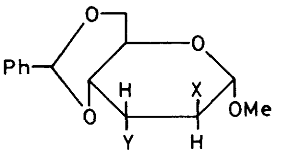
C-Stannylated Carbohydrate Derivatives. Part 3.† 1,2:5,6-Di-*O*-isopropylidene-3-*C*-(organostannyl)methyl-α-D-allofuranose Derivatives. Crystal and Molecular Structure of 3-*C*-(Dibutyliodostannyl)methyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose‡

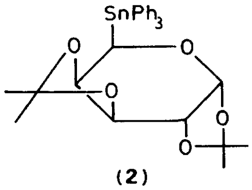
Philip J. Cox,[a] **Solange M. S. V. Doidge-Harrison,**[b] **R. Alan Howie,**[c] **Ian W. Nowell,**[b] **Oonah J. Taylor,**[c] **and James L. Wardell**[c]*
[a] *School of Pharmacy, Robert Gordon's Institute of Technology, Schoolhill, Aberdeen AB9 1FR, Scotland*
[b] *School of Chemistry, Robert Gordon's Institute of Technology, St. Andrews Street, Aberdeen AB1 1HG, Scotland*
[c] *Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland*

Reaction of $R_2R'SnCH_2Li$ (R = R' = Me or Bu) with 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*hexofuranos-3-ulose provides 1,2:5,6-di-*O*-isopropylidene-3-*C*-($R_2R'Sn$)methyl-α-D-allofuranose (**5**): the glucose isomer was not obtained. Despite a hydroxy group being in a β-position to tin in compound (**5**), no β-elimination products are obtained on reaction with CF_3CO_2H, reaction proceeding instead at the C(5)—C(6) protecting group. Cleavage of an alkyl–tin bond in (**5**) by iodine is aided by nucleophilic assistance of the β-hydroxy group. ^1H N.m.r. spectra of (**5**; R = Me, R' = I) in $CDCl_3$ indicate the formation of a four-membered chelate ring due to Sn---OH interaction. The crystal structure of (**5**; R = Bu, R' = I) was determined; there is a distorted trigonal bipyramidal arrangement about tin with I and O axial; Sn—O 2.68(2) Å.

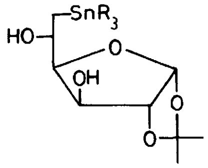
Organotin-substituted carbohydrate derivatives are attracting increasing attention.[1–3] Most activity has centred on tin–oxygen-bonded species,[1,3,4] with tin–carbon-bonded compounds having had a more limited study.[5–10] Among the tin–carbon-bonded derivatives which have been investigated are (1),[5] (2),[7] and (3).[8]



(**1**) X = $SnPh_3$, Y = OH
X = OH , Y = $SnPh_3$



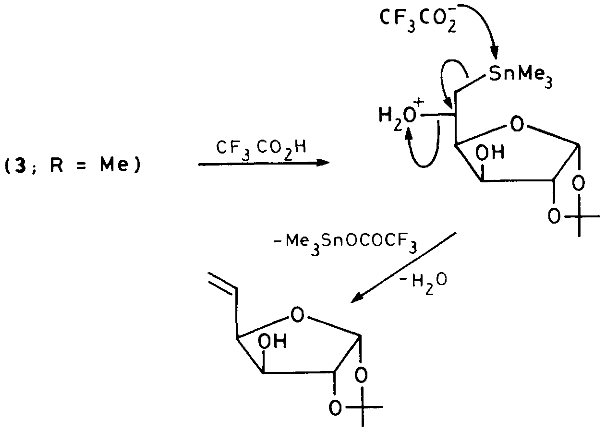
(**2**)



(**3**)

Recently we reported on the synthesis and reactions of 6-deoxy-1,2-*O*-isopropylidene-6-(trimethylstannyl)-α-D-glucofuranose (3; R = Me). Various reactions of this β-hydroxyalkyltin compound lead to the elimination of the unsaturated sugar (**4**), *e.g.* equation (1).

In the present publication, we report the synthesis and some reactions of 1,2:5,6-di-*O*-isopropylidene-3-*C*-($R_2R'SnCH_2$)-α-D-allofuranose (**5**; R = R' = Me or Bu) as well as the X-ray molecular structure of 3-*C*-(dibutyliodostannyl)methyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**5**; R = Bu, R' = I). Compound (**5**), like (**3**), has a HO group in a β-position to the tin centre; however, the molecular geometry prevents a *trans* arrangement of the HO and the SnR_2R' groups. We report some consequences of this.



(1)

(**4**)

Results and Discussion

Compounds (**5**; R = R' = Me or Bu) were obtained at −63 °C in Et_2O from $R_2R'SnCH_2Li$ [prepared[11] *in situ* from $R_2R'SnCH_2I$ and BuLi; equation (2)] and the keto sugar,

$$\mathrm{BuLi + R_2R'SnCH_2I \longrightarrow R_2R'SnCH_2Li + BuI} \qquad (2)$$

1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose (**6**), obtained from D-glucose.[12,13] The only addition product of the reaction between compound (**6**) and $R_2R'SnCH_2Li$ to be isolated was the allose product (**5**). The yields were low but were not optimized. In the synthesis of (**5**; R = R' = Me), other products isolated were 3-*C*-butyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**7a**) and the glucose isomer (**7b**) in the ratio *ca.* 4:1. These were obtained from reaction with residual BuLi – a

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† Part 2, Ref. 9.

