crystallize. The compound (200 mg) was dissolved in absolute methanol (10 ml) and was deacetylated with 1 *N* barium methoxide (0.1 ml) as described above. The solution was neutralized by stirring with Dowex 50W-X8, H^+ form, and the residue resulting from the evaporation of the filtrate was crystallized from methanol–ether and recrystallized from water–methanol–ether (1:5:20): yield 80 mg of VII; mp 204–205°; $[\alpha]^{18}D$ +38.5° (*c* 0.9, water). The ir spectrum showed bands at 3.0 (OH), 6.1, and 6.45 (amide), 11.2 (β-glycoside), and 11.45 μ (galactopyranose ring); tlc (benzene–methanol, 2:3), *R* (lactose) 0.5 and *R* (galactose) 0.31.

Anal. Calcd for $C_{14}H_{25}NO_{11}$: C, 43.86; H, 6.57; N, 3.64. Found: C, 43.62; H, 6.75; N, 3.58.

1,2,3,4-Tetra-*O*-acetyl-6-*O*-trityl-D-galactopyranose[6,11] was prepared by treating 6-*O*-trityl-D-galactopyranose[11] (10 g) with acetic anhydride (100 ml) in pyridine (300 ml) at room temperature for 48 hr. The reaction mixture was evaporated *in vacuo* and coevaporated several times with toluene. The product was eluted from a silica gel column with benzene–ethyl acetate, 150:30, and crystallized from isopropyl alcohol (10 ml) and hexane (100 ml): yield 10 g; mp 94–96°; $[\alpha]^{22}D$ −19.5° (*c* 1, chloroform); tlc (benzene–methanol, 8:2) R_f 0.85 and *R* (pentaacetylgalactose) 1.1, The nmr spectrum showed the expected ratio between aromatic and acetyl protons (15:12).

Anal. Calcd for $C_{33}H_{34}O_{10}$: C, 67.10; H, 5.80. Found: C, 67.09; H, 5.73.

1,2,3,4-Tetra-*O*-acetyl-D-galactopyranose[8] was now prepared in chromatographically pure form. After detritylation of the preceding compound with hydrogen bromide,[12] the residue resulting from the evaporation of the acetic acid *in vacuo* was chromatographed on a column of silica gel. Methylene chloride–ether (85:15) eluted an oil which showed a single spot on tlc, *R* (trityl derivative) 0.66. The nmr spectrum showed signals of four acetyl groups.

1,2,3,4-Tetra-*O*-acetyl-6-*O*-(2-deoxy-2-dichloroacetamido-3,4,-6-tri-*O*-benzoyl-β-D-galactopyranosyl)-D-galactopyranose (VIII).—The reaction of 3 mmol of III with 4 mmol of 1,2,3,4-tetraacetylgalactose and 1.8 mmol of mercuric cyanide was carried out as described for V. The residue (3.1 g) resulting from the evaporation of the chloroform was dissolved in methylene chloride and passed through a silica gel column (160 g). The product was eluted with methylene chloride–ether (94:6). It was crystallized from ether and recrystallized from alcohol: yield 2.1 g (75.5%); mp 156–157°; $[\alpha]^{23}D$ +4.0° (*c* 1.1, chloroform); tlc (benzene–methanol, 9:1), R_V 0.89. The nmr spectrum showed signals of 15 aromatic, 1 dichloroacetyl, and 12 acetyl protons.

Anal. Calcd for $C_{43}H_{43}Cl_2NO_{18}$: C, 55.37; H, 4.65; Cl, 7.60. Found: C, 55.23; H, 4.62; Cl, 7.38.

1,2,3,4-Tetra-*O*-acetyl-6-*O*-(2-acetamido-2-deoxy-3,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-D-galactopyranose (IX).—A solution of VIII (0.400 g) in warm alcohol (150 ml) was hydrogenated with 10% palladium on charcoal at 55 psi during 48 hr. The residue resulting from the evaporation of the filtrate was purified by chromatography on silica gel (30 g), using methylene chloride–ether (85:15) as eluent: yield 0.275 g (75%); tlc, R_{VIII} 0.85. The nmr spectrum showed signals of 15 aromatic and 15 acetyl protons (one more acetyl group than in VIII, but no signal for a dichloroacetyl proton). On deacylation, the resulting product was identical in every respect with VII.

Registry No.—I, 20072-85-9; II, 20072-86-0; V, 20072-87-1; VI, 20072-88-2; VII, 20072-89-3; 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-D-galactopyranose, 20072-90-6; VIII, 20072-91-7.

(11) M. Onuki, *Bull. Inst. Phys. Chem. Res.* (Tokyo), **12**, 614 (1933); *Chem. Abstr.*, **28**, 113 (1934).

(12) B. Helferich, L. Moog, and A. Junger, *Chem. Ber.*, **58**, 872 (1925).

2-Oxazolidinone Derivatives of D-Glucose and Glycolaldehyde[1]

W. E. DICK, JR., D. WEISLEDER, AND J. E. HODGE

Northern Regional Research Laboratory,[2] Peoria, Illinois 61604

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A 4-hydroxy-3-phenyl-5-(D-*arabino*-1,2,3,4-tetrahydroxybutyl)-2-oxazolidinone structure (**3**) is established for the compound previously registered as 2-carbanilino-D-glucose. Hydrolysis of *N*-(2-*O*-phenylcarbamoyl-β-D-glucopyranosyl)piperidine first forms 2-*O*-phenylcarbamoyl-D-glucopyranose which rapidly converts into **3** in alkaline solution. The mechanism proposed for this cyclization requires attack of the amido nitrogen on the adjacent carbonyl group. Cyclization of glycolaldehyde carbanilate to 4-hydroxy-3-phenyl-2-oxazolidinone in high yield at pH 4 requires a free carbonyl group. Treatment of **3** with methanolic hydrogen chloride produces an α-D-glucofurano-2-oxazolidinone derivative, 5-(D-*glycero*-1,2-dihydroxyethyl)tetrahydro-6-hydroxy-3-phenylfuro[2,3-*d*]oxazol-2-(3*H*)-one, isolated as a triacetate. The structure is assigned by nmr analysis.

In 1952, Hodge and Rist[3] reported the synthesis of a compound provisionally identified as 2-*O*-phenylcarbamoyl-D-glucose. It was isolated from *N*-(2-*O*-phenylcarbamoyl-β-D-glucopyranosyl)piperidine (**1b**) after hydrolysis with hydrochloric acid and neutralization with silver carbonate. The product gave the empirical formula of a hexose monocarbanilate and was not characterized beyond noting an atypical minimal mutarotation and low reducing power toward hot Fehling solution.

Investigations published since 1952 have demonstrated that the phenylcarbamoyl ester is a poor blocking group. Although these esters are easily prepared in crystalline form and are stable to hydrolysis,[4,5] they undergo acyl migrations in basic solutions[6] and readily cyclize[7-9] by displacements of sensitive neighboring groups. Because the urethan radical is an ambident nucleophile, two cyclization paths are available. Although a basic environment promotes formation of a 2-oxazolidinone by preferential nitrogen participation, an acidic medium favors formation of an unstable anil by carbonyl oxygen participation. Such selective displacements have been exploited by Baker, *et al.*, and others[10] to introduce nitrogen, oxygen, or

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(2) This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

(3) J. E. Hodge and C. E. Rist, *J. Amer. Chem. Soc.*, **74**, 1498 (1952).

