# Hydroxy group interactions in stannylated carbohydrates. Structures and thermal stabilities of 5-deoxy-5-*C*-($Ph_3Sn$)-1,2-*O*-isopropylidene-α-D-xylofuranose, 5-deoxy-5-*C*-($IPh_2Sn$)-1,2-*O*-isopropylidene-α-D- and -L-xylofuranose, and 5-deoxy-5-*C*-($I_2PhSn$)-1,2-*O*-isopropylidene-α-D- and -L-xylofuranose

**Lynne A. Burnett,[a] Vitor F. Ferreira,[b] R. Alan Howie,[a] Helena Rufino,[a] Janet M. S. Skakle,[a] James L. Wardell[a,c] and Solange M. S. V. Wardell[b]**

[a] *Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Scotland, UK AB24 3UE*
[b] *Departamento de Química Orgânica, Instituto de Química, Universidade Federal Fluminense, 24020–150 Niterói, RJ, Brazil*
[c] *Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CP 68563, 21945–970 Rio de Janeiro, RJ, Brazil*

***Received (in Cambridge, UK) 14th May 2002, Accepted 8th August 2002***
***First published as an Advance Article on the web 11th September 2002***

Structures and thermal stabilities of 5-deoxy-5-*C*-($Ph_3Sn$)-1,2-*O*-isopropylidene-α-D-xylofuranose, [(D)-**3**], 5-deoxy-5-*C*-($IPh_2Sn$)-1,2-*O*-isopropylidene-α-D- and -L-xylofuranose, [(D)-**4** and (L)-**4**], and 5-deoxy-5-*C*-($I_2PhSn$)-1,2-*O*-isopropylidene-α-D- and -L-xylofuranose, [(D)-**5** and (L)-**5**], are reported. The hydroxy groups in the stannylated xylofuranose derivatives, **3**–**5**, exhibit roles as Lewis bases, Brønsted acids and hydrogen bonding centres. The 5-deoxy-1,2-*O*-isopropylidene-α-D- and –L-xylofuran-5-yl ligands operate as $C^5,O^4$ chelating ligands (4-membered chelate rings) in **3**, $C^5,O^3$ chelating ligands in **4** (molecule 2) and **5** (5-membered chelate rings), and a $C^5,O^4,O^3$ tridentate ligand in **4** (molecule 1) [both 4- and 5-membered chelate rings]. Compounds **4**, in contrast to **3** and **5**, undergo slow proton-dephenylation reactions in chloroform solutions at ambient temperature. All decompose on heating at 145–155 °C with evolution of PhH, $Me_2CO$ and $H_2O$. The trigonal bipyramidal tin centres in (D)-**5** and (L)-**5** are chiral, at least in the solid state. Different modes of O–H–O bonding are found in **3**, **4** (molecule 2) and **5** compared to that in **4** (molecule 1).

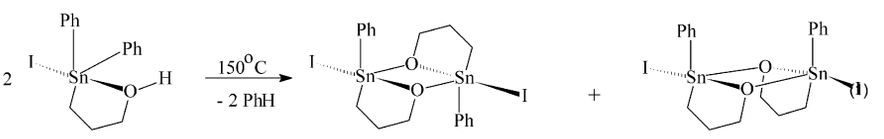
## Introduction

Acid/base behaviour and participation in H-bonding are characteristic properties of alcohols.[1] Specifically in organotin chemistry, the Lewis base interactions with organotin centres are illustrated[2–4] by the formation of stable intramolecular (hydroxy-alkyl- and -alkenyl-*C*,*O*)-stannane complexes, including some conformationally rigid tetraorganostannanes. While carbon–tin bonds, in general, are resistant to cleavage by alcohols, the Brønsted acidity has been illustrated with the more reactive carbon–tin bonds, *e.g.* alkynylstannanes,[5] $RSn(C{\equiv}CR')_3$, react at 60 °C with alcohols, R″OH, with the formation of alkoxides, $RSn(OR'')_3$, and HC≡CR′. Intramolecular reactions of (hydroxyalkyl)stannanes have also been reported; for example, $Bu_2(HOCH_2CH_2CH_2)_2Sn$,[3] stable at ambient temperature, undergoes proto-dealkylation at 200 °C to yield polymeric $[Bu_2SnCH_2CH_2CH_2O]_n$, while ($HOCH_2$-$CH_2CH_2$–*C*,*O*)$Ph_2SnI$ (**1**),[4] also stable at 25 °C, undergoes proto-de-phenylation at 150 °C to form dimers, **2**, $[IPhSnCH_2$-$CH_2CH_2O]_2$, see equation (1).

A study has been made of the acid/base and H-bonding properties of the HO groups in 5-deoxy-5-C-[$(iodo)_n(phenyl)_{3-n}$-stannyl]-1,2-*O*-isopropylidene-α-D-xylofuranose compounds, [$n$ = 0, (D)-**3**; $n$ = 1, (D)-**4**; $n$ = 2, (D)-**5**] and 5-deoxy-5-*C*-[$(iodo)_n$-$(phenyl)_{3-n}$stannyl]-1,2-*O*-isopropylidene-α-L-xylofuranose compounds, [$n$ = 0, (L)-**3**; $n$ = 1, (L)-**4**; $n$ = 2; (L)-**5**], see Fig. 1. The crystal structure of (L)-**3** has already been briefly reported.[6] The thermal stabilities of **3**–**5** and the structures of (D)-**3**, (D)-**4**, (D)-**5**, (L)-**4** and (L)-**5**, are now reported. In addition, some further details of the structure and H-bonding in 3-*C*-(triphenylstannyl)methyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose, (D)-**6**,[7] are also discussed and compared with those of **3**–**5**.

## Results and discussion

Compound (D)-**3** was obtained from (D)-**9** and $Ph_3SnLi$, after work-up, in adequate, if not good, yield, Scheme 1; (L)-**3** was prepared similarly from (L)-**9**. In contrast to the $Ph_3SnLi$ reaction, (D)-**9** and $R_3SnLi$ (R = Me or Bu) gave 3,5-anhydro-




**1** **2a**: Solid state structure; major component in solution **2b**: minor components in solution (1)

 DOI: 10.1039/b204675j

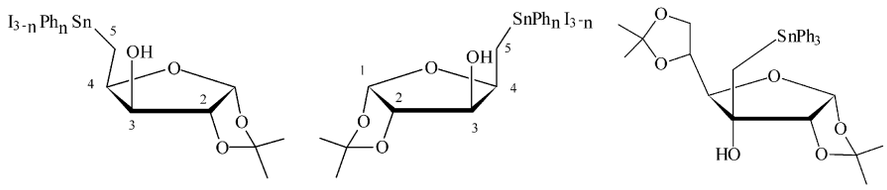
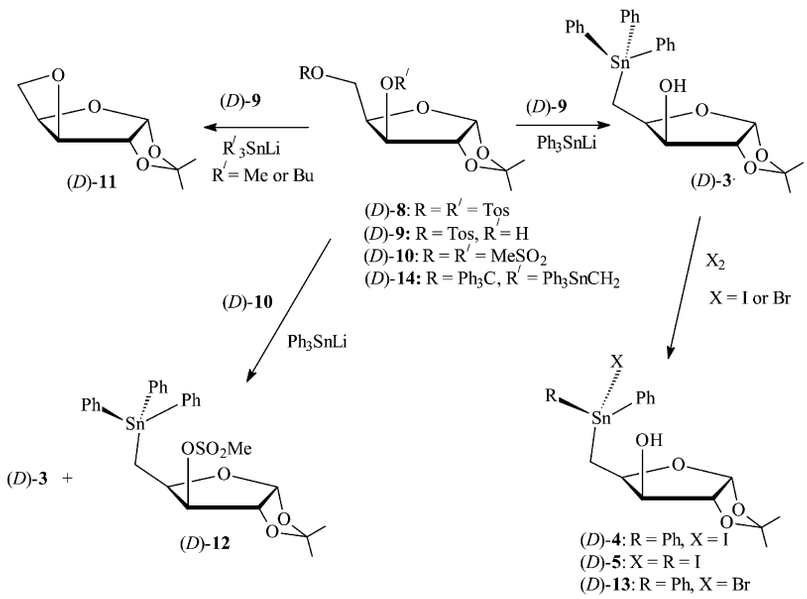



**Fig. 1**




**Scheme 1** (Tos = *p*-tolylsulfonyl).

1,2-*O*-isopropylidene-α-D-xylofuranose, (D)-**11**, rather than the stannylated substitution products. The formation of (D)-**11** from (D)-**9** and a base, *e.g.* NaOMe,[26] has previously been reported. Thus it appears, superficially at least, that $Ph_3SnLi$ is acting as a nucleophilic reagent, while $R_3SnLi$ (R = Me or Bu) is acting as a base towards (D)-**9** in abstracting *p*-$MeC_6H_4SO_3H$.

In contrast to the reaction of (D)-**9** with $Ph_3SnLi$, 1,2-*O*-isopropylidene-3,5-di-*O*-tolylsulfonyl-α-D-xylofuranose, (D)-**8**, was completely recovered from an attempted reaction with excess $Ph_3SnLi$ after 48 h at 20 °C. Nucleophilic substitution of the sulfonate groups at the primary C-5 site in 3,5-di-sulfonated xylose derivatives is generally much easier than at the more hindered secondary C-3 position. The lack of reaction, even at the C-5 site, results from the steric hindrance by the 3-sulfonate group to the approach of the bulky tin-lithium reagent to C-5 in an $S_N2$-type reaction. The reaction of the less hindered 1,2-*O*-isopropylidene-3,5-di-*O*-methylsulfonyl-α-D-xylofuranose, (D)-**10**, with $Ph_3SnLi$, however, did produce stannylated products, namely (D)-**3** and 5-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-5-*C*-triphenylstannyl-α-D-xylofuranose, (D)-**12**. While the formation of (D)-**12** was anticipated, that of (D)-**3** was not. As desulfonylation of (D)-**12** does not occur under the work-up conditions, the loss of the C-3-sulfonate group during the formation of (D)-**3** must have arisen from a precursor to (D)-**12** rather than from (D)-**12** itself, a possible precursor being the anhydro derivative, (D)-**11**. Compound (D)-**11** has been shown to undergo oxetane ring opening with various nucleophilic agents,[26] including $R_2CuLi$ reagents,[27a] the latter providing 5-deoxy-5-*C*-R-1,2-*O*-isopropylidene-α-D-xylofuranose. A similar reaction of (D)-**11** with $Ph_3SnLi$ would produce (D)-**3**. If this is indeed the case, it provides a clear contrast with reactions with trialkylstannyllithiums, since (D)-**11** was isolated from reactions involving trialkylstannyllithiums and (D)-**9**. Furthermore, there remains the possibility that the reactions of $Ph_3SnLi$ and (D)-**9** proceed partially or completely *via* (D)-**11**. 5-Deoxy-5-*C*-R-1,2-*O*-isopropylidene-α-D-xylofuranose compounds have also been obtained from (D)-**3** and excess R-Grignard reagents, in the presence of a copper(I) catalyst as well as from stoichiometric cuprates.[27]

Reactions of (D)-**3** and (L)-**3** with iodine, at both 1 : 1 and 1 : 2 mole ratios of **3**–$I_2$, proceeded at ambient temperature to give the iodophenylstannylated products, **4** and **5**, in quantitative yields. The (D)-**3**–$Br_2$ [1 : 1 mole ratio] reaction at 0 °C gave mainly (D)-**13** (90%) with also *ca.* 5% each of $Ph_3SnBr$ and an unknown tin-containing product, as shown by the $^{119}$Sn NMR spectrum. The (D)-**3**–$Br_2$ [1 : 2 mole ratio] reaction did not lead to any characterised stannylated-xylose product.

