[(2,3-*O*-Isopropylidene-5-*O*-(triphenylmethyl)-α-D-ribofuranosyl]-triphenylstannane

Lynne A. Burnett,⁽¹⁾ Philip J. Cox,⁽²⁾ and James L. Wardell⁽²⁾*

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The synthesis, IR, MS, solution and solid state NMR spectra and X-ray structure of $(2.3-O-isopropylidene-5-O-(triphenylmethyl)-\alpha$ -D-ribofuranosyl]triphenylstannane 1 (R₃Sn = Ph₃Sn) are reported. Compound, 1 (R₃Sn = Ph₃Sn), crystallizes in the orthorhombic space group C222₁ (Z = 8), with a = 8.935(4), b = 17.058(7), c = 47.94(5)Å. There are two short tin-oxygen separations, at 3.030(7) [involving O4, on an alpha carbon] and 3.094(7) Å [involving O2, on a beta carbon]. Only the O4 atom is considered to form a weak and additional bond to tin; this results in a deviation of the geometry at tin toward trigonal bypramid from tetrahedral, with O4 and C34 in the axial sites [C34-Sn-O4 = 152.3(3)°]. The conformation of the ribofuranosyl ring in the solid state is E_o [P, the phase angle of pseudorotation, = 268.4(9)° and τ_{max} , the puckering amplitude, = 38.0(6)°], while the isopropylidene ring conformation is between the envelope form, E_{C6} , and the twist form, O_{TC6} [P = 46.5(10)° and τ_{max} = 36.9(6)°]. In solution, the ribofuranosyl ring adopts a conformation between E_o and $^{1}T_{o}$.

KEY WORDS: Organostannanes; ribofuranose; conformation; solid state NMR, tin NMR.

Introduction

Furanose rings can exist in 10 twist (*T*) and 10 envelope (*E*) forms¹ (see Fig. 1). These forms interconvert with very low barriers (< 4 kcal/mol)^{2,3} to pseudorotation. Much interest has been shown in furanose ring conformations in carbohydrates, both in solution and in the solid state.^{2,4–6} Ribofuranosyl rings, in general, attract attention as a consequence of their presence in nucleosides and nucleotides, with β-D-ribofuranosyl derivatives^{2,5,6} being particular well studied. The number of β-D-ribofuranosyl derivatives, for example, listed in the Cambridge Crystallographic Data base, far exceeds the number of the α anomers.^{7,8} In particular, few structures of 2,3-*O*-isopropylidene- α -D-ribofuranosyl compounds have been reported.

As part of a study on stannylated carbohydrate drivatives, we have investigated the structure of

[(2,3-O-isopropylidene-5-O-(triphenylmethyl)- α -Dribofuranosyl]triphenylstannane, 1 (R₃Sn = Ph₃Sn), using a combination of X-ray crystallography, solution and solid state NMR spectroscopy.

Furanose ring conformations in solution may be deduced from NMR coupling constants and Karplus⁹ type equations, which relate the couplings to the appropriate dihedral angle, (θ) . The interpretation of the coupling constants, such as ${}^{3}J(H-H)$, is complicated since ring substitution alters the form of the Karplus equation and coupling constants can be averaged by the pseudorotation. Although conformations of carbohydrates in the solid state can be determined unambiguously by X-ray crystallography, these solid state conformations, frozen conformations, can be markedly different from those in solution, especially if differences in hydrogen bonding or crystal packing effects dominate. The absence of free hydroxyl groups in 1 removes the possibility of structural differences between solution and solid state structures, arising from H-bonding effects.

The presence of a stannyl group in 1 can be an advantage in providing an additional structural probe, but could conversely provide complications arising from

⁽¹⁾ Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB24 3UE, Scotland.

⁽²⁾ School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen, AB10 IFR, Scotland.

^{*} To whom correspondence should be addressed.



