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## 5-Deoxy-1,2-*O*-isopropylidene-5-*C*-triphenylstannyl- $\alpha$ -L-xylofuranose

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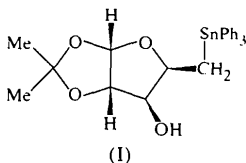
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### Abstract

In the title compound, [Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(C<sub>8</sub>H<sub>13</sub>O<sub>4</sub>)], the L-furanose ring adopts a C4-*endo*-envelope pucker, with C4 displaced 0.544 (3) Å from the mean plane of the remaining four atoms. The isopropylidene ring adopts a C6-envelope conformation, with C6 displaced -0.439 (3) Å from the mean plane of the remaining four atoms. The Ph<sub>3</sub>Sn group has an irregular propeller conformation and the Sn atom has slightly distorted tetrahedral geometry, with Sn—C distances in the range 2.131 (2)–2.150 (2) Å and C—Sn—C angles in the range 106.55 (8)–114.27 (8)°.

### Comment

As part of a study on organotin compounds containing chiral ligands (*e.g.* Buchanan *et al.*, 1997; Cox *et al.*, 1996), we have obtained both 5-deoxy-1,2-*O*-isopropylidene-5-*C*-triphenylstannyl- $\alpha$ -L-xylofuranose, (I), and 5-deoxy-1,2-*O*-isopropylidene-5-*C*-triphenylstannyl- $\alpha$ -D-xylofuranose. We are currently employing these compounds in the syntheses of enantiomeric organostannanes with chirality at the Sn centres, and as precursors of hydroxy- and halo(5-xylofuranosyl)stannanes for biological assays. Carbohydrate moieties, in general, form useful chiral ligands with the potential to act as chelating groups. Hydrogen bonding involving free hydroxyl groups can also have significant effects on the reactivities and structures of compounds. We report here on the structure and conformation of the  $\alpha$ -L-isomer.



A view of the molecule with the atomic numbering scheme is shown in Fig. 1. The analysis established the absolute structure of the compound unequivocally and shows that the xylofuranose is indeed the L-isomer. Molecular dimensions are unexceptional.

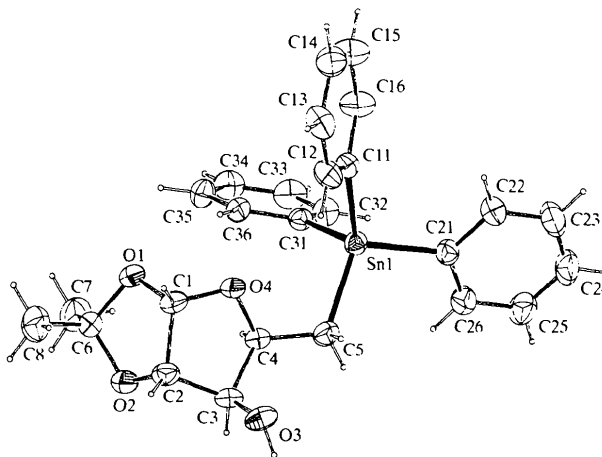


Fig. 1. A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The L-furanose ring adopts a C4-*endo*-envelope pucker, with C4 displaced 0.544 (3) Å from the mean plane of the remaining four atoms. The relevant Cremer and Pople puckering parameters (Cremer & Pople, 1975) are  $Q_2$  0.353 (2) Å and  $\Phi_2$  137.1 (4)°. The isopropylidene ring adopts a C6-envelope conformation, with C6 displaced -0.439 (3) Å from the mean plane of the remaining four atoms; puckering parameters are  $Q_2$  0.285 (2) Å and  $\Phi_2$  136.6 (5)°. While a search of the April 1998 release of the Cambridge Structural Database (Allen & Kennard, 1993) revealed that no other  $\alpha$ -L-xylofuranose systems have been reported, several  $\alpha$ -D-xylofuranose structures are known. The structure closest to the title compound is that of 1,2-*O*-isopropylidene-5-*O*-triphenylmethyl-3-*O*-[(triphenylstannyl)methyl]- $\alpha$ -D-xylofuranose (Burnett *et al.*, 1996); here the D-xylofuranose ring adopts a C3-envelope conformation [puckering parameters  $Q_2$  0.363 (5) and  $\Phi_2$  291.2 (8)°] and the isopropylidene ring has a C2-envelope conformation [ $Q_2$  0.251 (5) Å and  $\Phi_2$  247.8 (11)°]. [There was an error in the puckering parameter values quoted in the Burnett *et al.* (1996) publication; the correct values are reported here.]

The Ph<sub>3</sub>Sn group in the title compound has an irregular propeller conformation and the Sn atom has slightly distorted tetrahedral geometry, with Sn—C bond lengths in the range 2.131 (2)–2.150 (2) Å and C—Sn—C bond angles in the range 106.55 (8)–114.27 (8)°.

