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# On the characterization of the reaction of organotin compounds with D-glucuronic acid

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## ABSTRACT

$^{13}C$ NMR spectroscopy and mass spectrometry show that D-glucuronic acid forms trialkyltin glucuronate complexes upon reaction with bis(tributyltin) oxide but not with tributyltin or trimethyltin chlorides in $Me_2SO$ or the trimethyltin chloride in water. Analysis of the $^{13}C$ NMR chemical shifts of the tributyltin D-glucuronate formed indicates that appreciable interaction of the *d*-orbitals on tin occurs with primarily the O-4 hydroxyl group and to a lesser extent with ring oxygen at C-1. Previous incorrect assignments of the $^{13}C$ NMR signals for D-glucuronic acid are discussed.

## INTRODUCTION

Polysaccharides, which are constituents of cell surfaces, have been implicated as playing important roles in detoxification, transport, and adsorption of various substances[1–3]. D-Glucuronic acid has been shown to be a constituent of the polysaccharides of cell walls of marine microbes[4] and a common constituent saccharide of bacterial extracellular polysaccharides[5]. The structures of various compounds having metal ions bound to D-glucuronic acid have been examined using infrared spectroscopy, nuclear magnetic resonance spectrometry[6,7] and using potentiometric and electron paramagnetic spectroscopy[8] in attempts to document the mode of binding of metal ions to uronic acids in biological systems.

Trialkyltin compounds have been shown to be effective antifouling agents for materials in the marine environment[9]. The specification of tributyltin chloride, an effective antifouling reagent in sea water, has been reported[10]. The purpose of this report is to present the first findings which describe the interaction of organomet-

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als, specifically trialkyltin compounds, including tributyltin chloride, with D-glucuronic acid, the results of which could provide insight into (*1*) the interaction of organotin compounds with cell-wall and extracellular polysaccharides and (*2*) a possible mode of action describing its antifouling capability. Understanding this mode of interaction could lead to a fuller understanding of the mechanism of transport across the cell wall as well as have implications regarding the environmental fate of tributyltin compounds in marine epibiotic communities.

## EXPERIMENTAL

*Materials.*—Tributyltin chloride (TBTCl), trimethyltin chloride (TMTCl) and bis(tributyltin) oxide (TBTO) were obtained from Alpha Ventron Co. Deuterated water ($D_2O$), $Me_2SO$-$d_6$, 1,4-dioxane, and D-glucuronic acid (a mixture of $\alpha$ and $\beta$ anomers) were obtained from Aldrich Chemical Co. All reagents were used as received.

*$^{13}C$ NMR spectroscopy.*—All $^{13}C$ NMR spectra were obtained in 5-mm NMR tubes on either Jeol-GSX270 or Varian Galaxy 300 NMR spectrometers employing proton decoupling with 5-s delay times between acquisitions. Between 64 and 256 scans were used for each experiment. All spectra were referenced to an internal standard of 1,4-dioxane at 67.4 ppm ($Me_4Si = 0$).

*Mass spectrometry.*—All mass spectra were obtained by fast-atom bombardment (FABMS) with a Finnigan TSQ-70 triple quadrupole mass spectrometer. Samples consisted of approximate 0.5 $\mu$L of the analyte solution (corresponding to roughly 10 to 20 $\mu$g of the analyte) mixed with 1 $\mu$L of glycerol directly on the FABMS probe tip. The samples were then bombarded with an 8-keV Xe atom beam, and the sputtered ions were mass analyzed. At least 20 scans were averaged in each experiment, and both positive- and negative-ion mass spectra were measured. Tandem mass spectrometric (MS–MS) experiments were performed by selecting one $m/z$ ion from the ion source with the first quadrupole, colliding these species with Ar gas in the second (RF-only) quadrupole, and mass analyzing the resultant fragment ions with the third quadrupole.

