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[6-*O*-(1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranosyl)methyl]tin derivatives

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Abstract

A family of [6-*O*-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosyl)methyl]tin species $Ph_nSn(CH_2OR)_{4-n}$ (**1**n = 1–3), $Ph_nMe_{3-n}Sn(CH_2OR)$ (**2**n = 0–3) and Bu_3SnCH_2OR (**3**) have been prepared from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (ROH) and the iodomethyltin compounds $Ph_nSn(CH_2I)_{4-n}$ (n = 1–3), $Ph_nMe_{3-n}SnCH_2I$ (n = 1–3) and Bu_3SnCH_2I. The pyranose rings in these mono-, di- and trisaccharide derivatives, as well as in $IPh_nSn(CH_2OR)_{3-n}$ (**4**n = 0–2) and $IPh_nMe_{2-n}Sn(CH_2OR)$ (**5**n = 0, 1), have similar twist-boat conformations in solution. The solution $\delta\,^{119}Sn$ NMR values for the series (**1**n = 1–4) and (**4**n = 1–3) do not vary linearly with n. The X-ray diffraction study of (**4**n = 1) at 120 K revealed that only one of the sugar moieties acts as a *C*,*O*-bidentate ligand, via its pyranose ring oxygen. The tin centre in solid (**4**n = 1) is five-coordinate and has a trigonal bipyramidal geometry: the Sn–O and Sn–I bond lengths are 2.759(5) and 2.790(2) Å respectively, with the I–Sn–O valency angle of 173.5(1)°. As indicated by the solid state and solution $\delta\,^{119}Sn$ values (−177.8 and −130.7 ppm respectively), the solid state structure of (**4**n = 1) does not survive on dissolution. The two pyranose rings in solid (**4**n = 1) have similar conformations (intermediate between screw-boat $^{O}S_5$ and the twist-boat forms $^{O}T_2$ with deviations in the direction of the boat-form $B_{2,5}$). Compound (**1**n = 3) undergoes transmetallation with PhLi to give $LiCH_2OR$, which was trapped as the triphenylgermanium derivative Ph_3GeCH_2OR.

Keywords: Tin; Germanium; Pyranose derivatives; Crystal structure

1. Introduction

Carbohydrate derivatives comprise an interesting group of functionally substituted organic species. These chiral moieties, containing several oxygen (and possibly other donor) groups in well-defined stereo-arrangements, have considerable potential as ligands or substituents in metal compounds and complexes. For tin, compounds have been produced in which the tin and carbohydrate units are directly linked via Sn–O [1,2] or Sn–C [2,3] bonds, as well as more indirectly via Sn–CH_2–O (sugar) units [4–6]. The stannylated derivatives so-far reported have contained only one tin–carbohydrate link: no bis- or tris-saccharyl derivative of tin has yet been studied. In order to investigate the effect of more than one carbohydrate moiety on the properties and reactions of stannylated sugar derivatives, a number of [6-*O*-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosyl)methyl]tin compounds, $Ph_nSn(CH_2OR)_{4-n}$ (**1**n = 1–3), $Ph_nMe_{3-n}Sn(CH_2OR)$ (**2**n = 1–3) and Bu_3SnCH_2OR (**3**), have been synthesised from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (ROH) and the appropriate iodomethyltin compounds $Ph_nSn(CH_2I)_{4-n}$ (n = 1–3), $Ph_nMe_{3-n}SnCH_2I$ (n = 1–3) or Bu_3SnCH_2I.

In addition to these syntheses, the effects of the oxygen groups on the structures, NMR spectra and reactions are also reported.

2. Experimental

NMR spectra were obtained on a Bruker 250 MHz instrument; IR spectra were recorded on a Philips Analytical PU9800 Fourier-transform spectrometer. The following EPSRC services were used: solid state NMR spectroscopy, based at the University of Durham, and

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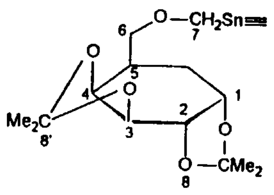
Table 1
^{1}H NMR data for compounds (**1**)–(**5**)



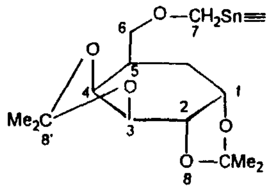
Compound	H-1 $J_{1,2}$	H-2 $J_{2,3}$	H-3 $J_{3,4}$	H-4 $J_{4,5}$	H-5 $J_{5,6}$	H-6 $J^{1}_{6,6}$	H-6^{1} $J^{1}_{5,6}$	H-7 $J^{1}_{7,7}$	H-7^{1} [J(Sn–H7)]	Me$_2$C	Other [$J(^{117,119}$Sn–H)]
(**1**, $n = 3$)[a]	5.59	4.35	4.60	4.19	4.01	3.67	3.74	4.44	5.51	1.36, 1.38	7.35–7.45 (Ph)
	5.0	2.35	7.9	1.8	6.75	9.7	5.8	10.2	[17]	1.48, 1.56	7.62–7.69
(**1**, $n = 2$)	5.55	5.32	4.59	4.19	3.97	3.60	3.66	4.27	4.35	1.34, 1.35	7.32–7.38 (Ph)
	5.0	2.4	7.9	1.8	6.7	9.7	5.9	10.4	[15]	1.46, 1.54	7.61–7.66
(**1**, $n = 1$)	5.51	4.28	4.56	4.18	3.92	3.51	3.58	4.12	4.19	1.32, 1.32	7.27–7.35 (Ph)
	5.0	2.3	7.9	1.6	6.6	9.7	6.0	10.4	[14]	1.43, 1.52	7.59–7.63
(**2**, $n = 2$)	5.57	4.34	4.61	4.21	4.00	3.61	3.68	4.21	4.27	1.36, 1.37	0.60 [55,53] (Me$_3$Sn) 7.34–7.40 (Ph)
	5.0	2.3	7.9	1.9	6.7	9.7	5.9	10.4	[16]	1.47, 1.56	7.58–7.61
(**2**, $n = 1$)	5.55	4.32	4.60	4.22	3.98	3.55	3.61	3.96	4.03	1.35, 1.35	0.37 [55,53] (Me$_3$Sn) 7.32–7.39 (Ph)
	5.0	2.3	8.0	1.8	6.5	9.6	5.8	10.5	[15]	1.46, 1.55	7.52–7.55
(**2**, $n = 0$)	5.54	4.31	4.61	4.24	3.97[b]	3.54[b]	3.54[b]	3.76	3.84	1.35, 1.35	0.15 [51,49] (Me$_3$Sn)
	5.0	2.2	7.7	1.2				[10.4]	[—]	1.45, 1.55	
(**3**)	5.53	4.31	4.60	4.25	3.95	3.48	3.56	3.79	3.83	1.34, 1.35	0.8–1.32
	5.0	2.4	7.9	1.9	6.3	9.6	6.3	[10.4]	—	1.46, 1.54	
(**4**, $n = 2$)	5.56	4.35	4.62	4.21	4.07	3.72	3.78	4.64	4.71	1.35, 1.37	7.32–7.56 (Ph)
	5.0	2.4	7.9	1.8	*ca.* 7	10	*ca.* 5	10.0		1.46, 1.56	7.65–7.80
(**4**, $n = 1$)	5.52	4.30	4.58	4.19	3.97	3.62	3.70	4.48	4.53	1.31, 1.31	7.32–7.50 (Ph)
	5.0	2.4	7.95	1.5	7.2	9.9	5.2	10.2		1.40, 1.50	7.65–7.80
(**4**, $n = 0$)	5.53	4.29	4.57	4.21	3.98	3.56	3.70	4.40	4.45	1.31, 1.32	—
	5.0	2.3	7.95	1.7	7.3	10.1	5.0	10.3		1.44, 1.53	
(**5**, $n = 1$)	5.52	4.33	4.60	4.21	4.01	3.66	3.74	4.46	4.51	1.34, 1.35	1.15 (MeSn); 7.30–7.50 (Ph)
	5.0	2.4	8.0	1.8	7.0	10.1	5.2	10.4		1.45, 1.45	[57,55] 7.60–7.75
(**5**, $n = 0$)	5.49	4.31	4.59	4.18	3.97	3.56	3.70	4.27	4.27	1.32, 1.32	0.97 (MeSn)
	5.0	2.4	7.9	1.7	7.6	10.6	4.8			1.45, 1.53	[57,55]
IMe$_2$SnCH$_2$OR	5.55	4.35	4.63	4.43	4.04	3.73	3.86	4.79	4.79	1.35, 1.35	1.73 (MeSn)
	5.0	2.4	7.9	1.9	7.0	10.3	5.0			1.48, 1.56	[57,55]
HOR[c]	5.54	4.32	4.59	4.26	3.80	3.66	3.76			1.32, 1.32	2.52 (Ph)
	5.0	2.4	7.9							1.43, 1.51	

