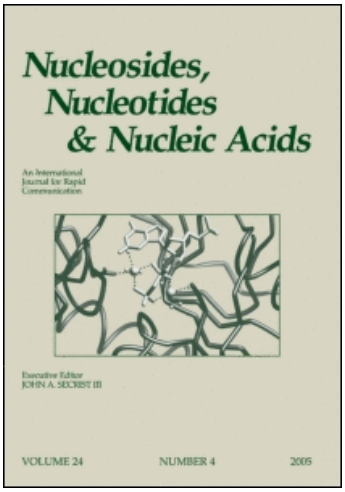

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Preparation of New Glycoheptofurano[2,1-d]Imidazolidine-2-Thiones., Isomerizations to Acyclic-Sugar C-Nucleoside Analogues of Imidazole

J. Fuentes Mota[a]; J. I. Fernández García-Hierro[b]; P. Areces Bravo[b]; F. Rebolledo Vicente[b]; J. A. Galbis Pérez[c]
[a] Department of Organic Chemistry, Faculty of Chemistry, University of Seville, Seville, Spain [b] Department of Organic Chemistry, Faculty of Sciences, University of Extremadura, Badajoz, Spain [c] Department of Organic Chemistry, Faculty of Pharmacy, University of Seville, Seville, Spain

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PREPARATION OF NEW GLYCOHEPTOFURANO[2,1-d]IMIDAZOLIDINE-2-THIONES. ISOMERIZATIONS TO ACYCLIC-SUGAR C-NUCLEOSIDE ANALOGUES OF IMIDAZOLE

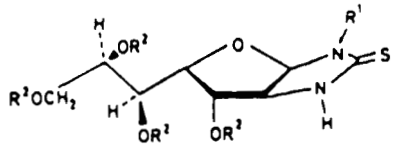
J. Fuentes Mota[*a], J.I. Fernández García-Hierro[b], P. Areces Bravo[b], F. Rebolledo Vicente[b], and J.A. Galbis Pérez[c].

a) Department of Organic Chemistry, Faculty of Chemistry, University of Seville. 41071 Seville (Spain)
b) Department of Organic Chemistry, Faculty of Sciences, University of Extremadura. 06071 Badajoz (Spain)
c) Department of Organic Chemistry, Faculty of Pharmacy, University of Seville. 41071 Seville (Spain)

ABSTRACT: 1-Methyl- and 1-aryl-(1,2-dideoxy-D-glycofurano)[2,1-d]-imidazolidine-2-thiones having the configurations β-D-glycero-L-gluco (4), β-D-glycero-D-ido (5-8), α-D-glycero-D-galacto (9-10) and β-D-glycero-D-talo (11,12) are prepared by reaction of 2-amino-2-deoxy-aldoses with methyl and aryl isothiocyanates. 1-Aryl-(1,2-dideoxy-β-D-glycero-L-gluco-heptofurano)[2,1-d]imidazolidine-2-thiones (1-3) have been converted into 1-aryl-4-(D-galacto-pentitol-1-yl)-4-imidazoline-2-thiones (24-26) by acid catalysed isomerization.

The reaction of 2-amino-2-deoxyaldoses with alkyl and aryl isothiocyanates gives 1-alkyl- and 1-aryl-(1,2-dideoxy-D-glycofurano)-[2,1-d]imidazolidine-2-thiones[1], which are useful intermediates in the synthesis of acyclic sugar imidazole C-nucleoside analogues[2]. We have already described[3] the preparation of 1-aryl-(1,2-dideoxy-β-D-glycero-L-gluco-heptofurano)[2,1-d]imidazolidine-2-thiones (1-3) by reaction of 2-amino-2-deoxy-D-glycero-L-gluco-heptose with aryl isothiocyanates.

By reaction of the 2-amino-2-deoxyheptoses, having the configurations D-glycero-L-gluco, D-glycero-D-ido, D-glycero-D-talo[4] and D-glycero-D-galacto, and of the new 2-(benzylamino)-2-deoxy-D-glycero-D-ido-heptose with methyl and aryl isothiocyanates, the imidazolidine-2-thiones (4-12) have been obtained. The structures of these compounds are supported by their elemental analyses and spectroscopic data (u.v.,



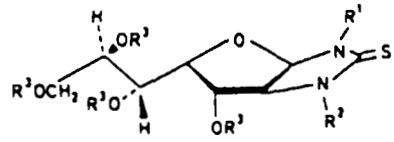
1 $R^1 = C_6H_5$, $R^2 = H$

2 $R^1 = p\text{-}CH_3\text{-}C_6H_4$, $R^2 = H$

3 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = H$

4 $R^1 = CH_3$, $R^2 = H$

13 $R^1 = CH_3$, $R^2 = Ac$



5 $R^1 = C_6H_5$, $R^2 = R^3 = H$

6 $R^1 = p\text{-}CH_3\text{-}C_6H_4$, $R^2 = R^3 = H$

7 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = R^3 = H$

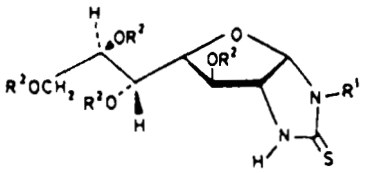
8 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = CH_2\text{-}C_6H_5$, $R^3 = H$

14 $R^1 = C_6H_5$, $R^2 = H$, $R^3 = Ac$

15 $R^1 = p\text{-}CH_3\text{-}C_6H_4$, $R^2 = H$, $R^3 = Ac$

16 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = H$, $R^3 = Ac$

17 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = CH_2\text{-}C_6H_5$, $R^3 = Ac$

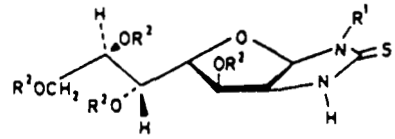


9 $R^1 = C_6H_5$, $R^2 = H$

10 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = H$

18 $R^1 = C_6H_5$, $R^2 = Ac$

19 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = Ac$

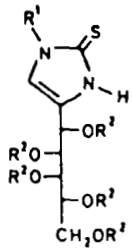


11 $R^1 = p\text{-}CH_3\text{-}C_6H_4$, $R^2 = H$

12 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = H$

20 $R^1 = p\text{-}CH_3\text{-}C_6H_4$, $R^2 = Ac$

21 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = Ac$



24 $R^1 = C_6H_5$, $R^2 = H$

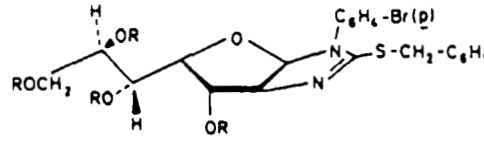
25 $R^1 = p\text{-}CH_3\text{-}C_6H_4$, $R^2 = H$

26 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = H$

27 $R^1 = C_6H_5$, $R^2 = Ac$

28 $R^1 = p\text{-}CH_3\text{-}C_6H_4$, $R^2 = Ac$

29 $R^1 = p\text{-}Br\text{-}C_6H_4$, $R^2 = Ac$



22 R = H

23 R = Ac

COMPOUND STRUCTURES

i.r., and ^{1}H- and ^{13}C-n.m.r.). Conventional treatment with pyridine--acetic anhydride yielded the tetraacetates (13–21), whose structures have also been completely established. Compounds 4–10 and 13–19 present a small value of $J_{2,3}$ (0–1.5 Hz) in accordance[5] with a trans arrangement of H-2,3, whereas compounds 11, 12, 20, and 21 exhibit values of $J_{2,3}$ = = 5–7 Hz in agreement with a cis arrangement of these protons. The ^{13}C-n.m.r. spectra of all these compounds contain a signal at ~181 ppm for the thiocarbonyl carbon atom which excludes the 2-mercaptoimidazoline structure[6]. The S-benzylation of 7 yielded the 2-benzylthio-2--imidazoline (22) whose acetylation gave 23; both compounds showed the signal of C-2 at ~160 ppm in their ^{13}C-n.m.r. spectra.

