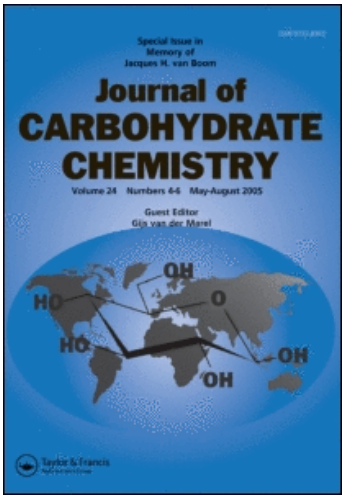

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Synthesis of Some Quaternary *N*-(1,4-anhydro-5-deoxy-D, L-ribitol-5-yl)ammonium Salts

Barbara Dmochowska,[1] Eugenia Skorupa,[1] Patrycja Świtecka,[1] Artur Sikorski,[1] Izabela Łącka,[2] Sławomir Milewski,[2] and Andrzej Wiśniewski[1]

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The successful removal of the isopropylidene-protecting group from 1,4-anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol and from quaternary *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)ammonium salts is reported. The structures of all isolates were determined by spectral analysis, including extensive 2-D NMR analyses. Single-crystal x-ray diffractions of 1,4-anhydro-5-*O*-tosyl-D,L-ribitol and its 2,3-*O*-isopropylidene derivatives are reported.

Keywords Quaternary ammonium salt; 1,4-Anhydro-D,L-ribitol; ^{1}H,^{13}C NMR, X-ray crystallography

INTRODUCTION

(+) Muscarine is an alkaloid of the poisonous fungus *Amanita muscaria*, a specific cholinomimetic.[1] Both the structure and chemico-biological properties of muscarine have been thoroughly examined and described in detail. However, the discovery of an association between cholinergic deficiency and Alzheimer's disease has renewed interest in muscarine.[2] Recently, more than 30 analogs of this alkaloid have been synthesized using carbohydrate and noncarbohydrate substrates.[3–9]

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In the search for muscarine analogs that would exhibit anti-Alzheimer activity, we synthesized quaternary ammonium salts, which have anhydroalditol as one of the substituents on the nitrogen atom. In this work we discuss the conditions for the de-*O*-isopropylidenation of the *O*-tosyl derivative of 1,4-anhydropentitol and some of its quaternary ammonium salts. Some of the obtained compounds, namely, those that contain free vicinal hydroxyl groups or are protected by an *O*-isopropylidene group in their structure, were tested for antifungal activity.

RESULTS AND DISCUSSION

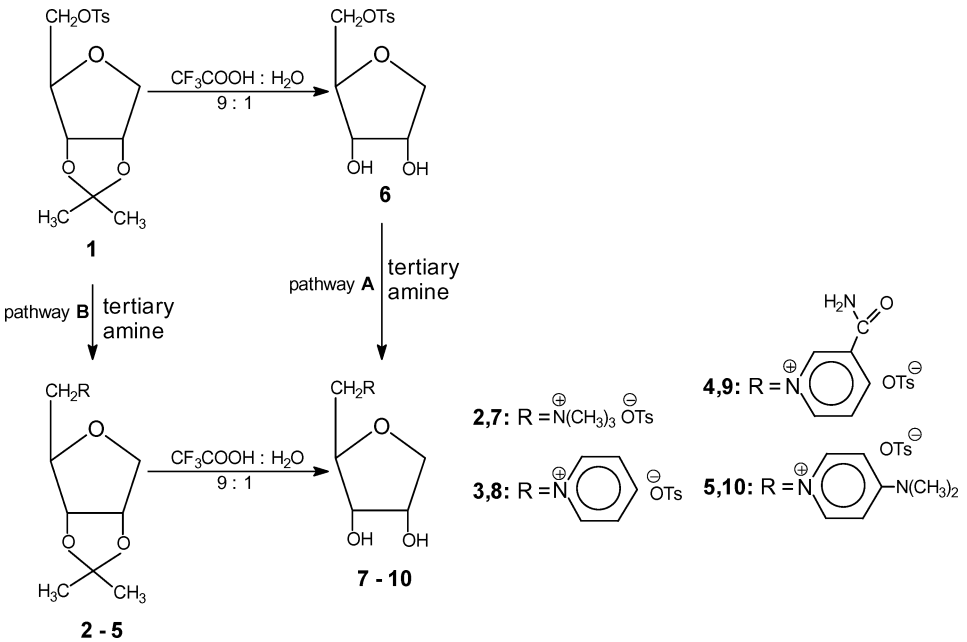
We have recently synthesized and characterized quaternary *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)ammonium salts with a tosylate and an iodide anion.[10,11]

