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NUCLEOPHILIC DISPLACEMENT REACTIONS OF SOME *N*-ACETYL-*N*-ARYL-β-D-XYLOPYRANOSYLAMINES

ZYGFRYD SMIATACZ
Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk (Poland)

AND ANTONINA MOCZULSKA
Department of Chemistry, The Pedagogical University, 76-200 Słupsk (Poland)

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ABSTRACT

The 4-*O*-methanesulphonyl (and toluene-*p*-sulphonyl), 3,4-di-*O*-methanesulphonyl (and toluene-*p*-sulphonyl), and 3,4-di-*O*-benzoyl-2-*O*-methanesulphonyl derivatives of *N*-acetyl-*N*-*p*-methoxyphenyl- and *N*-acetyl-*N*-*p*-chlorophenyl-β-D-xylopyranosylamine have been synthesised together with the *N*-acetyl-*N*-*p*-methoxyphenyl and *N*-acetyl-*N*-*p*-chlorophenyl derivatives of 3,4-di-*O*-benzoyl-2-*O*-methanesulphonyl-β-D-lyxopyranosylamine. The relative reactivity of the hydroxyl groups of the *N*-acetyl-*N*-aryl-β-D-xylopyranosylamines towards sulphonylation has been established. On heating the 2- and 4-mesylates of *N*-acetyl-*N*-aryl-β-D-xylopyranosylamines and the 2-mesylate of *N*-acetyl-*N*-aryl-β-D-lyxopyranosylamines with sodium azide in *N*,*N*-dimethylformamide or acetonitrile, either nucleophilic replacement of the mesyl groups or their solvolysis with participation of the *N*-acetyl group occurred. In this way, β-D-*xylo* compounds were converted into α-L-*arabino* and β-D-*lyxo* derivatives.

INTRODUCTION

The purpose of this study was to investigate the nucleophilic displacement reactions of derivatives of *N*-acetyl-*N*-aryl-β-D-xylopyranosylamines. The properties of these compounds resemble those of certain nucleosides[1]. The compounds are, however, less complex and more readily accessible. The *N*-acetyl-*N*-aryl-β-D-xylopyranosylamines are model compounds suitable for studying S_N2 reactions in *N*-glycosyl derivatives.

The displacement of the 2-sulphonate groups of glycopyranosides with charged nucleophiles is difficult[2–5], although it has been effected in the β-D-*manno* series[5,6]. In this context, we have studied *N*-glycosyl derivatives, recognising that an AcN-1 group under certain conditions might participate in the displacement of a 2-mesylate group.

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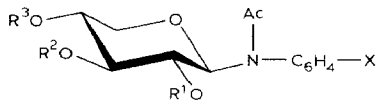
RESULTS AND DISCUSSION

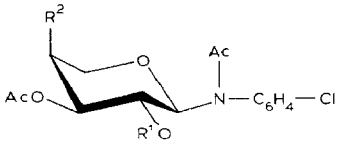
N-Acetyl-*N*-*p*-methoxyphenyl- (**1**) and *N*-acetyl-*N*-*p*-chlorophenyl-β-D-xylopyranosylamine[7] (**2**) were reacted with two equivalents of mesyl chloride in pyridine or dichloromethane in the presence of triethylamine[8]. In each reaction, *N*-acetyl-*N*-aryl-3,4-di- (**3** and **5**) and -4-*O*-methanesulphonyl-β-D-xylopyranosylamines (**4** and **6**) were the products that were isolated by chromatography. The mesylations in dichloromethane were not accompanied by formation of coloured side-products. Thus, the yields of the products, particularly the monosulphonates, were enhanced and their isolation was facilitated.

In order to determine the positions of free hydroxyl groups in **3–6**, the acetates (**7** and **8**) of **5** and **6** were prepared. The positions of unsubstituted hydroxyl groups in **3–6** were then established conventionally by comparison of the n.m.r. data (Table I). That HO-2 in **3–6** was unsubstituted was indicated by a large downfield shift (1.5–1.2 p.p.m.) of the H-2 signal on acetylation. Likewise, HO-3 in **4** and **6** was unsubstituted, because of the downfield shift (1.07–2.40 p.p.m.) of the signal for H-3 on acetylation.

Treatment of **1** with a large excess of tosyl chloride in pyridine or dichloromethane[8] afforded only 3,4-di-*O*- (**9**) and 4-*O*-tosyl (**10**) derivatives. As with the mesylation, higher yields were obtained when dichloromethane was the reaction solvent. As for **3–6**, the n.m.r. data (Table I) showed that HO-2,3 in **10** and HO-2 in **9** were unsubstituted.

