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ACYLATION OF GLYCOFURANO[2,1-*d*]IMIDAZOLIDINE-2-THIONES: A STRUCTURAL REVISION

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ABSTRACT

Acetylation of glycofurano[2,1-*d*]imidazolidine-2-thiones leads to the *O*-acetylated or *N*-acetylated, *O*-acetylated glycofurano[2,1-*d*]imidazolidine-2-thiones depending on the reaction conditions. The position of acetylation on the imidazolidine-2-thione ring was demonstrated by spectroscopic data and by transformation of C=S→C=O groups. The formation of a glycofuranoimidazolidine-2-thione by the reaction of a 2-amino-2-deoxyaldose with potassium thiocyanate has not been observed hitherto.

INTRODUCTION

The reaction of aminoaldoses with isothiocyanates has been studied extensively[1]. The structures 1-aryl- or 1-alkyl-2-mercapto-4-D-*arabino*-tetrahydroxybutylimidazole (**1**, R = aryl or alkyl) were proposed[2] for the products of reaction of 2-amino-2-deoxy-D-glucose hydrochloride with phenyl and allyl isothiocyanates. Later[3,4], the structure 2-mercapto-4(5)-D-*arabino*-tetrahydroxybutylimidazole (**1**, R = H) was assigned to the product of condensation of this amino sugar with potassium thiocyanate and subsequently confirmed[5]. However, the structure "1-aryl-4,5-(1,2-D-glucopyrano)imidazolidine-2-thione" (**2**, R = aryl) was proposed for the products of reaction of aryl isothiocyanates with 2-amino-2-deoxy-D-glucose and utilised by several authors[6–11]. Finally, the furanoid structure of these compounds (**3**, R = aryl) has been established by ^{1}H-n.m.r. spectroscopy[12], oxidation with periodate [12,13] and lead tetra-acetate[13], and by X-ray crystallography[14–16].

On heating with acetic acid[8,17], **3** rearranges into the isomeric monocyclic 4-(tetrahydroxybutyl)-4-imidazolidine-2-thione (**4**). These products were also obtained by the reaction of substituted 1-amino-1-deoxy-D-fructose with the thiocyanate ion[18]. A comparative structural study of these compounds has been reported[7].

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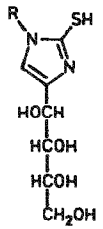

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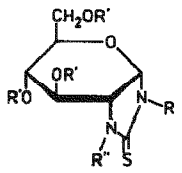

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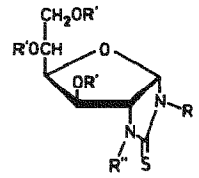
5 R'=R''=Ac



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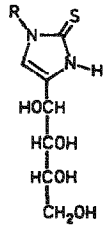

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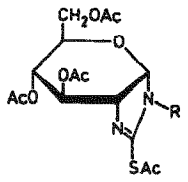

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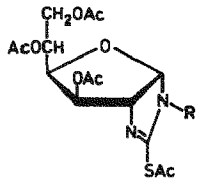

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The acetylation of **4** involves only the tetrahydroxybutyl side-chain[8], but the heterocyclic ring in **3** is acetylated[11]. These compounds have been formulated as tetra-acetates of tetrahydroimidazoles[11,13] (**5** and **6**) and dihydroimidazoles[7,11,19] (**7** and **8**). Therefore, the position of the acetyl group in the heterocycle remains uncertain.

We now report a structural investigation of a series of glycofuranoimidazolidine-2-thiones and their acetyl derivatives.

RESULTS AND DISCUSSION

The reaction of 2-amino-2-deoxy-α-D-glucopyranose hydrochloride with several isothiocyanates gave 1-alkyl(aryl)-(1,2-dideoxy-α-D-glucofurano)[2,1-*d*]-imidazolidine-2-thiones (**9–13**). Likewise, **14–17** have been prepared from 2-amino-2-deoxy-D-*glycero*-α-L-*gluco*-heptopyranose hydrochloride[20]. The structures assigned to these compounds are supported by chemical and spectroscopic properties. Thus, they had u.v. absorptions characteristic[21] of the C=S group [231–248 nm (ε_{mM} 9.0–21.0) for the $\pi \rightarrow \pi^*$ transition and ~268 nm (ε_{mM} 10.0) for the $n \rightarrow \pi^*$ transition], thus ruling out the 2-mercaptoimidazoline structure. The ^{1}H-n.m.r. signal for the NH of the imidazolidine-2-thione ring appeared at ~9 p.p.m. The chemical shifts of the signals for H-1′ depend on the N-1 substituent (see Table I). Thus, for 1-aryl-(1,2-dideoxyglycofurano)[2,1-*d*]imidazolidine-2-thiones, the signal for H-1′ is shifted downfield (~0.3 p.p.m.) with respect to that of H-1′ in the 1-alkyl analogue **9**. The $J_{2',3'}$ values of ~0 Hz (Table II) accorded with H-2′,3′ being *trans* in a furanoid structure. The ^{13}C-n.m.r. spectra (Table III) contained a signal at ~181 p.p.m. for the thiocarbonyl carbon atom, further con-