The *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)ammonium tosylates did not exhibit antifungal properties. Our intention was to find out whether this could have been due to the absence of free hydroxyl groups. This paper reports our attempts to find the best conditions for the removal of the 2,3-*O*-isopropylidene protecting group in 1,4-anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**1**) and in some of its quaternary *N*-(1,4-anhydro-5-deoxy-D,L-ribitol-5-yl)ammonium salts **2–5**. The removal of this group would enable molecules to be obtained that are smaller than and more similar in structure to muscarine (i.e., molecules containing free hydroxyl groups).

The titular quaternary ammonium salts **2–5** were prepared from 1,4-anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol **(1)**, all of which were then used as experimental models for their de-*O*-isopropylidenation. We deliberately chose such models with *O*-tosyl or ammonium residues at C-5 for our experimental studies because we wanted to compare and evaluate their electronic influence on the ease of de-*O*-isopropylidenation in **1** and **2**–**5**.

After a careful study of the conditions for deisopropylidenation, well known and described in the literature,[12–17] and taking into account our experimental experience, we decided to perform the conversion in trifluoroacetic acid solution.

Scheme 1 shows the synthesis pathway of quaternary ammonium salts **7–10**. Compounds **1–5** were each placed in five screw-capped ampoules to which 1.5 mL of a CF_3COOH–H_2O solution (9:1 v/v) was added. The reaction mixtures were left at rt and the progress of the reaction was controlled using the MALDI-TOF-MS technique (Table 1). The reaction was interrupted by neutralization with 50% aq NaOH in the presence of litmus paper. The inorganic salts formed precluded effective purification of the synthesized quaternary ammonium salts **7–10**. But the manner in which the reaction was stopped was



Scheme 1. Deprotection of the *O*-isopropylidene group from the *O*-tosyl derivative (**1**) and the quaternary ammonium salts (**2**–**5**).

sufficient to estimate its progress. Every product of the interrupted reaction was analyzed by MALDI-TOF-MS. For preparative purposes, we decided to interrupt each reaction by immediate freezing in a cooling bath and removing excess trifluoroacetic acid by freeze-drying.

The applied conditions enabled the preparative synthesis of pure compounds—1,4-anhydro-5-*O*-tosyl-D,L-ribitol **(6)** and four quaternary *N*-(1,4-anhydro-5-deoxy-D,L-ribitol-5-yl)ammonium salts **7–10**—in high yields (90%).

Table 1: Reaction times for the removal of the *O*-isopropylidene protecting group in compounds **1**–**5**.

	Time (min)							
Compound	**15**	**30**	**45**	**60**	**75**	**90**	**105**	**120**
1	+	−	−	−	−	−	−	−
2	+	+	+	+	+	−	−	−
3	+	+	+	+	+	+	+	−
4	+	+	+	+	+	+	+	−
5	+	+	+	+	+	−	−	−

+, the m/z signal corresponding to the cation with the *O*-isopropylidene group in the MALDI-TOF-MS spectrum was visible.
−, the m/z signal corresponding to the cation without the *O*-isopropylidene group in the MALDI-TOF-MS spectrum was visible.

The de-*O*-isopropylidenation of 1,4-anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**1**) lasted 30 min but the analogous reaction for all the salts lasted c. 90 min. This observation suggested the negative influence of the ammonium group at C-5 (with a positive charge on the nitrogen atom) on the ease of deisopropylidenation of quaternary ammonium compounds in relation to the influence of the *O*-tosyl group in **1**.

