Carbohydrate Research 346 (2011) 203–209

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

ESIMS and NMR studies on the selective deprotection of acetylated glucosides by dibutyltin oxide

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ARTICLE INFO

Article history:
Received 24 September 2010
Received in revised form 16 November 2010
Accepted 17 November 2010
Available online 21 November 2010

Keywords:
Dibutyltin oxide
O-Deacylation
Glucosides
Reaction mechanism

ABSTRACT

The reaction process for the selective deprotection of acetylated glucosides by dibutyltin oxide in methanol is investigated by using methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside as a model substrate with ESIMS and NMR techniques. According to the results, it is inferred that at first, dimeric 1,3-dimethoxytetrabutyldistannoxane is formed by the reaction of dibutyltin oxide with methanol, and then the tetraorganodistannoxane reacts with the acetylated glucoside to produce glucoside–organotin complex intermediates. Finally, the complex intermediates are hydrolyzed leading to the free-OH glucoside and organotin acetate derivatives. The reaction is affected by neighboring group participation and steric hindrance, which allow for high selectivities among different acetyl groups in acetylated glucosides.

1. Introduction

Selective protection and deprotection of functional groups are of great importance in organic synthesis. Selective O-deacylation of carbohydrates under mild conditions is not only necessary for the synthesis of some natural glycosides but also is of great synthetic value, as the products thus prepared may have further synthetic utility as versatile intermediates. Various methods and deacylating reagents have been introduced for this purpose.[1–5] Organotin compounds have been introduced for selective acylation, alkylation, and oxidation to prepare intermediates for carbohydrate synthesis. Dibutyltin oxide (DBTO) in methanol has been used in the selective O-acylation of ribonucleosides and in microwave-mediated N-acylation of 1,2- and 1,3-amino alcohols.[6] Furlán et al. reported that the cleavage of carboxylic esters by DBTO was inefficient compared with other organotin compounds.[7] However, selective deacylation of esters of glycosyl units using DBTO as the catalyst in the synthesis of glycosides has been little studied from the reverse viewpoint. Our own previous work on the cleavage of *O*-acetyl groups with DBTO in methanol showed that DBTO is an active catalyst for deacetylation of glycosides under mild conditions, which allows a variety of functional groups to be tolerated and gives rise to high selectivities among the acetyl groups present on the glycosides.[8–11] Over the past decades, the development of mass spectrometry and NMR spectroscopy has revolutionized modern chemistry. Structure determination of a typical organic or organometallic compound with a molecular mass of up to ~3000 Da (natural products, drugs, organic derivatives, transition metal complexes, etc.) has become a routine task. The power of mass spectrometry in determining chemical composition has been successfully combined with establishing atomic connectivity (COSY, TOCSY, HSQC, and HMBC) and three-dimensional structural analysis (NOESY, ROESY, and coupling constants) by NMR spectroscopy. In spite of well-established experience in the structure determination of stable compounds, mechanistic studies and the nature of transient species are still the subjects of debates and questions. Most of the dedicated mechanistic investigations carried out so far have been done by either of the two methods. Getting chemically reliable and mutually consistent mechanistic data by both methods for chemical reactions studied under the same conditions until recently was quite rare and remained a challenging problem. The importance of the development of a proper methodology for such joint studies is unquestionable in order to facilitate the solution of long-standing mechanistic problems and achieve further progress in the development of organic synthesis.[12] As a further study on the mechanism of the reaction, this paper deals with the reaction on a model glucoside, methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (**1**), (Scheme 1) using MS and NMR technologies. Our interest was focused in two directions: (a) the reactivity comparison among different acetyl groups in the model glucoside, and (b) the characterization of the reactions involved between the 'catalyst' DBTO and the model glucoside.

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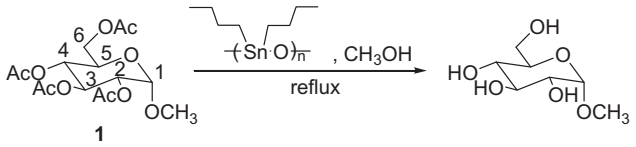
doi:10.1016/j.carres.2010.11.018



Scheme 1.

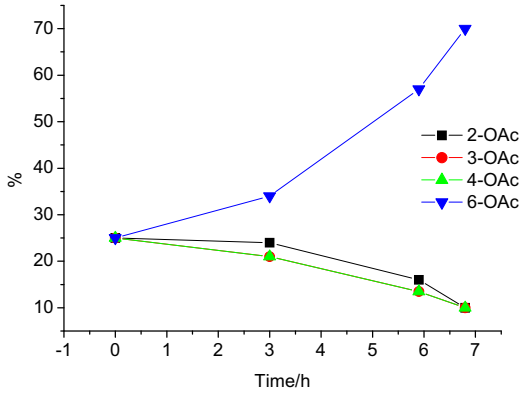


Figure 1. Relation between the percent of acetate and reaction time.

