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SYNTHESIS OF GLYCOFURANO[2,1-*d*]IMIDAZOLIDIN-2-ONES

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ABSTRACT

Several 2-(3-arylureido)-2-deoxyglycopyranoses (**13–16**) have been converted into the corresponding 1-aryl-(1,2-dideoxyglycofurano)[2,1-*d*]imidazolidin-2-ones (**17–20**) by acid-catalyzed cyclization. Acetylation of these compounds gave 1-aryl-(per-*O*-acetyl-1,2-dideoxyglycofurano)[2,1-*d*]imidazolidin-2-ones (**21–24**) or 3-acetyl-1-aryl-(per-*O*-acetyl-1,2-dideoxyglycofurano)[1,2-*d*]imidazolidin-2-ones (**25–28**) depending on the reaction. 3-Ethyl-1-phenyl-(1,2-dideoxy-D-*glycero*-β-D-*talo*-heptofurano)[2,1-*d*]imidazolidin-2-one (**33**) was obtained by the reaction of 2-deoxy-2-ethylamino-D-*glycero*-β-D-*talo*-heptopyranose with phenyl isocyanate, and converted into the tetra-acetate **34**.

INTRODUCTION

The reaction of aminodeoxyaldoses with isothiocyanates has been studied extensively[1–3], but the analogous reaction with isocyanates has received less attention. Steudel[4] proposed the structure 2-hydroxy-1-phenyl-4-D-*arabino*-tetrahydroxybutylimidazole (**1**) for the product of reaction of 2-amino-2-deoxy-D-glucose hydrochloride with phenyl isocyanate. Pauly and Ludwig[5] assigned the structure 4-D-*arabino*-tetrahydroxybutylimidazolin-2-one (**2**) for the product of condensation of this amino sugar with silver cyanate. Structure **3** was assigned by Heyns and Meinecke[6] to the product obtained by Steudel, but Micheel and Lengsfeld[7] obtained this compound in low yield and gave it the structure of 1-phenyl-4,5-(1,2-D-glucopyrano)imidazolidin-2-one (**4**) when they prepared its triacetate **5**. This structure was used by several authors[8–10], and Morel[9] prepared a tetra-acetate to which he assigned structure **6**. The isomeric structure **7** has been synthesized by the reaction of 1-alkyl(aryl)amino-1-deoxy-D-fructose with alkaline or ammonium cyanates[11–13]. Structures **8** and **9** were also proposed for one of the degradation products, in an acid medium, of the antitumour antibiotic streptozoto-

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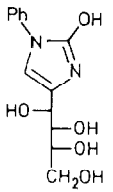
cin[14] (**10**) and for the antibiotic SF-1993[15] (**11**), respectively. Later, the glucofuranoid structure **12** was established by ^{1}H-n.m.r. spectroscopy[16,17] and oxidation with periodate[16], and subsequently confirmed by X-ray crystallography[18]. There appear to be no data on the reaction of 2-alkylamino-2-deoxyaldoses with aryl isocyanates.

We now describe the synthesis of several 1-aryl-(1,2-dideoxyglycofurano)-[2,1-*d*]imidazolidin-2-ones and their acetylated derivatives, and the correction of the structures erroneously assigned in the literature. The first 3-alkyl-1-aryl-(1,2-dideoxyglycofurano)[2,1-*d*]imidazolidin-2-one is also reported.



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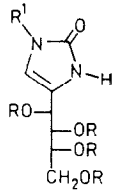
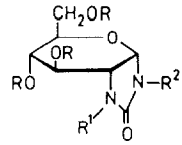
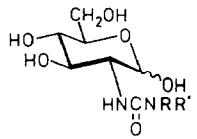


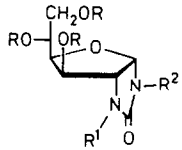
2 R = R^1 = H
3 R = H, R^1 = C_6H_5
7 R = Ac, R^1 = 4-$CH_3C_6H_4$



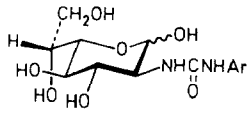
4 R = R^1 = H, R^2 = C_6H_5
5 R = Ac, R^1 = H, R^2 = C_6H_5
6 R = R^1 = Ac, R^2 = 4-$CH_3C_6H_4$
8 R = R^1 = H, R^2 = CH_3
9 R = R^1 = R^2 = H



10 R = NO, R' = CH_3
11 R = R' = H
13 R = H, R' = C_6H_5
14 R = H, R' = 4-ClC_6H_4



12 R and R^1 = H or Ac, R^2 = Aryl



15 Ar = C_6H_5
16 Ar = 4-ClC_6H_4

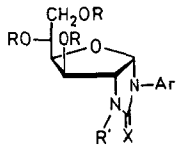
RESULTS AND DISCUSSION

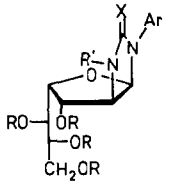
Heating solutions of the 2-arylureido-2-deoxy-D-glucopyranoses[19] **13** and **14** in dilute acetic acid gave the corresponding 1-aryl-(1,2-dideoxy-α-D-glucofurano)[2,1-*d*]imidazolidin-2-ones **17** and **18** in high yields. Likewise, the 2-arylureido-2-deoxy-D-*glycero*-L-*gluco*-heptopyranoses[19] **15** and **16** gave the 1-aryl-(1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[2,1-*d*]imidazolidin-2-ones **19** and **20**, respectively.