*Reactions.*—A typical reaction scheme is outlined as follows: to 0.1 mmol of D-glucuronic acid dissolved in 250 $\mu$L of a selected deuterated solvent was added 0.1 mmol of the selected organotin compound as either (*1*) a solid dissolved in 250 $\mu$L of a selected deuterated solvent, (*2*) a neat liquid or (*3*) a neat solid. All reactions were conducted in the NMR tube. After thorough mixing of the reagents the $^{13}C$ NMR and mass spectra were gathered, vide supra.

## RESULTS AND DISCUSSION

*$^{13}C$ NMR results.*—Prior to the examination of the reaction of D-glucuronic acid with the triorganotin compounds, spectra of the uronic acids in $D_2O$ and in $Me_2SO$-$d_6$ were examined. To determine the effect of solvent on the $^{13}C$ NMR

TABLE I

$^{13}C$ NMR chemical shifts of D-glucuronic acid as a function of solvent

| Atom | Solvent Composition (mole fraction $Me_2SO$-$d_6$) | | | | | | $\Delta\delta$ |
|---|---|---|---|---|---|---|---|
| | 0 | 0.06 | 0.14 | 0.28 | 0.50 | 1.0 | |
| α-D-Glucuronic acid | | | | | | | |
| C-1 | 93.16 | 93.25 | 93.31 | 93.45 | 93.62 | 93.88 | 0.72 |
| | 93.11 | 93.2 | 92.29 | | | | |
| C-2 | 71.86 | 71.97 | 72.11 | 72.35 | 72.61 | 73.02 | 1.16 |
| C-3 | 73.17 | 73.25 | 73.3 | 73.38 | 73.47 | 73.70 | 0.53 |
| C-4 | 72.28 | 72.40 | 72.50 | 72.63 | 72.78 | 73.02 | 0.74 |
| C-5 | 71.27 | 71.4 | 71.6 | 71.9 | 72.21 | 72.43 | 1.16 |
| C-6 | 173.19 | 172.98 | 172.67 | 172.22 | 171.71 | 171.58 | −1.61 |
| β-D-Glucuronic acid | | | | | | | |
| C-1 | 96.88 | 97.05 | 97.25 | 97.58 | 97.96 | 98.43 | 1.55 |
| | | | | 97.55 | 97.93 | 98.40 | |
| C-2 | 74.49 | 74.63 | 74.77 | 74.98 | 75.21 | 75.55 | 1.06 |
| C-3 | 76.09 | 76.19 | 76.28 | 76.46 | 76.70 | 77.10 | 1.01 |
| C-4 | 72.06 | 72.17 | 72.27 | 72.35 | 72.48 | 72.62 | 0.56 |
| C-5 | 75.33 | 75.50 | 75.72 | 76.07 | 76.41 | 76.76 | 1.43 |
| C-6 | 174.13 | 173.91 | 173.58 | 173.12 | 172.61 | 172.46 | −1.67 |

chemical shifts, $D_2O$–$Me_2SO$-$d_6$ solutions of D-glucuronic acid at various mole fractions of $Me_2SO$-$d_6$ were examined yielding the pattern of chemical shifts depicted in Table 1. The chemical shifts in $D_2O$ were assigned in agreement with previous reports[11]. Significant changes in chemical shifts in the NMR spectra of the uronic acids were observed as a function of solvent either $Me_2SO$-$d_6$ or $D_2O$. From the data in Table I, it is clear that the chemical shifts of both C-5 and C-6 of the α and β anomers are among the most affected by solvent, as expected. The $^{13}C$ NMR chemical shifts of the other carbons of D-glucuronic acid were also affected by solvent, especially C-1 of the β anomer. One of the trends that deserves close attention is that displayed by carbons α C-2 and β C-4. Both carbons shift downfield with increasing $Me_2SO$-$d_6$ content, but the rate of shift is different for each carbon. At one point, $Me_2SO$-$d_6$ mole fraction 0.28, α C-2 has shifted such that it overlaps the position of β C-4, 72.35 ppm. In pure $Me_2SO$-$d_6$, the α C-2 carbon is downfield of β C-4 in contrast to its upfield position in $D_2O$. Other changes in relative positions occur as the solvent changes from $D_2O$ to $Me_2SO$-$d_6$.