2. Results and discussion

2.1. Reaction of DBTO with model compound 1 in methanol-d_4 monitored by ^{1}H NMR spectroscopy

Survey spectra were obtained at intervals of 3, 6, 7, and 14 h, and the remaining 2-OAc, 3-OAc, 4-OAc, and 6-OAc groups in the substrate were quantified by integrating the 2-OAc resonances at 2.03 ppm, 3-OAc at 1.97 ppm, 4-OAc at 2.00 ppm, and 6-OAc at 2.05 ppm (Fig. 1). It is shown that: (a) 3-OAc and 4-OAc show the same reactivity, and (b) the reactivities of 3-OAc and 4-OAc are higher than that of 2-OAc, and the reactivities of 3-OAc, 4-OAc, and 2-OAc are much higher than that of 6-OAc.

2.2. ^{119}Sn NMR analyses of the reaction liquid of DBTO with compound 1

The ^{119}Sn NMR spectra for samples **2** and **3** exhibit several signals from −150 to −400 ppm relative to Me_4Sn (corrected values in the brackets in Table 1), suggesting that the crosslinks in the DBTO structure are disrupted and there are either five- or six-coordinate tin atoms in the samples.[13,14] The ^{119}Sn NMR spectrum for sample **2** exhibits three peaks in the field (−150, −175 ppm), and the expected sites are $Bu_2Sn[O]_3$, $Bu_2Sn[O]_2OH$, and $Bu_2Sn[O]_2OR$ corresponding to the unachieved hydrolysis and/or condensation reactions, while the two peaks at higher field (−175, −200 ppm) are assigned to $Bu_2SnO(OR)(OAc$ or $OR)$ according to the literature.[15] $Bu_2Sn[O]_2(OAc)$ is precluded since no resonance is found in the field (−200, −240 ppm). The ^{119}Sn NMR spectra for **2** consist of more than 91% pentacoordinated sites in the field (−150, −200 ppm) and 9% hexacoordinated sites in the field (−300, −400 ppm). The ^{119}Sn NMR spectra for **3** consist of more than 94% pentacoordinated sites and 6% hexacoordinated sites. It was therefore deduced that the intermediate species in the reaction may be, for the most part, five-coordinated tin atoms of $Bu_2Sn[O]_3$, $Bu_2Sn[O]_2OH$, $Bu_2Sn[O]_2OR$ along with a little $Bu_2SnO(OR)(OAc$ or $OR)$.

Table 1
^{119}Sn NMR data for samples **2**, and **3**[a]

Samples	δ
BBTO	−7.9 (82.4)
2	−249.5 (−159.2), −253.6 (−163.3), −256 (−165.7), −288.2 (−197.9), −290 (−199.7), −449.8 (−359.5)
3	−249 (−158.7), −254 (−163.76), −255.9 (−165.7), −259.9 (−169.7), −451.2 (−361)

[a] Experimental values (ppm) relative to external reference bis(tributyltin) oxide (BBTO) with corrected values relative to external reference Me_4Sn in parentheses (spectra are available on request).

2.3. MS, MS^2, and NMR analyses of the reaction of DBTO with methanol

According to reports in the literature,[16,17] the Sn–C bond and Sn–O bond are easily cleaved in the electrospray-ionization mass spectra (ESIMS) analysis of the organotin compounds. The MS for product **4** (Fig. 2a) shows an ion at m/z 319 with a relative abundance of 100% corresponding to $[CH_3O–Sn–O–Sn–OCH_3+H^+]$, an ion at m/z 347 with a relative abundance of 10% corresponding to $[CH_3O–H_2Sn–O–H_2Sn–OOH+Na^+]$, an ion at m/z 177 with a relative abundance of 18% corresponding to $[HO–Sn–OH+Na^+]$ by Sn–C bond and Sn–O bond cleavage. The mass data show that the $CH_3O–Bu_2Sn–O–Bu_2Sn–OCH_3$ group exists predominantly in product **4**.

By combining the ESIMS and NMR data (Supplementary data) for product **4**, the dimeric 1,3-dimethoxytetrabutyldistannoxane is considered as the main component (Scheme 2), which corresponds to the structure in report by Kohno et al.[18] It is a 'ladder-like' (entirely planar) or 'staircase' distannoxane, and the four tin atoms are pentacoordinated in two different ways (*endo* and *exo*).

2.4. Characterization of the intermediate species by MS and NMR spectroscopy

The ^{1}H NMR spectra for products **6** and **7** both present the resonances of both of the hydrogens of the glucoside group and those of the butyl groups. The signals due to the hydrogens of the glucoside group are shifted to a higher field when compared with the spectrum of compound **1**, which indicates that **6** and **7** should be the complexes of the glucoside and dimeric distannoxane (see Supplementary data for the ^{1}H NMR spectra of **6** and **7**).

