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STRUCTURAL ANALYSIS OF THE CONDENSATION PRODUCTS OF XYLAN WITH ORGANOTIN HALIDES

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ABSTRACT

Physical characterization of the products resulting from condensation of xylan with organostannanes halides is consistent with a tin-modified product. Results from elemental analysis shows the presence of tin consistent with the presence of the tin moiety. Results from control reactions are consistent with the product containing portions derived from both reactants. The presence of the Sn—O—R ether linkage is found by infrared spectroscopy. The presence of portions derived from both reactants is indicated by mass and infrared spectral results.

INTRODUCTION

Because the ready sources of feedstocks, such as coal and petroleum-based compounds, are being consumed at a faster rate than they are being discovered, there is a need for developing alternate renewable feedstocks. Polysaccharides, the most abundant class of naturally occurring organic compounds, represent one such readily available natural feedstock. Saccharides constitute three-

fourths of the dry weight of the plant world and are widely distributed in both plants and animals.

We previously reported on the modification of dextran with organostannane halides and titanocene dichloride (see, e.g., Refs. 1-5). Dextrans, branched storage polysaccharides of *D*-glucose connected mainly through the 1-6 sites, are primarily found in yeast and bacteria.

Xylans are components of plant cell walls. They mainly consist of 1,4-*D*-xylopyranose units. The chains, which may be linear or contain a few branches, are, along with cellulose, believed to exhibit a helical conformation. Woods generally contain about 10-25% dry weight of xylans. Annual plants, such as corn cobs, soybean stalks, and wheat straw, contain 25-35% xylan. Xylans are typically soluble in alkaline solutions. Similar to dextrans, and unlike celluloses, some xylans are also soluble in water. Xylans are composed of xylopyranose units that contain two hydroxyls per unit, whereas polysaccharides of *D*-glucose contain three hydroxyls per hexose unit.

Here we report the initial modification of xylan through condensation with organostannane halides. Our purposes in this study include the following. First, as noted above, xylans constitute a major renewable resource which is largely untapped, though they are employed in the production of furfural. Second, we have previously reacted organostannane halides with sugar to give products such that a major fraction was soluble, while the dextran-modified products are insoluble [1-6]. It is possible that the reaction with xylans may also give products that show some solubility since they have fewer hydroxyls per repeat unit. Further, the two hydroxyls are adjacent, which may encourage cyclization with the dihalostannanes rather than crosslinking. Third, information gained from such studies should allow a better understanding of the reaction dependencies involved in the use of natural polyhydroxylic materials as feedstocks in the production of useful materials. For instance, the analogous dextran and sugar materials modified through condensation with organostannane halides inhibit a wide variety of rot- and mildew-causing organisms (see, e.g., Ref. 7).

EXPERIMENTAL

Xylan (molecular weight 23 000-25 000 from larchwood; Sigma Chemical Co., U.S.A.), dibutyltin dichloride, tributyltin chloride, triphenyltin chloride, and triethylamine (Wako Pure Chemical Industries, Japan) were employed as received (from Tokyo Kasei Kogyo Co., Japan) unless otherwise noted.

Reactions were conducted in a one-quart Kimex emulsifying jar placed

upon a Waring Blendor (Model 7011G) with a "no-load" stirring rate of 20 000 rpm. The product was obtained as a precipitate by suction filtration. Repeated washings with water and organic liquids assisted in the purification of the product.

Infrared spectra were obtained by using Hitachi 260-10 and 270-30 spectrometers and a Digilab FTS-IMX FT-IR. The EI (70 eV) and CI (isobutane) mass spectra were obtained with a JEOL JMS-D300 GC mass spectrophotometer connected to a JAI JHP-2 Curie-Point Pyrolyzer (injector temperature 250°C; pyrolyzer temperature 590°C). Analysis for tin was carried out by the usual wet analysis procedures.

RESULTS AND DISCUSSION

The condensation of xylan with various organostannane halides results in the production of tin-containing products (Table 1). This paper presents the initial synthesis of these products and details their structural identification. It is reasonable to assume that the actual structure will vary from chain to chain, each chain composed of a mixture of modified and unmodified xylopyranose units such as depicted in Fig. 1.

Historical

As noted in the Introduction, analogous condensations, except for the use of cellulose and dextran, have been reported [1-5]. Further, the condensation of organostannane halides with xylan can be considered an extension of condensations involving poly(vinyl alcohol) [8-11].