The structures of **17–20** accord with the elemental analyses and spectroscopic

properties, and the structure of **17** has been confirmed by X-ray crystallography[18]. The ^{1}H-n.m.r. signal for NH appears at ~7.5 p.p.m. and the $J_{2',3'}$ value of ~0 Hz shows[2] the sugar ring to be furanoid (Tables I and II). The ^{13}C-n.m.r. spectrum (Table V) confirms these assumptions since C-1′ is the most deshielded glycosidic carbon, the signal for C-4′ also appears downfield (~79.5 p.p.m.), and C-2′ is the most shielded carbon. The signal at ~157 p.p.m., the u.v. absorption at 240 nm, and the i.r. bands at 1700–1660 cm^{-1}, all due to the carbonyl group, do not accord with a tautomeric structure of 2-hydroxyimidazolidine such as **1**.

Treatment of **17–20** severally with acetic anhydride and pyridine at <5° gave high yields of the *O*-acetylated derivatives **21–24**, each of which had an i.r. band at ~3300 cm^{-1} and a signal in the ^{1}H-n.m.r. spectra at ~6.6 p.p.m. due to the NH group. The chemical shift of the signal for H-1′ is practically constant since position 1′ is not involved in the acylation; instead, the presence of the 3′-acetate group induces a downfield shift (~1.2 p.p.m.) in the signal for H-3′ and, to a lesser extent (~0.2 p.p.m.), in that for H-2′. In the ^{13}C-n.m.r. spectra, the 3′-acetate group shifts the C-2′ signal upfield (~1.5 p.p.m.; β-effect), and that of C-4′ is shifted most (~3.5 p.p.m.) since the β-effect of the 5′-acetate group is added; conversely, the signal for C-3′ is shifted downfield (~1.0 p.p.m.; α-effect). The elemental analysis and the weak i.r. band at ~1690 cm^{-1} demonstrated that **23** crystallised with 1 mol of water[20,21].





17 R = R′ = H, X = O, Ar = C_6H_5
18 R = R′ = H, X = O, Ar = 4-ClC_6H_4
21 R = Ac, R′ = H, X = O, Ar = C_6H_5
22 R = Ac, R′ = H, X = O, Ar = 4-ClC_6H_4
25 R = R′ = Ac, X = O, Ar = C_6H_5
26 R = R′ = Ac, X = O, Ar = 4-ClC_6H_4
29 R = R′ = Ac, X = S, Ar = C_6H_5
31 R = R′ = H, X = S, Ar = C_6H_5

19 R = R′ = H, X = O, Ar = C_6H_5
20 R = R′ = H, X = O, Ar = 4-ClC_6H_4
23 R = Ac, R′ = H, X = O, Ar = C_6H_5
24 R = Ac, R′ = H, X = O, Ar = 4-ClC_6H_4
27 R = R′ = Ac, X = O, Ar = C_6H_5
28 R = R′ = Ac, X = O, Ar = 4-ClC_6H_4
30 R = R′ = Ac, X = S, Ar = C_6H_5
32 R = R′ = H, X = S, Ar = C_6H_5

On acetylation of **21–24** with acetic anhydride–zinc chloride, the heterocyclic nitrogen also reacted, giving the 1-acetyl-3-aryl-(per-*O*-acetyl-1,2-dideoxy-D-glycofurano)[1,2-*d*]imidazolidin-2-ones **25–28**.

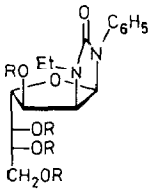
Micheel and Lengsfeld[7] and García González *et al.*[8], using the glycopyranoid structure **5**, described a triacetate of **17** but did not determine the structure. However, the physical constants {lit.[7] m.p. 152°, $[\alpha]_D$ +40° (ethanol); lit.[8] m.p. 151°} and the reagent used (acetic anhydride–zinc chloride) indicate the structure to be **25**.

The u.v. spectra of **25–28** are identical to those of **21–24**, but in the i.r. spectra the absorptions characteristic of the acetamido and heterocyclic carbonyl groups coincide. The ^{1}H-n.m.r. spectra contain three or four singlets (δ ~2.0) due to OAc groups and a singlet at δ ~2.60 due to the NAc group. The latter chemical shift probably reflects deshielding of the methyl group by the C=O bond of imidazolidin-2-one in the more stable antiperiplanar conformation of the NAc group, analogous to those found in 3-acetyl-2-oxazolidones[22,23] and in 1-acetyl-3-aryl-(per-*O*-acetyl-1,2-dideoxyglycofurano)[1,2-*d*]imidazolidine-2-thiones[2]. In the ^{13}C-n.m.r. spectra, the methyl signal of the NAc group appears at a lower field (δ ~24) than that (δ ~20) of the OAc groups.