TABLE I

^{1}H-N.M.R. CHEMICAL SHIFT DATA

Compound	*H-1'*	*H-2'*	*H-3'*	*H-4'*	*H-5'*	*H-6'*	*H-6''*	*H-7'*	*H-7''*	*N–CH$_3$*	*N–CH$_2$*	*N–H*	*Aromatic*	*OAc*	*NAc*
9[a,c]	5.66 d	3.97 d	3.98 d	←3.90–3.25 m→						2.93 s		8.59 s			
10[a,c]	5.97 d	4.18 d	4.13 d	←3.90–3.30 m→								9.07 s	7.60–7.20 m		
14[a,c]	5.93 d	4.18 d	←4.20–3.20 m→									9.07 s	7.60–7.10 m		
18[b,c]	5.77 d	4.22 dd	5.24 d	4.09 dd	5.28 qd	4.55 dd	4.13 dd			3.14 s		7.29 s		2.08 s (3 H) 2.07 s (3 H) 2.02 s (3 H)	
19[b,c]	6.00 d	4.35 dd	5.34 d	4.41 dd	5.29 qd	4.52 dd	4.13 dd					7.68 s	7.55–7.30 m	2.09 s (6 H) 2.04 s (3 H)	
21[b,c]	6.00 d	4.35 dd	5.32 d	4.39 dd	5.30 qd	4.61 dd	4.14 dd					7.26 s	7.65–7.30 m	2.10 s (3 H) 2.08 s (3 H) 2.04 s (3 H)	
23[b,c]	5.99 d	4.33 dd	5.35 m	4.35 m	←5.50–5.25 m→			4.50–4.20 m	3.94 dd			7.67 s	7.50–7.30 m	2.08 s (3 H) 2.06 s (6 H) 2.02 s (3 H)	
27[b,c]	5.70 d	4.72 d	5.60 d	3.89 dd	5.19 qd	4.49 dd	4.13 dd			3.19 s				2.09 s (3 H) 2.05 s (3 H) 1.99 s (3 H)	2.85 s (3 H)
28[b,c]	5.92 d	4.90 d	5.73 d	4.27 dd	5.20 qd	4.55 dd	4.08 dd						7.55–7.20 m	2.10 s (6 H) 2.02 s (3 H)	2.90 s (3 H)
32[b,c]	5.91 d	4.85 d	5.74 d	4.20 dd	←5.50–5.20 m→			4.31 dd	3.89 dd				7.60–7.10 m	2.11 s (3 H) 2.10 s (3 H) 2.05 s (3 H) 2.00 s (3 H)	2.89 s (3 H)
38[b,c]	5.98 d	4.63 d	5.73 d	4.23 dd	5.22 qd	4.50 dd	4.13 dd						7.70–7.20 m	2.11 s (3 H) 2.01 s (3 H) 1.97 s (3 H)	2.61 s (3 H)
39[b,c]	5.98 d	4.60 d	5.68 d	4.17 dd	←5.55–5.25 m→			4.31 dd	3.87 dd				7.70–7.10 m	2.12 s (3 H) 2.04 s (3 H) 2.00 s (3 H) 1.80 s (3 H)	2.59 s (3 H)
40[a,c]	5.63 dd	3.93 d	4.17 dd	←3.80–3.30 m→				←3.80–3.30 m→			5.26 d 4.36 d	9.18 d	7.32 s		
41[b,d]	5.71 dd	4.04 d	5.21 d	4.02 dd	←5.50–5.25 m→			4.31 dd	3.93 dd		5.45 d 4.44 d	7.04 d	7.55–7.20 m	2.14 s (3 H) 2.05 s (3 H) 2.03 s (3 H) 2.02 s (3 H)	

[a]In $(CD_3)_2SO$. [b]In $CDCl_3$. [c]At 80 MHz. [d]At 90 MHz.

TABLE II

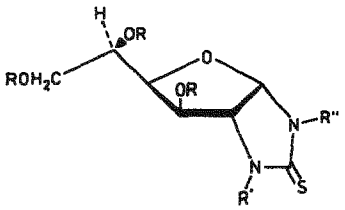
^{1}H-N.M.R. SPIN-COUPLING DATA[a] *(Hz)*

Compound	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'}$	$J_{5',6''}$	$J_{6',6''}$	$J_{6',7'}$	$J_{6'',7'}$	$J_{7',7''}$	$J_{2',NH}$	$J_{1',NH}$
9	6.5	0.0	2.7									
10	6.3	0.0										
14	6.3	0.0										
18	6.6	0.0	3.0	9.0	2.5	5.3	−12.3				1.2	
21	6.3	0.0	2.9	9.2	2.5	4.8	−12.4				1.3	
23	6.4	0.0							6.4	−11.5	1.2	
27	6.8	0.0	3.1	9.5	2.5	5.0	−12.3					
28	6.7	0.0	3.1	9.4	2.4	4.3	−12.4					
32	6.7	0.0	3.1	9.3				4.7	6.6	−11.8		
38	6.6	0.0	3.0	9.4	2.4	4.7	−12.4					
39	6.7	0.0	3.0	9.3				4.7	6.9	−11.6		
40	6.6	0.0	1.8									1.3
41	6.6	0.0	2.9	9.0[b]	3.0[b]			5.0	6.7	−11.5		1.2

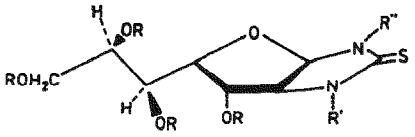
[a]Conditions described in Table I. [b]Values obtained after addition of $Eu(fod)_3$.

firming the imidazolidine-2-thione structure (*cf.* ~160 p.p.m. for the imine carbon atom in the 2-mercaptoimidazoline structure[22]). The sequence of glycosidic carbons is practically constant; C-1′ is the most deshielded (~94 p.p.m.), C-4′ also appears downfield (~79 p.p.m.), as generally occurs for a carbon atom closing the furanose ring, and C-2′ and C-6′ in **9–13**, and C-7′ in **14–17**, are the most shielded.

Treatment of **9–17** with acetic anhydride and pyridine at −20° led to the *O*-acetylated derivatives **18–26** in almost quantitative yields. However, at 40°, the



9 R = R′ = H, R″ = CH_3
10 R = R′ = H, R″ = C_6H_5
11 R = R′ = H, R″ = 4-ClC_6H_4
12 R = R′ = H, R″ = 4-BrC_6H_4
13 R = R′ = H, R″ = 4-$CH_3C_6H_4$
18 R = Ac, R′ = H, R″ = CH_3
19 R = Ac, R′ = H, R″ = C_6H_5
20 R = Ac, R′ = H, R″ = 4-ClC_6H_4
21 R = Ac, R′ = H, R″ = 4-BrC_6H_4
22 R = Ac, R′ = H, R″ = 4-$CH_3C_6H_4$
27 R = R′ = Ac, R″ = CH_3
28 R = R′ = Ac, R″ = C_6H_5
29 R = R′ = Ac, R″ = 4-ClC_6H_4
30 R = R′ = Ac, R″ = 4-BrC_6H_4
31 R = R′ = Ac, R″ = 4-$CH_3C_6H_4$



14 R = R′ = H, R″ = C_6H_5
15 R = R′ = H, R″ = 4-ClC_6H_4
16 R = R′ = H, R″ = 4-BrC_6H_4
17 R = R′ = H, R″ = 4-$CH_3C_6H_4$
23 R = Ac, R′ = H, R″ = C_6H_5
24 R = Ac, R′ = H, R″ = 4-ClC_6H_4
25 R = Ac, R′ = H, R″ = 4-BrC_6H_4
26 R = Ac, R′ = H, R″ = 4-$CH_3C_6H_4$
32 R = R′ = Ac, R″ = C_6H_5
33 R = R′ = Ac, R″ = 4-ClC_6H_4
34 R = R′ = Ac, R″ = 4-BrC_6H_4
35 R = R′ = Ac, R″ = 4-$CH_3C_6H_4$