[a] Ref. [10].

[b] Unresolved couplings.

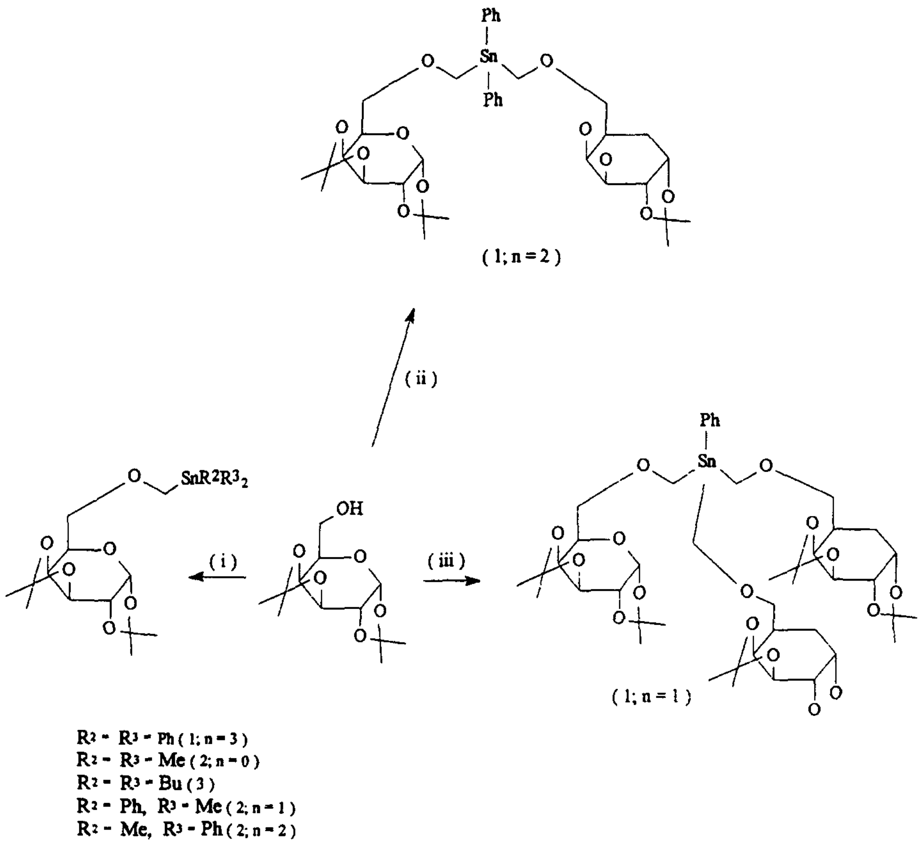
[c] 1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranose.

Table 2
^{13}C and ^{119}Sn NMR data for compounds (**1**)–(**5**)



Compound	δC-1	δC-2	δC-3	δC-4	δC-5	δC-6 [$J(^{117,119}Sn-^{13}C)$]	δC-7 [$J(^{117,119}Sn-^{13}C)$]	δC-8; C-8'	δCMe₂	Other (δ) [a] [$J(^{117,119}Sn-^{13}C)$]	δ ^{119}Sn
(**1**, *n* = 3)	96.3	70.6	70.6	71.1	66.6	74.1 [50]	64.2 [484,462]	108.5 109.1	24.4, 25.0 25.9, 26.1	128.4 [49], 128.9 [11] (Ph) 137.2 [36], 138.4 [499,477] (Ph)	−146.2
(**1**, *n* = 2)	96.3	70.6	70.5	71.0	66.5	73.8 [46]	63.7 [452,432]	108.4 109.1	24.3, 24.9 25.9, 26.1	128.2 [47], 128.7 [11] (Ph) 137.1 [34], 138.9 [466,446] (Ph)	−151.7
(**1**, *n* = 1)	96.2	70.6	70.5	71.0	66.4	73.4 [41]	63.2 [420,402]	108.4 109.0	24.4, 24.9 25.9, 26.1	128.0 [45], 128.4 [—] (Ph) 137.0 [33], 139.5 [429,410] (Ph)	−143.1
(**2**, *n* = 2)	96.3	70.6	70.6	71.1	66.6	73.8 [46]	64.0 [467,446]	108.5 109.1	24.4, 25.0 25.9, 26.1	128.3 [48], 128.6 [11] (Ph) 136.6 [35], 139.7 [—] (Ph) −11.0 [355,339] (Me)	−101.7
(**2**, *n* = 1)	96.3	70.6	70.6	71.1	66.5	73.5 [43]	63.8 [448,428]	108.5 109.1	24.4, 24.9 25.9, 26.0	128.1 [46], 128.2 [13] (Ph) 136.1 [35], 141.2 [—] (Ph) −10.7 [341,327] (Me)	−60.6
(**3**)	96.2	70.6	70.5	71.0	66.3	73.4 [39]	62.6 [365,349]	108.3 108.9	24.2, 24.8 25.8, 25.9	8.87 [320,306], 28.9 [20.2] (Bu) 72.1 [52], 13.5 [—] (Bu)	—
(**4**, *n* = 2)	96.2	70.4	70.5	71.0	66.6	73.6 [50]	68.2 [515,492]	108.5 109.2	24.4, 24.9 25.9, 26.1	128.8 [59], 129.9 [13] (Ph) 136.3 [47], 137.4 [511,489] (Ph)	−126.1
(**4**, *n* = 1)	96.2	70.5	70.5	71.0	66.7	73.1 [40]	68.7 [481,460]	108.6 109.3	24.3, 24.9 25.9, 26.1	129.0 [56], 129.6 [17] (Ph) 136.5 [45], 138.3 [465, 445] (Ph)	−130.7
(**4**, *n* = 0)	96.2	70.5	70.5	70.8	67.0	73.0 [33]	68.9 [417,399]	108.5 109.1	24.3, 24.9 25.9, 26.1	—	−106.4
(**5**, *n* = 1)	96.1	70.4	70.4	70.9	66.5	73.2 [44]	68.0 [506,484]	108.5 109.2	24.3, 24.9 25.8, 21.0	128.6 [57], 129.7 [13] (Ph) 135.7 [47], 138.1 (br) (Ph) −2.9 (Me)	−68.1 (br)
(**5**, *n* = 0)	96.0	70.3	70.4	70.7	67.1	72.8 [39]	68.4 [499,476]	108.6 109.1	24.2, 24.8 25.9, 26.0	−1.6 (Me) [333, 318]	−8.9
HOR [a]	96.2	70.5	70.6	71.4	68.1	62.1	—	108.6 109.3	24.2, 24.9 25.8, 25.9	—	
$I_2MeSnCH_2OR$											−177.7

[a] 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose.