The NAc group deshields (~0.4 p.p.m.) H-2′ and H-3′ in **25–28** compared to **21–24**, and the signals due to heterocyclic C=O, C-1′, and C-3′ are shifted to higher field (~6.0, ~3.6, and ~3.0–1.5 p.p.m., respectively) and that of C-2′ is shifted downfield (~2.2 p.p.m.). Furthermore, the NAc group has a marked effect on the $[\alpha]_D$ value. Thus, the $[\alpha]_D$ values of **21** and **22** are ~60° greater than those of **25** and **26**, and those of **23** and **24** are ~60° less than those of **27** and **28**.

The structures assigned to **25** and **27** were confirmed[2] by their synthesis from the thio-analogues **29** and **30**. Compounds **29** and **30** were obtained from **31** and **32**, the structures of which have been elucidated by X-ray crystallography[24,25].

The reaction of 2-deoxy-2-ethylamino-D-*glycero*-β-D-*talo*-heptopyranose[26] and phenyl isocyanate in an aqueous medium gave 51% of 3-ethyl-1-phenyl-(1,2-dideoxy-D-*glycero*-β-D-*talo*-heptofurano)[2,1-*d*]imidazolidin-2-one (**33**), the structure of which accorded with the elemental analysis and spectroscopic data. Compound **33** consumed 2 mol. equiv. of periodate, indicating that the structure 3-ethyl-1-phenyl-4-D-*manno*-pentahydroxypentylimidazolin-2-one can be discarded, and the formation of 1 mol. of formic acid confirmed the furanoid structure. Treatment of **33** with acetic anhydride–pyridine gave the tetra-acetate **34**, for which the $J_{2',3'}$ value of 5.8 Hz accords with a D-*glycero*-D-*talo* configuration, in which H-2′,3′ are *cis*[26].



33 R=H

34 R=Ac

EXPERIMENTAL

General methods. — Melting points were determined with a Gallenkamp apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer

141 polarimeter. U.v. spectra were recorded with a Pye-Unicam SP8-250 automatic spectrophotometer on solutions in aqueous 96% ethanol, and i.r. spectra (KBr disc) with a Perkin–Elmer 399 spectrophotometer. ^{1}H-N.m.r. spectra (internal Me_4Si or sodium 2,2-dimethyl-2-silapentane-5-sulfonate) were recorded with a Varian XL-200 (200 MHz), Perkin–Elmer R-32 (90 MHz), or Bruker WP-80-SY (80 MHz) spectrometer. ^{13}C-N.m.r. spectra were recorded with a Varian XL-200 (50.2 MHz) or Bruker WP-80-SY (20.15 MHz) spectrometer. P.c. (ascending) was performed on Whatman No. 1 paper, using 1-butanol–pyridine–water (1:1:1) and detection with silver nitrate–sodium hydroxide. T.l.c. was conducted on Silica Gel GF_{254} (Merck), using 3:1 ethyl acetate–ethanol and detection with iodine vapour and u.v. light at 254 nm. The consumption of oxidant and the release of formic acid on periodate oxidation of **33** were determined as described[27,28].

*1-Phenyl-(1,2-dideoxy-α-*D*-glucofurano)[2,1-*d*]imidazolidin-2-one* (**17**). — To a suspension of 2-deoxy-2-(3-phenylureido)-D-glucopyranose[19] (**13**; 2.3 g, 7.7 mmol) in water (5 mL) was added acetic acid (1 mL), and the mixture was stirred at ~100° for 30 min[9] and then filtered. The product (1.92 g, 89%) which crystallised on cooling was collected, washed with cold water and acetone, and recrystallised from water to give material having m.p. 214–216°, $[\alpha]_D$ +93°, $[\alpha]_{578}$ +98°, $[\alpha]_{546}$ +113°, $[\alpha]_{436}$ +214.5°, $[\alpha]_{365}$ +395.5° (*c* 0.5, pyridine); λ_{max} 235 nm (ε_{mM} 15.2); ν_{max} 3400–3300 (OH, NH), 1660 cm^{-1} (C=O); lit.[7] m.p. 211°, $[\alpha]_D$ +92° (*c* 1.25, aqueous 25% *N,N*-dimethylformamide). The ^{1}H- and ^{13}C-n.m.r. data are given in Tables I, II, and V.

*1-(4-Chlorophenyl)-(1,2-dideoxy-α-*D*-glucofurano)[2,1-*d*]imidazolidin-2-one* (**18**). — Obtained, as described for **17**, from 2-[3-(4-chlorophenyl)ureido]-2-deoxy-D-glucopyranose[9,19] (**14**; 2.0 g, 6.0 mmol) in aqueous 80% ethanol (65 mL) and acetic acid (6 mL), **18** (1.6 g, 85%) had m.p. 217–218° (from ethanol), $[\alpha]_D$ +116.5°, $[\alpha]_{578}$ +123°, $[\alpha]_{546}$ +141.5°, $[\alpha]_{436}$ +268°, $[\alpha]_{365}$ +492.5° (*c* 0.5, pyridine); λ_{max} 243 nm (ε_{mM} 15.3); ν_{max} 3500–3300 (OH, NH), 1670 cm^{-1} (C=O); lit.[9] m.p. 221–222°, $[\alpha]_D$ +145.9° (*c* 1, *N,N*-dimethylformamide). The ^{1}H- and ^{13}C-n.m.r. data are given in Tables I, II, and V.