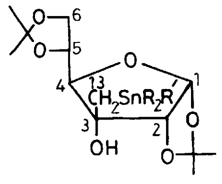
‡ *Supplementary data available:* see section 5.6.3 of Instructions for Authors, *J. Chem. Soc. Perkin Trans.*, 1988. Issue 1.

Table 1. ^1H n.m.r. spectral data for compounds (**5**) in $CDCl_3$ at 30 °C (δ rel. to Me_4Si; *J* in Hz)

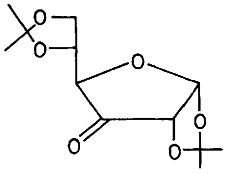
Compound (**5**)	1-H [$J(H^1–H^2)$]	2-H [$J(H^2–H^3)$]	4-H [$J(H^4–H^5)$]	5-H [$J(H^5–H^6)$] [$J(H^5–H^{6'})$]	6-H and 6′-H [$J(H^6–H^{6'})$]	OH [$J(H^{13'}–OH)$]	13-H and 13-H′ [$J(H^{13}–H^{13'})$]	CMe_2	Other
R = R′ = Ph	5.61 [3.7]	4.05	3.86 [7.9]	4.25 [5.2][6.2]	4.11, 3.96 [8.5]	3.08 [1.3]	2.16, 1.50 [13.3][a]	1.50, 1.38 1.32, 1.06	7.70—7.32 (Ph_3Sn)
R = R′ = Bu	5.68 [4.3]	3.98	3.81 [7.2]	4.17 [7.0][5.8]	4.08, 3.98 [7.7]	2.70	*b*	1.54, 1.40 1.33, 1.30	*b*
R = R′ = Me	5.68 [4.1]	4.03	3.78 [7.2]	4.16 [7.0][5.0]	4.07, 3.94 [7.9]	2.72	1.44, 0.85 [13.9]	1.57, 1.42 1.34, 1.32	0.16 (Me_3Sn)[c]
R = Bu, R′ = I	5.63 [4.1]	4.09	3.50 [8.2]	3.87 (m)[d,e,f]	4.01, 3.99[e]	2.93	2.13[13.9][f]	1.51, 1.34 1.29, 1.28	*g*
R = Me, R′ = I	5.72 [3.8]	4.19	3.63 [8.2]	3.99 [2.9][4.1]	4.10, 4.02 [8.8]	3.07	2.07, 1.72 [13.9]	1.54, 1.41 1.33, 1.33	1.04 (br), 0.98 (br) [$Me_2(I)Sn$][h]

[a] $J(^{119}Sn-^1H)$ 21 Hz. [b] δ 1.60—1.20 (m) and 1.10—0.7 (m) [29 H, 3 × Bu + CH_2SnBu_3]. [c] $J(^{119}Sn—^1H)$ 53 Hz. [d] m = multiplet. [e] = Couplings unresolved. [f] δ H^{13} masked by butyl absorptions. [g] ($^{\delta}Me–^{\gamma}CH_2–^{\beta}CH_2–^{\alpha}CH_2)_2SnI$ = δ 1.50 (m, β), 1.35 (m, α + γ), 0.94 (t, δ). [h] broad; varies with temperature.

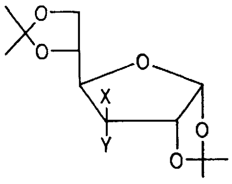
consequence of its incomplete reaction with Me_3SnCH_2I. Previously only (**7a**) was isolated from the direct reaction[14] of ketone (**6**) and BuLi on recrystallization of the work-up residue.



(**5**)



(**6**)



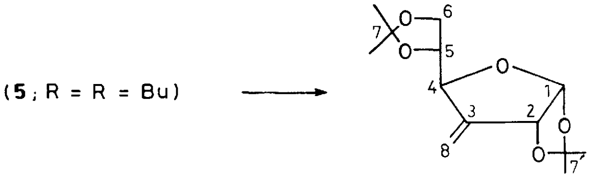
(**7**) **a**; X = Bu, Y = OH
b; X = OH, Y = Bu

In the electron-impact mass spectrum (e.i.m.s.) of (**5**; R = R′ = Me or Bu), the highest *m/z* values corresponded to loss of R. Fragmentations common to both derivatives included [$M^+ - Me_2CO$] and [$M^+ - CH_2CHOCMe_2O$]; other ions observed included R_3Sn^+, R_2Sn^+, RSn^+, and Sn^+. The ^1H n.m.r. spectral data of (**5**; R = R′ = Me, Bu, or Ph) are listed in Table 1. From the values of the coupling constants, similar conformations are suggested.

Reactions.—The reaction between equimolar amounts of (**5**; R = R′ = Me) and CF_3CO_2H in $CDCl_3$ was slow and initially produced acetone, released from the C(5)—C(6) isopropylidene protecting group. Notably the initial reaction did not proceed at the tin centre—in particular, no β-elimination reaction occurred. This contrasts with the rapid β-elimination reaction between compound (**3**; R = Me) and CF_3CO_2H [equation (1)]. Over a period of 4 days, the reaction mixture from compound (**5**; R = R′ = Me) and CF_3CO_2H became complex, with several sugar species present as well as three major methyltin compounds, including $Me_3SnOCOCF_3$ [δ_H 0.64; lit. values,[8,15] 0.65—0.68]. There was no spectral evidence for the elimination product, 3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-*C*-methylene-α-D-*ribo*-hexofuranose (**8**). As no methane was detected when the reaction was carried out in a sealed tube, cleavage of a methyl–tin bond appears not to arise; however, the formation of $Me_3SnOCOCF_3$ points to some cleavage of the Sn–CH_2 sugar bond.