Fig. 1. Pseudorotional pathway of the furanose ring in 1 ($R_3Sn = Ph_3Sn$).

steric or coordinating effects. A measure of the steric bulk of a substituent, X, is the A-factor, which is the free energy difference between conformers of cyclohexyl-X having X in equatorial and axial sites. A factors for the Ph₃Sn, Me and Bu^t groups are 1.44,¹⁰ 1.74,¹¹ and 4.9^{12} kcal/mol, respectively, clearly indicate the relatively small steric demands of the triphenylstannyl moiety. Only a few tetraorganotin molecules are known to contain other than four coordinate tin centres; for these molecules, intramolecular donor centres are usually held

in relatively rigid positions near to the tin centres.¹³⁻¹⁵ Examples of 5-coordinate tetraorganotin compounds are the (Z)-(2-hydroxyvinyl)-stannanes,¹⁴ and 1,2:5,6-di-*O*-isopropylidene-3-C-(triphenylstannylmethyl)- α -D-allofuranose **2** (R = R' = Ph).¹⁵

Experimental

Melting points were measured using a Kofler hotstage microscope and are uncorrected. NMR spectra





were obtained on a Bruker 250 MHz instrument; IR spectra were recorded on Phillips Analytical PU900 and Nicolet 205 Fourier-transform instruments. Mass spectra (EI) were obtained at 70 eV on a Kratos MS50 instrument; m/z measurements for tin-containing ions are quoted for the ¹²⁰Sn isotope. x-ray data for 1 (R₃Sn = Ph₃Sn) were collected by the EPSRC service, based at the University of Wales, Cardiff. Solid state NMR spectra were obtained by the EPSRC service at the University of Durham.

2,3-O-Isopropylidene-5-O-(triphenylmethyl)- α -Dribofuranosyl chloride (3)

Triphenylphosphine (14.0 g, 53.4 mmol) was added to a solution of 2,3-O-isopropylidene-5-O- trityl-D-ribofuranose¹⁶ (18.2 g, 42.1 mmol) in anhydrous DMF (40 ml) and CCl₄ (20 ml). The mixture was stirred at room temperature for 24 h, poured into a stirred mixture of light petroleum (b.p. 40-60°C, 75 ml), diethyl ether (75 ml) and ice-water (150 ml), and filtered through celite to remove the precipitate of triphenylphosphine oxide. The aqueous and organic layers were separated, and the aqueous solution was washed with light petroleum (b.p. 40-60°C)/diethyl ether (1:1 v:v, 150 ml). The combined organic extracts were concentrated to 75 ml, filtered through silica gel to remove remaining traces of triphenylphosphine oxide. The filtrate was dried over anhydrous sodium sulfate, rotary evaporated and the residue recrystallized from light petroleum (b.p. 40–60°C) to give 3 as colorless crystals (5.14 g, 27.1%), m.p. 113-115°C(lit.¹⁶ m.p. 114-115°C).

$[(2,3-O-isopropylidene-5-O-(triphenylmethyl)-\alpha-D-ribofuranosyl]triphenylstannane 1 (R₃Sn = Ph₃Sn)$

To a solution of triphenylstannyllithium, prepared from triphenyltin chloride (2.46 g, 6.0 mmol) and lithium (0.42 g, 60 mmol) in anhydrous THF (20 ml), was added a solution of 3 (1.35 g, 3.0 mmol) in anhydrous THF (10 ml), slowly with stirring. The mixture was stirred under nitrogen at room temperature for 24 h, hydrolyzed with aqueous buffer solution (100 ml, pH 6.6), and then extracted with chloroform (3×50) ml). The combined chloroform extracts were washed with water $(2 \times 50 \text{ ml})$, dried over anhydrous magnesium sulfate and evaporated in vacuo to leave a white residue. Purification on a chromatotron gave 1 (R₃Sn = Ph_3Sn) as a colorless solid (0.77 g, 34.7%). A further 1.46 g of product was isolated but was found to be contaminated with hexaphenylditin. Crystallization of the chromatographed material from ethanol gave the title compound as colorless needles (0.53 g, 23.9%), m.p. 150–152°C.

Chem. Analysis: Found C, 71.0; H, 5.6. Calculated for $C_{45}H_{42}O_4Sn: C, 70.6; H, 5.5\%$.

IR (*KBr*, *cm*⁻¹). 3074, 3034, 3016, 2939, 2875, 1490, 1448, 1429, 1373, 1269, 1206, 1160, 1089, 1077, 1061, 1033, 1008, 857, 759, 751, 729, 700, 632, 450.