(4) W. M. Hearon in "Methods in Carbohydrate Chemistry," Vol. 2, R. L. Whistler and M. L. Wolfrom, Ed., Academic Press, New York, N. Y., 1963, pp 239–241.

(5) H. Bredereck, A. Wagner, G. Faber, W. Huber, G. Immel, and H. Kreiselmeier, *Chem. Ber.*, **91**, 2819 (1958).

(6) H. O. Bouveng, *Acta Chem. Scand.*, **15**, 87, 96 (1961).

(7) M. E. Dyen and D. Swern, *Chem. Rev.*, **67**, 197 (1967).

(8) F. L. Scott, R. E. Glick, and S. Winstein, *Experientia*, **13**, 183 (1957).

(9) F. L. Scott and D. F. Fenton, *Tetrahedron Lett.*, 1681 (1964).

(10) B. R. Baker, K. Hewson, L. Goodman, and A. Benitez, *J. Amer. Chem. Soc.*, **80**, 6577 (1958); B. R. Baker and T. Neilson, *J. Org. Chem.*, **29**, 1057 (1964), and references cited therein.

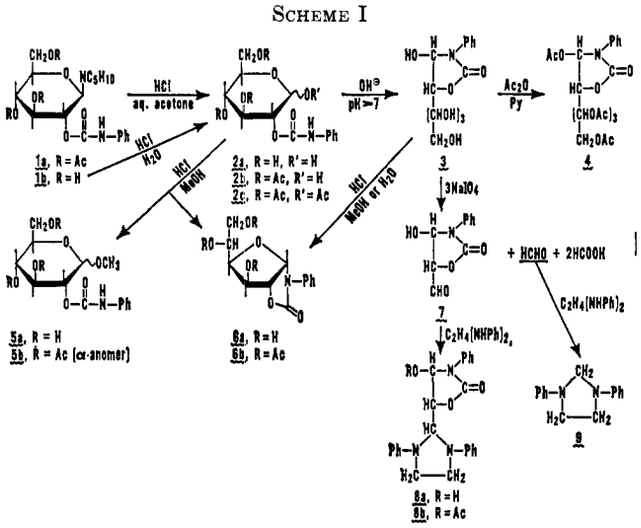
sulfur into selected nucleosides *via* cyclic intermediates (including 2-oxazolidinones) generated from neighboring urethano, ureido, or thiourethano substituents. Carbohydrate 2-oxazolidinones have also been prepared by indirect routes, often involving eliminations from carbobenzoxy derivatives of amino sugars.[11-17]

The literature cited above and the reported N cyclization of an acyloin during carbanilation[18] suggested that the compound of Hodge and Rist[3] may have undergone such a cyclization. The low reducing power, limited mutarotation, and absence of an amide II band in the ir spectrum of the compound supported this view. These unusual properties were sufficient to warrant further investigation.

Results and Discussion

The aqueous hydrolysis of **1b** (derived by deacetylation of **1a**) was monitored chromatographically (tlc and glpc) for 48 hr. Hydrolysis was complete within 24 hr and three products were identified (Scheme I).

SCHEME I



The major product in the acidic hydrolysate was the anticipated 2-*O*-phenylcarbamoyl-D-glucopyranose (**2a**). Smaller amounts of the oxazolidinone open-chain form (**3**) were present with still smaller amounts of the bicyclic oxazolidinone-D-glucofuranose derivative (**6a**). Increases in both temperature of hydrolysis and concentrations of acid caused a marked increase in he proportion of **6a** relative to **2a** and **3** (Table I).

The concentration of the reducing pyranose 2-carbanilate (**2a**) diminished slowly during the final 24 hr with a corresponding increase of **3**. At any given time the composition could be fixed by neutralizing the hydrolysis mixture with a weakly basic ion-exchange resin. The product mixtures were stable for 6 months or longer in the freezer, but they converted slowly into the oxazolidinone form (**3**) within several days at room temperature. If, however, the isolated product mixtures were made alkaline, a rapid increase in the rate of cyclization was noted. An 85% conversion into **3** was noted after 15 min at pH 11. This pH is quickly reached during neutralization of the hydrolysate with Ag_2CO_3; thereafter **3** was isolated.[3]

TABLE I

HYDROLYSIS OF **1b** AND VARIATION IN PRODUCT COMPOSITION[a]

Compd	Hydrolyst	Temp, °C	Time, hr	Base	Composn, % 2a[b]	3	6a	5a[b]
1b	0.1 *N* HCl	25	24	IR-45	83	10	8	
			48	IR-45	72	21	6	
			48	Ag_2CO_3	8	86	6	
1b	IR-120 (H^+) in aqueous acetone	25	20		67	32		
2a	H_2O	25	0.25	$NaHCO_3$	75	25		
			0.25	Na_2CO_3	15	80	5	
2a	0.5 *N* HCl	100	3	C_5H_5N	48	4	48	
2a	2% MeOH-HCl	25	48	IR-45			41	59
3	0.5 *N* HCl	100	3	IR-45		<5	>95	
3	2% MeOH-HCl	25	24	IR-45		<5	>95	

[a] Glpc of pertrimethylsilyl ethers at 200° with 3% JXR on Gas Chrom Q. [b] Sum of the α-D and β-D forms.

The identity of syrupy **2a** was confirmed by characterization of a crystalline fraction isolated after acetylation in pyridine. The physical properties and nmr spectrum were identical with those previously determined for a reference sample of 2-*O*-phenylcarbamoyl-1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (**2c**).

The hexose monocarbanilate reported by Hodge and Rist[3] proved to be 4-hydroxy-3-phenyl-5-(D-*arabino*-1,2,3,4-tetrahydroxybutyl)-2-oxazolidinone[19,20] (**3**). Structural assignments for **3** and its pentaacetate (**4**) were suggested by analyses of their nmr spectra. Application of double-resonance techniques established the spectral contributions of each alkyl chain proton. Chemical shifts and first-order coupling constants representing those portions of the spectra amenable to analysis are listed in Tables II and III.

TABLE II

CHEMICAL SHIFT DATA[a] FOR 2-OXAZOLIDINONE COMPOUNDS

Proton[b]	3[c]	4[d]	8a[c]	8b[d]	14a[c]	14b[d]
H-2′			3.99	3.93		
H-4	4.37	3.51	4.44	3.48	4.29	3.34
H-5	5.60	5.32	5.41	5.14	5.58	5.42
H-5′					5.95	5.76
H-6	6.20	4.42				
H-7	6.49[e]	4.51				
H-8		4.83				
H-9		5.76				
H-9′		5.91				
OH-4	3.17		3.35		3.18	
OH-6	4.97					
OH-7	5.48[e]					
OH-8						
OH-9						

[a] On τ scale. [b] Based on the systematic name. [c] In methyl sulfoxide-d_6. [d] In chloroform-*d*. [e] Complex multiplet.

