Its infrared spectrum was strikingly similar to that of II, except for an 807 cm.$^{-1}$ peak in III, absent in II. The 886 cm.$^{-1}$ band may be due to the C_1–H absorption of β-D-glucopyranose.[31] Hydrolysis of III (5 mg.) in 3 ml. of *N* sulfuric acid and subsequent paper chromatography of the hydrolyzate showed D-glucose and 2-amino-2-deoxy-D-galactose (D-galactosamine).

To determine the alkali stability of III, an amount of 5 mg. of III was treated with 1 ml. of 0.04 *N* sodium carbonate for 2 hr. at room temperature and the mixture was analyzed paper chromatographically. Aside from III, D-glucose and a Morgan–Elson[10] reactive sugar ($R_{glucose}$ 1.8), "anhydro-*N*-acetyl-D-galactosamine,"[11] different from 2-acetamido-2-deoxy-D-galactose ($R_{glucose}$ 1.2), were detected.

An amount of 100 mg. of III in 5 ml. of 50% methanol was added in portions, with stirring, to a solution of 40 mg. of sodium borohydride in 5 ml. of 0.1 *M* borate buffer (*p*H 8) at 0°. The mixture was stirred at 0° for 2 hr., an additional hr. at room temperature and acidified to *p*H 5 with acetic acid and passed through a column (100 × 13 mm., diam.) of mixed-bed resin (Amberlite MB-3[37]). A hygroscopic sirup was obtained after carbon[35] (Nuchar C unground[36]) column purification and solvent removal under reduced pressure; yield 60 mg. This product was found to be chromatographically identical, with three developers, to sirupy 3-*O*-β-D-glucopyranosyl-2-acetamido-2-deoxy-D-galactitol (IV) prepared from authentic chondrosine according to Davidson and Meyer.[4] The principal and non-reducing spot ($R_{glucose}$ 0.76) was unreactive to aniline hydrogen phthalate,[41] but was reactive to the alkaline silver nitrate[33] and (purple) to the Elson–Morgan[9,32] indicators. Traces of D-glucitol ($R_{glucose}$ 1.0) and Morgan–Elson[10] reactive "anhydro-*N*-acetyl-D-galactosaminol," ($R_{glucose}$ 1.8) also were detected, with alkaline silver nitrate,[33] in both preparations.

Besides IV and "anhydro-*N*-acetyl-D-galactosaminol,"[11] 2-acetamido-2-deoxy-D-glucitol[23] (*N*-acetyl-D-glucosaminol) also gave the characteristic purple color of the Morgan–Elson[10] reaction with the reagent.[32]

Characterization of 3-*O*-(Methyl Tri-*O*-acetyl-β-D-glucopyranosyluronate)-2-acetamido-tetra-*O*-acetyl-2-deoxy-D-galactitol (V).[42]—Substance V[17,18] gave a positive uronic acid assay[29] and a negative Elson–Morgan[9,43] reaction.

(41) S. M. Partridge, *Nature*, **164**, 443 (1949).

(42) Experimental work by Mr. J. N. Schumacher.

(43) J. W. Palmer, Elizabeth M. Smyth and K. Meyer, *J. Biol. Chem.*, **119**, 491 (1937).

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[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY]

The Reaction of Spruce Lignin with *t*-Butyl Hypochlorite; A Study of the Accessibility of Lignin in Wood

BY JUNZO NAKANO AND CONRAD SCHUERCH

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The reaction of spruce lignin with *t*-butyl hypochlorite has been studied at 30° in a series of fourteen organic liquids of moderate to poor solvent power for isolated lignins. The reaction on the model compounds ethylguaiacol and vanillyl alcohol is complete at the stage of disubstitution in about five hours, with the exception of ethylguaiacol in carbon tetrachloride. Some simultaneous oxidation of the phenols and direct or induced decomposition of the hypochlorite occurs. The reaction on lignin in wood proceeds similarly, with some simultaneous demethylation; however, the extent and rate of reaction is controlled by the solvent power of the liquid for lignin. Poor solvents do not permit any significant reaction, while reaction in fair solvents is approximately as fast as that of vanillyl alcohol. The accessibility of lignin in wood is affected by solvent–polymer interaction in the same manner as solubility phenomena in isolated lignins.

