ELSEVIER

Journal of Organometallic Chemistry 489 (1995) 161–164

Journal of Organometallic Chemistry

X-ray and NMR study of the structure of the organotin carbohydrate: 6-Deoxy-1,2-*O*-isopropylidene-6-(triphenylstannyl)-α-D-glucofuranose

Philip J. Cox [a,*], R. Alan Howie [b], Olga A. Melvin [a], James L. Wardell [b]

[a] *School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen, AB9 1FR, UK*
[b] *Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, UK*

Received 27 June 1994

Abstract

The crystal and molecular structure of the title compound has been determined by X-ray crystallography, ^1H NMR and ^{13}C NMR spectroscopy. In the crystals of the chiral carbohydrate the hydroxyl groups are held together by intramolecular H bonding, and there is an intermolecular link between one hydroxyl hydrogen atom and an oxygen of the isopropylidene ring. The tin atom is in a tetrahedral environment and the shortest Sn...O separation is 3.354(5) Å, an interaction that appears to have no effect on the stereochemistry of the metal. The ^1H NMR spectrum shows long-range splitting of a methylene proton by a hydroxyl hydrogen.

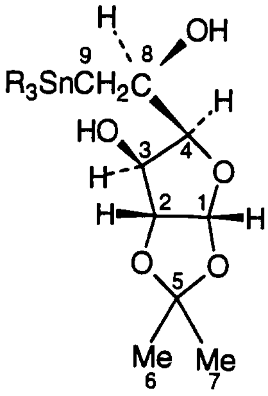
Keywords: X-ray diffraction; Molecular structure; Organotin; Carbohydrate; Tin; Crystal structure

1. Introduction

Carbohydrates provide an interesting array of functionally substituted ligands for use in metal and organometallic complexes. The availability of carbohydrate compounds having oxygen groups with fixed orientations allows for systematic study of the effects of their spatial arrangements on reactions and reactivities at the metal centres. Such facets as nucleophilic assistance (i.e. neighbouring group participation) and elimination reactions (β-, etc.) at the metal centres can thus be readily studied [1]. Additional features such as chirality, enhanced water solubility, biological activities and use in organic synthesis offer further stimulus for the study of these metallated saccharide species.

We have been carrying out a study of the preparations, reactivities, and structures of carbon–tin bonded carbohydrates [2–4]. Among the findings we have reported are the ready β-elimination reactions undergone by 6-deoxy-1,2-*O*-isopropylidene-6-(trimethylstannyl)-α-D-glucofuranose (**I**, R = Me) and the enhanced reactivity of phenyl–tin bonds in the phenyl analogue (**I**, R = Ph) in cleavage reactions with I_2 [5,6].

Compounds (**I**) contain two hydroxyl groups in β- and δ-positions, respectively, relative to the tin centre. As well as the β-hydroxyl group, the δ-hydroxyl group could also be involved in reactions at the tin centre, e.g. by providing nucleophilic assistance during reactions with electrophiles such as halogens. In order to obtain a measure of the separation of the β-HO- and



(I)

---

[*] Corresponding author.

SSDI 0022-328X(94)05144-5

δ-HO-groups from the tin atom, as well as their spatial arrangements, we have determined the crystal structure of (**I**, R = Ph). The ^{1}H NMR and ^{13}C NMR data have also been examined.

2. Experimental details

2.1. X-ray crystallography

The X-ray data were collected on a Nicolet P3 4-circle diffractometer by the θ–2θ scan method with scan widths in the range 2.4–2.7°. Two standard reflections were periodically monitored for crystal decay, and ψ scans showing approximately equal intensities indicated that an absorption correction was not required. The data were corrected for Lorentz and polarisation effects. The coordinates of the tin atom were fixed and the remaining atom coordinates were located from successive Fourier difference maps following least-squares refinement. All non-H atoms were refined freely with anisotropic temperature factors, while the hydrogen atoms were given common isotropic tempera-