*1-Phenyl-(1,2-dideoxy-*D*-glycero-α-*L*-gluco-heptofurano)[2,1-*d*]imidazolidin-2-one* (**19**). — A mixture of 2-deoxy-2-(3-phenylureido)-D-*glycero*-L-*gluco*-heptopyranose[19] (**15**; 1.4 g, 4.3 mmol), water (5 mL), and acetic acid (0.6 mL) was heated at ~100° for 30 min[9]. The solvent was removed under reduced pressure and the residual syrup was crystallised from ethanol. Recrystallisation of the product (1.09 g, 82%) from aqueous 96% ethanol gave **19** as large prisms, m.p. 211–212°, $[\alpha]_D$ −114.5°, $[\alpha]_{578}$ −120.5°, $[\alpha]_{546}$ −139.5°, $[\alpha]_{436}$ −266°, $[\alpha]_{365}$ −496° (*c* 0.5, pyridine); λ_{max} 236 nm (ε_{mM} 13.0); ν_{max} 3540, 3460–3200 (OH, NH), 1705 cm^{-1} (C=O). The ^{1}H- and ^{13}C-n.m.r. data are given in Tables I, II, and V.

Anal. Calc. for $C_{14}H_{18}N_2O_6$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.09; H, 6.06; N, 9.18.

*1-(4-Chlorophenyl)-(1,2-dideoxy-*D*-glycero-α-*L*-gluco-heptofurano)[2,1-*d*]-imidazolidin-2-one* (**20**). — A mixture of 2-[3-(4-chlorophenyl)ureido]-2-deoxy-D-

TABLE I

^{1}H-N.M.R. CHEMICAL SHIFT DATA[a] (δ, 200 MHz) FOR COMPOUNDS **17–20** AND **33**

Compound	*H-1'*	*H-2'*	*H-3'*	*H-4'*	*H-5'*	*H-6',6''*	*H-7',7''*	*NH*[e]	*Aromatic*	*OH-3*	*OH-5*	*OH-6*	*OH-7*	*Et*	
														CH_2	*CH_3*
17	5.97 d	4.00 d[c]	4.08 dd[d]	←	3.76–3.29 m	→		7.50 s	7.63–7.05 m	5.30 d	4.74 d	4.49 t			
18	5.97 d	4.00 d[c]	4.06 dd[d]	←	3.80–3.30 m	→		7.62 s	7.65–7.35 dd	5.33 d	4.75 d	4.50 t			
19	5.95 d	4.00 dd	4.06 dd	3.94 dd	←	3.86–3.30 m	→	7.50 s	7.64–7.06 m	5.22 d	4.32 d[b]	*4.29 d*[b]	4.50 t		
20	5.96 d	4.02 d[c]	4.07 m[d]	3.94 dd	←	3.87–3.30 m	→	7.61 s	7.67–7.35 dd	5.24 d	4.34 d[b]	4.30 d[b]	4.50 t		
33	5.85 d	4.18 t		3.97 d	←	3.48–3.31 m	→		7.70–7.00 m	5.44 d	4.53 m (2 H)		4.32 m	3.52 m (1 H)	1.11 t

[a]In $(CD_3)_2SO$. [b]Assignments may be interchanged. [c]Sharp doublet after deuteration with D_2O. [d]Doublet after deuteration with D_2O. [e]Broad singlets.

glycero-L-*gluco*-heptopyranose[19] (**16**; 2.5 g, 6.7 mmol) in aqueous 70% ethanol (30 mL) and acetic acid (5 mL) was heated at ~100° for 45 min[9], then concentrated. Treatment of the residual syrup with acetone gave crystalline **20** (1.39 g, 58%). Recrystallisation from water gave material having m.p. 192–194°, $[\alpha]_D$ −66.5°, $[\alpha]_{578}$ −71°, $[\alpha]_{546}$ −82°, $[\alpha]_{436}$ −156°, $[\alpha]_{365}$ −288° (*c* 1, pyridine); λ_{max} 241 nm (ε_{mM} 18.2); ν_{max} 3560–3100 (OH, NH), 1715, 1680 cm^{-1} (C=O). The ^1H- and ^{13}C-n.m.r. data are given in Tables I, II, and V.

Anal. Calc. for $C_{14}H_{17}ClN_2O_6 \cdot 0.5\ H_2O$: C, 47.53; H, 5.13; N, 7.92. Found: C, 47.52; H, 5.19; N, 7.74.