Comparison of the reaction times necessary for the *O*-isopropylidene group removal in quaternary ammonium salts (**2–5**, Table 1) shows only slight differences (within experimental error) and confirms the explanation suggested above.

In conclusion, we suggest that *N*-(1,4-anhydro-5-deoxy-D,L-ribitol-5-yl)ammonium tosylates **7–10** should be obtained using method A (Sch. 1), that is, beginning with the de-*O*-isopropylidenation of 1,4-anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol **(1)**, then converting the product into quaternary ammonium salts.

Examination of the molecular structure **1** and **6** has revealed that in the crystalline state compound **1** has a bicyclic structure, consisting of five-membered ring O-5/C-1/C-2/C-3/C-4 and five-membered ring O-18/C-2/C-3/O-19/C-20 with the disordered O18 atom, while compound **6** has a monocyclic structure, consisting of five-membered ring O-5/C-1/C-2/C-3/C-4 (Fig. 2). Both five-membered rings adopt conformations close to the E form[18,19]: envelope on O5 for **1** and envelope on C3 for **6** with ring puckering parameters[20,21] $\theta = 0.334(4)$ Å and $\varphi = 357.3(9)^\circ$ for compound **1** and $\theta = 0.400(2)$ Å and $\varphi = 112.9(2)^\circ$ for compound **6**; pseudorotation parameters ${}^3P = 88.1(4)^\circ$ and $\tau_m = 37.6(3)^\circ$ for the C-2—C-3 reference bond in **1** and $P = 204.8(1)^\circ$ and $\tau_m = 41.2(1)^\circ$ for the C-2—C-3 reference bond in **6**; and delta parameter[22] $\Delta = 630.2^\circ$ for **1** and $\Delta = 409.5^\circ$ for **6**.

The five-membered ring O-18/C-2/C-3/O-19/C-20 in compound **1** (with the disordered O18 atom) adopts two conformations very similar to the T form: twisted on O18A—C-20 for O-18A/C-2/C-3/O-19/C-20 ring (ring A) and twisted on C-2—O18B for O-18B/C-2/C-3/O-19/C-20 ring (ring B) with ring puckering parameters $\theta = 0.306(10)$ Å and $\varphi = 161.1(11)^\circ$ and $\theta = 0.370(16)$ Å and $\varphi = 89.1(13)^\circ$ for rings A and B, respectively; pseudorotation parameters ${}^3P = 248.0(8)^\circ$ and $\tau_m = 33.5(5)^\circ$ for the C-3—O-19 reference bond in ring A and $P = 179.9(11)^\circ$ and $\tau_m = 39.5(11)^\circ$ for the C-2—O-18B reference bond in ring B; and delta parameter[20] $\Delta = 496.1^\circ$ for ring A and $\Delta = 359.7^\circ$ for ring B.

Differences are visible in the crystal packing of both compounds. In the crystal lattice of **1** we can observe that neighboring molecules interact through weak C—H···O interactions (bifurcated on H14A) and form separated chains along the *bc* plane (Fig. 2, Table 3). Furthermore, compound **6** has a layered structure. Molecules in layer are linked via strong O—H···O and weak C—H···O hydrogen bonds as well as layers interacting between themselves (Fig. 3, Table 4).

It is well known that several quaternary ammonium compounds exhibit antimicrobial activity, especially against pathogenic fungi.[29] For this reason we considered it interesting to test representatives of the obtained compounds for antifungal activity. The experiments were performed using a microtiter serial dilution method. Compounds **3** and **8** were tested against *Candida albicans*, *Saccharomyces cerevisiae,* and *Candida tropicalis*. The former did not exhibit any antifungal activity at concentrations <10 000 μg/mL, while the latter inhibited growth of the yeast strains but the MIC value was very high (2500 μg/mL). The well-known antifungal agent fluconazole, tested in the same system, exhibited MIC = 16 μg/mL; we may therefore conclude that the novel compounds are very weak antifungals.

