By analogy with vinylacetylene, it is believed that the structure of the methoxy ketal from vinylethylacetylene is 1,3,3-trimethoxyhexane. The quantity of material available was not sufficient definitely to prove its structure.

Summary

1. Substituted allylacetylenes add two molecules of methanol, in the presence of mercuric oxide, boron fluoride and trichloroacetic acid, to yield 5,5-dimethoxy-1-alkenes. Vinylethylacetylene reacts, under these conditions, to form a trimethoxyalkane analogous to the trimethoxybutane derived from monovinylacetylene.

2. Conjugation of the triple and double bonds in alkenylacetylenes is apparently necessary for the addition of methanol to the ethylenic linkage.

3. Using mercuric oxide and boron fluoride as a catalyst, methyl vinyl ketone reacts with methanol to yield 4-methoxy-2-butanone.

4. The addition of methanol to divinylacetylene has not been effected with mercury–boron fluoride catalysts in this Laboratory.

5. Further evidence in favor of 1,4-addition of oxy compounds to vinylacetylenes is presented.

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[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Some Characteristics of Wood Lignins[2]

BY ELWIN E. HARRIS

In a former publication[3] it was reported that maple and spruce lignin isolated by the sulfuric acid method differed with respect to methoxyl content and reactions with chlorine. The present paper deals with an extension of the former work to determine if the same consistent differences exist in lignins from other species of hardwoods and softwoods. Lignins isolated by extraction with methyl alcohol acidified with hydrochloric acid were also included in this study.

The procedure used for the isolation of lignin by the sulfuric acid method was the same as that recommended in a previous publication[4] except for the oak which was first extracted with alcohol according to the modification of Ritter and Barbour[5] by which some materials not soluble in alcohol–benzene mixtures or water were removed.

The alcohol lignin was prepared by a modification of the Friedrich procedure,[6] in which the material was subjected to mild hydrolysis and fractionation during purification. Brauns and Hibbert[7] have more recently used methyl alcohol with acid as a means of removing lignin from wood.

As a further means of comparison, samples of the lignin by the two methods were methylated and chlorinated. Moist lignin was methylated by dimethyl sulfate in the presence of sodium hydroxide. Lignin, dried in a desiccator, was chlorinated with dry chlorine in dry carbon tetrachloride until it reached the second or light-colored stage. The chlorolignin showed about 20% increase in weight over the starting product.

Table I shows that, with the exception of the high yield of lignin from oak, a similarity exists among all the hardwood lignins. Another similarity exists among all the softwood lignins. Except for the methoxyl content of the fully methylated lignin and the chlorine content of chlorinated lignin, there are distinct differences between the hardwood and softwood lignins as shown especially in the average figures given in Table II.

The lignins isolated by the sulfuric acid method were partially soluble in alcohol or acetone: about 12% of hardwood and 2% of softwood lignin. These soluble fractions had the same methoxyl content, could be methylated to the same percentage of methoxyl, and gave chlorolignins with the same percentages of methoxyl and chlorine as the corresponding insoluble fraction from which they were separated.

The yield of extracted lignin, using methyl alcohol and hydrochloric acid, was low. This may be due to the fact that the reaction temperature was not high enough. To determine

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[1] Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

[2] Presented before the American Chemical Society at its 89th meeting in New York City, April 22–26, 1935.

[3] E. E. Harris, E. C. Sherrard and R. L. Mitchell, THIS JOURNAL, **56**, 889 (1934).

[4] E. C. Sherrard and E. E. Harris, *Ind. Eng. Chem.*, **24**, 103 (1932).

[5] G. J. Ritter and J. H. Barbour, *ibid.*, **7**, 238–240 (1935).

[6] A. Friedrich, *Z. physiol. Chem.*, **176**, 127–143 (1928).

[7] F. Brauns and H. Hibbert, THIS JOURNAL, **55**, 4720 (1933).

TABLE I

CHARACTERISTICS OF WOOD LIGNINS

Wood	Method of isolation	Yield[a] of lignin	MeO content of isolated lignin	MeO content of methylated lignin	Chlorolignin MeO	Chlorolignin Cl
		Hardwoods				
Sugar maple	70% H_2SO_4	21.0	20.7	32.0	11.8	27.0
Sugar maple	MeOH–HCl	6.0	25.3	32.2	15.0	26.0
Sugar maple[b]	70% H_2SO_4	..	17.3	..	..	..
Aspen	70% H_2SO_4	20.4	20.4	31.9	12.0	25.7
Aspen	MeOH–HCl	7.0	25.6	32.0	14.6	25.7
Aspen[b]	70% H_2SO_4	..	17.3	..	..	..
White oak	70% H_2SO_4	25.8	20.5	31.7	11.7	25.0
White oak	MeOH–HCl	7.0	25.4	31.9	14.5	25.6
Beech	70% H_2SO_4	22.5	20.6	31.9	11.7	26.0
Beech	MeOH–HCl	6.0	25.5	32.0	14.8	27.0
Beech[b]	70% H_2SO_4	..	17.3	..	..	..
Basswood	70% H_2SO_4	19.0	20.5	32.0	11.8	25.0
Basswood	MeOH–HCl	6.0	25.5	32.2	14.9	26.6
Basswood[b]	70% H_2SO_4	..	17.3	..	..	..
		Softwoods				
Spruce	70% H_2SO_4	26.9	17.0	32.0	8.8	26.8
Spruce	MeOH–HCl	4.0	21.5	32.0	12.1	26.3
Spruce[b]	70% H_2SO_4	..	14.5	..	..	..
Slash pine	70% H_2SO_4	25.5	16.9	31.9	8.5	25.3
Slash pine	MeOH–HCl	4.0	21.6	32.0	11.7	26.9
Slash pine[b]	70% H_2SO_4	..	14.5	..	..	..
Eastern hemlock	70% H_2SO_4	30.06	16.9	32.0	8.7	25.4
Eastern hemlock	MeOH–HCl	4.0	21.6	32.0	11.6	27.0
Eastern hemlock[b]	70% H_2SO_4	..	14.5	..	..	..

