5 Hz, C-CH_3). Refrigeration of a dichloromethane–pentane solution of **22** gave a crystalline substance[4], but this consisted mostly of a transformation product having a lower R_F value on silica gel than **22**.

Anal. Calc. for $C_{29}H_{31}NO_5$ (473.57): C, 73.55; H, 6.60; N, 2.96. Found: C, 73.89; H, 6.46; N, 2.52.

ACKNOWLEDGMENTS

This work was supported by the College of Agricultural and Life Sciences, University of Wisconsin–Madison, and by Grant No. AM-10588 from The National Institute of Arthritis, Metabolism, and Digestive Diseases, N.I.H. The Biochemistry 270-MHz NMR Facility was made possible by grants from the Graduate School and the National Science Foundation (No. BMS74-23826). We thank Professor W. A. Gibbons for making this facility available, and Mr. Sean Hehir for skilfully recording spectra. We also thank Prof. N. V. Riggs, Armidale, Australia, for helpful discussion.

REFERENCES

1 M. A. Nashed, C. W. Slife, M. Kiso, and L. Anderson, *Carbohydr. Res.*, 58 (1977) c13–c16.
2 R. U. Lemieux and H. Driguez, *J. Am. Chem. Soc.*, 97 (1975) 4063–4069.
3 K. L. Matta and O. P. Bahl, *Carbohydr. Res.*, 21 (1972) 460–464.
4 C. D. Warren, M. A. E. Shaban, and R. W. Jeanloz, *Carbohydr. Res.*, 59 (1977) 427–448.

5 P. ROLLIN AND P. SINAŸ, *J. Chem. Soc., Perkin Trans. 1*, (1977) 2513–2517.
6 R. T. LEE AND Y. C. LEE, *Carbohydr. Res.*, 37 (1974) 193–201.
7 M. BERGMANN AND L. ZERVAS, *Ber.*, 64B (1931) 975–980.
8 M. KISO AND L. ANDERSON, *Carbohydr. Res.*, 72 (1979) c12–c14.
9 J. GIGG AND R. GIGG, *J. Chem. Soc., C*, (1966) 82–86.
10 P. A. GENT, R. GIGG, AND R. CONANT, *J. Chem. Soc., Perkin Trans. 1*, (1973) 1858–1863.
11 C. D. WARREN AND R. W. JEANLOZ, *Carbohydr. Res.*, 53 (1977) 67–84.
12 M. A. E. SHABAN, V. N. REINHOLD, AND R. W. JEANLOZ, *Carbohydr. Res.*, 59 (1977) 213–233.
13 P. A. GENT, R. GIGG, AND R. CONANT, *J. Chem. Soc., Perkin Trans. 1*, (1972) 1535–1542.
13a J.-M. PETIT, J.-C. JACQUINET, AND P. SINAŸ, *Carbohydr. Res.*, 82 (1980) 130–134.
14 M. A. NASHED, *Carbohydr. Res.*, 71 (1979) 299–304.
15 R. GIGG AND C. D. WARREN, *J. Chem. Soc., C*, (1968) 1903–1911.
16 T. ISHIKAWA AND H. G. FLETCHER, JR., *J. Org. Chem.*, 34 (1969) 563–571.
17 M. A. E. SHABAN AND R. W. JEANLOZ, *Carbohydr. Res.*, 52 (1976) 103–114; 115–127.
18 J. E. WALLACE AND L. R. SCHROEDER, *J. Chem. Soc., Perkin Trans. 1*, (1976) 1938–1941.
19 K. L. MATTA AND J. J. BARLOW, *Carbohydr. Res.*, 53 (1977) 47–56.
20 E. WALKER-NASIR AND R. W. JEANLOZ, *Carbohydr. Res.*, 68 (1979) 343–363.
21 R. HARRISON AND H. G. FLETCHER, JR., *J. Org. Chem.*, 30 (1965) 2317–2321.
22 D. HORTON, *Methods Carbohydr. Chem.*, 6 (1972) 282–285.
23 N. PRAVDIĆ, I. FRANJIĆ-MIHALIĆ, AND B. DANILOV, *Carbohydr. Res.*, 45 (1975) 302–306.
24 J. M. MCLAREN, R. V. STICK, AND S. WEBB, *Aust. J. Chem.*, 30 (1977) 2689–2693.
25 E. W. THOMAS, *Carbohydr. Res.*, 13 (1970) 225–228.
26 A. YA. KHORLIN, M. L. SHUL'MAN, S. E. ZURABYAN, I. M. PRIVALOVA, AND YU. L. KOPAEVICH, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1968) 1987–1990.