The ^{1}H NMR spectrum for sample **8** presents the resonance regions of the $–CH_3$ hydrogens of $CH_3O–$, AcO–, and Bu– groups, respectively, centered at δ 3.34, 1.91, and 0.94 ppm, indicating that it contains $CH_3O–$, AcO–, and $Bu_2Sn–$ groups (see Supplementary data for the ^{1}H NMR spectrum of **8**). Quantitative analysis gives a relative proportion of 0.2:1:4.6 for the three areas. When compared with the spectrum for compound **1**, the signal due to AcO– (1.91 ppm) is shifted to a higher field by 0.1, which shows the bonding of the ester group and tin atom. The electrophilic inductive effect of the tin atom is lower than that of the carbon atom, causing the charge density of methyl protons in AcO– to increase, and the chemical shift to move toward the higher field. So, it is deduced that sample **8** is an organotin compound with some acetyl groups and traces methoxyl groups. Therefore, by the ^{1}H NMR results for samples **6**–**8**, it is reasonable that the acetylated glucoside organotin derivative intermediate is generated and finally is decomposed to the deprotected glucoside and organotin acetates.

ESIMS of sample **8** in methanol solution (Fig. 3a) showed a base peak at m/z 541, and after scanning the fragments at m/z 541, the product ion spectrum (Fig. 3b) showed ions at m/z 491, 427, 385, 311, 293, 256, 233, and 177, with relative abundances of 5%, 100%, 8%, 11%, 8%, 15%, 4%, and 5%, respectively. By combining these results with the MS results of catalytic entity **4**, the structure of the ion at m/z 541 and its fragments were determined as shown

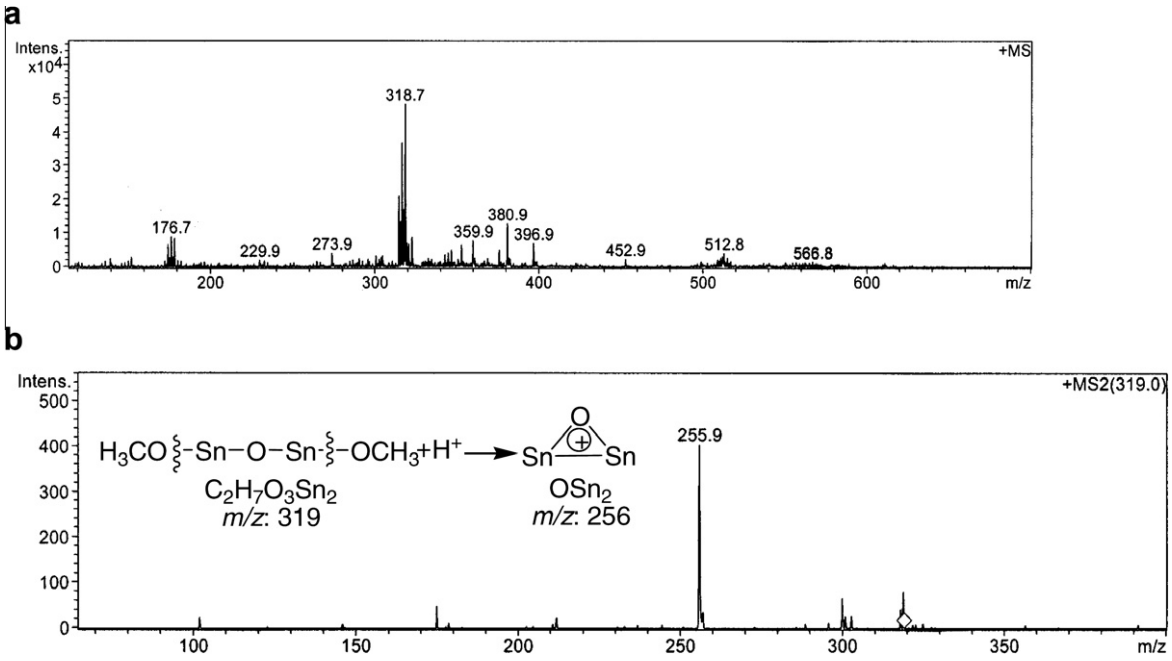
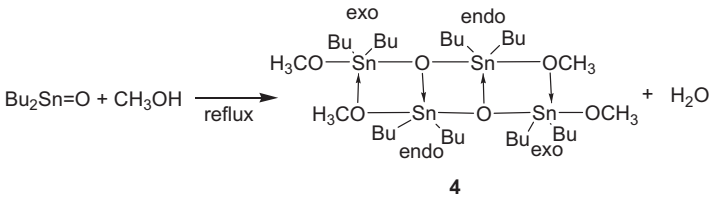


Figure 2. MS and MS^2 spectra of sample **4** in the positive-ion mode: (a) MS spectrum of sample **4**; (b) MS^2 fragmentation spectra of the ion at *m/z* 319.