Previous studies[11] have shown the $^{13}C$ NMR chemical shifts for D-glucuronic acid to be a function of pH; however, the literature is not completely clear on the absolute assignments of the carbons at high pH. Triorganotin complexes ($R_3SnX$) based on the nature of the X substituent are known to alter the pH of aqueous solutions[10]. Consequently, a study of the effect of pH on the chemical shifts of D-glucuronic acid, by titrating with an aqueous solution of NaOH, was carried out. The results are presented in Table II. Notice that both the C-5 and C-6 carbons of both anomers show significant chemical shifts as a function of pH. For example,

TABLE II

$^{13}C$ NMR chemical shifts of D-glucuronic acid as a function of pH

| Atom | [NaOH] (mmol) | | | | | $\Delta\delta$ |
|---|---|---|---|---|---|---|
| | 0 | 2.0 | 4.0 | 6.0 | 10.0 | |
| pH | 1.5 | | | | 6.5 | |
| α-D-Glucuronic acid | | | | | | |
| C-1 | 93.17 | 93.14 | 93.11 | 93.09 | 93.01 | −0.16 |
| C-2 | 71.83 | 71.85 | 71.91 | 71.93 | 72.04 | 0.21 |
| C-3 | 73.17 | 73.17 | 73.23 | 73.26 | 73.34 | 0.17 |
| C-4 | 72.23 | 72.31 | 72.45 | 72.55 | 72.77 | 0.54 |
| C-5 | 71.27 | 71.39 | 71.66 | 71.93 | 72.55 | 1.28 |
| C-6 | 173.14 | 173.76 | 174.49 | 175.16 | 176.40 | 3.26 |
| β-D-Glucuronic acid | | | | | | |
| C-1 | 96.84 | 96.78 | 97.76 | 96.70 | 96.70 | −0.14 |
| C-2 | 74.47 | 74.50 | 74.58 | 74.63 | 74.74 | 0.27 |
| C-3 | 76.06 | 76.09 | 76.17 | 76.20 | 76.30 | 0.24 |
| C-4 | 72.04 | 72.12 | 72.26 | 72.36 | 72.42 | 0.38 |
| C-5 | 75.25 | 75.52 | 75.87 | 76.20 | 76.76 | 1.51 |
| C-6 | 174.08 | 174.62 | 175.27 | 175.94 | 177.32 | 3.24 |

the β C-5 chemical shift changes from 75.25 to 76.76 ppm, while for comparison the β C-3 chemical shift changes slightly from 76.06 to 76.30 ppm. Previous assignments of carbon chemical shifts[11b] attributed to C-5 of the sodium salt at high pH values were therefore found to be incorrect. Similar incorrect assignments were noted by Angyal et al.[12] in the proton spectrum of sodium D-glucuronate. Carbon assignments were in agreement with those of Jacques et al.[11a] and Izumi[11c].

The difficulty of assigning the $^{13}C$ NMR peaks for the ring carbons is clearly illustrated by Figs. 1A, B, and C. Fig. 1A is the NMR spectrum (80–70 ppm) of D-glucuronic acid dissolved in $Me_2SO$-$d_6$, Fig. 1B is the NMR spectrum in $D_2O$, while Fig. 1C is the NMR spectrum of the reaction product of D-glucuronic acid plus TBTO in $Me_2SO$-$d_6$. Without prior knowledge of the effects of pH and solvent, assignments could easily be incorrect, leading to a misinterpretation of the data.

