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SYNTHESES OF D-RIBOSYLAMINES, D-RIBOPYRANOSYL ISOTHIOCYANATES, AND D-RIBOPYRANOSYLTHIOUREAS, AND THEIR TRANSFORMATIONS INTO HETEROCYCLIC COMPOUNDS*

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ABSTRACT

The synthesis of 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosylamine hydrobromide and 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosylamine from D-ribosylamine, *via* ribosylenamines, is reported. The reaction of 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosylamine hydrobromide with thiophosgene in a basic medium yields 2,3,4-tri-*O*-benzoyl-α-(**7**) and -β-D-ribopyranosyl isothiocyanate (**8**). 5-Methyl-1-(2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl)-4-imidazoline-2-thione was obtained by reaction of **8** with aminoacetone hydrochloride. Treatment of **7** and **8** with phenacylamine hydrochlorides gave the *N*-phenacyl-*N'*-(2,3,4-tri-*O*-benzoyl-α- and -β-D-ribopyranosyl)thioureas. The 5-aryl-2-(2,3,4-tri-*O*-benzoyl-α- and -β-D-ribopyranosylamino)thiazoles were prepared by cyclodehydration with acetic anhydride and phosphoric acid of the corresponding phenacylribopyranosylthioureas.

INTRODUCTION

The glycosylamines are of synthetic, biological, and pharmaceutical interest[2]. 2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosylamine has been used in syntheses of various aminoimidazole and pyrimidine nucleosides[3]. The usefulness of these syntheses depends on the availability of the ribofuranosylamine. Hitherto, 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosylamine hydrochloride has been obtained by reduction of

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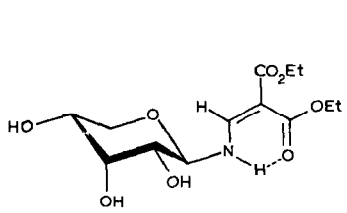

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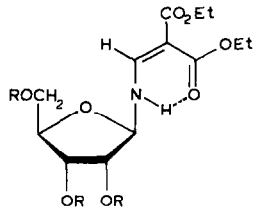

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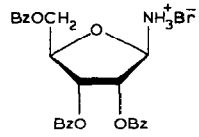
3 R = Ac



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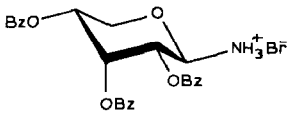

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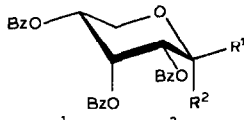
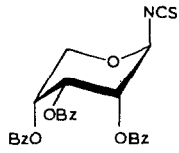


6 R^1 = NH_2, R^2 = H
7 R^1 = H, R^2 = NCS



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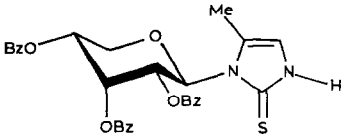

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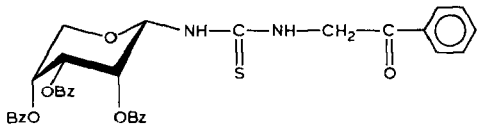

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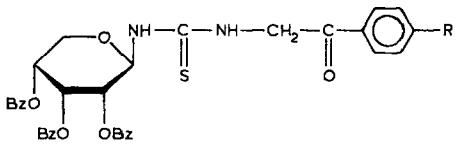
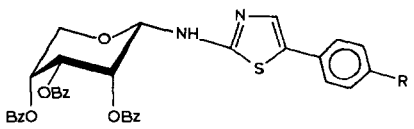
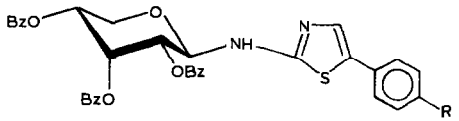


11 R = H, **12** R = Me
13 R = OMe, **14** R = Br



15 R = H, **16** R = Me
17 R = OMe, **18** R = Br



19 R = H, **20** R = Br

2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl azide[4]. We now describe a new and improved synthesis of this compound as the hydrobromide and also the preparation of 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosylamine (**6**).

Isothiocyanates and thioureas are valuable intermediates in the construction of heterocyclic compounds[5], and glucopyranosyl, galactopyranosyl, and ribofuranosyl derivatives have been widely used in syntheses of *N*-nucleosides and glycosylaminoheterocycles[6,7]. However, little attention has been directed to the ribopyrano-

syl derivatives. We now report the preparation of 2,3,4-tri-*O*-benzoyl-α- (**7**) and -β-D-ribopyranosyl isothiocyanate (**8**) from D-ribopyranosylamine by the method recently described for hexopyranosyl isothiocyanates[8].

The reactions of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate with aliphatic α-aminoketone hydrochlorides[9] and the reaction of 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl isothiocyanate with aminoacetaldehyde diethyl acetal[10] yield glycosylthiourea derivatives which give glycosylimidazolinethiones by cyclodehydration[11]. Similarly, when aromatic α-aminoketone hydrochlorides are used, phenacylglycosylthioureas are obtained [7,11]. These thioureas yield glycosylaminothiazoles by dehydration. We now describe syntheses of ribopyranosylimidazolinethione (**9**), ribopyranosylthioureas (**10–14**), and ribopyranosylaminothiazoles (**15–20**) from **7** and **8**.

