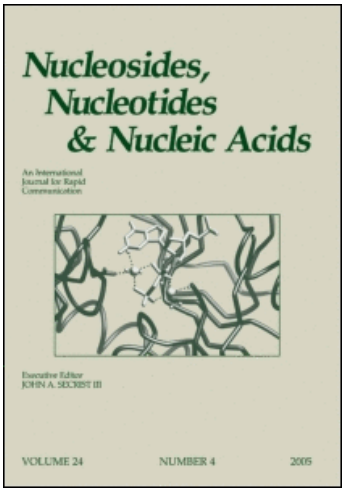

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Reaction of Glycosylisothiocyanates with 2-Chloroethylamine. Synthesis and Structure of N-Nucleoside Analogues

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REACTION OF GLYCOSYLISOTHIOCYANATES WITH 2–CHLOROETHYLAMINE. SYNTHESIS AND STRUCTURE OF N–NUCLEOSIDE ANALOGUES

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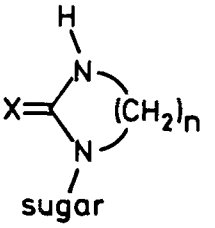
ABSTRACT

Per–*O*–acetyl–*β*–D–glycopyranosylisothiocyanates (**3** and **4**) were condensed with 2–chloroethylamine hydrochloride to afford *N,N'*–bis(per–*O*–acetyl––*β*–D–glycopyranosyl)–*N*–(2–thiazolin–2–yl)thioureas (**5** and **6**) through the glycosyl–aminoheterocycles (**7** and **8**) as intermediates. Compounds **7** and **8** were converted into *N*–(2–thiazolin–2–yl)urea or thioureas (**9–11**) by reaction with iso(thio)cyanates. Compounds **5**, **6** and **9–11** show a strong chelated structure due to an intramolecular hydrogen bond, which anchors the *E,Z* conformation in solution.

INTRODUCTION

Cyclic and saturated urea nucleosides **1** (n = 2,3,4) have been extensively prepared[1-3], but syntheses of their thioanalogues are scarce[4]. However, Ogura *et al.*[5] have reported a facile and high yield synthesis of *N*–nucleosides of imidazolidine–2––thione (**2**, n = 2), and hexahydropyrimidine–2–thione (**2**, n = 3) by reaction of per–*O*––acyl–D–glycosylisothiocyanates with 2–chloroethylamine. On the contrary, bibliogra–

phic data[6,7] on the reaction of alkyl(aryl)isothiocyanates with β–haloalkylamines show that 2–alkyl(aryl)amino–2–thiazolines are the only products formed. Likewise, we have recently corrected the research reported by Ogura in a preliminary communication[8], and this paper describes the detailed experimental procedures and spectroscopic data that support our results.

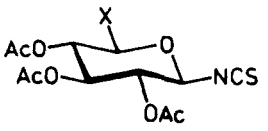


1 X = O
2 X = S

RESULTS AND DISCUSSION

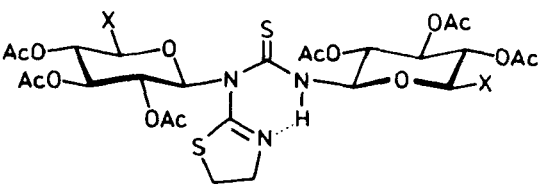
On treatment of per–*O*–acetyl–β–D–glucopyranosylisothiocyanates (**3** and **4**) with 2–chloroethylamine hydrochloride under the same conditions described by Ogura, new and unexpected products were isolated. The assigned structures to **5** and **6** are supported by analytical and spectral data. Thus, all glycosidic signals are duplicated in the ^{1}H– and ^{13}C–n.m.r. spectra, showing the presence of two sugar moieties. A signal at δ ~182 ppm and two absorptions at ~280 and 250 nm in the u.v. spectra indicate the presence of the N–C(=S)–N group[9,10]. The ^{13}C resonances at ~25 ppm (CH_2–S), ~55 ppm (CH_2–N=), and ~166 ppm (C=N), jointly with the i.r. absorption (~1600 cm^{-1}) support a structure of 2–thiazoline for the heterocyclic moiety[11-13].

The formation of **5** and **6** must involve the formation of a chloroethyl–thiourea, which undergoes a spontaneous intramolecular cyclization to per–*O*––acetyl–D–glycopyranosylaminothiazolines (**7** and **8**). The further addition of isothiocyanates **3** and **4** gives **5** and **6**.