Solution $^1$H, $^{13}$C and $^{119}$Sn NMR spectral data for (D)-**3**–**5** and (D)-**13** in $CDCl_3$ are listed in Table 1. The NMR spectra for the (D) and (L) forms of each of **3**–**5** and **13** are, as expected, essentially identical. The $\delta^{119}$Sn value [−107.3 ppm] and coupling constants, in particular $J(^{119}Sn–^{13}C_{ipso})$ and $J(^{119}Sn–^{13}C_5)$ values [515 and 371 Hz], indicate that compounds **3** have 4 co-ordinate Sn centres in solution [*cf.* $\delta^{119}$Sn, $^1J(^{119}Sn–^{13}C_{aryl})$ and $^1J(^{119}Sn–^{13}C_\alpha)$ values for $PrPh_3Sn$[28] of −101.0 ppm, 480 Hz and 398 Hz, respectively]. Similar comparisons indicate that compounds **4**, **5** and (D)-**13** are predominately 5 co-ordinate I(alkyl-*C*,*O*)$Ph_2Sn$, $I_2$(alkyl-*C*,*O*)PhSn and Br(alkyl-*C*,*O*)$Ph_2Sn$ species, respectively, in chloroform solution. For example, the $\delta^{119}$Sn and $^1J(^{119}Sn–^{13}C_\alpha)$ values [−111.5 ppm and 509 Hz] for **4** are much closer to the corresponding values in 5-coordinate **2** [−113.1 ppm and 493 Hz][4] than to those in 4-coordinate $IPrPh_2Sn$ [−54.1 ppm and 399 Hz].[28] The large $^1J(^{119}Sn–^{13}Ci)$ value [747 Hz] in **5**, markedly higher than that of 549 Hz, in 4-coordinate $I_2PhSnCH_2CH_2CH_2CH_2SnPhI_2$;[29] and the $\delta^{119}$Sn

**Table 1** NMR spectral data (ppm, Hz) in $CDCl_3$ at 25 °C

(a) $^1H$ and $^{119}Sn$ NMR data[f]

| | $\delta H_1$ [$JH_1$–$H_2$] | $\delta H_2$ [$JH_2$–$H_3$] | $\delta H_3$ [$JH_3$–$H_4$] | $\delta H_4$ [$JH_4$–$H_5$] [[$J$Sn–H]][a] | $\delta H_5$ [$JH_5$–$H_5'$] [[$J$Sn–H]] | $\delta H_5'$ [$JH_4$–$H_5'$] [[$J$Sn–H]] | $\delta$(OH) [$JH_3$–OH] | $\delta Me_2C$ | $\delta$(H) others | $\delta^{119}Sn$ |
|---|---|---|---|---|---|---|---|---|---|---|
| (D)-**9** | 5.88 | 4.51 | 4.35 | 4.35 | 4.15 | 4.35 | 2.30 | 1.29 | 7.80 (*o*-Ph) | |
| | [3.6] | [<0.5] | [nd] | [8.3] | [13.5] | [nd] | [7.5] | 1.45 | 7.36 (*m*-,*p*-Ph) | |
| | | | | | | | | | 2.45 (Me) | |
| (D)-**10** | 6.00 | 4.83 | 5.10 | 4.59 | 4.42 | 4.42 | — | 1.33 | 3.10, 3.14 (Me) | |
| | [3.7] | [< 0.5] | [2.9] | [6.4] | [10.5] | [5.8] | | 1.52 | | |
| (D)-**12** | 5.86 | 4.77 | 4.83 | 4.67 | 1.62 | 1.88 | — | 1.29 | 7.63 (*o*-Ph) | −106.2 |
| | [3.7] | [< 0.5] | [2.4] | [4.6] | [12.8] | [10.4] | | 1.31 | 7.33 (*m*-,*p*-Ph) | |
| | | | | [[nd]] | [[49]][a] | [[48]][a] | | | 2.96 (Me) | |
| (D)-**3** | 5.77 | 4.44 | 3.88 | 4.64 | 1.74 | 1.90 | 1.57 | 1.29 | 7.64 (*o*-Ph) | −107.3 |
| | [3.7] | [<0.5] | [2.4] | [7.3] | [12.8] | [7.7] | [6.7] | 1.39 | 7.40, (*m*-,*p*-Ph) | |
| | | | | [[39]] | [[60,57]][b] | [[59,57]][b] | | | | |
| (D)-**4** | 5.35 | 4.29 | 4.07 | 4.81 | 2.11 | 2.26 | 2.44 | 1.23 | 7.66 & 7.76(*o*-Ph) | −111.5 |
| | [3.7] | [< 0.5] | [2.4] | [3.8] | [13.6] | [4.8] | [4.3] | 1.45 | 7.36 (*m*-,*p*-Ph) | −119.4 (in $CD_2Cl_2$) |
| | | | | [[nd]] | [[73,70]][b] | [[62]][a] | | | | |
| (D)-**5** | 5.28 | 4.33 | 4.22 | 4.75 | 2.50 | 2.86 | 3.37 | 1.26 | 7.69 (*o*-Ph) | −244.0 |
| | [3.7] | [< 0.5] | [2.5] | [2.1] | [13.3] | [4.8] | [4.4] | 1.49 | 7.43 (*m*-,*p*-Ph) | |
| | | | | [[nd]] | [[nd]] | [[96]][a] | | | | |
| (D)-**13** | 5.27 | 4.25 | 4.02 | 4.84 | 1.95 | 2.10 | 3.74 | 1.20 | 7.56 (*o*-Ph) | −86.3 |
| | [3.5] | [< 0.5] | [nd] | [2.8] | [13.9] | [4.0] | (br) | 1.44 | 7.43 (*m*-,*p*-Ph) | |
| | | | | [[nd]] | [[74]][a] | [[63]][a] | | | | |
| (D)-**15** | 5.51 | 4.75 | 4.69 | 4.96 | 1.88 | 2.27 | — | 1.30 | 7.41 (Ph) | −149.0 |
| | [3.7] | [< 0.5] | [2.7] | [1.9] | [13.7] | [3.8] | | 1.51 | | |
| | | | | [[nd]] | [[nd]] | [[nd]] | | | | |
| (D)-**16** | 5.55 | 4.75 | 4.65 | 4.98 | 1.81 | 2.22 | — | 1.31 | 7.48 (Ph) | −130.9 |
| | [3.7] | [< 0.5] | [2.6] | [1.9] | [13.8] | [nd] | | 1.51 | | |
| | | | | [[nd]] | [[nd]] | [[nd]] | | | | |

(b) $^{13}C$ NMR data

| | $\delta C_1$ | $\delta C_2$ | $\delta C_3$ [$J$Sn–C][c] | $\delta C_4$ [$J$Sn–C][c] | $\delta C_5$ [$J$Sn–C][d] | $\delta C_i$ [$J$Sn–C][d] | $\delta C_o$ [$J$Sn–C][c] | $\delta C_m$ [$J$Sn–C][c] | $\delta C_p$ [$J$Sn–C][c] | $\delta CMe_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| (D)-**9** | 104.8 | 84.9 | 74.1 | 76.8 | 66.3 | 145.2 | 127.9 | 129.8 | 132.2 | |
| (D)-**10** | 104.7 | 80.5 | 83.0 | 76.1 | 65.6 | — | — | — | — | 26.3, 26.4 & 112.8 |
| | | | | | | | | | | 37.3 & 38.1 ($MeSO_3$) |
| (D)-**12** | 103.8 | 84.3 | 83.2 | 77.6 | 10.1 | 138.4 | 137.2 | 129.5 | 129.0 | 26.3, 26.4 & 112.3 |
| | | | [40] | [nd] | [365,349] | [520,498] | [37] | [51] | [11] | 38.4 ($MeSO_3$) |
| (D)-**3** | 103.8 | 85.7 | 76.2 | 78.7 | 10.1 | 138.6 | 136.9 | 128.4 | 128.8 | 26.2, 26.4 & 111.3 |
| | | | [27] | [18] | [371,353] | [515,492] | [37] | [50] | [11] | |
| (D)-**4** | 104.2 | 86.0 | 76.3 [nd] | 78.0 | 21.3 | 138.8[nd] & 140.4[nd] | 135.7, [46] & 136.5, [50] | 128.6, [60] & 128.3, [66] | 129.4, [nd] & 129.3, | 26.2, 26.6 & 112.0 |
| | | | | [48] | [509,488] | | | | [nd] | |
| (D)-**4** in $CD_2Cl_2$ | 105.1 | 85.8 | 76.9 | 78.6 | 22.6 | 140(br), [nd] & 142(br), [nd] | 136.5(br) [nd] | 129.0(br), [nd] & 129.8(br), [nd] | 129.9(br) [nd] | 26.6, 27.1 & 112.7 |
| | | | [19] | [50] | [531,509] | | | | | |
| (D)-**5** | 104.5 | 84.8 | 76.0 | 77.8 | 32.7 | 139.3 | 133.9 | 128.4 | 130.1 | 26.3, 26.8 & 112.7 |
| | | | [19] | [65] | [548,524] | [747,711] | [66] | [87,84] | [18.3] | |
| (D)-**13** | 104.4 | 84.9 | 76.0 | 77.3 | 20.4 | 141.7 [nd] | 136.1 [nd] | 129.2 [nd] | 130.6 [nd] | 26.2, 26.6 & 112.1 |
| | | | [18] | [50] | [532,507] | | | | | |
| (D)-**15** | 104.4 | 85.9 | 76.6 | 79.6 | 31.6 | 138.6 | 134.9 | 128.4 | 130.6 | 26.2, 26.6 & 112.0 |
| | | | [18] | [34 & 19] | [643,613] | [883,844] | [67] | [92] | [18] | |
| (D)-**16** | 104.5 | 85.9 | 75.4 | 79.0 | 27.3 [nd] | e | e | e | e | 26.1, 26.5 & 112.1 |
| | | | [23] | [36 & 11] | | | | | | |

[a] [[$J$($^{119,117}$Sn–$^1$H)]]; [b] [[$J$($^{119}$Sn–$^1$H), J($^{117}$Sn–$^1$H)]]; [c] [$J$($^{119,117}$Sn–$^{13}$C)]; [d] [$J$($^{119}$Sn–$^{13}$C), J($^{117}$Sn–$^{13}$C)]; [e] Not resolved. [f] br = broad; nd = not detected

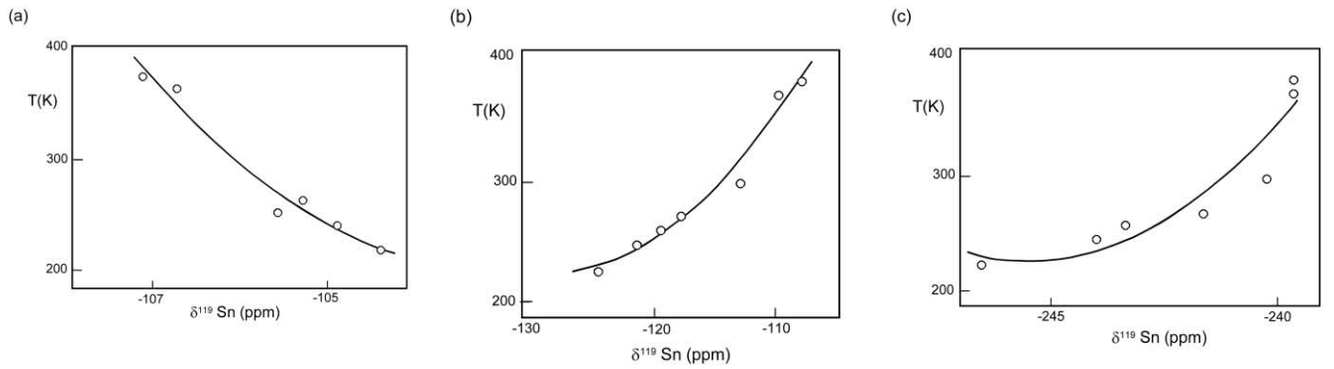



**Fig. 2** Changes in $\delta^{119}$Sn with temperature for (*a*) (D)-**3**, (*b*) (D)-**4**; (*c*) (D)-**5**.

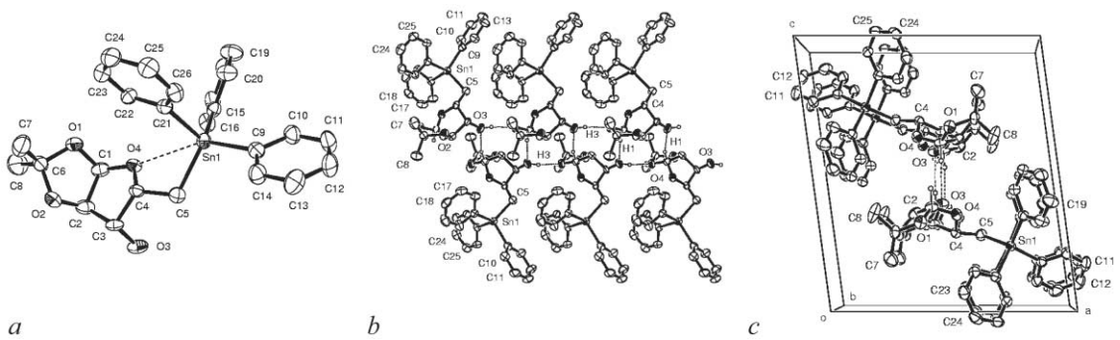



**Fig. 3** (D)-**3** showing (*a*) the molecule and labelling scheme (Sn–O contact shown as a dashed line), (*b*) a portion of a double chain of molecules propagated in the direction of *b* and (*c*) an end-on view of the zig-zag chain of molecules.

value [−244 ppm] in **5**, close to that of −228 ppm in $I_2PhSnCH_2CH_2CO_2$-cholesteryl,[30] are good indicators of a predominant 5-coordinate species in solution.