The molecules are linked into infinite chains along the *b* direction by intermolecular O—H...O hydrogen bonds [O...O 2.846 (3) Å]; there is also a possible C—H...O hydrogen bond involving C1—H and

the hydroxy O3 atom of an adjacent molecule (details in Table 2). Examination of the structure with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattice.

## Experimental

1,2-*O*-Isopropylidene-5-*O*-*p*-tosyl- $\alpha$ -L-xylofuranose was obtained from L-xylose on successive reactions with (i) Me<sub>2</sub>CO and anhydrous copper(II) sulfate in the presence of concentrated sulfuric acid, (ii) aqueous hydrochloric acid and (iii) *p*-toluenesulfonyl chloride in anhydrous pyridine. A solution of 1,2-*O*-isopropylidene-5-*O*-*p*-tosyl- $\alpha$ -L-xylofuranose (1.5 g, 4.1 mmol) in anhydrous tetrahydrofuran (THF; 10 ml) was added to a stirred solution of triphenylstannyl lithium prepared from triphenyltin chloride (5.1 g, 8.2 mmol) and lithium (0.6 g) in anhydrous THF (10 ml) under a nitrogen atmosphere. The mixture was stirred at 293 K for 48 h under a nitrogen atmosphere, hydrolysed with saturated ammonium chloride solution (75 ml) and extracted with diethyl ether (2 × 75 ml). The combined ether extracts were dried over calcium chloride and rotary evaporated. The resulting syrup was repeatedly dissolved in ether (20 ml portions) and the insoluble hexaphenylditin was removed by filtration after each extraction. The product was purified on a chromatotron using petroleum ether (333–353 K)/ethyl acetate as the eluent (initially 9:1 and subsequently 1:1 *v/v*). The product was crystallized from EtOH/CHCl<sub>3</sub> (2:1 *v/v*) as a white crystalline solid (yield 0.52 g, 25%; m.p. 431–433 K). Full details of the IR and NMR spectra are with the archived CIF. The <sup>119</sup>Sn NMR (CDCl<sub>3</sub>, 93.2 MHz)  $\delta$  value of -107.2 p.p.m. is in the region expected for a four-coordinate Sn species of the type (alkyl)Ph<sub>3</sub>Sn (Howie & Wardell, 1994). The  $\delta^{119}$ Sn value of the D-isomer, obtained by an analogous route, is, as expected, essentially the same (-107.4 p.p.m.).

### Crystal data

[Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(C<sub>8</sub>H<sub>13</sub>O<sub>4</sub>)]  
*M<sub>r</sub>* = 523.17  
 Monoclinic  
*P*2<sub>1</sub>  
*a* = 12.8086 (9) Å  
*b* = 6.6542 (4) Å  
*c* = 14.4143 (10) Å  
 $\beta$  = 97.679 (9)°  
*V* = 1217.53 (14) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.427 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  
 Gaussian (*ABSO* in  
*NRCVAX*; Gabe *et al.*,  
 1989)  
*T<sub>min</sub>* = 0.679, *T<sub>max</sub>* = 0.906  
 5788 measured reflections  
 5568 independent reflections

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25  
 reflections  
 $\theta$  = 9.47–19.76°  
 $\mu$  = 1.077 mm<sup>-1</sup>  
*T* = 294 (1) K  
 Lath  
 0.42 × 0.32 × 0.10 mm  
 Colourless

5052 reflections with  
 $I > 2\sigma(I)$   
*R<sub>int</sub>* = 0.009  
 $\theta_{\max}$  = 27.41°  
 $h$  = -16 → 16  
 $k$  = -8 → 8  
 $l$  = -18 → 18  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 5.3%

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.017$   
 $wR(F^2) = 0.040$   
*S* = 1.025  
 5568 reflections  
 282 parameters  
 H-atom parameters  
 constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0253P)^2$   
 $+ 0.0346P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.206 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.189 \text{ e } \text{\AA}^{-3}$   
 Extinction correction:  
*SHELXL97*  
 Extinction coefficient:  
 0.0030 (3)  
 Scattering factors from  
*International Tables for*  
*Crystallography* (Vol. C)  
 Absolute structure: Flack  
 (1983), 2541 Friedel pairs  
 Flack parameter =  
 -0.033 (12)

Table 1. Selected geometric parameters (Å, °)

Sn1—C5	2.150 (2)	Sn1—C21	2.138 (2)
Sn1—C11	2.131 (2)	Sn1—C31	2.144 (2)
C11—Sn1—C21	111.05 (8)	C5—Sn1—C11	114.27 (8)
C11—Sn1—C31	107.06 (8)	C5—Sn1—C21	109.12 (8)
C21—Sn1—C31	106.55 (8)	C5—Sn1—C31	108.46 (8)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3A...O1 <sup>i</sup>	0.82	2.05	2.846 (3)	164
C1—H1...O3 <sup>ii</sup>	0.98	2.33	3.284 (3)	165

Symmetry codes: (i)  $x, y - 1, z$ ; (ii)  $1 - x, \frac{1}{2} + y, 1 - z$ .