The trifluoroacetic acid catalysed isomerization of 1–3 gave 1--aryl-4-(D-galacto-pentitol-1-yl)-4-imidazoline-2-thiones (24–26) which can be considered to be new acyclic-sugar imidazole C-nucleoside analogues. The structures of these compounds are supported by elemental analyses, spectroscopic data, and by the preparation of their pentaacetates (27–29).

The stereochemistry of the tetrahydrofurane ring of 13–21 and 23 has been studied by comparing the experimental J values obtained from the ^{1}H-n.m.r. spectra of these compounds with sets of calculated[7] J values for the dihedral angles shown by the protons of the conformations presented by these systems, measured on molecular models[8]. The conformations used are the maximally puckered extremes which contain at least one dihedral angle of 60° (Table 6). We think that compounds 13–17, 20, and 21 present a conformation close to ^{4}E and $^{4}T_{0}$, whereas for 18 and 19 the most favored conformation of the furanoid ring must be between the ^{3}E, $^{3}T_{4}$, and E_{4} forms. Compound 23 seems to present a conformation near to $^{4}T_{0}$.

EXPERIMENTAL

General methods. Solutions were concentrated in vacuo at <40°. Melting points were determined with a Gallenkamp apparatus, and are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter (10-cm cell), i.r. spectra (KBr discs) with a Perkin-Elmer 399 spectrometer and u.v. spectra with a Beckman 25 instrument. ^{1}H-n.m.r. spectra were recorded with a Perkin-Elmer R-32 (90 MHz) and with a

Varian XL-200 (200 MHz) spectrometer. ^{13}C-n.m.r. spectra were recorded with a Bruker WP-80-SY spectrometer operated at 20.15 MHz and a Varian XL-200 spectrometer operated at 50.2 MHz. T.l.c. was conducted on silica gel GF-254 (Merck) with 3:1 ethyl acetate-ethanol (eluant a) and 3:1 benzene-ethanol (eluant b) and detection with u.v. light and iodine vapour. Preparative t.l.c. was conducted on plates coated with 1-mm, layers of silica gel 60 PF-254 with 3:2 benzene-ether as the eluant. Column chromatography was performed in the flash mode[9], with 3:1 ethyl acetate-ethanol (eluant a) or 3:1 benzene-ethanol (eluant b).

1-Methyl-(1,2-dideoxy-β-D-glycero-L-gluco-heptofurano)[2,1-d]imidazolidine-2-thione (4). To a solution of 2-amino-2-deoxy-D-glycero-L-gluco-heptose hydrochloride[4] (6.0 g, 24 mmol) in water (30 ml) were added sodium hydrogen carbonate (2 g, 24 mmol), methylisothiocyanate (2.2 g, 30 mmol), and 96% ethanol (25 ml). The mixture was heated for 9 h at 40°; acetic acid (5 ml) was added, and the solution was heated for a further 2.5 h at 50°, cooled, evaporated under diminished pressure, the residue treated with water (20 ml), the solution washed with ether (3 x 50 ml) and extracted with 3:1 benzene-ethanol (4 x 30 ml) and 3:1 ethyl acetate-ethanol (3 x 25 ml). The extracts were combined, dried ($MgSO_4$), evaporated and the residue subjected to flash chromatography (eluant a). The fraction containing 4 (R_F 0.55) was concentrated to give a syrup which was crystallised from 99% ethanol (1.8 g, 28%). Recrystallised from 99% ethanol, m.p. 125-127°, $[\alpha]_D^{17}$ + 19.8°, $[\alpha]_{578}^{17}$ + 20.9°, $[\alpha]_{546}^{17}$ + 26.4°, $[\alpha]_{436}^{17}$ + 67.8°, $[\alpha]_{365}^{17}$ + 166.0° (c 0.44, pyridine); $\lambda_{max}^{H_2O}$ 236 nm (ε_{mM} 12.9); ν_{max} 3350-3150 (NH, OH), 2970, 2945, and 2915 (CH), and 1480 cm^{-1} (C-N, NH); ^{13}C-n.m.r. data are given in Table 2.

Anal. Calc. for $C_9H_{16}N_2O_5S$: C, 40.90; H, 6.10; N, 10.59. Found: C, 40.92; H, 6.31; N, 10.27.

1-Methyl-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy-β-D-glycero-L-gluco-heptofurano)[2,1-d]imidazolidine-2-thione (13).- Conventional treatment of a suspension of 4 (0.135 g, 0.3 mmol) in pyridine (1.1 ml) and acetic anhydride (0.9 ml), with recrystallisation of the crude product (0.156 g, 71%) from 99% ethanol, gave 13, m.p. 162-163°, $[\alpha]_D^{17}$ - 24.5°,

$[\alpha]_{578}^{17}$ - 25.9°, $[\alpha]_{546}^{17}$ - 29.0°, $[\alpha]_{436}^{17}$ - 46.0°, $[\alpha]_{365}^{17}$ - 61.7° (c 0.53, pyridine); $\lambda_{max}^{96\%\ EtOH}$ 237 and 270 nm (ε_{mM} 14.3 and 9.0); ν_{max} 3300 (NH), 2980, 2960, 2865 (CH), 1745, 1730 (C=O), and 1245 cm^{-1} (C-O-C); ^{1}H-n.m.r. data are given in Table 3.

Anal. Calc. for $C_{17}H_{24}N_2O_9S$: C, 47.21; H, 5.59, N, 6.47. Found: C, 47.28; H, 5.83; N, 6.38.

1-Phenyl-(1,2-dideoxy-β-D-glycero-D-ido-heptofurano)[2,1-d]imidazolidine-2-thione (5).- It was prepared from 2-amino-2-deoxy-D-glycero-D-ido-heptose hydrochloride[4] (7.5 g, 30 mmol) and phenylisothiocyanate (4.35 ml, 37 mmol) as described for 4. Crude 5 (R_F 0.65)(0.9 g, 10%) was recrystallised from 99% ethanol, m.p. 185-187°, $[\alpha]_D^{13}$ + 21.4°, $[\alpha]_{578}^{13}$ + 21.8°, $[\alpha]_{546}^{13}$ + 27.5°, $[\alpha]_{436}^{13}$ + 72.9° (c 0.52, pyridine); $\lambda_{max}^{96\%\ EtOH}$ 239 nm (ε_{mM} 8.2); ν_{max} 3520-3250 (NH, OH), 2990, 2970, 2930, 2910 (CH), 1595, 1460 (C=C aromatic), and 1490 cm^{-1} (NH); ^{1}H- and ^{13}C-n.m.r. data are given in Tables 1 and 2.

Anal. Calc. for $C_{14}H_{18}N_2O_5S$: C, 51.52; H, 5.56; N, 8.58. Found: C, 51.54; H, 5.58; N, 8.37.

1-Phenyl-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy-β-D-glycero-D-ido-heptofurano)[2,1-d]imidazolidine-2-thione (14).- Conventional treatment of 5 (0.1 g, 0.31 mmol) with pyridine (2 ml) and acetic anhydride (2 ml) gave 14 (0.083 g, 55%). Recrystallised from 99% ethanol, m.p. 158-160°, $[\alpha]_D^{13}$ + 4.9°, $[\alpha]_{578}^{13}$ + 7.2°, $[\alpha]_{546}^{13}$ + 8.6°, $[\alpha]_{436}^{13}$ + 22.1°, $[\alpha]_{365}^{13}$ + 57.2° (c 0.49, pyridine); ν_{max} 3480 (NH), 2990, 2960 (C-H), 1600, 1500, 1460 (C=C aromatic), 1745 (C=O), and 1230 cm^{-1} (C-O-C); ^{1}H- and ^{13}C-n.m.r. data are given in Tables 3 and 4.