Scheme 1. Reagents (i) $R^2R^3_2$ $SnCH_2I$; NaH, DMF; (ii) $Ph_2Sn(CH_2I_2)$; NaH, DMF; (iii) $PhSn(CH_2I)_3$; NaH, DMF.

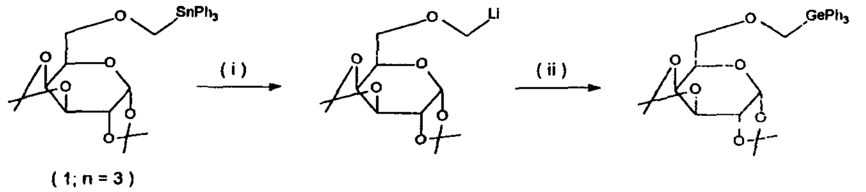
X-ray data collection, based at the University of Wales, Cardiff.

The iodomethylstannane reagents [7] 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose [8] and 1,2:3,4-di-*O*-isopropylidene-6-*O*-[(triphenylstannyl)methyl]-α-D-galactopyranose [6] were produced according to published procedures.

2.1. *Syntheses of [6-O-(1,2:3,4-di-O-isopropylidene-α-D-galactopyranosyl)methyl]tin species* $Ph_nSn(CH_2OR)_{4-n}$ *(1 n = 1–3),* $Ph_nMe_{3-n}Sn(CH_2OR)$ *(2 n = 0–2) or* Bu_3SnCH_2OR *(3)*

The following general procedure was adopted. To a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (3.80 g, 10 mmol) in dry DMF (20 ml) was successively added, under a nitrogen atmosphere, sodium hydride (1.0 g) and $Ph_nSn(CH_2I)_{4-n}$ [(4 − *n*) × 10 mmol], $Ph_nMe_{3-n}SnCH_2I$ (10 mmol) or Bu_3SnCH_2I (10 mmol). The stirred reaction mixture was monitored by TLC [irrigant petrol (60–80°C): EtOAc in ratios varying from 9 : 1 to 2 : 3 v/v]. On complete reaction (less than, 6 h), MeOH (10 ml) was slowly added, followed by H_2O (50 ml) and Et_2O (50 ml). The aqueous phase was separated and extracted with Et_2O (3 × 30 ml). The combined ethereal solutions were dried over $CaCl_2$ and rotary evaporated to leave oily residues: the pure products were obtained as oils after chromatotronic purification. Chemical analyses, IR spectra, yields of pure products and the solvent used as eluant in the chromatographic purification are given below.

(**1** *n* = 2). Yield 88%; eluant petrol (60–80°C): EtOAc 1 : 1.



Scheme 2. Reagents (i) PhLi, Et_2O, −64°; (ii) Ph_3GeBr.

Table 3
Crystal data and structure refinement for (**4** $n = 1$)

Empirical formula	$C_{32}H_{47}IO_{12}Sn$
Formula weight	869.29
Temperature (K)	120(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	10.842(8)
b (Å)	16.443(3)
c (Å)	11.126(7)
β (°)	114.64(4)
Volume (Å^3)	1803(2)
Z	2
Density (calculated) (Mg m^{-3})	1.601
Absorption coefficient (mm^{-1})	1.623
$F(000)$	876
Crystal size (mm^3)	0.28 × 0.32 × 0.30
θ range for data collection	2.07°–24.97°
Index ranges	$-12 \leqslant h \leqslant 12$; $-18 \leqslant k \leqslant 18$; $-10 \leqslant 13$
Reflections collected	7649
Independent reflections	4679 ($R_{int} = 0.0778$)
Observed reflections [$I > 2\sigma(I)$]	4507
Refinement method	Full-matrix least-squares on F^2
Number of parameters	417
Goodness-of-fit on F^2 (S)	1.084
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0400$, $wR_2 = 0.1032$
R indices (all data)	$R_1 = 0.0410$, $wR_2 = 0.1036$
Final weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2$ where $P = (F_o^2 + 2F_c^2)/3$
Absolute structure parameter	−0.04(3)
Residual diffraction max. (e Å^{-3})	1.728
Residual diffraction min. (e Å^{-3})	−0.586

Anal. Found: C, 56.2; H, 6.5. $C_{38}H_{52}O_{12}Sn$ Calc.: C, 55.7; H, 6.4%.

IR(cm^{-1}): 3067, 3050, 2990, 2930, 1481, 1458, 1429, 1383, 1258, 1213, 1169, 1071, 1003, 891, 866, 729, 698, 509, 442.

(**1**$n = 1$). Yield 53%; eluant petrol (60–80°C): EtOAc 2:1.

Anal. Found: C, 53.5; H, 6.9. $C_{45}H_{68}O_{18}Sn$ Calc.: C, 53.2; H, 6.7%.

(**2**$n = 2$). Yield 75%; eluant petrol (60–80°C): EtOAc 6:1.

Anal. Found: C, 55.2; H, 6.1. $C_{26}H_{34}O_6Sn$ Calc.: C, 55.6; H, 6.1%.

IR(cm^{-1}) 3065, 3046, 2988, 2930, 1482, 1456, 1429, 1383, 1256, 1211, 1171, 1073, 1003, 918, 893, 727, 700, 517, 448.

(**2**$n = 1$). Yield 83%; eluant petrol (60–80°C): EtOAc 9:1.

Anal. Found: C, 50.7: H, 6.4. $C_{21}H_{32}O_6Sn$ Calc.: C, 50.5; H, 6.5%.

IR(cm^{-1}): 3065, 2990, 2929, 1482, 1458, 1429, 1381, 1256, 1211, 1169, 1100, 1071, 1003, 918, 891, 866, 768, 727, 700.

(**2**$n = 0$). Yield 12%.

Anal. Found: C, 44.1; H, 6.8. $C_{16}H_{30}O_6Sn$ Calc.: C, 43.9; H, 6.9%.

(**3**). Yield 51%.

Anal. Found: C, 52.3; H, 8.5. $C_{25}H_{46}O_6Sn$ Calc.: C, 52.3; H, 8.6%.

