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Synthesis and structure of selected quaternary *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)ammonium salts

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Abstract—The syntheses have been developed for quaternary *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)ammonium salts derived from five aromatic amines, pyridine, 2-methylpyridine, 3-carbamoylpyridine, 4-(*N*,*N*-dimethylamino)pyridine, and quinoline, as well as two tertiary aliphatic amines, trimethylamine and triethylamine. Reactions of 1,4-anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol with tri-*n*-propylamine and tri-*n*-butylamine were unsuccessful. The products were identified on the basis of their ^{1}H and ^{13}C NMR spectra. The structure of *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate was additionally elucidated by X-ray diffractometry.

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

1. Introduction

Alditols and anhydroalditols are widespread in both the animal and plant kingdoms.[1,2] They also occur in human blood and urine and in the amniotic and cerebrospinal fluids.[3] These compounds and some of their derivatives have been used in medicine. For instance, 1,4:3,6-dianhydro-D-glucitol 2,5-dinitrate and 1,4:3,6-dianhydro-D-glucitol 5-nitrate, marketed under the trade names 'Sorbonit' and 'Mononit', are vasodilators used for the treatment of chronic circulatory insufficiency and stenocardia.[3] Intravenous infusions of D-mannitol have been used to control intraocular, intracranial, and cerebrospinal pressure, thus reducing brain edema. It is also used as an antidote for acute intoxications with, for instance, barbiturates.[3] Again, D-glucitol, commonly known as sorbitol, after intravenous administration acts as a diuretic and controls neurosis-dependent intestinal peristalsis.[4] Many alditols have also been used as stabilizing agents for antiviral vaccines[5] and as compounds that protect monoclonal antibodies from denaturation,[6] as well as protecting agents for red blood cells.[7]

Both animal and preliminary clinical tests have shown that 1,2:5,6-dianhydrogalactitol (DAG) is an effective drug for the treatment of some tumors, for instance those of the lung and brain, as well as leukemia.[8]

Both chemists and biologists are currently interested in pseudo-nucleosides in which the sugar residue is substituted by 1,4-anhydropentitol or 1,5-anhydrohexitol derivatives. Some of these compounds are effective against viruses, for instance against the HIV virus. Intense chemical and biological investigations are also conducted on analogues of DNA acids containing substituted 1,5-anhydrohexitols in place of 2-deoxy-D-ribose.[9,10]

Literature reports,[11–14] and in particular a paper devoted to the synthesis of (**3***S*)- and (**3***R*)-3-hydroxymuscarine,[12] a drug used in chemotherapy and for the treatment of Alzheimer's disease, encouraged us to synthesize quaternary ammonium salts with an anhydroalditol moiety as one of the substituents on the nitrogen atom.

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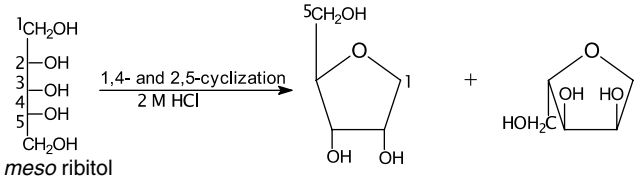
The selection of 1,4-anhydro-D,L-pentitol and particular amines for synthesizing the quaternary ammonium salts was done on the basis of the aforementioned literature reports and our own experience,[15] first of all bearing in mind the efficiency of the syntheses and expected bioactivities of the salts. The reactant used for the synthesis of the quaternary *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)ammonium salts was *meso*-ribitol, which upon intramolecular dehydration afforded 1,4-anhydro-D,L-ribitol.

The purpose of this contribution was to synthesize and determine the structure of some of these salts. Another purpose was to study their biological activities in order to select antibacterials that are not harmful to humans or the environment.

2. Results and discussion

The first literature reports on dehydration of pentitols appeared in 1945 and were devoted to xylitol, which upon treatment with 1% sulfuric or benzenesulfonic acid was converted to 1,4-anhydro-D,L-xylitol in 65% yield.[16] Later on, Baddiley and co-workers[17] obtained 1,4-anhydro-D,L-ribitol, a dehydration product of ribitol, with 2 M hydrochloric acid. Again, Kurszewska and co-workers[18,19] developed a method of the solvent-free thermal dehydration of alditols in the presence of 3 Å zeolites.

1,4-Anhydro-D,L-ribitol is here obtained by both methods, that is, through the solvent-free thermal dehydration of ribitol in the presence of 3 Å zeolites and through its dehydration in 2 M hydrochloric acid. The method of Baddiley and co-workers (Scheme 1) gave the highest yield (96%) of 1,4-anhydro-D,L-ribitol.

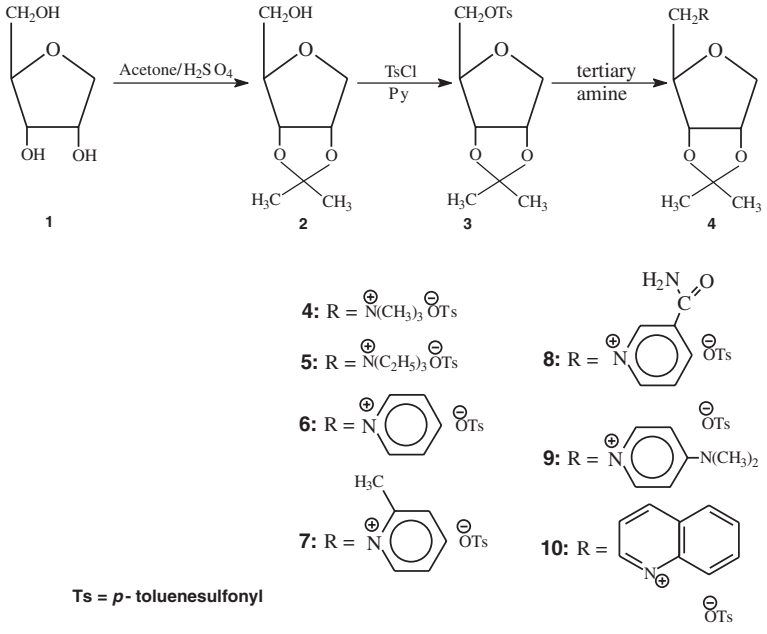


Scheme 1. 1,4- and 2,5-Cyclization of *meso* ribitol.