RESULTS AND DISCUSSION

N-(2,2-Diethoxycarbonylvinyl)-β-D-ribopyranosylamine (**1**) and the furanose analogue **2** were prepared from D-ribosylamine[3], using the method described for other glycosylenamines[12]. The major product **1** was amorphous and was characterised by analytical, i.r., and ^{1}H-n.m.r. data (Table I). The $J_{1,2}$ value (9.3 Hz) indicated **1** to be β. The minor product **2** was crystalline and gave a triacetate **3**, the ^{1}H-n.m.r. data of which are included in Table I. The chemical shift (4.38 p.p.m.) of the signal for H-4 was indicative[13] of the furanoid structure. The β configuration could not be deduced from the $J_{1,2}$ value[14,15] but was determined for **2** by X-ray crystallography[16].

Treatment of **2** with benzoyl chloride followed by reaction with bromine in chloroform[8,17] gave, in good yield, 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosylamine hydrobromide (**4**), the hydrochloride of which has been described[4]. Likewise, **1** gave 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosylamine hydrobromide (**5**). The structures **4** and **5** were assigned on the basis of analytical, i.r., and ^{1}H-n.m.r. (Table I) data. The ring sizes of **4** and **5** were indicated[13,18] by the chemical shifts of the resonance for H-4 (4.85 p.p.m. for the furanoid compound **4**, 5.40–5.60 p.p.m. for the pyranoid compound **5**).

The free base (**6**) obtained from **5** showed ^{1}H- (Table I) and ^{13}C-n.m.r. data (Table III) which accorded[13,19,20] with the β-D-ribopyranosyl structure. The values (8.5 and 10.6 Hz, respectively) of $J_{1,2}$ and $J_{4,5}$ were in the range for antiperiplanar protons and were indicative of the major $^4C_1$(D) conformation in solution. The chemical shift of the resonance of C-4, close to those for the resonances of C-2 and C-3, confirmed the ribopyranosyl structure[19,20].

During the treatment of **5** with base to obtain **6**, the α anomer was also detected by n.m.r. spectroscopy but not isolated. Mutarotational equilibria of glycosylamines[2,21] and *O*-protected glycosylamines[3,4,22] have been reported.

2,3,4-Tri-*O*-benzoyl-α- (**7**) and -β-D-ribopyranosyl isothiocyanate (**8**) were obtained from **5** (or **6**) by reaction with thiophosgene in a basic medium. The struc-

TABLE I

^{1}H-N.M.R. DATA (δ SCALE, J IN Hz) FOR **1-8** AT 200 MHz

Compound	*Chain*					
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*
1[c]	4.62t $J_{1,2}$ 9.3 $J_{1,NH}$ 9.3	3.65–3.25m	3.91t $J_{2,3}$ 2.2 $J_{3,4}$ 2.2	← 3.65–3.25m →		
2[a,c]	5.20dd $J_{1,2}$ 5.0 $J_{1,NH}$ 9.0	← 4.30–3.75m →				
3[b]	5.41dd $J_{1,2}$ 5.3 $J_{1,NH}$ 9.5	5.27t $J_{2,3}$ 5.3	5.37dd $J_{3,4}$ 2.6	4.38m	← 4.31–4.10m →	
4[c]	5.90d $J_{1,2}$ 4.9	5.95dd $J_{2,3}$ 3.2	5.45t $J_{3,4}$ 3.2	4.85m	← 4.75–4.50m →	
5[c]	← 5.60–5.40m →		6.22t $J_{2,3}$ 2.7 $J_{3,4}$ 2.7	5.60–5.40m	← 4.50–4.20m →	
6[c]	4.80m $J_{1,2}$ 8.5	5.24dd $J_{2,3}$ 2.8	6.16t $J_{3,4}$ 2.8	5.44ddd $J_{4,5}$ 10.6 $J_{4,5'}$ 5.3	4.19dd $J_{5,5'}$ 11.7	4.06dd
7[b]	5.86d $J_{1,2}$ 4.6	5.50dd $J_{2,3}$ 3.3	6.19td $J_{3,4}$ 3.3 $J_{3,5'}$ 0.9	5.44ddd $J_{4,5}$ 10.8 $J_{4,5'}$ 5.1	4.35t $J_{5,5'}$ 10.8	4.05ddd
8[b]	5.76d $J_{1,2}$ 4.4	5.53dd $J_{2,3}$ 3.9	5.96dd $J_{3,4}$ 3.5	5.59m $J_{4,5}$ 3.1 $J_{4,5'}$ 5.0	4.36dd $J_{5,5'}$ 12.2	4.20dd

[a] At 90 MHz. [b] In $CDCl_3$. [c] In $(CH_3)_2SO$.

tures of **7** (minor) and **8** (major) were assigned on the basis of analytical, i.r., and ^{1}H- and ^{13}C-n.m.r. data (Tables I and III). Compound **7** showed $J_{1,2}$ 4.6, $J_{4,5}$ 10.8, and $J_{3,5'}$ 0.9 Hz in agreement with the α configuration and the $^4C_1$(D) conformation. However, the $^3J_{H,H}$ values of the β-anomer **8** (see Table I) accorded with the $^1C_4$ (D) conformation or an equilibrium $^1C_4 \rightleftharpoons {}^4C_1$. The magnitude of $J_{5,5'}$ is dependent[23] on the orientation of the 4-acyl group (axial ~13 Hz, equatorial ~11 Hz). The $J_{5,5'}$ values (10.8 and 12.2 Hz) for **7** and **8** accorded with the conformations assigned.

