

**$^{119}\text{Sn}$ ,  $^{13}\text{C}$  AND  $^1\text{H}$  NMR SPECTRA OF TRIS(1-BUTYL)STANNYL D-GLUCURONATE**Antonin LYCKA<sup>a</sup>, Jaroslav HOLECEK<sup>b1</sup> and David MÍČAK<sup>b</sup><sup>a</sup> *Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitvi, Czech Republic, e-mail: slnmr@pol.upce.cz*<sup>b</sup> *Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, 532 10 Pardubice, Czech Republic, e-mail: <sup>1</sup>holecek@hlb.upce.cz*

Received April 1, 1997

Accepted April 21, 1997

*Dedicated to Dr Jaromir Plesek on the occasion of his 70th birthday.*

The  $^{119}\text{Sn}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of tris(1-butyl)stannyl D-glucuronate have been measured in hexadeuteriodimethyl sulfoxide, tetradeuteriomethanol and deuteriochloroform. The chemical shift values have been assigned unambiguously with the help of H,H-COSY, TOCSY, H,C-COSY and  $^1\text{H}$ - $^{13}\text{C}$  HMQC-RELAY. From the analysis of parameters of  $^{119}\text{Sn}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of the title compound and their comparison with the corresponding spectra of tris(1-butyl)stannyl acetate and other carboxylates it follows that in solutions of non-coordinating solvents (deuteriochloroform) the title compound is present in the form of more or less isolated individual molecules with pseudo-tetrahedral environment around the central tin atom and with monodentately bound carboxylic group. The interaction of tin atom with oxygen atoms of carbonyl group and hydroxyl groups of the saccharide residue – if they are present at all – are very weak. In solutions in coordinating solvents (hexadeuteriodimethyl sulfoxide or tetradeuteriomethanol), the title compound forms complexes with one molecule of the solvent. Particles of these complexes have a shape of trigonal bipyramid with the 1-butyl substituents in equatorial plane and the oxygen atoms of monodentate carboxylic group and coordinating solvent in axial positions.

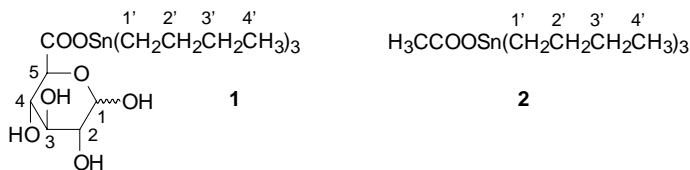
**Key words:** Tris(1-butyl)stannyl D-glucuronate;  $^{119}\text{Sn}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR.

Recently, Tiekink has published two fundamental review articles<sup>1,2</sup> on structure of organotin carboxylates of general formula  $\text{R}_n\text{Sn}(\text{OOCR}')_{4-n}$  in which he has summarized all the structural motives known so far to occur in crystals of these compounds. If the substituent  $\text{R}'$  of carboxylic group contains no donor atom able of a donor-acceptor interaction with the tin atom, the crystals of the organotin carboxylates are formed – depending on size of  $\text{R}$  and  $\text{R}'$  substituents – either by pseudotetrahedral isolated molecules or by molecular chelate complexes with the COO group bidentately bound to the tin atom, or by di-, oligo- or polymeric clusters in which COO groups play the role of bridges between the  $\text{R}_n\text{Sn}$  fragments. If the  $\text{R}'$  substituent contains a donor atom able of an intra- or intermolecular interaction, then chelate complexes or di-, oligo- or

polymeric clusters can be formed with its participation. Of course, it is obvious that the structure of crystals and particles forming them can be – as it is often the case – different from the structure of isolated particles found *e.g.* in the solutions after dissolution. Moreover, the structure of organotin carboxylates is usually affected significantly by the solvent nature, too.

