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Note

Phenacylthiourea and *N*-thiazolyl derivatives of 2-amino-2-deoxy-D-glucose*

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The glycosylthioureas have been widely used in syntheses of glycosylamino-heterocycles and *N*-nucleosides[1–12], but similar reactions for 2-deoxy-2-thioureido-aldoses have not been studied. Several 1,3,4,6-tetra-*O*-acetyl-2-[3-alkyl(aryl)-thioureido]-2-deoxy-α(β)-D-glycopyranoses have been prepared by the reactions of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose with aryl isothiocyanates[13,14] and 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-isothiocyanato-α(β)-D-glycopyranoses with simple alkyl(aryl)amines[15–19].

We now report the preparation of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(3-phenacylthioureido)-α(β)-D-glucopyranoses (**1–4**), followed by a cyclodehydration reaction to afford 1,3,4,6-tetra-*O*-acetyl-2-(5′-arylthiazol-2′-ylamino)-α(β)-D-glucopyranoses (**5–8**) according to the method described for phenacylglycosylthioureas[1,2].

The reactions of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-isothiocyanato-α-D-glucopyranose[19] and the β anomer[15] with phenacylamine and *p*-methylphenacylamine gave 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(3-phenacylthioureido)-α(β)-D-glucopyranoses (**1** and **3**) or 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-[3-(*p*-methyl)phenacylthioureido]-α(β)-D-glucopyranoses (**2** and **4**), in good yields.

The structures of **1–4** were demonstrated by elemental analyses, optical rotations, and u.v., i.r., ^{1}H-n.m.r. (Table I), and ^{13}C-n.m.r. (Table II) data. The α anomers **1** and **2** were more dextrorotatory than the β anomers **3** and **4**. Compounds **1–4** had u.v. absorptions at 250 nm, in agreement with data reported[12] for phenacyl- and *p*-methylphenacyl-glycosylthioureas, and i.r. bands at 1675–1690 cm^{-1} (C=O group in arylketones).

*Thiourea Derivatives of Carbohydrates, Part X. For Part IX, see ref. 2.