(11) K. Heyns, R. Harrison, and H. Paulsen, *Chem. Ber.*, **100**, 271 (1967).
(12) K. Brendel, P. H. Gross, and H. K. Zimmerman, Jr., *Ann. Chem.*, **691**, 192 (1966).
(13) S. R. Kulkarni and H. K. Zimmerman, Jr., *ibid.*, **684**, 223 (1965).
(14) P. H. Gross, K. Brendel, and H. K. Zimmerman, *Angew. Chem. Intern. Ed. Engl.*, **3**, 379 (1964).
(15) P. H. Gross, K. Brendel, and H. K. Zimmerman, Jr., *Ann. Chem.*, **680**, 159 (1964).
(16) P. R. Steyermark, U. S. Patent 3,120,510 (Feb 4, 1964); *Chem. Abstr.*, **60**, 9349 (1964).
(17) B. R. Baker and J. P. Joseph, *J. Amer. Chem. Soc.*, **77**, 15 (1955).
(18) N. R. Easton, D. R. Cassady, and R. D. Dillard, *J. Org. Chem.*, **27**, 2927 (1962).
(19) An alternative name is (*R*)-1-*C*-(*N*-carboxyanilino)-D-glucitol γ-lactone.
(20) We are grateful to Dr. K. L. Loening, Director of Nomenclature, Chemical Abstracts Service, who suggested the systematic names of **3** and **6a**.

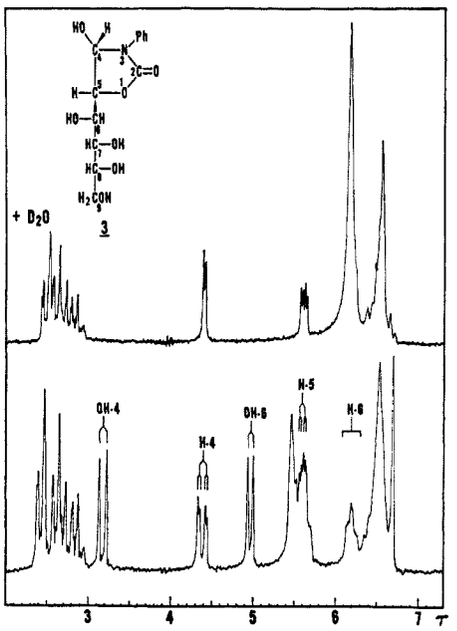


Figure 1.—The low-field portion of the 100-MHz spectrum of **3** in methyl sulfoxide-d_6 (bottom), and with added D_2O (top).

TABLE III

COUPLING CONSTANT DATA FOR 2-OXAZOLIDINONE COMPOUNDS

Coupling constant,[a] J	**3**[b]	**4**[c]	**8a**[b]	**8b**[c]	**14a**[b]	**14b**[c]
2′,5			1.8	1.3		
4,5	2	1	1.5	1.5	2	1.5
4,5′					6	5.5
5,5′					9.5	10.5
5,6	4.5	<1.5				
8,9		~3				
8,9′		~4				
9,9′		~12				
4,OH	9		8.5		8	
6,OH	6					

[a] In hertz. Numerical designations based on the systematic name. [b] In methyl sulfoxide-d_6. [c] In chloroform-d.

The nmr spectrum of **3** in methyl sulfoxide-d_6 is reproduced in Figure 1, before and after addition of D_2O. The integration curve (not included) indicated five hydroxyl groups. The two labeled groups and three others colocated with H-5 were verified by exchange with D_2O. The upper trace shows the simplified spectrum after exchange.

The presence of five acetyl groups in **4** was confirmed by acetyl analysis and by inspection of the integration curve in the methyl proton region of the nmr spectrum. Deshielding of all methine protons, but that of C-5 (C-2 of glucose chain), was observed owing to the presence of acetoxy substituents at these sites.

These spectra deny a 2-*O*-phenylcarbamoyl-D-glucose structure in pyranose, furanose, or acyclic *aldehydo* form. The ring forms would have yielded tetraacetates and the acyclic form a tetra- or hexaacetate. The absence of an amido proton in **3** or **4** was indicated by the lack of amide II bands in the ir spectra and the absence of NH resonances in the nmr spectra. N cyclization of the phenylcarbamoyl group with the adjacent reducing group of the isolated intermediate, 2-*O*-phenylcarbamoyl-D-glucopyranose (**2a**), formed a new hydroxyl group. This accounts for the fifth hydroxyl group observed. The deshielding of H-4 in the 2-oxazolidinone ring results from the combined effects of the vicinal OH-4 (or C-4 acetoxy) and N–Ph groups.

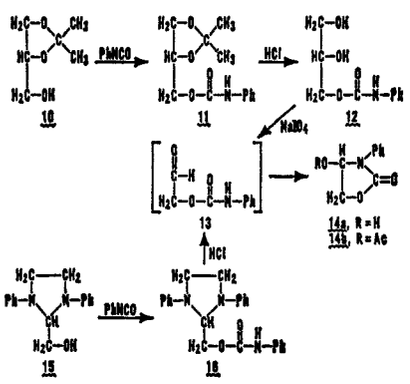
The small coupling constants for the vicinal ring protons (**3**, $J_{4,5}$ = 2 Hz; **4**, $J_{4,5}$ = 1 Hz) are consistent with a *trans* relationship on a five-membered 2-oxazolidinone ring; the configuration at C-4 is therefore *R*. These small values allow confidence in this assignment, although such decisions are questionable when the coupling constant exceeds 2 Hz.[21]

Each mole of **3** consumed 3 mol of $NaIO_4$, yielding 2 mol of formate and 1 mol each of formaldehyde and 5-*aldehydo*-4-hydroxy-3-phenyl-2-oxazolidinone (**7**). Both aldehydes were converted into stable 1,3-diphenyl-2-imidazolidinyl derivatives[22] and isolated. The formaldehyde derivative, 1,3-diphenyl-2-imidazolidine (**9**), was readily identified by comparison with the literature. The other, 4-hydroxy-5-(1′,3′-diphenyl-2′-imidazolidinyl)-3-phenyl-2-oxazolidinone (**8a**), and its derived monoacetate (**8b**) were examined by double-resonance nmr. All chain protons were identified and their coupling constants determined (Tables II and III). The ir spectra displayed the anticipated amide I, ester carbonyl, and phenyl (C=C skeletal and CH out of plane) absorptions. The absence of an amide II band confirmed the survival of the 3-phenyl-2-oxazolidinone ring structure.

The proposed mechanism for the conversion of **2a** into **3** requires that **2a** be in an acyclic form before an irreversible nucleophilic attack by the amido nitrogen. Two diastereoisomeric forms of **3** can be produced having H-4 and H-5 in a *cis* or *trans* relationship. The isolation of the *trans* form in high yield reflects the unfavorable steric effects in the *cis* form caused by eclipsing of the OH-4 and the tetrahydroxybutyl groups.