β-Elimination reactions of several functionally substituted alkyl–tin compounds (*e.g.* β-substituents = OH, OR, SR, NR_2, or PR_2) have been reported.[16] The ideal geometry for a concerted elimination has that with the leaving groups in a *trans*-arrangement. That compound (**5**; R = R′ = Me) did not give a β-elimination with CF_3CO_2H indicates that the *trans*-arrangement of HO and Me_3Sn groups is not attainable. From molecular models, it would appear that steric hindrance by the C(5)—C(6) side-chain inhibits such a configuration, with the result that these groups have a *cis*-orientation.

The butyl analogue (**5**; R = R′ = Bu) reacted similarly with CF_3CO_2H. The elimination product (**8**) was, however, isolated from the reaction of (**5**; R = R′ = Bu) with acetyl chloride in the presence of $Pd(Ph_3P)_4$ in hexamethylphosphoramide, equation (3). Various Pd cross-coupling reactions of organotins and organic electrophiles are known.[17] A cross-coupled ketosugar product, *e.g.* [**7**; X = MeC(O)CH_2, Y = HO], was indeed the aim of reaction (3). It remains unknown whether the elimination occurred from a tin or from a palladium species. The more usual preparation[18] of compound (**8**) involves a Wittig reaction of ketone (**6**) and Ph_3P=CH_2.

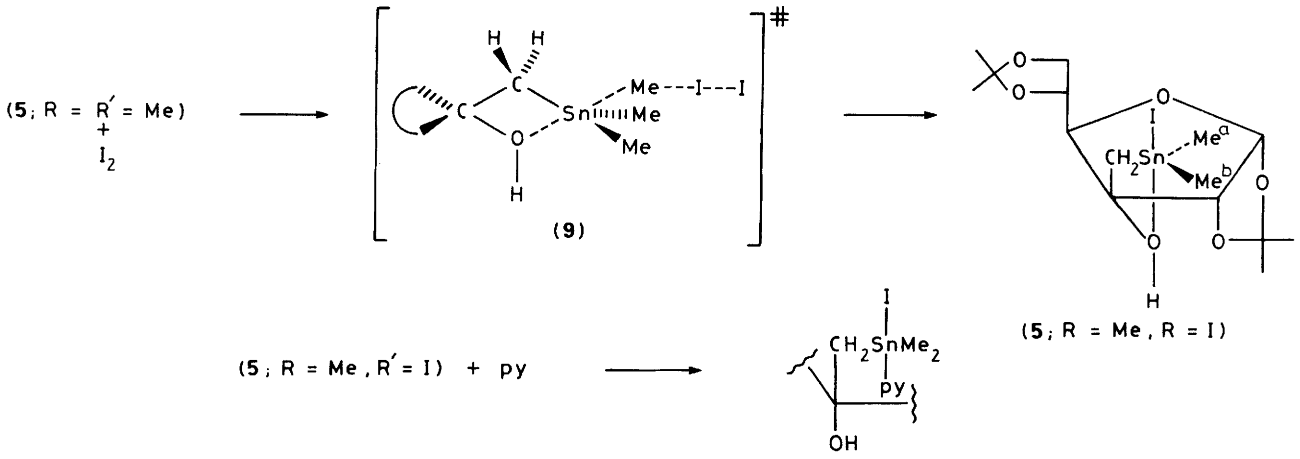


(3)

(**8**)

Reagents and conditions: CH_3COCl, $Pd(Ph_3P)_4$, 70 °C, 36 h

The *cis*-like arrangement of the HO and $R_2R'Sn$ groups in compound (**5**) has an impact on reactions with halogens; for example, compound (**5**; R = R′ = Me) reacts with I_2 to give MeI [and (**5**; R = Me, R′ = I)] at a faster rate than does Me_4Sn. Furthermore, in (**5**; R = Me, R′ = I) in $CDCl_3$ solution, the two methyl groups are inequivalent as shown by ^1H n.m.r. spectra (Scheme). [Note that all Me groups are equivalent in (**5**; R = R′ = Me)]. The inequivalence is a consequence of tin–oxygen co-ordination, which holds the methyl groups in different environments. In solution, the four-membered chelate ring can be broken either on raising the temperature or on addition of a strong electron donor such as



Scheme.

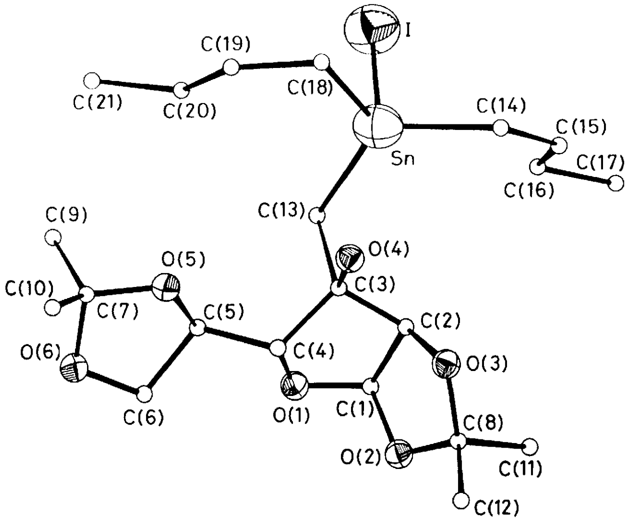


Figure. X-Ray molecular structure of compound (**5**; R = Bu, R′ = I)

