Derivatives of 2-Amino-2-deoxy-D-gulose: Synthetic and Conformational Studies

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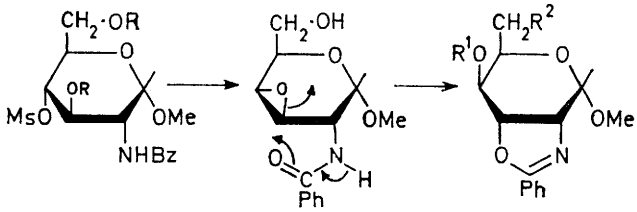
Methyl 2-benzamido-3,6-di-*O*-benzoyl-2-deoxy-4-*O*-methylsulphonyl-α-D-glucopyranoside (1) underwent two inversion reactions when treated with sodium methoxide to give an oxazoline derivative, methyl 2,3-dideoxy-3,2-(2-phenyl-1-oxa-3-azaprop-2-eno)-α-D-gulopyranoside (4) in high yield. The reaction proceeded *via* the *galacto*-3,4-epoxide (3) which underwent ring-opening with participation of the amide carbonyl group to give the *gulo*-oxazoline. Acid-catalysed opening of the oxazoline ring afforded, after *N*-acetylation, methyl 2-acetamido-3-*O*-benzoyl-2-deoxy-α-D-gulopyranoside (12), which was then de-*O*-benzoylated to give methyl 2-acetamido-2-deoxy-α-D-gulopyranoside (14).

The ^{1}H n.m.r. data of various *O*-substituted derivatives of the oxazoline showed that they adopted non-chair conformations. As would be expected the 2-acylamino-2-deoxygulopyranosides obtained by cleavage of the oxazoline ring existed in the C_1^4 conformation.

THE natural occurrence of 2-amino-2-deoxy-D-gulose (gulosamine) is limited to its presence in two antibiotics, streptothricin and streptolin B,[1] so that studies of this sugar have mainly relied on the availability of synthetic material. The amino-sugar has been synthesised from D-xylose by ascent of the series [2,3] and from the solvolysis of 3-sulphonates of methyl 2-acetamido-2-deoxy-D-galactopyranoside.[4] In an alternative synthesis Gross, Brendel, and Zimmerman [5] utilised a derivative of 2-amino-2-deoxy-D-glucose, namely benzyl 3,6-di-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-4-*O*-methylsulphonyl-α-D-glucopyranoside, from which they prepared a 3,4-epoxide by treatment with base. This compound underwent acid-catalysed epoxide ring-opening with participation by the neighbouring amide carbonyl group to give a 2,3-(oxazolidin-2-one) with the D-*gulo*-configuration. Subsequent hydrolysis of the oxazolidinone afforded 2-amino-2-deoxy-D-gulose.

The latter method, which employed a 4-sulphonate of a 2-acylamino-2-deoxyglucopyranoside, was of interest to us since we have recently achieved a convenient preparation of a related compound, methyl 2-benzamido-3,6-di-*O*-benzoyl-2-deoxy-4-*O*-methylsulphonyl-α-D-glucopyranoside (1) by selective benzoylation.[6] It was therefore of interest to see whether this could be conveniently converted into the related oxazoline (4) *via* the 3,4-epoxide (3). However, attempted formation of the 3,4-epoxide (3) from compound (1) by treatment with sodium methoxide at room temperature afforded a crystalline compound, in almost quantitative yield, which was an isomer of the epoxide (3). The i.r. spectrum contained no amide II band but showed strong absorptions at 1650 (amide I or oxazoline) and *ca.* 3500 cm.$^{-1}$ (OH). These properties indicated that the intermediary epoxide (3) had been transformed directly into the oxazoline (4). T.l.c. of the reaction mixture failed to detect any of the epoxide (3); the only intermediate detectable was the de-*O*-benzoylated starting material, methyl 2-benzamido-2-deoxy-4-*O*-methylsulphonyl-α-D-glucopyranoside (2), which could be isolated in the early stages of the reaction. The structure of the oxazoline was confirmed by the formation of a di-*O*-benzoyl derivative (5) and a di-*O*-methylsulphonyl derivative (6) and by the ^{1}H n.m.r. spectra of these and other derivatives (see later).