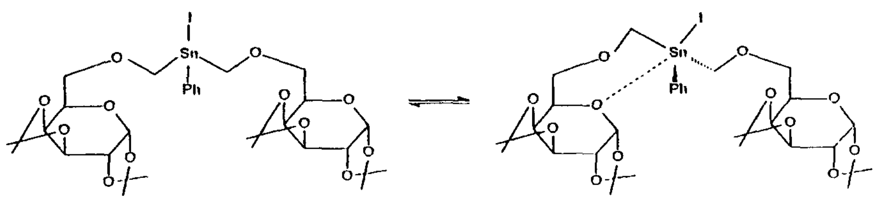
^1H, ^{13}C and ^{119}Sn solution NMR spectral data for **1**, **2** and **3** are displayed in Tables 1 and 2.

2.2. Preparation of 1,2:3,4-di-O-isopropylidene-6-O-triphenylgermanylmethyl-α-D-galactopyranose

To a solution of (**1**$n = 3$) (0.564 g, 0.905 mmol) in dry Et_2O (10 ml) at −64°C was added an excess of PhLi (1.36 mmol). After leaving the stirred reaction mixture for 15 min, a solution of Ph_3GeBr (0.312 g, 0.813 mmol) in Et_2O (10 ml) was added dropwise. After leaving overnight, the reaction mixture was hydrolysed with an aqueous solution buffered at pH 6.6 and extracted into CH_2Cl_2 (3 × 50 ml). The combined extracts were dried over $CaCl_2$, rotary evaporated and the residue chromatographed on a chromatotron, using hexane/Et_2O as eluant, to give the target molecule as a colourless oil: yield 0.198 g, 42.1%.

Anal. Found: C, 64.9; H, 6.1. $C_{31}H_{36}GeO_6$ Calc.: C, 64.5; H, 6.3%.

^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 24.4, 25.0, 26.0, 26.1 (4 × Me), 64.4 (C-7), 66.6 (C-5), 70.6, 70.8 (C-2 + C-3), 71.1 (C-4), 73.6 (C-6), 96.4 (C-1), 108.5, 109.1 (2 × CMe_2), 128.2, 129.0, 135.2 and 136.1 (aryl).



Solution structure (4 $n = 1$) **Solid state structure (4 $n = 1$)**

Fig. 1. Solution and solid state structures of (**4** $n = 1$).

Table 4
Selected NMR spectral data for XCH_2Sn (X = H, I or RO) compounds $\delta^{119}Sn/[J(^{119}Sn-^{13}C_i)]$ [b]/$[[J(^{119}Sn-^{13}C\alpha)]]$ [c,d]

Compound [a]	$n = 4$	$n = 3$	$n = 2$	$n = 1$	$n = 0$
$Ph_nSn(CH_2OR)_{4-n}$	−128.1 [516]	−146.2 [499] [[484]] [c]	−151.7 [466] [[452]] [c]	−143.1 [429] [[420]] [c]	—
$Ph_nSn(CH_2I)_{4-n}$	−128.1 [516]	−120.0 [545] [[348]] [c]	−104.4 [557] [[370]] [c]	−80.4 [586] [[388]] [c]	−47.7 — [40.0] [c]
Ph_nSnMe_{4-n}	−128.1	−92.4 [510] [[377]] [c]	−59.5 [487] [[365]] [c]	−28.7 [462] [[351]] [c]	0 [—] [[337]] [c]
$I\,Ph_nSn(CH_2OR)_{3-n}$	—	−112.8 [568]	−126.1 [511] [[515]] [c]	−130.7 [465] [[481]] [c]	−106.4 — [[417]] [c]
$I\,Ph_nSnMe_{3-n}$	—	−112.8 [568]	−68.8 [548] [[381]] [d]	−17.9 [524] [[367]] [d]	+39 — [[351]] [d]
$I\,Ph_nMe_{2-n}SnCH_2OR$	—	—	−126.1 [511] [[515]] [c]	−68.1 [c] [[506]] [c] [[341]] [d]	−8.9 — [[499]] [c] [[333]] [d]

[a] RO- = 6-*O*-(1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranosyl)-.
[b] Coupling to *ipso* carbon of Ph group.
[c] Coupling to CH_2OR or CH_2I.
[d] Coupling to Me group.
[e] Not measured.

2.3. Iodo-de-phenylations of 1 and 2 to give $IPh_nSn(CH_2OR)_{3-n}$ (4) and $IPh_nMe_{2-n}SnCH_2OR$ (5) respectively

2.3.1. Synthesis of bis[6-O-(1,2:3,4-di-O-isopropylidene-α-D-galactopyranosyl)methyl]phenyltin iodide (4 n = 1)

Solutions of (**1** $n = 2$) (0.993 g, 1.21 mmol) in $CHCl_3$ (3 ml) and I_2 (0.308 g, 1.21 mmol) in $CHCl_3$ (12 ml) were mixed and left to decolourise at room temperature. The volatiles were removed under vacuum to leave a colourless solid residue, which was recrystallised from $Et_2O/CHCl_3$: yield 70%; m.p. 145–146°C. Solution NMR spectal data for (**4**n = 1) are displayed in Tables 1 and 2.

Solid state ^{13}C NMR (75.431 MHz; relaxation delay 2.0 s; cross polarization contact time 1.0 s): δ 25.6, 26.3, 26.7, 27.1, 27.4, 27.8, 28.3, 70.1, 70.7, 71.1, 72.1, 73.5, 78.1, 97.2, 98.0, 109.1, 110.3, 129.3, 136.5, 144.1.

Solid state ^{119}Sn NMR (111.862 MHz; relaxation delay 1.0 ms; cross polarization with flip-back contact time 5.0 ms): δ −177.9 ppm.

2.3.2. Synthesis of 1,2:3,4-di-O-isopropylidene-6-O-[(iododiphenylstannyl)methyl]-α-D-galactopyranose (4 n = 2)

Solutions of (**1**n = 3) (0.500 g, 0.789 mmol) in $CHCl_3$ (3 ml) and I_2 (0.200 g, 0.789 mmol) in $CHCl_3$ (9 ml) were mixed and left until complete decolourisation. The volatiles were removed under vacuum to leave (**4**n = 2) as an oil, which decomposed on attempted crystallisation from petrol (60–80°C).

2.4. NMR scale

To a solution of **1** or **2** (ca. 100 mg) in $CDCl_3$ (0.33 ml) at 0°C was added an equivalent of iodine. The ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded after decolourisation and are displayed in Tables 1 and 2. Compound (**2**n = 2) (56 mg, 1 mmol) was also reacted

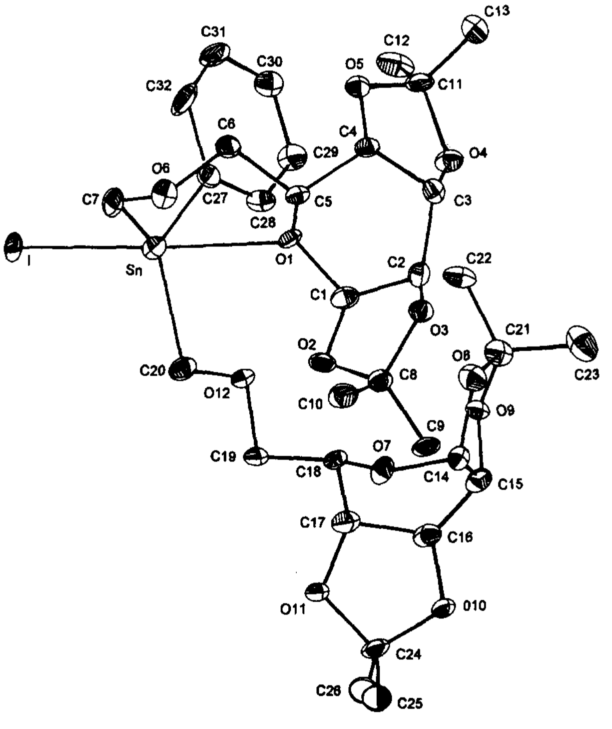


Fig. 2. Atom arrangement and numbering system for (**4** $n = 1$).

with I_2 (50 mg, 2 mmol) in $CDCl_3$ (0.33 ml) to give $I_2MeSnCH_2OR$.