Table 2. Fractional atomic co-ordinates (× 10^4) for (**5**; R = Bu, R′ = I) with e.s.d.s in parentheses

	x	*y*	*z*
I	−0.396 13(10)	0.000 00	−0.140 69(12)
Sn	−0.634 39(10)	0.010 10(41)	−0.217 30(10)
O(1)	−0.848 6(10)	−0.488 4(25)	−0.259 5(8)
O(2)	−0.957 1(17)	−0.445 7(18)	−0.146 0(12)
O(3)	−0.923 6(13)	−0.200 0(17)	−0.146 2(10)
O(4)	−0.851 3(10)	−0.089 6(15)	−0.301 4(10)
O(5)	−0.856 9(11)	−0.297 8(16)	−0.505 9(11)
O(6)	−0.913 8(11)	−0.515 4(21)	−0.598 9(10)
C(1)	−0.844 7(18)	−0.432 4(24)	−0.157 1(15)
C(2)	−0.822 5(15)	−0.267 7(24)	−0.149 4(13)
C(3)	−0.805 6(15)	−0.234 4(22)	−0.257 6(15)
C(4)	−0.869 4(15)	−0.363 3(23)	−0.329 4(13)
C(5)	−0.837 7(16)	−0.414 8(23)	−0.424 2(15)
C(6)	−0.913 5(17)	−0.536 4(21)	−0.493 3(14)
C(7)	−0.871 1(19)	−0.362 3(26)	−0.605 7(16)
C(8)	−0.989(2)	−0.309(3)	−0.114(2)
C(9)	−0.758(2)	−0.385(3)	−0.622(2)
C(10)	−0.970(2)	−0.281(3)	−0.693(2)
C(11)	−0.967(2)	−0.305(3)	0.006(2)
C(12)	−1.121(2)	−0.277(5)	−0.172(2)
C(13)	−0.671 8(14)	−0.221 6(26)	−0.249 3(16)
C(14)	−0.682(3)	0.153(5)	−0.099(3)
C(15)	−0.646(3)	0.122(5)	0.018(3)
C(16)	−0.583(3)	−0.012(5)	0.060(3)
C(17)	−0.592(3)	0.022(7)	0.175(3)
C(18)	−0.670(4)	0.149(5)	−0.357(3)
C(19)	−0.659(3)	0.058(5)	−0.454(3)
C(20)	−0.601(3)	−0.095(5)	−0.467(3)
C(21)	−0.585(3)	−0.162(5)	−0.575(3)

pyridine (Scheme). The cleavage of the Me–Sn bond in (**5**; R = R′ = Me) by iodine is aided by the nucleophilic assistance, in the transition state, afforded by the HO group. There have been a few reports[9,19–21] indicating the enhanced reactivity of carbon–tin bonds (towards electrophilic reagents) arising from nucleophilic assistance, *e.g.* that of the Me–Sn bond in $Me_3SnCH_2CH_2CO_2R$[19] and of Ph–Sn bonds in $Ph_3Sn(CH_2)_nSO_mAr$ ($n > 2$; $m = 0$—2)[20] and in triphenyltin derivatives of carbohydrates.[9] Indeed the usual reactivity sequences, such as alkyl–tin < R–Sn (R = aryl, vinyl, or benzyl), can be overturned with suitably sited donor substituents in the R groups.[21] The ideal geometry of the transition state in a nucleophilically assisted cleavage has both the donor group and the leaving group occupying axial sites,[22] as in intermediate (**9**) in the Scheme.

The butyl derivative (**5**; R = R′ = Bu) reacts similarly (even if *ca.* 7 times more slowly) with iodine to give BuI and (**5**; R = Bu, R′ = I). Proof of the intramolecular co-ordination in the solid state for the iodination products was achieved for (**5**; R = Bu, R′ = I). This compound could be more readily isolated as suitable crystals for a structure determination study than could (**5**; R = Me, R′ = I).

Structure of (**5**; R = Bu, R′ = I).—Single-crystal data are consistent with the atomic arrangement shown in the Figure. This shows a distortion from tetrahedral geometry induced by the approach of an oxygen atom, 0(4), of the hydroxy group at a tetrahedral face opposite the tin–iodine bond. Atomic co-ordinates are listed in Table 2, bond lengths in Table 3, valency angles in Table 4, and mean-plane calculations in Table 5.

The displacement of the tin atom from the equatorial plane [C(13), C(14), C(18)] is 0.466(1) Å, which compares with an ideal tetrahedral value of 0.76 Å based on an average tin–ligand bond length of 2.31 Å. This represents a 39% displacement toward a trigonal bipyramid arrangement. Also, the sum of the equatorial C–Sn–C angles is 346(2)° and the axial angle I–Sn---O(4) is 158.3(4)°. The dihedral angle between these equatorial and axial planes is 89°. Evidence of further distortion is shown by the apparent lengthening of the Sn–I bond [2.764(2) Å]. This lengthening cannot be due to intermolecular Sn---I interaction as there are no contacts < 4.3 Å. Com-

Table 3. Bond lengths (Å) for (**5**; R = Bu, R′ = I) with e.s.d.s in parentheses