5-Methyl-1-(2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl)-4-imidazoline-2-thione (**9**) was prepared by reaction[11] of **8** with aminoacetone hydrochloride and its structure was assigned on the basis of analytical, u.v., i.r., and ^{1}H- (Table II) and ^{13}C-n.m.r. (Table IV) data. Compound **9** had λ_{max} 274 nm[24], $\nu_{C=S}$ 1205 cm^{-1} (ref. 25),

Benzoyl						*Acetyl*
Ph	*OH*	*NH*	*HC=*	*CH_2*	*CH_3*	*CH_3*
	5.12d 4.96d 4.80d	9.10dd $J_{NH,=CH}$ 13.5	8.07d	4.14–4.03m	1.21t 1.20t	
	5.46d 5.20d 4.70t	9.52dd $J_{NH,=CH}$ 13.0	8.02d	4.30–3.75m	1.23t 1.21t	
		9.93dd $J_{NH,=CH}$ 12.7	7.98d	4.31–4.10m	1.37t 1.32t	2.25s (3 H) 2.12s (6 H)
8.30–7.30m		9.05 bs (3 H)				
8.14–7.25m		9.10 bs (3 H)				
8.15–7.25m		2.02 bs (2 H)				
8.25–7.25m						
8.20–7.20m						

and δ 6.19 for H-4[11] as reported for related imidazoline-2-thiones. The ^{13}C-n.m.r. spectrum contained a signal at 163.5 p.p.m. that was assigned to the C=S group. This value is different to those reported for **10–14** and for other thiourea derivatives of carbohydrates (183–185 p.p.m.)[8,26]. The $^3J_{H,H}$ values for **9** (Table II) showed that the $^4C_1$(D) conformation preponderated in a solution in chloroform.

N-Phenacyl-*N'*-(2,3,4-tri-*O*-benzoyl-α- and -β-D-ribopyranosyl)thioureas (**10–14**) were prepared by reaction of the mixture **7**+**8** with phenacylamine hydrochlorides. The reactions gave $\alpha\beta$-mixtures of ribopyranosylthioureas. The β anomers (**11–14**) were isolated in good yields (60–70%) by crystallisation. The α-anomer **10**, isolated by p.l.c., was also prepared by reaction of **7** with phenacylamine hydrochloride. The analytical, i.r., ^{1}H-n.m.r. (Table II) for **10–14**, and ^{13}C-n.m.r. (Table IV) data for **11–14** were consistent with the structures proposed.

TABLE II

^{1}H-N.M.R. DATA (δ SCALE, J IN Hz) FOR **9–20** IN $CDCl_3$ AT 200 MHz

Compound	*Chain*					
	H-1'	*H-2'*	*H-3'*	*H-4'*	*H-5'*	*H-5"*
9	7.19d $J_{1',2'}$ 9.9	5.82dd $J_{2',3'}$ 2.7	6.28t $J_{3',4'}$ 2.7	5.56ddd	← 4.40–4.18m →	
10	5.87dd $J_{1',2'}$ 4.4 $J_{1',NH}$ 6.8	5.66dd $J_{2',3'}$ 3.3 $J_{2',4'}$ < 1	6.10m $J_{3',4'}$ 4.1	5.52m $J_{4',5'}$ 7.9 $J_{4',5''}$ 4.4	4.37dd $J_{5',5''}$ 12.9	4.09dd
11	← 5.57–5.45m →		6.23t $J_{2',3'}$ 2.9 $J_{3',4'}$ 2.9	5.57–5.45m	← 4.35–4.20m →	
12	← 5.55–5.40m →		6.20t $J_{2',3'}$ 2.9 $J_{3',4'}$ 2.9	5.55–5.40m	← 4.35–4.20m →	
13	← 5.50–5.38m →		6.20t $J_{2',3'}$ 2.7 $J_{3',5'}$ 2.7	5.50–5.38m	← 4.35–4.20m →	
14	← 5.60–5.45m →		6.23t $J_{2',3'}$ 2.7 $J_{3',4'}$ 2.7	5.60–5.45m	← 4.35–4.20m →	
15	5.61dd $J_{1',2'}$ 3.1 $J_{1',NH}$ 8.9	5.78t $J_{2',3'}$ 3.1	5.95t $J_{3',4'}$ 3.1	5.55dt $J_{4',5'}$ 5.8 $J_{4',5''}$ 3.1	4.40dd $J_{5',5''}$ 12.6	4.08dd
16	5.60bdd $J_{1',2'}$ 3.1 $J_{1',NH}$ 9.0	5.78t $J_{2',3'}$ 3.1	5.95t $J_{3',4'}$ 3.1	5.55dt $J_{4',5'}$ 5.5 $J_{4',5''}$ 3.1	4.39dd $J_{5',5''}$ 12.6	4.05dd
17	5.60d $J_{1',2'}$ 3.3	5.79t $J_{2',3'}$ 3.4	5.95t $J_{3',4'}$ 3.4	5.57dt $J_{4',5'}$ 5.6 $J_{4',5''}$ 3.3	4.40dd $J_{5',5''}$ 12.7	4.06dd
18	5.60dd $J_{1',2'}$ 3.4 $J_{1',NH}$ 8.7	5.78t $J_{2',3'}$ 3.2	5.97t $J_{3',4'}$ 3.2	5.55dt $J_{4',5'}$ 5.8 $J_{4',5''}$ 3.2	4.39dd $J_{5',5''}$ 12.4	4.06dd
19	5.60d $J_{1',2'}$ 8.4	5.58–5.50m	6.23t $J_{3',4'}$ 2.7	5.58–5.50m	4.25dd $J_{4',5'}$ 4.7 $J_{4',5''}$ 9.3	4.20dd $J_{5',5''}$ 10.8
20	5.58d $J_{1',2'}$ 8.7	5.56–5.45m	6.22t $J_{3',4'}$ 2.8	5.56–5.45m	4.29dd $J_{4',5'}$ 4.4 $J_{4',5''}$ 9.4	4.20dd $J_{5',5''}$ 10.8