EXPERIMENTAL

General Methods

Reactions were monitored by thin-layer chromatography (TLC) on Kieselgel 60 F_{254} Silica Gel plates (E. Merck, 0.20 mm thickness). The spots were detected by spraying with 5% ethanolic H_2SO_4 and charring. The ^1H and ^{13}C NMR spectra ($CDCl_3$, D_2O, internal Me_4Si) were measured with a Varian Mercury 400 (400.49/100.70 MHz) instrument. Optical rotations were measured with a JASCO J-20 polarimeter. Elementary analyses were conducted with a Carlo Erba EA1108 elemental analyzer. Positive-ion mode MALDI-TOF mass spectra were obtained using a Bruker BiflexIII spectrometer with α-cyano-4-hydroxycinnamic matrix.

X-Ray crystallography

Diffraction data were collected at temperature 100K on a Gemini R-Ultra diffractometer[23] with CuKα radiation ($\lambda = 1.54184$ Å) using the $2\Theta/\omega$ scan mode. The initial phase angle determination was performed by the SHELXS.[24] All H atoms were placed geometrically and refined using a riding model with C–H = 0.95–1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and O–H = 0.84 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The crystallographic data,[31] data collection, and structure refinement are summarized in Table 2 and hydrogen bonds are summarized in Tables 3 and 4.

The crystal structure was refined to $R_1 = 0.0811$ (3630 reflections, all unique reflections) and $R_1 = 0.0481$ (1566 reflections with $F_0 > 2\sigma(F_0)$) by the full-matrix least-squares method using the program SHELXL-97[25] based on 212 parameters for compound **1** and $R_1 = 0.0327$ (16,663 reflections, all unique reflections) and $R_1 = 0.0303$ (2295 reflections with $F_0 > 2\sigma(F_0)$) for compound **6** by the full-matrix least-squares method using the program SHELXL-97 based on 173 parameters. The compound structures showing the conformations and

Table 2: Crystal data and structure refinement for **1** and **6**.

	1	**6**
Empirical formula	$C_{15}H_{20}O_6S$	$C_{12}H_{16}O_6S$
Formula weight	328.37	288.31
Temperature (K)	100(2)	100(2)
Wavelength (Å)	1.54184	1.54184
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/c$
Unit cell dimensions		
a (Å)	5.8959 (11)	14.5217 (4)
b (Å)	11.3436 (14)	10.6287 (3)
c (Å)	12.0455 (19)	8.4996 (2)
α(°)	93.476 (11)	90
β(°)	101.908 (14)	92.236 (2)
γ(°)	104.905 (13)	90
V (Å^3)	756.2 (2)	1310.89 (6)
Z	2	4
D_{calcd} (mg.m^{-3})	1.442	1.461
Absorption coefficient (mm^{-1})	2.157	2.405
F(000)	348	608
Crystal size (mm)	0.12 × 0.02 × 0.02	0.26 × 0.08 × 0.08
Θ Range for data collection (°)	3.78–66.50	3.05–66.50
Limiting indices	$-5\leq h\leq 5$, $-11\leq k\leq 11$, $-12\leq l\leq 12$	$-17\leq h\leq 17$, $-12\leq k\leq 12$, $-8\leq l\leq 9$
Reflections collected/unique	3630/1566 (R_{int} = 0.0481)	16,663/2295 (R_{int} = 0.0324)
Completeness 2Θ = 67.00° (%)	60.0	99.3
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1566/0/212	2295/0/173
Goodness-of-fit on F^2	0.924	1.102
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.048$ $wR_2 = 0.094$	$R_1 = 0.030$ $wR_2 = 0.083$
R indices (all data)	$R_1 = 0.081$ $wR_2 = 0.103$	$R_1 = 0.033$ $wR_2 = 0.084$
Largest diff. peak and hole (e Å^{-3})	0.216 and −0.222	0.301 and −0.311

atom numbering system are illustrated in Figure 1.[26] Molecular packing in the crystals, illustrated in Figures 2 and 3, were prepared by PLUTO-78.[27] The computational material for publication was prepared using the PLATON program.[28]

Table 3: Hydrogen bonds for **1** with distances (d): d(D...A) < R(D) + R(A) + 0.50Å; d(H...A) < R(H) + R(A) – 0.12 Å and angle (<) <D–H...A > 100.0°

D-H	**A**	**d(D–H)**	**d(H..A)**	**< D–H...A**	**d(D..A)**
C-14-H-14A	O-5^i	0.95	2.57	3.412 (5)	148
C-14-H-14A	O-7^i	0.95	2.58	3.218 (5)	125

Symmetry codes: (i) -1-x, y, z.