The carbonyl requirement was tested by preparing a model compound containing the requisite *O*-phenylcarbamoyl group adjacent to an aldehyde group. The model selected, *O*-phenylcarbamoylglycolaldehyde (**13**), is so reactive that it required generation *in situ* (Scheme II). Compound **13** was prepared by the action of aqueous $NaIO_4$ on 1-*O*-phenylcarbamoylglycerol (**12**). Concomitant cyclization was essentially complete in the weakly acidic solution, and racemic 4-hydroxy-3-phenyl-2-oxazolidinone (**14a**) was isolated in an overall yield greater than 80%.

SCHEME II



(21) E. Walton, F. W. Holly, G. E. Boxer, and R. F. Nutt, *J. Org. Chem.*, **31**, 1163 (1964), and references cited therein.

(22) H. W. Wanzlick and W. Löchel, *Chem. Ber.*, **86**, 1463 (1953).

Alternatively, glycolaldehyde was converted into 1,3-diphenyl-2-hydroxymethylimidazolidine (**15**), carbanilated, and hydrolyzed. Yields of **14a** were reduced, presumably because of decomposition reactions during hydrolysis.

The nmr spectra of **14a** and its monoacetate (**14b**) displayed the anticipated ABX patterns with the X proton (H-4 of **14a**) coupled to the hydroxyl proton (Table II). The BX coupling agrees with those values previously obtained for the *trans* vicinal ring protons (H-4, H-5), and the magnitude of AX agrees with the value reported for the comparable *cis* protons of **6b**.

The failure to isolate **13** at pH 4 stands in sharp contrast to the previously noted stability of **2a** at pH ≤ 7. Aqueous solutions of reducing carbohydrates generally contain small concentrations of *aldehydo* or *keto* forms. Glucose derivatives are predominately in a hemiacetal ring form at pH <7, although structural factors or high pH can produce more of the *aldehydo* form. Polarographic investigations have demonstrated that the carbonyl content increases markedly at alkaline pH values.[23,24] It is reasonable, therefore, to postulate that an elevated carbonyl content accounts for the sharp increase in the rate of N cyclization observed when solutions of **2a** are raised to pH >7.

Factors other than low free aldehyde content may retard the N cyclization of **2a** at pH ≤ 7, *e.g.*, steric effects, reduced nitrogen nucleophilicity, and formation of an intermediate acyloxonium species similar to that postulated for the anhydrous acid polymerization of 2,3,6-tri-*O*-phenylcarbamoyl-D-glucose.[25,26] These possibilities were not investigated. However, the spontaneous cyclization of **13** in a weakly acidic solution (pH 4) stands against lowered nitrogen nucleophilicity. Furthermore, the acyloxonium intermediate would form an unstable anil in aqueous solution with subsequent hydrolysis to produce aniline and a carbonate derivative. If anil formation represented a major reaction, large losses of **2a** would have occurred with an adverse effect on the over-all yields of **3**. No such losses were detected.

The role of **3** as a precursor in the formation of an oxazolidinone glucofuranose (**6a**) derivative was established by heating a pure sample in 0.5 *N* HCl while monitoring with tlc. During 3 hr, conversion into **6a** was essentially complete; thereafter, small amounts of degradation products formed. Use of 2% HCl in MeOH completely converted **6a** within 48 hr at 25° with less degradation (Scheme I). Purification by silica gel column chromatography yielded syrupy 5-(D-*glycero*-1,2-dihydroxyethyl)tetrahydro-3-phenylfuro-[2,3-*d*]oxazol-2-(3*H*)-one (**6a**) and from it a crystalline triacetate (**6b**). To designate its carbohydrate origin, **6a** also is named 4,5-(1′-amino-1′-deoxy-α-D-glucofuranosyl)-3-phenyl-2-oxazolidinone.

The structure of crystalline **6b** was deduced by nmr analysis (Figure 2). The chemical shifts and coupling constants are almost exactly duplicated in the spectrum of 3,4,6-tri-*O*-acetyl-1,2-*O*-isopropylidine-α-D-glucofuranose (**17**)[27,28] and the recently published spectra of analogous oxazolidinthiones[29,30] and imidazolidinones.[31] The nmr spectrum of **6a** is reproduced in Figure 2, and the data are compared with those for **17** in Table IV. A numbering system based on the six atoms of the glucose chain is used hereafter for the comparisons. Site numbers derived from the systematic name are given in parentheses either to achieve clarity or to allow other comparisons to be made.

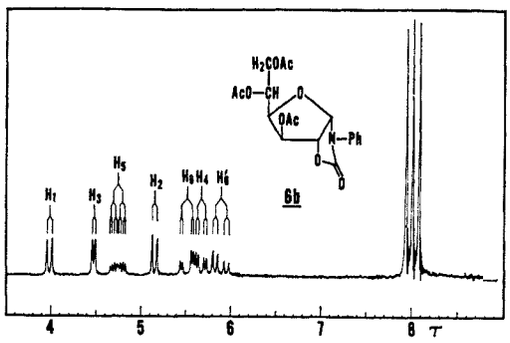


Figure 2.—The 100-MHz spectra of oxazolidinone glucofuranose triacetate (**6b**) in chloroform-*d*. For clarity, numbering is based on glucose.

TABLE IV

COMPARISON OF NMR DATA FOR **6b**[a] AND **17**[b]

Proton	Chemical shifts, τ 6b	17	Coupling constants,[c] Hz— J	6b	17
H-1	3.96	4.06	1,2	5.5	3.5
H-2	5.13	5.49	1,3	0.5	*d*
H-3	4.45	4.64	2,3	<0.5	<0.5
H-4	5.65	5.58	3,4	2.8	3.0
H-5	4.72	4.77	4,5	9.1	9.0
H-6′[e]	5.50	5.39	5,6	2.4	2.0
H-6′[e]	5.86	5.84	5,6′	5.2	6.3
			6,6′	12.3	12.3

[a] Measured in chloroform-*d*. [b] Data of Abraham, *et al.*,[27] in chloroform at 60 MHz. [c] By direct measurement of peak spacings. [d] Not reported. [e] The proton on C-6 giving the higher field signal is designated H-6′.

The nearly identical $J_{2,3}$ (<0.5 Hz) and $J_{3,4}$ (2.8 Hz, 3.0 Hz) suggest similar symmetrical twist conformations for **6b** and **17**. In **6b** a smaller dihedral angle is predicted between H-1 and H-2 (H-4 and H-5 of the 2-oxazolidinone ring) on the basis of a larger coupling constant (5.5 Hz). This greater eclipsing would be caused by less flexibility in the 2-oxazolidinone ring than in the isopropylidene ketal ring of **17**.

After formation of the furanose ring of **6a** from **3**, the only configurational change indicated was at C-1 (C-4); H-1 was brought into the *cis* relationship with H-2 by ring fusion. The possibility that **3** could have undergone an unsuspected epimerization to a *manno* configuration during the original cyclization was banished by observing the minimal $J_{2,3}$ (<0.5 Hz) value of **6b**, indicating a *trans* relationship of H-2 and H-3. This relationship is characteristic of the *gluco*

(23) W. G. Overend, A. R. Peacocke, and J. B. Smith, *J. Chem. Soc.*, 3487 (1961).