During the intramolecular dehydration of ribitol, which proceeds exclusively according to the S_N2 mechanism, as for instance in the hydrochloric acid solution, racemic 1,4-anhydroribitol is obtained, which is the sole reaction product (Scheme 1). Owing to the symmetry of the molecule, the 1,4- and 2,5-cyclizations with retention of configuration of the reactants afford a racemic mixture of 1,4-anhydro-D,L-ribitol. The homogeneity of the crude product as determined by gas chromatography (GC) amounts to 99%.

To obtain the quaternary ammonium salt with the *N*-C-5 linkage, vicinal hydroxyls were protected through *O*-isopropylidenization of 1,4-anhydro-D,L-ribitol with acetone in sulfuric acid (Scheme 2). The remaining hydroxyl group at C-5, upon reaction with *p*-toluenesulfonyl chloride (TsCl) in pyridine, gave the *O*-tosyl derivative (Scheme 2), 1,4-anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**3**).

By reaction of 1,4-anhydo-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**3**) with two tertiary aliphatic amines and five aromatic amines, the corresponding *N*-(1,4-



Scheme 2. Formation of *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)ammonium tosylates.

anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)-ammonium salts were obtained.

Under the applied experimental conditions for the synthesis of *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate, trimethylamine turned out to be an outstanding nucleophilic reagent. Thus, heating of 1,4-anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**3**) with 33% ethanolic trimethylamine during 15 min at 70 °C gave the expected salt (**4**) in 100% yield. Its identity was confirmed by ^{1}H and ^{13}C NMR spectral evidence and by X-ray diffractometry (Tables 1–5; Figs. 1 and 2).

The asymmetric unit of *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate contains one ammonium cation and one tosylate anion (see Fig. 1). The intermolecular interactions are shown in the drawing of the unit cell (Fig. 2). There are several C–H···O hydrogen bonds to the oxygen atoms of the anion. Most of them are charge assisted—the ones with C–H donors from the methyl groups of the trimethylammonium groups. These interactions are relatively strong with donor–acceptor distances of about 3.3 Å. The other interactions are weaker and probably play less important roles.

Using triethylamine in place of trimethylamine resulted in a dramatic reduction of the reaction rate. After heating the mixture for 16 h at 70 °C, the yield was only 46%. On the other hand, reactions of **3** with

Table 1. Crystal data and structure refinement for *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate

Empirical formula	$C_{18}H_{29}NO_6S$
Formula weight	387.48
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, P 2_1 2_1 2_1
Unit cell dimensions	
a (Å)	8.110(2)
b (Å)	9.537(2)
c (Å)	27.098(5)
Volume (Å^3)	2095.9(8)
Z	4
Calculated density (mg m^{-3})	1.228
Absorption coefficient (mm^{-1})	0.185
F(000)	832
Crystal size (mm)	0.30 × 0.25 × 0.10
Theta range for data collection (°)	1.50 θ 27.55
Index ranges, *h*, *k*, *l*	0 → 10, 0 → 12, 0 → 35
Reflections collected/unique	2764 / 2761
Reflections [$I > 2\sigma(I)$]	1057
Completeness to $\theta = 27.55$	0.993
Refinement method	Full-matrix least-squares refinement based on F^2
Data/restraints/parameters	1057/0/110
Goodness-of-fit on F^2	1.019
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0690$, $wR_2 = 0.1959$
R indices (all data)	$R_1 = 0.2588$, $wR_2 = 0.2570$
Largest difference peak and hole (e Å^{-3})	0.480/−0.386

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate[a]

	x	*y*	*z*	U_{eq}
S(1)	1857(2)	2232(3)	8261(1)	53(1)
O(1)	3443(7)	820(6)	8111(2)	67(2)
O(2)	633(8)	1222(7)	8338(2)	75(2)
O(3)	2213(8)	3081(7)	7944(2)	75(2)
O(4)	−1918(9)	6310(7)	8552(2)	82(2)
O(5)	−1047(9)	7317(8)	9251(3)	90(2)
N(1)	2813(8)	7397(7)	7493(2)	51(2)
C(1)	4198(15)	3816(13)	10305(4)	108(4)
C(2)	3723(10)	3362(9)	9793(3)	63(2)
C(3)	4272(12)	2086(10)	9609(3)	73(3)
C(4)	3868(10)	1658(10)	9145(3)	62(2)
C(5)	2855(10)	2465(8)	8855(2)	45(2)
C(6)	2306(11)	3738(8)	9024(3)	57(2)
C(7)	2757(12)	4145(9)	9493(3)	69(2)
C(8)	−2450(20)	5158(14)	9309(4)	132(5)
C(9)	−2392(12)	6562(9)	9052(3)	69(2)
C(10)	−3948(17)	7373(15)	9096(5)	127(5)
C(11)	−337(11)	8158(10)	8863(3)	65(2)
C(12)	1484(11)	7997(10)	8874(3)	66(2)
O(6)	1827(7)	6803(7)	8572(2)	68(2)
C(14)	685(9)	6851(9)	8173(2)	50(2)
C(15)	1246(9)	7816(8)	7755(3)	50(2)
C(16)	2721(11)	5915(8)	7298(3)	62(2)
C(17)	2999(12)	8364(10)	7060(3)	73(3)
C(18)	4307(11)	7506(10)	7815(3)	66(2)
C(13)	−889(11)	7422(10)	8404(3)	60(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (Å) for *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate

	Bond length
S(1)–O(2)	1.446(7)
S(1)–O(3)	1.450(6)
S(1)–O(1)	1.452(6)
S(1)–C(5)	1.783(7)
O(4)–C(13)	1.408(10)
O(4)–C(9)	1.429(10)
O(5)–C(9)	1.414(11)
O(5)–C(11)	1.444(10)
N(1)–C(18)	1.496(10)
N(1)–C(17)	1.501(11)
N(1)–C(15)	1.509(9)
N(1)–C(16)	1.512(10)
C(1)–C(2)	1.502(13)
C(2)–C(7)	1.353(11)
C(2)–C(3)	1.389(12)
C(3)–C(4)	1.363(11)
C(4)–C(5)	1.373(11)
C(5)–C(6)	1.372(10)
C(6)–C(7)	1.379(11)
C(8)–C(9)	1.510(14)
C(9)–C(10)	1.484(15)
C(11)–C(12)	1.485(12)
C(11)–C(13)	1.497(12)
C(12)–O(6)	1.431(10)
O(6)–C(14)	1.423(9)
C(14)–C(13)	1.522(11)
C(14)–C(15)	1.530(10)

Table 4. Selected valence angles (°) for *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate

	Valence angles
O(2)–S(1)–O(3)	114.3(4)
O(2)–S(1)–O(1)	111.2(4)
O(3)–S(1)–O(1)	113.0(4)
O(2)–S(1)–C(5)	105.1(4)
O(3)–S(1)–C(5)	106.1(3)
O(1)–S(1)–C(5)	106.4(4)
C(13)–O(4)–C(9)	107.7(7)
C(9)–O(5)–C(11)	108.2(7)
C(18)–N(1)–C(17)	109.3(7)
C(18)–N(1)–C(15)	113.0(5)
C(17)–N(1)–C(15)	106.8(6)
C(18)–N(1)–C(16)	108.0(7)
C(17)–N(1)–C(16)	107.7(6)
C(15)–N(1)–C(16)	111.8(6)
C(7)–C(2)–C(3)	116.9(8)
C(7)–C(2)–C(1)	123.0(9)
C(3)–C(2)–C(1)	120.1(9)
C(4)–C(3)–C(2)	121.1(9)
C(3)–C(4)–C(5)	120.3(9)
C(6)–C(5)–C(4)	119.9(7)
C(6)–C(5)–S(1)	119.8(6)
C(4)–C(5)–S(1)	120.3(6)
C(5)–C(6)–C(7)	118.1(8)
C(2)–C(7)–C(6)	123.5(9)
O(5)–C(9)–O(4)	103.9(7)
O(5)–C(9)–C(10)	111.1(8)
O(4)–C(9)–C(10)	113.1(9)
O(5)–C(9)–C(8)	107.5(10)
O(4)–C(9)–C(8)	107.2(8)
C(10)–C(9)–C(8)	113.4(11)
O(5)–C(11)–C(12)	108.9(8)
O(5)–C(11)–C(13)	103.0(7)
C(12)–C(11)–C(13)	105.5(8)
O(6)–C(12)–C(11)	105.3(8)
C(14)–O(6)–C(12)	106.4(6)
O(6)–C(14)–C(13)	104.3(6)
O(6)–C(14)–C(15)	112.8(6)
C(13)–C(14)–C(15)	109.7(7)
N(1)–C(15)–C(14)	116.0(6)
O(4)–C(13)–C(11)	107.1(7)
O(4)–C(13)–C(14)	110.1(7)
C(11)–C(13)–C(14)	104.9(7)

Table 5. Selected torsion angles (°) for *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate

C(7)–C(2)–C(3)–C(4)	0.8(12)
C(1)–C(2)–C(3)–C(4)	−179.4(8)
C(2)–C(3)–C(4)–C(5)	−2.3(13)
C(3)–C(4)–C(5)–C(6)	2.9(12)
C(3)–C(4)–C(5)–S(1)	−176.4(7)
O(2)–S(1)–C(5)–C(6)	−83.2(7)
O(3)–S(1)–C(5)–C(6)	38.2(7)
O(1)–S(1)–C(5)–C(6)	158.8(6)
O(2)–S(1)–C(5)–C(4)	96.0(7)
O(3)–S(1)–C(5)–C(4)	−142.5(7)
O(1)–S(1)–C(5)–C(4)	−21.9(7)
C(4)–C(5)–C(6)–C(7)	−2.0(12)
S(1)–C(5)–C(6)–C(7)	177.3(7)
C(3)–C(2)–C(7)–C(6)	0.0(13)
C(1)–C(2)–C(7)–C(6)	−179.7(8)
C(5)–C(6)–C(7)–C(2)	0.6(13)
C(11)–O(5)–C(9)–O(4)	32.2(9)
C(11)–O(5)–C(9)–C(10)	−89.7(10)
C(11)–O(5)–C(9)–C(8)	145.6(9)
C(13)–O(4)–C(9)–O(5)	−29.6(9)
C(13)–O(4)–C(9)–C(10)	91.0(10)
C(13)–O(4)–C(9)–C(8)	−143.2(10)
C(9)–O(5)–C(11)–C(12)	−133.7(8)
C(9)–O(5)–C(11)–C(13)	−22.1(9)
O(5)–C(11)–C(12)–O(6)	88.0(8)
C(13)–C(11)–C(12)–O(6)	−22.0(10)
C(11)–C(12)–O(6)–C(14)	36.7(8)
C(12)–O(6)–C(14)–C(13)	−35.9(8)
C(12)–O(6)–C(14)–C(15)	83.1(7)
C(18)–N(1)–C(15)–C(14)	−67.2(8)
C(17)–N(1)–C(15)–C(14)	172.5(6)
C(16)–N(1)–C(15)–C(14)	54.9(8)
O(6)–C(14)–C(15)–N(1)	63.4(8)
C(13)–C(14)–C(15)–N(1)	179.2(6)
C(9)–O(4)–C(13)–C(11)	16.1(9)
C(9)–O(4)–C(13)–C(14)	129.6(7)
O(5)–C(11)–C(13)–O(4)	3.4(9)
C(12)–C(11)–C(13)–O(4)	117.6(8)
O(5)–C(11)–C(13)–C(14)	−113.6(7)
C(12)–C(11)–C(13)–C(14)	0.5(10)
O(6)–C(14)–C(13)–O(4)	−93.8(7)
C(15)–C(14)–C(13)–O(4)	145.1(7)
O(6)–C(14)–C(13)–C(11)	21.1(9)
C(15)–C(14)–C(13)–C(11)	−100.0(8)