heterocyclic nitrogen was also acetylated (**27–35**). Compounds **29–32, 34**, and **35** were previously described[7,19,23] as 2-acetylthio-1-aryl-(1,2-dideoxy-3,5,6-tri-*O*-acetyl-α-D-glucopyrano)[2,1-*d*]-2-imidazolines (**7**) and 2-acetylthio-1-aryl-(1,2-di deoxy-3,5,6,7-tetra-*O*-acetyl-D-*glycero*-α-L-*gluco*-heptofurano)[2,1-*d*]-2-imidazolines (**36**). The structures of **18–35** were confirmed by spectroscopic data. Their u.v. spectra were similar to those of **9–17**, and **18–26** showed i.r. absorption bands at ~3300 and 1500 cm^{-1} (characteristic of NH); **27–35** lacked these absorptions, but showed absorption characteristic of the *N*-acetyl group at ~1690 cm^{-1} which coincides with that expected for the acetylthio group[24]. Hence, the structures **7, 8**, or **36** were erroneously assigned as **29–32, 34**, and **35**. The ^{13}C-n.m.r. spectra of **18–35** each contained a signal between 179.24 and 183.59 p.p.m. characteristic of the thiocarbonyl carbon. In addition, the signals of the carbonyl carbons of **18–35**, which appeared at 168–172 p.p.m., can be assigned to acetate and/or acetamido groups, but there was no signal at ~194 p.p.m. indicative of the acetylthio group[25]. The acetylation of heterocyclic nitrogen induces important differences in the chemical shifts of the sugar carbons. Thus, for **27–35**, C-1′ resonates at higher field (~4 p.p.m.) than for **18–26**, and this effect was inverted (~2.5 p.p.m.) for C-2′. In the ^1H-n.m.r. spectra of **18–35**, the signal for H-1′ appears at lower field (5.77–5.70 p.p.m.) for the *N*-methyl derivatives **18** and **27**, and at 6.00–5.90 p.p.m. for the *N*-aryl derivatives. For **18–26**, the signals of H-3′ and H-5′ have similar chemical shifts. For **27–35**, H-3′ is deshielded (~0.4 p.p.m.) by the *N*-acetyl group. Likewise, for H-2′ (4.35–4.22 p.p.m. for **18–26** and 4.90–4.72 for **27–35**). The chemical shift of the signal of H-4′ (see Table I) is affected by the N-1 substituent. The NH signals

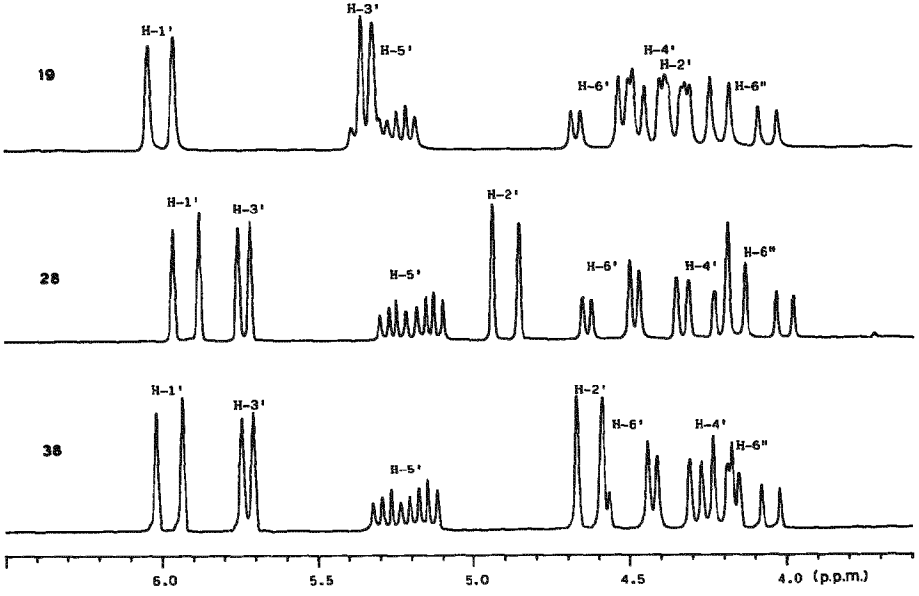


Fig. 1. ^1H-N.m.r. spectra (80 MHz) of the glycosidic moiety of compounds **19, 28**, and **38**.

TABLE III

^{13}C-N.M.R. DATA

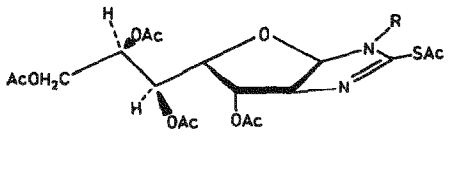
Compound	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*	*C-7'*	*C=S*	*C=O*	*Aromatic*	*OAc*		*NAc*	
											C=O	*CH_3*	*C=O*	*CH_3*
9[a]	93.20	64.32	74.16	79.28	68.32	63.57		181.84						
10[a]	94.41	65.02	73.89	79.39	68.22	63.59		181.10		138.82 128.10 126.67 126.22				
14[a]	94.41	65.18	73.91	78.83	66.28	70.84	62.58	181.12		138.90 128.10 126.92 126.26				
18[b]	94.78	63.14	75.86	76.46	67.72	63.24		183.59			170.51 169.82 169.60	20.66		
19[b]	95.69	63.76	75.79	76.51	67.62	63.19		183.17		138.09 129.06 127.88 127.15	170.50 169.76 169.59	20.68		
21[b]	95.49	63.67	75.54	76.61	67.61	63.08		182.94		137.15 132.29 128.51 121.69	170.51 169.94 169.61	20.66		
23[b]	95.66	63.64	75.25	76.21	67.51	69.75	62.14	183.00		138.11 129.00 127.67 126.67	170.30 169.85 169.70 169.49	20.69 20.56		

27[b]	90.28	65.54	74.34	76.42	67.14	63.19		179.24			171.14 170.33 169.71	20.70 20.60	168.38	26.63
28[b]	91.11	66.35	74.42	76.24	67.09	63.08		179.77		137.70 129.48 128.92 128.13	171.50 170.27 169.70	20.70 20.62	168.41	26.99
32[b]	91.16	66.28	74.15	76.15	67.14	69.86	62.30	179.65		137.73 129.45 128.80 127.79	171.53 170.19 169.71	20.73 20.56	168.58	26.98
38[b]	87.16	61.73	73.74	76.25	67.20	63.25			152.00	136.87 129.27 126.46 122.50	170.31 169.72	20.66 20.46	168.47	24.07
39[b]	87.00	61.72	73.52	75.97	67.13	69.76	62.15		151.88	136.82 129.29 126.24 121.88	170.24 169.70 169.47	20.73 20.55 20.30	168.61	24.07
40[a]	86.18	66.39	71.23[c]	78.70	70.41[c]	70.68[c]	62.50	182.27		136.38 128.27 127.50 127.18				
41[b]	86.84	69.36	72.64	75.80	77.41	69.75	62.10	183.60		135.78 128.83 128.22	170.30 169.80 169.26	20.58 20.42		

[a]In $(CD_3)_2SO$. [b]In $CDCl_3$. [c]These assignments can be interchanged.

of **18–26** appear at 7.70–7.25 p.p.m. (bs), and the acetate groups of **18–35** resonate at 2.11–1.99 p.p.m. For **27–35**, the singlet at ~2.90 p.p.m. is assigned to the acetamido group, because its chemical shift is coincident with that reported[26] for the acetamido group of *N*-acetylimidazolidine-2-thiones, and very different from that (~2.35 p.p.m.)[27,28] of an acetylthio group. The unusual chemical shift of the signal of this methyl group probably reflects deshielding by the C=S bond in the more-stable conformation (**37**) of the acetamido group which is similar to that found for 3-acetyl-2-oxazolidones[29,30] and other five-membered *N*-acylated heterocycles[31]. This disposition of the *N*-acyl carbonyl group is also responsible for the high deshielding of H-2′ and H-3′.