It is well established that a *trans*-acyloxy-group has a marked influence upon the direction of acid-catalysed ring-opening of a vicinal epoxide ring *via* the formation of intermediary acyloxonium ions.[7] The formation of our oxazoline can only be explained in an analogous way by the sequence (1) ⟶ (2) ⟶ (3) ⟶ (4).



(1) R = Bz
(2) R = H
(3)

Ms = mesyl; Ts = tosyl

(4) R^1 = H, R^2 = OH
(5) R^1 = Bz, R^2 = OBz
(6) R^1 = Ms, R^2 = OMs
(7) R^1 = H, R^2 = OTs
(8) R^1 = Ts, R^2 = OTs
(9) R^1 = H, R^2 = I
(10) R^1 = R^2 = H

Ring cleavage of the oxazoline (4) was conveniently effected by acid-catalysed methanolysis to give, presumably, methyl 2-amino-3-*O*-benzoyl-2-deoxy-α-D-gulopyranoside (11) hydrochloride. After neutralisation, the free base (11) was *N*-acetylated with acetic anhydride to give the 2-acetamido-3-*O*-benzoyl derivative (12) in good overall yield. The 3-*O*-benzoyl group was then removed to give methyl 2-acetamido-2-deoxy-α-D-gulopyranoside (14) in an overall yield of 31% from the readily available [6] starting material (1); thus this route

[1] E. E. Van Tamelen, J. R. Dyer, H. E. Carter, J. V. Pierce, and E. E. Daniels, *J. Amer. Chem. Soc.*, 1956, **78**, 4817.
[2] R. Kuhn and W. Bister, *Annalen*, 1958, **617**, 92.
[3] J. C. Sowden and M. L. Oftedahl, *J. Org. Chem.*, 1961, **26**, 2153; M. B. Perry and A. C. Webb, *Canad. J. Chem.*, 1969, **47**, 1245.
[4] Z. Tarasiejska and R. W. Jeanloz, *J. Amer. Chem. Soc.*, 1957, **79**, 4215; R. W. Jeanloz, *ibid.*, 1959, **81**, 1956.
[5] P. H. Gross, K. Brendel, and H. K. Zimmerman, *Annalen*, 1964, **680**, 155, 159.
[6] M. W. Horner, L. Hough, and A. C. Richardson, *J. Chem. Soc.* (*C*), 1970, 1336.
[7] J. G. Buchanan and J. C. P. Schwartz, *J. Chem. Soc.*, 1962, 4770; J. G. Buchanan and R. Fletcher, *ibid.*, 1965, 6316.

to gulosamine derivatives is more attractive than the methods described hitherto. Similarly, methyl 2-benzamido-3-*O*-benzoyl-2-deoxy-α-D-gulopyranoside (13) could be isolated, after the ring-opening of the oxazoline (4), by *N*-benzoylation of the amine (11) with benzoic anhydride. De-*O*-benzoylation of compound (13) afforded methyl 2-benzamido-2-deoxy-α-D-gulopyranoside (15) in 43% overall yield from compound (1).

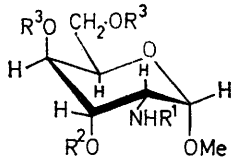
The oxazoline (4) may serve as a useful precursor of 6-substituted gulosamine derivatives, since we have found that it can be selectively *p*-tolylsulphonylated at the terminal position to give the 6-sulphonate (7) in 38% yield. This has been converted into the 6-iodo-derivative (9), which has been reduced to the 6-deoxy-oxazoline (10) with Raney nickel.