Table 1
Crystal data and structure refinement

Empirical formula	$C_{27}H_{30}O_5Sn$
Formula weight	553.20
Temperature	293 (2) K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	$P1$
Unit cell dimensions	$a = 6.631(2)$ Å $b = 9.120(3)$ Å $c = 11.492(4)$ Å $\alpha = 83.03(3)°$ $\beta = 108.02(3)°$ $\gamma = 107.36(3)°$
Volume	630.5(4) Å^3
Z	1
Density (calculated)	1.457 Mg m^{-3}
Absorption coefficient	1.047 mm^{-1}
$F(000)$	282
Crystal size	0.05 × 0.60 × 0.18 mm
θ range for data collection	1.86–25.05°
Index ranges	$0 \leq h \leq 7$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$
Independent reflections	2234
Observed reflections [$I > 2\sigma(I)$]	2232
Refinement method	Full-matrix least-squares on F^2
Number of parameters	299
Goodness-of-fit on F^2 (S)	1.228
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0268$, $wR2 = 0.0497$
R indices (all data)	$R1 = 0.0269$, $wR2 = 0.0498$
Final weighting scheme	$w = 1/\sigma^2\,(F_o^2)$
Absolute structure parameter	−0.03(2)
Residual diffraction max.	0.370 e Å^{-3}
Residual diffraction min.	−0.372 e Å^{-3}

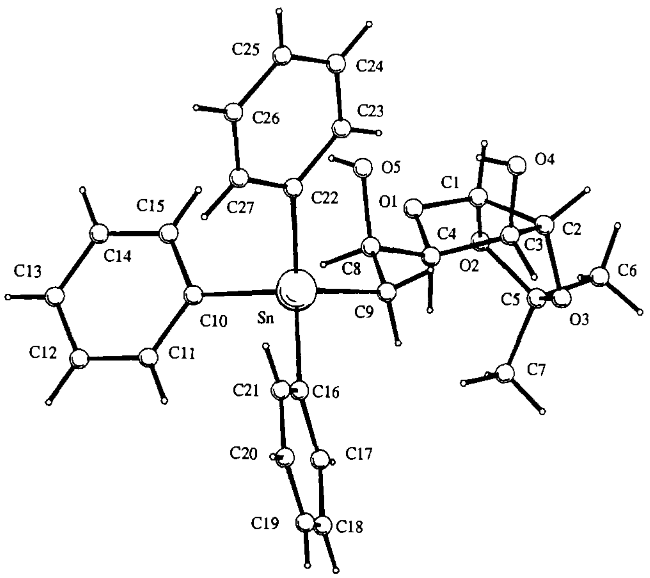


Fig. 1. The atomic arrangement in the molecule.

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq}
Sn	10000	10000	0	39(1)
O(1)	8550(6)	6959(4)	4187(3)	46(1)
O(2)	6107(7)	5585(5)	5255(5)	78(2)
O(3)	4299(6)	7410(5)	4528(4)	52(1)
O(4)	9298(8)	10287(6)	4380(4)	69(1)
O(5)	11292(7)	9150(5)	3015(5)	57(1)
C(1)	7738(9)	6947(7)	5165(5)	51(2)
C(2)	6589(9)	8227(7)	4930(5)	49(1)
C(3)	7330(9)	9152(6)	3881(5)	45(1)
C(4)	7619(8)	7932(6)	3218(5)	40(1)
C(5)	4008(10)	5869(7)	5007(6)	54(2)
C(6)	3399(12)	5680(9)	6181(6)	77(2)
C(7)	2336(14)	4827(9)	4045(7)	87(2)
C(8)	9055(9)	8410(6)	2365(5)	42(1)
C(9)	8265(10)	9529(7)	1356(5)	50(1)
C(10)	10675(9)	7945(6)	−298(5)	40(1)
C(11)	9632(11)	7166(7)	−1366(5)	57(2)
C(12)	10150(13)	5899(7)	−1588(6)	69(2)
C(13)	11748(13)	5359(8)	−695(7)	69(2)
C(14)	12778(13)	6101(9)	363(7)	71(2)
C(15)	12228(9)	7372(7)	568(6)	54(2)
C(16)	7910(9)	10593(7)	−1725(5)	48(1)
C(17)	5677(10)	9838(8)	−2068(6)	65(2)
C(18)	4309(13)	10231(10)	−3182(7)	82(2)
C(19)	5156(17)	11344(10)	−3928(7)	92(3)
C(20)	7300(19)	12071(9)	−3623(7)	99(3)
C(21)	8721(14)	11697(9)	−2516(6)	66(2)
C(22)	13112(9)	11685(6)	555(5)	46(1)
C(23)	13953(11)	12305(7)	1712(6)	63(2)
C(24)	16006(13)	13330(8)	2063(8)	80(2)
C(25)	17276(14)	13777(10)	1274(11)	96(3)
C(26)	16503(14)	13182(10)	145(10)	83(3)
C(27)	14443(10)	12137(7)	−206(7)	61(2)