Scheme 2.

in Scheme 3. Structural analysis of the other major ions shown in Figure 3a is also summarized in Scheme 3. It is deduced that organotin acetates, dimeric 1,3-dimethoxytetrabutyldistannoxane and its hydrolysis products are formed in the reaction process, which is consistent with the results of ^{119}Sn NMR analysis of the reaction mixture samples **2**–**3** (see Table 1).

ESIMS data of samples **4**–**8** in methanol solution are summarized in Table 2. The abundance of the ion at *m/z* 381 is the highest in sample **6**, followed by the ion at *m/z* 541. In sample **7**, the abundance of the ion at *m/z* 541 is the highest, followed by the ion at *m/z* 381. As for sample **8**, the abundance of the ion at *m/z* 541 is the highest, and that of *m/z* 381 is low. All of the three samples produce the ion at *m/z* 319 with abundances of 15%, 23%, and 11%, respectively. The structures of the ions at *m/z* 541, 381, and 319 are shown in Scheme 3. It is indicated that in the mid-term reaction, much $CH_3O–Bu_2Sn–O–Bu_2Sn–OH$ and some $CH_3O–Bu_2Sn–O–Bu_2Sn–OAc$ are generated. In the later reaction phase the content of $CH_3O–Bu_2Sn–O–Bu_2Sn–OAc$ has significantly increased, and by the end it exceeds that of $CH_3O–Bu_2Sn–O–Bu_2Sn–OH$. It is proposed that the intermediates that are mainly generated in the initial reaction are the organotin compounds with the $CH_3O–Bu_2Sn–O–Bu_2Sn–OCH_3$ structure. As the reaction proceeds, it gradually transforms products into organotin acetates, and synchronically the content of $CH_3O–Bu_2Sn–O–Bu_2Sn–OH$ formed by hydrolysis is also gradually increasing.

The ESIMS and the analysis results for the reaction solution sample **5** are shown in Figure 4 and Scheme 4. By comparison with the ESIMS spectra of samples **4** and **8**, the ions at *m/z* 217, 233, 259, 275, 385, and 401 should be due to carbohydrate products. According to the abundance of the ion at *m/z* 319 and 559 in sample **5**, the content of $CH_3O–Bu_2Sn–O–Bu_2Sn–OCH_3$ is significantly higher than that of $CH_3O–Bu_2Sn–O–Bu_2Sn–OAc$, which further confirms the supposition proposed in the previous context that the organotin compounds with $CH_3O–Bu_2Sn–O–Bu_2Sn–OCH_3$ structure are mainly generated in the initial reaction phase, and as the reaction progresses, products are gradually transformed into organotin acetates (a dimeric alkoxy, acyloxy distannoxane entity). The ions with low abundance related with the hydrolysis product of dimeric distannoxane ($CH_3O–Bu_2Sn–O–Bu_2Sn–OH$) are also found in the figure.

The ESIMS of sample **6** and analysis results of the mass spectra are shown in Figure 5 and Scheme 5. The ions related with the organotin complexes of carbohydrates further prove the generation of the intermediates with the $CH_3O–Bu_2Sn–O–Bu_2Sn–OCH_3$, $CH_3O–Bu_2Sn–O–Bu_2Sn–OAc$, and $CH_3O–Bu_2Sn–O–Bu_2Sn–OH$ structures. So it is supposed that in the reaction, DBTO first reacts with methanol to form **4**, then **4** reacts with **1** to form the carbohydrate organotin complexes, and the organotin complexes again react with the traces of water to generate the deprotected products.

2.5. Reaction process proposed for the selective deprotection of acetylated glucosides by DBTO

Based on the above NMR, MS, and MS^2 analysis results, it is inferred that the reaction is affected by neighboring group participation and steric hindrance. 3-OAc and 4-OAc, with the smallest