(24) S. M. Cantor and Q. P. Peniston, *J. Amer. Chem. Soc.*, **62**, 2113 (1940).

(25) I. J. Goldstein and T. L. Hullar, *Advan. Carbohyd. Chem.*, **21**, 440 (1966).

(26) E. Husemann and G. J. M. Müller, *Makromol. Chem.*, **91**, 212 (1966).

(27) R. J. Abraham, L. D. Hall, L. Hough, and K. A. McLauchlan, *Chem. Ind.* (London), 213 (1962); *J. Chem. Soc.*, 3699 (1962).

(28) L. D. Hall, *Advan. Carbohyd. Chem.*, **19**, 51 (1964).

(29) J. C. Jochims, A. Seeliger, and G. Taigel, *Chem. Ber.*, **100**, 845 (1967).

(30) J. Yoshimura and H. Hashimoto, *Bull. Chem. Soc. Jap.*, **41**, 261 (1968).

(31) H. Fritz, C. J. Morel, and O. Wacker, *Helv. Chim. Acta*, **51**, 569 (1968).

configuration. Epimerization at the other chain carbon atoms would be improbable.

Methanolysis of **2a** yields a mixture of compounds (Scheme I, Table I). The major component was **6a** isolated as **6b**. The other components were the methyl 2-*O*-phenylcarbamoyl-α,β-D-glucopyranosides (**5a**). A crystalline fraction isolated after acetylation of **5a** was identified as methyl 3,4,6-tri-*O*-acetyl-2-*O*-phenylcarbamoyl-α-D-glucopyranoside (**5b**) by comparison with an authentic sample.

An anomaly was observed in the ir spectra of derivatives containing the 2-oxazolidinone ring. Although the amide I carbonyl absorption usually falls in the 1740–1780-cm^{-1} range,[7] it is often observed at wavenumbers above 1760 cm^{-1}. However, this band was found between 1710 and 1735 cm^{-1} for the 4-hydroxy-3-phenyl forms (**3**, **8a**, **14a**). Substitution of the OH-4 caused a shift to higher frequencies. Participation as the furanose ring oxygen in **6a** raised the absorption band to 1750 cm^{-1}; acetylation caused an even greater shift to 1775–1780 cm^{-1} (**4**, **8b**). An alternative assignment of the higher frequency band as ester carbonyl is less probable, since carbohydrate acetates and carbanilates not containing 2-oxazolidinone rings have carbonyl absorptions at the usual 1740–1745 cm^{-1}.

Experimental Section

Nmr spectra were measured at 100 MHz on a Varian HA-100 spectrometer with tetramethylsilane (τ 10.0) as the internal standard. Chemical shifts and coupling constants are first-order values, measured directly from spectral spacings. Hydroxyl group resonances of compounds dissolved in methyl sulfoxide-d_6 were identified by exchange with added D_2O. Ir spectra were recorded with a Perkin-Elmer Model 621 spectrophotometer by the potassium bromide disk technique.

All samples for glpc were dissolved in pyridine and converted into their trimethylsilyl ethers approximately 18 hr before injection into an F & M research chromatograph, Model 700. The column was 4-ft, 1/8-in.-o.d. stainless steel tubing, packed with 3% JXR on Gas Chrom Q (trademark of the Applied Science Laboratories) (100–120 mesh). Operation was isothermal at 200° with helium as the carrier gas and flame ionization detection (Table V).

TABLE V

RELATIVE RETENTION VALUES OF 2-*O*-PHENYLCARBAMOYL-D-GLUCOSE AND DERIVATIVES[a]

Sample[b]	Anomer	Retention value[c]
2a	α-D	0.47
	β-D	0.61
3		0.53
5a	α-D	0.50
	β-D	0.55
6a		0.42
Maltose	β	1.00

[a] t/t_{std} at 200°, as pertrimethylsilyl ethers. [b] The order of appearance of the anomers is presumed to follow that observed for known compounds. [c] With 3% JXR on Gas Chrom Q.

Silica gel G (E. Merck, Darmstadt, Germany) was used for tlc without heat activation of the plates. Solvents were proportioned on a v/v basis. Reducing compounds were detected as red spots after spraying the chromatoplates with a saturated chloroform solution of 2,3,5-triphenyl-2*H*-tetrazolium chloride followed by 2.5 *N* alcoholic potassium hydroxide. Mild heat was applied when necessary. For column chromatography Baker Analyzed silica gel (J. T. Baker Chemical Co., Phillipsburg, N. J.) was used without pretreatment.

Melting points were determined in capillary tubes and are corrected. Solutions were evaporated below 40° under diminished pressure. Pyridine was removed from organic phases by repeated washes with 5% aqueous cupric sulfate.

***N*-(3,4,6-Tri-*O*-acetyl-2-*O*-phenylcarbamoyl-β-D-glucopyranosyl)piperidine (1a).**—The method of Hodge and Rist[3] was used to prepare **1a** (30 g) from β D-glucose pentaacetate (100 g). The pure compound was crystallized from methanol: mp 165–166° (lit. 164°);[3] nmr (pyridine-d_5) τ 2.11 (d, two Ph protons), 2.78 (m, three Ph protons), 4.31 (m, H-3), 4.52 (m, H-2), 4.64 (m, $J_{4,5}$ = ~10 Hz, H-4), 5.49 (pair of doublets, $J_{5,6}$ = 5 Hz, H-6), 5.68 (m, $J_{5,6'}$ = 2.8 Hz, $J_{6,6'}$ = 12.5 Hz, H-6'), 5.72 (d, $J_{1,2}$ = 8.5 Hz, H-1), 6.16 (m, H-5), 6.82 (m, 2 α protons, piperidine), 7.38 (m, 2 α′ protons, piperidine), 7.98–8.02 (m, three CH_3), 8.62 (m, 6 β, γ protons, piperidine).

***N*-(2-*O*-Phenylcarbamoyl-β-D-glucopyranosyl)piperidine (1b).**—An 18-g portion of **1a** was converted into **1b** by deacetylation in methanolic ammonia. One recrystallization from methanol gave 12.6 g of pure **1b**, mp 152–154° (lit. mp 153°).[3]

4-Hydroxy-3-phenyl-5-(D-*arabino*-1,2,3,6-tetrahydroxybutyl)-2-oxazolidinone (3).—A 9.5-g sample of **1b** was dissolved in 380 ml of 0.1 *N* HCl and held at room temperature. Tlc monitoring (5:1 ethyl acetate–methanol) indicated complete hydrolysis within 24 hr and no further changes during another 24 hr. The clear solution was neutralized by stirring 15 min with silver carbonate (10 g of Malinckrodt AR) then filtered. Residual silver salts were removed by treating the filtrate with 5 ml of pyridine and sweeping with hydrogen sulfide. The clear solution was reduced to one-half the original volume after filtration and extracted with three 100-ml portions of diethyl ether. After further evaporation to a thin syrup, **3** was again extracted with diethyl ether and dissolved in 99.5% ethanol. A final evaporation produced crude solids, which upon being twice recrystallized from 4:1 ethyl acetate–ethanol yielded 6.1 g (78%) of **3**: mp 166–167.5°; $[\alpha]^{20}D$ +42 → 46° (*c* 0.5, 50% aqueous CH_3OH); ir (KBr) 1710 (amide I C=O), 1600, 1500, 760, 690 cm^{-1} (Ph); for nmr data see Figure 1 and Tables II and III.