The position of acetylation on the heterocyclic ring was determined by C=S→C=O transformation[32], using sodium nitrite and hydrochloric acid. Thus, **38**



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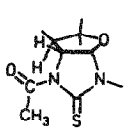

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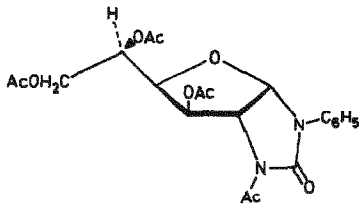

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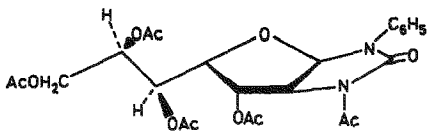

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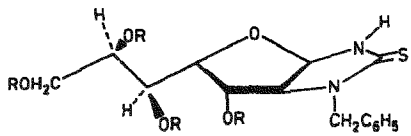

40 R = H
41 R = Ac

and **39** were obtained from **28** and **32**, respectively, and had λ_{max} at 238 nm (ε_{mM} ~14.00), due to the $\pi \rightarrow \pi^*$ transition of the carbonyl group of the imidazolidine-2-one ring, and ν_{max} at 1690 cm^{-1} (acetamido carbonyl). The ^{1}H-n.m.r. spectra of **38** and **39** are very similar to those of **28** and **32**, except in the chemical shift of the signal of the acetamido group which was shielded (~0.3 p.p.m.) in the former. The ^{13}C-n.m.r. spectra of **38** and **39** contained a characteristic signal at ~152 p.p.m. for C-2 of the imidazolidine-2-one ring. Furthermore, the signals of C-1′ and C-2′ were shifted (~4 p.p.m.) to high field compared to those of **28** and **32**. The structures of **38** and **39** were confirmed by their synthesis by acetylation of 1-phenyl-(1,2-dideoxy α-D-glucofurano)[2,1-*d*]imidazolidine-2-one and 1-phenyl-(1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[2,1-*d*]imidazolidine-2-one[33], respectively. Also, **19** was acetylated using a method reported for *N*-acylation of imidazolidine-2-thiones[26], and **28** was the sole product.

Treatment of 2-benzylamino-2-deoxy-D-*glycero*-L-*gluco*-heptose hydrochloride[34] with aqueous potassium thiocyanate at 100° gave 1-benzyl-(1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[1,2-*d*]imidazolidine-2-thione (**40**). All biblio-

graphical data on the reaction of 2-aminoaldoses and thiocyanate ion indicate that the products are polyhydroxyalkylimidazoline-2-thiones, probably formed from the intermediate glycofuranoimidazolidine-2-thiones.

Acetylation of **40** gave 1-benzyl-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[1,2-*d*]imidazolidine-2-thione (**41**). The imidazolidine-2-thione ring of **40** could not be acetylated.

The ^{1}H- and ^{13}C-n.m.r. spectra of **40** and **41** are very similar to those of the other bicyclic compounds described above. The furanoid ring size was indicated by the small value (0.0 Hz) of $J_{2',3'}$, and the imidazolidine-2-thione structure was confirmed by the λ_{max} at ~247 nm, the ν_{max} for NH at 1580 cm^{-1} for **40** and 3330 and 1590 cm^{-1} for **41**, the ^{1}H-n.m.r. signal for NH at 9.18 p.p.m. for **40** and 7.04 p.p.m. for **41**, and the ^{13}C-n.m.r. signal at ~183 p.p.m. for the thiocarbonyl carbon.

EXPERIMENTAL

General methods. — Melting points were determined with a Gallenkamp apparatus and are uncorrected. Optical rotations were measured at 20 ±5° with a Perkin–Elmer 141 polarimeter (10-cm, 5-mL cell). I.r. spectra (KBr disc) were recorded with a Perkin–Elmer 399 spectrophotometer and u.v. spectra with a Pye–Unicam SP8-250 instrument. T.l.c. was conducted on Silica Gel GF_{254} (Merck) with 3:1 ethyl acetate–ethanol or 3:2 benzene–ether, and detection with u.v. light or iodine vapour. ^{1}H-N.m.r. spectra were recorded with Bruker WP-80-SY (80 MHz, F.t.) and Perkin–Elmer R-32 (90 MHz, c.w.) spectrometers. ^{13}C-N.m.r. spectra were recorded with a Bruker WP-80-SY spectrometer (20.15 MHz). The e.i.-mass spectrum was obtained (70 eV) using an AEI MS-30 mass spectrometer.

1-(4-Chlorophenyl)-(1,2-dideoxy-D-glycero-α-L-gluco-*heptofurano)[2,1*-d]-*imidazolidine-2-thione* (**15**). — To a solution of 2-amino-2-deoxy-D-*glycero*-α-L-*gluco*-heptose hydrochloride (3.0 g, 12.2 mmol) in water (16 mL) were added sodium hydrogencarbonate (1.1 g, 13.0 mmol), 4-chlorophenyl isothiocyanate (2.5 g, 18.5 mmol), aqueous 96% ethanol (25 mL), and acetone (10 mL). The mixture was stirred for 8 h at 40°, acetic acid (7 mL) was added, and the solution was kept for 4 h more at 40°, then cooled, and concentrated under diminished pressure. The residue was extracted with water (20 mL), and the extract was washed with ether (3 × 25 mL) and concentrated to half volume to give **15** (3.15 g, 71%). Two recrystallisations from ethanol gave material having m.p. 186–187°, $[\alpha]_D$ −55.5° (*c* 1, pyridine); λ_{max}^{EtOH} 240 and 270 nm (ε_{mM} 18.0 and 6.8); ν_{max} 3500–3100 (OH, NH), 1590, 1490, and 820 cm^{-1} (aromatic).