The results of mesylation and tosylation show the reactivity sequence HO-4 > HO-3 > HO-2 for **1** and **2**, in contrast to the sequence HO-4 ≈ HO-3 > HO-2





1 X = OMe
2 X = Cl
} $R^1 = R^2 = R^3 = H$

3 X = OMe, $R^1 = H, R^2 = R^3 = Ms$

4 X = OMe, $R^1 = R^2 = H, R^3 = Ms$

5 X = Cl, $R^1 = H, R^2 = R^3 = Ms$

6 X = Cl, $R^1 = R^2 = H, R^3 = Ms$

7 X = Cl, $R^1 = Ac, R^2 = R^3 = Ms$

8 X = Cl, $R^1 = R^2 = Ac, R^3 = Ms$

9 X = OMe, $R^1 = H, R^2 = R^3 = Ts$

10 X = OMe, $R^1 = R^2 = H, R^3 = Ts$

11 X = OMe, $R^1 = Ms, R^2 = R^3 = Bz$

12 X = Cl, $R^1 = Ms, R^2 = R^3 = Bz$

13 $R^1 = Ac, R^2 = N_3$

14 $R^1 = H, R^2 = N_3$

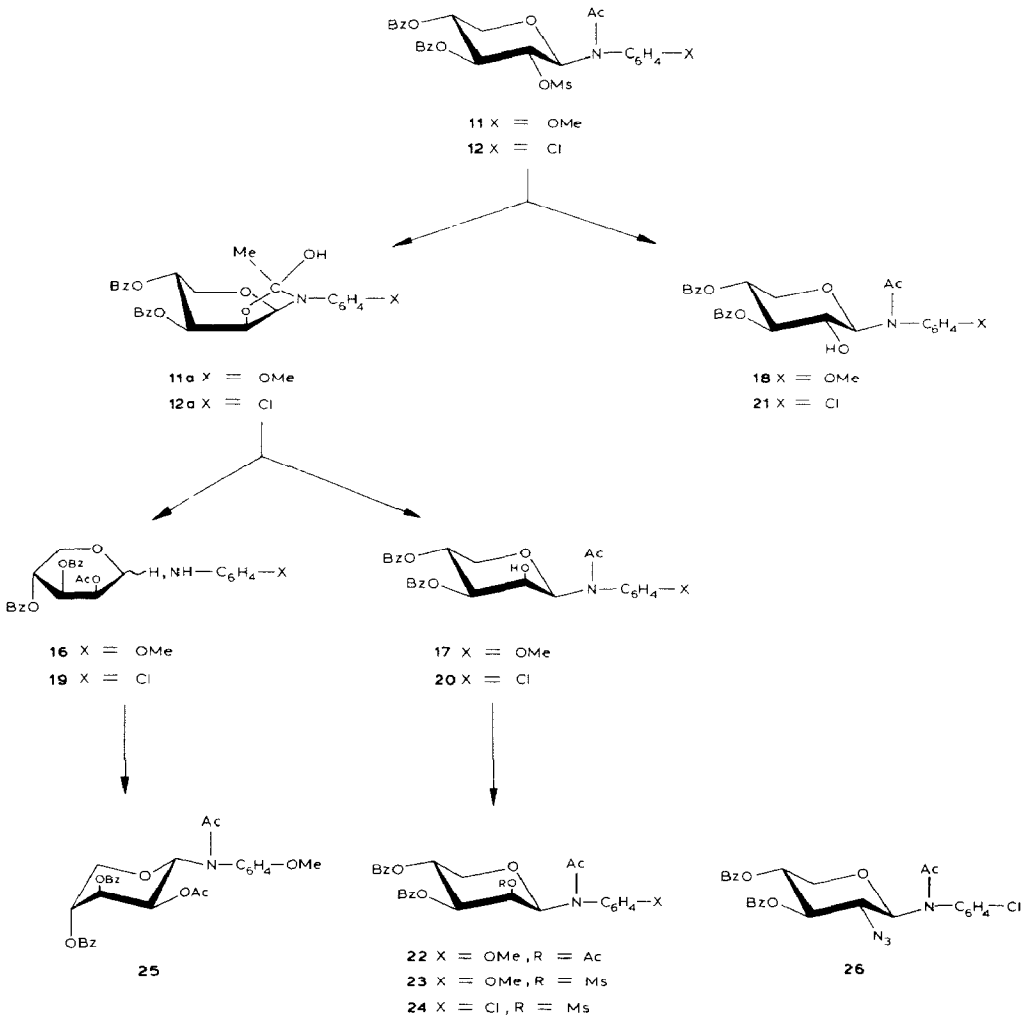
15 $R^1 = Ac, R^2 = NHAc$

TABLE I

^{1}H-N M.R DATA[a] FOR COMPOUNDS **3–6**

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*e	*H-5*a	$\Delta\delta_{H\text{-}5e,H\text{-}5a}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5e}$	$J_{4,5a}$	*NAc*	*OAc*	*OMs*
3	5.82d	3.25dd	4.80dd	4.10——	4.50m	3.90dd	—	10	10	10	—	10	1.75	—	2.97 and 3.05
4	5.73d	3.00dd	3.75dd	4.05——	4.47		—	10	10	10	—	—	1.90	—	3.37
5	5.85d	3.25dd	4.82dd	3.95——	4.40	3.57dd	—	10	10	10	—	10	1.73	—	2.90 and 3.05
6	5.75d	3.00dd	3.75dd	4.00——	4.40m		—	10	10	10	—	—	1.90	—	3.37
7	5.95d	4.57dd	4.85dd	4.00——	4.50	3.85dd	—	9	10	10	—	10	1.75	2.00	3.05 and 2.95
8	5.88d	4.45dd	5.15dd	4.30m	4.10dd	3.50dd	0.60	10	10	9	3	10	1.70	1.88 1.82	2.82
9	5.73d	3.05dd	4.57dd	4.10m	4.00dd	3.37dd	0.63	10	10	10	3	10	1.70	—	—
10	5.55d	2.87dd	3.25dd	4.00m	3.80dd	3.35dd	0.45	10	10	10	3	10	1.70	—	—
11	5.95d	4.85dd	5.75dd	5.00m	4.20dd	3.50dd	0.70	10	10	10	3	10	1.70	—	2.72
12	5.94d	4.80dd	5.77dd	5.00m	4.20dd	3.50dd	0.70	10	10	10	3	10	1.70	—	2.70
13	5.85d	4.70dd	5.05dd	4.00m	3.90dd	3.62dd	0.28	10	10	3	3	3	1.73	1.88 1.85	—
14	5.62d	3.30dd	5.10dd	4.10	—	3.70	—	10	10	—	—	—	1.80	2.00	—