*1-Aryl-(per-O-acetyl-1,2-dideoxyglycofurano)[2,1-*d*]imidazolidin-2-ones.* — A solution of each 1-aryl-(1,2-dideoxyglycofurano)[2,1-*d*]imidazolidin-2-one (1.5 mmol) in pyridine (4–6 mL) was heated gently and then cooled to 0°, and acetic anhydride was added (3 mL for **17** and **18**, 4.5 mL for **19** and **20**). Each mixture was stored for 10 h at 0° and then poured into ice–water, and the solid product was collected, washed with cold water, and dried *in vacuo*. The following compounds were prepared in this way.

1-Phenyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[2,1-*d*]imidazolidin-2-one (**21**, 82% from **17**), m.p. 109–110° (from aqueous 96% ethanol), $[\alpha]_D$ +95.5°, $[\alpha]_{578}$ +100°, $[\alpha]_{546}$ +116°, $[\alpha]_{436}$ +210°, $[\alpha]_{365}$ +355.5° (*c* 0.5, chloroform); λ_{max} 235 nm (ε_{mM} 14.3); ν_{max} 3310 (NH), 1745, 1720 (C=O ester), 1705 cm^{-1} (C=O heterocycle). The ^1H- and ^{13}C-n.m.r. data are given in Tables III–V.

Anal. Calc. for $C_{19}H_{22}N_2O_8$: C, 56.15; H, 5.46; N, 6.89. Found: C, 55.82; H, 5.53; N, 6.79.

1-(4-Chlorophenyl)-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[2,1-*d*]-imidazolidin-2-one (**22**, 86% from **18**), m.p. 96–98° (from aqueous 96% ethanol), $[\alpha]_{578}$ +99°, $[\alpha]_{546}$ +113.5°, $[\alpha]_{436}$ +206.5°, $[\alpha]_{365}$ +357° (*c* 1, chloroform); λ_{max} 243 nm (ε_{mM} 16.1); ν_{max} 3240 (NH), 1745, 1715 (C=O ester), 1700 cm^{-1} (C=O heterocycle). The ^1H- and ^{13}C-n.m.r. data are given in Tables III–V.

Anal. Calc. for $C_{19}H_{21}ClN_2O_8$: C, 51.77; H, 4.80; N, 6.35. Found: C, 51.50; H, 5.13; N, 6.12.

1-Phenyl-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[2,1-*d*]imidazolidin-2-one (**23**, 90% from **19**), m.p. 106–108° (from aqueous 50% ethanol), $[\alpha]_D$ −69.5°, $[\alpha]_{578}$ −73°, $[\alpha]_{546}$ −84.5°, $[\alpha]_{436}$ −155°, $[\alpha]_{365}$ −272° (*c* 0.5, chloroform); λ_{max} 234 nm (ε_{mM} 13.7); ν_{max} 3560–3180 (NH, H_2O), 1740 (C=O ester), 1695 (C=O heterocycle), 1645 cm^{-1} H_2O. The ^1H- and ^{13}C-n.m.r. data are given in Tables III–V.

Anal. Calc. for $C_{22}H_{26}N_2O_{10} \cdot H_2O$: C, 53.22; H, 5.68; N, 5.67. Found: C, 53.47; H, 5.62; N, 5.56.

1-(4-Chlorophenyl)-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[2,1-*d*]imidazolidin-2-one (**24**, 71% from **20**), m.p. 76–78° (from aqueous 90% ethanol), $[\alpha]_{578}$ −73.5°, $[\alpha]_{546}$ −76°, $[\alpha]_{436}$ −88.5°, $[\alpha]_{365}$ −287° (*c* 0.5, chloroform); λ_{max} 242 nm (ε_{mM} 17.1); ν_{max} 3440, 3220, 3140 (NH, OH), 1760, 1745 1730 cm^{-1} (C=O ester and heterocycle). The ^1H- and ^{13}C-n.m.r. data are given in Tables III–V.

TABLE II

^{1}H-N.M.R. SPIN-COUPLING DATA[a] (Hz) FOR COMPOUNDS **17–20** AND **33**

Compound	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{3',OH}$	$J_{5',OH}$	$J_{6',OH}$	$J_{7',OH}$	*Et*	
									J_{CH_2}	J_{CHCH}
17	6.2	0.0	1.8		4.6	5.5	5.6			
18	6.2	0.0[b]	1.8		4.6	5.5	5.6			
19	6.2	0.0[c]	2.4	9.5	4.8	3.2	1.8	5.5		
20	6.2	0.0	2.2[d]	9.5	4.4	3.6	1.9	5.3		
33	6.0	5.8	8.6	~0.0	5.4				−14.1	6.8

[a]Conditions described in Table I. [b]$J_{2',NH}$ ~0.8 Hz, [c]$J_{2',NH}$ 0.9 Hz. [d]Value obtained after addition of D_2O.