Anal. Calc. for $C_{14}H_{17}ClN_2O_5S$: C, 46.60; H, 4.75; Cl, 9.83; N, 7.76; S, 8.89. Found: C, 46.63; H, 4.77; Cl, 10.08; N, 7.69; S, 8.77.

*O-Acetylated 1-alkyl(aryl)-(1,2-dideoxy-α-*D-*glycofurano)[2,1-*d]*imidazolidine-2-thione.* — To a solution of each title compound (1 mmol) in pyridine (1 mL) at −20° was added acetic anhydride (2 mL). The mixture was kept at −20° for 12 h and then poured into ice–water. Solid products were collected, washed with cold

water, and crystallised from ethanol. Non-crystalline products were extracted by chloroform. The following compounds were prepared in this way.

1-Methyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[2,1-*d*]imidazolidine-2-thione (**18**, 93% from **9**[8]), isolated as a colourless syrup that solidified at 0°, $[\alpha]_D$ +47.5° (*c* 1, chloroform); λ_{max}^{EtOH} 242 nm (ε_{mM} 19.0); ν_{max} 3500–3200 (NH), 1740 (C=O ester), 1500 (NH), and 1230 cm^{-1} (ester). For n.m.r. data, see Tables I–III. The crude product appeared pure by t.l.c. and n.m.r. Mass spectrum: *m/z* 360.1026 (calc. for M^+ of $C_{14}H_{20}N_2O_7S$: 360.0990).

1-Phenyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[2,1-*d*]imidazolidine-2-thione (**19**, 98% from **10**[2]), m.p. 152–154°, $[\alpha]_D$ +87° (*c* 0.5, chloroform); λ_{max}^{EtOH} 240 nm (ε_{mM} 14.3); ν_{max} 3295 (NH), 1735, 1715, and 1700 (C=O ester), 1585, 1575, and 1490 (phenyl), 1480 (NH), 770 and 695 cm^{-1} (phenyl). For n.m.r. data, see Tables I–III.

Anal. Calc. for $C_{19}H_{22}N_2O_7S$: C, 54.02; H, 5.25; N, 6.63; S, 7.59. Found: C, 54.00; H, 5.26; N, 6.30; S, 7.86.

1-(4-Chlorophenyl)-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[2,1-*d*]-imidazolidine-2-thione (**20**, 94% from **11**[11]), m.p. 142–144°, $[\alpha]_D$ +82° (*c* 1, chloroform); λ_{max}^{EtOH} 238 and 266 nm (ε_{mM} 18.3 and 8.6); ν_{max} 3300 (NH), 1750 and 1740 (C=O ester), 1595, 1490 (aromatic), 1270–1200 (ester), and 820 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.71 (s, 1 H, NH), 7.55–7.30 (m, 4 H, aromatic), 5.92 (d, 1 H, $J_{1',2'}$ 6.5 Hz, H-1′), 5.32 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-3′), 5.27 (qd, 1 H, $J_{4',5'}$ 9.0, $J_{5',6'}$ 2.3, $J_{5',6''}$ 5.0 Hz, H-5′), 4.60 (dd, 1 H, $J_{6',6''}$ −12.0 Hz, H-6′), 4.40 (dd, 1 H, H-4′), 4.36 (d, 1 H, H-2′), 4.14 (dd, 1 H, H-6″), 2.07, 2.05, and 2.02 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{19}H_{21}ClN_2O_7S$: C, 49.95; H, 4.63; Cl, 7.66; N, 6.13; S, 7.02. Found: C, 49.86; H, 4.63; Cl, 7.81; N, 5.87; S, 7.21.

1-(4-Bromophenyl)-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[2,1-*d*]-imidazolidine-2-thione (**21**, 99% from **12**[19]), m.p. 229–231°, $[\alpha]_D$ +80° (*c* 0.5, chloroform); λ_{max}^{EtOH} 236 and 262 nm (ε_{mM} 21.0 and 8.8); ν_{max} 3290 (NH), 1735 and 1710 (C=O ester), 1585 and 1575 (aromatic), 1490 (NH), 1260, 1230, and 1210 (ester), and 830 cm^{-1} (aromatic). For n.m.r. data, see Tables I–III.

Anal. Calc. for $C_{19}H_{21}BrN_2O_7S$: C, 45.52; H, 4.22; Br, 15.94; N, 5.59; S, 6.40. Found: C, 45.33; H, 3.98; Br, 16.37; N, 5.47; S, 6.70.

1-(4-Methylphenyl)-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[2,1-*d*]-imidazolidine-2-thione (**22**, 93% from **13**[11]), m.p. 175–177°, $[\alpha]_D$ +92° (*c* 0.5, chloroform); λ_{max}^{EtOH} 238 nm (ε_{mM} 15.0); ν_{max} 3290 (NH), 1740 and 1710 (C=O ester), 1605 and 1510 (aromatic), 1480 (NH), 1250, 1235, and 1205 (ester), and 820 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.73 (s, 1 H, NH), 7.40–7.10 (m, 4 H, aromatic), 5.97 (d, 1 H, $J_{1',2'}$ 6.3 Hz, H-1′), 5.33 (d, 1 H, $J_{3',4'}$ 2.7 Hz, H-3′), 5.26 (m, 1 H, $J_{4',5'}$ 9.3, $J_{5',6'}$ 2.3, $J_{5',6''}$ 5.0 Hz, H-5′), 4.59 (dd, 1 H, $J_{6',6''}$ −12.3 Hz, H-6′), 4.40 (dd, 1 H, H-4′), 4.36 (d, 1 H, H-2′), 4.14 (dd, 1 H, H-6″), 2.38 (s, 3 H, Me), 2.10 and 2.04 (2 s, 6 and 3 H, 3 OAc).

Anal. Calc. for $C_{20}H_{24}N_2O_7S$: C, 55.04; H, 5.54; N, 6.42; S, 7.35. Found: C, 54.88; H, 5.75; N, 6.13; S, 7.62.

1-Phenyl-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-hepto-furano)[2,1-*d*]imidazolidine-2-thione (**23**, 84% from **14**[23]), m.p. 88–90°, $[\alpha]_D$ −28° (*c* 1, chloroform); λ_{max}^{EtOH} 239 nm (ε_{mM} 14.3); ν_{max} 3600–3100 (NH), 1730 (C=O ester), 1585, 1490 (phenyl), 1480 (NH), 1220 (ester), 760 and 695 cm^{-1} (phenyl). For n.m.r. data, see Tables I–III.

Anal. Calc. for $C_{22}H_{26}N_2O_9S$: C, 53.43; H, 5.30; N, 5.67; S, 6.48. Found: C, 53.26; H, 5.37; N, 5.56; S, 6.69.