Table 3
Bond lengths [Å] and angles [°]

Sn–C(22)	2.135(6)
Sn–C(10)	2.141(5)
Sn–C(9)	2.142(5)
Sn–C(16)	2.152(5)
O(1)–C(1)	1.386(6)
O(1)–C(4)	1.439(6)
O(2)–C(1)	1.400(7)
O(2)–C(5)	1.428(7)
O(3)–C(5)	1.425(7)
O(3)–C(2)	1.431(6)
O(4)–C(3)	1.407(7)
O(5)–C(8)	1.433(7)
C(1)–C(2)	1.530(8)
C(2)–C(3)	1.510(8)
C(3)–C(4)	1.509(7)
C(4)–C(8)	1.511(7)
C(5)–C(7)	1.491(10)
C(5)–C(6)	1.501(8)
C(8)–C(9)	1.522(7)
C(10)–C(11)	1.372(7)
C(10)–C(15)	1.373(7)
C(11)–C(12)	1.371(8)
C(12)–C(13)	1.391(9)
C(13)–C(14)	1.346(9)
C(14)–C(15)	1.380(9)
C(16)–C(21)	1.373(9)
C(16)–C(17)	1.385(8)
C(17)–C(18)	1.398(9)
C(18)–C(19)	1.352(11)
C(19)–C(20)	1.331(12)
C(20)–C(21)	1.402(10)
C(22)–C(27)	1.374(8)
C(22)–C(23)	1.391(8)
C(23)–C(24)	1.371(9)
C(24)–C(25)	1.369(12)
C(25)–C(26)	1.354(12)
C(26)–C(27)	1.383(10)
C(22)–Sn–C(10)	106.6(2)
C(22)–Sn–C(9)	112.6(2)
C(10)–Sn–C(9)	109.2(2)
C(22)–Sn–C(16)	112.8(2)
C(10)–Sn–C(16)	105.7(2)
C(9)–Sn–C(16)	109.7(2)
C(1)–O(1)–C(4)	108.6(4)
C(1)–O(2)–C(5)	111.0(5)
C(5)–O(3)–C(2)	109.1(4)
O(1)–C(1)–O(2)	112.1(5)
O(1)–C(1)–C(2)	108.1(4)
O(2)–C(1)–C(2)	105.5(4)
O(3)–C(2)–C(3)	110.6(4)
O(3)–C(2)–C(1)	103.0(5)
C(3)–C(2)–C(1)	102.9(4)
O(4)–C(3)–C(4)	114.0(5)
O(4)–C(3)–C(2)	107.8(5)
C(4)–C(3)–C(2)	101.7(4)
O(1)–C(4)–C(3)	104.0(4)
O(1)–C(4)–C(8)	108.6(4)
C(3)–C(4)–C(8)	119.2(5)
O(3)–C(5)–O(2)	105.3(5)
O(3)–C(5)–C(7)	108.4(5)
O(2)–C(5)–C(7)	110.0(6)
O(3)–C(5)–C(6)	111.8(5)
O(2)–C(5)–C(6)	108.7(5)
C(7)–C(5)–C(6)	112.6(6)
O(5)–C(8)–C(4)	111.1(4)
O(5)–C(8)–C(9)	107.3(4)
C(4)–C(8)–C(9)	112.0(4)
C(8)–C(9)–Sn	112.9(4)
C(11)–C(10)–C(15)	117.1(5)
C(11)–C(10)–Sn	122.0(4)
C(15)–C(10)–Sn	120.9(4)
C(10)–C(11)–C(12)	122.1(6)
C(11)–C(12)–C(13)	119.3(6)
C(14)–C(13)–C(12)	119.5(6)
C(13)–C(14)–C(15)	120.3(6)
C(10)–C(15)–C(14)	121.7(6)
C(21)–C(16)–C(17)	118.3(6)
C(21)–C(16)–Sn	122.0(5)
C(17)–C(16)–Sn	119.7(5)
C(16)–C(17)–C(18)	119.9(7)
C(19)–C(18)–C(17)	120.3(7)
C(20)–C(19)–C(18)	120.8(7)
C(19)–C(20)–C(21)	120.4(8)
C(16)–C(21)–C(20)	120.4(8)
C(27)–C(22)–C(23)	116.8(6)
C(27)–C(22)–Sn	120.6(4)
C(23)–C(22)–Sn	122.6(5)
C(24)–C(23)–C(22)	121.2(7)
C(25)–C(24)–C(23)	120.6(8)
C(26)–C(25)–C(24)	119.5(8)
C(25)–C(26)–C(27)	120.1(8)
C(22)–C(27)–C(26)	121.9(7)