In any chemical reaction upon a solid polymer, the degree to which the polymer molecules are accessible to the reactant determines the homogeneity and extent of the reaction. The formation of derivatives from cellulose has been especially thoroughly studied with this problem in mind[1] and it has been well demonstrated that the only important difference between reactions on cellulose and on low molecular weight analogs is related to the difficulty of making the entire supermolecular structure equally accessible to reagents. At best, one expects that a reaction on a solid polymer will proceed to completion in a bad solvent at a greatly reduced rate and that frequently the reaction will not go to completion at all.

There are a variety of technically and scientifically important chemical processes to which wood is subjected which are essentially reactions of lignin. These include pulping in aqueous and organic solvent systems, bleaching and defibering reactions, and holocellulose preparation; yet to our knowledge, there is no systematic study of the accessibility of lignin reported. It is, therefore, not clear whether these reactions proceed from the surface of the lignin or throughout the polymer matrix. To what extent do bleaching and holocellulose preparation, for example, actually require sequential chemical changes in multiple cleavage and extraction steps and to what extent do these reactions merely require the repeated exposure of fresh surface of the lignin? It is possible that the accessibility of lignin has attracted little attention because lignin is a relatively amorphous polymer and entering reagents do not have to overcome crystal lattice forces. Nevertheless, the amorphous regions of cellulose are not accessible to reagents dissolved in ethyl ether and one would not attempt to determine unsaturation in rubber particles suspended in an aqueous reagent. However, some reactions on lignin are carried out with as little thought of solubility considerations.

It is necessary to distinguish between penetration or permeation of wood with a solvent and the problem of accessibility. In large pieces of wood, it is not always a simple matter to fill all voids and wet all internal surfaces with liquid. This is a matter of penetration or permeation, and is primarily a problem of transferring air out of and liquid into the voids in the cellular structures. This exchange is not difficult in small particle size woodmeal. The accessibility of lignin or cellulose, however, is determined by solvent–polymer interaction when the polymer is thoroughly wet and essentially at equilibrium. This is the problem studied here.

(1) H. M. Spurlin in "Cellulose and Cellulose Derivatives," by E. Ott, H. M. Spurlin and M. W. Grafflin, Vol. II, Interscience Publishers, Inc., New York, N. Y., 1954, p. 673.

TABLE I

RATE OF DECOMPOSITION OF *t*-BUTYL HYPOCHLORITE IN ORGANIC SOLVENTS[a]

Solvent / Time, min.	Decomposed, % 10	20	30	40	60	90	120	180	240	300
Chloroform				0[b]	22.3	66.2	83.1			
Dioxane					44.2	54.9	70.1	81.3	83.9	86.6
Ethylene glycol	52.3	96.6								
Ethylene glycol monoethyl ether		43.0	60.8	95.5						
Ethylene glycol dimethyl ether					5.9		12.1		25.0	31.5
Acrylonitrile					9.8		16.3	22.2		33.7
Acetonitrile					4.0		8.1	12.2	16.1	20.5
Nitromethane					2.6		5.2		12.0	15.4

[a] Conditions: 1 ml. of *t*-butyl hypochlorite, 50 ml. of solvent, 30 ~ 30.3°. [b] Induction period observed.

The accessibility of cellulose is customarily determined by measuring the rate of a particular reaction and the extent to which it proceeds in a particular solvent system. Ideally, to measure the accessibility of lignin in wood, one should use a reaction which is specific for lignin, proceeds to a definite end-point, does not break covalent network bonds, has little effect on the polymer solvent interaction, and is identical in mechanism and course when carried out in a variety of solvents. A monosubstitution reaction on the aromatic rings therefore appears most appropriate and the phenol substitution reaction of *t*-butyl hypochlorite[2,3] was explored as a possible measure of accessibility of lignin in wood.

Preliminary experiments showed that *t*-butyl hypochlorite dissolved in ethyl acetate chlorinated wood but did not react with Whatman cellulose powder, birch xylan, dextrose or xylose at 30°. Chlorination of wood was therefore restricted to the lignin fraction. A series of experiments was then carried out to test the rate of decomposition of the hypochlorite in various organic solvents and the rates and extent of its reaction with model phenols in various solvents.