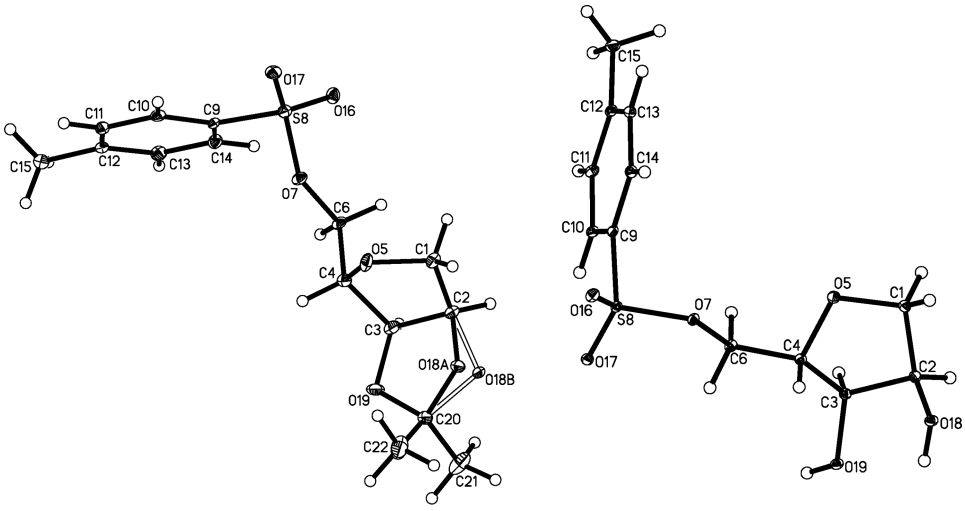
Table 4: Hydrogen bonds for **6** with distances (d): d(D...A) < R(D) + R(A) + 0.50Å; d(H...A) < R(H) + R(A) – 0.12 Å and angle (<) <D–H...A > 100.0°.

D-H	A	d(D–H)	d(H..A)	< D–H...A	d(D..A)
O-18-H-18A	O-17^{i}	0.84	2.12	2.879 (1)	151
O-19-H-19A	O-18^{ii}	0.84	1.95	2.786 (1)	176
C-1-H-1A	O-7^{iii}	0.99	2.48	3.431 (2)	160
C-6-H-6A	O-17^{iv}	0.99	2.55	3.196 (2)	123
C-15-H-15A	O-5^{v}	0.98	2.51	3.367 (2)	146

Symmetry codes: (i) 1-x, -y, 2-z; (ii) 1-x, 1/2+y, 5/2-z; (iii) x, -1/2-y, 1/2+z; (iv) x, 1/2-y, 1/2+z; (v) -x, -y, 2-z.

Determination of antifungal activity

Antifungal in vitro activity was determined using the serial twofold microdilution method in 96-well microtiter plates, according to the conditions recommended by NCCLS[30]; in Yeast Nitrogen Base (Difco) medium containing 2% glucose, or in the RPMI-1640 (with glutamine, without sodium bicarbonate, containing 2% glucose, buffered with 0.165 M MOPS to pH 6.0) medium. The inoculum size was 10^4 cells/mL. Plates were incubated for 48 h at 30°C and then the turbidity at 660 nm was measured in individual wells with a microplate reader (Labsystems, Multiscan Bichromatic). Minimal inhibitory concentration (MIC) was defined as a drug concentration at which at least an 80% decrease in turbidity, relative to that of the drug-free growth control well, was found.