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TABLE I

^{1}H-N M R. DATA (δ SCALE, J IN Hz) FOR **1–8** IN $CDCl_3$

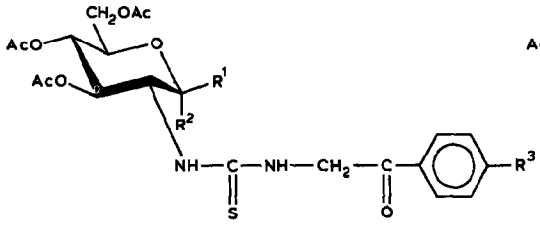
Compound	*Chain*							*Acetyl*	*Thiourea*				
	H-1'	*H-2'*	*H-3'*	*H-4'*	*H-5'*	*H-6''*	*H-6'*	CH_3	*NH*	*N'H*	CH_2	*Ph*	CH_3
1[a]	6.35d $J_{1',2'}$ 3.5	←——5.37–5.16m——→			←——4.12–4.02m→		4.29dd $J_{5',6'}$ 4.2 $J_{6',6''}$ 12.5	2.15s (3 H) 2.11s (3 H) 2.07s (3 H) 2.04s (3 H)	7.19t $J_{CH_2,NH}$ 3.0	6.65d $J_{2',N'H}$ 8.9	5.04d	8.00–7.35m	—
2[b]	6.37d $J_{1',2'}$ 3.0	←——5.50–5.10m——→			←—— 4.48–3.92m→		4.34dd $J_{5',6'}$ 4.3 $J_{6',6''}$ 12.7	2.12s (3 H) 2.09s (3 H) 2.08s (3 H) 2.02s (3 H)	7.20t $J_{CH_2,NH}$ 4.0	6.86d $J_{2',N'H}$ 8.0	5.01d	7.90–7.10m	2.40s
3[b]	5.82d $J_{1',2'}$ 9.0	4.85m $J_{2',3'}$ 9.0 $J_{2',N'H}$ 10.1	5.38t $J_{3',4'}$ 9.0	5.20–5.08m[c]	3.92m	4.33dd	4.17dd	2.18s (3 H) 2.14s (3 H) 2.12s (3 H) 2.08s (3 H)	7.22t $J_{CH_2,NH}$ 3.0	6.72d	5.10d	8.10–7.40m	—
4[a]	5.83d $J_{1',2'}$ 8.6	4.90m[c] $J_{2',3'}$ 9.0 $J_{2',N'H}$ 9.2	5.38t $J_{3',4'}$ 9.0	5.18t $J_{4',5'}$ 9.0	3.90m	4.14dd $J_{5',6''}$ 2.1	4.30dd $J_{5',6'}$ 4.5 $J_{6',6''}$ 12.0	2.14s (3 H) 2.10s (6 H) 2.04s (3 H)	7.25t[c] $J_{CH_2,NH}$ 4.7	6.97d	5.04m	7.90–7.20m	2.41s
									Thiazole				
									NH	*H-4*	*Ph*		CH_3
5[a]	6.37d $J_{1',2'}$ 3.6	4.40–4.20m	5.38t $J_{3',4'}$ 9.0	5.25t $J_{4',5'}$ 9.0	←—— 4.11–4.00m→		4.31dd $J_{5',6'}$ 4.1 $J_{6',6''}$ 12.4	2.17s (3 H) 2.10s (3 H) 2.05s (3 H) 1.97s (3 H)	5.33–5.25m	7.31s	7.40–7.20m		—
6[b]	6.36d $J_{1',2'}$ 3.3	4.01dd $J_{2',3'}$ 9.0	5.44t $J_{3',4'}$ 9.0	5.23t $J_{4',5'}$ 9.0	←—— 4.20–4.06m→		4.35dd $J_{5',6'}$ 4.4 $J_{6',6''}$ 13.3	2.11s (3 H) 2.06s (3 H) 2.05s (3 H) 1.95s (3 H)	5.35–5.25m	7.20s	7.35–7.13m		2.35s
7[b]	5.88d $J_{1',2'}$ 9.0	4.00t[d] $J_{2',3'}$ 9.0[e]	5.39t $J_{3',4'}$ 9.0	5.19t $J_{4',5'}$ 9.0	4.10–3.80m[e]	4.15dd $J_{5',6''}$ 2.9	4.36dd $J_{5',6'}$ 4.8 $J_{6',6''}$ 12.5	2.09s (3 H) 2.04s (6 H) 1.97s (3 H)	7.00–6.00m	7.27s	7.50–7.20m		—
8[b]	5.88d $J_{1',2'}$ 9.0	3.99t[e] $J_{2',3'}$ 9.0	5.30t $J_{3',4'}$ 9.0	5.19t $J_{4',5'}$ 9.0	4.12–3.80m[e]	4.13dd $J_{5',6''}$ 2.9	4.38dd $J_{5',6'}$ 4.8 $J_{6',6''}$ 12.5	2.10s (3 H) 2.04s (6 H) 1.98s (3 H)	7.00–6.00m	7.29s	7.40–7.05m		2.35s

[a] At 200 MHz. [b] At 90 MHz. [c] Overlapped signal. [d] By extrapolation to zero concentration of $Eu(fod)_3$. [e] In the presence of $Eu(fod)_3$.

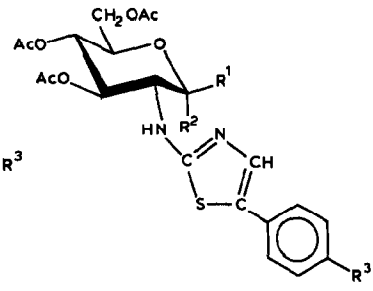
The ^{1}H-n.m.r. assignments (Table I) are based on the results of D_2O-exchange and double-resonance experiments. The J values are indicative of the preponderance of the $^4C_1$(D) conformation in solution. The chemical shifts (6.35–6.37 p.p.m.) of H-1′ and the small values (3–3.5 Hz) of $J_{1',2'}$ for **1** and **2** accord with the α configuration, whereas the corresponding data [δ 5.82–5.83 and large values (8.6–9.0 Hz) of $J_{1',2'}$] for **3** and **4** are indicative of the β configuration.

Table II gives the ^{13}C chemical shifts for **1–4**; C-1′ was more deshielded than the other ring carbons. The C-6′ and N–CH_2 signals were assigned on the basis of attached proton test (APT) spectra. The assignments of thiocarbonyl carbons (182.7–183.5 p.p.m.) and C-2′ are in agreement with data for other thiourea derivatives[19]. The resonances of C-1′,2′,3′,5′ in **3** and **4**, compared to the corresponding signals in **1** and **2** showed downfield shifts, according to those described for related pairs of anomers[20,21].