Anal. Calc. for $C_{22}H_{26}N_2O_9S$: C, 53.43; H, 5.29; N, 5.66. Found: C, 53.19; H, 5.24; N, 5.47.

1-p-Tolyl-(1,2-dideoxy-β-D-glycero-D-ido-heptofurano)[2,1-d]imidazolidine-2-thione (6).- It was prepared from 2-amino-2-deoxy-D-glycero-D-ido-heptose hydrochloride[4] (5 g, 20 mmol) as described for 4. Crude 6 (R_F 0.60) (0.3 g, 5%) was recrystallised from 99% ethanol, m.p. 161-

Table 1.- ^{1}H-n.m.r. data[a] (200 MHz) for compounds 5-9, and 22

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-7'	Aromatic	NH	OH	$-CH_2-C_6H_5$	$-C_6H_4-CH_3$
5	6.31 d $J_{1,2}$ 6.5	4.20 d $J_{2,3}$ 0.0	4.15 d[b] $J_{3,4}$ 2.4	3.87 dd	3.80 dd	← 3.60-3.30 m →			7.60-7.25 m (5H)	9.15 s	5.45 d (OH-3) 4.76 dd (OH-5,OH-6) 4.50 t (OH-7)		
6	5.99 d $J_{1,2}$ 6.6	4.20 d $J_{2,3}$ 0.0	4.15 d[b] $J_{3,4}$ 2.7	3.87 dd $J_{4,5}$ 6.2	3.77 dd $J_{5,6}$ 11.0	← 3.60-3.36 m →			7.37-7.17 dd (4H)	9.20 s	5.43 d (OH-3) 4.76 d (OH-6) 4.74 d (OH-5) 4.46 t (OH-7)		2.31 s
7	6.05 d $J_{1,2}$ 6.4	4.22 d $J_{2,3}$ 0.0	4.18 d[b] $J_{3,4}$ 2.5	3.90 dd $J_{4,5}$ 6.2	3.78 dd	← 3.60-3.40 m →			7.56 m (4H)	9.26 s	5.48 d (OH-3) 4.80 t (OH-5,OH-6) 4.60 t (OH-7)		
8	6.08 d $J_{1,2}$ 6.6	4.16 d $J_{2,3}$ 0.0	4.35 d[b] $J_{3,4}$ 2.6	3.90 dd	← 4.80-3.30 m →				7.65-7.50 m (4H) 7.40-7.34 m (5H)		5.55 d (OH-3) 4.76 d (OH-6) 4.72 d (OH-5) 4.40 t (OH-7)	5.40 d 4.59 d $J_{A,B}$ 15.6	
9	5.93 d $J_{1,2}$ 6.8	4.19 dd $J_{2,3}$ 1.9[b]	4.24 dd $J_{3,4}$ 4.5[b]	3.95 dd $J_{4,5}$ 3.5[b]	← 3.75-3.40 m →				7.60-7.25 m (5H)	9.23 s	5.50 d (OH-3) 4.63 d (OH-5) 4.53 d (OH-6) 4.41 t (OH-7)		
22	5.87 d $J_{1,2}$ 5.8	4.45 d $J_{2,3}$ 0.0	4.35 m	← 3.40-3.80 m →					7.70-7.20 m (9H)		5.34 d (OH-3) 4.62 d (OH-5) 4.30 m (OH-7)	4.30 s	

[a]Recorded in DMSO-d_6, δ scale, J in Hz.

[b]Values obtained by addition of D_2O.

Table 2.- ^{13}C-N.m.r. data[a] (20.15 MHz) for compounds 4-9, 11, and 22.

Comp.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C=S C-S-Bzl	Aromatic	-CH$_3$	Bzl -CH$_2$-	Bzl -C$_6$H$_5$
4[a]	93.1	64.4	74.2	78.7	66.4	70.8	62.6	181.7		30.4		
5[a]	93.7	65.5	75.3	79.9	70.5	71.9	62.5	180.9	138.9 (1C) 128.0 (2C) 126.6 (2C) 126.1 (1C)			
6[b]	95.6	67.0	76.6	80.8	71.5	73.0	63.2	183.3	140.2 (1C) 135.6 (2C) 131.0 (2C) 128.9 (1C)	21.3		
7[a]	93.6	65.6	75.3	80.1	70.5	71.9	62.6	180.8	183.3 (1C) 131.0 (2C) 128.5 (2C) 118.9 (1C)			
8[a]	91.1	69.3	72.8	79.7	70.4	71.5	62.4	180.7	136.0 (1C) 131.1 (2C) 127.5 (2C) 119.2 (1C)		48.9	138.5 (1C) 129.1 (2C) 128.4 (2C) 127.3 (1C)
9[b]	97.0	67.7	77.8	87.7	71.6	73.1	63.7	181.5	138.6 (1C) 130.4 (2C) 129.5 (2C) 128.6 (1C)			
11[a]	93.5	63.7	71.5	77.7	68.4	70.8	59.2	181.8	136.3 (1C) 135.5 (2C) 128.5 (2C) 126.9 (1C)	20.3		
12[b]	96.8	67.8	77.9	97.8	71.5	63.2	63.7	181.3	137.8 (1C) 133.3 (2C) 130.3 (2C) 122.2 (1C)			
22[a]	95.2	75.7*	77.8*	79.8*	71.7**	70.8**	72.6	159.3	137.3 (1C) 131.5 (2C) 126.3 (2C) 118.1 (1C)		34.8	137.2 (1C) 128.6 (2C) 128.1 (2C) 126.9 (1C)

[a] Recorded in DMSO-d$_6$. [b] Recorded in D$_2$O. *, ** The assignments may have to be interchanged.

Table 3.- ^{1}H-n.m.r. data[a] for compounds 13-21, and 23.

Comp.	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-7'	OAc	NH	Aromatic	N-CH_3	-CH_2-Ph	CH_3 Ph
13[b]	5.74 d	4.16 s	5.17 d	4.20 dd[c]	5.60-5.30 m		4.33 dd	3.95 dd	2.10 s (3H)	7.02 s		3.00 s (3H)		
	$J_{1,2}$ 6.6	$J_{2,3}$ 0.0	$J_{3,4}$ 2.7	$J_{4,5}$ 9.3			$J_{6,7}$ 4.9	$J_{6,7'}$ 7.3	2.09 s (3H)					
							$J_{7,7'}$ 11.9		2.05 s (3H)					
									2.03 s (3H)					
14[b]	5.97 d	4.38 d[c]	5.33 d	4.42 dd[c]	5.62 dd	5.10 m	4.45 dd[c]	7.14 dd	2.18 s (3H)		7.60-7.50 m (6H)			
	$J_{1,2}$ 6.3	$J_{2,3}$ 0.0	$J_{3,4}$ 3.0	$J_{4,5}$ 7.6	$J_{5,6}$ 4.3	$J_{6,7}$ 4.3	$J_{7,7'}$ 11.6		2.11 s (3H)					
						$J_{6,7'}$ 6.6			2.08 s (3H)					
									2.03 s (3H)					
15[d]	5.93 d	4.38 m	5.31 d	4.38 m	5.61 dd	5.07 m	4.37 m	4.15 dd	2.19 s (3H)		7.40-7.20 m (5H)			2.36 s
	$J_{1,2}$ 6.6	$J_{2,3}$ ~0.0	$J_{3,4}$ 3.3	$J_{4,5}$ 7.7	$J_{5,6}$ 3.7	$J_{6,7}$ 3.7	$J_{7,7'}$ 12.0		2.12 s (3H)					
						$J_{6,7'}$ 6.6			2.09 s (3H)					
									2.04 s (3H)					
16[b]	5.97 d	4.38 d	5.34 d	4.41 dd	5.63 dd	5.09 m	4.43 dd	4.15 dd	2.21 s (3H)		7.70-7.35 m (5H)			
	$J_{1,2}$ 6.6	$J_{2,3}$ ~0.0	$J_{3,4}$ 3.0	$J_{4,5}$ 7.3	$J_{5,6}$ 4.0	$J_{6,7}$ 4.3	$J_{7,7'}$ 12.6		2.14 s (3H)					
						$J_{6,7'}$ 7.2			2.10 s (3H)					
									2.07 s (3H)					
17[b]	5.23 d	3.77 d	5.36 d	4.06 m	5.68 dd	4.90 m	4.06 m	4.06 m	1.89 s (3H)		7.75-7.25 m 9(H)		5.50 d	
	$J_{1,2}$ 6.6	$J_{2,3}$ ~0.0	$J_{3,4}$ 3.0	$J_{4,5}$ 7.9	$J_{5,5}$ 3.3				1.72 s (6H)				4.65 d	
									1.69 s (3H)				$J_{A,B}$ 14.5	

[a] Recorded in $CDCl_3$. [b] Recorded at 90 MHz. [c] Values obtained by extrapolation back to zero concentration of Eu(fod)$_3$. [d] Recorded at 200 MHz.