TABLE 1

^{1}H N.m.r. spectra data. First-order chemical shifts (τ values) and coupling constants (Hz) at 100 MHz

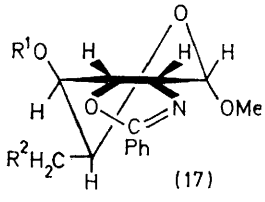
Compound:	(5)	(5)	(6)	(7)	(8)	(9)	(10)	(12)	(13)	(13)	(16)	(16)
Solvent	$CDCl_3$	C_5D_5N	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	C_5D_5N	C_5D_5N	$CDCl_3$	$CDCl_3$	C_5D_5N
H-1	4·90(d)	4·72(d)	4·96(d)	4·04(d) *	5·13(d)	4·98(d)	5·07(d) *	4·95(d)	4·83(d)	5·06(d)	5·12(d)	4·79(d)
H-2	5·40(q)	5·10(q)	5·35(q)	5·55(q) *	5·55(q)	5·54(q)	5·56(q) *	4·44(sex)	4·26(qui)	4·98(sex)	*ca.* 5·2 ‡	4·61(qui)
H-3	5·10(q) *	4·81(q)	5·02(q) *	5·29(q)	5·23(q)	5·28(q)	5·36(q)	4·01(t)	3·86(t)	4·52(t)	4·50(t)	3·88(t)
H-4	4·08(t) *	3·66 †	4·53(t) *		4·78(t)						4·55(d)	4·10(d)
H-5	5·45 ‡	5·15 ‡	5·57 ‡		5·8 ‡		5·87 ‡			5·87 ‡		4·97 §
H-6												5·2 ‡
H-6′							8·73(d)					
OMe	6·54(s)	6·64(s)	6·56(s)	6·64(s)	6·66(s)	6·54(s)	6·65(s)	6·56(s)	6·51(s)	6·46(s)	6·47(s)	6·50(s)
NAc								7·98(s)			8·09(s)	7·98(s)
O·SO_2Me			6·78(s) 6·94(s)									
ArMe				7·58(s)	7·57(s)							
NH								1·63(d)		3·41(d)	4·17(d)	1·36(d)
$J_{1,2}$	4·5	4·8	4·4	4·3	4·3	4·7	4·8	4·0	3·5	*ca.* 4	3·5	4·0
$J_{1,3}$	0	0	0	0	0	0	0	<1	<1	*ca.* 1	0·8	<1
$J_{2,3}$	9·5	9·2	10·2	9·5	10·0	9·0	9·0	3·8	*ca.* 3·5	*ca.* 4	3·4	4·0
$J_{3,4}$	4·6	4·8	6·7	4·7	6·3	3·5	3·5	*ca.* 4	*ca.* 3·4	*ca.* 4	3·5	3·5
$J_{4,5}$	*ca.* 4		*ca.* 6·0		*ca.* 6	3			<1		<1	*ca.* 1
$J_{5,6}$						7·0 6·5	6·5					
$J_{2,NH}$								9·0	*ca.* 9	8·5	8·5	*ca.* 8

* Assignment verified by spin decoupling. † Poorly resolved multiplet. ‡ Complex multiplet. § Complex quartet.



(11) $R^1 = R^3 = H$, $R^2 = Bz$
(12) $R^1 = Ac$, $R^2 = COPh$, $R^3 = H$
(13) $R^1 = R^2 = Bz$, $R^3 = H$
(14) $R^1 = Ac$, $R^2 = R^3 = H$
(15) $R^1 = Bz$, $R^2 = R^3 = H$
(16) $R^1 = Ac$, $R^2 = R^3 = Bz$

^{1}H N.m.r. spectral data for these gulopyranosides are listed in Table 1, and are of interest because the conformation of gulopyranosides has not been studied in any detail by n.m.r. spectroscopy. The spectra of the 2-acylamido-2-deoxygulopyranosides (12), (13), and (16) showed that they adopted a conformation approximating to the expected C_1^4 form [(11) *etc.*]. For example, the 2-acetamido-3,4,6-tri-*O*-benzoyl derivative (16) in deuteriopyridine gave a spectrum in which all the ring proton resonances were well separated and therefore amenable to first-order analysis. The two lowest field resonances were assigned to the methine protons adjacent to benzoyloxy-substituents (H-3 and H-4).[8] That due to H-3 was a triplet at τ 3·88 and that due to H-4 was observed as a broad doublet at τ 4·10. The very small coupling (<1 Hz) between H-4 and H-5 appears to be characteristic of an axial H-5 and an equatorial H-4 in hexopyranoses and has often been observed in galactopyranosides.[6,9] The H-2 resonance was easily distinguished since it occurred as a quintet at τ 4·61 as a result of being coupled to the amide proton as well as to the vicinal ring protons, and the H-1 signal occurred as a slightly broadened (long-range coupling to H-3) doublet at τ 4·79.