The single $\delta^{119}$Sn value for each of the isomers of **3**, **4** and **5** in solution at a given temperature suggests either the presence of a single species or a rapid equilibrium between species, including 4- and 5-coordinate compounds. The effects of changing the temperature on solution $\delta^{119}$Sn values of (D)-**3**, (D)-**4** and (D)-**5** are seen in Fig. 2. The changes are very small for (D)-**3** [$\Delta\delta$ = *ca.* −2.5 ppm], small for (D)-**5** [$\Delta\delta$ = *ca.* +8 ppm] and slightly larger for (D)-**4** [$\Delta\delta$ = *ca.* +18 ppm] in the temperature range from −40 to 100 °C. The values indicate no major changes in species, or proportions of species, present throughout the temperature range for any of the compounds, *i.e.* (D)-**3** remains essentially 4-coordinate, while (D)-**4** and (D)-**5** are at least 5-coordinate throughout the temperature range. Changes for (D)-**4** and (D)-**5** are in the direction of stronger Sn–O coordination as the temperature is lowered. Interestingly, the slight change in $\delta^{119}$Sn values for (D)-**3** is in the opposite sense, *i.e.* to lower field as the temperature is decreased.

The $J(H_1–H_2)$, $J(H_2–H_3)$ and $J(H_3–H_4)$ coupling constants, associated with the furanose rings, in **3**–**5** and **13** are in the same ranges reported for other 1,2-*O*-isopropylidene-α-xylofuranose derivatives.[31] While the changes from $Ph_3Sn$ to $X_nPh_{3-n}Sn$ at C-5 have no effect on these *J*(H–H) values, they do result in higher field shifts of H-1 and, to a lesser extent, of H-2, see Table 1. There are also changes to lower field for H-3. Significantly, both H-1 and H-2 are on the same side of the furanose ring as the stannyl substituents, while H-3 is on the opposite side. Coordination of the OH group to tin will hold the stannyl substituents in **4** and **5** close to the furanose ring and in positions to effect the shielding of the ring protons.

The presence of the chiral carbohydrate ligand in (D)-**4** and (L)-**4** results in the phenyl rings being diastereotopic as shown by the two sets of chemical shift values for the phenyl carbon and *ortho* hydrogen atoms in the NMR spectra at 25 °C. Raising the solution temperature (>50 °C) results in coalescence of these signals.

## Solid state structures of 3–5

**General features of the structures.** The general atom numbering scheme and atom arrangements are illustrated for (D)-**3** in Fig. 3a, for (L)-**4** (two independent molecules) in Figs. 4a and b, and for (D)-**5** and (L)-**5** in Figs. 5a and b. The arrangements in (L)-**3** and (D)-**4** are simply the mirror images of those shown for (D)-**3** and (L)-**4**. Enantiomers (D)-**5** and (L)-**5** are both depicted to illustrate the different chiralities at the tin centres in the two molecules.

As indicated by the pucker parameters,[32] calculated using the PLATON program,[25] Table 2, the xylofuranose ring conformations in solid **3**, **4** and **5** vary little within each of the (D)- and (L)-series, *e.g.* the $\phi$ ranges in the pseudorotational cycle[33] for furanose derivatives are 300(2) to 320(2)° [in the $E_4$ to $^3T_4$ region] and 123.7(16) to 137.1(4)° [the $^4E$ to $^4T_3$ region] for the (D)- and (L)-series, respectively, see Table 2. Pucker parameters for the related compounds, (D)-**8**, (D)-**9**[34] and 1,2-*O*-isopropylidene-3-*O*-(triphenylstannylmethyl)-5-*O*-triphenylmethyl-α-D-xylofuranose, (D)-**14**,[35] are also listed. The pucker parameters for the isopropylidene rings and the 5-membered chelate rings, when present, are also shown in Table 2.

**Specific features: compounds (D)-3 at 298(2) K and (L)-3 at 294(1) K.** Selected bond lengths and angles for (D)-**3**, and also those for (L)-**3**, largely as previously reported,[6] are listed in Table 3. The C–Sn–C bond angles at tin are close to tetrahedral, being in the ranges 106.8(4) to 113.8(4)° for (D)-**3**, and 106.55(8) to 114.27(8)° for (L)-**3**. However, in each molecule there is also a Sn ring-oxygen (O4) separation of 3.262(8) and 3.2520(14) Å in (D)-**3** and (L)-**3**, respectively, well within the sum of the van der Waals radii of 3.70 Å.[35]If these are considered as weak bonds, then the tin coordination number is increased to 5, with the O4 and C9 atoms in the quasi axial sites and thus the carbohydrate species acts here as a ligand creating a four membered chelate ring. The weakness of the Sn–O4 interactions is also clearly indicated from the *trans* axial O4–Sn–C9 and the axial–Sn–equatorial, O4–Sn–C5 angles [155.4(3) and 46.8(3) and

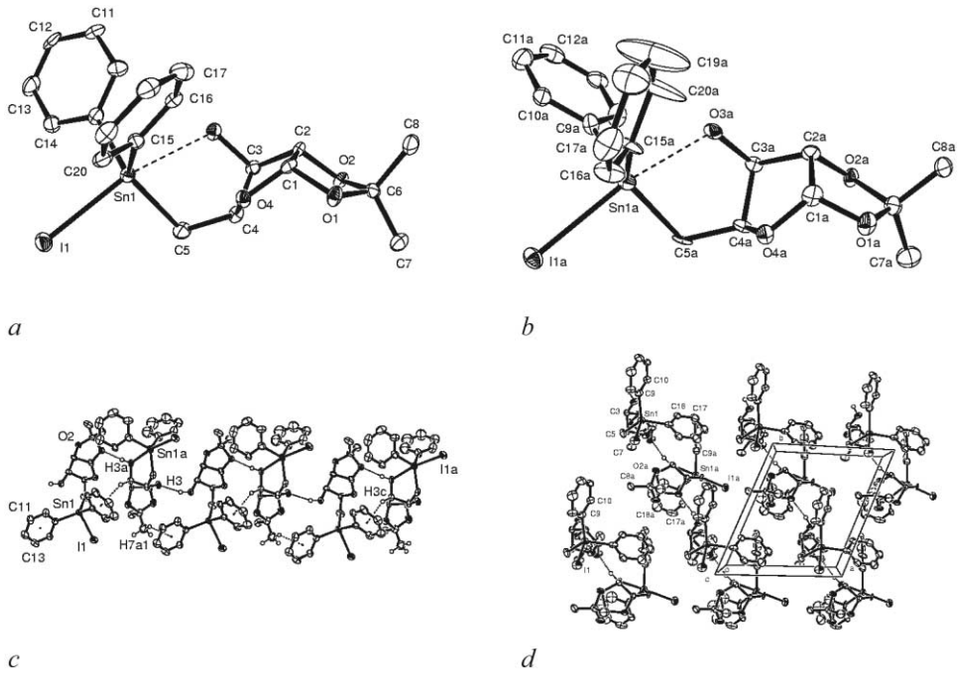



**Fig. 4** (L)-**4** showing the two independent molecules (*a*) molecule 1 and (*b*) molecule 2 [the (D)-**4** molecules are the mirror images of those shown], (*c*) a portion of a chain of molecules propagated in the direction [−1,1,0] and (d) the chains side-by-side in a layer of molecules parallel to (001), near $z = 0$.

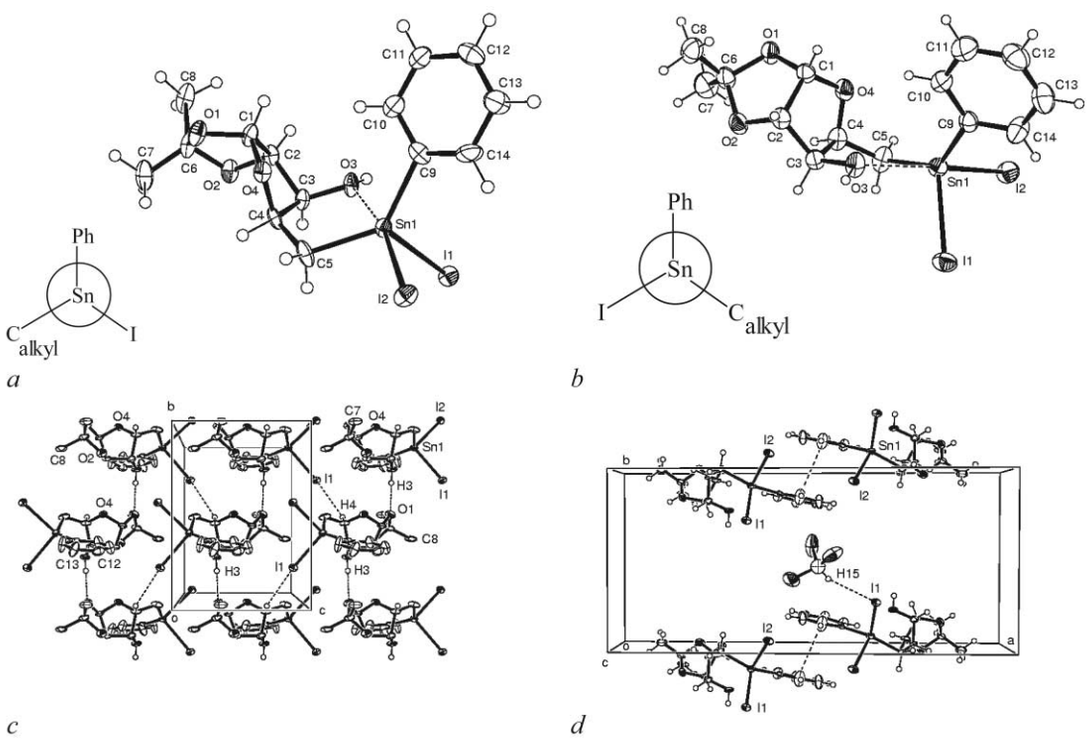



**Fig. 5** The molecule and numbering scheme for (*a*) (D)-**5** and (*b*) (L)-**5**. Insets illustrate the equatorial ligand arrangements about Sn looking down the I2⟶Sn⟶O3 *trans* axial bond. Also, for (D)-**5**, (*c*) a portion of a layer of molecules parallel to (001), centred on $z = 1/4$. and (*d*) π–π contacts between phenyl groups of adjacent layers also showing a representative chloroform solvate molecule.

155.68(6) and 47.21(6) in (D)-**3** and (L)-**3**, respectively] much reduced from the ideal angles of 180 and 90°. In contrast to the situations in solid **4** and **5**, see later, the shortest Sn–O distance is to the furanose ring oxygen rather than to O3 of the OH group. The Sn–O3 separations, at 4.931(10) and 4.9280(18) Å in the two isomers, are well outside the van der Waals radii sum. The average solid state $\delta^{119}$Sn NMR value for (D)-**3** and (L)-**3** at $-91.4 \pm 0.6$ ppm is at slightly lower field than the solution value of −107.3 ppm obtained for (D)-**3** in $CDCl_3$. However, this change in $\delta^{119}$Sn is considered merely to result from phase and not structural change.

Molecules of (D)-**3** or (L)-**3** are linked to form chains, in the direction of *b*, by intermolecular H-bonds of the form O3–H3–O1, see Table 3 and Figs. 3b and c. The molecules within the primary chains are related to one another purely by cell translation and as such the chains are linear rather than zig-zag in form. Further contacts, C1–H1–O3, link the primary chains in pairs as shown in Figs. 3b and c. Thus, in this case O3 serves both as donor and acceptor. The molecules take the form of a hydrophilic xylofuranose spine sheathed in hydrophobic methyl and phenyl groups and thus only van der Waals contacts arise when the chains are packed in the structure.