TABLE III

^{1}H-N.M.R. CHEMICAL SHIFT DATA (δ)[a] FOR COMPOUNDS **21–28** AND **34**

Compound	*H-1'*	*H-2'*	*H-3'*	*H-4'*	*H-5'*	*H-6'*	*H-6''*	*H-7'*	*H-7''*	*NH*	*NAc*	*Et*		*Ar*	*OAc*
												NCH$_2$	*CH$_3$*		
21[b]	5.99 d	4.19 d	5.33 d	4.42 dd	5.28 m	4.55 dd	4.16 dd			6.76 bd				7.63–7.16 m (5 H)	2.09 s (3 H) 2.02 s (3 H) 1.99 s (3 H)
22[b]	5.98 d	4.20 d	5.31 d	4.39 dd	5.27 m	4.55 dd	4.16 dd			6.62 bd				7.60–7.29 dd (4 H)	2.10 s (3 H) 2.03 s (3 H) 1.99 s (3 H)
23[b]	5.99 d	4.18 dd	5.25 d	4.34 dd	5.53–5.40 m			4.32 dd	3.94 dd	6.53 d				7.61–7.10 m (5 H)	2.12 s (3 H) 2.06 s (3 H) 2.03 s (3 H) 1.80 s (3 H)
24[b,d]	5.95 d	4.20 d	5.24 d	4.33 dd	5.45 dd	5.49 dd		4.33 dd	3.94 dd	6.56 bd				7.58–7.30 dd (4 H)	2.13 s (3 H) 2.07 s (3 H) 2.04 s (3 H) 1.82 s (3 H)

25[c]	5.98 d	4.63 d	5.73 d	4.23 dd	5.22 qd	4.50 dd	4.13 dd			2.61 s (3 H)			7.70–7.20 m (5 H)	2.11 s (3 H) 2.01 s (3 H) 1.97 s (3 H)
26[b]	5.96 d	4.64 d	5.73 d	4.22 dd	5.22 m	4.49 dd	4.14 dd			2.61 s (3 H)			7.59–7.35 dd (4 H)	2.12 s (3 H) 2.02 s (3 H) 1.98 s (3 H)
27[c]	5.98 d	4.60 d	5.68 d	4.17 dd	5.55–5.25 m			4.31 dd	3.87 dd	2.59 s (3 H)			7.70–7.10 m (5 H)	2.12 s (3 H) 2.04 s (3 H) 2.00 s (3 H) 1.80 s (3 H)
28[b]	5.94 d	4.62 d	5.69 d	4.15 dd	5.37 dd	5.47 m		4.32 dd	3.87 dd	2.60 s (3 H)			7.59–7.36 dd (4 H)	2.13 s (3 H) 2.05 s (3 H) 2.03 s (3 H) 1.84 s (3 H)
34[b]	5.90 d	4.38 dd-t	4.96 dd	4.25 dd	5.36 dd	5.26 m		4.38 dd	4.17 dd		3.60 m (1 H) 3.04 m (1 H)	1.17 t (3 H)	7.66–7.00 m (5 H)	2.17 s (3 H) 2.15 s (3 H) 2.03 s (3 H) 1.79 s (3 H)

[a]In $CDCl_3$. [b]At 200 MHz. [c]At 80 MHz. [d]Other signals: δ 3.72 (q, CH_2) and 1.25 (t, CH_3, *J* 7.0 Hz) from ethanol of crystallisation.

TABLE IV

^{1}H-N.M.R. SPIN-COUPLING DATA[a] (Hz) FOR COMPOUNDS **21–28** AND **34**

Compound	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'}$	$J_{5',6''}$	$J_{6'',6''}$	$J_{6',7'}$	$J_{6',7''}$	$J_{7',7''}$	*Et*	
											J_{CH_2}	J_{CHCH}
21	6.4	0.0	2.8	9.2	2.2	4.8	−12.4					
22	6.2	0.0	2.6	9.2	2.1	5.1	−12.5					
23	6.4	0.0[b]	2.8	9.3[c]	2.0			2.7[c]	7.0	−11.6		
24	6.4	0.0[d]	2.8	9.2	2.0				7.1	−11.5		
25	6.6	0.0	2.8	9.4	2.2	4.7	−12.4					
26	6.6	0.0	2.8	9.4	2.2	4.8	−12.2					
27	6.7	0.0	3.0	9.3				4.7	6.9	−11.6		
28	6.6	0.0	3.0	9.4	2.4			4.8	7.1	−11.8		
34	6.6	5.8	9.5	2.1	7.6			2.4	5.0	−12.4	−14.4	7.0

[a]Conditions described in Table III. [b]$J_{2',NH}$ 1.6 Hz. [c]At 90 MHz. [d]Broad doublet, $J_{2',NH}$ 1.7 Hz.