To assure that the assignments were correct in the examination of the reaction of D-glucuronic acid with TBTO in $Me_2SO$-$d_6$, 0.10 mmol of the uronic acid in $Me_2SO$ were reacted stepwise with TBTO until the Sn : uronic acid ratio reached 1 : 1, i.e., $5 \times 10^{-2}$ mmol of TBTO, Table III. Significant and consistent changes in chemical shifts were found for a number of the carbons. It is interesting to note that a similar difference in the rate of change of the chemical shifts was found here as was found in the $D_2O$–$Me_2SO$-$d_6$ titrations. The signals for β C-4 and α C-2 actually overlap in the $3 \times 10^{-2}$ mmol TBTO experiment as β C-4 shifts downfield from 72.62 to 73.24 ppm past the α C-2 signal which remains essentially unaffected at 73.05 ppm. A shift of similar magnitude is found for α C-4 as it shifts downfield from 73.02 to 73.65 ppm.

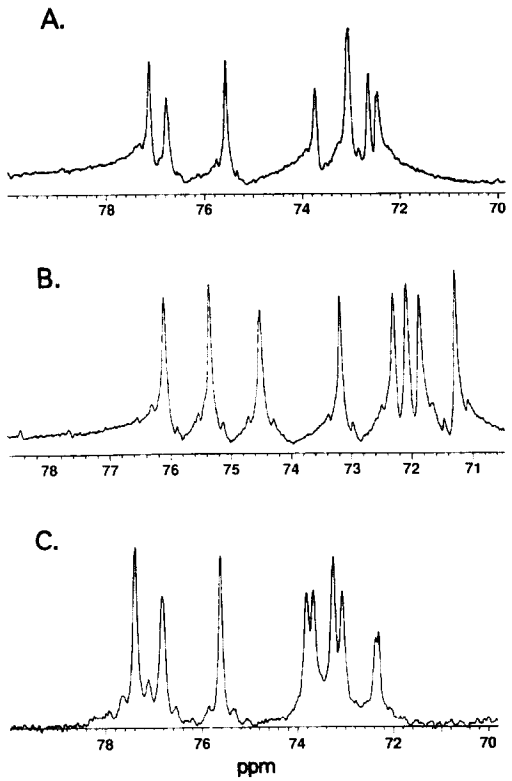



Fig. 1. $^{13}C$ NMR proton-decoupled spectra of carbons 2, 3 and 4 of $\alpha$- and $\beta$-D-glucuronic acid in (A) $Me_2SO$-$d_6$ and (B) $D_2O$. (C) $^{13}C$ NMR proton-decoupled spectra of carbons 2, 3 and 4 of tributyltin $\alpha$- and $\beta$-D-glucuronate in $Me_2SO$-$d_6$.

The changes in chemical shifts ($\Delta\delta$) of the carbons of the pyranose ring upon formation of the uronates give important clues to the nature of metal–hydroxyl interactions. These changes are similar for both the $\alpha$ anomer (Fig. 2) and the $\beta$ anomer. First, it is important to note small shifts, $\Delta\delta$, occurring in the $\beta$ C-5 and $\alpha$ C-5 signals upon complexation with the triorganotin cation (Table III). The $\Delta\delta$-values, 0.05 and $-0.07$ ppm, are much less than corresponding $\Delta\delta$-values of 0.62 and 0.63 ppm found for the C-4 signals and are also much less than the $\Delta\delta$-values (1.35 and 1.51) for formation of the D-glucuronate ion (Fig. 2A for the $\alpha$ anomer). This relationship between the $\Delta\delta$-values for C-4 and C-5 is the same as that found for the interaction of D-glucuronic acid with the Mo cation[7] wherein coordination with the C-4 was postulated, but it is in striking contrast to the situation observed upon sodium salt formation where the chemical shift of C-5 carbon is shifted significantly (Fig. 2B). The shifts found here for the C-4 carbons, 0.62 and 0.63, are not of the magnitude found for the Mo cation, 10.87 and 10.77, but it is still nonetheless reasonable to conclude that the triorganotin cation