Control Reactions

The term "control reaction" describes reaction sequences conducted in the usual manner except for omission of one of the reactants. For instance, in the modification of xylan through reaction with dibutyltin dichloride, these reaction sequences are carried except for the omission of one of the reactants. Neither reaction attempt produced precipitate, yet, when both reactants are present, a white precipitate is formed. This is consistent with the precipitate-containing components derived from both reactants.

TABLE 1. Results as a Function of Organostannane Halide^a

Organostannane	Amount of stannane, mmol	Yield		Sn, %
		g	%	
Bu ₂ SnCl ₂	4.00	0.43	58	11.6
Bu ₂ SnCl ₂	5.00	0.33	45	8.4
Ph ₃ SnCl	4.00	0.66	69	14.1
Ph ₃ SnCl	5.00	0.54	56	16.2
Bu ₃ SnCl	4.00	0.19	23	8.1
Bu ₃ SnCl	5.00	0.59	70	7.5

^aReaction conditions: Xylan (2.00 mmol) and triethylamine (4.00 mmol) dissolved in 50 mL water were added to stirred solutions containing organostannane chloride dissolved in 30 mL CCl₄ at 25°C with a stirring time of 60 s.

Mass Spectrophotometry

The four major ion fragments derived from xylan itself are given in Table 2 along with the relative ion abundances for the product derived from triphenyltin chloride. A good match exists. Similar comparative ion fragment comparisons are not valid for most aliphatic organostannanes since the ion fragmentation of most aliphatic hydrocarbons also produces fragments at these masses.

For the condensation product of triphenyltin chloride and xylan (Tables 3 and 4), ion fragments assigned to the presence of the phenyl moiety are present at 78 (most abundant ion), 51, 52, 77, 50, 39, 76, and 38 (given in descending order of abundance). Ion fragments at 114-117 are assigned to the ring xylopyranose moiety and/or the xylopyranose repeat unit minus one hydroxyl group. The presence of ion fragments at 96-98 is consistent with the presence of this repeat unit minus an additional oxygen and/or hydroxyl group, and ion fragments at 80-82 are assigned to the xylopyranose ring itself.

Absence of an ion fragment at 35 indicates the absence of the chloride ion, consistent with the absence of unreacted Sn-Cl moieties or chloride salts of triethylamine. It is also consistent with the product-purification process being satisfactory. The absence of an ion fragment at 86 is consistent with the absence of the triethylamine moiety.

The absence of ion fragments near 196, 272, and 348 indicates the absence

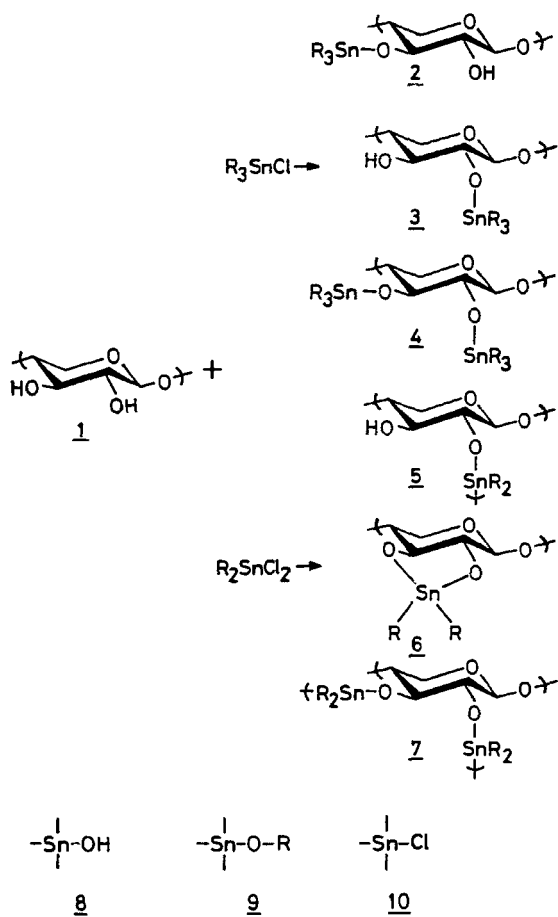


FIG. 1. Possible repeat unit structures for the condensation of xylan with mono- and dichloroorganostannanes.

TABLE 2. Abundance^a of Major Ion Fragments (relative abundances of 1% and greater) of Xylan and the Condensation Product of Xylan and Triphenyltin Chloride

	m/e			
	44	28	43	27
Xylan	100	33	33	17
ϕ_3Sn -xylan	100	32	22	15

^aRelative abundance based on m/e 44 = 100.