Benzoyl	*Heterocycle*		
Ph	*NH*	*H-4*	*CH_3*
8.31–7.15m	11.21bs	6.19s	2.43s

Thiourea

Ph	*N'H*	*CH_2*	*NH*	*CH_3*
← 8.20–7.24m →		5.24dd 5.06dd J_{gem} 19.1 $J_{CH_2,NH}$ 4.5	8.20–7.24m	
← 8.30–7.20m →		5.07 bs	6.25 bs	
← 8.20–7.20m →		5.05 bs	6.20 bs	2.43s
← 8.20–6.90m →		5.03 bs	6.20 bs	3.98s
← 8.20–7.20m →		5.02d	6.29 bs	

Heterocycle

Ph	*H-4*	*NH*	*CH_3*
← 8.01–7.61m →		6.34d	
← 8.05–7.14m →		6.32bd	2.35s
← 8.01–7.25m →		6.50–6.20 bs	3.81s
← 8.10–7.20m →		6.40 bd	
← 8.16–7.22m →		7.00 bs	
← 8.16–7.24m →		7.00 bs	

TABLE III

^{13}C-N.M.R. DATA (δ SCALE) FOR **6-8** IN $CDCl_3$ AT 20.15 MHz

Compound	*Chain*					*Benzoyl*		
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*Ph*	*C=O*	*N=C=S*
6	82.5	71.1	69.8	67.9	62.7	133.4–128.3	165.9 165.5 165.2	
7	80.6	67.8	67.8	66.4	59.1	133.7–128.5	165.7 165.4 165.1	142.2
8	83.6	69.7	66.7[a]	67.0[a]	63.8	133.5–128.3	166.5 166.3 165.9	144.1

[a] Assignments may have to be reversed.

The α-anomer **10** had values of $J_{1,2}$, $J_{2,3}$, $J_{3,4}$, and $J_{4,5'}$ in the range (3.3–4.4 Hz) for *gauche* protons, a $J_{2,4}$ value (~1 Hz) for protons in a planar W arrangement, and a $J_{5,5'}$ value (12.9 Hz) indicative[23] of an axial 4-acyloxy group. These data showed that the $^1C_4$(D) conformation preponderated in a conformational equilibrium in solution. Conformational assignments were not possible for the β thioureas (**11–14**) because only the $J_{2,3}$ and $J_{3,4}$ values could be measured.

Treatment of *N*-phenacyl-*N'*-(2,3,4-tri-*O*-benzoyl-$\alpha\beta$-D-ribopyranosyl)thioureas (β major) with acetic anhydride and phosphoric acid[7,26] afforded, after chromatography, 5-aryl-2-[2,3,4-tri-*O*-benzoyl-α- (**15–18**; average yields, 25%) and -β-D-ribopyranosylamino]thiazoles (**19** and **20**; average yields, 60%). The structures of **15–20** were assigned on the basis of elemental analyses, and u.v., i.r., ^{1}H-n.m.r. (Table II), and ^{13}C-n.m.r. (Table IV) data. Compounds **15–20** had λ_{max} 300 nm, characteristic of related arylsubstituted aminothiazoles[7,26,27].

The $J_{1',2'}$ values of **19** and **20** indicated H-1',2' to be antiperiplanar and established the β configuration. The $^3J_{H,H}$ values were consistent with the $^4C_1$(D) conformation. The value (10.8 Hz) of $J_{5',5''}$ indicated[23] an equatorial 4-acyloxy group. The $^3J_{H,H}$ and $^2J_{5',5''}$ values of the minor products **15–18** were consistent with the α configuration and the $^1C_4$(D) conformation. The ^{13}C-n.m.r. assignments were in agreement with those reported for ribopyranosides[19,20].

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were measured at 20 ±2°, using 1- and 10-cm cells. I.r. spectra were recorded for KBr discs. T.l.c. was performed on Silica Gel HF_{254} (Merck) with ether–hexane and detection by u.v. light, iodine vapour, or charring with sulphuric acid. Flash chro-

matography was conducted on Silica Gel 60 (Merck, 230 mesh). ^{1}H-N.m.r. spectra were recorded at 90 and 200 MHz. Assignments were confirmed by decoupling experiments and H/D exchange. ^{13}C-N.m.r. spectra were obtained at 20.15 and 50.30 MHz for solutions in $CDCl_3$ and $(CD_3)_2SO$. Proton-decoupled APT[27] and DEPT[28] spectra were obtained to assist in signal assignments.

N-(2,2-Diethoxycarbonylvinyl)-β-D-ribopyranosylamine (1) *and* N-*(2,2-diethoxycarbonylvinyl)-β-D-ribofuranosylamine* (2). — A suspension of D-ribosylamine[3] (13.5 g, 90.5 mmol) in methanol (100 mL) and diethyl ethoxymethylenemalonate (27 mL, 135 mmol) was stirred until dissolution was complete. The solution was stored for 48 h at room temperature and then concentrated to dryness, a solution of the residue in water (75 mL) was washed with ether–light petroleum (4:1, 5 × 50 mL) and extracted with ethyl acetate (5 × 50 mL), and the combined extracts were dried ($MgSO_4$) and concentrated to dryness. Crystallisation of the residue from 1,4-dioxane–ether gave 2 (2.4 g, 8.3%), m.p. 154–156°, $[\alpha]_D^{21}$ +41°, $[\alpha]_{578}^{21}$ +42°, $[\alpha]_{546}^{21}$ +46°, $[\alpha]_{436}^{21}$ +64°, $[\alpha]_{365}^{21}$ +59° (*c* 0.5, pyridine); $\lambda_{max}^{H_2O}$ 274 and 218 nm (ϵ_{mM} 27.5 and 12.5); ν_{max} 3500–3180 (OH, NH), 1688 and 1645 (C=O), and 1575 cm^{-1} (C=C). The ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{13}H_{21}NO_8$: C, 48.90; H, 6.63; N, 4.39. Found: C, 48.66; H, 6.67; N, 4.27.