¹*H NMR* (250 *MHz*, *CDCl*₃). δ : 1.05 & 1.32 [6H, 2 × s, 2 × CH₃], 3.20 [1H, dd, H5, J_{4,5} 4.8 Hz, J_{5,5'} 9.9 Hz], 3.29 [1H, dd, H5', J_{4,5} 4.1 Hz, J_{5,5'} 9.9 Hz], 4.40 [1H, br t, H4, J_{4,5} 4.9 Hz, J_{4,5'} 4.1 Hz], 4.77 [1H, dd, H3, J_{2,3} 6.1 Hz, J_{3,4} 0.8 Hz], 4.98 [1H, d, H1, J_{1,2} 3.8 Hz], 5.19 [1H, dd, H2, J_{1,2} 3.8 Hz, J_{2,3} 6.1 Hz], 7.29, & 7.44 [24H, 2 × m, aromatic-H], 7.73 [6H, m, *ortho*-aromatic-H (Ph₃Sn), J^{119,117}Sn⁻¹H 49 Hz].

¹³*C NMR* (62.9 *MHz*, *CDCl*₃). δ: 24.6 & 25.2 [2 × CH₃], 64.1 [C5], 81.9 [C1, J^{119,117}Sn⁻¹³C 502, 480 Hz], 83.0 [C3, J^{119,117}Sn⁻¹³C 27.5 Hz], 85.2 [C2, J^{119,117}Sn⁻¹³C 24.1 Hz], 85.9 [C4, J^{119,117}Sn⁻¹³C 45.8 Hz], 86.8 [*C*Ph₃], 111.8 [*C*Me₂], 126.9 [*C_p*, Ph₃C], 127.8 [*C_m*, Ph₃C], 128.2, 128.5 [*C*₀ (Ph₃C) & *C_m* (Ph₃Sn)], 128.7 [*C_p*, Ph₃Sn, J^{119,117}Sn⁻¹³C 11.2 Hz], 137.3 [*C_m*, Ph₃Sn, J^{119,117}Sn⁻¹³C 519, 496 Hz], 143.7 [*C_i*, Ph₃C].

¹³C NMR (75. 4 MHz, solid state:xpolar pulse sequence: cross polarization contact time 1.00 ms: relaxation delay 10.0 sec). δ: 24.7 & 26.7 [CH₃], 68.8 [C5], 83.0 & 84.8 (br) [C1, C2, C3 & C4], 87.5 [CPh₃], 111.1 [CMe₂], 126.1, 129.0 (br) [envelope with peaks at 28.1 and 129.5], & 137.4 (protonated aryl-C), 128.3, 138.6, 140.0, 142.2, 143.1 & 149.4 [nonprotonated aryl-C].

¹¹⁹Sn NMR (111.9 MHz, solid state:xpolar pulse sequence: cross polarization contact time 1.00 ms: relaxation delay 10.0 sec). δ : -169.5.

MS (70 ev) mass of tin-containing fragments based on Sn-120. m/z [% fragment]. 707 [4%, $M^+-C_2H_4O_2$, 632 [$M^+-Ph-C_3H_6O$], 533 [2%], 465 $[18\%, M^+-Ph_3C-C_3H_7O]$ 409 [7%], 351 [97%,Ph₃Sn⁺], 274 [2%, Ph₂Sn⁺], 243 [100%, Ph₃C⁺], 197 [17%, PhSn⁺], 165 [65%, C₁₂H₉], 154 [7%, Ph₂⁺], 120 [13%, Sn⁺], 105 [19%], 78 [17%, C₆H₆⁺], 77 [16%, $C_6H_5^+$], 43 [30%].

Iodo[(2,3-O-isopropylidene-5-O- $(triphenylmethyl)-\alpha-D$ $ribofuranosyl]diphenylstannane, 1 (R_3Sn =$ IPh₂Sn)

To a solution of compound 1 ($R_3Sn = Ph_3Sn$), (0.2 mmol), in CHCl₃ (6 ml) was added I₂ (0.51 g, 0.2 mmol). The solution was placed in the dark until decolorized. All volatiles were removed in vacuo and the NMR spectra of the residual oil taken.