TABLE 3. Ion Fragments for the Condensation Product of Xylan and Triphenyltin Chloride (relative ion fragments of 1% and greater)

m/e	% Abundance	Molecular formula of ion fragment	Derived from
26	1.2	C ₂ H ₂	Xy, ϕ
27	1.9	C ₂ H ₃	Xy
28	1.2	CO	Xy
37	1.0	C ₃ H	ϕ
38	1.9	C ₃ H ₂	
39	4.2	C ₃ H ₃	Xy, ϕ
41	1.7	C ₂ HO	Xy
44	3.9	CO ₂	Xy
49	1.1		
50	6.7	C ₄ H ₂	ϕ
51	7.8	C ₄ H ₃	ϕ
52	7.2	C ₄ H ₄	ϕ
63	1.4	C ₅ H ₃	ϕ
74	2.0	C ₆ H ₃	ϕ
76	1.7	C ₆ H ₄	ϕ
77	7	C ₆ H ₅	ϕ
78	37.7	C ₆ H ₆	ϕ
79	2.7	C ₆ H ₇	ϕ

of evolved organotin-containing moieties. There are seven (significant; >1%) naturally occurring isotopes of tin (Table 5). While there are ion fragments that correspond to most of these isotopes, the relative abundances are not consistent with the presence of tin as an evolved product. The absence of tin-associated evolved fragments is consistent with previous studies (see, e.g., Refs. 3, 7, 12) where tin remains as part of the residue. This is advantageous

TABLE 4. Ion Abundance Relationship for the Condensation Product of Xylan and Triphenyltin Chloride

m/e	Expected	Found
78	100	100
51	20	21
52	20	19
50	18	18
39	14	11
77	14	19
79	6	7
76	6	5
74	5	5
37	5	3
26	4	3
63	3	4
27	3	3

TABLE 5. Standard Relative Isotopic Abundance of Tin and Tin-Associated Ion Fragments

	m/z						
	120	118	116	119	117	124	122
Tin	100	73	42	27	21	18	15
Product from Ph_3Sn	100	127	92	88	113	88	0
Product from Bu_3Sn	100	70	30	145	70	0	30
Product from Bu_2Sn	100	83	26	155	103	14	16

TABLE 6. Ion Fragments Derived from the Condensation Product of Xylan and Dibutyltin Dichloride

m/e	% Abundance	Molecular formula of ion fragment	Derived from
26	3.9	C ₂ H ₂	Xy
27	9.7	C ₂ H ₃	Bu, Xy
28	8.9	CO	Xy
29	6.7	COH, C ₂ H ₅	Bu, Xy
38	1.0	C ₃ H ₂	Bu
39	7.2	C ₃ H ₃	Bu, Xy
40	1.2	C ₃ H ₄	Bu
41	14	C ₃ H ₅ , C ₂ HO	Bu, Xy
42	3.2	C ₃ H ₆	Bu
43	11	C ₂ H ₃ O, C ₃ H ₇	Bu, Xy
44	7.2	CO ₂ , C ₂ H ₄ O	Xy
53	1.1	C ₄ H ₆	Bu
55	3.5	C ₇ H ₇	Bu
56	4.6	C ₈ H ₈	Bu
57	1.3	C ₇ H ₉	Bu
58	1.6	C ₄ H ₁₀	Bu

in applications where tin-containing materials are employed in large amounts (such as industrial insulation) where fire may be a hazard.

The condensation product from tributyltin chloride and xylan gives ion fragments at 58, 57, 43, 41, 39, 29, 27, and 15, characteristic of the butyl moiety. Again, ion fragments about 116, 96, and 81 are consistent with the presence of the xylopyranose unit. The absence of an ion fragment at 35 is consistent with the absence of the chloride ion. The absence of an ion fragment at 86 is consistent with the absence of the triethylamine moiety. The absence of ion fragments near 176, 233, and 290 is consistent with the ab-

sence of evolved organotin fragments. Again, while ion fragments are present about 120, the relative abundances are not consistent with the presence of tin as an evolved product.

The product from dibutyltin dichloride and xylan (Table 6) also gives ion fragments at 58, 57, 43, 41, 39, 27, and 15, characteristic of the butyl moiety. Ion fragments about 116, 96, and 81 are consistent with the presence of the xylopyranose unit. Again, the absence of the chloride ion, triethylamine, evolved organotin fragments, and tin is indicated.