**Table 2** Cremer and Pople[32] pucker parameters and shapes of the 5 membered rings

| | Furanose ring[a] | | | Isopropylidene ring[b] | | | Chelate ring[c] | | |
|---|---|---|---|---|---|---|---|---|---|
| | Q(2) | $\phi$ | Conformation[d] | Q(2) | $\phi$ | Conformation[d] | Q(2) | $\phi$ | Conformation[d] |
| (L)-**3**[e] | 0.353(2) | 137.1(4) | $^4E \Leftrightarrow {}^4T_3$ | 0.285(2) | 136.6(5) | $^{C6}E \Leftrightarrow {}^{C6}T_{O2}$ | – | – | – |
| (L)-**4A**[f] | 0.363(10) | 123.7(16) | $^4T_3 \Leftrightarrow E_3$ | 0.285(10) | 94(2) | $^{C2A}T_{O2A} \Leftrightarrow E_{O2A}$ | 0.351(9) | 293.6(12) | $^{C4A}E \Leftrightarrow {}^{C4A}T_{C5}$ |
| (L)-**4B**[g] | 0.375(10) | 130.1(5) | $^4T_3 \Leftrightarrow {}^4E$ | 0.310(10) | 120.7(18) | $^{C6}T_{O2} \Leftrightarrow E_{O2}$ | 0.560(9) | 323.3(9) | $^{C5}E$ |
| (L)-**5** | 0.370(5) | 132.1(8) | $^4T_3 \Leftrightarrow {}^4E$ | 0.270(5) | 117.3(11) | $^{C6}T_{O2} \Leftrightarrow E_{O2}$ | 0.386(5) | 295.6(7) | $^{C4}E \Leftrightarrow {}^{C4}T_{C5}$ |
| (D)-**3** | 0.333(12) | 320(2) | $E_4 \Leftrightarrow {}^3T_4$ | 0.275(12) | 314(3) | $^{O2}T_{C6} \Leftrightarrow E_{C6}$ | – | – | – |
| (D)-**4A**[f] | 0.363(14) | 300(2) | $^3T_4 \Leftrightarrow {}^3E$ | 0.246(14) | 274(3) | $^{O2}T_{C2} \Leftrightarrow {}^{O2}E$ | 0.358(13) | 116.5(18) | $E_{C4A} \Leftrightarrow {}^{C5}T_{C4}$ |
| (D)-**4B**[g] | 0.382(14) | 307(2) | $^3T_4 \Leftrightarrow E_4$ | 0.289(14) | 297(3) | $^{O2}E \Leftrightarrow {}^{O2}T_{C6}$ | 0.554(12) | 146.1(14) | $E_{C5}$ |
| (D)-**5** | 0.400(8) | 310.8(12) | $^3T_4 \Leftrightarrow E_4$ | 0.272(8) | 298.9(17) | $^{O2}E \Leftrightarrow {}^{O2}T_{C6}$ | 0.380(8) | 115.3(11) | $E_{C4} \Leftrightarrow {}^{C5}T_{C4}$ |
| (D)-**6** | 0.376(13) | 325(2) | $E_4 \Leftrightarrow {}^oT_4$ | 0.262(14) | 323(3) | $E_{C6} \Leftrightarrow {}^{O2}T_{C6}$ | | | |
| (D)-**8**[h] | 0.350(5) | 294.2(8) | $^3E \Leftrightarrow {}^3T_4$ | 0.259(5) | 265.7(11) | $^{O2}T_{C2} \Leftrightarrow E_{C2}$ | | | |
| (D)-**9**[h] | 0.346(8) | 321.8(14) | $E_4 \Leftrightarrow {}^3T_4$ | 0.269(8) | 314.9(17) | $^{O2}T_{C6} \Leftrightarrow E_{C6}$ | | | |
| (D)-**14**[i] | 0.363(8) | 291.2(8) | $^3E \Leftrightarrow {}^3T_4$ | 0.251(5) | 247.8(11) | $E_{C2} \Leftrightarrow {}^{Cl}T_{C2}$ | | | |

[a] Ring atoms in cyclic order O4,C1,C2,C3,C4. [b] Ring atoms in cyclic order O1,C1,C2,O2,C6. [c] Ring atoms in cyclic order Sn,O3,C3,C4,C5. [d] T = twist, E = envelope, see ref. 6, conformation between the two quoted, but closer to the first. [e] Ref. 6. [f] Molecule 2. [g] Molecule 1. [h] Ref. 34. [i] (D)-**14**: 1,2-*O*-isopropylidene-5-*O*-triphenylmethyl-3-*O*-(triphenylstannylmethyl)-α-D-xylofuranose.[35]

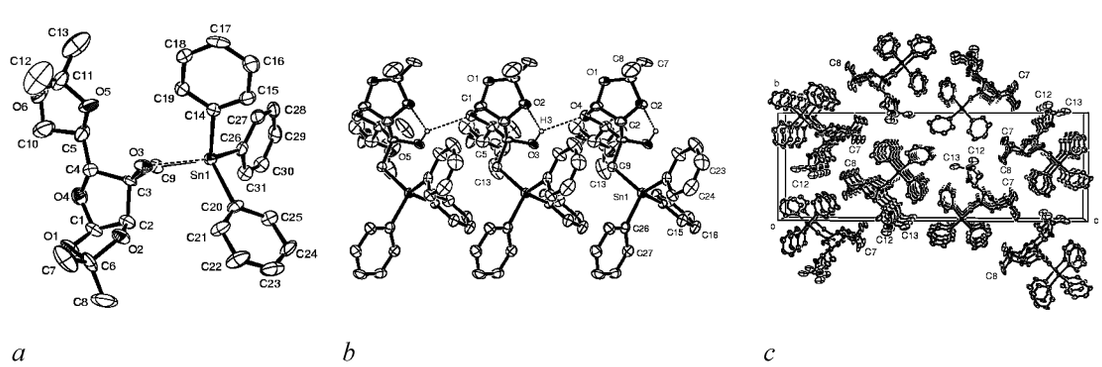
**Table 3** Selected bond lengths (Å) and angles (°) for (D)-**3**, (L)-**3** and (D)-**6** at 296(2) K

| | (D)-**3** | (L)-**3** | | (D)-**6** |
|---|---|---|---|---|
| Sn–C9 | 2.125(12) | 2.138(2) | Sn–C26 | 2.137(12) |
| Sn–C5 | 2.154(11) | 2.150(2) | Sn–C9 | 2.161(12) |
| Sn–C15 | 2.116(10) | 2.131(2) | Sn–C14 | 2.144(11) |
| Sn–C21 | 2.151(10) | 2.144(2) | Sn–C20 | 2.161(12) |
| Sn–O4 | 3.262(8) | 3.2520(14) | Sn–O3 | 2.977(10) |
| Sn–O3 | 4.931(10) | 4.9280(18) | Sn–O4 | 5.176(11) |
| C5–Sn–C15 | 113.8(4) | 114.27(8) | C9–Sn–C20 | 114.3(4) |
| C5–Sn–C21 | 108.1(4) | 108.46(8) | C9–Sn–C14 | 108.6(4) |
| C15–Sn–C21 | 106.9(4) | 107.06(8) | C14–Sn–C20 | 113.5(5) |
| C9–Sn–C5 | 109.4(4) | 109.12(8) | C26–Sn–C9 | 109.1(5) |
| C9–Sn–C15 | 111.5(4) | 111.05(8) | C26–Sn–C14 | 106.2(5) |
| C9–Sn–C21 | 106.8(4) | 106.55(8) | C26–Sn–C20 | 104.7(4) |
| O4–Sn–C5 | 46.8(3) | 47.21(6) | O3–Sn–C9 | 52.2(4) |
| O4–Sn–C9 | 155.4(3) | 155.68(6) | O3–Sn–C26 | 160.2(4) |
| O4–Sn–C15 | 79.9(3) | 80.53(6) | O3–Sn–C14 | 77.8(4) |
| O4–Sn–C21 | 89.4(3) | 89.28(6) | O3–Sn–C20 | 90.9(4) |

Intermolecular H-bonding contacts

| | D–H---A | *d*(D–H) | *d*(H---A) | *d*(D–A) | <(D–H---A) |
|---|---|---|---|---|---|
| (D)-**3** | O3–H3–O1[a] | 0.82 | 2.06 | 2.849(13) | 161.2 |
| | C1–H1–O3[b] | 0.98 | 2.34 | 3.0303(14) | 165.5 |
| (L)-**3** | O3–H3–O1[c] | 0.82 | 2.05 | 2.846(3) | 164.3 |
| | C1–H1–O3[d] | 0.98 | 2.33 | 3.284(3) | 164.7 |
| (D)-**6** | O3–H3–O2 | 0.82 | 2.18 | 2.634(11) | 114.9 |
| | O3–H3–O4[e] | 0.82 | 2.48 | 3.158(14) | 140.2 |

Symmetry operator: [a] $x, y + 1, z$. [b] $1 - x, y - ½, 1 - z$. [c] $x, y - 1, z$. [d] $1 - x, ½ + y, 1 - z$. [e] $x - 1, y, z$.




*a* *b* *c*

**Fig. 6** (D)-**6** showing (*a*) the molecule and labelling scheme (Sn–O contact shown as a dashed line) (*b*) a portion of a chain of molecules propagated in the direction of *a* and (*c*) the packing of the chains, viewed end-on, in the unit cell.

**Table 4** Selected geometric parameters (Å,°) for (D)-**4** and (L)-**4**

| | Molecule 1 | | | Molecule 2 | |
|---|---|---|---|---|---|
| | (D)-**4** at 298K | (L)-**4** at 150K | | (D)-**4** at 298K | (L)-**4** at 150K |
| Sn–O3 | 2.825(10) | 2.786(6) | SnA–O3A | 2.443(9) | 2.418(6) |
| Sn–I1 | 2.764(4) | 2.7630(8) | SnA–I1A | 2.826(5) | 2.8187(8) |
| Sn–C5 | 2.145(14) | 2.151(9) | SnA–C5A | 2.156(12) | 2.134(8) |
| Sn–C9 | 2.151(13) | 2.153(9) | SnA–C9A | 2.136(14) | 2.124(10) |
| Sn–C15 | 2.171(14) | 2.135(9) | SnA–C15A | 2.119(13) | 2.125(9) |
| Sn–O4 | 3.170(9) | 3.134(6) | SnA–O4A | 3.497(11) | 3.479(6) |
| O3–Sn–I1 | 157.1(2) | 158.70(13) | O3A–SnA–I1A | 169.6(2) | 170.25(15) |
| O3–Sn–C5 | 66.6(4) | 67.5(3) | O3A–SnA–C5A | 73.3(4) | 73.6(3) |
| O3–Sn–C9 | 78.5(4) | 78.3(3) | O3A–SnA–C9A | 84.8(4) | 84.8(3) |
| O3–Sn–C15 | 97.9(4) | 97.4(3) | O3A–SnA–C15A | 87.1(4) | 87.1(3) |
| O3–Sn–O4 | 55.9(2) | 56.61(15) | | | |
| O4–Sn–I1 | 125.0(2) | 124.59(11) | | | |
| O4–Sn–C5 | 49.0(4) | 49.9(3) | | | |
| O4–Sn–C9 | 132.9(4) | 133.4(3) | | | |
| O4–Sn–C15 | 72.1(4) | 71.7(3) | | | |
| I1–Sn–C5 | 96.5(4) | 96.8(3) | I1A–SnA–C5A | 96.3(3) | 96.7(2) |
| I1–Sn–C9 | 101.5(4) | 101.6(3) | I1A–SnA–C9A | 100.7(3) | 100.3(2) |
| I1–Sn–C15 | 104.0(4) | 102.9(2) | I1A–SnA–C15A | 99.1(4) | 98.7(2) |
| C5–Sn–C9 | 125.6(6) | 125.5(4) | C5A–SnA–C9A | 115.8(5) | 115.6(4) |
| C5–Sn–C15 | 118.1(5) | 118.8(4) | C5A–SnA–C15A | 127.8(5) | 126.9(4) |
| C9–Sn–C15 | 106.5(5) | 106.3(3) | C9A–SnA–C15A | 109.7(5) | 111.1(4) |
| O3–Sn–C5–C4 | −38.8(9) | 38.6(6) | O3A–SnA–C5A–C4A | −21.4(8) | 20.8(6) |
| Sn–C5–C4–C3 | 65.1(14) | −66.9(8) | SnA–C5A–C4A–C3A | 42.6(13) | −40.9(9) |
| C5–C4–C3–O3 | −40.9(15) | 44.4(9) | C5A–C4A–C3A–O3A | −40.3(13) | 39.0(9) |
| C4–C3–O3–Sn | 5.5(11) | −7.6(7) | C4A–C3A–O3A–SnA | 20.4(10) | −21.4(7) |
| C3–O3–Sn–C5 | 19.3(8) | −17.9(5) | C3A–O3A–SnA–C5A | −0.2(7) | 1.4(5) |

Intermolecular H-bonding contacts

| | D–H···A | *d*(D–H) | *d*(H···A) | D(D···A) | <(D–H···A) |
|---|---|---|---|---|---|
| (D-**4**) | O3A–H3A–O1 | 0.82 | 1.95 | 2.750(13) | 163.9 |
| (D-**4**) | O3–H3–O4[a] | 0.82 | 2.12 | 2.832(12) | 145.8 |
| (L-**4**) | O3A–H3A–O1 | 0.84 | 1.89 | 2.718(8) | 169.3 |
| (L-**4**) | O3–H3–O4A[b] | 0.84 | 1.97 | 2.773(8) | 160.1 |

Intermolecular C–H···π interactions[c]

| | | H···Cg | $H_{perpendicular}$ | $\gamma$ | X–H···Cg | X···Cg | Symmetry operation |
|---|---|---|---|---|---|---|---|
| (D)-**4** | C3A–H3C–Cg1 | 2.906 | 2.884 | 7.07 | 159.49 | 3.840 | $x, y, z$ |
| | C7A–H7A3–Cg2 | 2.734 | 2.690 | 10.27 | 147.47 | 3.598 | $x-1, y+1, z$ |
| (L)-**4** | CA–H3C–Cg1 | 2.827 | 2.807 | 6.82 | 158.30 | 3.775 | $x, y, z$ |
| | C7A–H7A1–Cg2 | 2.683 | 2.623 | 12.18 | 150.91 | 3.571 | $x+1, y-1, z$ |

Symmetry operator: [a] $x+1, y-1, z$. [b] $x-1, y+1, z$. [c] Cg1 and Cg2 are centroids for phenyl groups with C15 to C19 and C9 to C14, respectively; $\gamma$ is the angle at H between the vectors H–Cg and $H_{perpendicular}$.