The cyclodehydration reaction of **1–4** effected with acetic anhydride and phosphoric acid afforded the 1,3,4,6-tetra-*O*-acetyl-2-(5′-arylthiazol-2′-ylamino)-2-deoxy-$\alpha(\beta)$-D-glucopyranoses (**5–8**). The analytical and u.v., i.r., ^{1}H-n.m.r. (Table I), and ^{13}C-n.m.r. (Table II) data for **5–8** and the mass spectrum of **7** were consistent with the proposed structures. Compounds **5–8** had λ_{max} at 304–307 nm, characteristic of glycosylaminothiazoles[1,2] and the simple arylsubstituted aminothiazoles[22], no i.r. band for the Ar–C=O group, and chemical shifts for H-4 (7.20–7.31 p.p.m.) that were similar to those for glycosylaminothiazoles[1,2] and simple arylaminothiazoles[23]. The ^{13}C-n.m.r. data for **5–8** supported the formation of a thiazole ring when they were compared with data for **1–4**. In the spectra of **5–8**, the phenacyl (CH_2, C=O) and C=S resonances were replaced by signals at 132.8–134.1, 126.8–127.5, and 166.8–168.3 p.p.m., which were assigned to C-4, C-5, and C-2 of the thiazole ring, respectively. Also, a slight downfield shift (1.1–2.4 p.p.m.) for the C-2′ signal was observed.



1 R^1 = H, R^2 = OAc, R^3 = H
2 R^1 = H, R^2 = OAc, R^3 = Me
3 R^1 = OAc, R^2 = H, R^3 = H
4 R^1 = OAc, R^2 = H, R^3 = Me



5 R^1 = H, R^2 = OAc, R^3 = H
6 R^1 = H, R^2 = OAc, R^3 = Me
7 R^1 = OAc, R^2 = H, R^3 = H
8 R^1 = OAc, R^2 = H, R^3 = Me

TABLE II

^{13}C-N.M.R. DATA (δ SCALE) FOR **1–8** IN $CDCl_3$

Compound	*Chain*						*Acetyl*		*Phenyl*					*Thiourea*		
	C-1'	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*	*CH_3*	*C=O*	*C-1*	*C-2,C-6*	*C-3,C-5*	*C-4*	*Me*	*CH_2*	*C=O*	*C=S*
1	90.5	55.6	70.9[a]	67.5	69.4[a]	61.4	20.7 20.6 20.5 20.3	171.9 170.7 168.9 168.6	133.8	127.7	128.6	134.1	—	51.7	194.7	182.8
2	90.5	55.7	70.9[a]	67.5	69.5[a]	61.5	20.8 20.7 20.6 20.4	171.9 170.7 168.9 168.5	131.3	127.9	129.4	145.3	21.6	51.6	193.7	182.7
3	92.6	57.3	73.0[a]	67.8	72.3[a]	61.5	20.8 20.6 20.5 20.3	171.7 170.5 169.5 169.2	133.8	127.6	128.6	134.0	—	51.6	194.9	183.4
4	92.9	57.6	73.2[a]	68.1	72.7[a]	61.8	21.0 20.9 20.7 20.6	171.8 170.6 169.8 169.5	131.7	128.1	129.6	145.3	21.8	51.7	193.9	183.5

														Thiazole		
														C-4	*C-2*	*C-5*
5	90.2	56.7	71.0[a]	67.5	69.6[a]	61.4	20.7(2 C) 20.5(2 C)	171.1 170.2 168.9 168.5	132.0	125.4	128.8	127.0	—	134.1	167.0	127.6
6	90.1	56.9	70.9[a]	67.6	69.5[a]	61.3	20.5(3 C) 20.4(1 C)	171.0 170.5 169.1 168.5	128.7[a]	125.2	129.4	136.8	20.9	133.2	166.8	127.5[a]
7	92.5	59.5	72.8[a]	67.7	72.2[a]	61.3	20.4(1 C) 20.3(1 C) 20.2(2 C)	170.4 170.2 169.1 169.0	131.6	124.9	128.5	126.5	—	133.6	168.3	126.8
8	93.0	60.0	72.7[a]	68.1	71.1[a]	61.1	20.8(1 C) 20.7(1 C) 20.6(2 C)	171.0(2 C) 170.9(1 C) 169.4(1 C)	129.0[a]	125.3	129.5[a]	136.5	21.1	132.8	168.1	127.1

[a]Assignments may have to be reversed.

When the specific rotations, δ values of H-1′, $J_{1',2'}$ values, and ^{13}C-n.m.r. data for the α anomers **5** and **6** were compared with the corresponding data for the β anomers **7** and **8**, the differences were similar to those for α- (**1** and **2**) and β-thioureas (**3** and **4**).

