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Note

Crystal structure of *N*-(tri-*O*-acetyl-α-D-xylopyranosyl)pyridinium bromide

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Abstract

The structure of *N*-(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)pyridinium bromide was determined by X-ray crystallography and ^{1}H NMR spectroscopy. Two xylopyranosyl moieties crystallize with three water molecules and there is a novel pattern of Br^- and H_2O contacts. Both xylopyranosyl rings in the asymmetric unit have the $^1C_4$ conformation, with all three axial *O*-Ac groups.

Keywords: Pyridinium salt; ^{1}H NMR; X-ray crystallography

Only a few *N*-glycopyranosylpyridinium salts have been obtained previously, and none have been subjected to X-ray crystallography. Instead, they have been studied only by ^{1}H NMR spectroscopy.[1–7] Per-*O*-acetyl-glycopyranosyl bromides are suitable substrates for N-glycosylation (quaternization) of pyridine and its derivatives. Very recently we described the crystal structures of *N*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-pyridinium chloride[8] and *N*-(β-D-galactopyranosyl)pyridinium bromide and its per-*O*-acetylated derivative.[9] Now we report the crystal structure of *N*-(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)pyridinium bromide.

The reaction of 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl bromide with dry pyridine at ambient temperature produces a mixture of α and β anomers in a 3:1 ratio (Scheme 1).[10]

In our hands, the title compound was easily isolated after crystallization from 10:1 ethanol–ethyl acetate and recrystallized from acetone. Its high resolution ^{1}H NMR spectrum shows five broad pseudo-singlets from the sugar-ring hydrogen atoms which indicates the α anomeric configuration and the $^1C_4$-(D) conformation of the pyranoid ring in solution. The pyridyl residue, with its nitrogen atom formally bearing a +1 charge, has an equatorial orientation and all three *O*-acetyl groups of the sugar moiety are axial. The lack of a terminal primary alcohol group in these xylopyranosyl derivatives is probably responsible for the predominant formation of the α

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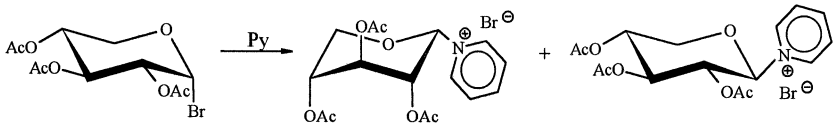
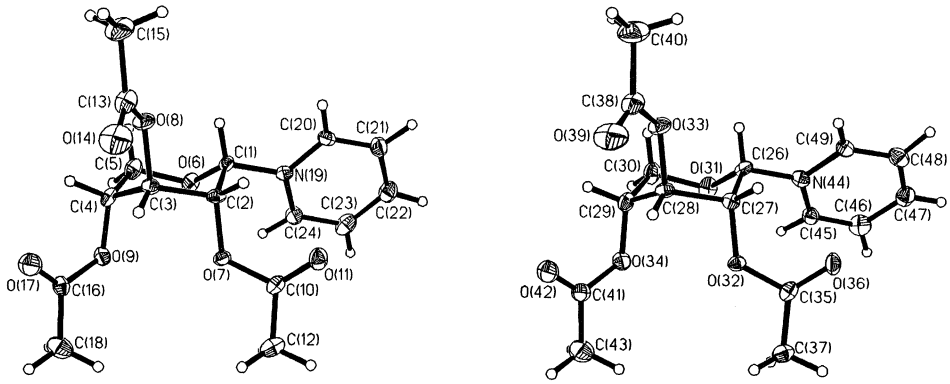


Scheme 1. Formation of *N*-(2,3,4-tri-*O*-acetyl-α- and -β-D-xylopyranosyl)pyridinium bromide.

anomer. Elemental analysis indicates that the title compound crystallizes as a hydrate in a ratio of two salts molecules to three of waters. This was confirmed by X-ray crystallography, which showed two molecules of the salt and three water molecules in the asymmetric unit. The two cations are shown in Fig. 1.

The details of the crystallographic determination are summarized in Table 1.

Bond lengths and angles agree well with expected values.[11] In the crystal, both cations (**A** and **B**) have six-membered pyranoid rings in the $^1C_4$-(D) conformation with axial acetyl groups, as found in solution. Ring puckering parameters are: $Q = 0.541(6)$, $\phi = -149(4)°$ and $Q = 0.560(7)$, $\phi = -150(5)°$, respectively.[12] The same $^1C_4$-(D) conformation for this compound was also concluded from the ^{1}H NMR spectrum in a solution.



cation A **cation B**

Fig. 1. View of two cations of molecules **A** and **B** forming independent cell showing 50% probability for ellipsoids.