tri-*n*-propylamine and tri-*n*-butylamine, carried out under various conditions, failed to afford the expected products. Evidently, tertiary aliphatic amines with *n*-propyl and *n*-butyl substituents enlarge the steric hindrance so much that the expected salts cannot be formed, even in trace amounts.

The reactions of **3** with the aromatic amines, pyridine, 2-methylpyridine, 3-carbamoylpyridine, 4-(*N*,*N*-dimethylamino)pyridine, and quinoline afforded the corresponding quaternary *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)ammonium salts (**6**–**10**). The reaction of **3** with pyridine gave *N*-(1,4-anhydro-5-deoxy-2,3–*O*-isopropylidene-D,L-ribitol-5-yl)pyridinium tosylate (**6**) in 94% yield, whereas the analogous reaction with 2-methylpyridine gave the 2-methylpyridinium tosylate (**7**) in 60% yield. The lower yield in this case can be explained in terms of the steric hindrance due to the presence of the methyl group. This hindrance makes difficult the attachment of the nucleophilic nitrogen atom to the reaction center to form the C_5–*N* bond. In similar terms, the reduced yield of the quinolinium salt (**10**) can be explained as compared to that of the pyridinium salt (**6**).

The rate of formation of the quaternary ammonium salts of aromatic amines is affected by electronic effects, as seen in the 45% yield of the *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)-3-carbamoylpyridinium tosylate (**8**). In this case the yield is rather low in spite of absence of the steric hindrance. It seems likely that the presence of the electron-withdrawing substituent at C-3 of the pyridine ring considerably suppresses the nucleophilicity of 3-carbamoylpyridine.

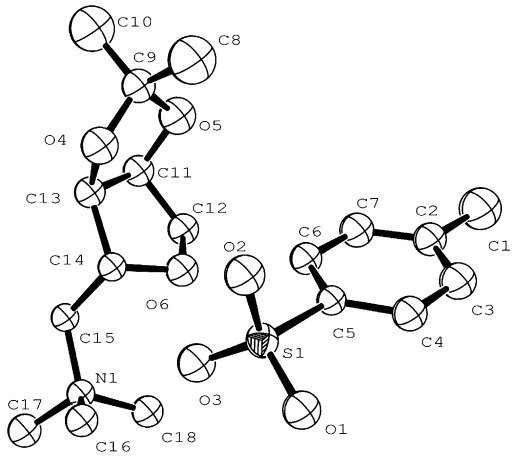


Figure 1. The X-ray structure of *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate.

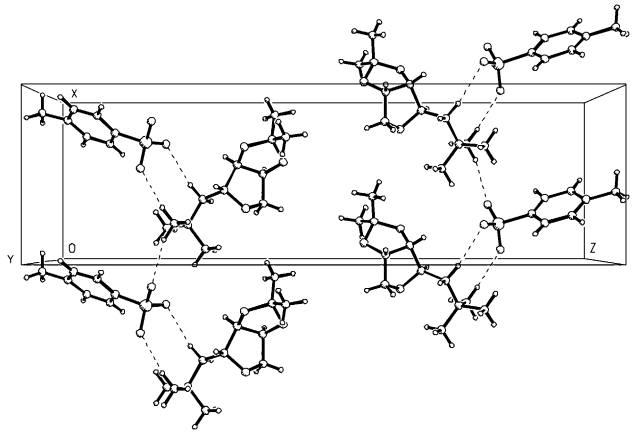


Figure 2. View of unit cell packing along the *b*-direction of *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate.

As expected, another base, 4-(*N*,*N*-dimethylamino)-pyridine reacts with **3** to afford the *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)-4-(*N*,*N*-dimethylamino)pyridinium salt in the highest yield (95%). The yield is due to the presence of the *N*,*N*-dimethylamino substituent at C-4 of the pyridine molecule.

The identity of the *N*-(1,4-anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)ammonium tosylates was confirmed by their ^{1}H and ^{13}C NMR spectra.

3. Experimental

3.1. General methods

Commercial ribitol (Fluka) was used. All 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. A Varian Mercury 400BB (400 MHz) spectrometer with D_2O as a solvent and acetone as an external standard, and 2D COSY and HSQC techniques at a temperature of 25 °C were used. GC separation of per-*O*-acetylated derivatives of ribitol was carried out using a VEGA 6180 (Carlo Erba) Gas Chromatograph equipped with a DB-23 fused silica capillary column (60 m × 0.258 mm I.D.) and flame ionization detector (FID). Hydrogen was used as a carrier gas. The running conditions were: initial temperature 140 °C, increase 4 °C/min to 160 °C, 6 °C/min to 200 °C, 8 °C/min to 240 °C, final hold 10 min, detector temperature 260 °C. Optical rotations were measured with a JASCO J-20 polarimeter. Elementary analyses were made with a Carlo Erba apparatus. Positive-ion mode MALDITOF mass spectra were obtained using a Bruker BiflexIII spectrometer with α-cyano-4-hydroxycinnamic acid as the matrix.