1 **6**

Figure 1. Structures of **1** and **6** showing 25% probability displacements for ellipsoids. H atoms are shown as small spheres of arbitrary radii.

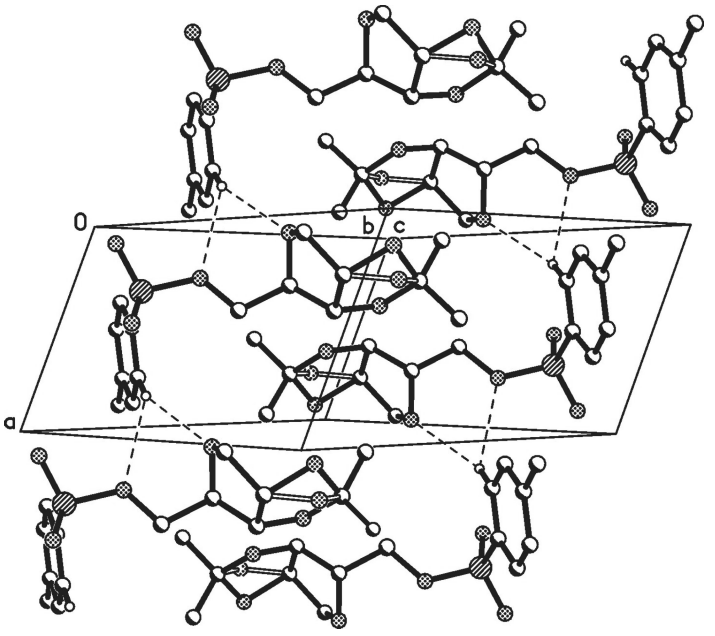


Figure 2. Molecular packing of **1** (view along *bc* plane). The hydrogen atoms not involved in C—H···O interactions have been omitted.

General de-O-isopropylidenation Procedure

N-[(1,4-Anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol)-5-yl] ammonium salts (0.15 mmol) were dissolved in 1.5 mL of aqueous solution $CF_3COOH:H_2O$ (9:1). The mixture was left at rt and the progress of the reaction was controlled on the MALDI-TOF spectra (Table 1). Finally, water and trifluoroacetic acid were removed by freeze-drying and the syrupy raw products were obtained: 49.5 mg (95%) of compound **7**, 52.4 mg (95%) of compound **8**, 49.3 mg (80%) of compound **9**, 55.4 mg (90%) of compound **10**, $R_f = 0.0$ (acetone–hexane 2:3).

1,4-Anhydro-5-O-tosyl-D,L-ribitol (6)

1,4-Anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (50 mg, 0.15 mmol) was dissolved in 1.5 mL of aqueous solution $CF_3COOH:H_2O$ (9:1). After 15 min, water and trifluoroacetic acid was removed by freeze-drying. The raw product was crystallized from $EtOH_{aq}$. The yield of colorless crystals (39.5 mg, 90%); m.p. 79.2–80.5, $R_f = 0.19$ (acetone–hexane 2:3). ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3H, PhMe), 2.90 (s *b*, 2H, OH), 3.77 (dd, 1H, $J_{1',2} = 2.0$, $J_{1,1'} = 10.3$, H-1′), 3.92 (m, 1H, $J_{4,5'} = 2.9$, H-4), 4.02 (dd, 1H, $J_{1,2} = 4.4$, H-1), 4.10 (dd, 1H, $J_{2,3} = 5.9$, H-3), 4.20 (2 × dd, 2H, $J_{5,5'} = 10.8$, H-5, H-5′), 4.25 (s *b*, 1H, H-2), 7.36 and 7.80 (2d, each 2H, Ph); ^{13}C NMR ($CDCl_3$): δ 145.40, 132.80, 130.20, 128.20 (C, Ph), 79.86 (C-4), 73.44 (C-1), 72.48 (C-3), 71.24 (C-2), 69.73 (C-5), 21.86 (C, PhMe). Anal.