The rate of decomposition as followed by iodometry was too rapid at 30° in a number of solvents to permit testing the substitution reaction. These solvents included the primary alcohols ethanol, butanol, ethylene glycol and its monomethyl ether and also chloroform, dioxane and dimethyl sulfoxide. Fourteen solvents were chosen, however, in which solvent-induced decomposition was negligible: hexane, carbon tetrachloride, chlorobenzene, nitrobenzene, 1,1,2-trichloroethane and ethyl acetate; or sufficiently slow that the substitution reaction could be followed: 1-nitropropane, 1-nitroethane, nitromethane, methyl ethyl ketone, acetone, acetonitrile, acrylonitrile and ethylene glycol dimethyl ether (Table I). In some cases the rate of decomposition of *t*-butyl hypochlorite without corresponding chlorination was greater in these solvents when another substance, either wood or hemicellulose or phenol, was present than when the hypochlorite and solvent were present alone. It was possible, however, to follow the chlorination of wood in all of these solvents, even though this variation in behavior obscured some quantitative aspects of the reaction.

For example, when vanillyl alcohol was permitted to react with *t*-butyl hypochlorite in eight of these solvents under conditions comparable to those used to measure solvent-induced decomposition, the consumption of the hypochlorite was very rapid during the first hour and proceeded at a much reduced and progressively slower rate thereafter. After four hours about 2.7 moles (54%) of hypochlorite had been consumed per mole of vanillyl alcohol in ethyl acetate and carbon tetrachloride, while in acetonitrile and acetone nearly four moles or 80% of the hypochlorite had been consumed. Other solvents gave intermediate values (Table II). When the concentration of vanillyl alcohol was reduced by one-half, the percentage decomposition of hypochlorite decreased correspondingly, but since the solvent-induced decomposition remained the same the molar consumption of hypochlorite per mole of vanillyl alcohol in acetonitrile appeared to increase to 5 moles per mole of phenol (in four hours). This ratio with decrease in substrate

TABLE II

RATE OF CONSUMPTION OF *t*-BUTYL HYPOCHLORITE BY VANILLYL ALCOHOL AND ETHYLGUAIACOL[a]

Solvent / Time, min.		60	120	180	240	300
Vanillyl alcohol						
Ethyl acetate	A	1.94	2.31	2.58	2.70	
	B	1.21	1.92	2.15	2.30	2.38
Carbon tetrachloride	A	2.23	2.63	2.75	2.84	
	B	1.98	2.41	2.59	2.71	2.76
Nitrobenzene	A	2.91	3.08	3.16	3.22	
	B	3.02	3.27	3.40	3.49	3.60
Nitropropane	A	3.02	3.15	3.20	3.25	
	B	3.25	3.56	3.69	3.81	3.85
Nitromethane	A	3.12	3.26	3.28	3.31	
	B	3.47	3.68	3.84	3.92	4.01
Nitroethane	A	3.16	3.30	3.35	3.37	
	B	3.78	3.99	4.05	4.10	4.18
Acetone	A	3.35	3.55	3.65	3.75	
	B	3.98	4.32	4.50	4.58	4.63
Acetonitrile	A	3.54	3.74	3.85	3.96	
	B	4.23	4.61	4.86	4.98	5.09
Ethylguaiacol						
Ethyl acetate		0.69	1.29	1.61	1.86	2.09
Carbon tetrachloride		0.00	0.11	0.12	0.15	0.20
Nitroethane		1.33	1.78	2.11	2.36	2.51

[a] Conditions: A 0.154 g. of vanillyl alcohol (0.001 mole), 0.6 ml. of *t*-BuOCl (0.005 mole), 25 ml. each solvent, 30 ~ 30.3°; B 0.077 g. of vanillyl alcohol (0.0005 mole) with the other quantities unchanged. 0.076 g. of ethylguaiacol (0.005 mole), 0.3 ml. of *t*-BuOCl (0.0025 mole), 25 ml. each solvent, 30 ~ 30.3°.

(2) D. Ginsburg, THIS JOURNAL, **73**, 702, 2723 (1951).

(3) *Cf.* B. F. Clark, Jr., *Chem. News*, **143**, 265 (1931).

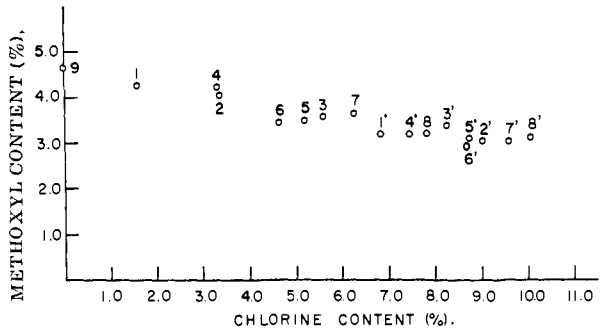

Fig. 1.—Relation between methoxyl content and chlorine content in chlorinated wood.