2.5. Crystal structure determination of (4 $n = 1$) at 120 K

A colourless crystal was used in the analysis. Data were collected on a Delft Instruments FAST diffractometer with monochromated Mo Kα radiation at 120 K. Corrections were made for Lorentz and polarisation effects only. The positions of the tin and iodine atoms were located from a Patterson vector map using SHELX-86 [9]. The positions of the remaining non-hydrogen atoms were located on successive difference Fourier maps using SHELXL-93 [10]. The positions of the hydrogen atoms were calculated from geometrical considerations. During refinement the hydrogen atoms were allowed to ride on their attached carbon atoms. Full-matrix least-squares calculations were carried out with anisotropic temperature factors for the Sn, I, O and C atoms and common isotropic temperature factors according to type (methyl, aryl, etc.). The absolute configuration is based on the known stereochemistry of the carbohydrate moiety and the absolute structure parameter −0.4(3). The diagram of the molecular structure was obtained by the program, ZORTEP [11]. Data collection and structure refinement parameters are given in Table 3. Tables of hydrogen atom coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

The procedure used previously [6] to obtain 1,2:3,4-di-*O*-isopropylidene-6-*O*-triphenylstannylmethyl-α-D-galactopyranose (**1** $n = 3$) was employed to produce compounds **1**–**3**. The sodium salt of 1,2:3,4-di-*O*-isopropylindene-α-D-galactopyranose (NaOR) readily reacted in DMF with the iodomethyltin compounds, in appropriate molar ratios, to give the stannylated carbohydrate derivatives **1**–**3** (Scheme 1). Nucleophilic substitution reactions of halomethylstannanes $XCH_2Sn\equiv$ (X = Cl, Br or I) have been particularly well used to obtain $YCH_2Sn\equiv$ with $Y = NR'_2$ [12], SeR′ [13,14], SR′ [14–16] and OR′ [4–6,16,17]. The alkoxymethylstannanes R_3SnCH_2OR', prepared from R_3SnCH_2I, include 1,2:5,6-di-*O*-isopropylidene-3-*O*-[(triorganostannyl)methyl]-α-D-glucofuranosides [4] and triorganostannylmethyl 2,3 : 5,6-di-*O*-isopropylidene-α-D-mannofuranosides [5] as well as (**1** $n = 3$) [6].

All the compounds (**1**–**3**), except (**1** $n = 3$), were obtained as oils, none of which crystallised even on prolonged standing.

3.1. Reactions

Iodides $IPh_nSn(CH_2OR)_{3-n}$ (**4**) and $IPh_nMe_{2-n}SnCH_2OR$ (**5**) were readily obtained from $Ph_nSn(CH_2OR)_{4-n}$ (**1**) and $Ph_nMe_{3-n}SnCH_2OR$ (**2**); diiodides, e.g. $I_2MeSnCH_2OR$, could also be obtained on use of additional I_2. The reactivities of **1** and **2** towards iodine clearly indicated that one, if not more, of the

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for (**4** $n = 1$)

Atom	x	y	z	U_{eq}
Sn	1864.2(5)	−4.2(3)	183.3(4)	23(1)
I	4360.1(5)	−773.1(3)	1531.1(5)	36(1)
O(1)	−445(5)	919(3)	−1072(4)	20(1)
O(2)	−1136(5)	785(3)	−3332(5)	27(1)
O(3)	−2740(5)	1735(3)	−3638(5)	25(1)
O(4)	−3265(6)	1154(3)	−751(5)	32(1)
O(5)	−1404(5)	1827(3)	648(5)	32(1)
O(6)	2049(5)	1864(3)	−135(5)	29(1)
O(7)	−2681(5)	−1219(3)	−4317(5)	26(1)
O(8)	−4206(5)	−820(3)	−3460(5)	29(1)
O(9)	−4536(5)	−2159(3)	−3188(5)	27(1)
O(10)	−4130(5)	−2768(3)	−6113(5)	26(1)
O(11)	−1828(5)	−2728(3)	−5115(5)	31(1)
O(12)	−15(5)	−1063(3)	−1934(5)	26(1)
C(1)	−1527(7)	675(4)	−2280(7)	24(2)
C(2)	−2823(7)	1179(4)	−2661(7)	25(2)
C(3)	−2925(7)	1697(4)	−1578(7)	24(2)
C(4)	−1582(7)	2085(4)	−638(7)	23(2)
C(5)	−372(7)	1807(4)	−891(7)	21(2)
C(6)	957(7)	1985(4)	250(7)	23(2)
C(7)	2869(7)	1169(4)	486(8)	29(2)
C(8)	−2107(8)	1291(4)	−4320(7)	26(2)
C(9)	−3098(8)	794(5)	−5434(7)	28(2)
C(10)	−1325(9)	1909(5)	−4772(8)	33(2)
C(11)	−2614(8)	1458(5)	574(7)	29(2)
C(12)	−2286(10)	752(6)	1520(9)	44(2)
C(13)	−3504(8)	2093(5)	814(8)	32(2)
C(14)	−4043(7)	−1236(4)	−4501(7)	22(2)
C(15)	−4617(7)	−2081(4)	−4499(7)	24(2)
C(16)	−3819(8)	−2766(5)	−4730(7)	27(2)
C(17)	−2254(8)	−2668(4)	−4057(7)	27(2)
C(18)	−1867(7)	−1839(4)	−3406(7)	22(2)
C(19)	−399(7)	−1612(5)	−3034(8)	27(2)
C(20)	1199(8)	−623(5)	−1695(7)	30(2)
C(21)	−4778(7)	−1359(4)	−2810(7)	26(2)
C(22)	−4001(9)	−1279(6)	−1337(8)	42(2)
C(23)	−6267(8)	−1190(5)	−3284(9)	37(2)
C(24)	−2945(7)	−3023(5)	−6278(7)	24(2)
C(25)	−2939(11)	−3931(5)	−6388(10)	49(2)
C(26)	−2943(8)	−2598(5)	−7470(8)	33(2)
C(27)	896(7)	−379(4)	1416(7)	22(2)
C(28)	−210(7)	−886(4)	947(7)	28(2)
C(29)	−780(8)	−1190(5)	1753(8)	32(2)
C(30)	−271(8)	−977(5)	3059(8)	33(2)
C(31)	834(9)	−437(6)	3558(7)	38(2)
C(32)	1416(8)	−162(6)	2754(8)	39(2)

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

Table 6
Bond lengths (Å) and angles (°) for (**4** $n = 1$)