3 X = CH_2OAc

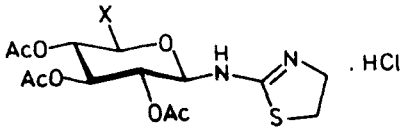
4 X = H



5 X = CH_2OAc

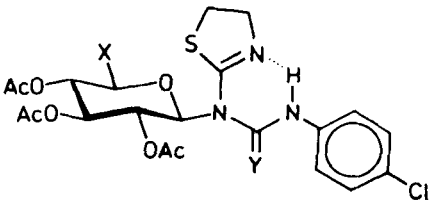
6 X = H

Glycosylaminoheterocycles **7** and **8** were prepared by reaction of **3** and **4** with an ethereal solution of 2–chloroethylamine. Under these conditions, the formation of hydrochlorides **7** and **8**, preserves further additions. These compounds were characterized through the preparation of compounds **9**–**11** by reaction with 4–chloro–phenyliso(thio)cyanate in pyridine.



7 X = CH_2OAc

8 X = H

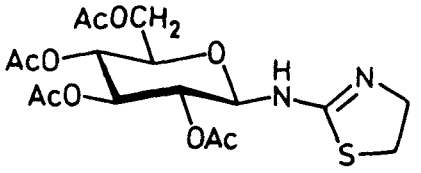


9 X = CH_2OAc, Y = O

10 X = CH_2OAc, Y = S

11 X = H, Y = O

The treatment of **7** with an aqueous solution of sodium hydrogen–carbonate in chloroform afforded the free base **12**, which showed the same chromato–graphic behavior and spectral data as **13**, previously described[5].



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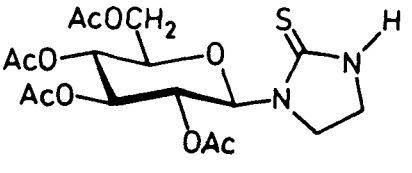
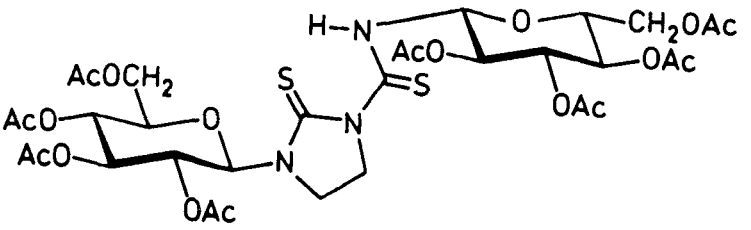


13

Alternative isomeric structure **13** must be ruled out due to the absence of the thiocarbonilic resonance in the ^{13}C–n.m.r. spectrum. Moreover, an unassignable i.r. absorption at 1625 cm^{-1}, which is also in disagreement with **13**, supports the C=N absorption for **12**. For a similar reason, structure **14** must be discarded instead of **5**.



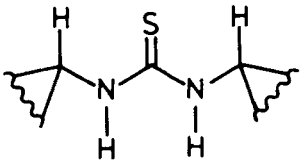
14

Our results can be explained on the basis of the HSAB principle. Thus, in the intramolecular cyclization of chloroethylthioureas, the soft sulphur atom attacks to the soft chloromethyl carbon instead to the hard nitrogen.

For a major clarity, we will denote rings A and B to the sugar moiety joined to *N* and *N'* atoms, respectively. A strong intramolecular hydrogen bond is present in compounds **5**, **6**, and **9**–**11**. This fact is supported by the large downfield shift of NH signals in ^1H–n.m.r. spectra (see Table I) and the shift at lower frequencies of NH ($\Delta\nu > 300$ cm^{-1}) and C=N ($\Delta\nu \sim 40$ cm^{-1}) with respect to other non–bonded thiazolines and 2–amino–2–thiazolines[14].

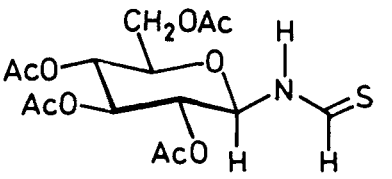
These chelated structures anchor the *E,Z*–conformation in the thiourea group. The $J_{1,NH}$ values prove that the relative disposition of B sugar residues in **5** and **6** is identical to those of *N,N'*–bis(glycosyl)thioureas (**15**)[15]. On the contrary, the upfield chemical shift of H–1 in the A sugar residue is close to that of the *E*–conformer[16] of **16**. In conclusion, we propose that **17** is the more stable conformer in solution for these compounds.