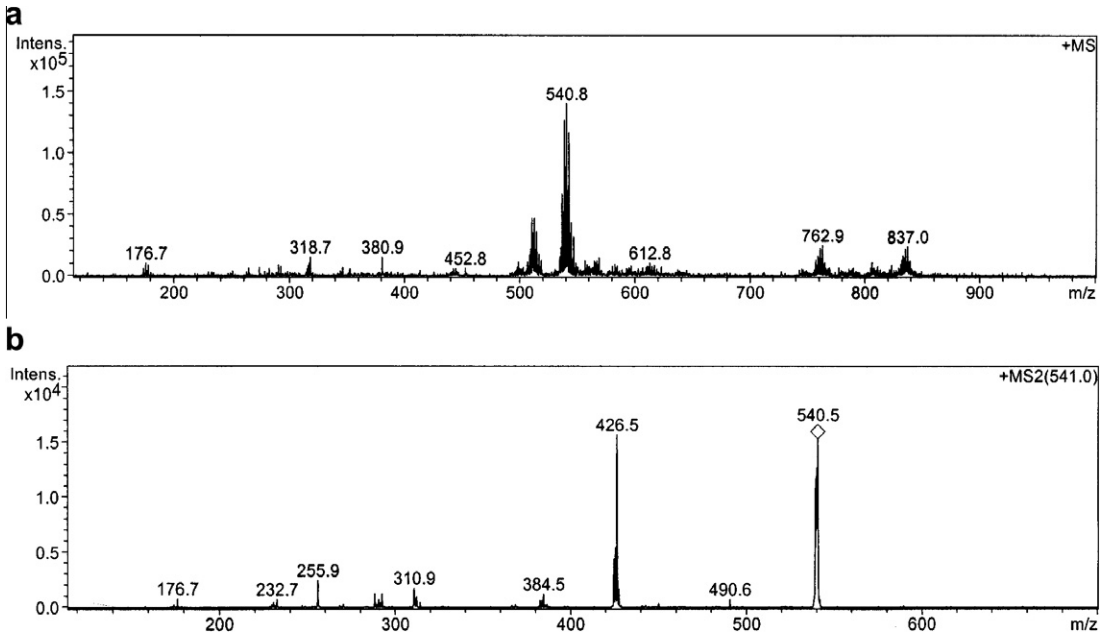
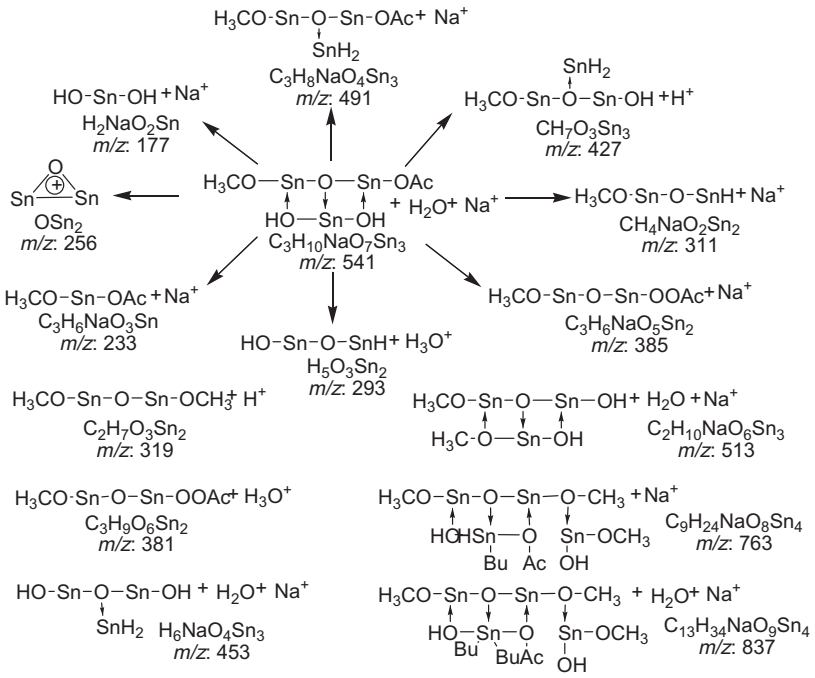


Figure 3. (a) ESIMS spectrum of sample **8**; (b) MS^2 fragmentation spectra of the ion at *m*/*z* 541.



Scheme 3.

Table 2
Main ions and their relative abundance for samples **4**–**8**[a]

Sample	Main ions
4	177(19), 319(100), 381(27), 397(14), 453(3), 513(8), 567(3)
5	217(100), 233(20), 259(47), 275(27), 319(37), 335(9), 385(12), 401(12), 411(9), 453(16), 495(13), 511(6), 559(7), 657(1)
6	319(15), 381(100), 453(28), 513(24), 541(42), 563(31), 589(33), 619(17), 635(16), 647(11), 663(11), 719(2)
7	179(21), 319(23), 381(68), 453(30), 512(44), 541(100), 563(23), 635(24), 763(50)
8	177(7), 319(11), 381(11), 453(2), 513(34), 541(100), 763(17), 837(17)

[a] *m*/*z* with relative abundance (%) in parentheses.

steric hindrance in the sugar and the most similar spatial positions, may follow the same reaction mechanism; 2-OAc and 6-AcO follow a different reaction mechanism from that of the 3-OAc and 4-OAc groups, and there is also a difference between 2-OAc and 6-OAc.