TABLE III

$^{13}C$ NMR chemical shifts of D-glucuronic acid upon reaction with tributyltin oxide (TBTO) [a]

| Atom | [TBTO] (mmol × $10^2$) | | | | | | $\Delta\delta$ |
|---|---|---|---|---|---|---|---|
| | 0 | 0.98 | 1.96 | 2.94 | 3.92 | 4.90 | |
| α-D-Glucuronic acid | | | | | | | |
| C-1 | 93.88 | 93.79 | 93.74 | 93.66 | 93.56 | 93.50 | −0.38 |
| C-2 | 73.02 | 73.02 | 73.01 | 73.04 | 73.06 | 73.05 | 0.03 |
| C-3 | 73.70 | 73.71 | 73.73 | 73.78 | 73.79 | 73.79 | 0.09 |
| C-4 | 73.02 | 73.24 | 73.27 | 73.40 | 73.56 | 73.65 | 0.63 |
| C-5 | 72.43 | 72.45 | 72.44 | 72.41 | 72.40 | 72.36 | −0.07 |
| | | 72.41sh | 72.40sh | 72.37sh | 72.33 | 72.30 | |
| C-6 | 171.58 | br | br | 173.01 | 173.49 | 173.77 | 2.19 |
| β-D-Glucuronic acid | | | | | | | |
| C-1 | 98.43 | 98.36 | 98.32 | 98.27 | 98.21 | 98.16 | −0.27 |
| | 98.41 | 98.29 | 98.27 | 98.22 | 98.15 | 98.10 | −0.31 |
| C-2 | 75.55 | 75.56 | 75.56 | 75.60 | 75.61 | 75.60 | 0.05 |
| C-3 | 77.10 | 77.18 | 77.20 | 77.30 | 77.36 | 77.38 | 0.28 |
| C-4 | 72.62 | 72.83 | 72.89 | 73.04 | 73.56 | 73.24 | 0.62 |
| C-5 | 76.76 | 76.80 | 76.80 | 76.81 | 76.83 | 76.81 | 0.05 |
| C-6 | 172.46 | br | br | 173.80 | 174.41 | 174.74 | 2.28 |
| | | | | | 174.39 | | |

[a] Abbreviations include: sh, shoulder, br, broad.

coordinates to some extent to O-4 of both anomers. The enhanced effect on the C-4 signals compared to the C-5 signals is evidence for interaction between the tin and O-4.

The chemical shifts of the C-1 carbons, (Fig. 2 and Table III) are affected also by the complexed tin atom, although to a lesser extent than the C-4 carbons but more than with anion formation. Therefore, it appears that some interaction between the tin and the ring oxygen on C-1 occurs.

Molecular mechanics modeling of tributyltin D-glucuronate using the Desktop Molecular Modeller (Version 1.2) and assuming an Sn–O bond length of 2.15 Å shows the rotation of the C-5–C-6 bond brings the Sn atom into proximity to the C-4 hydroxyl group (2.9 Å) or the ring oxygen (3.4 Å) consistent with the proposed interaction. In addition, organotin compounds have been observed to form five-coordinate structures in organotin carboxylates[14].

The characteristics of the NMR of the reaction of D-glucuronic acid with TBTO in $Me_2SO$-$d_6$ clearly indicate that complexation with the carboxyl group has occurred. The signals attributable to the carbonyl carbons (C-6) in the uncomplexed acid (β C-6, 172.46 ppm and α C-6, 171.58 ppm) both became very broad and nearly disappeared into the baseline, indicating a significant increase in relaxation time (spin polarization) resulting from coordination with an organometallic ion. The breadth of the carboxyl carbon signal observed in these experiments is similar to that observed with the carbonyl carbon of tributyltin acetate.