Probably, the intramolecular hydrogen bond is responsible of the fragmentation pathway in mass spectrometry. Compounds **9**–**11**, do not show the molecular ion peak; however, this ion may lose an iso(thio)cyanate molecule (base peak) *via* a McLafferty fragmentation process, to give the higher mass peak at m/z 432, for **9**



Z,Z

15



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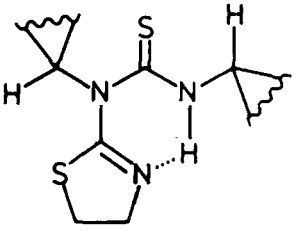


E,Z

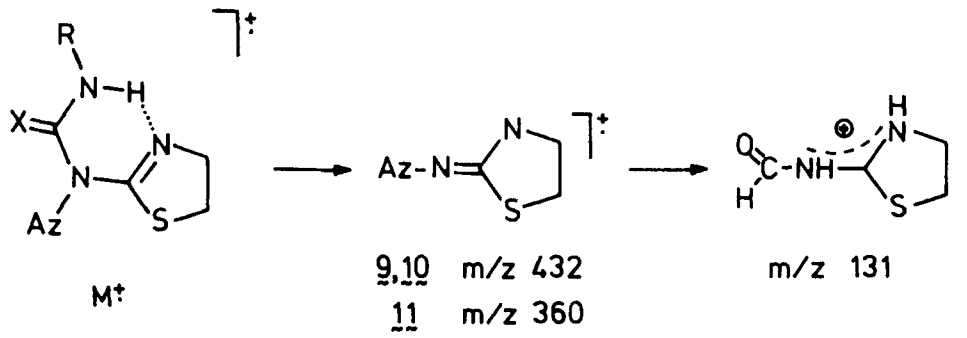
17

and 10, or 360 for 11 (Scheme I). These fragments undergo successive losses of ketene, acetyl, and acetoxyl groups, and acetic acid in a similar way to other per–*O*–acetylsugar derivatives[12,17].

Compounds 5, 6, and 9–11 can be considered a special class of *N*–nucleosides, in which the hydrogen bond closes a "heterocyclic moiety". Some "*N*–nucleosides" of this type, such as the Clytocine[18] and other analogous compounds, have been isolated from natural sources or detected in the interaction between DNA and carcinogenic amines[19,20].

EXPERIMENTAL

General Methods.– Solutions were concentrated *in vacuo* at <50°. 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 cell). I.r. spectra (KBr discs) were recorded with a Perkin–Elmer 399 spectrophotometer, and u.v. spectra with a Pye–Unicam SP8–250 instrument. ^{1}H–N.m.r. spectra were recorded with a Varian XL–200 (200 MHz) and a Bruker WM–360 (360 MHz) spectrometers.



SCHEME I

^{13}C–N.m.r. spectra (50.2 MHz) were recorded with a Varian XL–200 spectrometer. E.i.–mass spectra (35 and 70 eV) were obtained with a Kratos MS–80RFA mass spectrometer, using a direct–insertion probe heated at 30° below the m.p. for solids. T.l.c. was conducted on silica gel GF_{254} (Merck) with benzene–acetone (5:1) and benzene–methanol (5:1 or 5:2) as eluants using detection with u.v. light or iodine vapour. Preparative t.l.c. was conducted on plates coated with 1–mm, layers of silica gel 60 PF_{254} with benzene–methanol (5:1) as eluant. Elemental microanalyses were performed on a Perkin–Elmer 240C analyzer.

N,N'–Bis(2,3,4,6–tetra–O–acetyl–β–D–glucopyranosyl)–N–(2–thiazolin–2–yl)thiourea (**5**).– a) To a solution of 2–chloroethylamine hydrochloride (0.3 g, 2.6 mmol) in pyridine (6.0 mL) was added 2,3,4,6–tetra–*O*–acetyl–β–D–gluco–pyranosylisothiocyanate (**3**) (1.0 g, 2.6 mmol). The mixture was stirred at room temperature for 2 h, poured into ice–water, and the crude product (0.7 g, 64%) was purified by preparative t.l.c. to give (**5**) as a white foam (0.4 g, 37%); $[\alpha]_D$ –10°, $[\alpha]_{578}$ –9°, $[\alpha]_{546}$ –6.5°, $[\alpha]_{436}$ +48°, $[\alpha]_{365}$ +580° (*c* 0.6, chloroform); λ_{max}^{EtOH} 279 and 246 nm (ϵ_{mM} 16.2 and 11.7); ν_{max} 3000–2840 (NH), 1735 (C=O ester), 1600 (C=N), and 1535 cm^{-1} (NH). ^{1}H– and ^{13}C–n.m.r. data are given in Tables I–III.