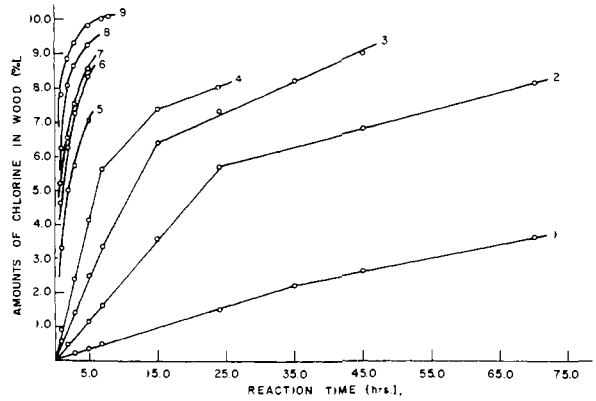

Fig. 2.—Rates of chlorination of woodmeal in various solvents (reaction temp. 30~30.3°; lignin:*t*-BuOCl = 1:11): 1, 1-nitropropane; 2, ethyl acetate; 3, nitroethane; 4, methyl ethyl ketone; 5, ethylene glycol dimethyl ether; 6, acrylonitrile; 7, acetone; 8, acetonitrile; 9, nitromethane.

increased smaller amounts or not at all in other solvents. Since the reactions in acetone and ethyl acetate were very different in their consumption of *t*-butyl hypochlorite, the products of the reactions of vanillyl alcohol with 5 moles of *t*-butyl hypochlorite in both solvents were isolated after a period of five hours. These were reddish-brown resins which contained in the case of the acetone 36.1% Cl and in the ester, 33.8% Cl, or slightly more than two chlorine atoms per vanillyl alcohol residue (disubstitution = 31.8% Cl). After two or three days the product in both cases still contained only about 36% Cl even when extra hypochlorite was used in the acetone (15–30 moles). This reaction is not completely simple, however, because the five-hour reaction product was shown by paper chromatography to be a mixture of several components and even still to include some 5-chlorovanillin and 5-chlorovanillyl alcohol (but not the 6-chloro compounds).

The reaction, therefore, although complex stopped at approximately a stage of disubstitution in both solvents and no marked differences were observed between the two reaction products. The fact that oxidation of the carbinol group also occurs and that more than one dichloro isomer may be present is of less significance for our purpose than the fact that the chlorination has a fairly definite end-point.

The rate of consumption of *t*-butyl hypochlorite by ethylguaiacol also was studied in nitroethane and ethyl acetate. Two and one-half moles of hypochlorite was consumed over a period of four to five hours and thereafter the reaction was slow in both solvents. (The similar period of rapid reaction with vanillyl alcohol was two hours.) In the non-polar solvent carbon tetrachloride, ethylguaiacol, however, consumed only 0.9 mole of *t*-butyl hypochlorite in twenty hours.

From these experiments on model compounds and a number of similar experiments on related compounds, it was concluded that the reaction of excess *t*-butyl hypochlorite with 4-substituted guaiacols in a number of polar organic solvents proceeds to about a stage of disubstitution in about four or five five hours. In very non-polar environment, the more unreactive phenols occasionally require longer times. The reaction is complicated by oxidation of α-carbinol groups and by some direct and probably some induced decomposition of hypochlorite which varies with the solvent system. However, since disubstitution can be expected to proceed rapidly in a variety of solvents bearing ester, ketone, nitro and nitrile groups, halogen content of lignin after reaction with excess *t*-butyl hypochlorite can be used as a measure of accessibility at least in these solvents.

This conclusion was in general confirmed in our experiments on wood. The reaction is again not entirely one of substitution but here the oxidative reaction results in the loss of methoxyl groups from the guaiacyl residues. The ratio of methoxyl lost to chlorine substituted was reasonably constant for a variety of solvents in which the rate of reaction was remarkably different (Fig. 1). If the reaction mechanism were greatly different in these solvents one would expect a substantial scatter in these ratios, or a real difference in the ratios between the slow and rapid reactions.