The mass spectrum of **7** showed the molecular peak at *m/z* 506, a peak at *m/z* 176 assigned to 2-amino-5-phenylthiazole, and significant peaks at *m/z* 161, 134, 121, 116, 102, and 60 characteristic of simple thiazoles[24]. There were losses of AcO·, acetic acid, and ketene typical of acetylated sugars[25].

The $^3J_{H,H}$ values for **5–8** (Table I) showed that the $^4C_1$(D) conformation preponderated in solutions in chloroform.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were measured at 5.895 and 5.461 Å, using a 1-cm cell. I.r. spectra were recorded for KBr discs. ^{1}H-N.m.r. spectra were obtained at 90 (continuous wave) and 200 MHz (F.t.). Assignments were confirmed by double-resonance experiments and H/D exchange. Overlapping signals were separated from each other by incremental additions of Eu(fod)$_3$. ^{13}C-N.m.r. spectra were recorded at 50.3 MHz for solutions in $CDCl_3$ which also served as the internal deuterium lock. Proton-decoupled APT spectra were obtained to assist in signal assignments. The e.i. mass spectrum was obtained at 70 eV, with an ion-source temperature of 200°. T.l.c. was performed on Silica Gel HF_{254} (Merck) with ether–hexane (6:1) and detection by u.v. light, iodine vapour, or charring with sulphuric acid. Flash chromatography was conducted on Silica Gel 60 (Merck, 230 mesh).

*1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(3-phenacylthioureido)-α(β)-*D*-glucopyranose* (**1–4**). — A solution of the phenacylamine hydrochloride (1.29 mmol) in water (5 mL) was neutralised with sodium hydrogencarbonate (1.29 mmol) and added to a solution of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-isothiocyanato-α(β)-D-glucopyranose (1.29 mmol) in acetone (12 mL) under nitrogen. The resulting solution was kept at room temperature for *t* h. The solvent was evaporated under diminished pressure, and the residue was washed with water and crystallised from ethanol. The following compounds were prepared in this manner.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(3-phenacylthioureido)-α-D-glucopyranose (**1**; 0.64 g, 95%; *t* 2 h), m.p. 98–100° (from ethanol), $[\alpha]_D^{21}$ +85° (*c* 0.85, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 242 nm (ε_{mM} 37.5); ν_{max} 3350 (NH), 3070, 2960, 2930, 1750 (CO ester), 1690 (CO ketone), 1540, 1225 (C–O–C and C=S), 760 and 690 cm^{-1} (CH aromatic). The ^{1}H- and ^{13}C-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{23}H_{28}N_2O_{10}S$: C, 52.66; H, 5.88; N, 5.34; S, 6.11. Found: C, 52.85; H, 5.70; N, 5.21; S, 5.87.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-[3-(*p*-methylphenacyl)thioureido]-α-D-glucopyranose (**2**; 0.42 g, 60%; *t* 4 h), m.p. 128–129° (from ethanol), $[\alpha]_D^{21}$ +76° (*c* 0.8, chloroform); $\lambda_{max}^{CH_2Cl_2}$ 247 nm (ε_{mM} 29.6); ν_{max} 3300 and 3280 (NH), 3050, 2980,

1740 (CO ester), 1675 (CO ketone), 1535, 1225 (C–O–C and C=S), and 810 cm^{-1} (CH aromatic). The ^1H- and ^{13}C-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{24}H_{31}N_2O_{10}S$: C, 53.52; H, 5.61; N, 5.20; S, 5.95. Found: C, 53.36; H, 5.63; N, 5.15; S, 6.20.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(3-phenacylthioureido)-β-D-glucopyranose (**3**; 0.51 g, 76%; *t* 2 h), m.p. 151° (from ethanol),$[\alpha]_{546}^{21}$ +6.8° (*c* 0.8, chloroform); $\lambda_{max}^{CH_2Cl_2}$ 252 nm (ε_{mM} 11.2); ν_{max} 3350 and 3330 (NH), 3070, 2980, 1760 (CO ester), 1690 (CO ketone), 1520, 1230 (C–O–C and C=S), 760 and 690 cm^{-1} (CH aromatic). The ^1H- and ^{13}C-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{23}H_{28}N_2O_{10}S$: C, 52.66; H, 5.38; N, 5.34; S, 6.11. Found: C, 52.67; H, 5.55; N, 5.30; S, 5.89.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-[3-(*p*-methylphenacyl)thioureido]-β-D-glucopyranose (**4**; 0.48 g, 69%; *t* 0.3 h), m.p. 138–139° (from ethanol), $[\alpha]_D^{21}$ +6.5° (*c* 1, chloroform); $\lambda_{max}^{CH_2Cl_2}$ 255 nm (ε_{mM} 18.0); ν_{max} 3320 and 3310 (NH), 3080, 2980, 1750 (CO ester), 1680 (CO ketone), 1530, 1220 (C–O–C and C=S), and 810 cm^{-1} (CH aromatic). The ^1H- and ^{13}C-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{24}H_{31}N_2O_{10}S$: C, 53.52; H, 5.61; N, 5.20; S, 5.95. Found: C, 53.56; H, 5.72; N, 4.91; S, 6.08.