Infrared Spectroscopy

Analysis of the infrared spectra of the products is consistent with the xylan being modified through formation of Sn–O–R ether linkages through condensation of the stannane at xylopyranose hydroxyl sites. Formation of the ether linkage is indicated by the presence of new bands between 660 and 690 (all band assignments are given in wavenumbers, cm^{-1}), which are characteristic of the asymmetric stretch of tin ethers, and a band(s) in the region of 550 to 600, attributed to the symmetric stretch of tin ethers (Table 7).

Bands characteristic of the organotin moiety are present. For instance, the products from dibutyltin dichloride and tributyltin chloride exhibit bands characteristic of methylene deformation near 1460 (1460 for Bu_2SnCl_2 , 1465 for Bu_3SnCl) and 1160; bands characteristic of the methyl group are present at 1420 (asymmetric stretching) and 1380 (symmetric stretching); a quartet of bands characteristic of the C–H stretch in *n*-butyl groups are present at 2850, 2870, 2920, and 2965. Bands attributed to the symmetric C–O stretching are present at 1010, 880, and 870, and bands attributed to asymmetric C–O stretching are present at near 1075 (1070 for Bu_2SnCl_2 , 1080 for Bu_3SnCl). A broad band centering around 3450 is attributed to the presence of unreacted hydroxyl groups. Bands characteristic of the presence of moieties derived from triethylamine are absent.

TABLE 7. Positions of Sn–O–R Associated Bands as a Function of Organostannane Used

Stannane moiety	Sn–O–R asymmetric stretch	Sn–O–R symmetric stretch
Bu_2Sn	685	600
Bu_3Sn	680	570
Ph_3Sn	660	570

The product derived from triphenyltin chloride and xylan exhibits a sharp, intense band at 1435 characteristic of Sn–Ph stretching. Bands at 700 and 725 are characteristic of C–H out-of-plane deformation for monosubstituted benzene. Bands at 3000–3070 are characteristic of C–H stretching from the phenyl groups, and those at 2850–2950 are characteristic of C–H stretching from the C–H groups in the xylopyranose. A broad band centering about 3450 is attributed to the presence of unreacted hydroxyl groups. Weak overtone bands characteristic of the phenyl groups are found centering about 1960, 1890, and 1820. Bands characteristic of the symmetric C–O stretching are present at 1005 and 860, and bands attributed to asymmetric C–O stretching are present at 1080.

In summary, infrared spectral results are consistent with the presence of tin ether groups, giving the products depicted in Fig. 1.

Solubility

The products from xylan and the monohaloorganostannanes are soluble in dipolar solvents such as DMSO. This is similar to the analogous products derived from cellulose and dextran through reaction with monochlorostannanes. However, the products from dibutyltin dichloride are also soluble in DMSO, unlike the analogous products derived from cellulose and dextran, but similar to the results derived from the reaction of sucrose with dihaloorganostannanes where major portions (typically 50–80 wt%) of the products are soluble in DMSO (e.g., **6** in Fig. 1).

The difference in solubility is probably due in part to the number of available hydroxyl groups present in each saccharide unit. Cellulose and dextran both have three hydroxyls per unit, while xylan has two hydroxyls per unit. Further, the two hydroxyls per unit present in the xylan are on adjacent carbons and may lead to a majority of the substituted units containing cyclized stannanes, such as pictured in **6**. Also, the extent of substitution is lower for the xylan products (roughly one stannane per three xylopyranose units) compared with the analogous products derived from dextran (typically one stannane per hexose unit; see, e.g., Refs. 1–4).

End Groups

There exist three possible organostannane structures. The presence of a major fraction of **10** can be discounted, based on mass spectral evidence, due to the lack of ion fragments characteristic of the chloride ion. The OH stretch in Sn–OH moieties can overlap the OH stretch present in the xylan itself. The shape and position of the band centering about 3500 cm^{-1} for the products correspond to that observed for xylan itself. Even so, the Sn–OH stretch also

centers about 3450 cm^{-1} so that little can be confidently concluded based on the present spectral evidence.

In fact, as previously noted, the majority of the stannane may be present as part of a five-membered ring as depicted in **6** for products derived from dichloroorganostannanes. Szmant and coworkers (see, e.g.; Ref. 13) reported that the preference for the formation of the five-membered stannylene ring by hexopyranosides is probably due to a favorable semiequatorial conformation of the *gem*-dibutyl groups. Additional reports relating the formation of cyclic organostannane ethers are given in Refs. 14-19.

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