Table 3 (Cont.).- ^{1}H-n.m.r. data[a] for compounds 13-21, and 23.

Comp.	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-7'	OAc	NH	Aromatic	N-CH_3	CH_2-Ph	CH_3 Ph
18[b]	5.98 d	4.35 m[c]	4.99 dd	4.45 m[c]	5.45 dd	5.31 m	4.55 m[c]	4.16 dd	2.26 s (3H)		7.70-7.20 m (6H)			
	$J_{1,2}$ 7.3	$J_{2,3}$ 1.3	$J_{3,4}$ 3.6	$J_{4,5}$ 3.0	$J_{5,6}$ 6.6	$J_{6,7}$ 3.0	$J_{7,7'}$ 12.5		2.15 s (3H)					
						$J_{6,7'}$ 5.3			2.07 s (3H)					
									2.05 s (3H)					
19[b]	5.93 d	4.35 m	4.93 dd	4.60 m	5.40 dd	5.25 m	4.35 m	4.12 dd	2.24 s (3H)		7.70-7.25 m (5H)			
	$J_{1,2}$ 6.7	$J_{2,3}$ 0.7	$J_{3,4}$ 3.3	$J_{4,5}$ 3.0	$J_{5,6}$ 6.6	$J_{6,7}$ 2.7	$J_{7,7'}$ 12.5		2.18 s (3H)					
						$J_{6,7'}$ 5.5			2.10 s (3H)					
									2.06 s (3H)					
20[b]	5.28 d	4.65 t	4.84 dd	4.33 dd[c]	5.45-5.25 m		4.55-4.05 m		2.15 s (3H)	7.66 s	7.45-7.05 m (4H)			
	$J_{1,2}$ 6.3	$J_{2,3}$ 5.6	$J_{3,4}$ 9.2	$J_{4,5}$ 3.0	$J_{5,6}$ 7.0	$J_{6,7}$ 3.0	$J_{7,7'}$ 13.0		2.10 s (3H)					
									2.06 s (6H)					
21[b]	5.85 d	4.67 t	4.84 dd		5.55-5.20 m				2.15 s (3H)	7.72 s	7.62-7.30 m (4H)			
	$J_{1,2}$ 7.0	$J_{2,3}$ 6.0	$J_{3,4}$ 9.0	$J_{4,5}$ 3.0	$J_{5,6}$ 7.0	$J_{6,7}$ 2.0	$J_{7,7'}$ 12.0		2.11 s (3H)					
						$J_{6,7'}$ 5.4			2.04 s (3H)					
23[d]	5.78 d	4.65 d	5.51 d	3.97 dd	5.56 dd	5.05 m	4.30 dd	4.18 dd	2.19 s (3H)		7.46-7.16 m (9H)		4.36 d	
	$J_{1,2}$ 5.6	$J_{2,3}$ 0.0	$J_{3,4}$ 2.5	$J_{4,5}$ 7.5	$J_{5,6}$ 3.9	$J_{6,7}$ 4.6	$J_{7,7'}$ 12.2		2.11 s (3H)					
						$J_{6,7'}$ 6.7			2.09 s (3H)					
									2.02 a (3H)					

[a] Recorded in $CDCl_3$. [b] Recorded at 90 MHz. [c] Values obtained by extrapolation back to zero concentration of Eu(fod)$_3$. [d] Recorded at 200 MHz.

Table 4.- ^{13}C-N.m.r. data (20.15 MHz) for compounds 14, 17, 23, and 25.

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C=S/C-S-Bzl	Aromatic	OAc C=O	OAc CH_3	Bzl $-CH_2-$	Bzl $-C_6H_5$
14[a]	94.9	64.3	76.8*	76.9*	69.8**	70.0**	61.8	183.1	138.2 (1C) 128.9 (2C) 127.5 (2C) 127.0 (1C)	170.5 170.4 169.6 169.5	20.7		
17[a]	91.7	68.0	63.9	76.7	69.6*	69.9*	61.5	182.5	136.0 (1C) 131.9 (2C) 128.6 (2C) 121.3 (1C)	170.1 169.5 169.3	20.6	50.0	137.9 128.6 128.2
23[a]	96.1	76.2	76.7	77.3	70.2	70.2	76.6	163.4	136.8 (1C) 129.2 (2C) 126.9 (2C) 120.5 (1C)	170.2 170.0 169.6 169.5	20.9 20.8 20.6	36.5	136.6 (1C) 128.7 (2C) 127.8 (2C) 127.5 (1C)

Compound	C-1'	C-2'	C-3'	C-4'	C-5'	C-2	C-4	C-5	Aromatic	$-CH_3$
25[b]	72.0*	69.9*	69.3*	64.1*	62.9	161.0	131.4	115.4	136.6 (1C) 135.5 (1C) 128.9 (2C) 125.0 (2C)	20.4

[a]Recorded in $CDCl_3$. [b]Recorded in DMSO-d_6.

*, ** The assignments may have to be interchanged

-163°, $[\alpha]_D^{11}$ + 15.7°, $[\alpha]_{578}^{11}$ + 16.8°, $[\alpha]_{546}^{11}$ + 19.6°, $[\alpha]_{436}^{11}$ + 57.4°, $[\alpha]_{365}^{11}$ + 158.0° (c 0.7, pyridine); $\lambda_{max}^{96\% \text{ EtOH}}$ 239 nm (ε_{mM} 12.9); ν_{max} 3500-3100 (NH, OH), 2920, 2870 (C-H), 1520, 1460 (C=C aromatic), and 1490 cm^{-1} (C-N, N-H); ^{1}H- and ^{13}C-n.m.r. data are given in Tables 1 and 2.

Anal. Calc. for $C_{15}H_{20}N_2O_5S$: C, 52.92; H, 5.92; N, 8.22. Found: C, 52.91; H, 5.91; N, 7.94.

1-p-Tolyl-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy-β-D-glycero-D-ido-hepto-furano)[2,1-d]imidazolidine-2-thione (15).- Conventional treatment of 6 (0.16 g, 0.54 mmol) with pyridine (2 ml) and acetic anhydride (1.5 ml) gave 15 as an amorphous solid (0.14 g, 60%), m.p. 63-66°, $[\alpha]_D^{19}$ + 8.1°, $[\alpha]_{578}^{19}$ + 10.9°, $[\alpha]_{546}^{19}$ + 13.9°, $[\alpha]_{436}^{19}$ + 30.3°, $[\alpha]_{365}^{19}$ + 77.5° (c 0.40, pyridine); ν_{max} 3350 (NH), 2970, 2930 (C-H), 1580, 1505, 1470 (C=C aromatic), 1745 (C=O), and 1230 cm^{-1} (C-O-C); ^{1}H-n.m.r. data are given in Table 3.

Anal. Calc. for $C_{23}H_{28}N_2O_9S$: C, 54.36; H, 5.55; N, 5.51. Found: C, 54.10; H, 5.67; N, 5.26.