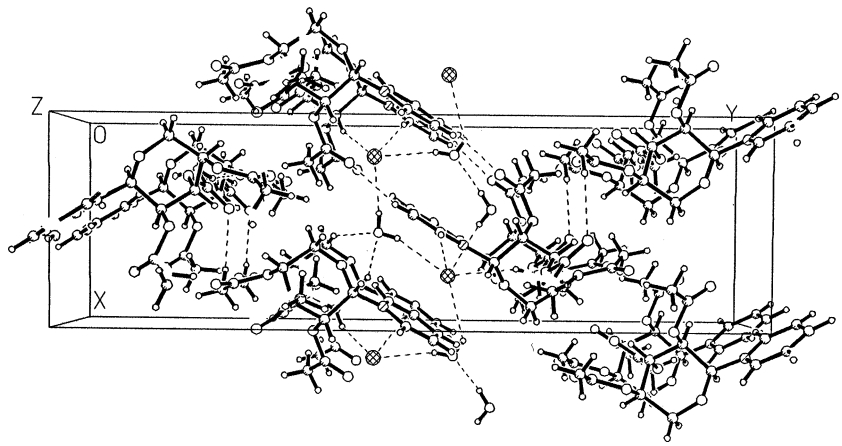


Fig. 2. Packing of *N*-(tri-*O*-acetyl-α-D-xylopyranosyl)pyridinium bromide hydrate (2:3) with hydrogen bonds and the shortest contacts shown (contacts between N^+ and neighboring Br^- lie within 4.22–5.13 Å).

Table 1
Crystal data and structure refinement for *N*-(tri-*O*-acetyl-α-D-xylopyranosyl)pyridinium bromide hydrate (2:3)

Empirical formula	$C_{16}H_{23}BrNO_{8.5}$ ($C_{16}H_{20}BrNO_7 \cdot 3/2\ H_2O$)
Formula weight	445.26
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	monoclinic, $P2_1$
Unit cell dimensions	
a (Å)	8.341(2)
b (Å)	27.711(6)
c (Å)	8.667(2)
β (°)	92.29(3)
V (Å^3)	2001.7(8)
Z	4
D_{calcd} (Mg m^{-3})	1.478
Absorption coefficient (mm^{-1})	2.097
$F(000)$	916
Crystal size (mm)	$0.3 \times 0.3 \times 0.5$
θ Range for data collection (°)	1.47–30.09
Index ranges	$-11 \le h \le 8,\ -39 \le k \le 0,\ -8 \le l \le 12$
Reflections collected/unique	6118/5867 [$R_{int} = 0.0681$]
Completeness to $\theta = 30.09$	97.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5867/3/478
Goodness-of-fit on F^2	1.020
Reflections [$I > 2\sigma > (I)$]	1063
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0389,\ wR_2 = 0.1018$
R indices (all data)	$R_1 = 0.2223,\ wR_2 = 0.1484$
Absolute structure parameter [a]	−0.024(11)
Largest difference peak and hole (e Å^{-3})	0.549 and −0.390

[a] The Flack's parameter together with NMR data and known configuration of substrate evidently indicate the configuration of the sugar moiety in the title salt.

Table 2
Selected bond lengths for two molecules of *N*-(tri-*O*-acetyl-α-D-xylopyranosyl)pyridinium bromide hydrate (2:3)

Molecule **A**		Molecule **B**	
Bond length (Å)			
C-1–O-6	1.389(7)	C-26–O-31	1.413(8)
C-1–N-19	1.485(8)	C-26–N-44	1.462(8)
C-1–C-2	1.518(9)	C-26–C-27	1.515(9)
C-2–O-7	1.440(6)	C-27–O-32	1.446(7)
C-2–C-3	1.515(9)	C-27–C-28	1.528(9)
C-3–O-8	1.446(7)	C-28–O-33	1.421(7)
C-3–C-4	1.522(9)	C-28–C-29	1.546(8)
C-4–O-9	1.416(7)	C-29–O-34	1.426(8)
C-4–C-5	1.527(9)	C-29–C-30	1.503(9)
C-5–O-6	1.423(8)	C-30–O-31	1.416(8)

The most important values of bond lengths and torsion angles describing molecules **A** and **B** are collected in Tables 2 and 3, respectively. The atomic coordinates of the non-hydrogen atoms are listed in Table 4.

We found the hydrogen bonding system that is displayed in Fig. 2. Hydrogen atoms of three water molecules and two bromide ions form a flat, ten-membered ring of hydrogen-bonded species. Each ring of this type is joined to the next ring by hydrogen bond formed between an exo-cyclic hydrogen atom of a water molecule and the bromide anion of the next ring. The rings form a chain along the *a*-direction (Fig. 2).