4-Acetoxy-3-phenyl-5-(D-*arabino*-1,2,3,6-tetraacetoxybutyl)-2-oxazolidinone (4).—A 1-g sample of **3** was dissolved in 50 ml of cold pyridine and mixed with 5 ml of acetic anhydride. After 12 hr at 0° and 36 hr at room temperature, the product was isolated from ethyl acetate. Two crystallizations from 95% ethanol produced **4**: mp 105–106°; $[\alpha]^{20}D$ +47° (*c* 0.55, $CHCl_3$); ir (KBr) 1780 (amide I C=O), 1745 (ester C=O), 1595, 1500, 685 cm^{-1} (Ph); for nmr data see Tables II and III.

Anal. Calcd for $C_{28}H_{27}NO_{12}$: C, 54.22; H, 5.34; N, 2.75; acetyl, 42.2. Found: C, 54.08; H, 5.37; N, 2.74; acetyl, 42.6.[32]

Reaction of 3 with $NaIO_4$. A. Reaction Stoichiometry.—Two samples of **3** (0.1805 and 0.0645 g) was dissolved in 25-ml portions of deionized water. Each solution was mixed with 25 ml of 0.091 *M* $NaIO_4$ and held in the dark at 25°. Aliquots (10 ml) were titrated at 5, 60, 120, and 240 min against 0.105 *M* $Na_2S_2O_3$. Reaction was complete within 5 min with no further periodate uptake for 4 hr. The periodate consumed was 2.98 and 2.80 mol/mol of **3**. Formic acid was determined titrimetrically after 6 and 22 hr, averaging 1.95 mol/mol of **3**. The presence of formaldehyde was indicated by chromotropic acid and verified by isolation in a derivative form (**9**) described below.

B. 5-*aldehydo*-4-Hydroxy-3-phenyl-2-oxazolidinone (7).—A solution containing 1 g of **3** and 2.5 g of $NaIO_4$ in 250 ml of water was allowed to react in the dark for 2 hr at 25°. The solution was concentrated to dryness with 99.5% ethanol so as to remove any residual water. The final solids were extracted serially with 100-ml portions of hot ethyl acetate, acetone, and ethanol. The bulk of the products was recovered from the ethyl acetate extract. A tlc examination (ethyl acetate) of the combined product mixture confirmed that **3** had reacted completely.

The entire product mixture was dissolved in 50 ml of methanol containing 2.6 g of *N*,*N*′-diphenyl-1,2-diaminoethane[22] and 1.4 ml of 50% aqueous acetic acid. The flask containing the solution was stoppered, immersed in a 60° water bath for 1 hr, and then stored 2 days at −5°. After the solids were collected, an examination by tlc (12:1 chloroform–acetone) revealed formic acid and two other components. One of the other components was the formaldehyde derivative, 1,3-diphenyl-2-imidazolidine (**9**). Crystallization from warm methanol yielded 0.23 g of **9**. Comparison with an authentic sample proved the identity: mp 125–

(32) M. L. Wolfrom and A. Thompson in "Methods of Carbohydrate Chemistry," Vol. 1, R. L. Whistler and M. L. Wolfrom, Ed., Academic Press, New York, N. Y., 1962, p 448.

127°, mixture melting point undepressed, identical R_f on tlc plates. The major component (**7**) was isolated as follows.

Isolation of 7 as 4-Hydroxy-5-(1′,3′-diphenyl-2′-imidazolidinyl)-3-phenyl-2-oxazolidinone (8a).—The original liquors and mixed solids were combined, evaporated, and fractionated on a silica gel column packed and irrigated with 12:1 chloroform–acetone. The fraction containing **8a** (1.4 g, 72%) also had traces of the original reagent. However, three recrystallizations from methanol gave the pure product: mp 175–177°; $[\alpha]^{20}D$ +57.4° (*c* 1.06, pyridine); ir (KBr) 3440 (OH), 1735 (amide I C=O), 1595, 1500, 690 cm^{-1} (Ph); for nmr data see Tables II and III.

Anal. Calcd for $C_{24}H_{23}N_3O_3$: C, 71.80; H, 5.77; N, 10.47. Found: C, 71.94; H, 5.97; N, 10.38.

Acetylation of 8a.—A 650-mg sample of **8a** was dissolved in 10 ml of cold pyridine and mixed with 1 ml of acetic anhydride. After 24 hr at room temperature, the product was isolated and recrystallized twice from 99.5% ethanol, mp 142.5–143.5°.

This derivative, 4-acetoxy-5-(1′,3′-diphenyl-2′-imidazolidinyl)-3-phenyl-2-oxazolidinone (**8b**), was unstable in a chloroform solution and decomposed within several weeks. In the solid state it remained unchanged for 6 months; for nmr data see Tables II and III.

Anal. Calcd for $C_{26}H_{25}N_3O_4$: C, 70.41; H, 5.68; N, 9.47. Found: C, 70.57; H, 5.92; N, 9.45.

Hydrolysis of 1b under Varying Conditions. A. Time.—A 2.5-g sample of **1b** was dissolved in 100 ml of 0.1 *N* HCl and held at 25°. Aliquots (25 ml) were removed after 24 and 48 hr, neutralized with Amberlite IR-45 resin (Malinckrodt), and evaporated to a thin syrup. A portion of each sample was converted into the pertrimethylsilyl ether form and analyzed by glpc (Table I). Three compounds (four peaks) were detected and later identified as **2a** (α and β forms), **3**, and **6a**. The decrease in the concentration of **2a** with an equivalent rise in that of **3** is in agreement with Scheme I.

B. Neutralization with Ag_2CO_3.—The balance of the hydrolysis solution (A) was neutralized with silver carbonate and treated as described earlier. The solution was concentrated, analyzed (Table I), and afforded pure **3** (0.6 g) by crystallization.

C. Use of Ion-Exchange Resin.—Duplicate 3-g samples of Amberlite IR-120 (H^+) resin were added to two previously prepared solutions containing 1 g of **1b** in 100 ml of 50% aqueous acetone. The first was stirred 20 hr at 25°, filtered, and concentrated. Glpc (Table I) showed **2a** and **3** in approximately a 2:1 ratio with trace amounts of **6a**. The duplicate mixture was stirred at reflux for 30 min to produce **2a**, **3**, and **6a** in approximately equal amounts (tlc estimation).

2-*O*-Phenylcarbamoyl-α,β-D-glucopyranose (2a).—A 5-g sample of **1b** was dissolved in 200 ml of 0.1 *N* HCl and allowed to stand 36 hr at 25°. The solution was neutralized with Amberlite IR-45 resin, the filtrate extracted twice with 100-ml portions of diethyl ether, and the extract evaporated to a thin syrup. All efforts to crystallize this syrup failed. Tlc examinations confirmed that **2a** was the major component and that 6-month storage in the freezer produced no change.