The rates of chlorination of the lignin in wood with *t*-butyl hypochlorite, however, varied in a striking manner with the solvent in which the reaction was carried out (Fig. 2, Tables III and IV). The reaction was most rapid in nitromethane, acetonitrile, acetone, acrylonitrile, and ethylene glycol dimethyl ether. Of these the rate in nitromethane appeared greatest, but in the other four solvents the concurrent decomposition of the hypochlorite unquestionably slowed down the reaction by removing more hypochlorite from the system. It may be, therefore, that there is no marked difference between the rates of chlorination in these five solvents. Chlorination occurred at a progressively slower rate in methyl ethyl ketone, nitroethane, ethyl acetate and nitropropane. In the latter case, less than one equivalent of chlorine per phenylpropane unit was introduced even after seventy hours. In 1,1,2-trichloroethane, nitrobenzene, chlorobenzene, carbon tetrachloride and hexane the reaction was almost negligible and proceeded to less than 0.07 mole of chlorine per phenylpropane unit in fifteen hours. This behavior is in marked contrast to that of the monomers for even in the one monomer–solvent system in which we observed a substantial decreased rate of reaction, ethylguaiacol in carbon tetrachloride, 0.9 mole of *t*-

TABLE III

CHLORINE CONTENT (%) OF WOODMEAL TREATED WITH *t*-BuOCl

Reaction temp. 30~30.3°; lignin:*t*-BuOCl, 1:5.5

Solvent Time, hr.	0.15	0.30	1	2	3	5	7	9	15	30	45	70
Hexane[a]			0.02	0.03		0.04	0.06		0.07	0.11		
Carbon tetrachloride[a]			.02	.03		.05	.06		.06	0.11		
Chlorobenzene[a]			.04	.08	0.08	.11	.16		.30			
Nitrobenzene[a]			.04	.08	.12	.13	.17					
1,1,2-Trichloroethane[a]			.13	.14	.16	.20	.24					
1-Nitropropane[a]			.11	.14	.20	.34	.44					4.21
Ethyl acetate[b]			.23	.40	.60	1.10	1.54		3.91	6.00	6.72	
Nitroethane[a]			.58	.93	1.36	2.50	3.33		6.49	7.55[d]		
Methyl ethyl ketone			.69	1.50	2.52	4.03	5.60	6.00	6.96[d]			
Ethylene glycol dimethyl ether[c]		1.54	3.22	4.92	5.59	6.55[d]	6.95[d]					
Acrylonitrile[b]		3.00	4.51	6.23	7.06	8.20[d]	8.72[d]					
Acetone[c]	1.77	3.32	5.17	6.51	7.44	7.66[d]						
Acetonitrile[b]		3.96	6.17	7.98	8.57	9.10[d]	9.27[d]					
Nitromethane[b]	3.74	6.10	7.74	8.81	9.31	9.73	9.97[d]	10.02[d]				

[a] Kraft lignin showed no solubility in these solvents. [b] Kraft lignin showed only slight solubility in these solvents. [c] Kraft lignin showed only partial solubility in these solvents. [d] A drop of reaction liquor no longer gave a positive starch–iodide paper test.

TABLE IV

CHLORINE CONTENT (%) OF WOODMEAL TREATED WITH *t*-BuOCl

Reaction temp. 30~30.3°; lignin:*t*-BuOCl, 1:11

Solvent Time, hr.	1	2	3	5	7	8	15	24	35	45	70
1-Nitropropane			0.22	0.35	0.50			1.52	2.22	2.63	3.60
Ethyl acetate		0.48		1.15	1.60		3.60	5.71		6.83	8.13
Nitroethane	0.56		1.40	2.49	3.35		6.40	7.31	8.20	9.01	
Methyl ethyl ketone	0.81		2.40	4.13	5.60		7.38	8.02			
Ethylene glycol dimethyl ether	3.31	5.00	5.75	7.05	7.44[a]						
Acrylonitrile	4.62	6.25	7.25	8.30	8.70[a]						
Acetone	5.20	6.55	7.52	8.55	8.75[a]						
Acetonitrile	6.25	8.05	8.65	9.25	9.60[a]						
Nitromethane	7.81	8.85	9.30	9.80	10.00	10.08					

[a] A drop of reaction liquor no longer gave a positive starch–iodide paper test.

butyl hypochlorite was consumed in twenty hours and in all other cases disubstitution was complete in about five hours. The results in nitromethane and the other better solvents suggest that lignin may be intrinsically nearly as reactive as vanillyl alcohol and the variation in rate of lignin chlorination can in no way be correlated with any solvent effect upon the reaction mechanism.

