Carbohydrate Research, 56 (1977) 404–406

Note

Conversion of acetylated glycosyl cyanides into *C*-glycosyl derivatives of benzothiazole and tetrazole

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(Received August 2nd, 1976; accepted for publication, September 15th, 1976)

Acetylated aldonitriles react readily with 2-aminothiophenol or azide ion to give 2-(polyacetoxyalkyl)benzothiazoles[1] or 5-(polyacetoxyalkyl)tetrazoles[2], respectively. However, this type of cyclization reaction has not hitherto been applied to acylated glycosyl cyanides.

Reaction of 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl cyanide[3], 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl cyanide[4], and 2,3,4-tri-*O*-benzoyl-β-D-ribopyranosyl cyanide[5] with 2-aminothiophenol in warm ethanol gave the corresponding acylated 2-β-D-glycosylbenzothiazoles in good yield, deacylation of which gave the crystalline 2-β-D-glycopyranosylbenzothiazoles shown in Table I.

The foregoing glycosyl cyanides also reacted with sodium azide and ammonium chloride in hot *N*,*N*-dimethylformamide to give the corresponding, crystalline, acylated 5-β-D-glycopyranosyltetrazoles (see Table I). However, the 5-β-D-glycopyranosyltetrazoles formed on deacylation of these compounds were hygroscopic, amorphous solids.

EXPERIMENTAL

Melting points were determined in capillary tubes and are uncorrected. Solutions were concentrated at 20 mmHg.

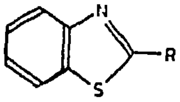
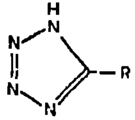
2-β-D-Glycopyranosylbenzothiazoles. — A solution of the acylated glycosyl cyanide (1 g) and 2-aminothiophenol (0.4 ml) in anhydrous ethanol (10–15 ml) was boiled for 4 h under a nitrogen atmosphere. The mixture was cooled, and the product was collected, and recrystallized from ethanol. Data on the crystalline products are given in Table I.

Saponification of the above esters with sodium methoxide, followed by crystallization of the products from ethanol, gave the glycosylbenzothiazoles shown in Table I.

Acylated 5-β-D-glycopyranosyltetrazoles. — A solution of the acylated glycosyl cyanide (1 g), sodium azide (~0.3 g), and ammonium chloride (0.23 g) in *N*,*N*-

TABLE I

DATA ON GLYCOSYL-BENZOTHIAZOLES AND -TETRAZOLES

R	*Yield* (%)	*M.p.* (*degrees*)	$[\alpha]_D$ (*degrees*)	*Formula*	*Found*		*Calc.*	
					N	*S*	*N*	*S*
								
2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl	65	162–163	+14 (C)[a]	$C_{21}H_{23}NO_9S$	3.10	6.66	3.01	6.89
2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl	57	161–162	−44 (C)	$C_{18}H_{19}NO_7S$	3.63	7.96	3.56	8.15
β-D-Galactopyranosyl		116	+26 (P)[a]	$C_{13}H_{15}NO_5S$	4.57	10.66	4.71	10.78
β-D-Xylopyranosyl		154	−48 (P)	$C_{12}H_{13}NO_4S$	5.31	11.94	5.24	12.00
β-D-Ribopyranosyl		213–214	−45 (P)	$C_{12}H_{13}NO_4S$	5.36	11.77	5.24	12.00
								
2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl	53	181–182	+43 (C)	$C_{15}H_{20}N_4O_9$	13.98		13.99	
2,3,4-Tri-*O*-acetyl-β-D-xylopyranosyl	43	173–174	−17 (C)	$C_{12}H_{16}N_4O_7$	17.18		17.07	
2,3,4-Tri-*O*-benzoyl-β-D-ribopyranosyl	58	115 (dec.)	−75 (C)	$C_{27}H_{22}N_4O_7$	10.94		10.89	

[a] C, chloroform; P, pyridine.

dimethylformamide (5 ml) was kept at 100° for 75–105 min. The reaction mixture was then concentrated to dryness and the residue was crystallized from aqueous methanol to give the products shown in Table I.

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