ture factors. The coordinates of the hydroxyl hydrogens were refined, but the remaining hydrogens were only allowed to ride on their attached atoms. Details of the crystal data and structure refinement using SHELXL-93 [7] are shown in Table 1. A plot of the atomic arrangement in the molecule (Fig. 1) was obtained with program SNOOPI [8]. Tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

2.2. NMR spectra

A Brucker spectrometer was used to record the spectra. Data were as follows.

2.2.1. ^1H NMR ($CDCl_3$, 250 MHz)

7.57 [m, 6H, $J(^{119}Sn-^{1}H)$ ca.50 Hz, O–H], 7.39 (m, 9H, *m*– + *p*–H), 5.94 [d, 1H, $J(H(1)-H(2)) = 3.62$ Hz, H(1)], 4.51 [d, 1H, $J(H(1)-H(2)) = 3.62$ Hz, H(2)], 4.45 [m, 2H, H(8) + H(04)], 4.17 [d, 1H, $J(H(3)-H(4)) = 3.24$ Hz, H(3)], 4.07 [t, 1H, $J(H(3)-H(4)) = 3.24$ Hz, $J(H(4)-H(8)) = 3.22$ Hz, H(4)], 2.89 [dd, 1H, $J(H(8)-H(05)) = 3.33$ Hz, $J(H(9B)-H(05)) = 2.16$ Hz, H(05)], 1.87 [dd, 1H, $J(H(9A)-H(9B)) = 13.10$ Hz, J(H(9A)–H(8)) = 11.10 Hz, $J(^{119}Sn-^{1}H) = 53$ Hz, H(9B)], 1.79 [ddd, 1H, $J(H(9A)-H(9B)) = 13.10$ Hz, $J(H(8)-H(9B)) = 4.96$ Hz, $J(H(9B)-H(05)) = 1.90$ Hz, $J(^{119}Sn-^{1}H) = 53$ Hz, H(9A)], 1.43 (s, 3H, Me), 1.32 (s, 3H, Me).

Table 4
Hydrogen bonding in (I)

	Distance (Å)		Angle (°)	Distance (Å)
O(4)...O(5)	2.789(7)	O(3)...O(5)^1		2.931(6)
O(4)-H(04)	0.73(7)	O(5)-H(05)		0.89(8)
O(5)...H(04)	2.11(7)	O(3)...H(05)^1		2.21(9)
O(4)-H(04)...O(5)			155(8)	
O(3)...H(05) ^{a}-O(5) ^{a}			138(8)	

[a] Coordinates transposed by $x-1$, y, z.

Long-range ^{1}H NMR coupling is observed between the hydroxyl hydrogen, H(05), and the methylene proton, H(9A) resulting in a split double doublet (ddd) for the H(9A) proton.

2.2.2. ^{13}C NMR ($CDCl_3$, 62.9 MHz)

138.3 [$J(^{119}Sn-^{13}C) = 518$ Hz, C*ipso*], 136.9 [$J(^{119}Sn-^{13}C) = 35.4$ Hz, CO], 128.9 [$J(^{119}Sn-^{13}C) = 49.8$ Hz, C*m*], 128.4 [$J(^{119}Sn-^{13}C)$ ca. 10 Hz, C*p*], 111.6 [CMe_2], 104.8 [C(1)], 85.2 [C(2) or C(3)], 82.7 [$J(^{119}Sn-^{13}C) = 65.8$ Hz, C(4)], 75.4 [C(3) or C(2)], 69.9 [$J(^{119}Sn-^{13}C] = 24.3$ Hz, C(8)], 26.0 and 26.7 (Me_2C), 15.7 [$J(^{119}Sn-^{13}C)$ 36.8 Hz, C(9)].