The O-deacylation pathways proposed for the 3-OAc and 4-OAc in compound **1** are shown in Scheme 6. The spatially adjacent and nucleophilic 3- and 4-carbonyl oxygens tend to simultaneously attack the same exocyclic tin atom with smaller steric hindrance present in compound **4**, giving rise to formation of the hexacoordinated sites via an Sn←O bond cleavage (see complex **I**). The coordination of the carbonyl oxygen to the neighboring tin site results in increased electropositivity of the carbonyl carbon, so it is more

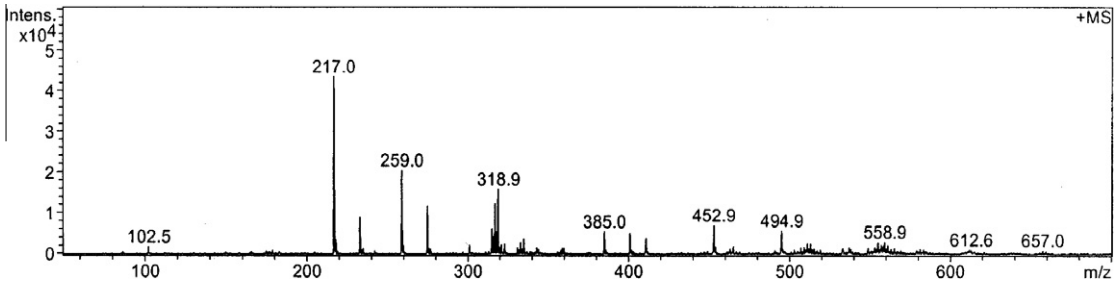
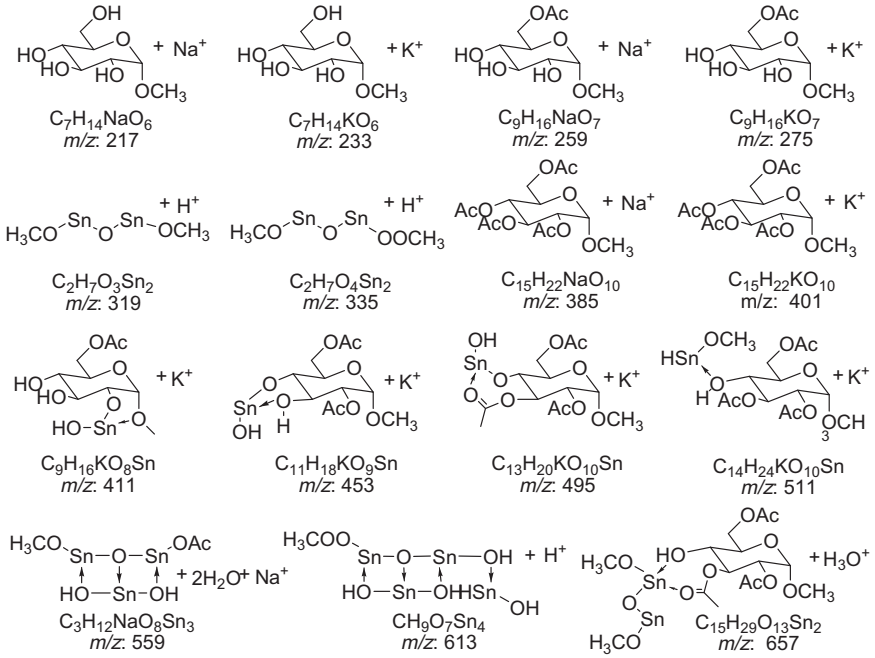


Figure 4. ESIMS spectrum of sample **5**.



Scheme 4.

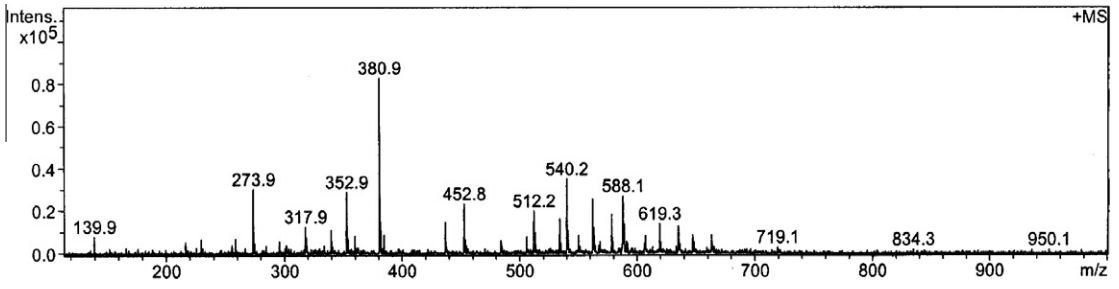


Figure 5. ESIMS spectrum of sample **6**.