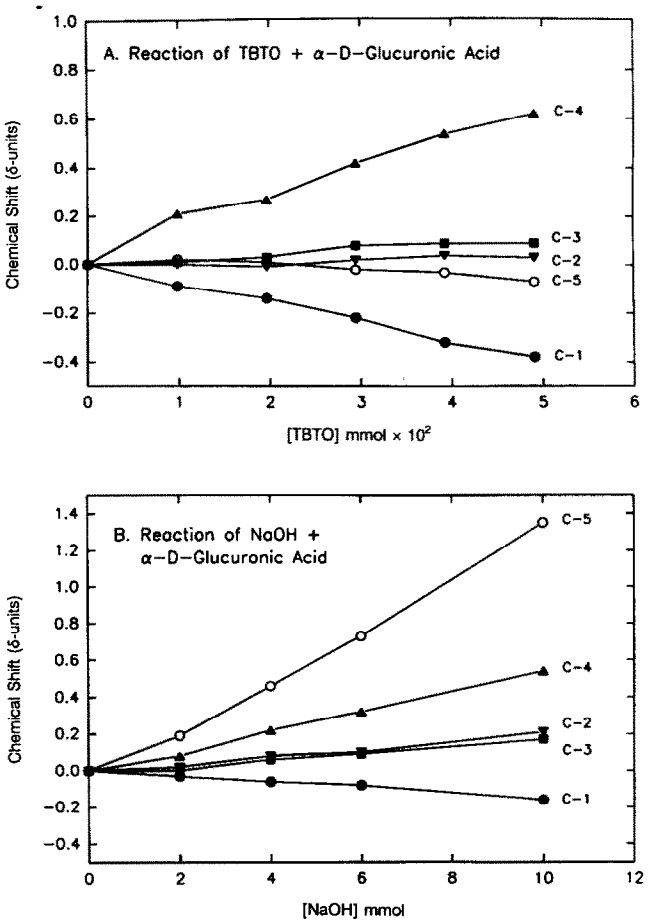



Fig. 2. Changes in $^{13}C$ NMR chemical shifts, $\Delta\delta$-values, observed for the pyranose ring carbons of α-D-glucuronic acid upon reaction with (A) bis(tributyltin) oxide and with (B) sodium hydroxide.

There is, however, some perplexing behavior associated with the signal attributable to α C-5 which was not found in the Mo cation study. Upon addition of $1 \times 10^{-2}$ mmol of TBTO, α C-5 appears as two closely spaced peaks, 72.45 and 72.41 ppm. The signal at 72.41 ppm is only a shoulder at this point. However, by the end of the titration the shoulder at 72.41 ppm becomes the dominant peak located at 72.30 ppm, and the once dominant peak at 72.45 now becomes the shoulder. The β C-1 signal, vide infra, also appears as two closely spaced peaks. This behavior of these carbons is not a this time readily explainable, but may result from cluster formation or aggregation.

The presence of a triorganotin cation apparently does not shift the equilibrium between the open ring and pyranose form of D-glucuronic acid since the change in chemical shift for β C-1 and α C-1 is small, less than 0.4 ppm and upfield; a chemical shift attributable to an aldehyde is not observed. However, the upfield

TABLE IV

$^{13}C$ NMR chemical shifts of the butyltin group [a]

| Compound | α-C | β-C | γ-C | δ-C |
|---|---|---|---|---|
| TBTO | 14.71 | 28.50 | 27.60 | 13.82 |
| TBTOAc | 19.29 | 28.68 | 27.58 | 14.68 |
| TBT–GlcA | 19.58 | 28.63 | 27.55 | 14.66 |

[a] Abbreviations include: TBTO, tributyltin oxide; TBTOAc tributyltin acetate; TBT–GlcA, tributyltin–D-glucuronic acid complex.

shift of 0.38 for α C-1 does indicate the presence of interaction of the triorganotin cation with the ring oxygen. The β C-1 signal appears as two peaks and both carbon signals shift upfield by approximately 0.3 ppm, again indicating the presence of interactions with the ring oxygen and the triorganotin cation. The direction and magnitude of the shifts of the C-1 carbons are the same as those found in the study of the D-glucuronic acid and Mo cation[7].