Compound (I) crystallized in the monoclinic system. Space groups *P*2<sub>1</sub> and *P*2<sub>1</sub>/*m* were both suggested by the systematic absences; *P*2<sub>1</sub> was adopted because the compound was known to be chiral. H atoms were treated as riding atoms (C—H 0.93–0.98 and O—H 0.82 Å).

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET4* and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX96* via Patterson heavy-atom method. Program(s) used to refine structure: *NRCVAX96* and *SHELXL97* (Sheldrick, 1997). Molecular graphics: *NRCVAX96*, *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *PRCIF97* (Ferguson, 1997).

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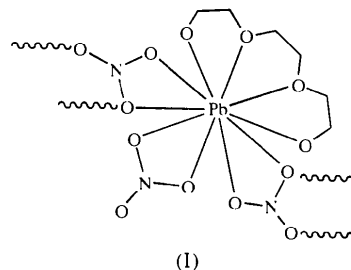
Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1213). Services for accessing these data are described at the back of the journal.

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gel processing of ceramic films containing Pb, *e.g.* PZT [Pb(Zr,Ti)O<sub>3</sub>], PLZT [(Pb,Lu)(Zr,Ti)O<sub>3</sub>], PT (PbTiO<sub>3</sub>) and PMN [Pb(Mg<sub>0.33</sub>Nb<sub>0.67</sub>O<sub>3</sub>)] (Sayer & Sreenivas, 1990; Schwartz, 1997).



These Pb-based perovskites, and their solid solutions with other oxides, are of great importance in a number of ferroelectric devices. The increased need for fine-tuned and well defined complex ceramics of a small size for electronics applications gives impetus for research into solution-based routes. Metal–organic complexes dissolved in organic solvents are thus of general use in various sol–gel processes and, when used for film preparation, the solution is usually deposited by the spin-coating technique, *i.e.* the precursor solution is added to a spinning substrate. The gel film thereby obtained is subsequently heat treated to produce the final ceramic film.

The object of using the present Pb(NO<sub>3</sub>)<sub>2</sub>(EO3) complex, where EO3 is triethylene glycol, was to obtain a precursor that is sufficiently soluble and stable during storage, as well as having a low organic content at higher temperatures. The weakly coordinating EO3 molecule was used to make insoluble Pb(NO<sub>3</sub>)<sub>2</sub> soluble in solvents which are suitable for the other precursors, *i.e.* Ti(O<sup>i</sup>Pr)<sub>4</sub> and Zr(O<sup>i</sup>Pr)<sub>4</sub>. Low organic content at the firing temperatures, where the gel is converted to oxide, should impede reduction of PbO to Pb, thus preventing damage to the Pt substrate which would hinder a good contact between the substrate and the PZT film. In a recent study, it was shown that the Pb(NO<sub>3</sub>)<sub>2</sub>(EO3) precursor could be used for the preparation of PZT films and powders at 823–973 K (Lashgari & Westin, 1998). The Bi analogue, dimeric [Bi(NO<sub>3</sub>)<sub>2</sub>(EO3)]<sub>2</sub> (Rogers *et al.*, 1992), has also been used as a precursor in the preparation of ZnO-based varistors, with good results (Ekstrand *et al.*, 1997).

In the solid state, the title compound shows some similarities with its congeners having longer polyglycol ligands. In particular, the compound Pb(NO<sub>3</sub>)<sub>2</sub>(EO4) (EO4 = tetraethyleneglycol; Rogers *et al.*, 1996) has structural features in common with Pb(NO<sub>3</sub>)<sub>2</sub>(EO3). Both compounds are polymeric and both have polyethylene and nitrate groups coordinated to Pb<sup>2+</sup>. The main difference between the two Pb coordination spheres is that the dissimilarity in chelating ability of the two

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## Pb(NO<sub>3</sub>)<sub>2</sub>(EO3), where EO3 is Triethylene Glycol

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### Abstract

A new polyglycol complex, *catena*-poly[[ (3, 6-dioxaoctane-1, 8-diol-κ<sup>4</sup>O)(nitrate-κ<sup>2</sup>O, O')lead(II)]-μ-(nitrate-O, O':O', O'')], [Pb(NO<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>14</sub>O<sub>4</sub>)]<sub>n</sub>, has been synthesized and structurally characterized by single-crystal X-ray diffraction and IR spectroscopy. The Pb atom is coordinated by ten O atoms from the polyglycol and nitrate groups. The compound is polymeric along the *a* axis, through bridging nitrate groups.

### Comment

New routes for synthesizing ferroelectric ceramics are of considerable interest and, of these methods, sol–gel processing using metal–organic precursors is one of the most potent and versatile (Chandler *et al.*, 1993; Schwartz, 1997). The title compound, (I), was prepared for use as a new type of precursor in sol–