Conversion of 2a into 3 by $NaHCO_3$ and Na_2CO_3.—Duplicate 75-mg portions of crude **2a** were dissolved in 5 ml of water containing 50 mg of $NaHCO_3$ (pH 8.1) or Na_2CO_3 (pH 11.4) and held 15 min at 25°. Excess acetic acid was added to each, and both samples were evaporated to dryness. The results of glpc analysis are summarized in Table I demonstrating the high pH required for the conversion in to **3**.

Acetylation of 2a.—A 1-g sample of **2a** was dissolved in 100 ml of cold pyridine containing 5 ml of acetic anhydride. After 48 hr, the product was isolated and crystallized from 95% ethanol. After an additional recrystallization, the ir and nmr spectra were identical, and the mp 197–199° was undepressed on admixture with authentic 1,3,4,6-tetra-*O*-acetyl-2-*O*-phenylcarbamoyl-α-D-glucopyranose (**2c**).

1,3,4,6-Tetra-*O*-acetyl-2-*O*-phenylcarbamoyl-α-D-glucopyranose (2c).—A 4-g sample of **1a** was dissolved in 50 ml of acetone and 10 ml of 1 *N* HCl. Hydrolysis was complete after the mixture was left overnight at 25° as judged by tlc examination (7:1 chloroform–acetone). The major component, 3,4,6-tri-*O*-acetyl-2-*O*-phenylcarbamoyl-α,β-D-glucopyranose (**2b**), weighed 1.5 g after purification on a silica gel column (1:1 ethyl acetate–benzene). The syrupy **2b** was acetylated in cold pyridine containing acetic anhydride and crystallized from 95% ethanol: mp 199–200.5°; $[\alpha]^{20}D$ +109° (*c* 0.5, $CHCl_3$); ir (KBr) 1750 (C=O ester and amide I), 1540 (amide II), 1595, 1495, 760, 695 cm^{-1} (Ph); nmr (chloroform-*d*) τ 2.78 (m, five Ph protons), 3.58 (d, $J_{1,2}$ = 3.7 Hz, H-1), 4.50 (m, $J_{3,4}$ = 9.5 Hz, H-3), 4.81 $J_{4,5}$ = ~9 Hz, H-4), 4.95 (m, $J_{2,3}$ = 10 Hz, H-2), 5.80 (m, H-6, H-6′), 5.97 (m, H-5), 7.87–8.03 (four CH_3).

Anal. Calcd for $C_{21}H_{25}NO_{11}$: C, 53.96; H, 5.39; N, 3.00; acetyl, 36.8. Found: C, 54.16; H, 5.56; N, 2.95; acetyl, 37.2.

2,3-*O*-Isopropylideneglycerol (10).—A mixture containing 18.5 g of glycerol, 60 ml of dry acetone, 11 g of anhydrous cupric sulfate, and 0.1 ml of concentrated H_2SO_4 was placed in a 250-ml round-bottomed flask and vigorously shaken 24 hr. The supernatant liquid was mixed with an equal volume of benzene, decanted, and dried over anhydrous potassium carbonate. The solution was mixed with 2 ml of pyridine and evaporated to a clear syrup (20 g, 73%) of satisfactory purity.

2,3-*O*-Isopropylidene-1-*O*-phenylcarbamoylglycerol (11).—A solution containing 20 g of **10** in 100 ml of pyridine was cooled to 0° and treated with 16 ml of phenyl isocyanate. After the solution stood 18 hr at 25°, 5 ml of water was added and the product isolated from ethyl acetate. Tlc (4:1 benzene–ethyl acetate) showed only traces of substances other than **11**. Evaporation yielded a tan syrup that spontaneously crystallized. Charcoal decolorization and crystallization from hexane gave the final product (31 g, 82%), mp 59–61° (lit.[33] mp 56–57°). Spots on the tlc plates were visualized either by exposure to iodine vapor or by spraying with water.

1-*O*-Phenylcarbamoylglycerol (12).—A 15-g sample of **11** was dissolved in 100 ml of acetone, 25 ml of water, and 1 ml of concentrated HCl, and then the solution refluxed 1 hr. Tlc (3:1 benzene–ethyl acetate) showed complete hydrolysis. After excess sodium acetate was added, the mixture was evaporated to a small volume and then dissolved in 200 ml of water. All colored material was removed by extraction with two 100-ml portions of diethyl ether. The aqueous layer was reconcentrated, taken up in 100 ml of acetone, and filtered. Evaporation afforded 11.5 g of syrupy product essentially free of impurities, assumed to be **12**.

4-Hydroxy-3-phenyl-2-oxazolidinone (14a).—A 4-g portion of **12** was dissolved in 400 ml of water containing 4 drops of glacial acetic acid and 5.3 g of $NaIO_4$. After 4 hr in the dark at 25°, the solution was evaporated to dryness and extracted with 250 ml of hot acetone. The acetone solution was cooled, filtered, evaporated to dryness, and extracted with three 50-ml portions of diethyl ether. The residual **14a** was washed with hexane and dried; it weighed 2.75 g (80%). The ether extract weighed 0.8 g of which **14a** was the major component admixed with formaldehyde and colored materials. Recrystallization from water gave pure **14a**: mp 116–117.5°; ir (KBr) 3420 (OH), 1715 (amide I C=O), 1595, 1495, 755, 690 cm^{-1} (Ph); for nmr data see Tables II and III.

Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.49; H, 5.01; N, 7.79.

4-Acetoxy-3-phenyl-2-oxazolidinone (14b).—A 2-g sample of **14a** was dissolved in a mixture containing 20 ml of pyridine, 10 ml of ethyl acetate, and 3 ml of acetic anhydride; the solution was left overnight at room temperature. Pure **14b** was crystallized from methanol–water: mp 69–71°; for nmr data see Tables II and III.

This compound, unstable at room temperature, eliminates acetic acid within several hours. Decomposition in chloroform-*d* was complete within 2 weeks. The solution then showed a two-proton multiplet at τ 3.10 and the CH_3 singlet of acetic acid at τ 7.95. The ABX system originally observed for **14b** could not be detected.

1,3-Diphenyl-2-hydroxymethylimidazolidine (15).—Dimeric glycolaldehyde (2.0 g) was dissolved in 200 ml of methanol containing 10.4 g of *N,N′*-diphenyl-1,2-diaminoethane and 3.0 ml of 50% aqueous acetic acid. The solution was heated in a closed flask for 2 hr at 60°, and then evaporated to solids under reduced pressure. This mixture was dissolved in methanol and stored 2 days at −5°. The precipitate, after being collected and washed twice with cold methanol, yielded 7.4 g (82%) of **15**. Tlc (10:1 chloroform–acetone) showed the product to be essentially homogeneous. Recrystallization gave pure **15**: mp 107–110°.