3. Discussion

Atomic coordinates are shown in Table 2, and bond lengths and angles for (I) in Table 3.

The geometry about the tin atom is tetrahedral. The $Sn-C_{aryl}$ bond lengths range from 2.135(5)–2.152(5) Å and the $Sn-C_{alkyl}$ bond length is 2.142(5) Å. The three $C_{aryl}-Sn-C_{aryl}$ angles range from 105.7(2)–112.8(2)°, and the three $C_{aryl}-Sn-C_{alkyl}$ angles range from 109.2(2)–112.6(2)°. The tin–oxygen separations are Sn...O(4) 5.240(5) Å and Sn...O(5) 3.354(5) Å. The latter is less than the sum of the van der Waal's radii (3.70 Å) [9] and the O(5)–C(8)–C(9)–Sn torsion angle is 65.3(5)°. If Sn is considered to be weakly coordinated to O(5) then the geometry can be regarded as a distorted square planar environment, with C(10) and C(22) on opposite sides of a mean plane as follows: atoms defining plane: Sn, −0.047(3); O(5), 0.032(2); C(9), −0.023(1); C(16) 0.038(2); atoms out of plane: C(10), −1.920(8); C(22) 1.473(9).

The more electronegative O(5) atom, however, would be expected to occupy the apical position and there is no apparent angular distortion away from a tetrahedral environment. Hence the above consideration is merely a geometrical artefact and the O(5) atom has a negligible influence on the tin coordination.

Hydrogen bonding is present in the molecule as shown Table 4. It will be seen that the intramolecular H bond involving the hydroxyl groups is stronger than the intermolecular H bond involving a hydroxyl group and an isopropylidene ring oxygen.

Various descriptors may be applied to the conformations of five-membered rings, and the Cremer–Pople puckering constants [10] obtained by program PUCKER [11] are shown in Table 5.

Table 5
Conformations of the five-membered rings

	Furanose	Isopropylidene
Cremer-Pople	$Q = q_2 = 0.368$ Å	$Q = q_2 = 0.231$ Å
Puckering constants	$\phi = 303.5°$	$\phi = 263.2°$
% twist (half-chair)	86 (axis through C(1))	62 (axis through O2))
% envelope	14 (C(3) at flap)	38 (O(3) at flap)

References

[1] J.L. Wardell, Formation and cleavage of the tin–carbon bond, in P.G. Harrison (ed.), *Chemistry of Tin*, Blackie, Glasgow, 1989, Ch. 5.

[2] L.A. Burnett, S.M.S.V. Doidge-Harrison, S.J. Garden, R.A. Howie, O.J. Taylor and J.L. Wardell, *J. Chem. Soc., Perkin Trans., 1* (1993) 1621.

[3] P.J. Cox, O.A. Melvin, S.J. Garden and J.L. Wardell, *J. Chem. Cryst.*, in the press.

[4] S.M.S.V. Doidge-Harrison, I.W. Nowell, P.J. Cox, R.A. Howie, O.J. Taylor and J.L. Wardell, *J. Organometallic Chem., 401* (1991) 273.

[5] O.J. Taylor and J.L. Wardell, *Recl. Trav. Chem. Pays-Bas, 107* (1988) 267.

[6] O.J. Taylor, J.L. Wardell and M. Muzhar, *Main Group Metal Chemistry, 12* (1989) 107.

[7] G.M. Sheldrick, SHELXL-93, *J. Appl. Cryst.*, in preparation.

[8] K. Davies, SNOOPI, *A program for producing molecular diagrams from X-ray data*, part of the Chemgraf package, 1983.

[9] P.G. Harrison (ed.), *Chemistry of Tin*, Blackie, Glasgow, 1989, p. 10.

[10] D. Cremer and J.A. Pople, *J. Am. Chem. Soc., 97* (1975) 1354.

[11] R.O. Gould and P. Taylor, PUCKER, *A program for calculating Cremer-Pople ring puckering parameters*, University of Edinburgh, Scotland, 1994.