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Note

Some *N*-acetyl-*N*-aryl-α-L-arabinopyranosylamines*

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Although glycosylamines derived from primary aromatic amines are too unstable for use as model compounds for investigations of the relative reactivity of their hydroxyl groups, the *N*-acetyl derivatives are suitable for this purpose and have found application in structural studies of nitrogen glycosides[1–7]. Numerous *N*-acetyl-*N*-glycosides have been described[5–7], and the deacetylation of their *N,O*-acetyl derivatives investigated. The mechanism of *O*- and *N*-deacetylation has been elucidated[8]. We now report on a series of *N*-acetyl-*N*-aryl-α-L-arabinopyranosylamines.

The *N*-acetyl derivatives of *N*-*p*-chlorophenyl- (**1**), *N*-*p*-bromophenyl- (**2**), and *N*-*p*-nitrophenyl-α-L-arabinopyranosylamines (**3**) (Table I) were obtained by treatment of the corresponding triacetates[9] with methanolic dimethylamine[10] at room temperature for 36 h. The products, which contained (t.l.c.) small quantities of *N*-aryl-L-arabinopyranosylamines and incompletely deacetylated material, were purified by column chromatography.

Compounds **1**–**3** had i.r. absorptions at 1640–1665, 910–915, and 760–770 cm^{-1} due, respectively, to acetamido C=O, and asymmetrical and symmetrical vibrations of the pyranoside ring[11], and like the analogous derivatives of D-glucose[5], D-galactose[5], and D-xylose[6] were dextrorotatory and did not mutarotate even in the presence of an acidic catalyst. On oxidation of **1**–**3** severally with periodate, ~2 mol. of oxidant were consumed and ~1 mol. of formic acid was released, as expected for pyranosides. The magnitude of the coupling constants ($J_{1,2} = J_{2,3} = 10$, $J_{3,4}$ 3 Hz) for **1** and **2** indicated H-1, H-2, and H-3 to be *ax*, and H-4 to be *eq*, thus confirming the pyranoside structure, *C1* conformation, and α-L configuration.

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were determined with a Hilger–Watts polarimeter.

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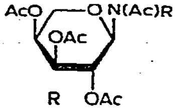
*Ester and ether derivatives of glycopyranosylamines: Part III. For Part II, see *Rocz. Chem.*, 47 (1973) 1389.

TABLE I

DATA ON *N*-ACETYL-*N*-ARYL-α-L-ARABINOPYRANOSYLAMINES

	*Yield* (%)	*M.p.* (*degrees*)	$[\alpha]_D^{20\,a}$ (*degrees*)	*Formula*	*Calc.*		
					C	*H*	*N*
1 *p*-Chlorophenyl	70	155–157	+94	$C_{13}H_{16}ClNO_5$	51.75	5.34	4.64
2 *p*-Bromophenyl	70	194–196	+73	$C_{13}H_{16}BrNO_5$	45.10	4.64	4.04
3 *p*-Nitrophenyl	55	146–148	+88	$C_{13}H_{16}N_2O_7$	50.00	5.12	8.97

[a]Ethanol (*c* 0.5). [b]Carbon tetrachloride–acetone (1:1.5).

T.l.c. was carried out on Kieselgel G, using carbon tetrachloride–acetone (1:1.5), and detection was effected with 5% ethanolic sulphuric acid at ~110°. For column chromatography, Kieselgel (<0.08 mm) was used.

N.m.r. spectra were obtained using a Tesla BS-487 (80 MHz) spectrometer at ambient temperature for solutions in acetone-d_6 containing tetramethylsilane as internal standard. I.r. spectra were recorded with a Perkin–Elmer 257 spectrophotometer on suspensions in paraffin oil.

N-*Acetyl*-N-*aryl*-α-L-*arabinopyranosylamines* (**1–3**). — A solution of 0.01 mole of *N*-acetyl-2,3,4-tri-*O*-acetyl-*N*-*p*-chlorophenyl-α-L-arabinopyranosylamine[9] (or the *p*-bromo or *p*-nitro analogue[9]) in dry methanol (~25 ml) containing 31.5 mmoles of dimethylamine was stored at room temperature and monitored by t.l.c. (carbon tetrachloride–acetone, 3:1). When the starting material had disappeared, the mixture was concentrated under diminished pressure and the residue was eluted from Kieselgel with carbon tetrachloride–acetone (1:1.5).

Compounds **1–3** were crystallised from ethanol, and data on these compounds are recorded in Table I.

Oxidation of **1–3** with periodate was carried out on aqueous solutions by using the method of Jackson and Hudson[11].

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Found			$R_F{}^b$	ν_{max} (*cm*$^{-1}$)	*Periodate oxidation*	
C	*H*	*N*			*Formic acid (mol.)*	*Oxidant uptake (mol.)*
51.25	5.45	4.70	0.30	1665 vs, 915 m, 760 m	1.0	2.0
44.87	4.72	4.15	0.45	1640 vs, 910 m, 765 m	1.1	2.1
49.85	5.18	9.09	0.35	1660 vs, 915 m, 770 m	1.0	2.0

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