1-(p-Bromophenyl)-(1,2-dideoxy-β-D-glycero-D-ido-heptofurano)-[2,1-d]-imidazolidine-2-thione (7).- It was prepared from 2-amino-2-deoxy-D--glycero-D-ido-heptose hydrochloride[4] (4 g, 16 mmol) and p-bromophenyl-isothiocyanate (4.1 g, 20 mmol) as described for 4. Crude 7 (R_F 0.71) (1.25 g, 20%) was recrystallised from 99% ethanol, m.p. 145-147°, $[\alpha]_D^{14}$ + 1.8°, $[\alpha]_{578}^{14}$ + 2.0°, $[\alpha]_{546}^{14}$ + 1.0°, $[\alpha]_{436}^{14}$ + 9.5°, $[\alpha]_{365}^{14}$ + 45.1° (c 0.64, pyridine); $\lambda_{max}^{H_2O}$ 239 nm (ε_{mM} 19.6); ν_{max} 3500-3200 (NH, OH), 2970, 2940, 2910, 2880 (C-H), 1505, 1440 (C=C aromatic), and 1495 cm^{-1} (N-H, C-N); ^{1}H- and ^{13}C-n.m.r. data are given in Tables 1 and 2.

Anal. Calc. for $C_{14}H_{17}BrN_2O_5S$: C, 41.49; H, 4.23; N, 6.91. Found: C, 41.46; H, 4.53; N, 6.70.

1-(p-Bromophenyl)-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy-β-D-glycero-D-ido--heptofurano)[2,1-d]imidazolidine-2-thione (16).- Conventional treatment of 7 (0.17 g, 0.42 mmol) with pyridine (1.5 ml) and acetic anhydride (1.13 ml) gave 16 (0.211 g, 88%). Recrystallised from 1:1 ethanol-water,

m.p. 202-204°, $[\alpha]_D^{20}$ +11.6°, $[\alpha]_{578}^{20}$ + 13.0°, $[\alpha]_{546}^{20}$ + 15.6°, $[\alpha]_{436}^{20}$ + 33.7°, $[\alpha]_{365}^{20}$ + 79.0° (c 0.43, pyridine); ν_{max} 3280 (NH), 2970, 2960 (C-H), 1495, 1405 (C=C aromatic), 1745 (C=O), and 1230 cm^{-1} (C-O-C); ^{1}H-n.m.r. data are given in Table 3.

Anal. Calc. for $C_{22}H_{25}BrN_2O_9S$: C, 46.08; H, 4.39; N, 4.88. Found: C, 46.11; H, 4.35; N, 4.69.

3-(Benzylamino)-1-(p-bromophenyl)-(1,2-dideoxy-β-D-glycero-D-ido-hepto-furano)[2,1-d]imidazolidine-2-thione (8).- A solution of 2-(benzylamino)--2-deoxy-D-glycero-D-ido-heptononitrile[10] (12 g, 40 mmol) in M hydrochloric acid (50 ml) was hydrogenated at atmospheric pressure and room temperature in the presence of 10% $Pd/BaSO_4$ (2.5 g) for 24 h, then filtered, and concentrated until crystals of ammonium chloride appeared. These were removed, the filtrate was concentrated and ethanol and benzene were repeatedly evaporated from the syrupy residue to yield amorphous 2-(benzylamino)-2-deoxy-D-glycero-D-ido-heptose hydrochloride impurified by 2-amino-2-deoxy-D-glycero-D-ido-heptose hydrochloride. A solution of the crude product in water (30 ml), was treated with p-bromophenylisothiocyanate (4.1 g, 20 mmol) as described for 4. Column chromatography (eluant b) of the product gave 7 (0.56 g, 4%), R_F 0.71, and 8 (2.18 g, 11%), R_F 0.78, which was recrystallised from 99% ethanol, m.p. 85-87°, $[\alpha]_D^{19}$ - 35.3°, $[\alpha]_{578}^{19}$ - 38.6°, $[\alpha]_{546}^{19}$ - 47.0°, $[\alpha]_{436}^{19}$ - 91.8°, $[\alpha]_{365}^{19}$ - 166.6° (c 0.48, pyridine); $\lambda_{max}^{96\% EtOH}$ 250 nm (ε_{mM} 21.1) ν_{max} 3450-3250 (OH), 2980, 2920, 2880 (C-H), 1450, 1405 (C=C aromatic), and 1490 cm^{-1} (C-N); ^{1}H- and ^{13}C-n.m.r. data are given in Tables 1 and 2.

Anal. Calc. for $C_{21}H_{23}BrN_2O_9S$: C, 50.91; H, 4.67; N, 5.65. Found: C, 50.52; H, 4.64; N, 5.39.

3-(Benzylamino)-1-(p-bromophenyl)-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy--β-D-glycero-D-ido-heptofurano)[2,1-d]imidazolidine-2-thione (17).- Conventional treatment of a solution of 8 (0.5 g, 1.0 mmol) in pyridine (1.1 ml) and acetic anhydride (0.9 ml), with recrystallisation of the crude product (0.4 g, 61%) from 99% ethanol, gave 17, m.p. 115-117°, $[\alpha]_D^{19}$ - 41.1°, $[\alpha]_{578}^{19}$ - 43.7°, $[\alpha]_{546}^{19}$ - 95.0°, $[\alpha]_{365}^{19}$ - 173.4° (c

0.54, pyridine); ν_{max} 2990, 2980, 2960, 2880 (C-H), 1745 (C=O), 1495, 1450, 1405 (C=C aromatic), and 1230 cm^{-1} (C-O-C); ^{1}H- and ^{13}C-n.m.r. data are given in Tables 3 and 4.

Anal. Calc for $C_{29}H_{31}BrN_2O_9S$: C, 52.49; H, 4.70; N, 4.22. Found: C, 52.28; H, 4.75; N, 4.22.

2-(Benzylamino)-2-deoxy-D-glycero-D-galacto-heptononitrile and 2-(benzylamino)-2-deoxy-D-glycero-D-talo-heptononitrile.- A suspension of D-manosse (5.4 g, 30 mmol) in 99% ethanol (20 ml) was treated with benzylamine (4 ml, 40 mmol) and heated under reflux to dissolution. The mixture was cooled to room temperature and then anhydrous hydrogen cyanide (3 ml, 80 mmol) was added and the mixture kept in a refrigerator to crystallise a mixture of heptononitriles. The crystals (2.2 g, 54%) were collected, washed with cooled 99% ethanol and ether and recrystallised from 99% ethanol.

Anal. Calc. for $C_{14}H_{20}N_2O_5$: C, 56.74; H, 6.70; N, 9.45. Found: C, 56.77; H, 6.70; N, 9.34.

2-Amino-2-deoxy-D-glycero-D-galacto-heptose hydrochloride and 2-amino-2-deoxy-D-glycero-D-talo-heptose hydrochloride.- A mixture of 2-(benzylamino)-2-deoxy-D-glycero-D-galacto and 2-(benzylamino)-2-deoxy-D-glycero-D-talo-heptononitriles (30 g, 0.1 mol) in M hydrochloric acid (250 ml) was hydrogenated at atmospheric pressure and room temperature in the presence of 10% $Pd/BaSO_4$ (12.5 g). After 6 days, the catalyst was filtered off, and the filtrate was concentrated until crystals of ammonium chloride appeared; these were filtered off, the filtrate was evaporated and the syrupy residue was repeatedly treated and evaporated with 99% ethanol, to yield an almost pure, amorphous mixture of heptose hydrochlorides (15 g, 61%) that was used in the next step without purification.