If, however, one attempts to correlate the rates of the chlorination reaction with the known solvent power of these solvents for isolated lignins,[4] a relationship is immediately apparent. All solvents in which the reaction is negligibly slow are solvents in which isolated lignins are insoluble (Tables III and IV). Solvents in which the reaction proceeds rapidly are solvents in which isolated lignins show at least some solubility. Higher members of homologous series are poorer lignin solvents and in them reaction proceeds at lower rates. Reaction of lignin with *t*-butyl hypochlorite in dimethylformamide, an excellent lignin solvent, has been investigated by W. Erby and will be reported in detail later. However the reaction follows a course similar to the reaction in nitromethane and stops at the same degree of substitution. There can be little doubt that the degree to which an organic solvent penetrates into and is miscible with the lignin phase can determine rates of reaction in the solvent and presumably also the homogeneity or heterogeneity of reaction.

If one places solvents on a graph of cohesive energy density and hydrogen bonding capacity it can be seen that the solvents in which the chlorination rate is rapid, those in which it is intermediate in rate and those in which it is slow or negligible fall in three different areas of the plot (Fig. 3). A similar correlation has been made between these properties of solvents and their power to dissolve isolated lignins.[4,5]

Water is of course a poor lignin solvent and it would be of considerable interest to learn whether lignin reactions in aqueous media are also restricted in rate by inadequate accessibility. Certainly the comparatively low rate of chlorination of lignin by aqueous chlorine is in marked contrast to the nearly instantaneous reactions of phenols with chlorine water. At any rate, it is clear that any reaction on lignin in wood from which structural conclusions are to be drawn or any reaction used to degrade lignin completely should be carried out under solvent conditions which allow the lignin to be in an accessible form.

Experimental

Preparation of *t*-Butyl Hypochlorite.—A solution of 200 ml. of *t*-butyl alcohol in 2.85 l. of sodium hypochlorite (active

(4) C. Schuerch, THIS JOURNAL, **74**, 5061 (1952).

(5) E. C. Jahn, C. V. Holmberg and C. Schuerch, *Chemistry in Canada*, 35 (1953).

TABLE V

COLOR REACTION BY SPRAYING AGENT

Model compound	Diazotized *p*-nitroaniline	Overspray with 20% Na_2CO_3	2,4-Dinitrophenyl-hydrazine	Fluorescence, no spray
Vanillyl alcohol	Yellow-brown	Purple		None
5-Chlorovanillin	Light yellow brown	Dark reddish purple	Orange-brown	Purple
6-Chlorovanillin	Light yellow brown	Dark reddish purple	Yellow-brown	Purple
5-Chlorovanillyl alcohol	Orange-brown	Dark reddish purple		None
6-Chlorovanillyl alcohol	Yellow-brown	Dark reddish purple		None

chlorine 5.25%) was stirred mechanically and chilled in a 4-l. round-bottomed flask to 0°; 125 ml. of glacial acetic acid was added dropwise over 20 minutes with stirring. The upper oily layer was separated, washed with 50-ml. portions of 10% sodium carbonate until the washings were no longer acidic to congo red, then washed four times with water and dried over calcium chloride. The yield was 151 g. and the product was used without further purification.[6]

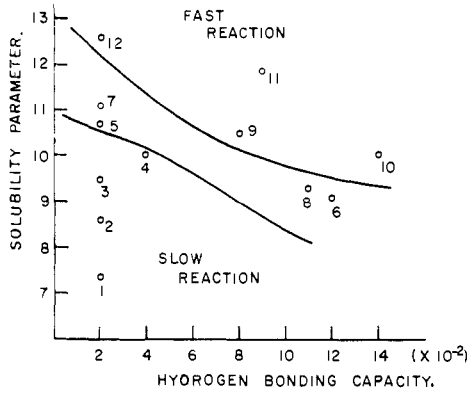

Fig. 3.—Relation between solvent properties and chlorination rate: 1, hexane; 2, carbon tetrachloride; 3, chlorobenzene; 4, nitrobenzene; 5, nitropropane; 6, ethyl acetate; 7, nitroethane; 8, methyl ethyl ketone; 9, acrylonitrile; 10, acetone; 11, acetonitrile; 12, nitromethane.

Stability Tests.—Fifty ml. of each organic solvent was sealed in an amber bottle with 1.0 ml. of *t*-butyl hypochlorite and shaken in a 30–30.3° water-bath. The *t*-butyl hypochlorite remaining after various periods of time was determined by iodometric titration of aliquots. Under these conditions the hypochlorite was stable in carbon tetrachloride, chlorobenzene, nitrobenzene, nitroethane, nitropropane, hexane, ethyl acetate and acetone for at least five hours. It reacted instantaneously and violently with ethanol, butanol, and dimethyl sulfoxide. The results with other solvents are listed in Table I.