TABLE V

^{13}C-N.M.R. CHEMICAL SHIFT DATA (P.P.M.) FOR COMPOUNDS **17–28, 33** AND **34**

Compound	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′	NCNO	Aromatic				AcO		Et		AcN	
									C-1	C-3,5	C-4	C-2,6	CH_3	CO	CH_2	CH_3	CH_3	CO
17[a,c]	89.76	60.67	74.32	79.47	68.72	63.93		157.34	139.39	128.89	123.06	119.41						
18[a,c]	89.51	60.65	74.24	79.54	68.65	63.86		157.09	138.35	128.56	126.33	120.63						
19[a,c]	89.69	60.78	74.28	78.86	66.37	70.85	62.61	157.35	139.48	128.62	122.96	119.42						
20[a,c]	89.46	60.77	74.22	78.94	66.32	70.81	62.57	157.13	138.43	128.51	126.77	120.67						
21[a,d]	90.76	59.34	75.30	75.70	67.22	63.05		157.84	137.63	128.77	124.59	120.64	20.59	170.48				
													20.54	169.58				
													20.48	169.54				
22[a,d]	90.54	59.34	75.27	75.85	67.21	62.95		157.52	136.24	128.80	129.82	121.53	20.58	170.46				
													20.53	169.67				
													20.47	169.51				
23[a,d]	90.43	59.28	75.21[f]		67.02	69.20	61.70	157.51	137.47	128.77	124.49	120.21	20.82	170.31				
													20.47	169.83				
													20.39	169.53				
													20.15	169.42				
24[a,d,g]	90.50	59.49	75.31	75.53	67.17	69.33	61.97	157.52	136.34	128.98	129.93	121.44	20.82	170.56				
													20.68	170.10				
													20.58	169.76				
													20.40	169.60				
25[b,d]	87.16	61.73	73.74	76.25	67.20	63.25		152.00	136.87	129.27	126.46	122.50	20.66[f]	170.31[f]			24.07	168.47
													20.46	169.72				
26[a,d]	86.70	61.26	73.00	75.79	66.57	62.84		151.47	135.02	129.10	131.57	122.99	20.59	170.29			24.08	168.39
													20.50	170.08				
													20.44	169.61				
27[b,d]	87.00	61.72	73.52	75.97	67.13	69.76	62.15	151.88	136.82	129.29	126.24	121.88	20.73	170.24[f]			24.07	168.61
													20.55[f]	169.70				
													20.30	169.47				
28[a,d]	86.86	61.28	72.71	75.48	66.51	69.09	61.90	151.43	134.92	129.05	131.62	122.57	20.61	170.27			24.05	168.55
													20.45	170.05				
													20.40	169.56				
													20.23	169.43				
33[a,c]	87.78	57.83	72.73[e]	81.03[e]	72.18[e]	69.16[e]	64.42	158.37	139.70	129.60	124.38	120.55			38.79	12.91		
34[a,d]	87.14	54.81	72.40	73.82	66.60	69.59	61.71	158.08	137.97	128.71	123.96	119.37	20.50	170.37	38.46	12.11		
													20.42	170.11				
													20.35	169.64				
														169.44				

[a]At 50 MHz. [b]At 20.15 MHz. [c]In $(CD_3)_2SO$. [d]In $CDCl_3$. [e]Assignments may be interchanged. [f]Signal for two carbons. [g]Other signals: δ 58.23 and 18.33 from ethanol of crystallisation.

Anal. Calc. for $C_{22}H_{25}ClN_2O_{10}\cdot EtOH$: C, 51.57; H, 5.59; N, 5.01. Found: C, 51.52; H, 5.61; N, 4.99.

*1-Acetyl-3-aryl-(per-O-acetyl-1,2-dideoxyglycofurano)[1,2-*d*]imidazolidin-2-ones.* — Each 1-aryl-(1,2-dideoxyglycofurano)[2,1-*d*]imidazolidin-2-one (2.0 mmol) was added to a solution of anhydrous, freshly fused zinc chloride (0.2 g) in acetic anhydride (5.7 mL). The mixture was kept for 48 h at room temperature or for 12 h at 40°, then poured into ice–water. The solid product was collected, washed with cold water, and dried *in vacuo*. The following compounds were prepared in this way.

1-Acetyl-3-phenyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[1,2-*d*]-imidazolidin-2-one (**25**, 90% from **17**), m.p. 153–155° (from ethanol), $[\alpha]_D$ +32.5°, $[\alpha]_{578}$ +34°, $[\alpha]_{546}$ +38.5°, $[\alpha]_{436}$ +65°, $[\alpha]_{365}$ +102.5° (*c* 0.5, chloroform); λ_{max} 238 nm (ε_{mM} 13.3); ν_{max} 1740 (C=O ester), 1700 cm^{-1} (C=O amide and heterocycle). The ^1H- and ^{13}C-n.m.r. data are given in Tables III–V.

Anal. Calc. for $C_{21}H_{24}N_2O_9$: C, 56.25; H, 5.39; N, 6.25. Found: C, 56.19; H, 5.45; N, 6.18.

1-Acetyl-3-(4-chlorophenyl)-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[1,2-*d*]imidazolidin-2-one (**26**, 72% from **18**), m.p. 130–132° (from ethanol), $[\alpha]_D$ +44°, $[\alpha]_{578}$ +47.5°, $[\alpha]_{546}$ +54°, $[\alpha]_{436}$ +98°, $[\alpha]_{365}$ +168° (*c* 0.5, chloroform); λ_{max} 244 nm (ε_{mM} 17.0); ν_{max} 1750 (C=O ester), 1690 cm^{-1} (C=O amide and heterocycle). The ^1H- and ^{13}C-n.m.r. data are given in Tables III–V.