I–Sn	2.764(2)	Sn–C(13)	2.14(3)
Sn–C(14)	2.22(4)	Sn–C(18)	2.13(5)
O(1)–C(1)	1.41(3)	O(1)–C(4)	1.41(3)
O(2)–C(1)	1.44(3)	O(2)–C(8)	1.39(4)
O(3)–C(2)	1.39(3)	O(3)–C(8)	1.41(3)
O(4)–C(3)	1.45(3)	O(5)–C(5)	1.46(3)
O(5)–C(7)	1.38(3)	O(6)–C(6)	1.39(3)
O(6)–C(7)	1.48(3)	C(1)–C(2)	1.50(4)
C(2)–C(3)	1.52(3)	C(3)–C(4)	1.53(3)
C(3)–C(13)	1.61(3)	C(4)–C(5)	1.48(3)
C(5)–C(6)	1.52(3)	C(7)–C(9)	1.48(4)
C(7)–C(10)	1.55(4)	C(8)–C(11)	1.49(4)
C(8)–C(12)	1.57(4)	C(14)–C(15)	1.47(6)
C(15)–C(16)	1.43(7)	C(16)–C(17)	1.56(5)
C(18)–C(19)	1.54(6)	C(19)–C(20)	1.58(6)
C(20)–C(21)	1.60(6)		

Table 4. Valency angles (°) for (**5**; R = Bu, R′ = I) with e.s.d.s in parentheses

I–Sn–C(13)	100.0(5)	I–Sn–C(14)	104.7(10)
I–Sn–C(18)	103.0(12)	C(13)–Sn–C(14)	127.5(12)
C(13)–Sn–C(18)	115.4(13)	C(14)–Sn–C(18)	103.2(16)
C(1)–O(1)–C(4))	105.7(18)	C(1)–O(2)–C(8)	109.1(18)
C(2)–O(3)–C(8)	107.7(17)	C(5)–O(5)–C(7)	109.1(16)
C(6)–O(6)–C(7)	107.3(15)	O(1)–C(1)–O(2)	109.0(16)
O(1)–C(1)–C(2)	111.3(17)	O(2)–C(1)–C(2)	103.6(16)
O(3)–C(2)–C(1)	106.6(16)	O(3)–C(2)–C(3)	109.5(15)
C(1)–C(2)–C(3)	102.0(16)	O(4)–C(3)–C(2)	112.8(15)
O(4)–C(3)–C(4)	112.2(15)	O(4)–C(3)–C(13)	102.6(15)
C(2)–C(3)–C(4)	102.8(15)	C(2)–C(3)–C(13)	113.1(15)
C(4)–C(3)–C(13)	113.7(16)	O(1)–C(4)–C(3)	104.8(14)
O(1)–C(4)–C(5)	104.4(16)	C(3)–C(4)–C(5)	121.5(16)
O(5)–C(5)–C(4)	111.1(17)	O(5)–C(5)–C(6)	99.2(14)
C(4)–C(5)–C(6)	116.1(16)	O(6)–C(6)–C(5)	107.1(16)
O(5)–C(7)–O(6)	105.7(16)	O(5)–C(7)–C(9)	110.6(18)
O(5)–C(7)–C(10)	108.8(18)	O(6)–C(7)–C(9)	104.2(20)
O(6)–C(7)–C(10)	105.8(17)	C(9)–C(7)–C(10)	120.4(20)
O(2)–C(8)–O(3)	106.4(18)	O(2)–C(8)–C(11)	111.2(21)
O(2)–C(8)–C(12)	111.3(23)	O(3)–C(8)–C(11)	111.3(20)
O(3)–C(8)–C(12)	108.8(23)	C(11)–C(8)–C(12)	107.8(21)
Sn–C(13)–C(3)	103.4(13)	Sn–C(14)–C(15)	123.1(30)
C(14)–C(15)–C(16)	120.5(36)	C(15)–C(16)–C(17)	90.9(35)
Sn–C(18)–C(19)	110.0(28)	C(18)–C(19)–C(20)	135.2(34)
C(19)–C(20)–C(21)	127.6(34)		

Table 5. Mean-plane calculations* (Å) for (**5**; R = Bu, R′ = I)

(1) *Sn* 0.466(1), C(13) 0.00, C(14) 0.00, C(18) 0.00
(2) *I* 0.782(2), *O*(4) −0.708(2), Sn 0.00, C(13) 0.00, C(3) 0.00
(3) *C*(4) 0.54(3), O(1) 0.00(2), C(1) −0.01(3), C(2) 0.01(3), C(3) −0.01(3)
(4) *C*(5) −0.49(4), 0(5) 0.01(2), 0(6) 0.02(2), C(6) −0.02(3), C(7) −0.04(4)
(5) *C*(8) 0.35(4), O(2) 0.02(2), C(1) −0.04(3), C(2) 0.03(3), O(3) −0.01(2)

* Italicized atoms not included in derivation of mean plane.

parable Sn–I bonds in other tetrahedral tin compounds range from 2.69(3)—2.729(3) Å.[23–27]

The distance Sn---O(4) [2.68(2) Å] is considerably larger than the sum of the covalent radii (2.13 Å) but is well within the sum of the van der Waals radii (3.70 Å). The normal Sn–O covalent bond is *ca.* 2.0 Å[28] and an Sn---O distance of 2.69 Å has been observed in a 1:1 adduct of dichlorodimethyltin(IV) and salicylaldehyde.[29] Intramolecular Sn---O distances ranging from 2.263(6)—3.071(2) Å have been reported.[30–33] A maximum Sn---O(4) interaction of 2.58 Å would have been achieved if O(4), C(3), C(13), and Sn [torsion angle 32(1)°] were coplanar. The configuration found enables the close approach of Sn and O(4) while at the same time accommodating the sugar, iodine, and butyl ligands. The three rings in the sugar unit adopt envelope conformations with flap atoms C(4), C(5), and C(8) (Table 5).