Reaction with Monomeric Phenols.—Ethylguaiacol (0.076 g., 0.0005 mole) was dissolved in 25 ml. of various solvents containing *t*-butyl hypochlorite (0.3 ml., 0.0025 mole) and shaken in amber bottles at 30.0–30.3°. Vanillyl alcohol (0.154 g., 0.001 mole) and *t*-butyl hypochlorite (0.6 ml., 0.005 mole) were dissolved in 25 ml. of various solvents and treated similarly. The decrease of *t*-butyl hypochlorite concentration was followed by iodometry. The results after several hours are listed in Table II. The same procedure was carried out using 0.076 to 0.078 g. of vanillyl alcohol with the other quantities unchanged (Table II).

After five hours the products obtained from the reaction of vanillyl alcohol (0.770 g.) with *t*-butyl hypochlorite (3.0 ml.) in 40 ml. of two different solvents, acetone and ethyl acetate, were isolated by evaporation of solvent. The chlorine contents of the reddish-brown resins were found to be, respectively, 36.1 and 33.8% Cl. Reactions continued for two days gave products from each solvent containing 36.0 ± 0.6% Cl. In the case of the acetone this was with a molar ratio of 1:30. The five-hour products were separated into benzene-soluble and benzene-insoluble fractions. The benzene-soluble fraction in both cases showed the presence of some 5-chlorovanillin and 5-chlorovanillyl alcohol by paper chromatography together with other unidentified products.

(6) *Cf. Org. Syntheses*, **32**, 20 (1952).

Reaction with Woodmeal.—Air-dried Norway spruce woodmeal (40–80 mesh, ethanol–benzene extracted, 27.4% Klason lignin on a moisture-free basis) was dried at least 24 hours *in vacuo* at 40° over phosphorus pentoxide. One-gram samples of dried woodmeal were sealed in amber bottles with 25 ml. of various solvents containing 0.97 or 1.94 ml. of *t*-butyl hypochlorite (0.008 or 0.016 mole). (One gram of wood contains 0.00145 mole of lignin phenylpropane units of mol. wt. 188.) The bottles were shaken at 30–30.3° for various periods of time. The wood residues were filtered off, and washed with these various solvents in order: the reaction solvent, *t*-butyl alcohol, water, *t*-butyl alcohol and benzene. Wood residues varied in color from almost an unchanged appearance to light brown. The wood meal was recovered quantitatively, dried and analyzed for chlorine and methoxyl. To determine rates of reaction, a number of identical experiments were carried out on separate samples for different periods of time.

Analytical Determinations.—Chlorine content was determined by fusion with sodium peroxide in a Paar bomb, of samples dried at least 24 hours *in vacuo* at 40° over phosphorus pentoxide. Methoxyl content was determined by the method of Gran[7] using an improved alkoxyl apparatus developed for this purpose.[8]

Paper Chromatography of Chlorinated Phenols.—Vanillyl alcohol, 5- and 6-chlorovanillyl alcohol and 5- and 6-chlorovanillin were chromatographed on Whatman No. 1 filter paper using the buffer technique of Gardon and Leopold[9] and butanol saturated with buffer as developer. For detection of spots, chromatograms were sprayed with diazotized *p*-nitroaniline in sodium acetate and with 2,4-dinitrophenylhydrazine. R_f values are reported in Fig. 4. Colors are shown in Table V.

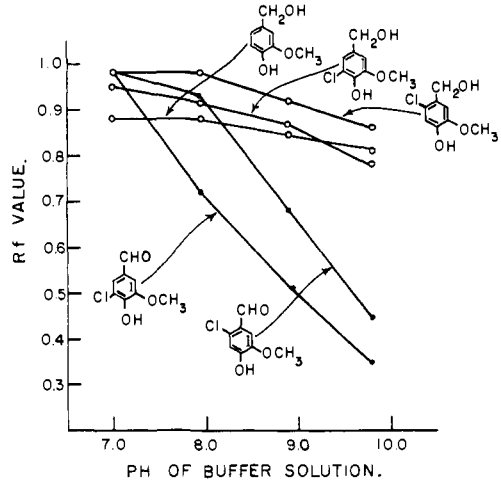

Fig. 4.—Relation between R_f value and *p*H of stationary phase.