Column chromatography (ethyl acetate–ether–acetone, 1:1:1) of the material in the mother liquor gave amorphous 1 (14 g, 48%), $[\alpha]_D^{21}$ +2°, $[\alpha]_{578}^{21}$ +2°, $[\alpha]_{546}^{21}$ +3°, $[\alpha]_{436}^{21}$ +13°, $[\alpha]_{365}^{21}$ +43° (*c* 0.3, chloroform); λ_{max}^{EtOH} 274 and 218 nm (ϵ_{mM} 33.0 and 16.0); ν_{max} 3500–3220 (OH, NH), 1670 and 1650 (C=O), and 1600 cm^{-1} (C=C). The ^{1}H-n.m.r. data are given in Table I.

Anal. Found: C, 48.89; H, 6.72; N, 4.23.

2,3,5-Tri-O-acetyl-N-(2,2-diethoxycarbonylvinyl)-β-D-ribofuranosylamine (3). — Conventional treatment of 2 (0.30 g, 0.94 mmol) with pyridine (3 mL) and acetic anhydride (3 mL) gave amorphous 3 (0.38 g, 91%), m.p. 63–65°, $[\alpha]_D^{24}$ +147° (*c* 0.6, dichloromethane), ν_{max} 3290 (NH), 1760, 1720, 1680 and 1670 (C=O), and 1605 cm^{-1} (C=C). The ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{19}H_{27}NO_{11}$: C, 51.23; H, 6.11; N, 3.14. Found: C, 51.08; H, 6.13; N, 3.14.

2,3,5-Tri-O-benzoyl-β-D-ribofuranosylamine hydrobromide (4). — Conventional treatment of 2 (0.5 g, 1.57 mmol) with pyridine (1.25 mL) and benzoyl chloride (1.25 mL) gave the syrupy 2,3,5-tribenzoate, which was treated gradually with a 4% solution of bromine in chloroform (6.5 mL, 1.62 mmol) and water (0.03 mL, 1.72 mmol). The mixture was kept for 24 h at room temperature and then concentrated, and the residue was crystallised from chloroform–hexane to give 4 (0.73 g, 86%), m.p. 136–139° (dec.), $[\alpha]_D^{22}$ +75°, $[\alpha]_{578}^{22}$ +81°, $[\alpha]_{546}^{22}$ +93°, $[\alpha]_{436}^{22}$ +171°, $[\alpha]_{365}^{22}$ +294° (*c* 0.5, methyl sulfoxide); ν_{max} 3050–2750 (NH_3^+), 1725 (C=O), and 1600 cm^{-1} (C=C aromatic). The ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{26}H_{24}BrNO_7$: C, 57.58; H, 4.46; N, 2.58. Found: C, 57.49; H, 4.42; N, 2.43.

TABLE IV

^{13}C-N.M.R. DATA (δ SCALE) FOR **9** AND **11–20** IN $CDCl_3$ AT 50.3 MHz

Compound	*Chain*					*Benzoyl*	
	C-1'	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*Ph*	*C=O*
9	81.3	69.2	67.6	66.9	64.3	129.9–128.1	165.4 165.0 164.7
11	80.7	69.0	69.0	67.1	62.8	133.8–127.9	166.2 165.4 165.1
12	80.7	69.0	69.0	67.1	62.8	133.6–128.1	165.6 164.7 164.3
13	80.7	69.0	69.0	67.1	62.8	134.0–128.1	165.7 165.4 165.1
14	80.8	69.0	69.0	67.1	62.8	133.5–128.2	166.1 165.4 165.1
15	80.9	68.9	67.7	66.5	61.7	135.0–128.0	165.7 165.5 165.3
16	80.8	68.9	67.7	66.5	61.7	135.0–128.0	165.6 165.2 (2 C)
17	81.3	69.1	68.0	66.5	61.7	133.7–128.2	165.6 165.4 165.1
18	80.8	68.8	68.7	66.9	66.2	133.5–125.0	166.4 166.0 165.6
19	82.1	69.1	67.1	68.9	62.5	133.4–128.2	166.0 165.7 165.2
20	82.1	69.1	67.1	68.8	62.5	133.5–128.2	166.9 165.7 165.2

Phenyl				*Heterocycle*			
C-1	*C-2, C-6*	*C-3, C-5*	*C-4*	*Me*	*C-4*	*C-5*	*C=S*
				11.1	112.2	126.5	163.5
Thiourea							
				Me	*CH_2*	*C=O*	*C=S*
133.9	← 130.1–127.9 →		134.1		51.9	193.9	183.3
130.7	← 130.0–128.1 →		145.4	21.7	50.4	192.8	182.5
126.8	130.8–128.1	114.0	164.4	55.5	51.7	192.2	183.1
132.7	130.0–128.2	132.1	130.0–128.2		52.0	192.9	183.2
Heterocycle							
				Me	*C-4*	*C-2*	*C-5*
131.8	125.7	130.0–128.0	127.1		134.2	165.0	130.0–128.0
130.0–128.0	125.5	130.0–128.0	135.0–133.0	21.0	135.0–133.0	165.0	130.0–128.0
124.0–114.0	127.0	114.2	158.7	55.4	124.0–114.0	165.0	124.0–114.0
131.3	← 129.0–125.0 →		119.1		135.6	164.2	129.9–125.0
131.7	125.5	129.8–128.2	126.9		133.9	165.0	129.8–128.2
130.7	← 129.8–126.9 →		120.6		134.6	165.0	129.8–126.9