A molecule of D-glucuronic acid contains beside two oxygen atoms of carboxylic group four more oxygen atoms of hydroxylic groups and one oxygen atom of the pyranose cycle. Theoretically, all of them can interact with the central tin atom and increase its coordination number by forming donor–acceptor connections. In 1992, Guard *et al.*<sup>3</sup> published a communication dealing with <sup>13</sup>C NMR spectra of tris(1-butyl)stannyl D-glucuronate (**1**) in hexadeuteriodimethyl sulfoxide. On the basis of differences between the  $\delta(^{13}\text{C})$  chemical shifts of this compound and the corresponding parameters of starting D-glucuronic acid they made a conclusion that the increase in coordination number of tin atom was due to the coordination of O(4) and possibly also O(1) oxygen atoms in the coordination sphere of the central tin atom. In our opinion these conclusions are not quite correct since they were made on the basis of an insufficient source of information, and also the application of strongly coordinating solvent to the purpose of evaluation of intramolecular coordination in the molecule of the compound studied is at least doubtful with regard to the highly probable interactions between tin and solvent itself.

With regard to these facts and to our long-term programme of studies of organotin carboxylates having O, S and N donor atoms in their R' group<sup>4–6</sup>, we considered it useful to verify the conclusions of paper<sup>3</sup> by a somewhat more detailed study using <sup>119</sup>Sn, <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy in a non-coordinating solvent (deuteriochloroform) and coordinating solvents of different Lewis basicities and to interpret the results by confronting them with the data of a typical representative of tris(1-butyl)stannyl carboxylates, *viz.* tris(1-butyl)stannyl acetate ((1-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnOCOCH<sub>3</sub>, **2**).



## EXPERIMENTAL

Tris(1-butyl)stannyl D-glucuronate (**1**) was prepared by a reaction of D-glucuronic acid (1 g) dissolved in warm ethanol (100 ml) with hexa(1-butyl)distannoxane (1.54 g) added with stirring within 30 min. The reaction mixture was stirred for another 1 h and then concentrated to half volume in vacuum. After several hours, crystals of the product began to separate from the solution. Yield 2.1 g (85%), m.p. 38–41 °C. For C<sub>18</sub>H<sub>36</sub>O<sub>7</sub>Sn (483.2) calculated: 44.75% C, 7.51% H, 24.56% Sn; found:

44.64% C, 7.56% H, 24.54% Sn. The compound was kept in cold since it decomposes slowly at room temperature. The decomposition is accompanied by a colour change to yellow and then to brown. Tris(1-butyl)stannyl acetate (**2**) was prepared in a known way<sup>7</sup>.

The <sup>119</sup>Sn, <sup>13</sup>C and <sup>1</sup>H NMR spectra were measured with a Bruker AMX 360 apparatus at 134.28, 90.56 and 360.13 MHz, respectively, at room temperature. The values of  $\delta(^1\text{H})$  and  $\delta(^{13}\text{C})$  chemical shifts were referenced to the internal tetramethylsilane ( $\delta$  0.00), those of  $\delta(^{119}\text{Sn})$  to external tetramethylstannane ( $\delta$  0.00) in a coaxial capillary. Positive values of the chemical shifts denote down-field shifts with respect to the standards.

The solutions for the measurements were prepared by dissolving compounds **1** and **2** (ca 50 mg) in the above-mentioned solvents (0.6 ml).

## RESULTS AND DISCUSSION

Compound **1** is a mixture of its  $\alpha$  and  $\beta$  anomers. The values of  $\delta(^1\text{H})$  chemical shifts for both anomers in all the solvents used are presented in Table I, those of  $\delta(^{13}\text{C})$  and  $\delta(^{119}\text{Sn})$  chemical shifts and  $^nJ(^{119}\text{Sn}, ^{13}\text{C})$  coupling constants similarly in Table II.

Relative populations of the anomers (Table I) were determined by integrating the signals of protons at position 1. According to ref.<sup>8</sup>, the signals with the coupling constants  $^3J(^1\text{H}(1), ^1\text{H}(2))$  of about 3.5 and 7.7 Hz are due to the  $\alpha$  and  $\beta$  anomers, respectively (Table I). The signals corresponding to protons at position 1 formed starting points for the H,H-COSY and TOCSY analyses which were used for an unambiguous assignment of the <sup>1</sup>H chemical shifts. The <sup>13</sup>C chemical shifts were assigned on the basis of the H,C-COSY spectra in the cases where the proton signals were separated. When the proton signals were overlapped, we used the <sup>1</sup>H-<sup>13</sup>C HMQC-RELAY experiment<sup>9</sup> for the assignment.