1-(4-Chlorophenyl)-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[2,1-*d*]imidazolidine-2-thione (**24**, 96% from **15**), m.p. 163–164°, $[\alpha]_D$ −32° (*c* 1, chloroform); λ_{max}^{EtOH} 238 and 264 nm (ε_{mM} 19.1 and 8.8); ν_{max} 3320 (NH), 1750, 1740, 1720 (C=O ester), 1495 (aromatic), 1480 (NH), 1245, 1230 (ester), and 820 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.73 (s, 1 H, NH), 7.55–7.30 (m, 4 H, aromatic), 5.95 (d, 1 H, $J_{1',2'}$ 6.3 Hz, H-1′), 5.60–5.30 (m, 2 H, H-5′,6′), 5.40 (d, 1 H, $J_{3',4'}$ 2.7 Hz, H-3′), 4.50–4.25 (m, 1 H, H-7′), 4.35 (m, 1 H, H-4′), 4.34 (d, 1 H, H-2′), 3.92 (dd, 1 H, $J_{6',7'}$ 6.7, $J_{7',7''}$ −11.7 Hz, H-7″), 2.07, 2.04, and 2.01 (3 s, 3, 6, and 3 H, 4 OAc).

Anal. Calc. for $C_{22}H_{25}ClN_2O_9S$: C, 49.95; H, 4.76; Cl, 6.70; N, 5.30; S, 6.06. Found: C, 50.02; H, 4.79; Cl, 6.98; N, 5.26; S, 5.97.

1-(4-Bromophenyl)-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[2,1-*d*]imidazolidine-2-thione (**25**, 98% from **16**[23]), m.p. 174–176°, $[\alpha]_D$ −32° (*c* 1, chloroform); λ_{max}^{EtOH} 236 and 262 nm (ε_{mM} 21.3 and 9.7); ν_{max} 3300 (NH), 1740, 1730, 1705 (C=O ester), 1485 (NH), 1240, 1220 (ester), and 825 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.65 (s, 1 H, NH), 7.55–7.25 (m, 4 H, aromatic), 5.90 (d, 1 H, $J_{1',2'}$ 6.3 Hz, H-1′), 5.55-5.20 (m, 2 H, H-5′,6′), 5.38 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-3′), 4.45–4.15 (m, 1 H, H-7′), 4.30 (m, 1 H, H-4′), 4.28 (d, 1 H, H-2′), 3.90 (dd, 1 H, $J_{6',7'}$ 7.0, $J_{7',7''}$ −11.3 Hz, H-7″), 2.05, 2.02, and 1.98 (3 s, 3, 6, and 3 H, 4 OAc).

Anal. Calc. for $C_{22}H_{25}BrN_2O_9S$: C, 46.08; H, 4.39; Br, 13.94; N, 4.89; S, 5.59. Found: C, 46.04; H, 4.40; Br, 14.28; N, 4.82; S, 5.61.

1-(4-Methylphenyl)-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[2,1-*d*]imidazolidine-2-thione (**26**, 99% from **17**[23]), m.p. 203–205°, $[\alpha]_D$ −32° (*c* 0.5, chloroform); λ_{max}^{EtOH} 238 nm (ε_{mM} 16.0); ν_{max} 3300 (NH), 1740, 1730, and 1710 (C=O ester), 1505 (aromatic), 1480 (NH), 1240 and 1225 (ester), and 815 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.52 (s, 1 H, NH). 7.40–7.15 (m, 4 H, aromatic), 5.96 (d, 1 H, $J_{1',2'}$ 6.3 Hz, H-1′), 5.55–5.25 (m, 2 H, H-5′,6′), 5.40 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-3′), 4.50–4.20 (m, 1 H, H-7′), 4.35 (d, 1 H, H-2′), 4.35 (m, 1 H, H-4′), 3.95 (dd, 1 H, $J_{6',7'}$ 6.5, $J_{7',7''}$ −12.0 Hz, H-7″), 2.38 (s, 3 H, Me), 2.10, 2.07, and 2.03 (3 s, 6, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{23}H_{28}N_2O_9S$: C, 54.32; H, 5.55; N, 5.51; S, 6.31. Found: C, 54.45; H, 5.59; N, 5.42; S, 6.63.

O-*Acetylated 1-acetyl-3-alkyl(aryl)-1,2-dideoxy-α-*D-*glycofurano)[1,2-*d]-

imidazolidine-2-thione. — To a solution of each title compound (1.5 mmol) in pyridine (3 mL) was added acetic anhydride (3 mL). The solution was kept at 40° for 12 h and then poured into ice–water, to afford a solid which was washed with cold water and recrystallised from ethanol. The following compounds were prepared in this way.

1-Acetyl-3-methyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[1,2-*d*]-imidazolidine-2-thione (**27**, 52% from **9**), m.p. 160–161°, $[\alpha]_D$ −36° (*c* 0.5, chloroform); λ_{max}^{EtOH} 231 and 264 nm (ε_{mM} 11.3 and 11.6); ν_{max} 1745 (C=O ester), 1680 (C=O amide), and 1225 cm^{-1} (ester). For n.m.r. data, see Tables I–III.

Anal. Calc. for $C_{16}H_{22}N_2O_8S$: C, 47.75; H, 5.51; N, 6.96; S, 7.97. Found: C, 47.96; H, 5.58; N, 6.84; S, 8.02.

1-Acetyl-3-phenyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucofurano)[1,2-*d*]-imidazolidine-2-thione (**28**, 95% from **10**), m.p. 190–191°, $[\alpha]_D$ +27.5° (*c* 0.6, chloroform); λ_{max}^{EtOH} 238 nm (ε_{mM} 12.7); ν_{max} 1750 (C=O ester), 1690 (C=O amide), 1595, 1590, 1500 (phenyl), 1240 (ester), 760 and 690 cm^{-1} (phenyl). For n.m.r. data, see Tables I–III.

Anal. Calc. for $C_{21}H_{24}N_2O_8S$: C, 54.30; H, 5.21; N, 6.03; S, 6.90. Found: C, 54.14; H, 5.22; N, 5.99; S, 7.13.

1-Acetyl-3-(4-chlorophenyl)-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-gluco-furano)[1,2-*d*]imidazolidine-2-thione (**29**, 97% from **11**), m.p. 183–184°, $[\alpha]_D$ +31.5° (*c* 0.6, chloroform); λ_{max}^{EtOH} 238 and 270 nm (ε_{mM} 16.9 and 8.8); ν_{max} 1755 (C=O ester), 1680 (C=O amide), 1490 (aromatic), 1240 (ester), and 830 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.55–7.15 (m, 4 H, aromatic), 5.89 (s, 1 H, $J_{1',2'}$ 6.3 Hz, H-1′), 5.70 (d, 1 H, $J_{2',3'}$ 0.0, $J_{3',4'}$ 3.3 Hz, H-3′), 5.18 (qd, 1 H, $J_{4',5'}$ 9.3, $J_{5',6'}$ 2.3, $J_{5',6''}$ 4.3 Hz, H-5′), 4.87 (d, 1 H, H-2′), 4.55 (dd, 1 H, $J_{6',6''}$ −12.0 Hz, H-6′), 4.23 (dd, 1 H, H-4′), 4.07 (dd, 1 H, H-6″), 2.86 (s, 3 H, NAc), 2.07 and 1.98 (2 s, 6 and 3 H, 3 OAc).