¹H NMR (250 MHz, CDCl₃). δ: 1.00 & 1.28 [6H, $2 \times s$, $2 \times CH_3$], 3.15 [1H, dd, H5, $J_{4.5}$ 4.4 Hz, $J_{5.5}$ 10.0 Hz], 3.29 [1H, dd, H5', J_{4.5'} 4.0 Hz, J_{5.5}' 10.0 Hz], 4.39 [1H, br s, H4], 4.76 [1H, m, H3,], 5.15 [2H, br.s, H1 & H2], 7.32, 7.70 & 7.82 [25H, $3 \times m$, aromatic-H].

 ^{13}C NMR (62.9 MHz, CDCl₃). δ : 24.4 & 25.1 [2] \times CH₃], 64.4 [C5], 83.1 [C3, J^{119,117}Sn-¹³C 31.6 Hz], 84.4 [C2, $J^{119,117}Sn^{-13}C$ 28.3 Hz], 86.2 [C4, $J^{119,117}Sn^{-13}C$ 56.3 Hz], 87.1 [CPh₃], 88.5 [C1, J^{119,117}Sn⁻¹³C 570, 545 Hz], 112.5 [*C*Me₂], 127.0 [C_p, Ph₃C], 127.9 [C_m, Ph₃C], 128.6 [C_o, (Ph₃C)], 128.7 $[C_m (Ph_3C)], 129.8 [C_p, Ph_3Sn, J^{119,117}Sn^{-13}C 13.6]$ Hz], 137.4 [C_o, Ph₃Sn, $J^{119,117}$ Sn $-^{13}$ C 45.5 Hz], 138.9 [C_b Ph₃Sn], 143.5 [C_i, Ph₃C].

¹¹⁹Sn NMR (93.3 MHz, CDCl₃). δ-142.4.

Crystal structure determination of 1 ($R_3Sn =$ $Ph_{3}Sn$

The crystal used for the determination was grown from ethanol solution. The unit cell and intensity data were collected on a Delft Instruments FAST diffractometer with monochromated Mo- $K\alpha$ radiation using the routines, ENDEX, REFINE, and MADONL in the using the routines ENDEX, REFINE and MADONL in the The structure was solved with SHELXS86¹⁹⁸ and refined with SHELXL93.²⁰ The nonhydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were allowed to ride on their attached carbon atoms with isotropic temperature factors either unrestrained (methyl) or 1.2 times that of their host (nonmethyl). No absorption corrections absorption were applied. The molecular plot was obtained with ZORTEP.21 Crystal data and refinement details are listed in Table 1.

Results and discussion

Compound 1 ($R_3Sn = Ph_3Sn$) was prepared from the reaction of Ph₃SnLi with 2,3-O-isopropylidene-5-O-trityl- β -D-ribofuranosyl chloride, equation 1. Only $1 (R_3 Sn = Ph_3 Sn)$, the product of inversion of configuration at the anomeric carbon atom, was isolated.

The molecular structure of 1 ($R_3Sn = Ph_3Sn$)

The atomic arrangements of 1 ($R_3Sn = Ph_3Sn$) and the numbering system are shown in Fig. 2. Atomic coordinates are listed in Table 2, selected bond lengths, valency and torsion angles are shown in Table 3. The C-Sn-C valency angles are spread between 100.6(4) and $119.6(4)^{\circ}$. The four Sn-C bond lengths are between 2.118(11) and 2.164(9) Å, *i.e.*, in normal range found for tin-carbon bonds in tetraorganotin species. The two shortest Sn---O separations involve 04, on the α -carbon and O2 on a β -carbon atom: Sn---O4 and Sn---O2 are 3.030(7) and 3.094(7) Å, respectively. While these are considerably longer than a Sn-O bond (ca. 2.0 Å), they are well within the sum of the van der Waals radii (ca. 3.70 Å).²² From X-ray diffraction studies of other Ph₃SnCHROR' compounds,²³ the Sn--- O_{α} separations have been found to be in the region of 2.9-3.0 Å The geometries about tin in these compounds is always near tetrahedral, with the C-Sn-C valency angles more closely grouped around the ideal tetrahedral angle of 109.5°, and typically between 106 and 113°; no positive signs could be found to indicate tin-oxygen interactions, which would, of course, produce highly strained three-membered chelate rings.