Figure 1 shows the <sup>13</sup>C NMR spectrum of compound **1** in (CD<sub>3</sub>)<sub>2</sub>SO in which it is possible to observe signals of standard half-width (in contrast to ref.<sup>3</sup> giving very broad signals) with no signs of splitting and existence of  $^nJ(^{119}\text{Sn}, ^{13}\text{C})$  coupling constants.

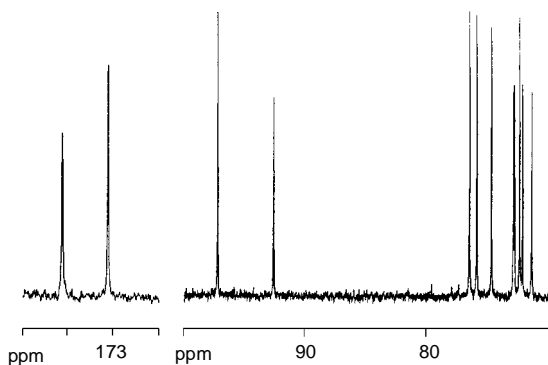


Fig. 1  
<sup>13</sup>C NMR spectrum of compound **1** in (CD<sub>3</sub>)<sub>2</sub>SO

The anomers ratio is *ca* 1 : 0.7, hence the different intensities enable an easy differentiation between the signals due to the individual anomers. As the  $\beta$  anomer predominates in the mixture (which was proved by the  $^1\text{H}$  NMR spectrum), it is obvious that the assignment of COO signals must be opposite to that given in ref.<sup>3</sup>.

The carbon signals, except for those of COO groups and C(1) atom, are found in a relatively narrow interval of chemical shifts. Guard *et al.*<sup>3</sup> adopted the assignment method based on gradual addition of one of the reactants and monitoring of changes in  $^{13}\text{C}$  chemical shifts. Two-dimensional NMR spectroscopy enables an unambiguous assignment of signals by means of a combination of techniques such as H,H-COSY and H,C-COSY inclusive of the optimization for long-range couplings. In our case it was very helpful to adopt the inverse  $^1\text{H}$ - $^{13}\text{C}$  HMQC-RELAY experiment<sup>9</sup> which makes it possible both to determine the connectivity of protons and to assign the  $^{13}\text{C}$  chemical shifts (Fig. 2) from a single 2D spectrum. If we start the assignment from the proton in position 1 of the  $\beta$  anomer, we have the carbon resonance assigned, parallel to F2 axis the position of cross-peak determines the resonance of the adjacent proton, at the parallel line to F1 axis we find the cross-peak determining the resonance of C(2) atom. Similarly we proceed till the C(5) atom. For the  $\alpha$  anomer we found unambiguously the respective connectivities for the following pairs: (H(1)/C(1) / (H(2)/C(2)) and (H(5)/C(5) / (H(4)/C(4)). The remaining signals correspond to H(3)/C(3).

TABLE I

$^1\text{H}$  NMR chemical shifts in tris(1-butyl)stannyl D-glucuronate (**1**) in various solvents