15	6.25d	4.50dd	4.90dd	5.30m	3.90dd	3 62dd	0.28	10	10	3	—	3	1.35 1.70	1.87	—
16	5.78 ——				3.30m	—	—	—	—	—	—	—	—	1.87	—
17	5.67s	4.45dd	5.32dd	5.45m	4.25dd	3.50dd	0.75	—	2	10	3	10	1.67	—	—
18	6.00d	3.30dd	5.62dd	5.04m	4.22dd	3.60dd	0.62	10	10	10	4	10	1.75	—	—
19	5.75 ——					3.22m	—	—	—	—	—	—	—	1.87	—
20	5.70s	4.47dd	5.35dd	5.47m	4.25dd	3.50dd	0.75	—	2	10	3	10	1.67	—	—
21	5.98d	3.30dd	6.55dd	5.05m	4.20dd	3.60dd	0.60	10	10	10	3.5	10	1.75	—	—
22	6.12d	5.69dd	—— 5.45m ——		4.32dd	3.62dd	0.70	2	2	—	3	10	1.37	1.67	—
23	5.90s	5.75d	4.30 ——			3.50m	—	—	2.5	—	—	—	1.63	—	2.7
24	5.97s	5.67m	4.35 ——			3.75m	—	—	—	—	—	—	1.62	—	2.87
25	6.30d	4.65dd	5.62dd	5.05m	4.20dd	4.00dd	0.20	10	3	2.5	3	3	1.67	1.80	—
26	5.70d	3.05dd	5.60dd	4.96m	4.10dd	3.52dd	0.58	10	10	10	3	10	1.75	—	—

[a]Chemical shifts (δ scale): s, singlet; d, doublet; m, multiplet. Coupling constants (±0.5 Hz) were determined by first-order analysis.



for benzoylation[9]. In sulphonylation reactions, there is a more pronounced difference in the reactivities of HO-4 and HO-3. Further, trisulphonates were not formed, whereas tribenzoates are easily obtained[9].

Compounds **11** and **12** were obtained by mesylation of the *N*-acetyl-*N*-*p*-methoxyphenyl and *N*-acetyl-*N*-*p*-chlorophenyl derivatives, respectively, of 3,4-di-*O*-benzoyl-β-D-xylopyranosylamine in pyridine[9]. Attempts to synthesise 2-tosylates under these conditions failed.

On heating **8** in *N*,*N*-dimethylformamide containing sodium azide, MsO-4 was displaced by azide ion, and the main product was *N*-acetyl-2,4-di-*O*-acetyl-4-azido-*N*-*p*-chlorophenyl-4-deoxy-α-L-arabinopyranosylamine (**13**). Under these conditions, AcO-2 was cleaved to a small extent, to give **14**. The $^4C_1$ structure of **13** and **14** was supported by the n.m.r. data ($J_{1,2}$ 10, $J_{2,3}$ 10, $J_{3,4} = J_{5a,4}$ = 3 Hz, $\Delta\delta_{5e,5a}$