The coordination of a beta hydroxyl group to a tin center, to give a four member chelate, in a tetraorganotin species has been indicated¹⁴ for both 2 (R=R'=Ph) and $(Z)-MeCH=C(SnPh_3)CMe_2OH$ (4).

Empirical formula	C48H43O4Sn	Formula weight	765.48
Temperature (K)	150(2)	Wavelength (Å)	0.71069
Crystal system	Orthorhombic	Space group	C2221
Unit cell dimensions		Volume (Å ³)	7306(8)
<i>a</i> (Å)	8.935(4)	Ζ	8
<i>b</i> (Å)	17.058(7)	Density (calc) (mg/m ³)	1.392
<i>c</i> (Å)	47.94(5)	Absorption coefft (mm ⁻¹)	0.743
<i>F</i> (000)	3152	Crystal size (mm)	$0.22 \times 0.07 \times 0.11$
Theta range for data coll (°)	2.39 to 24.98	Reflections collected	
Index ranges		Independent reflections	4966
h	$-9 \leq h \leq 10$	Observed reflections	4028 (I>2σ(I)
k	$0 \leq k \leq 19$	Goodness-of-fit (S)	1.080 (on F ²)
l	$0 \le l \le 53$	Refinement method	Full-matrix L.S. on F ²
Final R indices $[l > 2\sigma(l)]$	R1 = 0.0667, wR2 = 0.1442	Number of parameters	453
R indices (all data)	R1 = 0.0917, wR2 = 0.1740	Flack parameter	0.00(5)
Residual diffraction max/min (e/A ³)	2.109 (at Sn) -0.663	Final weighting scheme	$w = 1/[\sigma^{2}(Fo^{2}) + (0.0609P)^{2}]$ where $P = (Fo^{2} + 2Fc^{2})/3$





Fig. 2. Atom arrangement and atom numbering scheme for 1 ($R_3Sn = Ph_3Sn$).

Table 2. Atomic coordinates (\times 10⁴) and equivalent isotropic displacement parameters (Å \times 10³) for 1 (R₃Sn=Ph₃Sn)^a

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C(36) 2670(12) 6697(6) 8645(3) 27(3)
C(37) 3404(12) 6226(6) 8827(3) 32(3)
C(38) 3335(11) 6373(5) 9112(2) 30(3)
C(39) 2495(11) 7019(5) 9213(3) 25(2)
C(40) 600(12) 8380(5) 9626(2) 210	2)
C(41) 1610(12) 8785(6) 9791(2) 27(3)	3)
C(42) 1595(14) 8698(6) 10078(3) 43(3)
C(43) 608(15) 8200(6) 10206(2) 390	3)
C(44) = -399(14) = 7780(7) = 10047(2) = 420	3)
C(45) -411(14) 7875(6) 9756(2) 32(3)

a	$U_{(eq)}$	is	defined	as	one	third	of	the	trace	of	the	orthogonalized
	$U_{}$ te	ens	or.									