3.2. 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[23] and refined employing the full matrix least-squares method implemented in the SHELXL program.[24] The reflecting power of the crystal was poor, so the number of observed reflections was relatively small. In order to keep the data-to-parameter ratio reasonable, all atoms except the sulfur atom were refined isotropically. Hydrogen atoms were included isotropically as riding on the relevant heavy atoms. Because only the unique octant of the Ewald sphere was recorded, no information on the absolute configuration from this diffraction experiment can be elucidated. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography (1993). Molecular illustrations were drawn using the ORTEP program.[25]

3.3. 1,4-Anhydro-D,L-ribitol(1), (method 1[20])

Ribitol (0.39 g) was heated under an argon atmosphere over type 3 Å molecular sieves (0.3 g) at 290 °C for 2 h. After cooling to 0 °C, an oily product spontaneously crystallized. After recrystallization from 2-propanol, **1** (0.154 g, 45%) was obtained: mp 70–75 °C [lit.[21] mp 74–75 °C], $R_f = 0.28$ (3:2:1 Et_2O–$CHCl_3$–MeOH), $[\alpha]_D^{20}$ 0 (*c* 0.97; H_2O).

3.4. 1,4-Anhydro-D,L-ribitol(1), (method 2[22])

Ribitol (2.00 g) was dissolved in dilute hydrochloric acid (in 100 mL of 20 mL of concentrated acid + 80 mL of H_2O). The solution was heated at 100 °C for 48 h in a

10-mL sealed glass ampoule. After cooling, the contents of the ampoule was transferred to a round-bottomed flask, and the solvent was removed under reduced pressure to leave an oil, that spontaneously crystallized. In this way, **1** (1.58 g, 90%) was obtained: mp 72–75 °C [lit.[21] mp 74–75 °C], $R_f = 0.28$ (3:2:1 Et_2O–$CHCl_3$–MeOH), $[\alpha]_D^{20}$ 0 (*c* 0.97, H_2O). The homogeneity of the product was confirmed by capillary gas chromatography (GC) following exhaustive *O*-acetylation. $T_R = 12.95$ min. ^1H NMR (D_2O): δ 3.66 (dd, 1H, $J_{1,2}$ 5.2, $J_{1,1'}$ 12.4, H-1), 3.81 (dd, 1H, H-5), 3.82 (dd, 1H, $J_{1',2}$ 2.8, H-1′), 3.88 (m, 1H, $J_{2,3}$ 7.2, H-2), 4.08 (dd, 1H, $J_{5,5'}$ 10.4, H-5), 4.11 (dd, 1H, $J_{3,4}$ 5.0, H-3), 4.30 (m, $J_{4,5}$ 2.6, $J_{4,5'}$ 4.2, 1H, H-4); ^{13}C NMR (D_2O): δ 82.65 (C-4), 73.28 (C-1), 72.69 (C-3), 72.11 (C-2), 62.46 (C-5). Anal. Calcd for $C_5H_{10}O_4$ (134.13): C, 44.77; H, 7.52. Found: C, 44.50; H, 7.23; MALDITOF-MS (CHCA): *m*/*z* 157.0 ($[M+Na]^+$).

3.5. 1,4-Anhydro-2,3-*O*-isopropylidene-D,L-ribitol (2)

1,4-Anhydro-D,L-ribitol (**1**) (0.70 g, 5.20 mmol) was dissolved in absolute acetone (15 mL), and the solution was cooled in an ice bath. Then, concentrated H_2SO_4 (0.6 mL) was added dropwise, the temperature being held between 5 and 10 °C. The mixture was then stirred at ambient temperature for 5 h. After cooling the solution in an ice bath, a 50% NaOH solution (6 mL) was added to neutralize the acid. The precipitate that fell out was filtered off, and the filtrate was extracted with $CHCl_3$ to give pure **2** (0.52 g, 69%) as an oil: $R_f = 0.35$ (2:3 acetone–hexane). ^1H NMR (D_2O): δ 1.35 and 1.53 (2s, each 3H, CMe_2), 3.58 (dd, 1H, $J_{4,5'}$ 6.4, H-5), 3.68 (dd, 1H, $J_{5,5'}$ 12.0, H-5′), 3.98 (m, 2H, H-1, H-1′), 4.14 (m, 1H, $J_{4,5}$ 4.4, H-4), 4.63 (dd, 1H, $J_{3,4}$ 2.0, H-3), 4.83 (m, 1H, $J_{1',2}$ 2.8, $J_{2,3}$ 6.4, H-2); ^{13}C NMR (D_2O): δ 113.49 (C, CMe_2), 85.41 (C-4), 82.38 (C-3), 81.56 (C-2), 73.37 (C-1), 62.30 (C-5), 27.19 and 25.47 (Me_2, CMe_2). Anal. Calcd for $C_8H_{14}O_4$ (174.19): C, 55.62; H, 8.10. Found: C, 55.25; H, 7.87; MALDITOF-MS (CHCA): *m*/*z* 197.2 ($[M+Na]^+$).