Anal. Calc. for $C_{32}H_{43}N_3O_{18}S_2$: C, 46.77; H, 5.27; N, 5.11. Found: C, 46.48; H, 5.31; N, 4.83.

b) To a solution of 2,3,4,6–tetra–*O*–acetyl–β–D–glucopyranosylisothiocyanate (**3**) (0.4 g, 1.0 mmol) in chloroform (10 ml) was added 2–chloroethylamine hydrochloride (0.1 g, 1.0 mmol) and anhydrous sodium acetate (0.1 g, 1.0 mmol). The mixture was stirred at room temperature for 2 h, and then washed with water and dried over anhydrous magnesium sulphate. The solution was concentrated to dryness and the residue was purified by preparative t.l.c. to give (**5**) (0.15 g, 37%)

2–(2,3,4,6–Tetra–O–acetyl–β–D–glucopyranosyl)amino–2–thiazoline hydrochloride (**7**).– To a solution of 2–chloroethylamine hydrochloride (0.75 g, 6.5 mmol) in water (10 ml), was added diethyl ether (15 ml) and a solution of 1M sodium hydroxide (15 ml). The organic layer was separated, and the extraction was repeated with more diethyl ether (4x15 ml). The combined extracts were dried ($MgSO_4$), and then was added (**3**) (1.0 g, 2.6 mmol). The mixture was stored at room temperature for 12 h, and the solvent was evaporated to give (**7**) (1.2 g, 100%) as an amorphous and hygroscopic foam. This product was used inmediately without further purification in the next steps. To a solution of (**7**) (0.1 g, 0.2 mmol) in water (20 ml) was added chloroform (20 ml) and sodium hydrogencarbonate (0.1 g, 1.4 mmol). The mixture was stirred at room temperature for 2 h, and extracted with more chloroform (3x20 ml). The combined extracts were dried ($MgSO_4$) and evaporated to dryness. The syrupy residue was purified by preparative t.l.c., to give the free base (**12**) (0.1 g, 90%) as a colorless oil. Spectral data are in agreement with those reported by Ogura for the N–nucleoside (**13**).

N–*(2,3,4,6–tetra–O–acetyl–β–D–glucopyranosyl)*–N'–*(4–chlorophenyl)*–N–*(2–thiazolin–2–yl)urea* (**9**).– To a solution of (**7**) (0.5 g, 1.1 mmol) in pyridine (6 ml) was added 4–chlorophenylisocyanate (0.2 g, 1.1 mmol). After 24 h at room temperature, the mixture was poured into ice–water, and the resulting white solid (0.4 g, 70%) was recrystallized from ethanol; m.p. 197–199° ; $[\alpha]_D$ –51.5°, $[\alpha]_{578}$ –53.5°, $[\alpha]_{546}$ –60.5°, $[\alpha]_{436}$ –101.5°, $[\alpha]_{365}$ –157° (*c* 0.9, chloroform); λ_{max}^{EtOH} 260, 245, and 230 nm (ϵ_{mM} 11.6, 16.6, and 14.3); ν_{max} 3140–2900 (NH), 1740 (C=O ester), 1685 (C=O urea), 1595 (C=N), 1595 and 825 (aromatic) and 1540 cm^{-1} (NH). ^1H– and ^{13}C–n.m.r.

TABLE I

^{1}H–N.M.R. CHEMICAL SHIFTS OF COMPOUNDS 5, 6, AND 9–12[a]