Carbanilation of 15.—A 5.5-g sample of **15** was dissolved in a solution containing 50 ml of benzene, 10 ml of pyridine, and 2

(33) V. A. Welch and P. W. Kent, *J. Chem. Soc.*, 2266 (1962); prepared in three steps from **10**.

ml of phenyl isocyanate. The product, isolated after 18 hr at room temperature, was 6.4 g of the monocarbanilate (**16**). Tlc (ethyl acetate–benzene 1:9 or methanol–benzene 1:9) showed complete reaction. After two recrystallizations from 99.5% ethanol, **16** had mp 122–124°.

Anal. Calcd for $C_{33}H_{23}N_3O_2$: C, 73.97; H, 6.21; N, 11.25. Found: C, 73.94; H, 6.19; N, 11.28.

Hydrolysis of 16.—A 1-g sample of **16** was dissolved in 25 ml of 1,2-dimethoxyethane and treated with 5 ml of 6 *N* HCl. A heavy precipitate formed in the flask, which was stoppered and shaken 1 hr. The mixture was diluted with an equal volume of acetone and filtered; the solids were rinsed with additional acetone. The filtrate was neutralized with $NaHCO_3$, refiltered, and evaporated to dryness. Extraction with 100 ml of hot acetone and filtration removed the residual salts. The filtrate was reconcentrated, diluted with 100 ml of water, and decolorized with charcoal. Filtration and concentration to 20 ml produced **14a** (0.150 g, 31%), mp 116–117°.

5-(D-*glycero*-1,2-Dihydroxyethyl)tetrahydro-6-hydroxy-3-phenylfuro[2,3-*d*]oxazol-2-(3*H*)-one (6a).—Crystalline **3** (5.0 g) was dissolved in 200 ml of methanol, treated with 3 ml of acetyl chloride, and stored 24 hr in the dark at 25°. The colorless solution was neutralized with Amberlite IR-45 resin, filtered, and concentrated. Tlc examination (5:1 ethyl acetate–methanol) showed complete conversion into **6a**. Quantitation by glpc gave the results shown in Table I. Attempts to crystallize **6a** from a variety of solvents were unsuccessful.

Aqueous Production of 6a.—A 0.5-g sample of **3** was dissolved in 50 ml of 0.5 *N* HCl and heated 3 hr at 100°. The sample was analyzed by glpc after isolation (Table I) and found to duplicate the methanolysis results.

6-Acetoxy-5-(D-*glycero*-1,2-diacetoxyethyl)tetrahydro-3-phenylfuro[2,3-*d*]oxazol-2-(3*H*)-one (6b).—A pyridine solution (50 ml) containing **6a** (2 g) and acetic anhydride (5 ml) was held at 0° for 48 hr and the product was isolated from ethyl acetate. After two recrystallizations from 95% ethanol, **6b** gave mp 130.5–131.5°; $[\alpha]^{20}D$ +44.9° (*c* 0.55, $CHCl_3$); ir (KBr) 1770 (amide I C=O), 1735 (ester C=O), 1600, 1500, 755, 690 cm^{-1} (Ph); for nmr data see Figure 2 and Table IV.

Anal. Calcd for $C_{19}H_{21}NO_9$: C, 56.02; H, 5.20; N, 3.44. Found: C, 56.31; H, 5.40; N, 3.42.

Methyl 2-*O*-Phenylcarbamoyl-D-glucopyranoside (5a).—A 1-g sample of **2a** was dissolved in 50 ml of 2% methanolic HCl and held 48 hr at 25°. Tlc (20:3 ethyl acetate–methanol) showed two compounds, **6a** and **5a**. Results of glpc quantitation are listed in Table I. No change in product composition was observed after diluting to 100 ml with fresh methanol and refluxing 2 hr. The solution was neutralized with Amberlite IR-45 resin, concentrated, and acetylated in pyridine.

The acetylated products were separated on a silica gel column irrigated with 4.5:10 acetone–hexane, and crystallized from 95% ethanol: **6b**, mp 130–131.5°; **5b**, mp 167.5–169°, mixture melting point with the authentic α-glucoside (**5b**) undepressed. All physical properties matched those of authentic **5b** (see below).

Methyl 3,4,6-Tri-*O*-acetyl-α-D-glucopyranoside (19).—A solution containing 6 g of 3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl chloride (**18**)[34] in 200 ml of methanol and 20 ml of pyridine was allowed to stand 20 hr at 25°. Tlc monitoring (3:2 ethyl acetate–benzene) showed the reaction to be essentially complete within 2–3 hr and to have no apparent change thereafter. Glpc was used to identify and quantitate the reaction components after deacetylation and conversion to the trimethylsilyl ethers. The calculated yield of **19** was 84% and that of the β anomer, 6.5%; these percentages closely approximate earlier estimates based on optical rotations.[35,36] The reaction solution was evaporated to a thin syrup, dissolved in 500 ml of ethyl acetate, and freed of pyridine.

Methyl 3,4,6-Tri-*O*-acetyl-2-*O*-phenylcarbamoyl-α-D-glucopyranoside (5b).—The crude **19** was dissolved in 100 ml of benzene and treated with 5 ml of phenyl isocyanate. Water (5 ml) was added after the solution had been stored 24 hr at 25° and then it was evaporated to dryness. The solids were extracted with 100 ml of cold diethyl ether and filtered; the residual solids were crystallized from methanol. Yield was 5 g (62%): mp 167.5–169°; $[\alpha]^{20}D$ +112.6° (*c* 0.76, $CHCl_3$); nmr (acetone) τ 2.72 (three multiplets, Ph), 4.50 (unsymmetrical t, $J_{3,4}$ = 9.5 Hz, H-3), 4.91 (m, H-4), 4.94 (d, $J_{1,2}$ = 3.5 Hz, H-1), 5.09 (pair of doublets, $J_{2,3}$ = 10 Hz, H-2), 5.69 (m, $J_{5,6}$ = 5 Hz, $J_{5,6'}$ = 2.4 Hz, H-6), 5.90 (m, $J_{6,6'}$ = 12 Hz, H-6'), 6.02 (m, H-5), 6.59 (OCH_3).

Anal. Calcd for $C_{20}H_{25}NO_{10}$: C, 54.67; H, 5.72; N, 3.19; OCH_3, 7.06; acetyl, 29.4. Found: C, 54.76; H, 5.68; N, 3.22; OCH_3 7.80; acetyl, 29.1.

Registry No.—**1a**, 20147-90-4; **2c**, 20-126-09-4; **3**, 20-126-18-5; **4**, 20-126-19-6; **5b**, 20-126-10-7; **6b**, 20-126-17-4; **8a**, 20-126-11-8; **8b**, 20-126-12-9; **14a**, 20-126-13-0; **14b**, 20-126-14-1; **15**, 20-126-15-2; **16**, 20-126-16-3.

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(34) R. U. Lemieux and J. Howard in "Methods of Carbohydrate Chemistry," Vol. 2, R. L. Whistler and L. M. Wolfrom, Ed., Academic Press, New York, N. Y., 1963, p 401.

(35) W. J. Hickenbottom, *J. Chem. Soc.*, 1676 (1929).

(36) F. H. Newth and G. O. Phillips, *ibid.*, 2904 (1953).