Anal. Calc. for $C_{21}H_{23}ClN_2O_8S$: C, 50.55; H, 4.65; Cl, 7.11; N, 5.61; S, 6.43. Found: C, 50.32; H, 4.62; Cl, 7.42; N, 5.50; S, 6.21.

1-Acetyl-3-(4-bromophenyl)-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-gluco-furano)[1,2-*d*]imidazolidine-2-thione (**30**, 99% from **12**), m.p. 205–206°, $[\alpha]_D$ +37.5° (*c* 0.6, chloroform); λ_{max}^{EtOH} 240 and 270 nm (ε_{mM} 19.0 and 9.3); ν_{max} 1740 (C=O ester), 1675 (C=O amide), 1485 (aromatic), 1235 and 1215 (ester), and 825 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.75–7.10 (m, 4 H, aromatic), 5.90 (d, 1 H, $J_{1',2'}$ 6.6 Hz, H-1′), 5.72 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-3′), 5.20 (qd, 1 H, $J_{4',5'}$ 9.3, $J_{5',6'}$ 2.3, $J_{5',6''}$ 4.7 Hz, H-5′), 4.90 (d, 1 H, H-2′), 4.56 (dd, 1 H, $J_{6',6''}$ −12.0 Hz, H-6′), 4.24 (dd, 1 H, H-4′), 4.08 (dd, 1 H, H-6″), 2.89 (s, 3 H, NAc), 2.09 and 1.99 (2 s, 6 and 3 H, 3 OAc).

Anal. Calc. for $C_{21}H_{23}BrN_2O_8S$: C, 46.42; H, 4.27; Br, 14.71; N, 5.16; S, 5.90. Found: C, 46.29; H, 4.23; Br, 15.02; N, 5.16; S, 6.09.

1-Acetyl-3-(4-methylphenyl)-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-D-gluco-furano)[1,2-*d*]imidazolidine-2-thione (**31**, 93% from **13**), m.p. 139–140°, $[\alpha]_D$ +46° (*c* 0.6, chloroform); λ_{max}^{EtOH} 236 and 265 nm (ε_{mM} 15.9 and 9.6); ν_{max} 1745 (C=O

ester), 1685 (C=O amide), 1515 (aromatic), 1245, 1220 (ester), and 820 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.50–7.05 (m, 4 H, aromatic), 5.86 (d, 1 H, $J_{1',2'}$ 6.7 Hz, H-1'), 5.69 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-3'), 5.22 (m, 1 H, H-5'), 4.87 (d, 1 H, H-2'), 4.53 (dd, 1 H, $J_{5',6'}$ 2.3, $J_{6',6''}$ −12.0 Hz, H-6'), 4.22 (dd, 1 H, $J_{4',5'}$ 9.2 Hz, H-4'), 4.06 (dd, 1 H, $J_{5',6''}$ 4.3 Hz, H-6''), 2.86 (s, 3 H, NAc), 2.35 (s, 3 H, Me), 2.03 and 1.96 (2 s, each 3 H, 2 OAc).

Anal. Calc. for $C_{22}H_{26}N_2O_8S$: C, 55.22; H, 5.48; N, 5.85; S, 6.70. Found: C, 55.07; H, 5.71; N, 5.81; S, 6.51.

1-Acetyl-3-phenyl-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[1,2-*d*]imidazolidine-2-thione (**32**, 99% from **14**), m.p. 204–206°, $[\alpha]_D$ +29.5° (*c* 1, chloroform); λ_{max}^{EtOH} 237 and 270 nm (ε_{mM} 14.3 and 9.0); ν_{max} 1750 (C=O ester), 1690 (C=O amide), 1595, 1585, 1500 (phenyl), 1245, 1220 (ester), 760 and 690 cm^{-1} (phenyl). For n.m.r. data, see Tables I–III.

Anal. Calc. for $C_{24}H_{28}N_2O_{10}S$: C, 53.72; H, 5.25; N, 5.22; S, 5.97. Found: C, 53.77; H, 5.43; N, 5.29; S, 5.89.

1-Acetyl-3-(4-chlorophenyl)-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[1,2-*d*]imidazolidine-2-thione (**33**, 94% from **15**), m.p. 163–165°, $[\alpha]_D$ +25.5° (*c* 1, chloroform); λ_{max}^{EtOH} 239 and 270 nm (ε_{mM} 19.0 and 9.9); ν_{max} 1750 (C=O ester), 1695 (C=O amide), 1490 (aromatic), 1245, 1220 (ester), and 830 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.55–7.15 (m, 4 H, aromatic), 5.85 (d, 1 H, $J_{1',2'}$ 6.5 Hz, H-1'), 5.74 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-3'), 5.55–5.25 (m, 2 H, $J_{5',6'}$ 2.3 Hz, H-5',6'), 4.82 (d, 1 H, H-2'), 4.31 (dd, 1 H, $J_{6',7'}$ 5.0, $J_{7',7''}$ −12.0 Hz, H-7'), 4.18 (dd, 1 H, $J_{4',5'}$ 9.3 Hz, H-4'), 3.86 (dd, 1 H, $J_{6',7''}$ 7.0 Hz, H-7''), 2.87 (s, 3 H, NAc), 2.08, 2.03, and 1.99 (3 s, 6, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{24}H_{27}ClN_2O_{10}S$: C, 50.48; H, 4.77; Cl, 6.21; N, 4.91; S, 5.62. Found: C, 50.66; H, 4.84; Cl, 6.42; N, 4.89; S, 5.73.

1-Acetyl-3-(4-bromophenyl)-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[1,2-*d*]imidazolidine-2-thione (**34**, 96% from **16**), m.p. 180–182°, $[\alpha]_D$ +17.5° (*c* 0.6, chloroform); λ_{max}^{EtOH} 241 and 270 nm (ε_{mM} 19.6 and 10.0); ν_{max} 1750 (C=O ester), 1690 (C=O amide), 1490 (aromatic), 1245, 1220 (ester), and 820 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.60–7.20 (m, 4 H, aromatic), 5.91 (d, 1 H, $J_{1',2'}$ 6.6 Hz, H-1'), 5.78 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-3'), 5.55–5.30 (m, 2 H, H-5',6'), 4.88 (d, 1 H, H-2'), 4.35 (dd, 1 H, $J_{6',7'}$ 4.6, $J_{7',7''}$ −12.0 Hz, H-7'), 4.23 (dd, 1 H, $J_{4',5'}$ 9.5 Hz, H-4'), 3.93 (dd, 1 H, $J_{6',7''}$ 6.6 Hz, H-7''), 2.90 (s, 3 H, NAc), 2.14, 2.07, and 2.05 (3 s, 6, 3, and 3 H, 4 OAc).