Comp.	Ring[b]	H–1	H–2	H–3	H–4	H–5	H–5'	H–6	H–6'	=NC$\underline{H}_x$H$_y$	=NCH$_x$$\underline{H}_y$	–S–C$\underline{H}_u$H$_v$	N–H
5	A	4.34d	5.40dd	5.24t	5.07t	3.75m		4.21dd	4.08dd	5.01m	4.35m	3.10m	12.47d
	B	5.73dd	5.46t	5.24t	5.06t	3.75m		4.17dd	4.05dd				
6	A	4.34d	5.28t	5.2–5.0m	5.2–5.0m	4.14t	3.45dd			5.2–5.0m	4.35m	3.17m	12.68d
	B	5.72t	5.32t	5.41t	5.2–5.0m	4.11t	3.40dd						
9		4.52d	5.4–5.2m		5.16m	3.86m		4.30dd	4.21dd	4.47m	4.13m	3.21m	11.58s
10		4.53d	5.33t	5.24t	5.13t	3.86m		4.30dd	4.15dd	5.03m	4.60m	3.23m	13.61s
11		4.46d	5.23t	5.31t	5.07t	4.16dd	3.46t			4.39m	4.07m	3.20t	11.85s
12		4.84d	4.92t	5.22t	5.03t	3.76m		4.23dd	4.06dd		3.86m	3.28t	5.67s

[a]In $CDCl_3$. [b]Rings A and B are the sugar moiety joined to N and N' atoms respectively.

TABLE II

^{1}H–N.M.R. COUPLING CONSTANTS OF COMPOUNDS 5, 6, AND 9–12[a]

Comp.	Ring	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	$J_{1,NH}$	J_{H_x,H_u}	J_{H_x,H_v}	J_{H_x,H_y}	J_{H_y,H_u}
5	A	8.6	10.0	9.6	10.0			6.0	2.5	–11.0	8.3	2.6	7.1	–11.2	6.8
	B	8.1	10.0	9.6	10.0			5.1	2.5	–11.0					
6	A	8.0	9.2		10.8	2.6	–11.0				8.2			–11.9	7.7
	B	8.5	9.2	9.0	10.8	2.5	–11.0								
9		8.0		10.0	8.0			5.0	5.1	–12.4		3.4	6.0	–13.2	
10		8.2	9.6	9.2	9.4			4.0	2.4	–12.0		4.0	8.0	–12.0	
11		8.0	9.2	9.3	10.0	6.1	–10.8					5.4	6.1	–12.3	
12		9.0	8.8	9.2	9.6			4.4	2.1	–12.4					

[a]In $CDCl_3$.

TABLE III

^{13}C–N.M.R. CHEMICAL SHIFTS OF COMPOUNDS 5,6, AND 9–12[a,b]

Comp.	Ring	C–1	C–2	C–3	C–4	C–5	C–6	C=O	C=S	C=N	C–N=	C–S
5	A	89.38	71.72	73.58	68.17	73.35	61.89		181.97	165.76	54.61	24.85
	B	82.62	69.46	73.35	68.09	72.55	61.84					
6	A	89.99	71.87	72.70	69.11	64.57			182.14	165.60	54.66	25.15
	B	83.24	69.82	72.30	69.05	64.39						
9		90.08	72.24	73.46	68.13	72.84	61.71	150.01		165.71	54.69	24.89
10		89.71	72.08	73.59	68.04	72.62	61.63		178.76	165.55	54.69	24.89
11		91.10	72.58	72.45	69.00	64.47		150.30		165.03	49.01	25.82
12		85.24	70.98	72.97	68.05	72.86	61.85			163.72	55.37	33.41

[a]Assignments of C–3, C–4, and C–5 resonances may be interchanged. [b]In $CDCl_3$.

data are given in Tables I–III. Mass spectrum: m/z 432 (0.5%), 389 (1), 373 (11), 313 (8), 271 (3), 253 (3), 239 (3), 169 (7), 155 (34), 153 (100), 145 (8), 131 (13), 127 (16), 125 (32), 115 (5), 109 (7), 90 (20), and 43 (30).

Anal. Calc. for $C_{24}H_{28}ClN_3O_{10}S$: C, 49.19; H, 4.82; N, 7.17. Found: C, 49.14; H, 4.83; N, 7.05.