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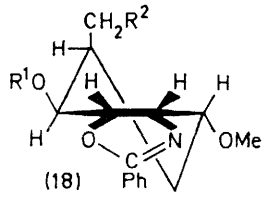

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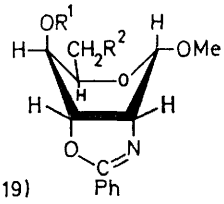

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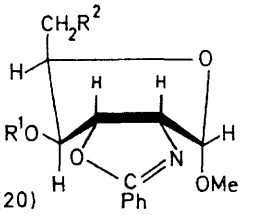

(20)

The ^{1}H n.m.r. spectra of the various oxazoline derivatives showed that these pyranosides adopted non-

[8] J. M. Williams and A. C. Richardson, *Tetrahedron*, 1967, **23**, 1369.

[9] J. Hill, L. Hough, and A. C. Richardson, *Carbohydrate Res.*, 1968, **8**, 7, 19; H. Libert, I. Schuster, and L. Schmidt, *Chem. Ber.*, 1968, **101**, 1902.

chair conformations owing to the restraint of the oxazoline ring. The spectrum of the parent oxazoline (4) was too complex for meaningful interpretation, but derivatives (5)—(10) gave good spectra in which the resonances due to H-1, H-2, H-3 and, sometimes, H-4 were clearly discernible, so that precise values of $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ could be determined (Table 2). The value

TABLE 2

Coupling constants and molecular rotations

	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$[M]_D$
Dibenzoate (5)	4·5	9·5	4·6	*ca.* 4	+68°
Dimesylate (6)	4·4	10·2	6·7	*ca.* 6	+67
6-Tosylate (7)	4·3	9·5	4·7		+24
Ditosylate (8)	4·3	10·0	6·3	*ca.* 6	+50
6-Iodo-compound (9)	4·7	9·0	3·5	3·0	+27
6-Deoxy-compound (10)	4·8	9·0	3·5		+24
Oxazoline (4)					+19

TABLE 3

Dihedral angles for various conformations

	HC_5^0 (17)	HC_0^5 (18)	$B^{1,4}$ (19)	$B_{1,4}$ (20)
$\phi_{1,2}$	*ca.* 30°	*ca.* 30°	60°	60°
$\phi_{2,3}$	0	0	0	0
$\phi_{3,4}$	*ca.* 90	*ca.* 150	60	180
$\phi_{4,5}$	*ca.* 50	*ca.* 50	60	60

for $J_{2,3}$ in these derivatives is unusually large (9·0—10·2 Hz) for *cis*-protons attached to a pyranoside ring, corresponding to small dihedral angles approaching[10] zero, rather than the 60° required for the C_1^4 chair conformation. Such a dihedral angle is consistent with C-1, C-2, C-3, and C-4 being in or near one plane, as found in the two half-chair conformations, (17) and (18), and in the two boat conformations, (19) and (20) (see Table 3).

If the anomeric effect were operative, then the methoxy-group would adopt an axial or quasi-axial orientation, which would favour the $B_{1,4}$ (20) or the HC_5^0 (17) conformations. Neither conformation satisfies the experimental data completely (Table 2) suggesting either the observation of a time-averaged spectrum of (17) and (20) or the presence of an intermediate conformation. Few ^{1}H n.m.r. data are available for other pyranose oxazolines, but $J_{1,2}$ values of 7·8 and 6·5 have been reported for 3,4,6-tri-*O*-acetyl-1,2-dideoxy-1,2-(2-phenyl-1-oxa-3-azaprop-2-eno)-α-D-glucopyranoside and -galactopyranoside, respectively, suggesting that these compounds have non-chair conformations in which $\phi_{1,2}$ is small.[11]