1-Phenyl-(1,2-dideoxy-α-D-glycero-D-galacto-heptofurano)[2,1-d]imidazolidine-2-thione (9).- A solution of the epimeric mixture of 2-amino-2-deoxy-D-glycero-D-galacto- and 2-amino-2-deoxy-D-glycero-D-talo-heptose hydrochlorides (15 g, 60 mmol) in water (40 ml), was treated with phenylisothiocyanate (8.7 ml, 74 mmol) as described for 4. The resulting residue was subjected to column chromatography (eluant b). The

fractions containing the component of R_F 0.30 were concentrated to give 9 (3.9 g, 20%); recrystallised from 99% ethanol, m.p. 178-180°, $[\alpha]_D^{19}$ + 46.1°, $[\alpha]_{578}^{19}$ + 47.6°, $[\alpha]_{546}^{19}$ + 54.0°, $[\alpha]_{436}^{19}$ + 88.7° (c 0.67, pyridine); $\lambda_{max}^{96\%\ EtOH}$ 240 nm (ε_{mM} 12.6); ν_{max} 3550-3050 (NH, OH), 2940, 2880 (CH), 1595, 1460, 1440 (C=C aromatic), and 1495 cm^{-1} (NH, CN); ^{1}H- and ^{13}C-n.m.r. data are given in Tables 1 and 2.

Anal. Calc. for $C_{14}H_{18}N_2O_5S$: C, 51,52; H, 5.56; N, 8.58. Found: C, 51.76; H, 5.71; N, 8.56.

1-Phenyl-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy-α-D-glycero-D-galacto-heptofurano)[2,1-d]imidazolidine-2-thione (18).- Conventional treatment of 9 (0.15 g, 0.46 mmol) with pyridine (1.5 ml) and acetic anhydride (0.8 ml) gave 18 as an amorphous solid (0.15 g, 68%), m.p. 68-70°, $[\alpha]_D^{19}$ + 60.4°, $[\alpha]_{578}^{19}$ + 62.9°, $[\alpha]_{546}^{19}$ + 71.1°, $[\alpha]_{436}^{19}$ + 113.6°, $[\alpha]_{365}^{19}$ + 150.0° (c 0.55, pyridine); ν_{max} 3340 (NH), 2950 (C-H), 1745 (C=O), 1595, 1500, 1450 (C=C aromatic), and 1220 cm^{-1} (C-O-C); ^{1}H-n.m.r. data are given in Table 3.

Anal. Calc. for $C_{22}H_{26}N_2O_9S$: C, 53.43; H, 5.29; N, 5.66. Found: C, 55.15; H, 5.36; N, 5.58.

1-(p-Bromophenyl)-(1,2-dideoxy-α-D-glycero-D-galacto-heptofurano)[2,1--d]imidazolidine-2-thione (10) and 1-(p-bromophenyl)-(1,2-dideoxy-β-D--glycero-D-talo-heptofurano)[2,1-d]imidazolidine-2-thione (12).- A solution of 2-amino-2-deoxy-D-glycero-D-galacto- and 2-amino-2-deoxy--D-glycero-D-talo-heptose hydrochlorides (7 g, 28 mmol) in water (20 ml), was neutralised with 5N NaOH, and p-bromophenylisothiocyanate (7.38 g, 36 mmol) was added. The mixture was heated for 24 h at 40°; acetic acid (17 ml) was added, and the solution heated for a further 7 h at 40°, cooled, evaporated under diminished pressure and the residue treated as described for 4. The resulting amorphous solid was subjected to column chromatography (eluant b). The fraction with R_F 0.35 was crystallised from 99% ethanol to yield 10 (0.56 g, 5%), m.p. 102-105°, $[\alpha]_D^{14}$ + 70.6°, $[\alpha]_{578}^{14}$ + 76.0°, $[\alpha]_{546}^{14}$ + 84.4°, $[\alpha]_{436}^{14}$ + 147.9°, $[\alpha]_{365}^{14}$ + 238.9° (c 0.48, pyridine); $\lambda_{max}^{96\%\ EtOH}$ 238 nm (ε_{mM} 12.2); ν_{max} 3600-

3000 (NH, OH), 2980, 2920, 2890 (C-H), 1600, 1510, 1450 (C=C aromatic), and 1495 cm^{-1} (CN, NH).

Anal. Calc. for $C_{14}H_{17}BrN_2O_5S$: C, 41.49; H, 4.23; N, 6.91. Found: C, 41.43; H, 4.26; N, 6.63.

The fraction with R_F 0.29 was crystallised from 99% ethanol to yield 12 (0.6 g, 6%), m.p. 184-185°, $\lambda_{max}^{96\%\ EtOH}$ 239 nm (ε_{mM} 14.9); ν_{max} 3600-3000 (NH, OH), 2965, 2940, 2900 (C-H), 1590, 1460 (C=C aromatic), and 1495 cm^{-1} (NH, CN); ^{13}C-n.m.r. data are given in Table 2.

Anal. Calc. for $C_{14}H_{17}BrN_2O_5S$: C, 41.49; H, 4.23; N, 6.91. Found: C, 41.20; H, 4.29; N, 6.63.

1-(p-Bromophenyl)-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy-α-D-glycero-D-galacto-heptofurano)[2,1-d]imidazolidine-2-thione (19).- Conventional treatment of 10 (0.12 g, 0.30 mmol) with pyridine (1.2 ml) and acetic anhydride (0.75 ml), gave 19 as an amorphous solid (0.12 g, 69%), m.p. 75-77°, $[\alpha]_D^{14}$ + 57.4°, $[\alpha]_{578}^{14}$ + 60.7°, $[\alpha]_{546}^{14}$ + 67.1°, $[\alpha]_{436}^{14}$ + 106.4°, $[\alpha]_{365}^{14}$ + 111.0° (c 0.54, pyridine); ν_{max} 3350 (NH), 2970 (C-H), 1750 (C=O), 1500, 1430 (C=C aromatic), and 1225 cm^{-1} (C-O-C); ^{1}H-n.m.r. data are given in Table 3.

Anal. Calc. for $C_{22}H_{25}BrN_2O_9S$: C, 46.08; H, 4.39; N, 4.88. Found: C, 45.95; H, 4.45; N, 4.70.

1-(p-Bromophenyl)-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy-β-D-glycero-D-talo-heptofurano)[2,1-d]imidazolidine-2-thione (21).- Conventional treatment of 12 (0.16 g, 0.4 mmol) with pyridine (1.6 ml) and acetic anhydride (0.85 ml), gave 21 as an amorphous solid (0.18 g, 80%), m.p. 78-80°, $[\alpha]_D^{14}$ - 61.5°, $[\alpha]_{578}^{14}$ - 64.5°, $[\alpha]_{546}^{14}$ - 74.7°, $[\alpha]_{436}^{14}$ - 185.5°, $[\alpha]_{365}^{14}$ - 239.6° (c 0.4, pyridine); ν_{max} 3350 (NH), 2970 (C-H), 1745 (C=O), 1580, 1490, 1430 (C=C aromatic), and 1220 cm^{-1} (C-O-C); ^{1}H-n.m.r. data are given in Table 3.

Anal. Calc. for $C_{22}H_{25}BrN_2O_9S$: C, 46.08; H, 4.39; N, 4.88. Found: C, 45.90; H, 4.38; N, 4.69.

1-p-Tolyl-(1,2-dideoxy-β-D-glycero-D-talo-heptofurano)[2,1-d]imidazolidine-2-thione (11).- A solution of 2-amino-2-deoxy-D-glycero-D-talo- and 2-amino-2-deoxy-D-glycero-D-galacto-heptose hydrochlorides (10 g,

40 mmol) in water (150 ml) was treated with p-tolylisothiocyanate (6 g, 40 mmol) as described for 4. The resulting residue was subjected to column chromatography (eluant b). The fraction with R_F 0.31 was crystallised from 99% ethanol to yield 11 (1.41 g, 10%), m.p. 115-118°, $[\alpha]_D^{19}$ - 138.0°, $[\alpha]_{578}^{19}$ - 144.6°, $[\alpha]_{546}^{19}$ - 165.5°, $[\alpha]_{436}^{19}$ - 293.5°, $[\alpha]_{365}^{19}$ - 490.4° (c 0.67, pyridine); $\lambda_{max}^{96\% \text{ EtOH}}$ 240 nm (ε_{mM} 14.6); ν_{max} 3550-3000 (NH,OH), 2980, 2920, 2900 (C-H), 1610, 1510, 1450 (C=C aromatic), and 1500 cm^{-1} (C-N, N-H); ^{13}C-n.m.r. data are given in Table 2.