N–(*2,3,4,6–Tetra*–O–*acetyl*–*β*–D–*glucopyranosyl*)–N'–(*4–chlorophenyl*)–N–(*2–thiazolin–2–yl*)*thiourea* (**10**).– To a solution of (**7**) (0.35 g, 0.75 mmol) in pyridine (5 ml), was added 4–chlorophenylisothiocyanate (0.1 g, 0.8 mmol). The mixture was processed as described for (**9**) to give (**10**) (0.3 g, 60%). Recrystallized from ethanol had m.p. 145–146°; $[\alpha]_D$ –21°, $[\alpha]_{578}$ –18.5°, $[\alpha]_{546}$ –20.5°, $[\alpha]_{436}$ +13° (*c* 0.5, chloroform); λ_{max}^{EtOH} 280, 273, and 225 nm (ϵ_{mM} 15.5, 15.2, and 17.9); ν_{max} 3070–2800 (NH), 1730, (C=O ester), 1600 (C=N), 1565 and 825 (aromatic), and 1540 cm^{-1} (NH). ^1H– and ^{13}C–n.m.r. data are given in Tables I–III. Mass spectrum: m/z 432 (1%), 389 (2), 373 (13), 313 (9), 253 (4), 171 (34), 169 (100), 145 (9), 131 (15), 111 (29), 103 (11), 75 (12), 60 (9), and 43 (28).

Anal. Calc. for $C_{24}H_{28}ClN_3O_9S_2$: C, 47.88; H, 4.69; N, 6.98. Found: C, 48.09; H, 4.81; N, 6.93.

N,N'–*Bis*(*2,3,4–tri*–O–*acetyl*–*β*–D–*xylopyranosyl*)N–(*2–thiazolin–2–yl*)–*thiourea* (**6**).– To a solution of 2–chloroethylamine hydrochloride (0.4 g, 3.15 mmol) in pyridine (6 ml), was added (**4**) (1.0 g, 3.15 mmol). The mixture was kept at room temperature for 6 h, poured into ice–water, and the resulting white solid (0.8 g, 79%) was recrystallized from 96% ethanol showing m.p. 119–121°; $[\alpha]_D$ –20°, $[\alpha]_{578}$ –20°, $[\alpha]_{546}$ –20°, $[\alpha]_{436}$ +1.5°, $[\alpha]_{365}$ +281° (*c* 0.5, chloroform); ν_{max} 3120–2800 (NH, CH), 1740 (C=O ester), 1595 (C=N), and 1545 cm^{-1} (NH). ^1H– and ^{13}C–n.m.r. data are given in Tables I–III.

Anal. Calc. for $C_{26}H_{35}N_3O_{14}S_2$: C, 46.08; H, 5.21; N, 6.20. Found: C, 46.13; H, 5.12; N, 6.04.

2–(2,3,4–Tri–O–acetyl–β–D–xylopyranosyl)amino–2–thiazoline hydrochloride (**8**).– To a solution of 2–chloroethylamine hydrochloride (0.8 g, 7.0 mmol) in water (10 ml), was added diethyl ether (15 ml), and a solution of 1M sodium hydroxide (15 ml). The aqueous layer was decanted and extracted with more diethyl ether (4x15 ml). The combined extracts were dried ($MgSO_4$) and then, a solution of (**4**) (0.8 g, 2.65 mmol) in diethyl ether (10 ml) was added. The mixture was kept at room temperature for 15 mn, and then at 0° for 48 h. The solvent was evaporated to give (**8**) as an hygroscopic white foam (1.0 g, 95%), which was used in the next step without further purification.

N–(*2,3,4–Tri–O–acetyl–β–D–xylopyranosyl*)–N'–(*4–chlorophenyl*)–N–(*2–thiazolin–2–yl*)*urea* (**11**).– To a solution of (**8**) (0.5 g, 1.3 mmol) in pyridine (6 ml) was added 4–chlorophenylisocyanate (0.2 g, 1.3 mmol). The mixture was kept at room temperature for 8 h, poured into ice–water, and the white solid (0.5 g, 81%) was recrystallized from ethanol; m.p. 190–192°; $[\alpha]_D$ –70°, $[\alpha]_{578}$ –72.5°, $[\alpha]_{546}$ –82.5°, $[\alpha]_{436}$ –149°, $[\alpha]_{365}$ –254° (*c* 1.0, chloroform); ν_{max} 3200–2800 (NH, CH), 1735 (C=O ester), 1685 (C=O urea),1595 (C=N), 1595 and 820 (aromatic) 1535 cm^{-1} (NH). ^1H– and ^{13}C–n.m.r. data are given in Tables I–III. Mass spectrum: m/z 360 (2%), 301 (21), 257 (1), 241 (12), 199 (5), 181 (8), 155 (33), 153 (100), 145 (15), 131 (27), 127 (15), 125 (32), 97 (21), 90 (18), and 43 (33).

Anal. Calc. for $C_{21}H_{24}ClN_3O_8S$: C, 49.08; H, 4.71; N, 8.18. Found: C, 48.80; H, 4.67; N, 8.12.

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