Sn–O(1)	**2.759(5)**		
Sn–C(27)	2.136(7)	O(12)–C(20)	1.426(9)
Sn–C(20)	2.160(7)	O(12)–C(19)	1.436(9)
Sn–C(7)	2.172(7)	C(1)–C(2)	1.531(10)
Sn–I	2.790(2)	C(2)–C(3)	1.517(11)
O(1)–C(1)	1.425(8)	C(3)–C(4)	1.534(10)
O(1)–C(5)	1.471(8)	C(4)–C(5)	1.522(10)
O(2)–C(1)	1.414(9)	C(5)–C(6)	1.500(10)
O(2)–C(8)	1.430(9)	C(8)–C(9)	1.500(11)
O(3)–C(8)	1.419(9)	C(8)–C(10)	1.536(11)
O(3)–C(2)	1.452(9)	C(11)–C(12)	1.507(12)
O(4)–C(11)	1.433(9)	C(11)–C(13)	1.519(11)
O(4)–C(3)	1.437(8)	C(14)–C(15)	1.522(10)
O(5)–C(11)	1.417(10)	C(15)–C(16)	1.506(10)
O(5)–C(4)	1.427(9)	C(16)–C(17)	1.551(11)
O(6)–C(6)	1.430(9)	C(17)–C(18)	1.518(10)
O(6)–C(7)	1.436(9)	C(18)–C(19)	1.515(10)
O(7)–C(14)	1.404(8)	C(21)–C(23)	1.501(11)
O(7)–C(18)	1.448(9)	C(21)–C(22)	1.504(11)
O(8)–C(14)	1.418(9)	C(24)–C(25)	1.498(11)
O(8)–C(21)	1.437(9)	C(24)–C(26)	1.500(11)
O(9)–C(15)	1.431(9)	C(27)–C(28)	1.373(10)
O(9)–C(21)	1.438(8)	C(27)–C(32)	1.401(10)
O(10)–C(16)	1.432(9)	C(28)–C(29)	1.377(10)
O(10)–C(24)	1.433(9)	C(29)–C(30)	1.368(11)
O(11)–C(17)	1.437(9)	C(30)–C(31)	1.407(12)
O(11)–C(24)	1.439(9)	C(31)–C(32)	1.369(12)
O(1)–Sn–C(20)	**84.4(2)**	**O(1)–Sn–I**	**173.5(1)**
O(1)–Sn–C(7)	**83.1(2)**	**O(1)–Sn–C(27)**	**84.2(2)**
C(27)–Sn–C(20)	115.4(3)	O(3)–C(8)–C(9)	112.5(6)
C(27)–Sn–C(7)	120.4(3)	O(2)–C(8)–C(9)	111.2(6)
C(20)–Sn–C(7)	120.8(3)	O(3)–C(8)–C(10)	106.9(6)
C(27)–Sn–I	98.6(2)	O(2)–C(8)–C(10)	107.8(6)
C(20)–Sn–I	99.5(2)	C(9)–C(8)–C(10)	113.2(6)
C(7)–Sn–I	90.5(2)	O(5)–C(11)–O(4)	104.9(6)
C(1)–O(1)–C(5)	112.7(5)	O(5)–C(11)–C(12)	110.2(6)
C(1)–O(2)–C(8)	109.4(5)	O(4)–C(11)–C(12)	108.7(6)
C(8)–O(3)–C(2)	105.7(5)	O(5)–C(11)–C(13)	109.6(6)
C(11)–O(4)–C(3)	107.1(6)	O(4)–C(11)–C(13)	110.2(6)
C(11)–O(5)–C(4)	109.5(5)	C(12)–C(11)–C(13)	112.9(7)
C(6)–O(6)–C(7)	112.9(5)	O(7)–C(14)–O(8)	110.7(6)
C(14)–O(7)–C(18)	112.7(5)	O(7)–C(14)–C(15)	115.0(6)
C(14)–O(8)–C(21)	109.9(5)	O(8)–C(14)–C(15)	104.4(5)
C(15)–O(9)–C(21)	105.9(5)	O(9)–C(15)–C(16)	108.1(6)
C(16)–O(10)–C(24)	108.4(5)	O(9)–C(15)–C(14)	103.5(5)
C(17)–O(11)–C(24)	108.8(5)	C(16)–C(15)–C(14)	114.7(6)
C(20)–O(12)–C(19)	113.3(5)	O(10)–C(16)–C(15)	106.9(6)
O(2)–C(1)–O(1)	109.4(5)	O(10)–C(16)–C(17)	103.8(5)
O(2)–C(1)–C(2)	105.0(5)	C(15)–C(16)–C(17)	115.5(6)
O(1)–C(1)–C(2)	114.1(6)	O(11)–C(17)–C(18)	109.5(6)
O(3)–C(2)–C(3)	106.8(6)	O(11)–C(17)–C(16)	104.9(6)
O(3)–C(2)–C(1)	102.3(6)	C(18)–C(17)–C(16)	110.7(6)
C(3)–C(2)–C(1)	116.5(6)	O(7)–C(18)–C(19)	106.4(6)
O(4)–C(3)–C(2)	106.4(6)	O(7)–C(18)–C(17)	109.3(5)
O(4)–C(3)–C(4)	104.3(6)	C(19)–C(18)–C(17)	113.7(6)
C(2)–C(3)–C(4)	114.4(6)	O(12)–C(19)–C(18)	106.6(6)
O(5)–C(4)–C(5)	109.2(6)	O(12)–C(20)–Sn	109.2(5)
O(5)–C(4)–C(3)	104.6(6)	O(8)–C(21)–O(9)	104.4(5)
C(5)–C(4)–C(3)	113.3(6)	O(8)–C(21)–C(23)	109.6(6)
O(1)–C(5)–C(6)	106.7(5)	O(9)–C(21)–C(23)	111.5(6)
O(1)–C(5)–C(4)	108.8(5)	O(8)–C(21)–C(22)	109.4(6)
C(6)–C(5)–C(4)	112.5(6)	O(9)–C(21)–C(22)	108.1(6)
O(6)–C(6)–C(5)	110.0(6)	C(23)–C(21)–C(22)	113.5(7)

Table 6 (continued)

O(6)–C(7)–Sn	117.6(5)	O(10)–C(24)–O(11)	104.5(5)
O(3)–C(8)–O(2)	104.7(5)	O(10)–C(24)–C(25)	109.7(7)
O(11)–C(24)–C(25)	112.3(7)	C(28)–C(27)–Sn	121.2(5)
O(10)–C(24)–C(26)	107.9(6)	C(32)–C(27)–Sn	121.4(5)
O(11)–C(24)–C(26)	109.0(6)	C(27)–C(28)–C(29)	122.1(7)
C(25)–C(24)–C(26)	113.0(7)	C(30)–C(29)–C(28)	120.5(7)
C(28)–C(27)–C(32)	117.3(7)	C(29)–C(30)–C(31)	118.8(7)
		C(32)–C(31)–C(30)	120.0(7)
		C(31)–C(32)–C(27)	121.3(7)

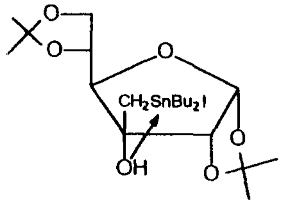
oxygen groups within the carbohydrate unit(s) was providing nucleophilic assistance in the cleavage step. Reactions of **1** and **2** with F_3CCO_2H also led to initial cleavage of a Ph–Sn bond, with formation of PhH, but secondary reactions within the carbohydrate moieties prevented identification of the primary stannyl-carbohydrate product. Reactions of (**2** $n = 0$) with electrophiles were not generally regiospecific, e.g. Br_2 reacted to give both $BrMe_2SnCH_2OR$ [δMe = 0.85 ppm, $J(^{119}Sn-^{1}H)$ = 59 Hz] and Me_3SnBr [δMe = 0.72 ppm, $J(^{119}Sn-^{1}H)$ = 58 Hz], in a molar ratio of 1 : 0.7. Reaction of (**2** $n = 0$) with I_2 did give predominately IMe_2SnCH_2OR, identical with the product obtained from (**2** $n = 1$).