Anal. Calc. for $C_{15}H_{20}N_2O_5S$: C, 52.92; H, 5.92; N, 8.23. Found: C, 52.62; H, 5.80; N, 7.98.

1-p-Tolyl-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy-β-D-glycero-D-talo-heptofurano)[2,1-d]imidazolidine-2-thione (20).- Conventional treatment of 11 (0.1 g, 0.34 mmol) with pyridine (1 ml) and acetic anhydride (0.7 ml), gave 20 (0.11 g, 65%). Recrystallised from 99% ethanol, m.p. 59-60°, $[\alpha]_D^{11}$ - 72.7°, $[\alpha]_{578}^{11}$ - 74.4°, $[\alpha]_{546}^{11}$ -86.1°, $[\alpha]_{436}^{11}$ -157.5°, $[\alpha]_{365}^{11}$ - 249.3° (c 0.41, pyridine); ν_{max} 3350 (NH), 2960 (C-H), 1745 (C=O), 1510, 1480 (C=C aromatic), and 1220 cm^{-1} (C-O-C); ^{1}H-n.m.r. data are given in Table 3.

Anal. Calc. for $C_{23}H_{28}N_2O_9S$: C, 54.36; H, 5.55; N, 5.51. Found: C, 54.33; H, 5.46; N, 5.41.

2-(Benzylthio)-1-(p-bromophenyl)-(1,2-dideoxy-β-D-glycero-D-ido-heptofurano)[2,1-d]-2-imidazoline (22).- To a suspension of 7 (0.3 g, 0.75 mmol) in 90% ethanol (4 ml) were added sodium hydrogen carbonate (0.06 g, 0.75 mmol), and benzyl chloride (0.1 ml, 0.75 mmol). The mixture was boiled under reflux for 1 h, and then evaporated to a dryness. Water was added to a solution of the residue in ethanol, to incipient turbidity and the mixture stored for 24 h at 0° to give 22 (0.28 g, 76%). Recrystallised from 1:1 ethanol-water, m.p. 72-75°, $[\alpha]_D^{14}$ - 46.0°, $[\alpha]_{578}^{14}$ -53.7°, $[\alpha]_{546}^{14}$ - 63.6°, $[\alpha]_{436}^{14}$ - 141.4°, $[\alpha]_{365}^{14}$ -326.7° (c 0.58, pyridine); $\lambda_{max}^{96\% \text{ EtOH}}$ 259 nm (ε_{mM} 15.6); ν_{max} 3600-3000 (OH), 2950, 2910 (C-H aliphatic), 1535, 1480, and 1450 cm^{-1} (C=C aromatic); ^{1}H- and ^{13}C-n.m.r. data are given in Tables 1 and 2.

Anal. Calc. for $C_{21}H_{23}BrN_2O_5S$: C, 50.91; H, 4.68; N, 5.65. Found: C, 50.84; H, 4.55; N, 5.33.

2-(Benzylthio)-1-(p-bromophenyl)-(3,5,6,7-tetra-O-acetyl-1,2-dideoxy--β-D-glycero-D-ido-heptofurano)[2,1-d]-2-imidazoline (23).- Conventional treatment of 22 (0.13 g, 0.20 mmol) with pyridine (1 ml) and acetic anhydride (1 ml) gave 23 (0.16 g, 95%). Recrystallised from 99% ethanol, m.p. 58–60°, $[\alpha]_D^{14}$ -8.5°, $[\alpha]_{578}^{14}$ -10.4°, $[\alpha]_{546}^{14}$ -13.2°, $[\alpha]_{436}^{14}$ - 38.1°, $[\alpha]_{365}^{14}$ - 105.5° (c 0.78, pyridine); ν_{max} 3050, 3010 (C-H aromatic), 2960, 2910 (C-H aliphatic), 1735 (C=O), 1550, 1480 (C=C aromatic), and 1220 cm^{-1} (C-O-C); ^1H- and ^{13}C-n.m.r. data are given in Tables 3 and 4.

Anal. Calc. for $C_{29}H_{31}BrN_2O_9S$: C, 52.49; H, 4.70; N, 4.22. Found: C, 52.20; H, 4.85; N, 4.01.

4-(D-Galacto-pentitol-1-yl)-1-phenyl-4-imidazoline-2-thione (24).- A solution of 13 (1 g, 3.06 mmol) in 50% ethanol (10 ml) was treated with trifluoroacetic acid (2 ml), and the mixture was boiled under reflux for 2.5 h and then concentrated to dryness. Ethanol was repeatedly evaporated from the residue, and the resulting residue was crystallised from water to give 24 (0.44 g, 44%). Recrystallised from 1:1 acetone-water, m.p. 190–192°, $[\alpha]_D^{28}$ + 25.6°, $[\alpha]_{578}^{28}$ + 27.0°, $[\alpha]_{546}^{28}$ + 31.0°, $[\alpha]_{436}^{28}$ + 58.6°, $[\alpha]_{365}^{28}$ + 112.2° (c 0.52, pyridine); $\lambda_{max}^{H_2O}$ 265 nm (ε_{mM} 10.0); ν_{max} 3330–3220 (NH, OH), 2910, 2890 (C-H), 1590, 1495, and 1460 cm^{-1} (C=C aromatic).

Anal. Calc. for $C_{14}H_{18}N_2O_5S$. ½ H_2O: C, 50.14; H, 5.71; N, 8.35. Found: C, 49.88; H, 5.43; N, 8.28.

4-(Penta-O-acetyl-D-galacto-pentitol-1-yl)-1-phenyl-4-imidazoline-2--thione (27).- Conventional treatment of 24 (0.16 g, 0.48 mmol) with pyridine (1.6 ml) and acetic anhydride (1.12 ml) gave 27 (0.17 g, 68%), which was purified by preparative t.l.c. (3:2 benzene-ether), m.p. 118--120°, $[\alpha]_D^{28}$ + 135.5°, $[\alpha]_{578}^{28}$ + 141.7°, $[\alpha]_{546}^{28}$ + 163.2°, $[\alpha]_{436}^{28}$ + 306.7° (c 0.49, pyridine); ν_{max} 1740 (C=O), 1590, 1495 (C=C aromatic), and 1210 cm^{-1} (C-O-C); ^1H-n.m.r. data are given in Table 5.

Table 5.- ^{1}H-N.m.r. data[a] (90 MHz) for compounds 27, 28, and 29

Compound	H-1'	H-2'	H-3'	H-4'	H-5'	H-5"	OAc	H-5	NH	Aromatic	$-C_6H_4-CH_3$
27	5.91 s	← 5.60-5.20 m →			4.25 dd $J_{4',5'}$ 5.5 $J_{5',5''}$ 12.0	3.87 dd $J_{4',5''}$ 7.5	2.15 s (3H) 2.13 s (3H) 2.10 s (3H) 2.05 s (3H) 2.02 s (3H)	6.81 s		7.60-7.25 m (5H)	
28	5.88 d $J^b_{1',2'}$ 3.0	← 5.46-5.16 m →	$J^b_{2',3'}$ 9.3	$J^b_{3',4'}$ 2.0	4.22 dd $J_{4',5'}$ 5.6 $J_{5',5''}$ 11.3	3.84 dd $J_{4',5''}$ 7.0	2.13 s (3H) 2.11 s (3H) 2.07 s (3H) 2.02 s (6H)	6.76 s	11.88	7.50-7.15 m (4H)	2.39 s (3H)
29	5.90 s	← 5.50-5.20 m →			4.26 dd $J_{4',5'}$ 6.0 $J_{5',5''}$ 12.0	3.85 dd $J_{4',5''}$ 7.0	2.14 s (6H) 2.10 s (3H) 2.04 s (6H)	6.79 s	11.80 s	7.70-7.32 m (4H)	

[a]Recorded in $CDCl_3$. [b]Values obtained by addition of $Eu(fod)_3$.