TABLE II

PRODUCTS OF SOLVOLYSIS OF COMPOUNDS **11** AND **12**

Compound	*Yield (%) in*		*M p. (degrees)*	$[\alpha]_D$ *(c 0 5) (degrees)*	ν_{max} *(cm^{-1})*				R_F[a]	*Molecular formula*	*Analysis (%)*					
	CH_3CN	$HCONMe_2$			*OH*	*NH*	*C=O (ester*	*C=O (amide)*			*C*		*H*		*N*	
											Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
16	65	60	140–145	−52	—	3380	1735	—	0 80		66.53	66.70	5 34	5.56	2 77	2.91
17	17	18	172–175	−65	3280	—	1735	1630	0 62	$C_{28}H_{27}NO_8$	66 53	66.24	5.34	5 46	2.77	3 00
18	5	6	193–195	−47	3270	—	1725	1640	0 56		66.53	66.30	5 34	5.20	2.77	2.80
			lit.[9] 195–196	lit [9] −45	lit [9] 3270		lit.[9] 1720	lit [9] 1640								
19	20	22	syrup	−80	—	3380	1735	—	0 66		63 59	63.45	4.71	4 80	2.75	2 81
20	63	64	194–198	−54	3285	—	1740	1640	0 47	$C_{27}H_{24}ClNO_7$	63.59	63 44	4.71	4.58	2 75	2 70
21	6	6	76–78	−17	3350	—	1730	1650	0 75		63 59	63 42	4 71	4 62	2.75	2 70
			lit [9] 72–75	lit [9] −16	lit [9] 3360		lit [9] 1725	lit [9] 1668								

[a]Solvent C

~0.28 p.p.m.). Hydrogenolysis of **13** over Pd/C and acetylation of the product gave 4-acetamido-*N*-acetyl-2,3-di-*O*-acetyl-*N*-*p*-chlorophenyl-4-deoxy-α-L-arabino-pyranosylamine (**15**). Attempts to displace MsO-4 of **8** in acetonitrile by azide ion failed.

In *N,N*-dimethylformamide or acetonitrile at 80°, **11** reacted with azide ion to give the D-*lyxo* products **16** and **17**, and the D-*xylo* product **18**. Similarly, **12** afforded **19, 20** (D-*lyxo*), and **21** (D-*xylo*). The structures of **16** and **19** were elucidated as follows. Each compound showed i.r. absorption for NH but not for amide C=O. The n.m.r. spectra indicated the presence of an *O*-acetyl group (δ ~1.87, Table I), but neither the configuration nor the conformation could be established on the basis of the n.m.r. data. Acetylation of **16** gave *N*-acetyl-2-*O*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-methoxyphenyl-α-D-lyxopyranosylamine (**25**), which was identified on the basis of the i.r. band at 1690 cm^{-1} (amide C=O) and the n.m.r. data [δ ~1.80 (OAc) and ~1.67 (NAc); $J_{1,2}$ 10, $J_{2,3}$ 3, $J_{3,4}$ 2.5 Hz, $\Delta\delta_{5e,5a}$ ~0.20 p.p.m.]. The results accord with those reported[10] for *N*-acetyl-*N*-aryl-α-D-lyxopyranosylamines ($^1C_4$).

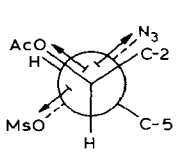
The identification of the solvolysis products **17** and **20** as *N*-acetyl-*N*-aryl-3,4-di-*O*-benzoyl-β-D-lyxopyranosylamines with the $^4C_1$ conformation was also based on the i.r. [ν_{max} 3280 (OH) and 1635 cm^{-1} (C=O amide) and ^{1}H-n.m.r. data [δ ~1.67 (NAc), $J_{2,3}$ 2, $J_{3,4} = J_{4,5a}$ = 10 Hz, $\Delta\delta_{5e,5a}$ ~0.7 p.p.m.]. The n.m.r. data accorded with those[10] of the *N*-acetyl-*N*-aryl-β-D-lyxopyranosylamines ($^4C_1$). That HO-2 in **17** and **20** was unsubstituted was established by comparison of the n.m.r. data with those of **22–24**. There is a downfield shift (~1 p.p.m.) of the H-2 signal on acetylation or mesylation (Table I).

The properties of **18** and **21** resemble those of the *N*-acetyl-*N*-*p*-methoxyphenyl and *N*-acetyl-*N*-*p*-chlorophenyl derivatives of 3,4-di-*O*-benzoyl-β-D-xylopyranosylamine, respectively[9] (Table II).

Thus, heating solutions of **11** and **12** in *N,N*-dimethylformamide or in acetonitrile containing sodium azide results mostly in solvolysis of MsO-2 with participation of the *N*-acetyl group, *O*-desulphonylation (→**18** and **21**) occurring to only a small extent. The displacement of MsO-2 by azide does not occur, probably due, as for glycosides[3], to unfavourable steric and polar interactions in the transition state (see **28**).