In 4, the C-Sn-C valency angles vary between 103.9(1) and $128.3(4)^{\circ}$: other geometric data for 4 were Sn - O = 3.012(3) Å, and O - Sn - C valency angles of 49.3(1) [the chelate angle], 77.9(1), 100.0(2), and $149.5(1)^{\circ}$ [the latter can be considered to be the axial-Sn-axial angle]. The O2-Sn-Cangles in (1: R₃Sn=Ph₃Sn) are 51.2(3) [the chelate angle], 77.7(3), 92.3(3) and 152.3(3) Å, *i.e.*, comparable to those in 3. Selected geometric data for 2 (R=R'=Ph) are 3.01(1) Å [Sn---O] and 160.8(3)° [O-Sn-C(ax)]. As similarly argued by Gielen et al. for 4, the structure of 1 ($R_3Sn=Ph_3Sn$) shows a deviation toward trigonal bipyramid from tetrahedral geometry due to the weak tin-oxygen interaction. The weaknesses of the tin-oxygen interactions in 1 and 3 result from the strain in creating four-membered chelate rings and also from the weak Lewis acid character of tin centers in tetraorganotin compounds. Stronger tin-oxygen interactions and more linear C(ax)-Sn-O(ax) angles are realized in tetraorganotin compounds when five-membered chelates are formed, ¹⁴ e.g., as in (Z)-17-(2-triphenylstannylvinyl) 4-estren-17-ol [Sn---O = 2.77 Å and O-Sn-C(ax)] = $168(1)^{\circ}$] and in (Z)-(p-XC₆H₄)₃SnCH=CHCR₂OH $[R_2 = -(CH_2)_6)$ -] [Sn---O/O-Sn-C(ax) values are 2.742(3) $\text{\AA}/167.7(1)^{\circ}$ (X=H) and 2.768(3) $\text{\AA}/$ $168.4(1)^{\circ}$ (X=Me]. Stronger four-membered chelate rings have been found in appropriate triorganotin halides, e.g., in 3-C-(dibutyliodostannyl)methyl-1,2:5,6-di-*O*-isopropylidene- α -D-allofuranose,²⁴ 2 (R=Bu, R' = I), the Sn-O bond length is 2.68(2) Å, while the I(ax) - Sn - (ax) valency angle is $158.3(4)^{\circ}$.

The solution and solid state δ^{119} Sn values for 1 (R₃Sn=Ph₃Sn) are -153.4 and -169.5 ppm, respectively. The slight difference, $\Delta \delta^{119}$ Sn (= δ^{119} Sn_{solution}- δ^{119} Sn_{solid}) = 16.1 ppm suggests little structural change at tin on dissolution. However, the finding for a number of triorganostannylsaccharides, all four coordinate species in both phases, is that $\Delta \delta^{119}$ Sn is normally negative, *e.g.*, $\Delta \delta^{119}$ Sn = -27.7 and -13.3 for methyl 5-deoxy-2,3-*O*-isopropylidene-5-*C*-triphenylstannyl- β -Dribofuranoside (two independent molecules), (**5**),³⁰ -7.0 for methyl 2,3-*O*-isopropylidene-5-*O*-triphenylstannylmethyl- β -D-ribofuranoside, (**6**)³⁰ and -1.5 ppm for 1,2-*O*-isopropylidene-3-*O*-triphenylstannylmethyl-5-*O*-triphenylmethyl- α -D-xylofuranose, (**7**).³¹

In the ¹³C solid state NMR spectrum, the number of aryl-C signals reveals the inequivalence of the three phenyl substituents on tin. Comparisons of the solid state and solution ¹³C NMR spectra indicate some significant shifts: *e.g.*, C5 shows a shift of 4.7 ppm,

(a) Bond lengths			
Sn-C34	2.118(11)	Sn-C28	2.143(11)
Sn-C40	2.123(9)	Sn-Cl	2.164(9)
Sn—O2	3.094(7)		
O2-C2	1.421(12)	C4-C5	1.490(14)
O2-C6	1.443(12)	C3-C4	1.550(13)
O3-C3	1.409(12)	C2-C3	1.557(14)
O3-C6	1.427(13)	C1-C2	1.499(13)
O4-C4	1.437(11)	O5-C9	1.461(11)
O4-C1	1.439(12)	O5-C5	1.441(11)
(b) Bond angles			
C34-Sn-C40	105.7(4)	C34-Sn-C28	110.7(4)
C40-Sn-C28	112.6(4)	C34-Sn-C1	107.5(4)
C40-Sn-C1	119.6(4)	C28-Sn-C1	100.6(4)
C1-Sn-O2	51.2(3)	C28-Sn-O2	92.3(3)
C34-Sn-O2	152.3(3)	C40-Sn-O2	77.7(3)
C2-O2-C6	107.6(8)	C3-O3-C6	108.0(8)
C4-O4-C1	106.5(7)	C5-O5-C9	115.0(7)
O4-C1-C2	106.3(7)	O4-C1-Sn	113.0(6)
C2-C1-Sn 113.2(6)		O2-C2-C1	112.0(8)
02-C2-C3 104.5(8)		O3-C3-C4	110.0(8)
O3-C3-C2	103.7(9)	C4-C3-C2	102.9(8)
O4-C4-C5 114.4(8)		O4-C4-C3	105.4(8)
C5-C4-C3 114.6(9)		O5-C5-C4	107.7(7)
O3-C6-O2	103.2(8)		
(c) Torsion angles			
C4-O4-C1-C2	36.2(10)	C3-C2-O2-C6	-17.5(10)
O4-C1-C2-C3	-20.7(10)	C2-O2-C6-O3	33.1(10)
C1-C2-C3-C4	-1.0(10)	02-C6-O3-C3	-36.7(11)
C2-C3-C4-O4	22.3(10)	C6-O3-C3-C2	25.4(10)
C3-C4-O4-C1	-36.6(9)	O3-C3-C2-O2	-4.6(10)
C4 - O4 - C1 - Sn	161.0(10)	O4-C4-C5-O5	-64.4(10)
Sn-Cl-C2-C3	-145.3(7)	Sn-C1-O4-C4	161.0(6)
C3-C4-C5-O5	57.4(11)	H1 - C1 - C2 - H2	-26.1(4)
H2-C2-C3-H3	-2.2(4)	H3-C3-C4-H4	-101.1(3)