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The Constitution of the Hemicelluloses of Sitka Spruce (*Picea sitchensis*). III. Structure of an Arabomethoxyglucuronoxylan[1]

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Methylation of sitka spruce hemicelluloses obtained by potassium hydroxide extraction of a chlorite holocellulose preparation yielded a homogeneous sample after fractional precipitation. Hydrolysis yielded 2,3,4-tri-*O*-methyl-D-xylose (1 mole), 2,3,5-tri-*O*-methyl-L-arabinose (0.4 mole), 2,3-di-*O*-methyl-D-xylose (10 moles), 2-*O*-methyl-D-xylose (0.3 mole), 3-*O*-methyl-D-xylose (1.2 moles) and 2-*O*-(2,3,4-tri-*O*-methyl-D-glucuronosyl)-3-*O*-methyl-D-xylose (3.4 moles). The structural features of the polysaccharide are discussed.

Previous papers in this series have reported on the nature of the aldobiouronic acid[2] and the mannan portion[3] of sitka spruce hemicelluloses. The present paper reports the constitution of an arabomethoxyglucuronoxylan. The current status of research on the constitution of hemicelluloses from coniferous trees has recently been summarized[4] and is not repeated here.

Sitka spruce sawdust was treated with sodium chlorite and the resulting holocellulose extracted with 5% potassium hydroxide.[2] The mixed hemicelluloses were methylated, first with methyl sulfate and sodium hydroxide and finally with Purdie reagents. The partly methylated polysaccharide did not separate from the aqueous solution during the Haworth methylations and had to be recovered by dialysis and evaporation. The fully methylated product was fractionated from chloroform solution with petroleum ether and the results are shown in Table II. Fraction 23b appeared to be homogeneous and was used in the subsequent experiments. Methanolysis with 2% hydrogen chloride in methanol cleaved the polysaccharide which was separated into neutral and acidic components by the use of ion-exchange resins. The methyl ester of the acidic component was reduced with lithium aluminum hydride and yielded crystalline methyl 2-*O*-(2,3,4-tri-*O*-methyl-D-glucopyranosyl)-3-*O*-methyl-D-xyloside identical with that originally obtained from western hemlock[5] and since obtained from sugar maple.[6] The neutral sugars were resolved on a cellulose–hydrocellulose column[7] using butanone–water azeotrope as the solvent.[8] Three fractions were obtained and paper chromatography showed these to contain 2,3,5-tri-*O*-methyl-L-arabinose, 2,3,4-tri-*O*-methyl-D-xylose, 2,3-di-*O*-methyl-D-xylose and two monomethyl-D-xyloses. The first two have very similar R_f values and may be separated either by using a benzene–ethanol–water solvent[9] or by taking advantage of the preferential furanoside formation of the arabinose derivative.[5] The latter method of separation was used and the xylose derivative was characterized as the crystalline 2,3,4-tri-*O*-methyl-N-phenyl-D-xylosylamine[10] and the arabinose derivative by paper chromatography after hydrolysis of the furanoside. The 2,3-di-*O*-methyl-D-xylose, which formed the major component, was identified as the crystalline sugar.[11] The 2- and 3-*O*-methyl-D-xyloses did not separate sufficiently well to enable crystalline derivatives to be prepared but enough of each sugar was obtained chromatographically pure to permit comparison with authentic samples.

From the above experimental evidence it is clear that the main structural feature of the hemicellulose is a chain of D-xylopyranose units linked through positions 1 and 4. Since hydrolysis involves an increase in rotation it is presumed that β-linkages are involved. The isolation of the known crystalline disaccharide glycoside from the acidic component shows that the uronic acid occupies a terminal position and that the uronic acid is joined to C_2 of the main xylose chain thus confirming our previous results.[2] The linkage in the aldobiuronic acid was judged to be α because of the high positive rotation and this now has been proved by lead tetraacetate degradation.[12] Since arabinose was only isolated in the form of 2,3,5-tri-*O*-methyl-L-arabinose it is clear that the arabofuranose units must also occupy terminal positions and strongly suggests that the arabinose is an integral part of the molecule. No free uronic acid was observed after methanolysis and hydrolysis and thus the monomethylxylose units must represent branch points or artifacts caused by incomplete methylation or demethylation during hydrolysis. In view of the relative amounts of the two isomers obtained it is possible that the arabinose is linked to position 3 of the main chain and that there is limited branching at position 2.

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