Transmetallation reactions generally occurred between PhLi and **1**–**3**, with transfer of the alkoxymethyl unit. This is illustrated by the reaction with (**1** $n = 3$); the organolithium product was trapped as the triphenylgermanium derivative Ph_3GeCH_2OR (Scheme 2).

3.2. *Solution structure and NMR spectra of 1–5*

The ^{1}H, ^{13}C and ^{119}Sn NMR spectral details for **1**–**5** in $CDCl_3$ solution are displayed in Tables 1 and 2. Only one set of signals is observed for the carbohydrate atoms in the bis- and tris-saccharide compounds. Comparison of the $^{3}J(^{1}H-^{1}H)$ values in Table 1 indicates that the pyranose rings in all the compounds, as well as that in the non-stannylated sugar precursor 1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranose (ROH), have similar conformations in solution and that these are twist-boat conformations as previously established [18] for a variety of non-metallated 1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranoses derivatives. The organotin substituents clearly do not effect the pyranose ring conformation. The $\delta^{119}Sn$ and $^{1}J(^{119}Sn-^{13}C)$ values for **1** and **2** are as expected for four-coordinate species. Comparisons of the $^{2}J(^{119}Sn-^{1}H)$ and $\delta^{119}Sn$ values for (**1**) and (**2**) with those of related series are shown in Table 4. Tetraorganotin compounds of the form $R_nSnR'_{4-n}$ (R, R′ = alkyl or aryl) usually show [19] regular changes in $\delta^{119}Sn$ as n varies; e.g. see data for $Ph_nSn(CH_2I)_{4-n}$ and Ph_nSnMe_{4-n} as well as for $Ph_nMe_{3-n}SnCH_2OR$ in Table 4. However, for **1** the maximum value of $\delta^{119}Sn$ is seen for $n = 2$. Two opposing influences on the $\delta^{119}Sn$ values are considered to be operating on replacement of phenyl groups by the CH_2OR units: these are a reduction in shielding due to the inductive effect of the CH_2OR group and an increase in shielding arising from a through-space interaction between the vacant d-orbitals on tin and a lone pair of electrons on the α-oxygen atom. The variation can be accounted for if the latter reaches saturation when $n = 2$. It is of interest to note that the $^{1}J(^{119}Sn-$

Table 7
Values of Sn–I and Sn–O bond lengths (Å) and I–Sn–O valency angles (°) in pentacoordinate (*C*, *O*)-chelated triorganotin iodides

Compounds	Sn–I	Sn–O	I–Sn–O	Chelate ring size	Ref.
	2.764(2)	2.68(2)	158.3(4)	4	[3a]
$IPh_2Sn(CH_2)_3OH$	2.857(1)	2.487(8)	168.3(2)	5	[29]
$IPh_2Sn(CH_2)_2CO_2Me$	2.811(2)	2.55(2)	170.5(3)	5	[27]
1-MeO_2C-2-IMe_2Sn-cyclohexadiene	2.830(7)	2.391(5)	172.5(1)	5	[28]
$IPh_2Sn(CH_2OR)_2$ [a]	2.790(2)	2.759(5)	173.5(1)	6	[b]
$IPh_2Sn(CH_2)_3SO_2Tol$ [c]	2.809(1)	2.625(8)	177.1(2)	6	[30]

[a] ROH = 1,2 : 3,4-di-*o*-isopropylidene-α-D-galactopyranose.
[b] This study.
[c] Tol = C_6H_4Me-*P*.

^{13}C) values for the CH_2OR carbons in **1–3** are considerably larger than those for the Me and CH_2I carbons in Ph_nSnMe_{4-n} and $Ph_nSn(CH_2I)_{4-n}$ respectively.

The δ^{119}Sn and ^1J(Sn–C) values for the monoiodides **4** and **5** exhibit similar trends as found for the tetraorganotin species **1** and **2**, see Table 4. The δ^{119}Sn and ^1J(Sn–C) values suggest that **4** and **5** also contain tetracoordinate tin in solution, i.e. the sugar units are remaining monodentate. The tin diiodide $I_2MeSnCH_2$-OR also appears to be four-coordinate from the δ^{119}Sn value of − 177.7 ppm, which is similar to that (− 159 ppm) for I_2SnMe_2, a four-coordinate species [20].

The compound $IPhMeSnCH_2OR$ (**5** $n = 1$) should be formed from (**2** $n = 2$) in principle as a mixture of diastereoisomers. Its δ^{119}Sn signal (centred at −68.1 ppm) at ambient temperature was broad (ca. 3 ppm width at half peak height), indicative of an exchange reaction at the tin centre. The exchange process was also indicated by the broadening of the Me signals in the ^{1}H and ^{13}C NMR spectra. As a result of the exchange process, no asymmetric induction at the tin centre by the chiral R group was attained. Racemisation of the diastereoisomers of (**5** $n = 1$) is considered to be promoted by the nucleophilic oxygen atoms in the sugar residues and to occur via a similar addition–elimination mechanism as proposed for other chiral triorganotin halides [21].

A comparison of the solid state and solution ^{13}C and ^{119}Sn NMR spectra of (**4** $n = 1$) indicated that a structural change occurred on dissolution. The δ^{119}Sn solid state value of − 177.8 ppm, compared with the value of − 130.7 ppm in $CDCl_3$ solution, indicated a higher coordination number for tin (i.e. 5) in the solid state; this was confirmed by a crystal structure determination, see below. The ^{13}C solid state spectrum of (**4** $n = 1$) indicated two sets of δ^{13}C values for the sugar groups,

Table 8
Selected torsional angles (°) and Cremer–Pople puckering parameters for the rings in (**4** $n = 1$)