3.6. 1,4-Anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (3)

1,4-Anhydro-2,3-*O*-isopropylidene-D,L-ribitol (**2**) (0.90 g, 5.20 mmol) was dissolved in anhydrous pyridine (22.5 mL), and the solution was cooled down to 0 °C. Then, TsCl (1.21 g, 1.2-fold excess) was slowly added, the mixture stirred for 17 h at ambient temperature, and the solution was then poured into a beaker with ice. The white precipitate that fell out was filtered off and washed copiously with ice-cold H_2O to give crude **3**. After crystallization from EtOH, **3** (1.26 g, 74%) was obtained: mp 92–93 °C and $R_f = 0.54$ (2:3 acetone–hexane). ^1H NMR (D_2O): δ 1.32 and 1.48 (2s, each 3H, CMe_2), 2.46 (s, 3H, PhMe), 3.90 (dd, 1H, $J_{1',2}$ 4.0, $J_{1,1'}$ 10, H-1′), 3.96 (dd, 1H, $J_{1,2}$ 1.6, H-1), 4.11 (m, 2H, $J_{5,5'}$ 10.8, H-5, H-5′), 4.19 (td, 1H, $J_{4,5}$ 4.4, H-4), 4.66 (dd, 1H, $J_{3,4}$ 1.6, H-3), 4.82 (m, 1H, $J_{2,3}$ 6.0, H-2), 7.37 and 7.79 (2d, each 2H, Ph); ^{13}C NMR (D_2O): δ 145.40, 132.78, 130.20, 128.17 (C, Ph), 113.24 (C, CMe_2), 82.34 (C-4), 82.29 (C-3), 81.36 (C-2), 74.31 (C-1), 69.99 (C-5), 26.80 and 25.14 (Me_2, CMe_2), 21.86 (C, PhMe). Anal. Calcd for $C_{15}H_{20}O_6S$ (328.38): C, 54.86; H, 6.14; S, 9.76. Found: C, 54.78; H, 6.21; S, 9.79; MALDITOF-MS (CHCA): *m*/*z* 351.1 ($[M+Na]^+$).

3.7. *N*-(1,4-Anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)trimethylammonium tosylate (4)

Compound **3** (0.07 g, 0.22 mmol) and 33% methanolic Me_3N (4.56 mL) were heated in a glass ampoule for 15 min at 70 °C until compound **3** was dissolved. The solution was then cooled, and EtOH, together with the excess of Me_3N, were removed in vacuo. The yield of colorless crystals with mp 212.0–213.4 °C, $R_f = 0.0$ (2:3 acetone–hexane) was **3** (0.086 g, 100%). A single crystal of the compound suitable for X-ray diffractometry was obtained by crystallization from an EtOH–acetone mixture. ^1H NMR (D_2O): δ 1.39 and 1.56 (2s, each 3H, CMe_2), 2.42 (s, 3H, MePh), 3.23 (s, 9H, NMe_3), 3.49 (dd, 1H, $J_{4,5}$ 2.0, $J_{5,5'}$ 14.0, H-5′), 3.63 (dd, 1H, $J_{4,5'}$ 11.2, H-5), 4.05 (dd, 1H, $J_{1',2}$ 3.6, H-1′), 4.15 (d, 1H, $J_{1,1'}$ 12.0, H-1), 4.74 (m, 2H, $J_{4,5'}$ 10.8, H-3, H-4), 5.03 (t, 1H, $J_{2,3}$ 5.6, H-2), 7.41 and 7.32 (2s, each 2H, Ph); ^{13}C NMR (D_2O): δ 142.70, 139.76, 129.67, 125.61 (C, Ph), 113.75 (C, CMe_2), 83.53 (C-3), 80.41 (C-2), 79.57 (C-4), 71.38 (C-1), 63.47 (C-5), 54.15 (C, NMe_3), 25.49 and 23.75 (Me_2, CMe_2), 20.70 (C, PhMe). Anal. Calcd for $C_{18}H_{29}NO_6S$ (387.48): C, 55.81; H, 7.49; N, 3.62; S, 8.27. Found: C, 55.62; H, 7.58; N, 3.74; S, 8.56; MALDITOF-MS (CHCA): *m*/*z* 216.2 ($[M-OTs]^+$).

3.8. *N*-(1,4-Anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)triethylammonium tosylate (5)

1,4-Anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**3**) (0.04 g, 0.13 mmol) and Et_3N (3 mL) were heated in a sealed ampoule at 70 °C for 16 h. Then Et_3N was removed in vacuo, H_2O was added to the residue (solidified oil) H_2O (1.5 mL), and the unreacted reagent was extracted twice with $CHCl_3$ (15-mL portions). The layer was concentrated under reduced pressure below 40 °C, and the colorless crystals were dried over P_2O_5 in a vacuum desiccator. The yield of compound **5** was 24 mg (46%): $R_f = 0.0$ (2:3 acetone–hexane). ^1H NMR (D_2O): δ 1.29 (t, 9H, Me_3), 1.39 and 1.55 (2s, each 3H, CMe_2), 2.42 (s, 3H, MePh), 3.52 (m, 8H, $(CH_2)_3$, H-5, H-5′), 4.06 (dd, 1H, $J_{1',2}$ 3.6, H-1′), 4.14 (d, 1H, $J_{1,1'}$ 12.0, H-1), 4.52 (d b, 1H, $J_{4,5'}$ 10.0, H-4), 4.74 (dd, 1H, $J_{3,4}$ 2.0, H-3), 5.00 (dd, 1H, $J_{2,3}$ 6.0, H-2), 7.40

and 7.73 (2s, each 2H, Ph); ^{13}C NMR (D_2O): δ 142.62, 139.97, 129.69, 125.64 (C, Ph), 114.05 (C, CMe_2), 83.98 (C-3), 80.38 (C-2), 79.09 (C-4), 72.03 (C-1), 55.37 (C-5), 53.87 (C, $(CH_2)_3$), 25.66 and 23.90 (Me_2, CMe_2), 20.73 (C, PhMe), 7.01 (C, $(CH_3)_3$). Anal. Calcd for $C_{21}H_{35}NO_6S$ (429.57): C, 58.72; H, 8.21; N, 3.26; S, 7.46. Found: C, 58.47; H, 8.03; N, 3.09; S, 7.23; MALDITOF-MS (CHCA): *m*/*z* 258.4 ([M−OTs]$^+$).