In our oxazoline derivatives the substituent at C-4 has a marked effect upon the value of $J_{3,4}$. Those compounds with bulky sulphonate groups [(6) and (8)] give the largest values (6·7 and 6·3 Hz, respectively), suggesting a conformational change towards the boat form (20) in which the bulky group is equatorial. This conformational effect is supported by a relationship between the molecular rotations of oxazolines (5)—(10) and the value of $J_{3,4}$ (Table 2). The sulphonates (6) and (8) both have high molecular rotations whereas the unsubstituted 4-hydroxy-derivatives give much lower values. The dibenzoate (5) is exceptional since it has a low $J_{3,4}$ value (4·5 Hz) and a high $[M]_D$ value, but optical rotations of benzoates are unreliable for comparison purposes because these compounds exhibit a strong Cotton effect in the u.v.[12]

[10] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11; R. J. Abrahams and K. A. McLauchlan, *Mol. Phys.*, 1962, **5**, 513; L. D. Hall, *Adv. Carbohydrate Chem.*, 1964, **19**, 51.

[11] N. Pravdić, T. D. Inch, and H. G. Fletcher, *J. Org. Chem.*, 1967, **32**, 1815.

[12] A. C. Richardson, J. C. P. Schwarz, and J. M. Williams, unpublished results.

EXPERIMENTAL,

For general procedures see ref. 6.

Methyl 2,3-*Dideoxy*-3,2-(2-*phenyl*-1-*oxa*-3-*azaprop*-2-*eno*)-α-D-*gulopyranoside* (4).—Methyl 2-benzamido-3,6-di-*O*-benzoyl-2-deoxy-4-*O*-methylsulphonyl-α-D-glucopyranoside [6] (1) (6 g.) was dissolved in methylene chloride (40 ml.) and treated with 1·6N-sodium methoxide solution (40 ml.). The mixture was kept at room temperature for 20 hr., then diluted with water (100 ml.) and extracted continuously with methylene chloride for 12 hr. The resulting syrup was then extracted several times with light petroleum in order to remove methyl benzoate. The residue crystallised during this procedure to give the *oxazoline* (2·73 g., 95%), m.p. 142—144°, which was usually sufficiently pure for the next stage. Recrystallisation from chloroform–light petroleum afforded material (2·2 g., 77%) with m.p. 144—145·5° and $[\alpha]_D$ +69° (*c* 1·4) (Found: C, 60·1; H, 6·1; N, 4·8. $C_{14}H_{17}NO_5$ requires C, 60·2; H, 6·1; N, 5·0%).

Methyl 4,6-*Di*-O-*benzoyl*-2,3-*dideoxy*-3,2-(2-*phenyl*-1-*oxa*-3-*azaprop*-2-*eno*)-α-D-*gulopyranoside* (5).—A solution of the oxazoline (4) (1·5 g.) in pyridine (20 ml.) was cooled to 0° and benzoyl chloride (1·4 ml.) was added with stirring. The temperature was maintained at 0° for 2 hr. and the mixture was then decomposed with water; the product was isolated by extraction into ether. Pyridine was removed from the extract by washing with aqueous 10% copper(II) sulphate until a deep blue colour was no longer formed. The resulting syrup was purified on a column of silica gel (75 g.) with ether–light petroleum (2 : 1 v/v) as eluant to give the 4,6-*di*-O-*benzoate* (1·6 g., 61%), m.p. 140—141° (from di-isopropyl ether), $[\alpha]_D$ +139·4° (*c* 1) (Found: C, 68·6; H, 5·2; N, 2·8. $C_{28}H_{25}NO_7$ requires C, 68·9; H, 5·1; N, 2·8%).

Methyl 2,3-*Dideoxy*-4,6-*di*-O-*methylsulphonyl*-3,2-(2-*phenyl*-1-*oxa*-3-*azaprop*-2-*eno*)-α-D-*gulopyranoside* (6).—The oxazoline (4) (4 g.) in pyridine (40 ml.) was methylsulphonylated in the usual way with methanesulphonyl chloride (4·9 g.); the reaction mixture was decomposed with water after 3 hr. The *di*-O-*methanesulphonate* (from ethanol) (5·2 g., 83%) had m.p. 106—108°, $[\alpha]_D$ +154·4° (*c* 1·2) (Found: C, 44·9; H, 4·7; N, 3·1. $C_{16}H_{21}NO_9S_2$ requires C, 44·5; H, 4·8; N, 3·2%).