The yields of the D-*lyxo* products are dependent on the nature of the aglycon (Table II), which is likely to affect the polarity of the O–C and N–C bonds in the cyclic intermediates (**11a** and **12a**), which, in turn, is crucial for the direction of ring opening. Consequently, **11** afforded mostly **16**, a product of cleavage of the C–N bond in **11a**, whereas **12** gave **20** in a higher yield, arising by rupture of the C–O bond in **12a**.

Despite unfavourable interactions in the transition state (see **29**), azide displacement of MsO-2 in **24** occurs when *N,N*-dimethylformamide is the reaction solvent. Under these conditions, the exclusive product was *N*-acetyl-2-azido-3,4-di-*O*-benzoyl-*N*-*p*-chlorophenyl-2-deoxy-β-D-xylopyranosylamine (**26**), which



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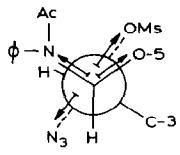

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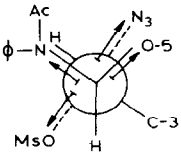

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adopts the $^4C_1$ conformation as demonstrated by the i.r. [ν_{max} 2100 cm^{-1} (N_3)] and n.m.r. data ($J_{1,2} = J_{2,3} = 10$ Hz; diamagnetic shift of the H-2 signal by ~1.6 p.p.m.). Compounds **23** and **24** were stable when heated in acetonitrile in the presence of the azide ion, probably because of the *cis*-relationship of the MsO-2 and *N*-Ac groups.

It is concluded that the reactivity of the OMs group declines in the series MsO-4 (β-D-*xylo*, **7**) > MsO-2 (β-D-*lyxo*, **24**) > MsO-2 (β-D-*xylo*, **11** or **12**). The observed differences in the reactivity of this group can be elucidated in terms of Richardson's findings[3] concerning the steric and polar interactions in the transition state. The interactions are illustrated by viewing projections along the C-3–C-4 (β-D-*xylo*, **27**), C-1–C-2 (β-D-*lyxo*, **28**), and C-1–C-2 (β-D-*xylo*, **29**) bonds.

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were determined (Hilger–Watt instrument) for solutions in chloroform. T.l.c. was performed on silica gel G with *A*, carbon tetrachloride–acetone (1:1); *B*, carbon tetrachloride–acetone (3:1); or *C*, benzene–acetone (6:1). Column chromatography was performed on Kieselgel (<0.08 mm). ^{1}H-N.m.r. spectra ($CDCl_3$, internal Me_4Si) were recorded with a Tesla BS 487C (80 MHz) spectrometer. I.r. spectra were recorded for Nujol mulls with a Perkin–Elmer 257 spectrophotometer.

N-*Acetyl*-N-*aryl*-O-*sulphonyl*-β-D-*xylopyranosylamines* (**3–8**). — (*a*) To a solution of *N*-acetyl-*N*-*p*-methoxyphenyl-β-D-xylopyranosylamine[7] (**1**, 0.01 mol) in dry pyridine (15 mL) at 0° was added methanesulphonyl chloride (0.02 mol) in pyridine (3 mL), and the solution was kept for 6 h at room temperature. T.l.c. (solvent *A*) then indicated almost complete conversion of **1** into two major products and four other products. The mixture was poured into ice–water (100 mL), the brown precipitate was collected and washed with water, and a solution in chloroform (150 mL) was washed with water, dried ($MgSO_4$), and concentrated to dryness. Column chromatography of the residue (solvent *A*) gave first *N*-acetyl-3,4-di-*O*-methanesulphonyl-*N*-*p*-methoxyphenyl-β-D-xylopyranosylamine (**3**, 15%), m.p. 60°, $[\alpha]_D^{20}$ +26°, R_F (solvent *C*) 0.60; ν_{max} 3300 (OH), 1660 (amide C=O), and 1163 cm^{-1} (OMs).

Anal. Calc. for $C_{16}H_{23}NO_{10}S$: C, 42.38; H, 5.07; N, 3.09. Found: C, 42.67; H, 5.00; N, 3.01.

Eluted second was *N*-acetyl-4-*O*-methanesulphonyl-*N*-*p*-methoxyphenyl-β-D-

xylopyranosylamine (**4**, 19%), m.p. 151–154°, $[\alpha]_D^{20}$ +45°, R_F 0.50; ν_{max} 3260 (OH), 1645 (amide C=O), and 1165 cm^{-1} (OMs).

Anal. Calc. for $C_{15}H_{21}NO_8S$: C, 48.00; H, 5.06; N, 3.73. Found: C, 48.18; H, 5.02; N, 3.87.