2,3,4-Tri-O-benzoyl-β-D-ribopyranosylamine (**6**) *and its hydrobromide* (**5**). — A solution of **1** (9.0 g, 28.20 mmol) was processed as described for the preparation of **4**, to give **5** (12.8 g, 84%), m.p. 161–164° (dec.), $[\alpha]_D^{15}$ −21°, $[\alpha]_{578}^{15}$ −20°, $[\alpha]_{546}^{15}$ −23°, $[\alpha]_{436}^{15}$ −31°, $[\alpha]_{365}^{15}$ −34° (*c* 0.5, methyl sulfoxide); ν_{max} 3050–2700 (NH_3^+), 1720 (C=O), and 1600 cm^{-1} (C=C aromatic). The ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{26}H_{24}BrNO_7$: C, 57.58; H, 4.46; N, 2.58. Found: C, 57.40; H, 4.41; N, 2.46.

To a suspension of **5** (2.5 g, 4.61 mmol) in chloroform (75 mL) was added a solution of sodium carbonate (0.5 g, 4.5 mmol) and sodium hydrogencarbonate (0.5 g, 6.00 mmol) in water (15 mL), and the mixture was stirred vigorously for 10 h. The organic layer was separated, the aqueous layer was extracted with chloroform (3 × 25 mL), the combined chloroform solutions were dried ($MgSO_4$) and concentrated to dryness, and the residue was crystallised from ether to give **6** (1.6 g, 75%), m.p. 125–127°, $[\alpha]_D^{15}$ −33°, $[\alpha]_{578}^{15}$ −35°, $[\alpha]_{546}^{15}$ −41°, $[\alpha]_{436}^{15}$ −72°, $[\alpha]_{365}^{15}$ −118° (*c* 0.5, chloroform); ν_{max} 3420 and 3350 (NH_2), 1735 (C=O), 1620 and 1595 cm^{-1} (C=C aromatic). The ^{1}H- and ^{13}C-n.m.r. data are given in Tables I and III, respectively.

Anal. Calc. for $C_{26}H_{23}NO_7$: C, 67.67; H, 5.02; N, 3.04. Found: C, 67.34; H, 4.98; N, 3.31.

2,3,4-Tri-O-benzoyl-α- (**7**) *and -β-D-ribopyranosyl isothiocyanate* (**8**). — To a heterogeneous mixture of **5** (8.0 g, 14.70 mmol), chloroform (80 mL), calcium carbonate (4.4 g, 44.30 mmol), and water (30 mL) was added thiophosgene (2.5 mL, 22.20 mmol). The mixture was stirred vigorously for 48 h and then filtered, the organic layer was washed with water, dried ($CaCl_2$), and concentrated, and the residue was crystallised from chloroform–hexane. Preparative t.l.c. (ether–hexane, 1:2) then gave **7** and **8**.

Compound **7** (1.1 g, 15%) had $[\alpha]_D^{21}$ −57° (*c* 0.6, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 280, 273, and 235 nm (ϵ_{mM} 2.6, 3.3, and 17.8); ν_{max} 3070, 2995, 2720 (CH), 2120 (NCS), 1725 (C=O), 1605, 1585, 1495, 1455 (C=C aromatic), 1270 (C–O–C), 750 and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{27}H_{21}NO_7S$: C, 64.40; H, 4.20; N, 2.78. Found: C, 64.00; H, 4.22; N, 3.05.

Compound **8** (4.6 g, 62%) had $[\alpha]_D^{21}$ −187° (*c* 0.6, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 280, 273, and 235 nm (ϵ_{mM} 2.6, 3.3, and 17.8); ν_{max} 3070, 2990, 2770 (CH), 2120 (NCS), 1725 (C=O), 1600, 1585, 1500, 1465 (C=C aromatic), 1270 (C–O–C), 750 and 710 cm^{-1} (CH aromatic).

Anal. Found: C, 64.20; H, 4.13; N, 3.01.

The ^{1}H- and ^{13}C-n.m.r. data for **7** and **8** are given in Tables I and III, respectively.

Compounds **7** (20%) and **8** (68%) were also obtained from **6** (0.25 g, 0.54 mmol) in a similar manner.

5-Methyl-1-(2,3,4-tri-O-benzoyl-β-D-ribopyranosyl)-4-imidazoline-2-thione (**9**). — A solution of aminoacetone hydrochloride (2.29 mmol) in water was neutra-

lised with sodium hydrogencarbonate (2.29 mmol) and added to a solution of 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl isothiocyanate (**8**) (2.29 mmol) in acetone (20 mL) under nitrogen. The resulting solution was kept for 20 min at room temperature and then concentrated. Column chromatography (ether–hexane gradient) of the residue gave **9** (0.12 g, 34%) which, after recrystallisation from ethanol, had m.p. 125–126°, $[\alpha]_D^{20}$ −15° (*c* 0.85, chloroform); $\lambda_{max}^{CHCl_3}$ 274 and 240 nm (ϵ_{mM} 11.8 and 17.4); ν_{max} 3130 (NH), 1720 (C=O), 1623 (C=C imidazoline), 1596, 1578, 1490 (C=C aromatic, NH), 1265 (C–O–C), 1205 (C=S), 753 and 709 cm^{-1} (CH aromatic). The ^1H- and ^{13}C-n.m.r. data are given in Tables II and IV, respectively.