The position of the alpha carbon of the butyl group attached to the tin previously has been shown to be sensitive to the nature of the X group attached to the tin[13]. The NMR data collected find the alpha carbons of tributyltin acetate, TBTO–D-glucuronic acid complex and bis(tributyltin) oxide at 19.29, 19.58 and 14.71 ppm, respectively (Table IV). The similarity in the chemical shift of the alpha carbon of the butyl groups of tributyltin in the presence of D-glucuronic acid to that of the alpha carbons of the butyl groups of tributyltin acetate is strong evidence for complexation of the Sn with the carboxyl group of uronic acid to form a carboxylate type compound.

In the experiment with $5 \times 10^{-2}$ mmol of TBTO added to the D-glucuronic acid, the Sn : uronic acid ratio was 1 : 1. In an attempt to study reactions at higher Sn to uronic acid ratios, 0.1 mmol of D-glucuronic acid in 500 μL of $Me_2SO$-$d_6$ were reacted with 0.1 mmol of TBTO, yielding an Sn : uronic acid ratio of 2 : 1. Additional peaks, other than those observed from the tributyltin glucuronates of Table III, were observed at 102.6, 96.94, 77.87 and 77.35 ppm. Peaks in this region of the carbon NMR spectrum can be attributable to furanose ring carbons and can be assigned tentatively as follows to the β C-1 at 102.6, the α C-1 at 96.94, the β C-4 at 77.87 and the α C-4 at 77.35 of the furanose form. In addition to the appearance of the new peaks, a deep yellow color developed in the solution approximately 2 h after the addition of the TBTO. Further examination of this rearrangement of the sugar induced by an excess of tributyltin compound is underway.

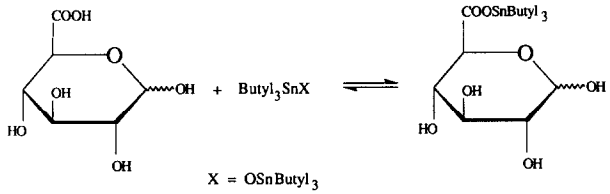
In addition to reactions between TBTO and D-glucuronic acid, reactions with tributyltin chloride in $Me_2SO$-$d_6$ and with trimethyltin chloride in $D_2O$ were also explored. The NMR evidence indicated no reaction between either of these Sn compounds and D-glucuronic acid. For example, in $D_2O$ the methyl group of TMTCl appears at 4.2 ppm, while the methyl group of TMTCl in the presence of D-glucuronic acid appears at 4.1 ppm, indicating minimal or no reaction or

coordination. In $Me_2SO$ the alpha carbon of the butyl groups attached to TBTCl appears at 21.97 ppm, while the alpha carbon of TBTCl in the presence of D-glucuronic acid appears at 21.76 ppm, again indicating minimal or no reaction or coordination of the Sn with the sugar. Further confirmation of the absence of reaction is found in that the carbonyl carbon of D-glucuronic acid does not shift or become broad in the presence of the triorganotin chloride compounds. Apparently then the reaction between the triorganotin compounds and the sugar is specific for the leaving group attached to the Sn, with the Cl compounds being unreactive and the oxide possessing selective reactivity.

*Mass spectrometry.*—Positive-ion FABMS of the sample consisting of the mixture of D-glucuronic acid and TBTO (1:1 sugar:tin molar ratio) yields a wide variety of abundant tin-containing ions, the identification of which is simplified by the unique tin isotope distribution. Some of the more abundant ions correspond to fragments of the TBTO: $[SnBu_3]^+$ at $m/z$ 291; $[SnBu_2 + H]^+$ at $m/z$ 235; $[SnBu]^+$ at $m/z$ 177; and $[Sn + H]^+$ at $m/z$ 121 (where Bu represents an *n*-butyl group and the $m/z$ value is that of the most abundant peak in a particular distribution, i.e., $^{120}Sn$). In addition, an abundant series of peaks is observed with the most intense ion at $m/z$ 485 and a pattern corresponding to that of a species containing one Sn atom. The molecular weight of the D-glucuronic acid–tributyltin adduct (reaction product) is 484. Because the sample matrix is glycerol and sugar compounds usually are desorbed from glycerol as protonated molecules, it is likely that $m/z$ 485 corresponds to the protonated D-glucuronic acid–tributyltin molecule.