Likewise, *N*-acetyl-*N*-*p*-chlorophenyl-β-D-xylopyranosylamine[7] (**2**) gave *N*-acetyl-*N*-*p*-chlorophenyl-3,4-di-*O*-methanesulphonyl-β-D-xylopyranosylamine (**5**, first fraction, 14%), m.p. ~70°, $[\alpha]_D^{20}$ +22°, R_F 0.68; ν_{max} 3300 (OH), 1670 (amide C=O), and 1165 cm^{-1} (OMs).

Anal. Calc. for $C_{15}H_{20}ClNO_9S$: C, 39.34; H, 4.37; N, 3.06. Found: C, 39.51; H, 4.56; N, 3.20.

The second fraction was *N*-acetyl-*N*-*p*-chlorophenyl-4-*O*-methanesulphonyl-β-D-xylopyranosylamine (**6**, 17%), m.p. 183–185°, $[\alpha]_D^{20}$ −8°, R_F 0.51; ν_{max} 3260 and 3350 (OH), 1660 (amide C=O), and 1170 cm^{-1} (OMs).

Anal. Calc. for $C_{14}H_{18}ClNO_7S$: C, 44.26; H, 4.74; N, 3.69. Found: C, 44.42; H, 4.94; N, 3.72.

Conventional treatment of **5** with acetic anhydride–pyridine and crystallisation of the crude product from methanol afforded *N*-acetyl-2-*O*-acetyl-*N*-*p*-chlorophenyl-3,4-di-*O*-methanesulphonyl-β-D-xylopyranosylamine (**7**, 50%), m.p. 183–185°, $[\alpha]_D^{20}$ +30°, R_F (solvent *A*) 0.75; ν_{max} 1760 (ester C=O), 1695 (amide C=O), and 1168 cm^{-1} (OMs).

Anal. Calc. for $C_{17}H_{22}ClNO_{10}S$: C, 40.84; H, 4.40; N, 2.80. Found: C, 40.83; H, 4.44; N, 2.99.

Likewise, **6** gave *N*-acetyl-2,3-di-*O*-acetyl-*N*-*p*-chlorophenyl-4-*O*-methanesulphonyl-β-D-xylopyranosylamine (**8**, 67%), m.p. 159–162°, $[\alpha]_D^{20}$ +6°, R_F 0.78; ν_{max} 1765 (ester C=O), 1680 (amide C=O), and 1165 cm^{-1} (OMs).

Anal. Calc. for $C_{18}H_{22}ClNO_9S$: C, 46.60; H, 4.75; N, 3.02. Found: C, 46.91; H, 5.01; N, 3.30.

(*b*) To a solution of **1**[7] (0.01 mol) in dichloromethane (15 mL) at 0° was added mesyl chloride (0.02 mol) followed, after 3 min, by triethylamine (1 mL) with stirring. The mixture was kept for 6 h at room temperature. T.l.c. (solvent *A*) then revealed the conversion of most of **1** into two major products. Ice–water (250 mL) was added to the mixture, the aqueous layer was decanted, and a solution of the sticky precipitate in chloroform (150 mL) was dried ($MgSO_4$) and concentrated. Column chromatography of the residue (solvent *A*) gave **3** (22%) and **4** (29%), respectively.

Likewise, **2** gave **5** (19%) and **6** (25%), respectively.

(*c*) Compound **1**[7] (0.01 mol) was treated with chloride (0.04 mol) as in (*a*). The crude product was chromatographed (solvent *A*) to give, first, *N*-acetyl-*N*-*p*-methoxyphenyl-3,4-di-*O*-toluene-*p*-sulphonyl-β-D-xylopyranosylamine (**9**, 18%), m.p. 80–86°, $[\alpha]_D^{20}$ +19°, R_F (solvent *A*) 0.72; ν_{max} 3400 (OH) and 1670 cm^{-1} (amide C=O).

Anal. Calc. for $C_{28}H_{31}NO_{10}S$: C, 55.53; H, 5.12; N, 2.31. Found: C, 55.17; H, 5.32; N, 2.33.

Eluted second was *N*-acetyl-*N*-*p*-methoxyphenyl-4-*O*-toluene-*p*-sulphonyl-β-D-xylopyranosylamine (**10**, 15%), m.p. 148–150°, $[\alpha]_D^{20}$ +39°, R_F 0.48; ν_{max} 3460 and 3360 (OH), and 1690 cm^{-1} (amide C=O).

Anal. Calc. for $C_{21}H_{25}NO_8S$: C, 55.87; H, 5.54; N, 3.10. Found: C, 56.14; H, 5.69; N, 3.46.

(*d*) Compound **1**[7] (0.01 mol) was treated with tosyl chloride (0.04 mol) in dichloromethane (20 mL) in the presence of triethylamine (1 mL) as in (*b*). Column chromatography of the crude product (solvent *A*) gave **9** (22%) and **10** (28%), respectively.