Experimental

M.p.s were measured on a Kofler hot-stage and are uncorrected. ^{1}H n.m.r. spectra (for $CDCl_3$ solutions) were obtained on a Perkin Elmer R34 (220 MHz) spectrometer and at the SERC n.m.r. unit, run by the University of Edinburgh. Mass spectra were obtained using an AEI MS 30 spectrometer: *M* of tin-containing peaks was based on ^{120}Sn.

Diethyl ether and tetrahydrofuan (THF) were dried over $LiAlH_4$ and distilled prior to use. 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose[11] [m.p. 107—109 °C (from cyclohexane)], 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose[12] (**6**) (b.p. 118—121 °C at 0.3 mmHg), and tetrakis(triphenylphosphine)palladium[34] were obtained by published procedures.

Preparation of a Zinc–Copper Couple.—Granular zinc (13.0 g, 0.2 mol) and copper(II) sulphate (0.18 g) in acetic acid (10 ml) were heated on a steam-bath for 2 min. The solution was decanted and the zinc was heated with more acetic acid (10 ml), washed with diethyl ether (3 × 15 ml), and dried in a stream of dry nitrogen.

Preparation of (Iodomethyl)trimethyltin.—A solution of di-iodomethane (53.75 g, 0.2 mmol) in THF (50 ml) was added dropwise under nitrogen to a stirred mixture of the zinc-copper couple, prepared above, and THF (30 ml). After addition was complete, the reaction mixture was stirred for a further 4 h, cooled to 0 °C, and filtered under nitrogen through glass wool. A solution of trimethyltin chloride (21.25 g, 0.1 mol) in THF (60 ml) was slowly added to the filtrate. The reaction mixture was stirred overnight, and 5% hydrochloric acid (70 ml) and benzene (30 ml) were successively added. The organic layer was collected, washed with more 5% hydrochloric acid (3 × 70 ml), dried over anhydrous sodium sulphate, and finally the solvent was removed on a rotary evaporator. The product was distilled (26.1 g, 85%), b.p. 66—70 °C at 14 mmHg (lit.,[35] 54—55 °C at 0.5 mmHg).

Preparation of Tributyl(iodomethyl)tin.—This was prepared from tributyltin chloride (32.5 g, 0.1 mmol) and (iodomethyl)zinc iodide, generated from a zinc–copper couple [obtained from zinc (9.75 g, 0.15 mol) and di-iodomethane (40.2 g, 0.15 mol)] by an analogous procedure to that described for (iodomethyl)-trimethyltin. The product was distilled; b.p. 120—125 °C at 0.1 mmHg (lit.,[36] 100—110 °C at 0.01 mmHg).

Preparation of compound (**5**; R = R′ = Bu).—To a solution of (tributylstannyl)methyl-lithium [prepared from tributyl-(iodomethyl)tin (4.31 g, 0.01 mol) and butyl-lithium (7 ml of 1.5M-solution in hexanes)] in dry diethyl ether (30 ml) at −63 °C under nitrogen was added a solution of ketone (**6**) (2.58 g, 0.01 mol) in dry diethyl ether (15 ml). The reaction mixture was allowed to warm to room temperature overnight, then hydrolysed with aqueous (pH 6.6) buffer solution (300 ml) and extracted into dichloromethane (3 × 150 ml). The combined extracts were dried over magnesium sulphate and the solvent was removed to leave a syrup. Purification, using a chromatotron [eluant: diethyl ether–hexane (1:1)], gave a *syrup* (1.62 g, 29%) (Found: C, 53.5; H, 8.5. $C_{25}H_{48}O_6Sn$ requires C, 53.3; H, 8.6%); δ_H (see Table 1); *m/z* (20 eV) (%, fragment) 507 (4, $M - Bu^+$), 449 (8, 507 $-Me_2CO$), 391 (10, 449 $-Me_2CO$), 331

(28, −449 −$CH_2CHOCMe_2O$ − OH), 291 (19, Bu_3Sn^+), 251 (100, Bu_2SnOH^+), 234 (10, Bu_2Sn^+), 177 (8, $BuSn^+$), and 101 (18, $CH_2CHOCMe_2O^+$).

Preparation of compound (**5**; R = R′ = Me).—This was obtained from (trimethylstannyl)methyl-lithium [prepared from (iodomethyl)trimethyltin (3.05 g, 0.01 mol) and butyl-lithium (4 ml of 2.5M-solution in hexanes)] and ketose (**6**) (2.58 g, 0.01 mol) by an analogous procedure to that used for the tributyltin derivative.

Isolated from the chromatotron were:

(i) Unchanged ketone (**6**) (0.46 g, 18% recovery).

(ii) *target compound* (**5**; R = R′ = Me) (0.83 g, 19%), m.p. 125—129 °C (from hexane) (Found: C, 44.2; H, 7.0. $C_{16}H_{30}O_6Sn$ requires C, 44.0; H, 6.9%); δ_H (see Table 1). *m/z* (20 eV) (%, fragment) 423 (5, M^+ − Me), 365 (10, 423 − Me_2CO), 307 (10, 423 − Me − CH_2 − $CHOCMe_2O$), 277 (12), 259 (3), 241 (15, M^+ − Me_3SnCH_2OH), 223 (15), 165 (74, Me_3Sn^+), and 101 (100, $CH_2CHOCM_eO^+$).