Anal. Calc. for $C_{24}H_{28}N_2O_{10}S$: C, 53.72; H, 5.26; N, 5.22. Found: C, 53.70; H, 5.08; N, 5.10.

4-(D-Galacto-pentitol-1-yl)-1-p-tolyl-4-imidazoline-2-thione (25).- It was prepared from 2[3] (0.96 g, 2.82 mmol) and trifluoroacetic acid (2 ml) as described for 24. Crude 25 (0.32 g, 33%) was recrystallised from 1:1 acetone-water, m.p. 207-209°, $[\alpha]_D^{21}$ + 18.5°, $[\alpha]_{578}^{21}$ + 18.3°, $[\alpha]_{546}^{21}$ + 21.9°, $[\alpha]_{436}^{21}$ + 44.0° (c 0.51, pyridine); $\lambda_{max}^{H_2O}$ 266 nm (ε_{mM} 9.0); ν_{max} 3340, 3210 (NH, OH), 2940, 2920 (C-H), 1510, and 1465 cm^{-1} (C=C aromatic); ^{13}C-n.m.r. data are given in Table 4.

Anal. Calc. for $C_{15}H_{20}N_2O_5S$: C, 52.92; H, 5.92; N, 8.22. Found: C, 53.13; H, 5.63; N, 8.54.

4-(Penta-O-acetyl-D-galacto-pentitol-1-yl)-1-p-tolyl-4-imidazoline-2--thione (28).- Conventional treatment of 25 (0.14 g, 0.21 mmol) with pyridine (1.4 ml) and acetic anhydride (1.1 ml) gave 28 (0.15 g, 66%), which was purified by preparative t.l.c. (3:2 benzene-ether), m.p. 101--103°, $[\alpha]_D^{21}$ + 136.3°, $[\alpha]_{578}^{21}$ + 142.7°, $[\alpha]_{546}^{21}$ + 164.1°, $[\alpha]_{436}^{21}$ + 314.7° (c 0.48, pyridine); ν_{max} 3440 (NH), 1735 (C=O), 1500, 1455 (C=C aromatic), and 1210 cm^{-1} (C-O-C); ^{1}H-n.m.r. data are given in Table 5.

Anal. Calc. for $C_{25}H_{30}N_2O_{10}S$: C, 54.51; H, 5.49; N, 5.09. Found: C, 54.74; H, 5.82; N, 5.11.

1-(p-Bromophenyl)-4-(D-galacto-pentitol-1-yl)-4-imidazoline-2-thione (26).- It was prepared from 3[3] (0.64 g, 1.6 mmol) and trifluoroacetic acid (1.3 ml) as described for 24. Crude 26 (0.34 g, 50%) was recrystallised from 1:1 acetone-water, m.p. 209-211°, $[\alpha]_D^{20}$ + 14.9°, $[\alpha]_{578}^{20}$ + 15.1°, $[\alpha]_{546}^{20}$ + 18.4°, $[\alpha]_{436}^{20}$ + 36.8° (c 0.55, pyridine); $\lambda_{max}^{H_2O}$ 273 nm (ε_{mM} 7.5); ν_{max} 3340-3200 (NH, OH), 2940, 2920, 1485, and 1460 cm^{-1} (C=C aromatic).

Anal. Calc. for $C_{14}H_{17}BrN_2O_5S$: C, 41.48; H, 4.19; N, 6.91. Found: C, 41.70; H, 4.39; N, 6.67.

1-(p-Bromophenyl)-4-(penta-O-acetyl-D-galacto-pentitol-1-yl)-4-imidazoline-2-thione (29).- Conventional treatment of 26 (0.19 g, 0.47 mmol)

Table 6.- Experimental and calculated[a] J values for compounds 13-21, and 23.

	Experimental J values			Calculated[a] J values for different conformations													
				$^4T_0$			^4E			^3E			$^3T_4$			E_4		
Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$
13	6.6	0.0	2.7	5.36	1.02	1.37	6.53	1.36	0.65	3.58	9.10	0.65	5.36	8.44	0.65	6.53	7.04	0.65
14	6.3	0.0	3.0															
15	6.6	0.0	3.3															
16	6.6	0.0	3.0															
17	6.6	0.0	3.0															
18	7.3	1.3	3.6	6.48	7.06	8.31	6.53	8.85	8.52	5.33	1.30	2.22	6.48	0.77	2.22	6.53	0.75	2.22
19	6.7	0.7	-															
20	6.3	5.6	9.2	5.36	6.23	8.31	6.53	8.35	8.52	3.58	1.91	2.22	5.36	2.87	2.22	6.53	4.35	2.22
21	7.0	6.0	9.0															
23	5.6	0.0	2.5	5.36	1.02	1.37	6.53	1.36	0.65	3.58	9.10	0.65	5.36	8.44	0.65	6.53	7.04	0.65

[a] The J values have been calculated for models[7] by applying the Altona[8] equation.

with pyridine (1.7 ml) and acetic anhydride (1.33 ml) gave 29 (0.22 g, 74%). which was purified by preparative t.l.c. (3:2 benzene-ether), m.p. 146-148°, $[\alpha]_D^{28}$ + 118.5°, $[\alpha]_{578}^{28}$ + 122.9°, $[\alpha]_{546}^{28}$ + 143.4°, $[\alpha]_{436}^{28}$ + 271.4°, (c 0.48, pyridine); ν_{max} 1745 (C=O), 1495, 1470 (C=C aromatic), and 1215 cm^{-1} (C-O-C); ^{1}H-n.m.r. data are given in Table 5.

Anal. Calc. for $C_{24}H_{27}BrN_2O_{10}S$: C, 46.81; H, 4.42; N, 5.55. Found: C, 46.62; H, 4.49; H, 4.17.

REFERENCES

1 F. García González, J. Fernández-Bolaños, and F. J. López Aparicio, Synthetic Methods for Carbohydrates, Am. Chem. Soc.,Symp. Ser., 39, 207 (1976).

2 J. A. Galbis Pérez, P. Areces Bravo, F. Rebolledo Vicente, J. I. Fernández García-Hierro, and J. Fuentes Mota, Carbohydr. Res., 126, 91 (1984).

3 F. García González, J. A. Galbis Pérez, J. I. Fernández García-Hierro, and J. Fernández-Bolaños, An. Quím., 75, 1002 (1979).

4 J. A. Galbis Pérez, R. M. Pinto Corraliza, E. Román Galán, and M. Gómez Guillén, An. Quím., 75, 387 (1979).

5 J. A. Galbis Pérez, J. C. Palacios Albarrán, J. L. Jiménez Requejo, M. Avalos González, and J. M. Fernández-Bolaños, Carbohydr. Res., 131, 71 (1984) and references therein.

6 M. Avalos González, J. L. Jiménez Requejo, J. C. Palacios Albarrán, M. D. Ramos Montero, J. A. Galbis Pérez, Carbohydr. Res., 161, 49 (1987).

7 C. A. G. Haasnoot, F. A. A. M. De Leeuw, and C. Altona, Tetrahedron, 36, 2783 (1980).

8 B. Coxon, Methods Carbohydr. Chem., 6, 513 (1972).

9 W. C. Still, M. Khan, and A. Mitra, J. Org. Chem., 43, 2923 (1978).

10 J. A. Galbis pérez, J. I. Fernández García-Hierro, and P. Areces Bravo, An. Quím., 72, 820 (1976).

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