3.9. *N*-(1,4-Anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)pyridinium tosylate (6)

1,4-Anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**3**) (0.05 g, 0.16 mmol) and anhydrous pyridine (1 mL) were heated in a sealed ampoule at 70 °C for 23 h. After cooling the mixture in an ice bath, white needles fell out that were filtered off, dried, and recrystallized from pyridine to give **6** (60 mg, 94% yield): mp 135–137 °C, R_f = 0.0 (2:3 acetone–hexane). ^{1}H NMR (D_2O): δ 1.42 and 1.53 (2s, each 3H, CMe_2), 2.41 (s, 3H, MePh), 4.17 (d, 2H, $J_{1',2}$ 2.8, H-1, H-1′), 4.57 (dt, 1H, $J_{4,5}$ 2.0, H-4), 4.70 (dd, 1H, $J_{4,5'}$ 11.2 H-5′), 4.86 (dd, 1H, $J_{5,5'}$ 13.2, H-5), 4.95 (dd, 1H, $J_{3,4}$ 1.2, H-3), 5.13 (dq, 1H, $J_{2,3}$ 6.0, $J_{1,2}$ 10.4, H-2), 7.39 and 7.72 (2s, each 2H, Ph), 8.13, 8.64, 8.83 (5H, Py); ^{13}C NMR (D_2O): δ 146.55, 144.95, 128.54 (C, Py), 142.67, 139.77, 129.67, 125.61 (C, Ph), 113.75 (C, CMe_2), 83.93 (C-4), 82.13 (C-3), 80.94 (C-2), 71.49 (C-1), 59.34 (C-5) 25.46 and 23.83 (Me_2, CMe_2), 20.70 (C, PhMe). Anal. Calcd for $C_{20}H_{25}SO_6N$ (407.48): C, 58.97; H, 6.14; N, 3.44; S, 7.86. Found: C, 59.06; H, 6.19; N, 3.46; S, 7.82; MALDITOF-MS (CHCA): *m*/*z* 236.1 ([M−OTs]$^+$).

3.10. *N*-(1,4-Anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)-2-methylpyridinium tosylate (7)

1,4-Anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**3**) (0.051 g, 0.16 mmol) and 2-methylpyridine (1 mL) were heated in a sealed ampoule at 70 °C for 94 h. TLC analysis (2:3 acetone–hexane) showed the absence of the starting reagents. 2-Methylpyridine was removed in vacuo to leave a brown, solidified oil that was dissolved in H_2O and heated with charcoal for 5 min. The charcoal was filtered off, and the solvent was evaporated to give **7** (0.039 g, 60%) as a solidified yellow oil: R_f = 0.0 (2:3 acetone–hexane). ^{1}H NMR (D_2O): δ 1.42 and 1.53 (2s, each 3H, CMe_2), 2.39 (s, 3H, MePh), 2.86 (s, 3H, MePy), 4.17 (d, 2H, $J_{1',2}$ 2.4, H-1, H-1′), 4.53 (dt, 1H, $J_{4,5'}$ 10.8, H-4), 4.63 (dd, 1H, $J_{5,5'}$ 14.0, H-5′), 4.85 (dd, 1H, $J_{4,5}$ 2.4, H-5), 4.95 (dd, 1H, $J_{3,4}$ 1.6, H-3), 5.12 (dq, 1H, $J_{2,3}$ 6.0, $J_{1,2}$ 10.4, H-2), 7.37 and 7.11 (2s, each 2H, Ph), 7.90, 7.95, 8.43, 8.62 (4H, Py); ^{13}C NMR (D_2O): 155.78, 146.03, 145.79, 130.50, 125.75 (C, Py), 142.61, 139.84, 129.66, 125.61 (C, Ph), 113.77 (C, CMe_2), 83.15 (C-4), 82.43 (C-3), 80.97 (C-2), 71.69 (C-1), 55.96 (C-5), 25.56 and 23.91 (Me_2, CMe_2), 20.70 (C, PhMe), 20.04 (MePy). Anal. Calcd for $C_{21}H_{27}NO_6S$ (421.51): C, 59.84; H, 6.46; N, 3.32; S, 7.61. Found: C, 59.70; H, 6.23; N, 3.18; S, 7.39; MALDITOF-MS (CHCA): *m*/*z* 250.3 ([M−OTs]$^+$).

3.11. *N*-(1,4-Anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)-3-carbamoylpyridinium tosylate (8)

1,4-Anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**3**) (0.033 g, 0.10 mmol), 3-carbamoylpyridine (0.01 g, 0.08 mmol) and CH_3CN (1.5 mL) were heated at 70 °C for 312 h in a sealed ampoule. After removing the solvent in vacuo, H_2O (1.5 mL) was added to the dry residue, and the solution was extracted with $CHCl_3$ (15-mL portions) to remove unreacted **3**. The aq layer was then evaporated to dryness in vacuo below 40 °C to give **8** (0.02 g, 45%) as a solidified oil: R_f = 0.0 (2:3 acetone–hexane). ^{1}H NMR (D_2O): δ 1.42 and 1.53 (2s, each 3H, CMe_2), 2.39 (s, 3H, MePh), 4.20 (dd, 2H, $J_{1',2}$ 3.6, H-1, H-1′), 4.60 (dd b, 1H, $J_{4,5}$ 1.8, H-4), 4.79 (m, 1H, $J_{4,5'}$ 11.2, H-5′), 4.93 (m, 2H, $J_{3,4}$ 0.8, H-3, H-5), 5.13 (dd b, 1H, $J_{2,3}$ 5.6, H-2), 7.37 and 7.70 (2s, each 2H, Ph), 7.63, 8.28, 9.01, 9.29 (4H, Py); ^{13}C NMR (D_2O): δ 151.69, 147.58, 144.96, 137.07, 128.68, 124.61 (C, Py), 142.62, 140.00, 129.64, 125.58 (C, Ph), 113.70 (C, CMe_2), 83.83 (C-4), 82.14 (C-3), 80.95 (C-2), 71.57 (C-1), 59.94 (C-5), 25.47 and 23.83 (Me_2, CMe_2), 20.68 (MePy). Anal. Calcd for $C_{21}H_{26}N_2O_7S$ (450.51): C, 55.98; H, 5.81; N, 6.22; S, 7.12. Found: C, 55.96; H, 5.95; N, 6.28; S, 7.33; MALDITOF-MS (CHCA): *m*/*z* 279.4 ([M−OTs]$^+$).