Table 3. Selected bond lengths (Å), bond and torsion angles (°) for 1 $(R_3Sn=Ph_3Sn)$



while one of the aryl C_{ipso} carbons experiences a large shift of at least 6 ppm to 149.4 ppm. The separation of the chemical shifts of C1, C2, C3 and C4 in the solid state spectrum were not sufficient to assign the individual signals.

Furanose ring conformations

The conformation of the furanose ring in solid 1 ($R_3Sn = Ph_3Sn$) was calculated to be E_0 from the torsional angles in the furanose ring: the pseudorotational parameters P, phase angle of pseudorotation, and the τ_m puckering amplitude,⁵ were found to be 268.4(9)° and 38.0(6)°, respectively. This conformation has also been established for all the 2.3-Oisopropylidene- α -D-ribofuranosyl compounds listed in the Cambridge Crystallographic Data base, namely, [8: $X = (CN) = NOSO_2C_6H_4Me_{-p}^{25}$ $Y = OCPh_3$ $X = CH_2CN$, $Y = O_2CC_6H_4Br-p$,²⁶ $X = NHCOC_6H_4$ - $CO_2Me \cdot oY$, = $O_2C_6H_4NO_2 \cdot p$,²⁷, and 2,5-bis[(1deoxy-2,3-O-isopropylidene- α -D-ribofuranosyl)amino]-3,6-difluoro-p-benzoquinone.²⁸

The solution ${}^{3}J(H-H)$ values associated with the furanose ring in 1 (R₃Sn=Ph₃Sn) are ${}^{3}J(H1-H2) =$ 3.8, ${}^{3}J(H2-H3) = 6.1$ and ${}^{3}J(H3-H4) = 0.8$ Hz. These values are within the regions [3.5 to 4.0, 6.0 to 6.5, and 0 to 1.0 Hz, respectively] determined for 8 [Y=Ph₃CO, X=CH(CO₂Me)₂, CH₂CO₂Me or CH₂CN; Y=OH, X=CH₂CO₂Me or CH₂CN] and for 8 (Y=OH, X=imidazol or uracil moiety).²⁹ This indicates that the 2,3-O-isopropylidene- α -D-ribofuranosyl compounds, 1 (R₃Sn=Ph₃Sn) and 8, despite the different substituents at C1 and C5, undergo similar conformational equilibria in solution.

Ohrui and co-worker suggested²⁷ from their Xray crystallographic and NMR spectral data that the conformation of 8 ($Y = OCPh_3$, $X = CH_2CN$) does not on dissolution. The H1 - C1 - C2 - H2, alter H2-C2-C3-H3 and H3-C3-C4-H4 torsional angles for 1 ($R_3Sn = Ph_3Sn$) calculated from the Xray data are -26.1 (4), -2.3 (4), and $-101.1(3)^{\circ}$, respectively. The ${}^{3}J(H-H)$ values, calculated from the H1-C1-C2-H2 and H2-C2-C3-H3 torsional angles and Karplus equations,⁹ differed from those directly observed in the ¹H NMR spectrum. To account for the solution ³J(H1-H2) and ³J(H2-H3) values recorded for 1 ($R_3Sn = Ph_3Sn$), we believe that the numerical values of both H1-C1-C2-H2 and H2-C2-C3-H3 must increase on dissolution, e.g., to about 40-45 and 30-35°, respectively, as would



($R_3Sn = Ph_3Sn$).

result on the conformation moving along the pseudorotational pathway toward the twist form, ${}^{1}T_{o}$ from the solid state E_{o} conformation.