N-*Acetyl*-N-p-*methoxyphenyl* (**11**) *and* N-*acetyl*-N-p-*chlorophenyl* (**12**) *derivatives of 3,4-di*-O-*benzoyl-2*-O-*methanesulphonyl*-β-D-*xylopyranosylamine.* — A solution of *N*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-methoxyphenyl-β-D-xylopyranosylamine[9] (0.01 mol) in pyridine (20 mL) at 0° was treated with methanesulphonyl chloride (0.04 mol). The mixture was kept for 1 h at ~0° and then for 3 h at 20°. T.l.c. (solvent *B*) then indicated complete conversion of the substrate into one product. Water (3 mL) was added and, after 20 min, the solution was poured into ice–water (250 mL). The crude sulphonate was collected, washed with water, and crystallised from methanol to afford **11** (78%), m.p. 136–141°, $[\alpha]_D^{20}$ −66°, R_F (solvent *B*) 0.72; ν_{max} 1725 (ester C=O) and 1680 cm^{-1} (amide C=O).

Anal. Calc. for $C_{29}H_{29}NO_{10}S$: C, 59.69; H, 4.97; N, 2.40. Found: C, 59.59; H, 4.90; N, 2.40.

Likewise, *N*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-chlorophenyl-β-D-xylopyranosylamine[9] gave **12** (62%), m.p. 139–145°, $[\alpha]_D^{20}$ −56°, R_F (solvent *B*) 0.70; ν_{max} 1730 (ester C=O) and 1680 cm^{-1} (amide C=O).

Anal. Calc. for $C_{28}H_{26}ClNO_9S$: C, 57.19; H, 4.42; N, 2.38. Found: C, 57.10; H, 4.48; N, 2.86.

When tosylation of the *N*-acetyl-*N*-aryl-3,4-di-*O*-benzoyl-β-D-xylopyranosylamines was attempted under these conditions, no reaction occurred.

N-*Acetyl-2,3-di*-O-*acetyl-4-azido*-N-p-*chlorophenyl-4-deoxy-* (**13**) *and* N-*acetyl-3*-O-*acetyl-4-azido*-N-p-*chlorophenyl-4-deoxy*-α-L-*arabinopyranosylamine* (**14**). — A mixture of **8** (1.5mmol) and sodium azide (60 mmol) in *N,N*-dimethylformamide (15 mL) was heated at ~125° for 8 h. T.l.c. (solvent *C*) then indicated complete conversion of **8** into two major products and a small proportion of a third product. The mixture was treated with ether, filtered, diluted with chloroform (200 mL), washed with water (3 × 50 mL), dried (Na_2SO_4), and concentrated to dryness. Column chromatography of the residue (solvent *C*) gave, first, **13** as a syrup (~50%), $[\alpha]_D^{22}$ −32°, R_F (solvent *C*) 0.43; ν_{max} 2100 (N_3), 1750 (ester C=O), and 1680 cm^{-1} (amide C=O).

Anal. Calc. for $C_{17}H_{19}ClN_4O_6$: C, 49.69; H, 4.62; N, 13.64. Found: C, 49.90; H, 4.58; N, 13.48.

Eluted second was **14** (syrup, 10%), $[\alpha]_D^{22}$ +83°, R_F 0.30; ν_{max} 3350 (OH), 2100 (N_3), 1750 (ester C=O), and 1670 cm^{-1} (amide C=O).

Anal. Calc. for $C_{15}H_{17}ClN_4O_5$: C, 49.24; H, 4.61; N, 15.19. Found: C, 49.38; H, 4.87; N, 14.86.

*4-Acetamido-*N*-acetyl-2,3-di-*O*-acetyl-*N*-p-chlorophenyl-4-deoxy-α-*L*-arabinopyranosylamine* (**15**). — A solution of **13** (6 mmol) in methanol (15 mL) was stirred under hydrogen (1 atmos.) in the presence of 5% Pd/C (200 mg) for 6 h at ~20°. The catalyst was than removed, the filtrate was concentrated, and the residue was treated with pyridine–acetic anhydride. The product was crystallised from ethanol to give **15** (53%), m.p. 110–112°, $[\alpha]_D^{20}$ +43°, R_F (solvent *B*) 0.24; ν_{max} 3260 (NH), 1750 (ester C=O), 1660 and 1760 cm^{-1} (amide C=O).

Anal. Calc. for $C_{19}H_{23}ClN_2O_7$: C, 53.33; H, 5.61; N, 6.55. Found: C, 53.37; H, 5.48; N, 6.19.