3.12. *N*-(1,4-Anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)-4-(*N*,*N*-dimethylamino)pyridinium tosylate (9)

1,4-Anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**3**) (0.027 g, 0.08 mmol), 4-(*N*,*N*-dimethylamino)pyridine (0.013 g, 0.11 mmol) and CH_3CN (1 mL) were heated in a sealed ampoule at 70 °C for 311 h. TLC analysis (2:3 acetone–hexane) showed the absence of the starting reagent. The CH_3CN was removed in vacuo, and the dry residue was crystallized from EtOH–acetone mixture to give **9** (0.035 g, 94.8%): mp 187–189 °C, R_f = 0.0 (2:3 acetone–hexane). ^{1}H NMR (D_2O): δ 1.40 and 1.52 (2s, each 3H, CMe_2), 2.36 (s, 3H, MePh), 3.17 (s, 6H, Me_2NPy), 4.12 (m, 3H, $J_{1',2}$ 3.2, H-5′, H-1, H-1′), 4.27 (dd, 1H, $J_{4,5}$ 3.4, $J_{5,5'}$ 14.0, H-5), 4.43 (dd, 1H, $J_{4,5'}$ 9.6, H-4), 4.83 (dd, 1H, $J_{3,4}$ 0.8, H-3), 5.06 (dd, 1H, $J_{2,3}$ 6.0, H-2), 6.83, 7.93 (4H, Py), 7.33, 7.68 (2s, each 2H, Ph); ^{13}C NMR (D_2O): δ 156.55, 141.71, 107.78 (C, Py), 142.46, 139.95, 129.61, 125.59 (C, Ph), 113.48 (C, CMe_2) 83.87 (C-4), 82.03 (C-3), 80.91 (C-2), 71.28 (C-1), 55.20 (C-5), 39.61 (C, NMe_2), 25.49 and 23.82 (Me_2, CMe_2), 20.71 (MePy). Anal. Calcd for $C_{22}H_{30}N_2O_6S$ (450.55): C, 58.65; H, 6.71; N, 6.22; S,

7.12. Found: C, 58.32; H, 6.47; N, 6.07; S, 6.90; MALDITOF-MS (CHCA): *m/z* 279.3 ($[M-OTs]^+$).

3.13. *N*-(1,4-Anhydro-5-deoxy-2,3-*O*-isopropylidene-D,L-ribitol-5-yl)quinolinium tosylate (10)

1,4-Anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol (**3**) (0.033 g, 0.11 mmol) and quinoline (2 mL) were heated in a sealed ampoule at 70 °C for 121 h. After removing the quinoline in vacuo, a solidified oil was obtained that was dissolved in H_2O (2 mL) and extracted twice with $CHCl_3$ (2-mL portions) to remove unreacted reagent. The aq layer was concentrated in vacuo at temperature below 40 °C to leave a residue that, after drying, gave **10** (0.38 g, 82.6%) as a solidified oil: $R_f = 0.0$ (2:3 acetone–hexane). ^{1}H NMR (D_2O): 1.44 and 1.49 (2s, each 3H, CMe_2), 2.34 (s, 3H, MePh), 4.18 (t, 1H, $J_{1,2}$ 12.0, H-1′), 4.27 (dd, 1H, $J_{1',2}$ 3.6, $J_{1,1'}$ 11.6, H-1), 4.65 (d b, 1H, $J_{4,5'}$ 11.2, H-4), 4.94 (m, 1H, $J_{5,5'}$ 14.0, H-5), 5.08 (d, 1H, H-3), 5.18 (m, 1H, $J_{2,3}$ 6.4, H-2), 5.45 (dd, 1H, $J_{4,5}$ 2.6, H-5′), 7.31 and 7.65 (2s, each 2H, Ph), 8.06, 8.31, 8.49, 9.16 (7H, quinoline); ^{13}C NMR (D_2O): δ 149.47, 148.80, 137.76, 131.80, 130.46, 127.49, 126.78, 121.67, 117.86 (C, quinoline), 142.54, 139.73, 129.58, 125.53 (C, Ph), 113.76 (C, CMe_2), 82.97 (C-4), 82.23 (C-3), 80.97 (C-2), 71.69 (C-1), 55.75 (C-5), 25.52 and 23.92 (Me_2, CMe_2), 20.65 (MePy). Anal. Calcd for $C_{24}H_{27}NO_6S$ (457.53): C, 63.00; H, 5.95; N, 3.06; S, 7.01. Found: C, 63.25; H, 6.28; N, 3.30; S, 7.32; MALDITOF-MS (CHCA): *m/z* 286.3 ($[M-OTs]^+$).

4. Supplementary material

Full crystallographic details, excluding structure features, have been deposited (deposition no. CCDC 222216) with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Tel.: +44 1223 336408; fax: +44 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.

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