The relevant lengths and angles of the hydrogen bond system are collected in Table 5.

1. Experimental

General methods.—A Mercury-400BB (400 MHz) spectrometer with D_2O as solvent and acetone as the external standard, and 2D

Table 3
Selected torsion angles (°) for two molecules of *N*-(tri-*O*-acetyl-α-D-xylopyranosyl)pyridinium bromide hydrate (2:3)

Molecule **A**		Molecule **B**	
*Dihedral angle (°)*a			
N-19–C-1–C-2–O-7	−62.7(6)	N-44–C-26–C-27–O-32	−61.1(6)
N-19–C-1–C-2–C-3	−177.5(5)	N-44–C-26–C-27–C-28	−177.1(5)
O-7–C-2–C-3–O-8	174.6(4)	O-32–C-27–C-28–O-33	176.3(4)
C-1–C-2–C-3–O-8	−67.9(5)	C-26–C-27–C-28–O-33	−64.7(6)
O-7–C-2–C-3–C-4	−69.4(6)	O-32–C-27–C-28–C-29	−69.4(6)
C-1–C-2–C-3–C-4	48.1(6)	C-26–C-27–C-28–C-29	49.6(6)
O-8–C-3–C-4–O-9	−167.9(4)	O-33–C-28–C-29–O-34	−171.9(5)
C-2–C-3–C-4–O-9	76.0(6)	C-27–C-28–C-29–O-34	73.6(6)
C-2–C-3–C-4–C-5	−44.7(7)	C-27–C-28–C-29–C-30	−46.9(7)
C-3–C-4–C-5–O-6	49.3(7)	C-28–C-29–C-30–O-31	52.3(7)
O-6–C-1–N-19–C-20	152.9(5)	O-31–C-26–N-44–C-49	160.1(5)

Table 4
Atomic coordinates and equivalent isotropic displacement parameters for *N*-(tri-*O*-acetyl-α-D-xylopyranosyl)pyridinium bromide hydrate (2:3)

	x	*y*	*z*	U_{eq}
C-1	3227(7)	1155(2)	798(6)	32(1)
C-2	4423(7)	1548(2)	439(6)	35(1)
C-3	3513(7)	1981(2)	−208(6)	33(1)
C-4	2092(7)	2127(2)	735(6)	37(1)
C-5	1121(8)	1685(3)	1180(9)	49(2)
O-6	2111(5)	1313(2)	1832(5)	43(1)
O-7	5209(5)	1714(2)	1850(4)	36(1)
O-8	2841(6)	1834(2)	−1699(4)	46(1)
O-9	2607(5)	2372(2)	2102(5)	40(1)
C-10	6711(7)	1532(3)	2243(7)	38(1)
O-11	7333(6)	1235(2)	1488(6)	52(1)
C-12	7373(9)	1764(3)	3645(9)	61(2)
C-13	3334(9)	2055(3)	−2973(8)	49(2)
O-14	4327(9)	2364(3)	−2918(6)	84(2)
C-15	2506(12)	1867(4)	−4400(8)	74(3)
C-16	2974(8)	2844(2)	1947(8)	41(2)
O-17	2875(7)	3045(2)	739(6)	65(1)
C-18	3559(11)	3058(3)	3443(9)	68(2)
N-19	4029(6)	725(2)	1503(6)	36(1)
C-20	4637(8)	393(2)	543(7)	42(2)
C-21	5465(9)	15(3)	1110(9)	53(2)
C-22	5714(9)	−38(3)	2691(9)	55(2)
C-23	5091(9)	300(3)	3657(9)	60(2)
C-24	4233(8)	686(2)	3037(7)	44(2)
Br-25	−1712(1)	−583(1)	−3888(1)	86(1)
C-26	1757(7)	−816(2)	−55(7)	40(2)
C-27	521(7)	−1207(2)	−388(6)	32(1)
C-28	1345(7)	−1634(2)	−1139(6)	34(1)
C-29	2892(7)	−1789(2)	−229(7)	41(2)
C-30	3902(8)	−1354(3)	175(9)	50(2)
O-31	3021(5)	−992(2)	924(5)	47(1)
O-32	−103(5)	−1389(1)	1031(4)	35(1)
O-33	1865(5)	−1461(2)	−2579(5)	48(1)
O-34	2518(6)	−2033(2)	1160(5)	44(1)
C-35	−1560(7)	−1224(3)	1492(8)	39(2)
O-36	−2214(5)	−890(2)	835(6)	51(1)
C-37	−2104(8)	−1497(3)	2782(8)	50(2)
C-38	1416(9)	−1694(3)	−3882(7)	52(2)
O-39	630(9)	−2045(3)	−3905(6)	89(2)
C-40	2094(13)	−1439(4)	−5211(9)	86(3)
C-41	2104(7)	−2505(3)	1032(8)	45(2)
O-42	2090(7)	−2710(2)	−180(6)	63(1)
C-43	1738(12)	−2709(3)	2499(10)	74(2)
N-44	1089(6)	−401(2)	740(6)	38(1)
C-45	1263(9)	−338(2)	2269(8)	43(2)
C-46	596(10)	30(3)	2996(9)	58(2)
C-47	−278(9)	373(3)	2135(9)	57(2)
C-48	−465(9)	308(3)	561(9)	52(2)
C-49	217(8)	−80(2)	−117(8)	44(2)
Br-50	2386(1)	531(1)	−3121(1)	86(1)
O-51	5768(9)	1179(3)	−3065(10)	112(3)
O-52	−1605(9)	610(4)	−3736(13)	155(4)
O-53	4564(15)	−524(4)	−2619(18)	209(7)