(iii) 3-*C*-Butyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**7a**) (0.53 g, 17%), m.p. 98—101 °C (from cyclohexane) [lit.,[14] 98—99 °C] (Found: C, 60.5; H, 9.1. Calc. for $C_{16}H_{28}O_6$: C, 60.7; H, 8.9%); δ_H ($CDCl_3$; 220 MHz) 5.67 (1 H, d, $J_{1,2}$ 3.6 Hz, 1-H), 4.35 (1 H d, $J_{1,2}$ 3.6 Hz, 2-H), 4.09 (2 H, m, 6-H_2), 3.89 (1 H, m, $J_{4,5}$ 8.4 Hz, 5-H), 3.77 (1 H, d, $J_{4,5}$ 8.4 Hz, 4-H), 2.53 (1 H, s, OH), 1.56, 1.42, 1.39, 1.33 (12 H, all s, 2 × CMe_2), and [1.81—1.32 (6 H) and 0.90 (3 H, t, *J* 8 Hz) (Bu)].

(iv) 3-C-*Butyl*-1,2:5-6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (**7b**), syrup (0.13 g, 4%) (Found: C, 60.4; H, 8.6%); δ_H ($CDCl_3$; 220 MHz) 5.81 (1 H, d, $J_{1,2}$ 3.1 Hz, 1-H), 4.26 (1 H, d, $J_{1,2}$ 3.1 Hz, 2-H), 4.25 (1 H, m, $J_{4,5}$ 7.0, $J_{5,6}$ 6.7, $J_{5,6'}$, 5.3 Hz, 5-H), 4.09 (1 H, dd, $J_{5,6}$ 6.7 $J_{6,6'}$ 8.9 Hz, 6-H), 3.95 (1 H, dd, $J_{5,6'}$ 5.3, $J_{6,6'}$ 8.9 Hz, 6-H′), 3.78 (1 H, d, $J_{4,5}$ 7.0 Hz, 4-H), 2.05 (1 H, s, OH), 1.48, 1.41, 1.33, 1.30 (12 H, all s, 2 × CMe_2), and [1.80—1.23 (6 H, m) and 0.91 (3 H, t, *J* 7 Hz) (Bu)].

Reactions of Compound (**5**; R = R′ = Me) *with iodine*.—Iodine (17.2 mg, 6.77 × 10^{-5} mol) was added to a solution of compound (**5**; R = R′ = Me) (29.6 mg, 6.77 × 10^{-5} mol) in $CDCl_3$ (0.5 ml). Decolourization was complete after 3.5 h at room temperature in the dark. The ^1H n.m.r. spectrum indicated the clean cleavage of a methyl–tin bond with formation of MeI (δ 2.15) and the iodide (**5**; R = Me, R′ = I). The signal for the Me_2SnI moiety appeared as a poorly resolved, doublet at δ *ca.* 1.00 at 30 °C. On lowering the temperature, the splitting and resolution of the doublet increased; and on raising the temperature, the doublet collapsed to a broad singlet. Addition of [$^2H_5$]pyridine (*ca.* 0.05 ml) gave rise to a sharp singlet [δ_H 0.98 $J(^{119}Sn—^1H)$ 60 Hz]; see Table 1 for ^1H n.m.r. spectrum of compound (**5**; R = Me, R′ = I).

Reactions of Compound (**5**; R = R′ = Bu).—(i) *With iodine*. A solution of iodine (0.067 g, 2.60 × 10-4 mol) and compound (**5**; R = R′ = Bu) (0.154 g, 2.74 × 10^{-4} mol) in CCl_4 (5 ml) was maintained at room temperature in the dark for 3 weeks until colourless. ^1H N.m.r. spectroscopy indicated cleavage of a butyl–tin bond with formation of the iodide (**5**; R = Bu, R′ = I) and iodobutane [δ_H 3.13 (t, 2 H, *J* Hz $CH_3CH_2CH_2I$)]. Removal of volatiles on the rotary evaporator and crystallization of the residue from aqueous ethanol gave crystals of the *iodide* (**5**; R = Bu, R′ = I), m.p. 98—101 °C (Found: C, 39.9; H, 6.3. $C_{21}H_{39}IO_6Sn$ requires C, 39.8; H, 6.2%); δ_H, see Table 1; *m/z* (20 eV) (% fragment) 577 (2, M^+ − Bu), 519 (3, 577 − Me_2CO), 461 (3, 519 − Me_2CO), 431 (3), 361, (19, Bu_2SnI^+), 269 (14), 241 (16 M^+ − Bu_2ISnCH_2 − H_2O), 177 (4, $BuSn^+$), 101 (100, $CH_2CHOMe_2O^+$), and 57 (71, Bu^+).