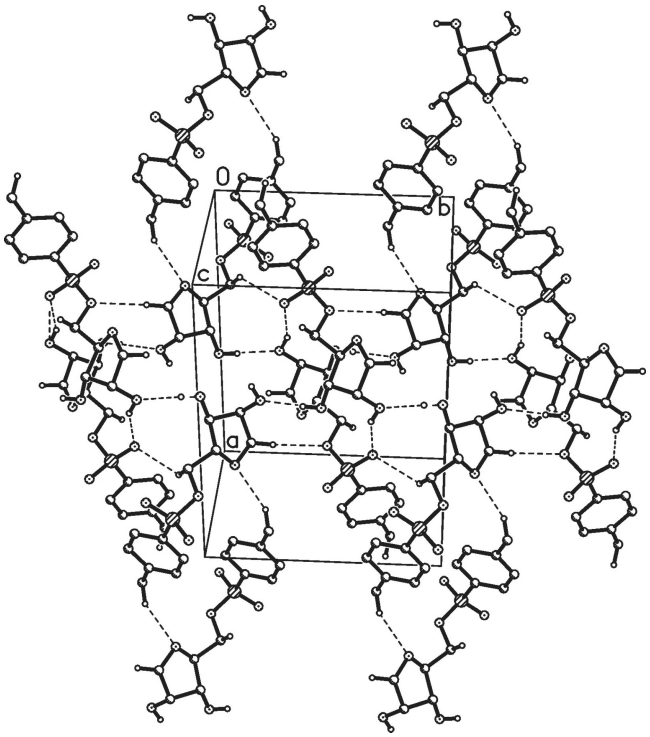


Figure 3. Molecular packing of **6** (view along *c*-axis). The hydrogen atoms not involved in O—H···O and C—H···O interactions have been omitted.

Calcd for $C_{12}H_{16}SO_6$ (288.32): C, 49.99; H, 5.59; S, 11.12. Found: C, 49.82; H, 5.40; S, 10.92; MALDI-TOF-MS (CCA): *m/z*311.1 $[M + Na]^+$).

N-(1,4-anhydro-5-deoxy-D,L-ribitol-5-yl)trimethylammonium tosylate (7)

^{1}H NMR (D_2O): δ 2.26 (s, 3H, MePh), 3.06 (s *b*, 10H, NMe_3+ H-3), 4.12 (dd, 1H, $J_{2,3} = 4.4$, H-2), 3.44 (m, 1H, H-4), 4.06 (dd, 1H, $J_{5,5'} = 14.0$, H-5′), 3.72 (d, 1H, $J_{1,1'} = 10.3$, H-1), 3.84 (dd, 1H, $J_{4,5} = 4.9$, H-5), 4.00 (dd, 1H, $J_{1',2} = 3.9$, H-1′), 7.56 and 7.24 (2d, each 2H, Ph); ^{13}C NMR (D_2O): δ 142.63, 139.58, 129.60, 125.49 (C, Ph), 74.46 (C-5), 73.49 (C-1), 69.38 (C-2), 68.96 (C-3), 54.05 (C-4), 54.02 (C, NMe_3), 20.61 (C, PhMe). Anal. Calcd for $C_{15}H_{25}NSO_6$ (347.43): C, 51.86; H, 7.25; N, 4.03; S, 9.23. Found: C, 51.29; H, 7.03; N, 4.29; S, 8.97; MALDI-TOF-MS (CCA): *m/z*176.2 ($[M - OTs]^+$).

N-(1,4-anhydro-5-deoxy-D,L-ribitol-5-yl)pyridinium tosylate (8)

^{1}H NMR (D_2O): δ 2.18 (s, 3H, MePh), 3.64 (d, 1H, $J_{1',1} = 10.3$, H-1), 3.90 (m, 2H, H-1′, H-3), 4.02 (td, 1H, $J_{4,5} = 2.0$, H-4), 4.10 (s *b*, 1H, H-2), 4.49 (dd, 1H, $J_{4,5'} = 8.3$ H-5′), 4.74 (dd, 1H, $J_{5,5'} = 13.7$, H-5), 7.17 and 7.49 (2d, each 2H, Ph), 7.87, 8.37, 8.65 (5H, Py); ^{13}C NMR (D_2O): δ 146.35, 144.90, 128.31