Anal. Calc. for $C_{24}H_{27}BrN_2O_{10}S$: C, 46.84; H, 4.42; Br, 12.98; N, 4.55; S, 5.21. Found: C, 46.54; H, 4.65; Br, 12.60; N, 4.83; S, 5.36.

1-Acetyl-3-(4-methylphenyl)-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-D-*glycero*-α-L-*gluco*-heptofurano)[1,2-*d*]imidazolidine-2-thione (**35**, 92% from **17**), m.p. 197–198°, $[\alpha]_D$ +16.5° (*c* 0.6, chloroform); λ_{max}^{EtOH} 235 and 268 nm (ε_{mM} 14.8 and 9.2); ν_{max} 1750 (C=O ester), 1690 (C=O amide), 1520 (aromatic), 1255, 1230, 1215 (ester), and 820 cm^{-1} (aromatic). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.40–7.20 (m, 4 H, aromatic), 5.87 (d, 1 H, $J_{1',2'}$ 6.6 Hz, H-1'), 5.75 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-3'), 5.50–

5.25 (m, 2 H, H-5′,6′), 4.85 (d, 1 H, H-2′), 4.31 (dd, 1 H, $J_{6',7'}$ 5.0, $J_{7',7''}$ −12.0 Hz, H-7′), 4.23 (dd, 1 H, $J_{4',5'}$ 9.5 Hz, H-4′), 3.90 (dd, 1 H, $J_{6',7''}$ 6.6 Hz, H-7″), 2.92 (s, 3 H, NAc), 2.14, 2.11, 2.06, and 2.02 (4 s, each 3 H, 4 OAc).

Anal. Calc. for $C_{25}H_{30}N_2O_{10}S$: C, 54.32; H, 5.49; N, 5.08; S, 5.82. Found: C, 54.34; H, 5.42; N, 5.16; S, 6.10.

*1-Acetyl-3-phenyl-(3,5,6-tri-*O*-acetyl-1,2-dideoxy-α-*D*-glucofurano)[1,2-*d*]-imidazolidine-2-one* (**38**). — To a vigorously stirred solution of **28** (0.2 g, 0.43 mmol) in chloroform (5 mL) was added 4M hydrochloric acid (5 mL) and then sodium nitrite (1.0 g, 11.8 mmol). The mixture was stirred for 1 h, and the organic layer was then separated, washed with water, dried (Na_2SO_4), filtered, and concentrated to dryness under diminished pressure. The residual oil crystallised from ethanol. Recrystallisation of the product (0.12 g, 62%) gave **38**, m.p. 153–155°, $[\alpha]_D$ +31° (*c* 1, chloroform); λ_{max}^{EtOH} 238 nm (ε_{mM} 13.2); ν_{max} 1740 (C=O ester), 1695 (C=O amide and C=O of imidazolidine-2-one), 1595, 1585, 1495 (phenyl), 1260, 1235 (ester), 740 and 690 cm^{-1} (phenyl). For n.m.r. data, see Tables I–III.

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-phenyl-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-*D*-glycero-α-*L*-gluco-heptofurano)[1,2-*d*]imidazolidine-2-one* (**39**). — Treatment of **32** as described for **28** afforded **39** (0.09 g, 26%), m.p. 149–150° (from ethanol), $[\alpha]_D$ −7.5° (*c* 1, chloroform); λ_{max}^{EtOH} 239 nm (ε_{mM} 14.9); ν_{max} 1740 (C=O ester), 1690 (C=O amide and C=O of imidazolidine-2-one), 1595, 1585, 1500 (phenyl), 1260, 1220, 1210 (ester), 740 and 700 cm^{-1} (phenyl). For n.m.r. data, see Tables I–III.

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-Benzyl-(1,2-dideoxy-*D*-glycero-α-*L*-gluco-heptofurano)[1,2-*d*]imidazolidine-2-thione* (**40**). To a solution of 2-benzylamino-2-deoxy-*D*-*glycero*-α-*L*-*gluco*-heptose hydrochloride[31] (4.0 g, 13.4 mmol) in water (25 mL) was added potassium thiocyanate (3.2 g, 32.9 mmol). The solution was heated under reflux for 8 h and then concentrated. The residue was extracted with ethanol, and the extract was concentrated. Column chromatography (chloroform–methanol, 5:1) of the residue yielded **40** (0.91 g, 28%), m.p. 195–196° (from ethanol), $[\alpha]_D$ +46.5° (*c* 1, pyridine); λ_{max}^{EtOH} 247 nm (ε_{mM} 8.6); ν_{max} 3600–3100 (NH, OH), 1600, 1575 (phenyl), 1490 (NH), 735 and 695 cm^{-1} (phenyl). For n.m.r. data, see Tables I–III.

Anal. Calc. for $C_{15}H_{20}N_2O_5S$: C, 52.93; H, 5.92; N, 8.23; S, 9.42. Found: C, 52.75; H, 6.10; N, 8.12; S, 9.29.

*1-Benzyl-(3,5,6,7-tetra-*O*-acetyl-1,2-dideoxy-*D*-glycero-α-*L*-gluco-hepto-furano)[1,2-*d*]imidazolidine-2-thione* (**41**). — (*a*) Prepared by the general procedures described above, **41** required extraction with chloroform and then crystallised (47%) from ether–light petroleum. Recrystallisation from ether gave material having m.p. 55–57°, $[\alpha]_D$ −19.5° (*c* 1, chloroform); λ_{max}^{EtOH} 248 nm (ε_{mM} 18.4); ν_{max} 3330 (NH), 1735 (C=O ester), 1600, 1580 (phenyl), 1490 (NH), 1220 (ester), 735 and 700 cm^{-1} (phenyl). For n.m.r. data, see Tables I–III.

Anal. Calc. for $C_{23}H_{28}N_2O_9S$: C, 54.32; H, 5.55; N, 5.51; S, 6.30. Found: C, 54.10; H, 5.59; N, 5.41; S, 6.57.

(*b*) Compound **40** (0.34 g, 1.0 mmol) was treated with acetic anhydride (3.0 mL) and anhydrous zinc chloride (0.11 g) for 12 h at 40°. The mixture was poured into ice–water, to afford **41** (0.425 g, 84%).

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