One test of this assignment is to analyze the negative ions produced by FABMS. In this experiment, in addition to some TBTO fragment ions, an abundant $m/z$ 483 is observed, in a distribution of ions with the Sn isotope pattern. This ion is probably the deprotonated D-glucuronic acid–tributyltin molecule. It is important to note that neither the $m/z$ 485 (positive ion) nor the $m/z$ 483 (negative ion) are observed in the FABMS of pure TBTO in glycerol or from pure D-glucuronic acid in glycerol. In addition, these ions are not observed in the FABMS of the mixture of D-glucuronic acid with TBTCl, thus supporting the NMR results, which indicated that these compounds do not react.

A tandem mass spectrometric (MS–MS) experiment was performed to investigate further the identity of the possible D-glucuronic acid–tributyltin adduct ions. The MS–MS analysis of the $m/z$ 485 positive ion at low collision energy ($< 10$ eV, laboratory frame) and single collision conditions, yields a fragment-ion mass spectrum in which the most abundant species corresponds to the loss of 18 amu, which is probably a water molecule from the sugar moiety, because the protonated D-glucuronic acid molecule dissociates in the same manner. At higher collision energies, other fragment ions of $m/z$ 485 are produced in greater abundances, including those at $m/z$ 429 (loss of 56 amu) and $m/z$ 291 (loss of 194 amu). The former fragment ion could result from breaking a Sn–C bond with a rearrangement to lose a butene species. The latter fragment ion could arise from cleavage of




Scheme 1.

the O–Sn bond of the adduct and a rearrangement to result in the net loss of the neutral D-glucuronic acid molecule (194 amu) and a stable tributyltin cation, $[SnBu_3]^+$. Both of these are reasonable low-energy dissociation processes. At very high collision energies (keV on a double-focusing sector mass spectrometer) or with multiple collisions, extensive fragmentation can be induced resulting in further losses of butyl groups, resulting in, finally, the tin atomic cation.

An interesting comparison can be made with the MS–MS analysis of $m/z$ 383, which is likely the glycerol–tributyltin adduct ion (92 + 291 amu). The most abundant fragment ion at low collision energy corresponds to loss of the neutral glycerol molecule, which is in contrast to the loss of water from the sugar moiety of the D-glucuronic acid–tributyltin ion under the same conditions. If we take these fragmentations to represent to lowest energy dissociation pathways, we can postulate that the glycerol–tributyltin species is a weakly bound adduct (or cluster), and the D-glucuronic acid–tributyltin species is more strongly bound (possibly covalently bonded).

## CONCLUSIONS

Bis(tributyltin) oxide reacts readily with D-glucuronic acid to form tributyltin D-glucuronate in $Me_2SO$ (Scheme 1). The $^{13}C$ NMR spectra clearly indicate that the tin is bound to the carboxyl group of the uronic acid. Positive- and negative-ion FABMS confirms the formation of the organotin glucuronate, and a tandem mass spectrometric experiment suggests that this compound is not just a loosely associated cluster. The $^{13}C$ NMR chemical shifts for the ring carbons of the tributyltin D-glucuronate when compared to D-glucuronic acid and the sodium salt indicate that the Sn also interacts, presumably through expansion of its octet with involvement of $d$-orbitals, with the hydroxyl group on C-4 and more weakly with an oxygen on C-1.

Tributyltin chloride does not react with D-glucuronic acid in $Me_2SO$-$d_6$ nor does trimethyltin chloride react with D-glucuronic acid in water. Apparently the equilibrium favors the uronic acid in reactions with organotin chlorides, but when two moles of uronic acid react with TBTO the equilibrium favors the tin uronate.

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