Proton	$(\text{CD}_3)_2\text{SO}$		$\text{CD}_3\text{OD}$		$\text{CDCl}_3$	
	$\alpha$ -anomer <sup>a</sup>	$\beta$ -anomer <sup>a</sup>	$\alpha$ -anomer <sup>a</sup>	$\beta$ -anomer <sup>a</sup>	$\alpha$ -anomer <sup>a</sup>	$\beta$ -anomer <sup>a</sup>
H-1	4.95(6.37) <sup>b</sup>	4.32(6.68) <sup>b</sup>	5.11	4.46	5.28	4.61
H-2	3.17	2.95(4.91) <sup>b</sup>	3.39	3.17	3.57	3.39
H-3	3.46	3.17	3.68	3.36	3.87	3.61
H-4	3.25	3.26	3.39	3.45	3.55	3.56
H-5	3.92	3.49	4.14	3.67	4.29	3.81
H-1'	1.08	1.08	1.19	1.19	1.29	1.29
H-2'	1.57	1.57	1.63	1.63	1.57	1.57
H-3'	1.39	1.39	1.33	1.33	1.29	1.29
H-4'	0.89	0.89	0.91	0.91	0.87	0.87

<sup>a</sup> The  $\alpha$  :  $\beta$  anomer ratios: 0.7 in  $(\text{CD}_3)_2\text{SO}$ , 1.6 in  $\text{CD}_3\text{OD}$ , 2.4 in  $\text{CDCl}_3$ . <sup>b</sup>  $^1\text{H}$  NMR chemical shift of the proton of directly bound hydroxyl group.

The values of  $\delta(^{119}\text{Sn})$  chemical shifts of both anomers of compound **1** (139.7 and 142.2) in solutions of non-coordinating solvent (deuteriochloroform) are typical<sup>10</sup> of tris(1-butyl)stannyl compounds with the coordination number at the central tin atom equal to 4. Also the values of C–Sn–C bond angles of about  $109^\circ$  calculated from the values<sup>11</sup> of coupling constants  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  (347.6 Hz) indicate an almost ideal tetrahedral arrangement around the tin atom. On the basis of the values of both these NMR parameters, which are fundamental in structure evaluation of organotin compounds, we must exclude any significant intra- or intermolecular interaction of any further donor oxygen atoms present in the particles of compound **1** in this solvent. Moreover, the findings given indicate a monomolecular character of the particles of both anomers at the given conditions. The distinct upfield shift by *ca* 120–150 ppm in the  $\delta(^{119}\text{Sn})$  values of both anomers of compound **1** accompanying the transition from a non-coordinating solvent to coordinating ones is due to the coordination of one molecule of this solvent in the coordination sphere of the central tin atom with formation of complexes having the coordination number of the tin atom equal to five<sup>10</sup>. The immediate vicinity of the tin atom in these complexes has a shape of *trans*-trigonal bipyramid with the 1-butyl substituents situated in the equatorial plane (the values of bond angles calculated according to ref.<sup>11</sup> from the values of  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  coupling constants 447.6 and 479.1 Hz (see Table I) are about  $119^\circ$  and  $122^\circ$ , respectively) and the oxygen atoms of carboxylic group and coordinating solvent at the axial positions. The differences in  $\delta(^{119}\text{Sn})$  chemical shifts and  $^1J(^{119}\text{Sn}, ^{13}\text{C})$  coupling constants of the complexes depend-

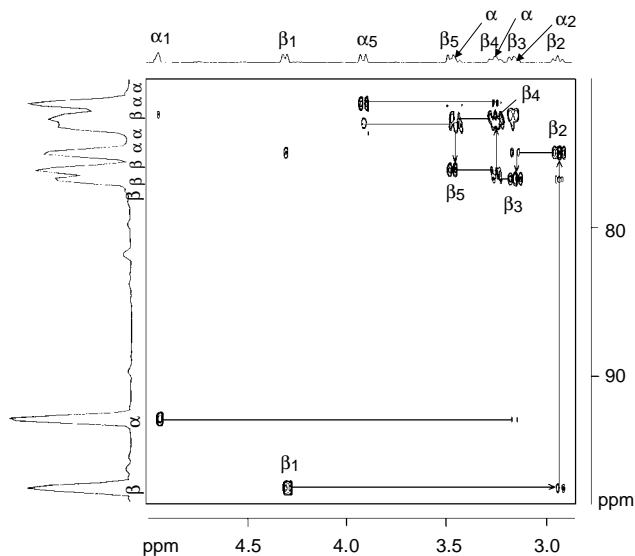


Fig. 2

$^1\text{H}$ - $^{13}\text{C}$  HMQC-RELAY spectrum of compound **1** in  $(\text{CD}_3)_2\text{SO}$

ing on the type of the coordinating solvent used are merely a consequence of the shift of the equilibrium reaction of formation of these complexes according to Eq. (1).