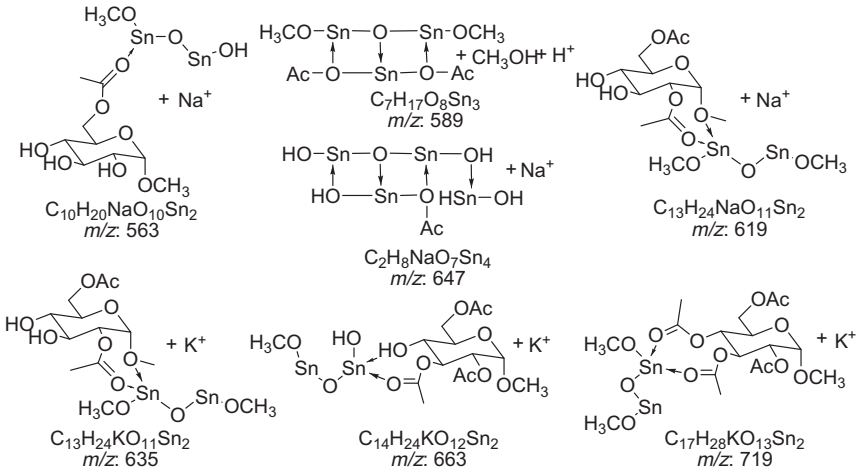
vulnerable to nucleophilic attack. The tin atom and oxygen atom of the other one molecular **4** subsequently attack the alkoxy oxygen and carbonyl carbon of 4-OAc or 3-OAc of the carbohydrate, respectively, resulting in the formation of a carbohydrate organotin complex **II** or **III** through the acyl–oxygen bond cleavage of 4-OAc or 3-OAc, and the Sn–O bond cleavage of compound **4**. Thereafter the complex **II** or **III** is hydrolyzed into the 4-deacetylated carbohydrate **IV**, **V** and organotin acetate **VI**.

In the deprotection process for the 2-OAc group, the methoxy oxygen at the ortho position may participate in the coordination of the tin atom, giving rise to the formation of complex **VII** (Scheme 7), a process that also accelerates the deprotection reaction of the 2-OAc group, but the intensity of action is less than that for the 3-OAc and 4-OAc positions, so its reaction rate is lower. And 6-OAc, having no spatially adjacent group (Scheme 7, **VIII**), cannot participate in the coordination of the tin atom together with the ortho-group of the bonding radical of the tin atom, so its reaction rate is much lower than that of 3-OAc, 4-OAc, and 2-OAc.

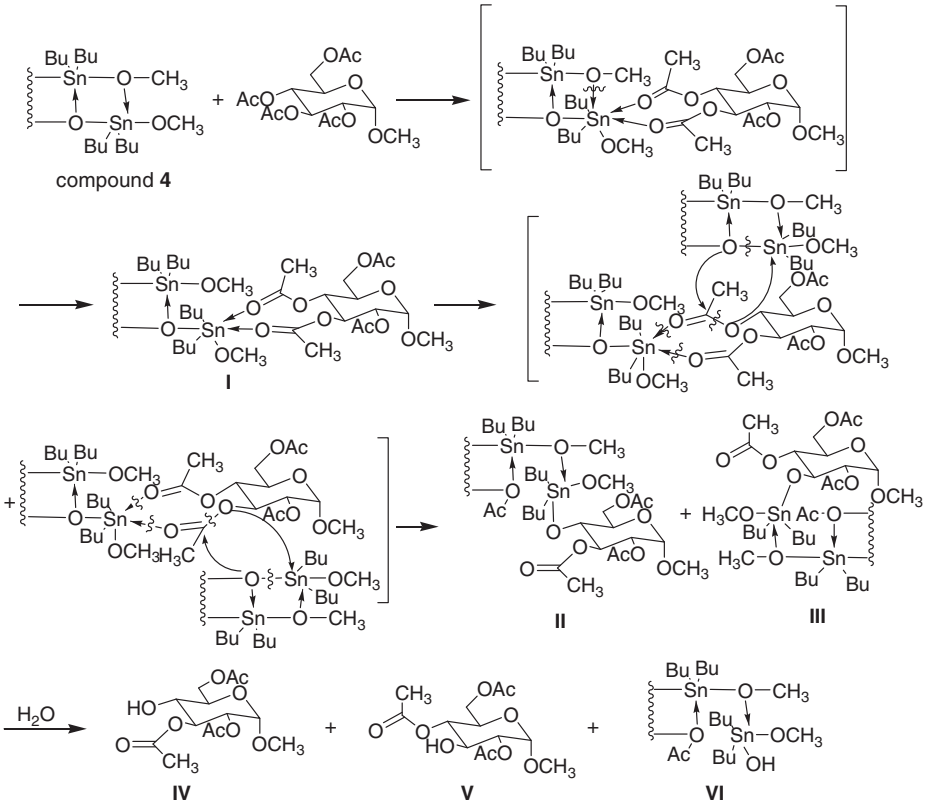
3. Experimental

3.1. General methods

Compound **1** and DBTO were commercial products and were used without purification. MeOH-d_4 was from E. Merck. All solvents and reagents were of analytical grade and were dried by

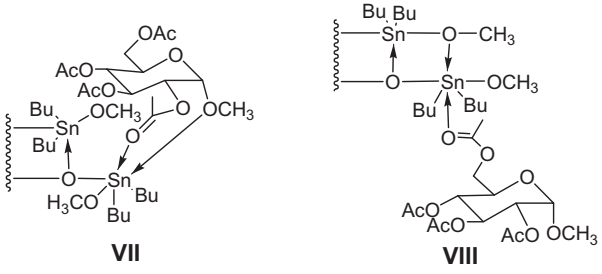


Scheme 5.