Anal. Calc. for $C_{30}H_{26}N_2O_7S$: C, 64.50; H, 4.69; N, 5.01. Found: C, 64.50; H, 4.85; N, 4.93.

N-*Phenacyl*-N'-*(2,3,4-tri*-O-*benzoyl-β-*D-*ribopyranosyl)thioureas* (**11–14**). — A solution of phenacylamine hydrochloride (1.07 mmol) in water (5 mL) was neutralised with sodium hydrogencarbonate (1.29 mmol) and added to a solution of crude 2,3,4-tri-*O*-benzoyl-α,β-D-ribopyranosyl isothiocyanates (1.07 mmol) in acetone (12 mL) under nitrogen. The resulting solution was kept at room temperature for *t* h and then concentrated under diminished pressure, and the residue was crystallised from ethanol. The following compounds were prepared in this manner.

N-Phenacyl-*N'*-(2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl)thiourea (**11**; 0.49 g, 72%; *t* 0.5 h), m.p. 168–169°, $[\alpha]_D^{21}$ ~0° (*c* 1, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 238 and 273 nm (ϵ_{mM} 30.9 and 5.6); ν_{max} 3340 and 3300 (NH), 1725 (CO ester), 1675 (CO ketone), 1595 and 1545 (C=C aromatic), 1280 (C–O–C and C=S), 760 and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{35}H_{30}N_2O_8S$: C, 65.81; H, 4.73; N, 4.38; S, 5.02. Found: C, 65.58; H, 4.95; N, 4.21; S, 5.24.

N-(*p*-Methylphenacyl)-*N'*-(2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl)thiourea (**12**; 0.48 g, 58%; *t* 0.5 h), m.p. 179–180°, $[\alpha]_D^{21}$ ~0° (*c* 0.8, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 236 and 252 nm (ϵ_{mM} 46.7 and 37.1); ν_{max} 3320 and 3280 (NH), 1720 (CO ester), 1665 (CO ketone), 1590 and 1540 (C=C aromatic), 1280 (C–O–C and C=S), 810, 760, and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{36}H_{32}N_2O_8S$: C, 66.24; H, 4.94; N, 4.29; S, 4.91. Found: C, 65.83; H, 5.17; N, 4.15; S, 5.18.

N-(*p*-Methoxyphenacyl)-*N'*-(2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl)thiourea (**13**; 0.4 g, 56%; *t* 4 h), m.p. 173–174°, $[\alpha]_D^{21}$ ~0° (*c* 0.6, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 232 and 280 nm (ϵ_{mM} 42.8 and 28.0); ν_{max} 3340 and 3280 (NH), 1725 (CO ester), 1670 (CO ketone), 1545 and 1515 (C=C aromatic), 1270 (C–O–C and C=S), 830, 760, and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{36}H_{32}N_2O_9S$: C, 64.66; H, 4.82; N, 4.19; S, 4.80. Found: C, 64.88; H, 4.75; N, 4.02; S, 5.23.

N-(*p*-Bromophenacyl)-*N'*-(2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl)thiourea (**14**; 0.28 g, 37%; *t* 5.5 h), m.p. 174°, $[\alpha]_D^{21}$ ~0° (*c* 0.6, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 235 and 250 nm (ϵ_{mM} 35.4 and 22.9); ν_{max} 3340 and 3290 (NH), 1725 (CO ester), 1675 (CO ketone), 1585 and 1545 (C=C aromatic), 1280 (C–O–C and C=S), 815, 770,

and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{35}H_{29}BrN_2O_8S$: C, 58.58; H, 4.07; N, 3.90; S, 4.47; Br, 11.13. Found: C, 58.83; H, 4.22; N, 3.98; S, 4.10; Br, 11.12.

The ^1H- and ^{13}C-n.m.r. data for **11–14** are given in Tables II and IV, respectively.

N-Phenacyl-N'-(2,3,4-tri-O-benzoyl-α-D-ribopyranosyl)thiourea (**10**). — A solution of **7** (0.11 mmol) was processed as described for the preparation of **11–14**, to give amorphous **10** (0.04 g, 60%; *t* 2 h), $[\alpha]_D^{21}$ +7° (*c* 0.3, dichloromethane). The ^1H-n.m.r. data are given in Table II.

Anal. Calc. for $C_{35}H_{30}N_2O_8S$: C, 65.81; H, 4.73; N, 4.38; S, 5.02. Found: C, 65.60; H, 4.90; N, 4.25; S, 5.30.

Compound **10** was also isolated from the mother liquor of crystallisation of **11** by preparative t.l.c. (ether–hexane, 3:1).

5-Aryl-2-(2,3,4-tri-O-benzoyl-α- and *-β-D-ribopyranosylamino)thiazoles* (**15–20**). — To *N*-phenacyl-*N'*-(2,3,4-tri-*O*-benzoyl-α,β-D-ribopyranosyl)thiourea (0.68 mmol) in acetic anhydride (6.8 mL) was added phosphoric acid (0.34 mL). The solution was stirred at room temperature for *t* h. Each reaction was monitored by t.l.c. The resulting solution was poured into ice–water (160 mL) and the crude solids were purified as indicated.