Obviously, this equilibrium in hexadeuteriodimethyl sulfoxide is shifted in favour of the products more than it is in tetradeuteriomethanol. It is also noteworthy that in the complexes of compound **1** with a molecule of any of the coordinating solvent there disappear the differences in the values of  $^{119}\text{Sn}$  and  $^{13}\text{C}$  NMR spectral parameters of the central tin atom and 1-butyl substituents in the individual anomers. The differences in the values of  $\delta(^{13}\text{C})$  chemical shifts of the residues of both anomers of D-glucuronic acid, although they are maintained, have no effect on the arrangement in the vicinity of tin atom. Also this fact indicates the non-existence of any significant interaction of any donor atom of oxygen with the central tin atom, at least so in the medium of a coordinating solvent. In our opinion, the incorrect conclusion of the authors<sup>3</sup> about the inter-

TABLE II  
 $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR chemical shifts and  $^nJ(^{119}\text{Sn}, ^{13}\text{C})$  coupling constants (the values in Hz in brackets) in tris(1-butyl)stannyl D-glucuronate (**1**) in various solvents

Atom	$(\text{CD}_3)_2\text{SO}$		$\text{CD}_3\text{OD}$		$\text{CDCl}_3$	
	$\alpha$ -anomer	$\beta$ -anomer	$\alpha$ -anomer	$\beta$ -anomer	$\alpha$ -anomer	$\beta$ -anomer
C-1	92.76	97.35	94.11	98.51	92.45	96.62
C-2	72.24	74.79	73.51	76.06	71.71	74.13
C-3	73.01	76.55	74.61	77.88	72.67	75.62
C-4	72.84	72.43	74.05	73.75	72.11	71.82
C-5	71.51	75.97	72.21	76.94	70.09	74.24
COO	173.91	172.96	176.99	175.81	175.76	174.65
C-1'	18.82 (479.1)	18.82 (479.1)	18.71 (447.6)	18.71 (447.6)	16.97 (347.6)	16.97 (347.6)
C-2'	27.87 (27.3)	27.87 (27.3)	29.18 (27.4)	29.18 (27.4)	27.62 (18.8)	27.62 (18.8)
C-3'	28.82 (77.1)	28.82 (77.1)	28.19 (75.9)	28.19 (75.9)	26.92 (65.2)	26.92 (65.2)
C-4'	13.91	13.91	14.14	14.14	13.51	13.51
Sn <sup>a</sup>	-20.8	-20.8	19.1	19.1	139.7	142.2

<sup>a</sup>  $\delta(^{119}\text{Sn})$ .

action of oxygen atoms bound to carbon at 1 and/or 4 positions of pyranose ring with the tin atom was caused by the overestimation of the changes in  $\delta(^{13}\text{C})$  chemical shifts of these carbon atoms as compared with the corresponding values of the other carbon atoms (up to *ca* 0.5 ppm) and by the underestimation of the general and specific solvent effects. This fact is clearly seen when comparing the values of parameters of  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra of compound **1** with the corresponding parameters of compound **2** (Tables II and III), no such interaction being possible in the latter. The striking similarities of values of mutually corresponding parameters and their comparable changes both in magnitude and direction of shifts on the one hand and the absolute magnitudes of changes in these parameters when changing the solvents, which are several times higher than the changes observed by the authors of paper<sup>3</sup>, cast serious doubt on their interpretation. On the other hand, it cannot be fully excluded that there exists a very weak interaction of the carbonyl oxygen atom of COO group in the isolated molecules of tris(1-butyl)stannyl D-glucuronate in the medium of deuteriochloroform (anisobidentate character of carboxylic group), which could be concluded from the values of  $\delta(^{13}\text{C})$  chemical shifts of COO groups (175.76 and 174.65 ppm) (Table II) close to the respective values found with the alkali salt of this acid<sup>3</sup> (176.40 and 177.32 ppm, respectively), and from their upfield shifts on going from deuteriochloroform to hexadeuteriodimethyl sulfoxide (173.91 and 172.96 ppm, respectively) due to vanishing of the anisobidentate function of COO group as a consequence of replacement of the weak interaction  $-\text{C}=\text{O}\dots\text{Sn}$  by a stronger donor-acceptor connection with a solvent molecule<sup>4</sup>.