(ii) *With acetyl chloride, in the presence of tetrakis*(*triphenylphosphine*)*palladium*. A solution of compound (**5**; R = R′ = Bu) (0.302 g, 5.36 × 10^{-4} mol), acetyl chloride (0.042 g, 5.36 × 10^{-4} mol), and tetrakis(triphenylphosphine)palladium (3.1 mg, 2.68 × 10^{-6} mol) in hexamethylphosphoramide (2 ml) was heated at 70 °C and stirred for 18 h. T.l.c. indicated incomplete reaction. More acetyl chloride (0.010 g) and tetrakis(triphenylphosphine)palladium (1 mg) were added and the mixture was heated for another 18 h, after which all the starting material (**5**; R = R′ = Bu) had been consumed. Water (2 ml) was added and the organics were extracted into diethyl ether (3 × 10 ml). The extracts were treated with methanolic KF (to remove Bu_3SnCl as insoluble Bu_3SnF), and the solution was filtered, dried over magnesium sulphate, and evaporated to dryness. The residue was dissolved in diethyl ether and the supernatant was chromatographed on a chromatotron to yield 3-deoxy-1,2:5,6-di-*O*-isopropylidene-3-*C*-methylene-α-D-*ribo*-hexofuranose (**8**) (81 mg, 59%) as a syrup (Found: C, 60.7; H, 8.1. Calc. for $C_{13}H_{20}O_5$: C, 60.9; H, 7.9%); δ_H ($CDCl_3$; 360 MHz) 5.78 (1-H, d, $J_{1,2}$ 4.0 Hz, 1-H), 5.48 (1 H, dd, $J_{8,8'}$ 2.1, $J_{2,8}$ = $J_{4,8}$ 1.2 Hz, 8-H), 5.42 (1 H, dd, $J_{8,8'}$ 2.1, $J_{2,8'}$ = $J_{4,8}$ = 1.0 Hz, 8-H′), 4.87 (1-H, ddd, $J_{1,2}$ 4.0, $J_{2,8}$ 1.2, $J_{2,8'}$ 1.0 Hz, 2-H), 4.63 (1 H, ddd, $J_{4,5}$ 6.3, $J_{4,8}$ 1.2, $J_{4,8'}$ 1.0 Hz, 4-H), 4.04 (1 H, m, 5-H), 4.03 (1 H, dd, $J_{5,6}$ 6.2, $J_{6,6'}$ 4.9 Hz, 6-H), 3.92 (1 H, dd, $J_{5,6'}$ 2.5, $J_{6,6'}$ 4.9 Hz, 6-H′), 1.50, 1.42, 1.35, and 1.34 (4 × 3 H, s, 2 × CMe_2). [lit.,[18d] ($CDCl_3$) 5.78 (1 H, d, $J_{1,2}$ 3.8 Hz, 1-H), 5.55—5.35 (2 H, m, 8-H_2), 4.81 (1 H, d, 2-H), 4.70—3.78 (4 H, m, 4- and 5-H, 6-H_2), 1.50 (3 H, s), 1.42 (3 H, s), and 1.37 (6 H, s) (together 2 × CMe_2); δ_C ($CDCl_3$; 90 Hz) 146.8 (C-3), 113.3 (C-8), 112.5 and 109.7 (C-7 and -7′), 104.5 (C-1), 82.1, 79.2, and 77.2 (C-2, -4, and -5), 66.7 (C-6), 27.3, 27.0, 26.5, and 25.3 (4 × Me).

Crystal Structure Determination of Compound (**5**; R = Bu, R′ = I).—*Crystal data*. $C_{21}H_{39}IO_6Sn$, M = 633.1, monoclinic, space group $P2_1$, a = 12.256(6), b = 8.950(7), c = 13.012(6) Å, β = 109.91(4)°, V = 1350.3 Å^3, Z = 2, D_c = 1.72 g cm^{-3}, D_m = 1.73 g cm^{-3}, $F(000)$ = 616, μ(Mo-K_α) = 19.6 cm^{-1}, λ = 0.710 69 Å, T = room temperature.

Data collection and processing. Colourless crystal, 0.9 × 0.3 × 0.2 mm. The cell dimensions were obtained from setting angles of 12 independent reflexions with $2\theta \simeq 20°$ on a Nicolet P3 automated diffractometer using monochromated Mo-K_α radiation. 3 615 Unique intensities were measured with $\theta < 60°$ as θ–2θ scans; 1958 reflexions had $F > 6\sigma(F)$. Range of *hkl*: $0 \le h \le 16$, $0 \le k \le 11$, $-17 \le l \le 17$. The data were corrected for Lorentz and polarization effects but absorption was ignored. Two reference reflexions, monitored periodically, showed no significant variation in intensity.

Structure analysis and refinement. The structure was determined by the heavy-atom method (Patterson function) which revealed the approximate positions of the tin and iodine atoms. The remaining non-hydrogen atoms were located[37] from successive Fourier difference maps using SHELX76. All hydrogen atoms, with the exception of the butyl hydrogens, were located but given ideal geometry. Full-matrix least-squares calculations on F with anisotropic thermal parameters for the tin, iodine, oxygen, and non-butyl carbons and isotropic thermal parameters for the butyl carbons and hydrogens converged at R 0.059, R_w 0.056. Atomic scattering factors were from SHELX76. Final $w = 2.34/\sigma^2(|F_0|)$, $\Delta/\sigma < 0.2$, final $\Delta\rho_{max.} = 0.9$, $\Delta\rho_{min.} = -0.7$ e A^{-3}. Molecular geometries were generated by the GX package.[38]

Location of the carbon atoms in the butyl chains proved to be difficult since these atoms are associated with large thermal parameters. This problem has been encountered in other tin compounds.[39]

Additional material deposited, with the Cambridge Crystallographic Data Centre, comprises lists of anisotropic thermal parameters, H-atom positions, and torsion angles.

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