Solvolyses of N*-acetyl-*N*-p-methoxyphenyl* (**11**) *and* N*-acetyl-*N*-p-chlorophenyl* (**12**) *derivatives of 3,4-di-*O*-benzoyl-2-*O*-methylsulphonyl-β-*D*-xylopyranosylamine.* — A mixture of **11** (0.01 mol), sodium azide (0.04 mol), and *N,N*-dimethylformamide or acetonitrile (15 mL) was stirred at ~80° for 6 h. Complete conversion of **11** into three new products was then revealed by t.l.c. (solvent *C*). The mixture was treated with anhydrous ether, filtered, diluted with chloroform (250 mL), washed with water (3 × 40 mL), dried ($MgSO_4$), and concentrated to dryness. Column chromatography of the residue (solvent *C*) gave 2-*O*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-methoxyphenyl-D-lyxopyranosylamine (**16**), *N*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-methoxyphenyl-β-D-lyxopyranosylamine (**17**), and *N*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-methoxyphenyl-β-D-xylopyranosylamine (**18**), respectively (see Table II).

Likewise, **12** gave 2-*O*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-chlorophenyl-D-lyxopyranosylamine (**19**), *N*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-chlorophenyl-β-D-lyxopyranosylamine (**20**), and *N*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-chlorophenyl-β-D-xylopyranosylamine (**21**) (see Table II).

Conventional treatment of **17** with acetic anhydride–pyridine and crystallisation of the crude product from ethanol afforded *N*-acetyl-2-*O*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-methoxyphenyl-β-D-lyxopyranosylamine (**22**, 82%), m.p. 124–131°, $[\alpha]_D^{21}$ −51°, R_F (solvent *C*) 0.72; ν_{max} 1760 and 1740 (ester C=O), and 1690 cm^{-1} (amide C=O).

Anal. Calc. for $C_{30}H_{29}NO_9$: C, 65.81; H, 5.30; N, 2.55. Found: C, 65.68; H, 5.46; N, 2.98.

Compound **17** (1 mmol) was treated with methanesulphonyl chloride (5 mmol) in pyridine as described in (*a*) for **1**. Chromatography (solvent *C*) of the crude product gave *N*-acetyl-3,4-di-*O*-benzoyl-2-*O*-methanesulphonyl-*N*-*p*-methoxyphenyl-β-D-lyxopyranosylamine (**23**, 90%), m.p. 83–86°, $[\alpha]_D^{20}$ −62°, R_F (solvent *C*) 0.69; ν_{max} 1740 (ester C=O) and 1670 cm^{-1} (amide C=O).

Anal. Calc. for $C_{29}H_{29}NO_{10}S$: C, 59.69; H, 4.97; N, 2.40. Found: C, 59.70; H, 4.78; N, 2.53.

Likewise, **20** gave *N*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-chlorophenyl-2-*O*-

methanesulphonyl-β-D-lyxopyranosylamine (**24**, 85%), m.p. 94–100°, $[\alpha]_D^{20}$ −60°, R_F (solvent *C*) 0.54; ν_{max} 1740 (ester C=O) and 1675 cm^{-1} (amide C=O).

Anal. Calc. for $C_{28}H_{26}ClNO_9S$: C, 57.19; H, 4.42; N, 2.38. Found: C, 57.21; H, 4.61; N, 2.20.

Treatment[11] of **16** (1 mmol) with acetic anhydride (15 mL) and zinc chloride (0.05 g) afforded *N*-acetyl-2-*O*-acetyl-3,4-di-*O*-benzoyl-*N*-*p*-methoxyphenyl-α-D-lyxopyranosylamine (**25**, 55%), m.p. 165–169°, $[\alpha]_D^{20}$ −54°, R_F (solvent *C*) 0.75; ν_{max} 1750 and 1725 (ester C=O), and 1680 cm^{-1} (amide C=O).

Anal. Calc. for $C_{30}H_{29}NO_9$: C, 65.81; H, 5.30; N, 2.55. Found: C, 66.02; H, 5.28; N, 2.47.

N-*Acetyl-2-azido-3,4-di-*O*-benzoyl-*N-p-*chlorophenyl-β-D-xylopyranosylamine* (**26**). — (*a*) A mixture of **24** (3 mmol) and sodium azide (12 mmol) in *N,N*-dimethylformamide (5 mL) was stirred at ~130° for 48 h. Complete conversion of **24** into one new major product and a very small proportion of two other products was then revealed by t.l.c. (solvent *C*). The mixture was processed as described above for **13** and **14**. Column chromatography (solvent *C*) of the crude product furnished **26** as a syrup (30%), $[\alpha]_D^{22}$ −56°, R_F (solvent *C*) 0.68; ν_{max} 2120 (N_3), 1735 (ester C=O), and 1685 cm^{-1} (amide C=O).

Anal. Calc. for $C_{27}H_{23}ClNO_6$: C, 60.61; H, 4.30; N, 10.47. Found: C, 60.35; H, 4.52; N, 10.26.

(*b*) A solution of **23** or **24** (3 mmol) and sodium azide (12 mmol) in acetonitrile (5 mL) was heated at 80° for 48 h. T.l.c. (solvent *C*) then indicated that no reaction had occurred.

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