(*a*) A suspension of the crude product in saturated aqueous sodium hydrogencarbonate (20 mL) at room temperature was stirred for 10 min, acetone (80 mL) was then added, and the resulting solid was crystallised from ethanol. The following compounds were prepared in this manner.

5-Phenyl-2-(2,3,4-tri-*O*-benzoyl-α-D-ribopyranosylamino)thiazole (**15**; 0.071 g, 24%; *t* 20 h), m.p. 200–202°, $[\alpha]_D^{22}$ +27° (*c* 0.6, chloroform); $\lambda_{max}^{CHCl_3}$ 298, 284, and 242 nm (ϵ_{mM} 23.0, 20.9, and 18.2); ν_{max} 3350 (NH), 1725 (CO), 1600, 1580, 1550 and 1510 (C=C aromatic, NH), 1280 (C–O–C), 750 and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{35}H_{28}N_2O_7S$: C, 67.73; H, 4.55; N, 4.51; S, 5.17. Found: C, 67.31; H, 4.49; N, 4.53; S, 5.54.

5-(*p*-Tolyl)-2-(2,3,4-tri-*O*-benzoyl-α-D-ribopyranosylamino)thiazole (**16**; 0.074 g, 25%; *t* 17 h), m.p. 205–207°, $[\alpha]_D^{22}$ +30° (*c* 0.7, chloroform); $\lambda_{max}^{CHCl_3}$ 304, 285, and 233 nm (ϵ_{mM} 8.8, 6.9, and 15.6); ν_{max} 3420 (NH), 1715 (CO), 1600, 1580, and 1510 (C=C aromatic, NH), 1265 (C–O–C), 820, 750, and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{36}H_{30}N_2O_7S$: C, 68.12; H, 4.76; N, 4.41; S, 5.05. Found: C, 67.68; H, 4.90; N, 4.36; S, 5.18.

5-(*p*-Methoxyphenyl)-2-(2,3,4-tri-*O*-benzoyl-α-D-ribopyranosylamino)thiazole (**17**; 0.069 g, 24%; *t* 22 h), m.p. 190°, $[\alpha]_D^{20}$ +20° (*c* 0.7, chloroform); $\lambda_{max}^{CHCl_3}$ 296, 282, and 240 nm (ϵ_{mM} 17.4, 16.6, and 19.6); ν_{max} 3340 (NH), 1720 (CO), 1600, 1550, and 1505 (C=C aromatic, NH), 1270 (C–O–C), 820, 750, and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{36}H_{30}N_2O_8S$: C, 66.45; H, 4.65; N, 4.31. Found: C, 66.64; H, 4.55; N, 3.98.

5-(*p*-Bromophenyl)-2-(2,3,4-tri-*O*-benzoyl-α-D-ribopyranosylamino)thiazole (**18**; 0.062 g, 21%; *t* 24 h), m.p. 197–198°, $[\alpha]_D^{20}$ +26° (*c* 0.3, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 307, 282, and 226 nm (ϵ_{mM} 8.8, 5.5, and 15.5); ν_{max} 3340 (NH), 1730 (CO), 1600, 1560, and 1525 (C=C aromatic, NH), 1270 (C–O–C), 820 and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{35}H_{27}BrN_2O_7S$: C, 60.10; H, 3.89; N, 4.00; S, 4.58; Br, 11.42. Found: C, 60.38; H, 4.06; N, 3.96; S, 4.77; Br, 11.48.

The ^1H- and ^{13}C-n.m.r. data for **15–18** are given in Tables II and IV, respectively.

(*b*) A solution of the crude product in chloroform (40 mL) was washed with saturated aqueous sodium hydrogencarbonate (3 × 15 mL) and then water, dried ($MgSO_4$), and concentrated. Solutions of the residues in aqueous 96% ethanol were treated with Amberlist IR-45 (HO^-) resin (8 mL), filtered,and concentrated. Column chromatography (ether–hexane, 6:1) of the residue then gave the α and the following β anomers.

5-Phenyl-2-(2,3,4-tri-*O*-benzoyl-β-D-ribopyranosylamino)thiazole (**19**; 0.16 g, 56%; *t* 20 h), obtained as an amorphous solid, had $[\alpha]_D^{20}$ +55° (*c* 0.5, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 302, 284, and 232 nm (ϵ_{mM} 15.8, 12.7, and 30.3); ν_{max} 3340 (NH), 1730 (CO), 1600, 1585, and 1520 (C=C aromatic, NH), 1270 (C–O–C), 755 and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{35}H_{28}N_2O_7S$: C, 67.63; H, 4.55; N, 4.51. Found: C, 68.10; H, 4.78; N, 4.22.

5-(*p*-Bromophenyl)-2-(2,3,4-tri-*O*-benzoyl-β-D-ribopyranosylamino)thiazole (**20**; 0.17 g, 60%; *t* 24 h), obtained as an amorphous solid, had $[\alpha]_D^{20}$ +56° (*c* 0.5, chloroform); $\lambda_{max}^{CH_2Cl_2}$ 305, 282, and 234 nm (ϵ_{mM} 10.3, 6.9, and 11.2); ν_{max} 3340 (NH), 1730 (CO), 1600, 1560, and 1525 (C=C aromatic, NH), 1270 (C–O–C), 820 and 710 cm^{-1} (CH aromatic).

Anal. Calc. for $C_{35}H_{27}BrN_2O_7S$: C, 60.10; H, 3.89; N, 4.00. Found: C, 59.86; H, 4.03; N, 3.69.

The ^1H- and ^{13}C-n.m.r. data for **19** and **20** are given in Tables II and IV, respectively.

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