1,3,4,6-Tetra-O-acetyl-2-(5'-arylthiazol-2'-ylamino)-2-deoxy-α(β)-D-glucopyranoses (**5–8**). — To a solution of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-(3-phenacylthioureido)-α(β)-D-glucopyranose (**1–4**, 0.68 mmol) in acetic anhydride (6.8 mL) was added phosphoric acid (0.34 mL). The mixture was stirred at room temperature for *t* h. The reactions were monitored by t.l.c. The resulting solution was poured into ice–water (80 mL), the solid products were collected, and solutions in dichloromethane (40 mL) were 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 (OH^-) resin (8 mL), filtered, and concentrated, and the resulting syrup was purified as indicated. The following compounds were prepared in this manner.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(5'-phenylthiazol-2'-ylamino)-α-D-glucopyranose (**5**; 0.12 g, 35%; *t* 2 h), m.p. 112–114° (from ether), $[\alpha]_D^{21}$ +61° (*c* 0.6, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 307 nm (ε_{mM} 19.2); ν_{max} 3370 (NH), 3050, 2940, 1745 (CO ester), 1525, 1225 (C–O–C), 755 and 690 cm^{-1} (CH aromatic). The ^1H- and ^{13}C-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{23}H_{26}N_2O_9S$: C, 54.53; H, 5.17; N, 5.53; S, 6.33. Found: C, 54.31; H, 4.97; N, 5.41; S, 6.78.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-[5'-(*p*-tolyl)thiazol-2'-ylamino]-α-D-glucopyranose (**6**; 0.32 g, 90%; *t* 8 h), isolated as an amorphous solid by column chromatography (6:1 ether–hexane), $[\alpha]_D^{21}$ +50° (*c* 0.9, dichloromethane); $\lambda_{max}^{CH_2Cl_2}$ 306 nm (ε_{mM} 12.3); ν_{max} 3420 and 3330 (NH), 3020, 2940, 1745 (CO ester), 1505, 1220 (C–O–C), and 810 cm^{-1} (CH aromatic). The ^1H- and ^{13}C-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{24}H_{28}N_2O_9S$: C, 55.37; H, 5.42; N, 5.38; S, 6.16. Found: C, 54.94; H, 5.52; N, 5.04.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(5′-phenylthiazol-2′-ylamino)-β-D-glucopyranose (**7**; 0.21 g, 60%; *t* 22 h), m.p. 165–166° (from ethanol), $[\alpha]_{546}^{21}$ −25° (*c* 0.5, chloroform); $\lambda_{max}^{CHCl_3}$ 306 nm (ε_{mM} 23.0); ν_{max} 3415 (NH), 3060, 2990, 1740 (CO ester), 1525, 1220 (C–O–C), 750 and 680 cm^{-1} (CH aromatic). The ^1H- and ^{13}C-n.m.r. data are given in Tables I and II. Mass spectrum: *m/z* 506 (1%), 200 (15), 176 (31), 161 (10), 134 (24), 121 (12), 116 (8), 102 (35), 60 (53), and 43 (100).

Anal. Calc. for $C_{23}H_{26}N_2O_9S$: C, 54.53; H, 5.17; N, 5.53; S, 6.33. Found: C, 54.40; H, 4.99; N, 5.40; S, 6.66.

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-[5′-(*p*-tolyl)thiazol-2′-ylamino]-β-D-glucopyranose (**8**; 0.16 g, 45%; *t* 19 h), m.p. 194–196° (from ethanol), $[\alpha]_D^{21}$ −16° (*c* 0.5, chloroform); $[\alpha]_{546}^{21}$ −26° (*c* 0.5, chloroform); $\lambda_{max}^{CHCl_3}$ 304 nm (ε_{mM} 109); ν_{max} 3405 (NH), 3020, 2960, 1755 (CO ester), 1520, 1220 (C–O–C), and 810 cm^{-1} (CH aromatic). The ^1H- and ^{13}C-n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{24}H_{28}N_2O_9S$: C, 55.37; H, 5.42; N, 5.38; S, 6.16. Found: C, 55.35; H, 5.70; N, 5.15; S, 6.50.

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