A four membered chelate ring and an intramolecular Sn–O interaction have been reported in the tetraorganotin (D)-**6**.[7] The structure of (D)-**6**, Cambridge Structural Database (CSD) reference code SUKNUH01, has been re-refined more completely here using the original intensity data and structural model. The hydroxy H has been located in this refinement, see Fig. 6a. The interacting oxygen group in (D)-**6** is the OH group [Sn–OH = 2.977(10) Å], in contrast to the furanose ring oxygen, which is involved in **3**. The angles subtended at tin in (D)-**6** are however similar to those in **3**, see Table 3. The OH group is involved in both intramolecular and intermolecular H-bonds. The latter connect the molecules into linear chains in the direction of *a*, see Figs. 6b and c. The packing of the chains appears to be controlled purely by van der Waals forces, but the hydrophobic sheath of methyl and phenyl groups is not as complete as it was in (D)-**3** and (L)-**3**.

**Specific features: compounds (D)-4 and (L)-4.** The structures of (D)-**4** and (L)-**4** were determined at 298 and 150 K, respectively. In each of (D)-**4** and (L)-**4**, there are two quite distinct molecular arrangements in the unit cell, as illustrated by the two distinct sets of intramolecular Sn–O3 and Sn–O4 separations and modes of participation of O4 in H-bond formation, see Table 4. Any differences in the geometric parameters between the enantiomers arise from the different temperatures of data collection. In molecule 2, the tin–oxygen distances, SnA–O3A and SnA–O4A, are 2.443(9) and 3.497(11) Å in (D)-**4**, while in (L)-**4**, the distances are 2.418(6) and 3.479(6) Å. These distances all are within the van der Waals radii sum of 3.70 Å. With O3A and O4A (and likewise O3 and O4) being relatively close together in the same molecule, strong bonding with one, *e.g.* O3A, would be expected to result in the other, *e.g.* O4A, also being drawn closer to tin.

A feature common to the structures of both (D)- and (L)-**4** is the extreme nature of the anisotropic displacement associated with C19A and C20A of the phenyl group of molecule 2 of which they are part. It is interpreted as resulting from libration in which the motion of the phenyl group has two components. The first is rotation about the Sn–C bond and the second a

fan-like wagging with the direction of motion perpendicular to the plane of the benzene ring.

Considering SnA–O3A as the only significant Sn–O bond, along with the other four bonds to tin [3 carbon atoms and 1 iodine atom], a distorted trigonal bipyramidal geometry at tin is realised, with I1A and O3A in the *trans* axial positions [O3A–SnA–I1A = 169.6(2) and 170.25(15)° in (D)-**4** and (L)-**4**, respectively]. Here the carbohydrate groups in **4** are acting as 5-membered chelating ligands with bite angles of 73.3(4) and 73.6(3)°, the small bite angles resulting in the distortion away from ideal trigonal bipyramidal structures. The SnA–I1A bond lengths, 2.826(5) and 2.8187(8) Å, are longer than the sum of the covalent radii for Sn and I (2.73 Å) as expected for an axial iodide ligand in a trigonal bipyramidal array.

In molecules 1 of **4**, the Sn–O3 separations are much longer, but the Sn–O4 distances are now shorter, compared to the situations in molecules 2: Sn–O3 and Sn–O4 distances being 2.825(10) and 3.170(9) Å in (D)-**4**, and 2.786(6) and 3.134(6) Å in (L)-**4**. Thus here it is apparent that the weakening of Sn–O3 is compensated by the strengthened Sn–O4 interaction. This strongly indicates that both oxygen atoms in molecules 1 should be considered as interacting with the tin centres, which thus gives rise to six coordinate triorganotin halides with tridentate carbohydrate-(*C*,*O*,*O*)-ligands, with both 4- and 5-membered chelate rings, in an irregular arrangement. The Sn–I1 bond lengths [2.764(4) and 2.7630(8) Å] in molecules 1 are appreciably shorter than in molecules 2, and indeed are only a little longer than a single Sn–I bond [2.73 Å]. Hexa-co-ordinate triorganotin halides have been reported rarely, one example being bis[8-(dimethylamino)-1-naphthyl]methyltin iodide.[37]

The chelate rings, Sn–O3–C3–C4–C5, in the two independent molecules in **4** have distinct conformations: the rings in molecules 1 are envelopes with flaps at C-5, while those in molecules 2 are more flattened envelopes with flaps at C4A, see Table 2. The differences between the two molecules is also clearly observed in the solid state MAS–CP NMR spectra, *e.g.* there are two distinct $^{119}$Sn chemical shift values of −67.7 and −145.6 ppm.

Molecules 1 and 2 are linked alternating into chains by H-bonds in the direction [−1,1,0]. For molecule 2, these are of the form O3A–H3A–O1 and occur within the asymmetric unit and for molecule 1 of the form O3–H3–O4A. Thus molecules 1 and 2 differ in terms of the type of oxygen atom which they provide as H-bond acceptors, see Figs. 4c and d. The arrangement of the molecules within the zig-zag chains also permits C–H–π interactions. In these the participation of C3A of the furanose ring and methyl C7A both of molecule 2 and the phenyl groups of molecule 1 further differentiates between the two molecules. The chains can be perceived as lying side by side, with only van der Waals contacts between them, to form layers parallel to (001). Adjacent layers, again with only van der Waals contacts between them, are related by cell translation and stacked in the direction of *c*.

**Specific features: compounds (D)-5 and (L)-5.** The structures of (D)-**5** and (L)-**5**, determined at 298 and 108 K, respectively, again exhibit small differences in some geometric parameters, see Table 5. For example in the (D) form with the lower temperature data, the Sn–O3 bond is shorter and the Sn–I2 bond longer. In each case there is only one independent molecule. As in compounds **4**, the Sn–O3 and Sn–O4 distances are both within the van der Waals radii sum, 3.70 Å, [Sn–O3 and Sn–O4 = 2.562(6) and 3.449(6) Å in (D)-**5**, and 2.588(4) and 3.461(4) Å in (L)-**5**]. All in all, the geometries of molecules, (D)- and (L)-**5**, are very similar to molecules 2 of (D)- and (L)-**4**, including the conformations of the chelate rings, Sn–O3–C3–C4–C5. The Sn–O4 distances in (D)- and (L)-**5** are only *ca.* 0.15 Å less than the van der Waals radii sum. As with molecules 2 in compounds **4**, consideration of only the shorter Sn–O3 distance as a bond would again provide slightly distorted trigonal biypramidal tin geometries with the axial sites being occupied by I2 and O3 [Sn–I2 = 2.7789(12) Å, Sn–O3 = 2.562(6) Å and I2–Sn–O3 = 168.45(13)° in (D)-**5**, while in (L)-**5**, the corresponding parameters are 2.7684(5) Å, 2.588(4) Å and 168.20(8)°], see Table 5. However, the Sn–O4 separation cannot be totally ignored. As stated above, since O3 and O4 are relatively close together in the same molecule, interaction with one of these oxygen atoms will influence the position of the other relative to the tin centre. The Sn–O4 distances in **5** are marginally less than those in molecules 2 of compounds **4**, despite the Sn–O3 distances being greater. A weak, even if extremely small, compensatory effect seems to be at play here: *i.e.* as the Sn–O3 interaction weakens so the Sn–O4 interaction develops. Overall, the structures of **5** are best considered as trigonal bipyramids, with an additional very weak interaction with O4.

A consequence of having three different groupings [Ph, alkyl group and I] in the equatorial plane in solid **5**, is the formation of chiral tin centres. Based on the priority sequence of the equatorial groups, and looking down the I–Sn–O3 *trans* axial bond, the tin centre in solid (D)-**5** has the (*S*)-configuration, while that in (L)-**5** has the (*R*) configuration, see Fig. 5a and b. Thus, in the solid state at least, (D)-**5** and (L)-**5** are complete enantiomers.

The molecules are interconnected first of all by O3–H3–O1 H-bonds to form zig-zag chains propagated in the direction of *b* and the chains, layered side by side, are further interconnected by C4–H4–I1 contacts (Table 5, Fig. 5c). In this way the molecules form layers parallel to (100) centred on $x = ¼$ and ¾ with the phenyl groups protruding on either side of the layer. Adjacent layers are related by the operation of crystallographic 2-fold screw axes parallel to *a* or, equivalently and more significantly, by 2-fold rotation axes parallel to *c*. This brings about overlap of the phenyl groups from adjacent layers in pairs with the overlap or π–π stacking parameters given in Table 5 and as shown in Fig. 5d. The Figure also shows how the chloroform solvate molecules, present in both structures, are disordered over two sites of equal occupancy related by one of the crystallographic 2-fold rotation axes mentioned above and only one member of the disordered pair being shown, are also present in cavities between the layers of molecules and participate in contacts of the form C15–H15–I1 (Table 5).

## Thermal stabilities

Compounds **3** and **5**, unlike **4** and **13**, were stable in chloroform solution at ambient temperature for weeks. Complete decomposition of (D)-**4** occurred within 1 month at ambient temperature in chloroform solution to give the proto-dephenylation product, (D)-**15** and PhH, see Fig. 7. The loss of PhH arises from the OH group acting as a Brønsted acid, in a manner analogous to that shown in the formation of **2**[4] [eqn. (1)]. The greater ease of proto-dephenylation in **4** compared to **3** in solution is considered a consequence of the Sn–OH coordination present in **4** but absent in **3**. Thus the OH group is ideally sited in **4** to cleave a phenyl–tin bond. On the other hand, the greater stability of **5** compared to that of **4** in solution follows the general trend of electrophilic cleavage of carbon–tin bonds, *i.e.* that a carbon–tin bond in a monoorganotin compound is more resistant to reaction than that in a diorganotin compound. Compound (D)-**15** was sufficiently stable to survive in solution, but unfortunately work up using chromatography and fractional recrystallisation resulted in its decomposition. Characterisation of (D)-**15** rested solely on its NMR spectra, see Table 1. Distinct from the case of **2**, only a single stereoisomer of (D)-**15** was indicated in solution from the single $\delta^{119}$Sn value. The two $J(^{119}\text{Sn}–^{13}\text{C})$ values (19 and 34 Hz) to C4 suggested that (D)-**15** may be present in solution as dimeric compounds, *e.g.* see Fig. 7. In this dimer, C4 has couplings, $^2J$ to Sn and $^3J$ to Sn′. Other significant NMR parameters for (D)-**15**