Anal. Calc. for $C_{21}H_{23}ClN_2O_9$: C, 52.24; H, 4.80; N, 5.80. Found: C, 52.13; H, 4.77; N, 5.67.

1-Acetyl-3-phenyl-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[1,2-*d*]imidazolidin-2-one (**27**, 95% from **19**), m.p. 149–150° (from ethanol), $[\alpha]_D$ −7.5° (*c* 1, chloroform); λ_{max} 239 nm (ε_{mM} 14.9); ν_{max} 1740 (C=O ester), 1690 cm^{-1} (C=O amide and heterocycle). The ^1H- and ^{13}C-n.m.r. data are given in Tables III–V.

Anal. Calc. for $C_{24}H_{28}N_2O_{11}$: C, 55.38; H, 5.42; N, 5.38. Found: C, 55.73; H, 5.45; N, 5.31.

1-Acetyl-3-(4-chlorophenyl)-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[1,2-*d*]imidazolidin-2-one (**28**, 88% from **20**), m.p. 160–162° (from ethanol), $[\alpha]_D$ −27.5°, $[\alpha]_{578}$ −27.5°, $[\alpha]_{546}$ −32°, $[\alpha]_{436}$ −61.5°, $[\alpha]_{365}$ −118° (*c* 0.5, chloroform); λ_{max} 245 nm (ε_{mM} 17.9); ν_{max} 1750 (C=O ester), 1695 cm^{-1} (C=O amide and heterocycle). The ^1H- and ^{13}C-n.m.r. data are given in Tables III–V.

Anal. Calc. for $C_{24}H_{27}ClN_2O_{11}$: C, 51.95; H, 4.90; N, 5.05. Found: C, 52.21; H, 4.92; N, 4.91.

*3-Ethyl-1-phenyl-(1,2-dideoxy-*D-glycero-β-D-talo-*heptofurano)[2,1-*d*]imidazolidin-2-one* (**33**). — To a solution of 2-deoxy-2-ethylamino-D-*glycero*-β-D-*talo*-heptopyranose hydrochloride[26] (2.74 g, 10.0 mmol) in water (9 mL) was added sodium hydrogencarbonate (0.84 g, 10.0 mmol). The mixture was stirred vigorously, and phenyl isocyanate (1.1 mL, 10.0 mmol) and aqueous 96% ethanol (6

mL) were added. After 3 h, *N,N'*-diphenylurea was removed and p.c. of the filtrate showed that a large quantity of amino sugar still remained. The mixture was concentrated to a thick syrup and diluted with ethanol (10 mL), and phenyl isocyanate (1.1 mL) was added. After several hours, the *N,N'*-diphenylurea was removed, the filtrate was concentrated, and an aqueous solution of the residue was extracted with ether (2 × 15 mL), then concentrated, and stored for several days at room temperature. A mixture (2.97 g) of **33** and sodium chloride crystallised. Recrystallisation from ethanol gave **33** (1.74 g, 51%). A second recrystallisation from aqueous 96% ethanol gave material having m.p. 184–185°, $[\alpha]_D$ −143°, $[\alpha]_{578}$ −150°, $[\alpha]_{546}$ −174°, $[\alpha]_{436}$ −328°, $[\alpha]_{365}$ −600° (*c* 0.5, pyridine); λ_{max} 240 nm (ε_{mM} 18.1); ν_{max} 3500–3200 (OH), 1665 cm^{-1} (C=O heterocycle). The ^1H- and ^{13}C-n.m.r. data are given in Tables I, II, and V. Compound **33** consumed 2.1 mol. equiv. of periodate and released 1.0 mol. equiv. of formic acid.

Anal. Calc. for $C_{16}H_{22}N_2O_6$: C, 56.80; H, 6.55; N, 8.28. Found: C, 56.58; H, 6.91; N, 8.44.

*3-Ethyl-1-phenyl-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-*D-glycero-*β*-D-talo-heptofurano)[2,1-*d*]imidazolidin-2-one* (**34**). — Conventional treatment of **33** (0.5 g, 1.5 mmol) with acetic anhydride (3.2 mL) in pyridine (3.0 mL) gave **34** (0.73 g, 97%), m.p. 111–112° (from aqueous 60% ethanol), $[\alpha]_D$ −120°, $[\alpha]_{578}$ −126°, $[\alpha]_{546}$ −144.5°, $[\alpha]_{436}$ −259.5°, $[\alpha]_{365}$ −442° (c 0.5, chloroform); λ_{max} 236 nm (ε_{mM} 15.8); ν_{max} 1740, 1730 (C=O ester), 1690 cm^{-1} (C=O heterocycle). The ^1H- and ^{13}C-n.m.r. data are given in Tables III–V.

Anal. Calc. for $C_{24}H_{30}N_2O_{10}$: C, 56.91; H, 5.97; N, 5.53. Found: C, 57.03; H, 5.97; N, 5.62.

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