Torsion angles		*Monodentate sugar*	
Bidentate sugar		*Pyranose ring*	
Pyranose ring			
C(5)–O(1)–C(1)–C(2)	−37.8(8)	C(18)–O(7)–C(14)–C(15)	−36.1(8)
O(1)–C(1)–C(2)–C(3)	−15.8(9)	O(7)–C(14)–C(15)–C(16)	−18.3(9)
C(1)–C(2)–C(3)–C(4)	37.3(9)	C(14)–C(15)–C(16)–C(17)	38.8(9)
C(2)–C(3)–C(4)–C(5)	−5.8(9)	C(15)–C(16)–C(17)–C(18)	−5.7(9)
C(3)–C(4)–C(5)–O(1)	−44.9(8)	C(16)–C(17)–C(18)–O(7)	−46.6(8)
C(4)–C(5)–O(1)–C(1)	70.0(7)	C(17)–C(18)–O(7)–C(14)	71.3(7)
Sn–C(7)–O(6)–C(6)	57.9(7)	Sn–C(20)–O(12)–C(19)	169.2(5)
C(7)–O(6)–C(6)–C(5)	−110.4(6)	C(20)–O(12)–C(19)–C(18)	−163.9(6)
O(6)–C(6)–C(5)–O(1)	72.3(7)	O(12)–C(19)–C(18)–O(7)	86.9(7)
H(1)–C(1)–C(2)–H(2)	−19.5(3)	H(14)–C(14)–C(15)–H(15)	−20.7(3)
H(2)–C(2)–C(3)–H(3)	−70.6(2)	H(15)–C(15)–C(16)–H(16)	−70.9(2)
H(3)–C(3)–C(4)–H(4)	−8.0(3)	H(16)–C(16)–C(17)–H(17)	−8.4(3)
H(4)–C(4)–C(5)–H(5)	−48.4(2)	H(17)–C(17)–C(18)–H(18)	−50.2(3)
Puckering parameters		*Puckering parameters*	
$Q = 0.640$ Å; $\phi = 323.3°$; $\varphi = 77.5°$		$Q = 0.648$ Å; $\phi = 321.0°$; $\varphi = 73.4°$	
1,3-Dioxolane ring		*1,3-Dioxolane ring*	
O(2)–C(8)–O(3)–C(2)	−35.8(7)	O(8)–C(21)–O(9)–C(15)	−33.0(7)
C(8)–O(3)–C(2)–C(1)	33.9(7)	C(21)–O(9)–C(15)–C(14)	34.1(7)
O(3)–C(2)–C(1)–O(2)	−19.5(7)	O(9)–C(15)–C(14)–O(8)	−22.2(7)
C(2)–C(1)–O(2)–C(8)	−1.6(7)	C(15)–C(14)–O(8)–C(21)	2.3(7)
C(1)–O(2)–C(8)–O(3)	22.9(7)	C(14)–O(8)–C(21)–O(9)	18.5(7)
Puckering parameters		*Puckering parameters*	
$Q = 0.332$ Å; $\phi = 250.8°$		$Q = 0.321$ Å; $\phi = 257.0°$	
1,3-Dioxolane ring		*1,3-Dioxolane ring*	
O(4)–C(11)–O(5)–C(4)	26.4(7)	O(10)–C(24)–O(11)–C(17)	27.0(7)
C(11)–O(5)–C(4)–C(3)	−10.8(7)	C(24)–O(11)–C(17)–C(16)	−12.3(7)
O(5)–C(4)–C(3)–O(4)	−8.8(7)	O(11)–C(17)–C(16)–O(10)	−7.0(7)
C(4)–C(3)–O(4)–C(11)	25.0(7)	C(17)–C(16)–O(10)–C(24)	24.0(7)
C(3)–O(4)–C(11)–O(5)	−32.0(7)	C(16)–O(10)–C(24)–O(11)	−32.0(7)
Puckering parameters		*Puckering parameters*	
$Q = 0.282$ Å; $\phi = 18.6°$		$Q = 0.20$ Å; $\varphi = 22.2°$.	

as required for a structure in which one sugar moiety is acting as a bidentate ligand and the other remains monodentate (Fig. 1).

3.3. Crystal structure of (4 $n = 1$)

The atomic arrangement of (4 $n = 1$) and the crystallographic numbering system are shown in Fig. 2. Atomic coordinates are listed in Table 5, bond lengths and valency angles are shown in Table 6. The tin atom in (4 $n = 1$) is pentacoordinated as a result of one of the sugar moieties acting as a *C*, *O*-bidentate ligand (to form, via the pyranose ring oxygen atom, a six-membered chelate ring). The geometry at the tin centre is trigonal bipyramidal with I and O in the axial sites: the Sn–I and Sn–O(1) bond lengths are 2.790(2) and 2.759(5) Å respectively, with an O(1)–Sn–I valency angle of 173.5(1)°. The sum of the C–Sn–C valency angles is 356.6°, with a bite angle of the chelate ligand of 83.1(2)°. Tin–iodine bond lengths in tetrahedral, tetracoordinate R_3SnI fall [22] in the range 2.69–2.73 Å, although a value of 2.54(1) Å has been reported for tricyclohexyltin iodide [23]. The sum of covalent radii for Sn and O is 2.06 Å; a single S–O covalent bond length is taken [24] to be ca. 2.0 Å, although a bond length of 1.940(1) Å has been determined [25] in $Me_3SnOSnMe_3$. Intramolecular Sn · · · O separations up to 3.071(2) Å have been taken with varying degrees of confidence to indicate Sn–O bonding [26].

Comparisons of the Sn–I and Sn–O axial bond lengths, and I–Sn · · · O valency angle in (4 $n = 1$) with the corresponding values in other pentacoordinate (*C*, *O*)-chelated triorganotin iodides are made [3a,27–30] in Table 7. The longer Sn–I bond lengths are generally associated with the shorter Sn–O distances. The I–Sn–O valency angles are dependent on the size of the chelate ring.

The conformations of the two sugar residues are similar, despite one sugar moiety acting as a chelating ligand, see Table 8. Pyranose rings in 1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranose derivatives have been generally found [31] by X-ray crystallography, to have conformations between the screw-boat $^{O}S_5$ and twist-boat $^{O}T_2$ forms, with deviations in the direction of the boat-form $B_{2,5}$ (see Fig. 3). This is also true for both pyranose rings in (4 $n = 2$): the puckering parameters of Cremer and Pople [32], as calculated [33] by the program PUCKER for the complexed ring, are $Q = 0.648$ Å, $\phi = 321.0°$ and $\varphi = 78.4°$, while those for the uncomplexed ring are $Q = 0.640$ Å, $\phi = 323.3°$ and $\varphi = 77.5°$. The isopropylidene rings have near envelope to twist conformations; the O(2)–C(8)–O(3)–C(2)–C(1), O(4)–C(11)–O(5)–C(4)–C(3), O(8)–C(21)–O(9)–C(15)–C(14) and O(10)–C(24)–O(11)–C(17)–C(16) rings have mainly $E_{O(3)}$, $^{O(4)}T_{C(11)}$, $E_{O(9)}$ and $^{O(10)}T_{C(24)}$ conformations respectively.

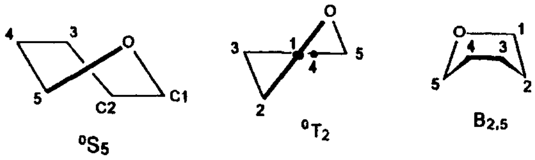


Fig. 3. Schematic forms of the $^{O}S_5$, $^{O}T_2$ and $B_{2,5}$ conformations of pyranose rings.

4. Conclusions

An impact of the oxygen groups in tetrahedral **1**–**3** is felt in their enhanced reactivity [compared with non-functionalised species $Ph_nSn(alkyl)_{4-n}$] towards electrophiles. However, the [6-*O*-(1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranosyl)methyl] unit is only able to act as a stable chelating group in **4** and **5** in the solid state. In general, the organotin substituents have no influence on the conformations of the sugar rings.

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