**Table 5** Selected geometric parameters [Å,°] for (D)-**5** at 108 K and (L)-**5** at 298 K

| | (D)-**5** | (L)-**5** |
|---|---|---|
| Sn–O3 | 2.562(6) | 2.588(4) |
| Sn–I2 | 2.7789(12) | 2.7684(5) |
| Sn–C5 | 2.132(8) | 2.127(5) |
| Sn–C9 | 2.134(8) | 2.115(5) |
| Sn–I1 | 2.7251(13) | 2.7121(5) |
| Sn–O4 | 3.449(6) | 3.461(4) |
| O3–Sn–I2 | 168.45(13) | 168.20(8) |
| O3–Sn–C5 | 72.8(3) | 72.31(17) |
| O3–Sn–C9 | 87.0(2) | 86.47(16) |
| O3–Sn–I1 | 85.29(13) | 85.45(8) |
| I2–Sn–C5 | 96.2(2) | 96.22(15) |
| I2–Sn–C9 | 103.7(2) | 104.02(14) |
| I2–Sn–I1 | 95.67(5) | 96.329(17) |
| C5–Sn–C9 | 134.7(3) | 134.4(2) |
| C5–Sn–I1 | 111.0(3) | 110.53(19) |
| C9–Sn–I1 | 107.1(2) | 107.32(14) |
| C4–C3–O3–Sn | 22.2(8) | −21.6(5) |
| C3–O3–Sn–C5 | −0.6(5) | 0.3(3) |
| O3–Sn–C5–C4 | −22.4(6) | 23.0(4) |
| Sn–C5–C4–C3 | 46.0(10) | −47.9(7) |
| C5–C4–C3–O3 | −43.9(10) | 44.4(7) |

Intermolecular H-bonding contacts

| | D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | <(D–H···A) |
|---|---|---|---|---|---|
| (D)-**5** | O3–H3–O1[a] | 0.84 | 1.96 | 2.802(8) | 178.5 |
| | C4–H4–I1[b] | 1.00 | 3.05 | 3.791(8) | 132.3 |
| | C15–H15–I1[c] | 1.00 | 3.05 | 3.92(2) | 146.7 |
| (L)-**5** | O3–H3–O1[d] | 0.82 | 2.00 | 2.819(5) | 179.7 |
| | C4–H4–I1[e] | 0.98 | 3.09 | 3.833(5) | 133.9 |
| | C15–H15–I1[f] | 0.98 | 3.12 | 4.020(17) | 153.5 |

π–π interactions[g]

| | *A* | *α* | *β* | *γ* | *B* | *C* | *O* | Symmetry operation |
|---|---|---|---|---|---|---|---|---|
| (D)-**5** | 3.773 | 9.67 | 12.82 | 12.82 | 3.679 | 3.679 | 0.837 | $-x, 1-y, z$ |
| (L)-**5** | 3.804 | 5.36 | 14.78 | 14.78 | 3.677 | 3.677 | 0.975 | $2-x, 1-y, z$ |

Symmetry operator:[a] $-\frac{1}{2}-x, y-\frac{1}{2}, 1-z$. [b] $\frac{1}{2}-x, \frac{1}{2}+y, -z$. [c] $\frac{1}{2}+x, \frac{1}{2}-y, -z$. [d] $\frac{3}{2}-x, y+\frac{1}{2}, 1-z$. [e] $\frac{3}{2}-x, y-\frac{1}{2}, 2-z$. [f] $x-\frac{1}{2}, \frac{3}{2}-y, 2-z$. [g] For rings 1 and 2 with centroids P and P′ respectively and points Q [Q′] defined as the foot of the perpendicular from P [P′] on the plane of ring 2 [1] then A=P–P′; α = angle between the planes of the rings; β = the angle Q–P–P′ and γ = Q′–P′–P; B=P–Q and C=P′–Q′ and O is the relative displacement of the centroids in a plane whose orientation is intermediate between those of the rings of the pair. The identity of the beta/gamma and B/C value pairs arises because the rings of the pair are related by the operation of a crystallographic 2–fold axis.

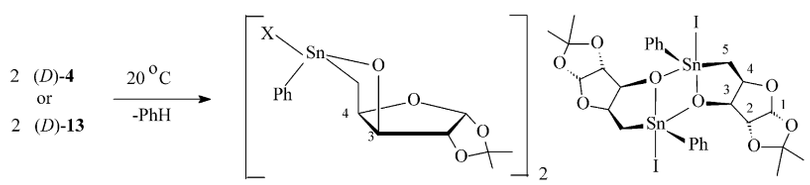



**Fig. 7** Formation of (D)-**15** and (D)-**16**.

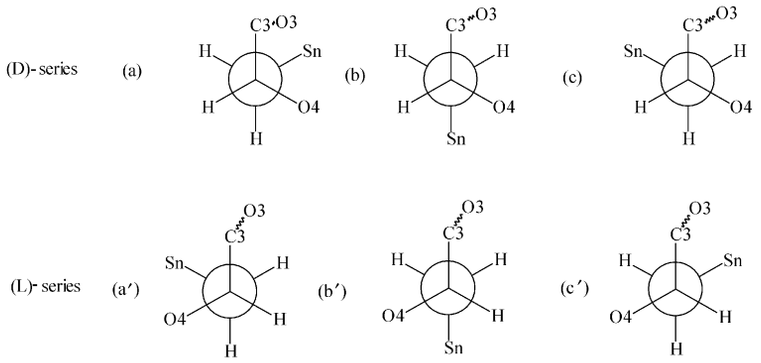
are the $\delta^{119}$Sn and $\delta^{13}$C5 values of −149.0 and 31.6 ppm, respectively, compared to corresponding values of −111.5 and 21.3 ppm in (D)-**4**, and the $J(^{119}\text{Sn}–^{13}\text{C})$ values for C5 and C-*i* of 643 and 883 Hz, respectively. These are as expected for the formation of a trigonal $C_2O_2I$-coordinated tin centre in (D)-**15** from a trigonal $C_3OI$-coordinated centre in (D)-**4**. Compound (L)-**4** reacted similarly to (D)-**4**, while (D)-**13** underwent a similar but slower decomposition on standing in solution to give (D)-**16**.

All compounds, **3**–**5** decomposed at or near their melting points, *ca.* 150 °C. Volatile products evolved at temperatures between 150 and 400 °C, as identified by TGA/MS, were PhH, $H_2O$ and $Me_2CO$. Benzene is produced by proto-dephenylation reactions, while the acetone is derived from breakdown of the isopropylidene group.

## Conclusions

The hydroxy groups in the stannylated xylofuranose derivatives, **3**–**5** and **13**, exhibit roles as Lewis bases, Brønsted acids and hydrogen bonding centres. In compounds **3**–**5**, the 5-deoxy-1,2-*O*-isopropylidene-α-D- and -L-xylofuran-5-yl ligands operate as $C^5,O^4$ chelating ligands [4-membered chelate rings] in **3**, $C^5,O^3$ chelating ligands in **4** (molecule 2) and **5** [5-membered chelate rings], and a $C^5,O^4,O^3$ tridentate ligand in **4** (molecule 1) [both 4- and 5-membered chelate rings]. The conformations about the C4–C5 bonds in **3**–**5** are shown in Table 6. Compounds **4** and **13**, in contrast to **3** and **5**, undergo slow proton-dephenylation reactions in chloroform solutions at ambient temperature. However **3**–**5** decompose on heating at temperatures *ca.* 150 ± 5 °C with the evolution of PhH, $Me_2O$ and $H_2O$. Different modes

**Table 6** Conformation about the C4–C5 bond in **3**–**5** shown in the schematics looking down from C4 to C5




| Compound | Sn–C5–C4–C3 | Sn–C5–C4–O4 | Conformation around the C4–C5 bond |
|---|---|---|---|
| (D)-**3** | 177.0(8) | 57.5(10) | b |
| (L)-**3** | −175.54(16) | −58.89(15) | b′ |
| (D)-**4** | | | |
| Molecule 1 | 65.1(14) | −49.1(12) | a |
| Molecule 2 | 42.6(13) | −71.9(11) | a |
| (L)-**4** | | | |
| Molecule 1 | −66.9(8) | 49.5(8) | a′ |
| Molecule 2 | −40.9(9) | 70.9(7) | a′ |
| (D)-**5** | 46.0(10) | −70.1(7) | a |
| (L)-**5** | −47.9(7) | 69.4(5) | a′ |

of H-bonding are found in **3**, **4** (molecule 2) and **5** compared to that in **4** (molecule 1). The *ν*(OH) bands for solid (D)-**3** [$\nu_{max}$ 3463 $cm^{-1}$] and (D)-**5** [$\nu_{max}$ 3349 $cm^{-1}$], in which there is only a single type of H-bond, have much smaller widths at half-peak heights [*ca.* 175 and 180 $cm^{-1}$, respectively], than that [350 $cm^{-1}$] of the asymmetric peak for (D)-**4** [$\nu_{max}$ 3372 $cm^{-1}$], in which there are two distinct H-bonding modes.

## Experimental

Solution NMR spectra were obtained on a Varian 400 MHz instrument and IR spectra on Philips Analytical PU 9800 FTIR and Nicolet 205 FTIR instruments. TG/MS experiments were carried out on a Mettler Toledo TGA/SDTA 851$^e$ instrument coupled with a Balzers Thermostar mass spectrometer. Solid state NMR spectra were recorded by the EPSRC service, based at the University of Durham, England and the X-ray diffraction data were collected variously on a Nicolet P3 4-circle diffractometer, or a Bruker SMART 1000 area detector diffractometer or by the EPSRC service based at either the University of Wales, Cardiff or the University of Southampton, England.

1,2-*O*-Isopropylidene-α-D-xylofuranose, (D)-**7**, 1,2-*O*-isopropylidene-3,5-di-*O*-*p*-tosyl-α-D-xylofuranose, (D)-**8**, and 1,2-*O*-isopropylidene-5-*O*-*p*-tosyl-α-D-xylofuranose, (D)-**9**, were prepared from (D)-xylose by published procedures.[8] Analogous procedures were used to prepare (L)-**7**–**9** from (L)-xylose. 3-*C*-(Triphenylstannyl)methyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose, (D)-**6**, was a recrystallised sample from an earlier study.[7]

### 1,2-*O*-Isopropylidene-3,5-di-*O*-methylsulfonyl-α-D-xylofuranose, (D)-10

A solution of methanesulfonyl chloride (10 ml) and (D)-**7**[8] (3.0 g, 14 mmol) in anhydrous pyridine (25 ml) was stirred overnight. Water (500 ml) was added and the mixture extracted with $CHCl_3$ (3 × 100 ml). The organic extracts were successively washed with 0.05 M $H_2SO_4$ and water (2 × 100 ml), dried over $CaCl_2$ and rotary evaporated to leave an oily residue, which was crystallised from ethanol, mp 65–67 °C, yield 6.2 g, 93%. Anal. Found. C, 34.6; H, 5.4%. $C_{10}H_{18}O_9S_2$ requires C, 34.7; H, 5.2%. $^1$H and $^{13}$C NMR spectral data in $CDCl_3$ solution are provided in Table 1.

### 5-Deoxy-1,2-*O*-isopropylidene-5-*C*-triphenylstannyl-α-D-xylofuranose, (D)-3

A solution of 1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-D-xylofuranose, (D)-**9**,[8] (3.50 g, 9.6 mmol) in anhydrous THF (20 ml) was slowly added to a stirred solution of triphenylstannyllithium, prepared from lithium (0.62 g, 90 mmol) and triphenyltin chloride (7.50 g 19 mmol), in anhydrous THF (55 ml). The mixture was stirred under nitrogen for 24 h at room temperature and then hydrolysed with buffer solution (100 ml, pH 6.6). The mixture was extracted with EtOH (3 × 100 ml) and the combined extracts were washed with water (2 × 50 ml), dried over anhydrous $CaCl_2$ and evaporated *in vacuo*. The oily residue (4.44 g) was dissolved in $Et_2O$ and the solution filtered to remove insoluble hexaphenylditin. The residue, on evaporating the filtrate, was purified on a Chromatotron using petroleum ether (60–80 °C)–ethyl acetate mixtures as eluents and was crystallised from methanol–chloroform (2 : 1 v/v) as colourless crystals (1.25 g, 47.7%), mp 155–157(dec) °C. Anal. Found. C, 59.6; H, 5.4%. $C_{26}H_{28}O_4Sn$ requires C, 59.7; H, 5.4%. IR (KBr, $cm^{-1}$): 3463, 3063, 2986, 1482, 1429, 1375, 1258, 1211, 1163, 1136, 1096, 1076, 1053, 1030, 992, 932, 885, 783, 733, 698, 635, 503, 448. $^1$H, $^{13}$C and $^{119}$Sn NMR spectral data in $CDCl_3$ solution are provided in Table 1. Solid state $^{13}$C NMR (MAS-CP, 75.4 MHz): *δ*: *ca.* 8 (v br, C-5), 26.8 (Me), 27.2 (Me), 76.5 (C-3), 80.1 (C-4), 88.4 (C-2), 104.3 (C-1), 110.9 (*C*Me$_2$), 128.4 (C-*m*), 130.1 (C-*p*), 137.9 (C-*i*), 138.7 (br,C-*o*), 139.3 (C-*i*), 140.9(C-*i*). Solid state $^{119}$Sn NMR (MAS-CP, 111.8 MHz): *δ*: −92.0.