Methyl 2,3-*Dideoxy*-3,2-(2-*phenyl*-1-*oxa*-3-*azaprop*-2-*eno*)-4,6-*di*-O-p-*tolylsulphonyl*-α-D-*gulopyranoside* (8).—The oxazoline (4) (0·5 g.) in pyridine (5 ml.) was cooled to 0°, treated with toluene-*p*-sulphonyl chloride (1 g.), and then set aside at room temperature for 20 hr. Addition of ice–water gave a solid, which yielded the *disulphonate* (0·6 g.,

57%), m.p. 128—130° (from propan-2-ol), $[\alpha]_D$ +89° (*c* 1·55) (Found: C, 57·0; H, 4·8; N, 2·2; S, 10·9. $C_{28}H_{29}NO_9S_2$ requires C, 57·2; H, 4·9; N, 2·4; S, 10·9%).

Methyl 2,3-*Dideoxy*-3,2-(2-*phenyl*-1-*oxa*-3-*azaprop*-2-*eno*)-6-O-p-*tolylsulphonyl*-α-D-*gulopyranoside* (7).—A solution of the oxazoline (4) (4 g.) in pyridine (30 ml.) was cooled to 0°, treated with a solution of toluene-*p*-sulphonyl chloride (2·26 g., 1·1 equiv.), and kept at 0° for 3 days. The mixture was decomposed with water, and the product was isolated by extraction with chloroform; pyridine was removed from the organic layer by washing with 10% copper(II) sulphate solution as before. The resulting syrup was shown to be a mixture of three components by t.l.c. The major component, the 6-O-*toluene*-p-*sulphonate*, was isolated by fractional crystallisation from methanol. The product, isolated as two crops (1·75 g., 38%), had m.p. 192—195°, $[\alpha]_D$ +55·6° (*c* 1·3) (Found: C, 58·3; H, 3·15; N, 7·5. $C_{21}H_{23}NO_7S$ requires C, 58·2; H, 3·2; N, 7·4%).

Methyl 2,3,6-*Trideoxy*-6-*iodo*-3,2-(2-*phenyl*-1-*oxa*-3-*azaprop*-2-*eno*)-α-D-*gulopyranoside* (9).—The 6-*O*-*p*-tolylsulphonyl derivative (7) (0·43 g.) was dissolved in butanone (10 ml.), redistilled from potassium iodide,[13] and heated under reflux with sodium iodide (0·6 g.) for 15 hr. The mixture was then diluted with water and the product was isolated by extraction with chloroform. The extract was washed with water and 10% sodium thiosulphate solution, dried ($MgSO_4$), and concentrated to dryness. The crystalline product gave the 6-*iodo*-*derivative* (9) as fine white needles (0·27 g., 70%), m.p. 117—118° (from di-isopropyl ether), $[\alpha]_D$ +72° (*c* 0·7) (Found: C, 43·0; H, 4·5; N, 3·0. $C_{14}H_{16}INO_4$ requires C, 43·2; H, 4·1; N, 3·6%).

Methyl 2-*Acetamido*-3-O-*benzoyl*-2-*deoxy*-α-D-*gulopyranoside* (12).—A solution of the oxazoline (4) (1·6 g.) in methanol (60 ml.) containing hydrochloric acid (3 ml.) was stirred for 30 hr. at room temperature. The acid was then neutralised with an excess of lead carbonate. As soon as the solution was neutral, acetic anhydride (0·36 ml.) was added, and the mixture was stirred for a further 30 min., then filtered and concentrated to dryness. Initially it was considered advisable that the acetic anhydride should be added as soon as neutralisation was complete, so that *O*→*N* benzoyl migration did not occur before *N*-acetylation. Subsequently we examined the reaction mixture, after the addition of lead carbonate, by t.l.c., and found that this migration was slow at room temperature and that the lead carbonate could be filtered off before the addition of the acetic anhydride. The resulting syrup was dissolved in water and deionised on a column of mixed Amberlite IR-120(H^+) and IR-45(OH^-) resins. Concentration of the eluate gave a syrupy residue which was dissolved in propan-2-ol, and the solution was carefully treated with di-isopropyl ether to turbidity. The product slowly crystallised to afford the 2-*acetamido*-3-O-*benzoyl derivative* (1·3 g., 67%), m.p. 157—158°, $[\alpha]_D$ +20° (*c* 1·2 in MeOH) (Found: C, 56·6; H, 6·2; N, 4·1. $C_{16}H_{21}NO_7$ requires C, 56·6; H, 6·2; N, 4·3%).