(C, Py), 142.52, 139.70, 129.59, 125.49 (C, Ph), 79.21 (C-4), 73.36 (C-3), 73.06 (C-1), 70.99 (C-2), 63.01 (C-5), 20.62 (C, PhMe). Anal. Calcd for $C_{17}H_{21}NSO_6$ (367.42): C, 55.57; H, 5.76; N, 3.81; S, 8.73. Found: C, 55.45; H, 5.61; N, 3.80; S, 8.23; MALDI-TOF-MS (CCA): m/z196.1 ($[M - OTs]^+$).

N-(1,4-anhydro-5-deoxy-D,L-ribitol-5-yl)-3-carbamoylpyridinium tosylate (9)

^{1}H NMR (D_2O): δ 2.20 (s, 3H, MePh), 3.68 (dd, 1H, $J_{1',1} = 10.3$, H-1′), 3.96 (m, 2H, H-1, H-3), 4.06 (td, 1H, $J_{3,4} = 2.0$, $J_{4,5}$ 8.3, H-4), 4.14 (s *b*, 1H, H-2), 4.60 (dd, 1H, $J_{4,5'} = 8.8$, H-5′), 4.86 (dd, 1H, $J_{5,5'} = 14.2$, H-5) 7.17 and 7.49 (2d, each 2H, Ph), 8.01, 8.73, 8.86, 9.14 (4H, Py); ^{13}C NMR (D_2O): δ 165.69, 147.21, 144.92, 139.60, 128.49, 125.48 (C, Py), 144.62, 142.57, 133.96, 129.59 (C, Ph), 79.11 (C-4), 73.48 (C-3), 73.16 (C-1), 71.03 (C-2), 63.67 (C-5), 20.62 (C, PhMe). Anal. Calcd for $C_{18}H_{22}N_2SO_7$ (410.44): C, 52.67; H, 5.40; N, 6.83; S, 7.81. Found: C, 52.22; H, 4.90; N, 6.88; S, 7.04; MALDI-TOF-MS (CCA): m/z239.1 ($[M - OTs]^+$).

N-(1,4-anhydro-5-deoxy-D,L-ribitol-5-yl)-4-(N,N-dimethylamino)pyridinium tosylate (10)

^{1}H NMR (D_2O): δ 2.18 (s, 3H, MePh), 2.98 (s, 6H, Me_2NPy), 3.63 (d *b*, 1H, $J_{1',1} = 10.8$, H-1), 3.80 (m, 1H, $J_{3,4} = 1.9$, H-3), 3.86 (dq, 1H, $J_{1',2} = 3.9$, H-1′), 3.90 (td, 1H, $J_{4,5'} = 7.8$, H-4), 4.00 (m, 1H, $J_{4,5} = 1.5$, H-5), 4.05 (m, 1H, $J_{2,3} = 5.9$, H-2), 4.23 (d *b*, 1H, $J_{5',5} = 14.2$, H-5′), 6.62, 7.76 (4H, Py), 7.12, 7.47 (2d, each 2H, Ph); ^{13}C NMR (D_2O): δ 156.47, 141.84, 107.55 (C, Py), 142.42, 139.69, 129.52, 125.47 (C, Ph), 79.41 (C-4), 73.02 (C-3), 72.74 (C-1), 70.95 (C-2), 58.64 (C-5), 39.50 (C, NMe_2), 20.61 (C, PhMe). Anal. Calcd for $C_{19}H_{26}N_2SO_6$ (410.49): C, 55.59; H, 6.38; N, 6.82; S, 7.81. Found: C, 55.39; H, 6.11; N, 7.02; S, 7.07; MALDI-TOF-MS (CHCA): m/z239.2 ($[M - OTs]^+$).

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32. Full crystallographic details, excluding structures features, have been deposited (deposition No. CCDC 671323 for 1 and deposition No. CCDC 671324 for 6 with the Cambridge Crystallographic Data Center). 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).