### 5-Deoxy-1,2-*O*-isopropylidene-5-*C*-triphenylstannyl-α-L-xylofuranose, (L)-3

This was prepared analogously to (D)-**3** from 1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-α-L-xylofuranose, (L)-**9**, (1.50 g, 4.1 mmol) in anhydrous THF (10 ml) and triphenylstannyllithium,

prepared from lithium (0.31 g, 45 mmol) and triphenyltin chloride (5.10 g, 8.2 mmol), in anhydrous THF (10 ml). Yield of pure product was 0.52 g, 25%, mp 157–159(dec) °C. $^{1}$H, $^{13}$C and $^{119}$Sn NMR spectra in $CDCl_3$ solution were identical with those of (D)-**3**. Solid state $^{119}$Sn NMR (MAS-CP, 111.8 MHz): $\delta$: −90.8.

### Reaction of (D)-9 with tributylstannyllithium. Preparation of 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose, (D)-11

The reaction between (D)-**9** (1.03 g, 3 mmol) in anhydrous THF (12 ml) and tributylstannyllithium, prepared from lithium (0.62 g, 90 mmol) and tributyltin chloride (2.93 g, 9 mmol), in anhydrous THF (30 ml), with a similar work-up to that used in the preparation of (D)-**3**, produced 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose, (D)-**11**, (0.51 g) as a viscous oil.

The $^{1}$H NMR spectrum in solution was identical with that previously reported.[9] $^{13}$C NMR (62.9 MHz, $CDCl_3$) $\delta$: 27.0, & 27.7 (2 × Me), 78.2. 78.4, 84.5 & 87.4 (C2 + C3 + C4 + C5), 108.0 (C1), 113.8 ($Me_2C$). The same product was also isolated from the reaction between (D)-**9** and $Me_3SnLi$.

### 5-Deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-5-*C*-triphenylstannyl-α-D-xylofuranose, (D)-12

The reaction between 1,2-*O*-isopropylidene-3,5-di-*O*-methylsulfonyl-α-D-xylofuranose, (D)-**10**, (2.50 g, 7.2 mmol) in anhydrous THF (20 ml) and triphenylstannyllithium, prepared from lithium (0.62 g, 90 mmol) and triphenyltin chloride (1.0 g, 28 mmol), in anhydrous THF (30 ml), with a similar work-up to that used in the preparation of (D)-**3**, produced a mixture (0.50 g) of (D)-**3** and 5-deoxy-1,2-*O*-isopropylidene-3-*O*-methylsulfonyl-5-*C*-triphenylstannyl-α-D-xylofuranose, (D)-**12**, in a 5 : 3 molar ratio as indicated by the $^{1}$H NMR spectrum. The product mixture was treated with methylsulfonyl chloride (1 ml) in anhydrous pyridine (2 ml) and stirred for 24 h, water was added (2 ml) and the mixture extracted with $CHCl_3$ (2 × 20 ml). The $CHCl_3$ extracts were successively washed with 0.05 M $H_2SO_4$ (3 × 10 ml) and water (2 × 10 ml), dried over $CaCl_2$, and rotary evaporated. Compound, (D)-**12**, was isolated from the syrupy residue by TLC, with petroleum ether (60–80 °C)–diethyl ether (1 : 1 v/v) as eluent, yield 1.19 g. $^{1}$H, $^{13}$C and $^{119}$Sn NMR spectral data in $CDCl_3$ solution are provided in Table 1.

### Reactions of (D)-3 or (L)-3 with halogens

To a solution of (D)-**3** or (L)-**3** (0.2 mmol) in $CHCl_3$ (6 ml), was added the appropriate molarity (1 or 2 mole equivalents) of the halogen. The solutions were maintained at 0 °C. After decolourisation, all volatiles were removed under reduced pressure to leave colourless syrups, which were crystallised from suitable solvents.

The $^{1}$H, $^{13}$C and $^{119}$Sn NMR spectral data for the halo derivatives, (D)-**4**, (D)-**5** and (D)-**13** in $CDCl_3$ solutions are given in Table 1. The NMR spectra of the (L)-isomers were essentially identical.

**5-Deoxy-5-*C*-iododiphenylstannyl-1,2-*O*-isopropylidene-α-D-xylofuranose (D)-4.** (D)-**4**, recrystallised from petroleum ether (60–80) °C–$CHCl_3$ as colourless needles, mp 154–156 °C (dec). Anal. Found. C, 41.9; H, 3.9%. $C_{20}H_{23}IO_4Sn$ requires C, 41.8; H, 4.0%. IR (KBr, $cm^{-1}$): 3372(br), 3065, 2986, 1479, 1429, 1381, 1373, 1321, 1259, 1217, 1159, 1073, 1015, 995, 926, 855, 791, 729, 696, 654. Solid state $^{13}$C NMR (MAS-CP, 75.4 MHz): $\delta$ *ca*. 22.4 (v br, C-5), 27.2, 27.9 & 29.2 (Me), 74.8 & 75.8 (C-3), 78.8 (C-4), 84.8 & 86.0 (C-2), 103.6 & 105.4 (C-1), 113.4 & 114.6 ($CMe_2$), 128.9, 130.2 & 136.4 (protonated phenyl-C), 135.8, 138.3 & 142.9 (C-*i*).Solid state $^{119}$Sn NMR (MAS-CP, 111.8 MHz): $\delta$ −67.7 and −145.6.

**5-Deoxy-5-*C*-diiodophenylstannyl-1,2-*O*-isopropylidene-α-D-xylofuranose·0.5CHCl$_3$ [(D)-5·0.5CHCl$_3$].** [(D)-**5**·0.5$CHCl_3$], recrystallised from $CHCl_3$ as colourless needles, mp 156–158 °C (dec). Anal. Found. C, 25.5; H, 2.6%. $C_{14}H_{18}I_2O_4Sn$ + ½ $CHCl_3$ requires C, 25.6; H, 2.9%. IR (KBr, $cm^{-1}$): 3349 (br), 2989, 2937, 2885, 1430, 1375, 1310, 1269, 1216, 1160, 1074, 997, 930, 857, 791, 726, 689, 648.

**5-Deoxy-5-*C*-iododiphenylstannyl-1,2-*O*-isopropylidene-α-L-xylofuranose (L)-4.** (L)-**4**, recrystallised from petroleum ether (60–80) °C–$CHCl_3$ as colourless needles, mp 154–156 °C (dec). Anal. Found. C, 41.6; H, 3.9%. $C_{20}H_{23}IO_4Sn$ requires C, 41.8; H, 4.0%. Identical IR spectrum to that of (D)-**4**.

**5-Deoxy-5-*C*-diiodophenylstannyl-1,2-*O*-isopropylidene-α-L-xylofuranose·0.5CHCl$_3$ [(L)-5·0.5CHCl$_3$].** [(L)-**5**·0.5$CHCl_3$], recrystallised from $CHCl_3$ as colourless needles, mp 156–158 °C (dec). Anal. Found. C, 25.5; H, 2.7%. $C_{14}H_{18}I_2O_4Sn$ + ½ $CHCl_3$ requires C, 25.6; H, 2.9%. Identical IR spectrum to that of [(L)-**5**: 0.5$CHCl_3$].

5-*C*-Bromodiphenylstannyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranoside, (D)-**13**, was obtained from the 1 : 1 reaction between (D)-**3** and $Br_2$ as an oil in *ca*. 97% purity after washing the reaction residue with cold petroleum ether to remove the more soluble $Ph_3SnBr$ and other by-products.

No characterised product was obtained from the (D)-**3**–bromine (1 : 2) reaction.

### Thermal analysis

TG/MS experiments were carried out with 10–15 mg samples and heating rates of 5 °C per minute.

### Crystal structure determinations†

**Data collection.** Unit cell and intensity data for (D)-**5** were obtained at 108 K on the Delft Instruments FAST diffractometer of the EPSRC's crystallography service, then based at University of Wales, Cardiff. The unit cell was determined and the intensity collected using the routines ENDEX, REFINE and MADONL of the MADNES software[10] and data reduction carried out using ABSMAD.[11] Full procedural details are available elsewhere.[12] DIFABS[13] was used to apply correction for absorption. Data for (L)-**5** at 301 K were obtained by means of a Bruker SMART 1000 CCD area detector diffractometer using programs SMART, SAINT and SADABS for data collection, data reduction and cell refinement and multi-scan (semi-empirical from equivalent reflections) absorption correction respectively.[14] For (L)-**4**, data was obtained at 150 K by means of the Enraf Nonius KappaCCD area detector diffractometer of the EPSRC's crystallography service, based at the University of Southampton. The entire process of data collection, cell refinement and data reduction was then accomplished by means of DENZO[15] and COLLECT.[16] Correction for absorption by a procedure very like that used by SADABS was by means of SORTAV.[17]

Unit cell and intensity data for (D)-**3** and (D)-**4** were obtained at 298 K by means of a Nicolet P3 4-circle diffractometer. Cell refinement and data collection were by means of Nicolet P3 software[18] and data reduction by means of the local program RDNIC.[19] Correction for absorption was not applied in these cases.

In the case of (D)-**5** and (L)-**5**, interchange of cell edges *a* and *c* as initially determined and re-indexing of the intensity data by means of the row-wise transformation matrix 0 0 −1; 0 1 0; 1 0 0 was applied for conformity with the standard setting of

† CCDC reference number(s) 185948–185953. See http://www.rsc.org/suppdata/p1/b2/b204675j/ for crystallographic files in .cif or other electronic format.