Isopropylidene ring

The pseudorotational parameters of the isopropylidene ring in solid 1 (R₃Sn=Ph₃Sn) are $P = 46.5(10)^{\circ}$ and τ_m , = 36.9(6)⁰: this corresponds to a conformation between the envelope form, E_{c6} , and the twist form, ${}^{O3}T_{c6}$.

Rotamer populations about the C4-C5 bond

The rotamer arrangement about the C4–C5 bond in solid 1 (R₃Sn=Ph₃Sn) can be described as *gauchegauche* (*gg*) (see Fig 3). The rotamer populations about the C4–C5 bond in CHCl₃ solution can be estimated from ³J(H4–H5) and ³J(H4–H5') values. As found by Serianni *and* co-workers,³¹ the proton at C5 with the more downfield signal is the pro-S proton in ribofuranosyl compounds, *i.e.*, for 1 (R₃Sn=Ph₃Sn) the proton designated as H5 corresponds to H5R and H5' to H5S. Using these assignments, estimates of the coupling constants of the individual rotamers, and equations³¹ 2–4, the C4–C5 bond rotamer [*gg: gt; tg*] populations (*t* = *trans*), were calculated to be at 25°C = 0.51 : 0.22 : 0.27.

1.3 $gg + 2.7 gt + 11.7 tg = {}^{3}J(H4-H5S) = 4.4$ (2)

$$1.3 gg + 11.5 gt + 5.8 tg = {}^{3}J(H4-H5R) = 4.8 (3)$$

$$gg + gt + tg = 1 \quad (4)$$

Other solution NMR spectra

The ${}^{1}J({}^{119}Sn - {}^{13}C_{\alpha})$ and ${}^{1}J({}^{119}Sn - {}^{13}C_{i})$ values of 502 and 519 Hz, respectively, for 1 (R₃Sn=Ph₃Sn)

are similar to those determined for 4 [509 and 512 Hz]: ${}^{1}J({}^{119}Sn - {}^{13}C_{\alpha})$ value (519 Hz) for 2 (R = R' = Ph) is also in the same region. The solution ${}^{3}J({}^{119}Sn - {}^{13}C)$ values associated with C-3 and C-4 are 27.5 and 45.8 Hz, respectively. A Karplus-type equation relating ³J(¹¹⁹Sn-¹³C) and Sn-C-C-C dihedral angles has been established for rigid trimethylstannanes.³² Related equations for other stannanes, such as triphenylstannanes, have yet to be developed due to the lack of data for compounds with welldefined structures in solution. While the values of the dihedral angles, $Sn-C1-C2-C3 = -145.3(7)^{\circ}$ and Sn - C1 - O4 - C4 [= 161.0(6)°], have been determined in the solid state for 1 ($R_3Sn = Ph_3Sn$), their values probably do not pertain in solution due to the slight structural alterations on dissolution.

Compound 1 ($R_3Sn = IPh_2Sn$)

Compound 1 ($R_3Sn = IPh_2Sn$) was isolated from the reaction of 1 ($R_3Sn = Ph_3Sn$) with I_2 (1:1 mol ratio) in CHCl₃ as a oily solid. Attempts to obtain suitable crystals for X-ray crystallography all failed. The resolution in the ¹H NMR spectrum was not sufficient to obtain values for ³J(H-H) in the furanose ring. Selected solution NMR parameters for 1 ($R_3Sn=IPh_2Sn$) – $\delta^{119}Sn = -142.4$ ppm and ¹J(¹¹⁹Sn-¹³C_{α}) = 570 Hz -indicate a five-coordinate tin center.

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Supplementary material. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1003/5360. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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