TABLE III  
 $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR chemical shifts and  $^nJ(^{119}\text{Sn},^{13}\text{C})$  coupling constants (the values in Hz in brackets) in tris(1-butyl)stannyl acetate (**2**) in various solvents

Atom	$(\text{CD}_3)_2\text{SO}$	$\text{CD}_3\text{OD}$	$\text{CDCl}_3^a$
$\text{CH}_3$	22.35	22.64	21.29
COO	174.36	178.99	176.76
C-1'	18.01 (459.0)	18.44 (442.4)	16.27 (360.7)
C-2'	27.46 (26.8)	29.22 (26.9)	27.73 (20.7)
C-3'	26.29 (73.2)	28.23 (74.4)	26.95 (67.7)
C-4'	13.28	14.26	13.5
$\text{Sn}^b$	-21.1	21.3	106.9

<sup>a</sup> Ref.<sup>10</sup>. <sup>b</sup>  $\delta(^{119}\text{Sn})$ .

## CONCLUSION

In a non-coordinating solvent, the particles of dissolved tris(1-butyl)stannyl D-glucuronate are present as simple isolated pseudotetrahedral molecules (the coordination number of central tin atom is equal to four) without any distinct side bonding interaction of any oxygen atom of pyranose system with the central tin atom. If a very weak interaction of this kind exists at all, then it probably consists in a connection of carbonyl oxygen atom with the tin atom. In solutions in coordinating solvents, *trans*-trigonally bipyramidal complexes of tris(1-butyl)stannyl D-glucuronate with one solvent molecule are formed; in these complexes, the 1-butyl substituents assume equatorial positions and oxygen atoms of COO groups and solvent assume axial positions.

The study presented again documents that a detailed characterization of organotin compounds in solution can only be achieved by measuring the NMR spectra of all the relevant nuclei ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$ ) in coordinating and non-coordinating solvents.

*The authors wish to thank the Grant Agency of Czech Republic for financial support (Grant No. 203/97/0502)*

## REFERENCES

1. Tiekink E. R. T.: *Appl. Organomet. Chem.* 5, 1 (1991).
2. Tiekink E. R. T.: *Trends Organomet. Chem.* 1, 71 (1994).
3. Guard H. E., Coleman W. M., Ross M. M.: *Carbohydr. Res.* 235, 41 (1992).
4. Holecek J., Nadvornik M., Handlir K., Pejchal V., Vitek R., Lycka A.: *Collect. Czech. Chem. Commun.* 62, 279 (1997).
5. Gajda-Schranz K., Nagy L., Kuzmann E., Vertes A., Holecek J., Lycka A.: *J. Chem. Soc., Dalton Trans.* 1997, 2201.
6. Lebl T., Holecek J., Lycka A.: *Sci. Pap. Univ. Pardubice, A* 2, 5 (1996).
7. Van der Kerk G. J. M., Luijten J. G. A.: *J. Appl. Chem.* 6, 49 (1957).
8. Van Halbeck H. in: *Encyclopedia of Nuclear Magnetic Resonance* (D. M. Grant and R. K. Harris, Eds), p. 1107. Wiley, New York 1996.
9. Bax A., Subramanian S.: *J. Magn. Reson.* 67, 565 (1986).
10. Nadvornik M., Holecek J., Handlir K., Lycka A.: *J. Organomet. Chem.* 275, 43 (1984).
11. Holecek J., Lycka A.: *Inorg. Chim. Acta* 118, L15 (1986).