**Table 7** Crystal data and structure refinement[a]

| | (D)-**3** | (D)-**4** | (L)-**4** | (D)-**5** | (L)-**5** | (D)-**6** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{26}H_{28}O_4Sn$ | $C_{20}H_{23}IO_4Sn$ | $C_{20}H_{23}IO_4Sn$ | $C_{14.50}H_{18.50}Cl_{1.50}I_2O_4Sn$ | $C_{14.50}H_{18.50}Cl_{1.50}I_2O_4Sn$ | $C_{31}H_{36}O_6Sn$ |
| Formula weight | 523.17 | 572.97 | 572.97 | 682.46 | 682.46 | 623.29 |
| $T$ /K | 298(2) | 298(2) | 150(2) | 108(2) | 301(2) | 298(2) |
| Crystal system | Monoclinic | Triclinic | Triclinic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | $P2_1$ | $P\bar{1}$ | $P\bar{1}$ | $P2_12_12$ | $P2_12_12$ | $P2_12_12_1$ |
| Cell dimension $a$ (Å) | 12.820(10) | 9.566(14) | 9.4450(3) | 23.904(9) | 24.2808(15) | 6.070(4) |
| $b$ (Å) | 6.658(6) | 10.366(10) | 10.2372(3) | 10.824(4) | 10.8472(7) | 13.074(12) |
| $c$ (Å) | 14.427(12) | 12.983(19) | 12.8723(6) | 7.954(6) | 8.0682(5) | 37.69(3) |
| $\alpha$ (°) | 90 | 104.99(9) | 105.1242(12) | 90 | 90 | 90 |
| $\beta$ (°) | 97.78(6) | 111.71(11) | 111.3979(12) | 90 | 90 | 90 |
| $\gamma$ (°) | 90 | 65.14(9) | 65.334(3). | 90 | 90 | 90 |
| Volume (Å$^3$) | 1220.1(18) | 1077(2) | 1044.38(7) | 2058.0(19) | 2125.0(2) | 2991(4) |
| $Z$ | 2 | 2 | 2 | 4 | 4 | 4 |
| Calculated density /Mg m$^{-3}$) | 1.424 | 1.767 | 1.822 | 2.203 | 2.133 | 1.384 |
| Absorption coefficient/mm$^{-1}$ | 1.075 | 2.639 | 2.722 | 4.450 | 4.310 | 0.894 |
| $F$(000) | 532 | 556 | 556 | 1276 | 1276 | 1280 |
| Crystal size /mm | 0.46 × 0.24 × 0.18 | 0.60 × 0.30 × 0.22 | 0.10 × 0.06 × 0.03 | 0.30 × 0.20 × 0.20 | 0.50 × 0.39 × 0.36 | 0.50 × 0.16 × 0.08 |
| Theta range for data collection (°) | 2.00 to 25.05 | 1.70 to 25.05 | 2.96 to 30.82 | 2.07 to 25.08 | 1.68 to24.01 | 1.08 to 25.00 |
| Index range | 0<= $h$ <= 15, −7<= $k$ <= 7, −17<= $l$ <= 17 | 0<= $h$ <= 11, −10<= $k$ <= 12, −15<= $l$ <= 14 | −12<= $h$ <= 12, −13<= $k$ <= 14, −17<= $l$ <= 17 | −27<= $h$ <= 26, −11<= $k$ <= 12, −9<= $l$ <= 7 | −26<= $h$ <= 27, −8<= $k$ <= 12, −9<= $l$ <= 9 | 0<= $h$ <= 7, 0<= $k$ <= 15, 0<= $l$ <= 44 |
| Reflections collected/unique | 4310/4215 [R(int) = 0.1248] | 3825/3823 [R(int) = 0.0079] | 15230/9477 [R(int)=0.0480] | 8938/3226 [R(int) = 0.1013] | 11487/3361 [R(int) = 0.0222] | 3077/3063 [R(int)= 0.0213] |
| Completeness to 2theta | 25.05 99.9% | 25.05 100% | 30.82 81.8% | 25.08 91.2% | 24.01 100% | 25.00 100.0% |
| Absorption correction | None | None | Semi-empirical from equivalents | Empirical (DIFABS) | Semi empirical from equivalents | None |
| Max/min. transmission | — | — | 0.960/ 0.935 | 0.4698/ 0.3487 | 0.928/0.624 | — |
| Data/restraints/parameters | 4215/1/283 | 3823/3/ 473 | 9477/3/473 | 3226/0/223 | 3361/0/228 | 3063/0/348 |
| Goodness-of-fit on $F^2$ | 1.056 | 1.059 | 1.010 | 1.056 | 1.127 | 0.984 |
| Final $R$ indices [$I$>2sigma($I$)] | $R1$ = 0.0679, $wR2$ = 0.1513 | $R1$ = 0.0459, $wR2$ = 0.1127 | $R1$ = 0.0468, $wR2$ = 0.1003 | $R1$ = 0.0395, $wR2$ = 0.0968 | $R1$ = 0.0237, $wR2$ = 0.0565 | $R1$ = 0.0560, $wR2$ = 0.0940 |
| $R$ indices (all data) | $R1$ = 0.0889, $wR2$ = 0.1659 | $R1$ = 0.0517, $wR2$ = 0.1173 | $R1$ = 0.0834, $wR2$ = 0.1163 | $R1$ = 0.0418, $wR2$ = 0.0977 | $R1$ = 0.0251, $wR2$ = 0.0570 | $R1$ = 0.1312, $wR2$ = 0.1116 |
| Absolute structure parameter | −0.06(6) | 0.01(4) | −0.04(3) | −0.01(5) | 0.03(3) | −0.05(7) |
| Largest diff. peak/hole eA$^{-3}$ | 2.099/−1.613 | 1.608/−1.565 | 0.859/−1.315 | 2.444/−1.093 | 0.311/−0.692 | 0.481/−0.786 |

[a] Wavelength: 0.71073 Å; all crystals were colourless; refinement: Full matrix least squares on $F^2$.

the space group $P2_12_12$ (no. 18). Likewise *a* and *b* of the initially determined cell of (L)-**4** were reversed in direction in order to render the originally acute cell angles $\alpha$ and $\beta$ obtuse for conformity with the cell adopted previously for (D)-**4** and the intensity data correspondingly re-indexed with the transformation matrix −1 0 0; 0 −1 0; 0 0 1.

**Structure solution and refinement.** For (D)-**3**, (D)-**4** and (D)-**5**, initial partial solutions obtained by the heavy atom method as implemented in SHELXS-86[20] were completed by iterated SHELXL-97[21] difference map and peak search calculations to yield positions for all non-H atoms. Starting parameters for the refinement of (L)-**5** and (L)-**4** were simply the coordinates obtained for the corresponding D structures suitably inverted. The re-refinement of the known structure of (D)-**6** (CSD ref. codes SUKNUH[7a] and SUKNUH01[7b]) simply employed coordinate data for SUKNUH01 extracted, *via* the Chemical Database Service of the EPSRC at Daresbury,[22] from the Cambridge Structural Database[23] as starting parameters. Refinement in all cases was by means of SHELXL-97 with refinement of anisotropic displacement parameters for all non-H atoms excepting only C of the molecule of chloroform solvent of (D)-**5** and, in the final stages, H atoms introduced in calculated positions and refined with a riding model. Further details of data collection and structure refinement are given in Table 7. In particular values of the Flack[24] x parameter close (within 3 × esd) to zero are evident confirming the correctness of all of the structures in an absolute sense. This is supported in the case of (L)-**4**, (D)-**5** and (L)-**5** by the presence of 1296, 1407 and 4113 Friedel pairs, respectively and by much higher (non-zero) values of the Flack x parameter for the 'wrong' inverted forms of all six structures whose refinement is reported here and finally confirmed as entirely consistent with the known stereochemistry of the constituent sugars by the results obtained with the PLATON[25] geometry program.

## Acknowledgements

The authors thank the Carnegie Trust (Scotland) (LAB), JNICT (Portugal) (HR), FAPERJ (Brazil) (VFF), and CPNq (Brazil) (JLW and SMSVW) for support. Also thanked are the EPSRC X-ray Crystallography Service, formerly based at the University of Wales, Cardiff and currently at the University of Southampton, the EPSRC Solid State NMR service, based at the University of Durham, and the Chemical Database Service at Daresbury.

## References

1 C. H. Rochester, in *The Chemistry of the Hydroxyl Group*. ed. S. Patai, Wiley, Chichester, 1971, p. 369.
2 (*a*) H. Pan, R. Willem, J. Meunier-Piret and M. Gielen, *Organometallics*, 1990, **9**, 349; (*b*) R. Willem, A. Delmotte, I. deBolger, M. Biesemans, M. Gielen, F. Kayser and E. R. T. Tiekink, *J. Organomet. Chem.*, 1994, **480**, 255; (*c*) F. Z. Fu, H. Y. Li, D. S. Zhu, Q. X. Fang, H. A. Pan, E. R. T. Tiekink, F. Kayser, M. Biesemans, I. Verbruggen, R. Willem and M. Gielen, *J. Organomet. Chem.*, 1995, **496**, 163; (*d*) F. Kayser, M. Biesemans, A. Delmotte, I. Verbruggen, I. DeBorger, M. Gielen, R. Willem and E. R. Tiekink, *Organometallics*, 1994, **13**, 4026; (*e*) F. Kayser, M. Biesemans, H. Pan, M. Gielen and R. Willem, *Magn. Reson. Chem.*, 1992, **30**, 877; (*f*) F. Kayser, M. Biesemans, H. Pan, M. Gielen and R. Willem, *J. Chem. Soc., Perkin Trans. 2*, 1994, 297; (*g*) F. Kayser, M. Biesemans, A. Delmotte, R. Hendrix, P. Malschaert, I. Verbruggen, I. Mahieu, R. Willem and M. Gielen, *Bull. Chim. Soc. Belg.*, 1994, **103**, 273; (*h*) F. Kayser, M. Biesemans, A. Delmotte, R. Willem and M. Gielen, *Bull. Chim. Soc. Belg.*, 1995, **104**, 27; (*i*) F. Kayser, M. Biesemans, F. X. Fu, H. A. Pan, M. Gielen and R. Willem, *J. Organomet. Chem.*, 1995, **486**, 263; (*j*) M. Biesemans, R. Willem, S. Damoun, P. Geerlings, E. R. T. Tiekink, M. Lahcini and B. Jousseaume, *Organometallics*, 1998, **17**, 90; (*k*) H. C. Dai, Q. H. Ying, X. H. Wang, S. M. Yue, H. D. Pan and X. Chen., *Polyhedron*, 1998, **12**, 2503; (*l*) P. J. Cox, S. M. S. V. Doidge-Harrison, R. A. Howie, I. W. Nowell, O. J. Taylor and J. L. Wardell, *J. Chem. Soc., Perkin Trans. 1*, 1989, 2017; (*m*) C. C. C. Chibesakunda, P. J. Cox, H. Rufino and J. L. Wardell, *Acta Crystallogr., Sect. C Cryst. Struct. Commun.*, 1998, **54**, 893.
3 B. R. Laliberte, W. Davidson and M. C. Henry, *J. Organomet. Chem.*, 1966, **5**, 526.
4 A. R Forrester, S. J. Garden, R. A. Howie and J. L. Wardell, *J. Chem. Soc., Dalton Trans.*, 1992, 2615.
5 (*a*) P. Jaumier, B. Jousseaume, M. Lahcini, F. Ribot and C. Sancher, *Chem Commun.*, 1998, 369; (*b*) see also V. S. Zavgorodnii, B. I. Ionin and A. A. Petrov, *J. Gen. Chem., USSR*, 1967, **37**, 898.
6 H. Rufino, J. L. Wardell, J. N. Low, R. Falconer and G. Ferguson, *Acta Crystallogr., Sect. C, Cryst. Struct. Commun*, 1998, **54**, 1792.
7 (*a*) F. Caruso, M. Bol-Schoenmakers and A. H. Penninks, *J. Med. Chem.*, 1993, **36**, 1168; (*b*) S. M. S. V. Doidge-Harrison, L. A. Burnett, S. J. Garden, R. A. Howie, O. J. Taylor and J. L. Wardell, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1621.
8 P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, 1933, **102**, 317.
9 H. Paulsen and M. Budzis, *Chem. Ber.*, 1974, **107**, 1998.
10 J. W. Pflugrath and A. Messerschmidt, MADNES, Version 11, Delft Instruments, Delft, The Netherlands, September, 1989.
11 A. I. Karaulov, ABSMAD, Program for FAST Data Processing. University of Wales, Cardiff, Wales, 1992.
12 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.
13 N. Walker and D. Stuart, *Acta Crystallogr., Sect A: Found. Crystallogr.*, 1983, **39**, 158.
14 Bruker, SADABS, SMART and SAINT, Bruker AXS Inc., Madison, Wisconsin, USA, 1999.
15 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.
16 R. Hooft, COLLECT, Nonius BV, Delft, The Netherlands, 1998.
17 (*a*) R. H. Blessing, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1995, **51**, 33; (*b*) R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421.
18 Nicolet, Nicolet P3/R3 Data Collection Operator's Manual, Nicolet XRD Corporation, 10061 Bubb Road, Cupertino, CA 95014, U.S.A, 1980.
19 R. A. Howie, RDNIC, Data Reduction Program for the Nicolet P3 Diffractometer. University of Aberdeen, Scotland, 1980.
20 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467.
21 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement. University of Göttingen, Germany, 1997.
22 D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746.
23 F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 1–31.
24 H. D. Flack, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1983, **39**, 876.
25 A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 34.
26 R. L. Whistler, T. J. Luttenegger and R. M. Powell, *J. Org. Chem.*, 1968, **33**, 396.
27 (*a*) J.-R. Pougny, *Tetrahedron Lett.*, 1984, **25**, 2363; (*b*) J.-R. Pougny and P. Sinay, *Tetrahedron Lett.*, 1978, 3301.
28 R. A. Howie and J. L. Wardell, *Main Group Met. Chem.*, 1994, **17**, 571.
29 S. M. S. V. Doidge-Harrison, R. A. Howie, J. N. Low and J. L. Wardell, *J. Chem. Crystallogr.*, 1997, **27**, 291.
30 H. J. Buchanan, P. J. Cox and J. L. Wardell, *Main Group Met. Chem.*, 1998, **21**, 751.
31 J.-R. Neeser, J. M. J. Tronchet and E. J. Charollais, *Can. J. Chem.*, 1983, **61**, 1387.
32 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.
33 S. Cros, C. Herve de Penhoat, S. Perez and A. Imberty, *Carbohydr. Res.*, 1993, **248**, 81.
34 P. J. Cox, R. A. Howie, H. Rufino and J. L. Wardell, *Acta Crystallogr., Sect. C Cryst. Struct. Commun.*, 1997, **53**, 1939.
35 L. A. Burnett, P. J. Cox and J. L. Wardell, *J. Chem. Crystallogr.*, 1996, **26**, 591.
36 A. Bondi, *J. Chem. Phys.*, 1964, **68**, 441.
37 J. T. B. H. Jastrzebski, P. A. van der Schaaf, J. Boersma, G. van Koten, D. J. A. de Ridder and D. Heijdenrijk, *Organometallics*, 1992, **11**, 1521.