COSY technique at temperature of 25 °C were used.

X-ray crystallography.—X-Ray measurements were carried out on a KUMA KM-4 four circle diffractometer. The structures were solved by direct methods with the SHELXS program[13] and refined employing full-matrix least-squares method implemented in the SHELXL program.[14] Anisotropic displacement coefficients were applied to all non-hydrogen atoms. Hydrogen atoms of the sugar moieties were refined in idealized positions with isotropic factors 1.2 times the equivalent isotropic temperature factor of adjacent C atoms. Water molecules were refined as rigid with H–O distance of 0.82 and H–H distance of 1.3 Å. The atomic scattering factors were taken from the International Tables for X-ray Crystallography (1993). Molecular illustrations were drawn using the ORTEP program.[15]

N-*(Tri*-O-*acetyl*-α-D-*xylopyranosyl)pyridinium bromide*.—2,3,4-Tri-*O*-acetyl-α-D-glucopyranosyl bromide (1 g, 2.9 mmol) was dissolved in dry pyridine (1.9 mL), without addition of a catalytic amount of *m*-cresol as suggested in the literature,[10] and the reaction mixture was kept at rt. After 12 h, the solvent was evaporated and the raw crystalline residue was crystallized from 10:1 EtOH–EtOAc resulting in a mixture of *N*-(tri-*O*-acetyl-α- and -β-D-xylopyranosyl)pyridinium bromide (1.2 g). Recrystallization from acetone gave the title compound (0.49 g, yield 40%), mp 120–126 °C (lit.,[10] 169–170°); $[\alpha]_D^{20}$ −40° (*c*, 0.8 $CHCl_3$) (lit.,[10] $[\alpha]_D^{20}$ −45.7° (*c*, 0.8 $CHCl_3$)); ^1H NMR (D_2O) δ: 7.99–8.98 (m, 5 H, Py), 6.38 (ps, 1 H, H-1), 5.15 (ps, 1 H, H-2), 5.17 (ps, 1 H, H-3), 4.78 (ps, 1 H, H-4), 4.32 (ps, 2 H, H-5, H-5′), 2.16–1.80 (9 H, 3 × *O*Ac). Anal. Calcd for $C_{16}H_{20}BrNO_7 \cdot 3/2\ H_2O$ (445.26): C, 43.16; H, 5.22; N, 3.15. Found: C, 42.20; H, 5.25; N, 3.08 (lit.,[10] Anal. Calcd for $C_{16}H_{20}BrNO_7$: C, 45.95; H, 4.8; N, 3.35. Found C, 46.25; H, 5.05; N, 3.4).

2. Supplementary material

Full crystallographic details, excluding structural features, have been deposited (CCDC no. 152348) with the Cambridge Crys-

Table 5
Hydrogen bonds for *N*-(tri-*O*-acetyl-α-D-xylopyranosyl)pyridinium bromide hydrate (2:3)

D-H	d(D–H)	d(H···A)	(D–H–A)	d(D···A)	A
O-51–H-51A	0.820	2.048	148.36	2.780(11)	O-52[$x+1$, y, z]
O-51–H-51B	0.820	2.578	155.71	3.342(7)	Br-50
O-52–H-52A	0.820	2.779	129.16	3.358(8)	Br-50
O-52–H-52B	0.820	2.578	149.45	3.311(10)	Br-25
O-53–H-53A	0.820	2.584	153.91	3.340(11)	Br-25[$x+1$, y, z]
O-53–53-B	0.820	2.679	159.54	3.460(12)	Br-50

Hydrogen bonds with H···A < r(A) + 2.000 Å and < DHA > 110°. Br-25, Br-50, O-51, O-52, O-53, those atoms are not inserted in Fig. 1.

tallographic Data Centre. These data may be obtained, on request, from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: +44-1223-336408; fax +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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