Methyl 2-*Benzamido*-3-O-*benzoyl*-2-*deoxy*-α-D-*gulopyranoside* (13).—The oxazoline (4) (0·5 g.) was treated with methanol (20 ml.) and hydrochloric acid (1 ml.) as in the previous experiment. After neutralisation ($PbCO_3$) the solution was treated with benzoic anhydride (0·6 g.) and, after 1 hr., concentrated to dryness. The resulting syrup was then fractionated between chloroform and water, and the dried organic phase was concentrated to a syrup which was chromatographed on a column of silica gel (50 g.) with ether–light petroleum (4 : 1 v/v) as eluant. The 2-*benzamido*-3-O-*benzoyl derivative* was obtained as a chromatographically homogeneous syrup (0·55 g., 77%), $[\alpha]_D$ −51·4° (*c* 0·9) (Found: C, 63·0; H, 5·9; N, 3·4. $C_{21}H_{23}NO_7$ requires C, 62·8; H, 5·75; N, 3·5%).

Methyl 2-*Acetamido*-2-*deoxy*-α-D-*gulopyranoside* (14).—The 2-acetamido-3-*O*-benzoate (12) in methanol (10 ml.) was mixed with methanolic 0·5N-sodium methoxide (1 ml.); the solution was kept at room temperature for 1 hr. then concentrated to dryness and fractionated between water and ether in order to remove methyl benzoate. The aqueous layer was washed further with ether, then neutralised with Amberlite IR-120(H^+) resin, and concentrated to dryness. The syrup so obtained was dissolved in acetone and ether was added to turbidity. At 0° overnight the *guloside* (0·26 g., 60%) crystallised out, m.p. 84—85°, $[\alpha]_D$ +79° (*c* 1·4 in H_2O) (Found: C, 45·9; H, 7·2; N, 5·8. Calc. for $C_9H_{17}NO_6$: C, 46·0; H, 7·2; N, 6·0%) [lit.,[4] m.p. 79—82°, $[\alpha]_D$ +72° (in MeOH)].

Methyl 2-*Benzamido*-2-*deoxy*-α-D-*gulopyranoside* (15).—The 2-benzamido-3-*O*-benzoate (13) (0·3 g.) was dissolved in methanolic 0·025N-sodium methoxide (10 ml.) and kept at room temperature for 1 hr. The solution was then concentrated to dryness and washed several times with light petroleum to remove methyl benzoate. The syrupy product crystallised and yielded the 2-*benzamido*-*guloside* (0·16 g., 72%), m.p. 131—135° (from ethanol–light petroleum), $[\alpha]_D$ +61° (*c* 1 in MeOH) (Found: C, 56·6; H, 6·4; N, 4·4. $C_{14}H_{19}NO_6$ requires C, 56·6; H, 6·4; N, 4·7%).

Methyl 2-*Acetamido*-3,4,6-*tri*-O-*benzoyl*-2-*deoxy*-α-D-*gulopyranoside* (16).—A cooled (0°) solution of the 2-acetamido-3-*O*-benzoate (12) (1·0 g.) in pyridine (10 ml.) was mixed with benzoyl chloride (1·67 g.) and then kept at room temperature for 20 hr. The mixture was then decomposed with water, and the product was isolated by extraction with ether as a syrup, which was purified on a column of silica gel (100 g.), with ether–light petroleum (3 : 1 v/v) as eluant. The resulting syrupy *tri*-O-*benzoate* (0·5 g.) had $[\alpha]_D$ +43° (*c* 1·2) (Found: C, 66·0; H, 5·2; N, 2·6. $C_{30}H_{29}NO_9$ requires C, 65·8; H, 5·3; N, 2·6%).

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[13] A. C. Richardson, *J. Chem. Soc.*, 1964, 5364.