Scheme 6.

standard procedures. Reactions were monitored by TLC on silica gel (TLC, Qingdao, China), using 1:1 ethyl acetate/cyclohexanone mixtures and detected by charring with sulfuric acid. ESIMS was carried out on a Bruker Esquire 3000 mass spectrometer. Survey spectra including ^{1}H NMR, ^{13}C NMR, homonuclear correlation (COSY), heteronuclear single quantum coherence spectra (HSQC), heteronuclear multiple bond correlation spectra (HMBC) and DEPT were obtained on a Bruker DPX-400 instrument with Me_4Si as the internal standard. The chemical shifts are reported in ppm downfield from Me_4Si. ^{119}Sn NMR spectra were recorded on a Bruker DPX-400 spectrometer operating at 149.2 MHz from −2000 to 2500 ppm with an external reference of BBTO (−7.87 ppm).



Scheme 7.

3.2. Reaction of DBTO with model compound 1 in MeOH-d_4

DBTO (16 μmol), **1** (17 μmol), and MeOH-d_4 (2 mL) were added to an NMR tube, and then the tube was sealed by fusing in air. The tube was heated in a water bath at 66 °C, and the reaction was monitored by 400 MHz ^{1}H NMR spectroscopy.

3.3. Reaction of DBTO with model compound 1 in MeOH

Equimolar amounts of DBTO (0.6 mmol) and **1** were heated under reflux in dry MeOH (30 mL) until **1** disappeared as determined by TLC monitoring (about 130 min). Aliquots (5 mL) of the reaction mixtures were taken at 75 min and at the end of the reaction. Then most of the solvent was removed under reduced pressure to give the residue mixtures **2** and **3** (each about 0.5 mL). $CDCl_3$ was added to the residue mixtures, and ^{119}Sn NMR spectra were obtained at room temperature.

Equimolar amounts of DBTO (0.6 mmol) and **1** were heated under reflux in 30 mL of dry MeOH, and 10-mL aliquots of the clear reaction solutions were taken at intervals of 30, 55, and 80 min, respectively (35%, 55% and 90% conversion as determined by TLC monitoring). The reaction sample for 30 min was analyzed as sample **5**. The reaction solutions for 55 and 80 min were cooled to room temperature, and transparent needle-like crystals crystallized out. After washing with MeOH and drying overnight under reduced pressure at 35 °C, products **6** and **7** were obtained. The ^{1}H NMR spectra and ESIMS determination of **6** and **7** were then carried out.

3.4. Reaction of DBTO with MeOH

DBTO (0.6 mmol) and 30 mL of dry MeOH were mixed, and the mixture was stirred and boiled under reflux until the suspension of DBTO disappeared. After cooling, transparent needle-like crystals of **4** were obtained. The ^{1}H NMR and ^{119}Sn NMR spectra characterization and ESIMS determination of **4** were then carried out.

3.5. Reaction of DBTO with 2′,3′,4′,6′,2″,3″,4″,6″-octa-*O*-acetyl-3,19-di-*O*-β-D-glucopyranosylandrographolide in MeOH

A control experiment was made with the deacetylation of 2′,3′,4′,6′,2″,3″,4″,6″-octa-*O*-acetyl-3,19-di-*O*-β-D-glucopyranosylandrographolide (0.6 mmol) to give 3,19-di-*O*-β-D-glucopyranosylandrographolide by equimolar amount of DBTO under reflux in 30 mL of dry MeOH for 16 h.[11] At a later point in the reaction, white solid precipitated out from the clear reaction solution. The precipitated product was isolated by filtration and dried at the end of the reaction, and a solid white power (**8**) was obtained and analyzed using NMR and ESIMS.

4. Conclusions

It is deduced that it is the dimeric 1,3-dimethoxytetrabutyldistannoxane is produced at first by the reaction of DBTO with MeOH, then the tetraorganodistannoxane reacts with the acetylated glucoside to produce glucoside organotin complex intermediates. Finally, the complex intermediates are hydrolyzed easily, which leads to the free-OH glucoside and organotin acetate derivatives. It is the neighboring group participation that accelerates the deprotection of the 3-OAc, 4-OAc, and 2-OAc groups, and the intensity of action of the 2-OAc group is less than that of the 3-OAc and 4-OAc positions. Because of the lack of neighboring group participation, the reaction rate of the 6-OAc is much lower than that of the 3-OAc, 4-OAc, and 2-OAc groups. So, the acetyl groups of the sugar moieties of glucosides can be selectively cleaved by adjusting the reaction time, temperature, or solvent as in our previous studies.[8,9]

Acknowledgments

This research was supported by the National Natural Science Foundation of China (No. 20272054) and the Natural Science Foundation of Henan Province (No. 0111030300).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2010.11.018.

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