[a] Yield calculated from the dried extracted wood. [b] Sample was that remaining after extracting four times with MeOH–HCl.

TABLE II

AVERAGE COMPOSITION OF WOOD LIGNIN AND LIGNIN DERIVATIVES

Material analyzed		Hardwood lignin		Softwood lignin	
		Found, %	Calcd. number of group	Found, %	Calcd.[a] number of group
MeO in lignin from residue after extraction with MeOH–HCl		17.3	5.02[a]	14.5	4.14[a]
MeO in lignin from wood by 70% H_2SO_4		20.5	6.04[a]	16.9	4.91[a]
MeO in lignin from wood by MeOH–HCl		25.5	7.63[a]	21.6	6.42[a]
MeO in fully methylated lignin		32.0	10.0	32.0	10.0
Chlorinated H_2SO_4 lignin	MeO	11.8	4.18[b]	8.7	3.05[b]
	Cl	25.7	7.98	25.5	7.85
Chlorinated MeOH–HCl lignin	MeO	14.8	5.25[b]	11.8	4.18[b]
	Cl	26.2	8.1	26.7	8.15

[a] Calculated on the basis of ten methoxyl groups in fully methylated lignin. [b] Calculated on the basis of 1100 for the molecular weight of the chlorolignin with four methoxyl groups.

the effect of higher boiling solvents on the yield, dioxane and cellosolve were used in place of methyl alcohol on maple wood. Methyl cellosolve gave a yield of 19% of lignin or 90% of the total in the wood. Dioxane gave a 10% yield or about 50% of the lignin. The methoxyl content is higher in the methyl alcohol and methyl cellosolve lignins. Brauns and Hibbert[7] concluded that this increase was due to methylation of one of the hydroxyl groups in lignin during isolation. No increase in alkoxyl content was found when dioxane was used. These products were easily methylated to give derivatives with the same percentage of methoxyl as that found in the methylated sulfuric acid lignin, indicating that the total number of possible hydroxyl groups were the same.

Methyl alcohol, methyl cellosolve, and dioxane with hydrochloric acid must also have acted as a demethylating agent because the lignin left in the wood after treatment contained less methoxyl. These materials when methylated gave a product with 32% methoxyl. Demethylation has been observed by other investigators[8] but under conditions much more drastic and without simultaneous methylation.

During chlorination both hardwood and softwood lignins lost methoxyl. Sulfuric acid lignin from hardwoods lost about one-third of its methoxyl and from softwoods about two-fifths. Methyl alcohol lignins from hardwoods lost about two-sevenths of their methoxyl and from softwoods about one-third. On the basis of ten methoxyls in fully methylated lignin, this loss in each case is two methoxyl groups. After correcting for the loss of methoxyl groups, the weight of the chlorine introduced into lignin during chlorination was about the same as the total increase in weight of the chlorolignin. It seems therefore that chlorine reacted by addition or substitution rather than by oxidation.

In a former publication[3] the fully methylated compound containing 32% methoxyl was assigned ten methoxyl groups. Table II shows the values for the numbers of methoxyl groups in the isolated lignin and lignin derivatives calculated on the basis of ten methoxyl groups in the fully methylated derivatives. The values for the methoxyl groups are close to whole numbers except for the lignins isolated by the action of methyl alcohol and hydrochloric acid. These values are intermediate between two whole numbers and therefore the products must have been mixtures of lignin derivatives with different numbers of methoxyl groups.[9] The "monomethylated" product described by Brauns and Hibbert[7] must also have been a mixture. Hardwood lignin as it occurs in wood contains six methoxyl groups and when fully methylated contains ten methoxyls. Softwood lignin contains five methoxyls and is methylated to a compound containing ten. When the lignin is isolated by extraction with methyl alcohol and hydrochloric acid some of the hydroxyl groups are methylated. At least one of the methoxyls introduced in this manner is resistant to the action of chlorine. There are two methoxyl groups in the sulfuric acid lignin and two in the methyl alcohol lignin from both hardwoods and softwoods which are removed by the action of dry chlorine.

Conclusions

The previously reported differences between maple and spruce lignins by the sulfuric acid method have been found to exist between the lignins from other hardwoods and softwoods; four other hardwoods being very similar to maple and two other softwoods very similar to spruce.

On the basis of ten methoxyl groups in the fully methylated lignin, hardwood lignins isolated by the sulfuric acid method contain six and softwood five methoxyl groups.

About 30% of the lignin in hardwoods and 15% in softwoods is removed by the action of methyl alcohol–hydrochloric acid. With both hardwoods and softwoods the part removed is methylated by about one and one-half groups and the insoluble residue is demethylated by about one group. All these fractions from both hardwoods and softwoods by either the methyl alcohol–hydrochloric acid or sulfuric acid method of isolation can be methylated by dimethyl sulfate to ten methoxyl groups.

Lignins from hardwoods or softwoods by either the sulfuric acid or alcohol methods lost two methoxyl groups when treated with dry chlorine.

MADISON, WISCONSIN RECEIVED MARCH 19, 1936

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[8] E. Heuser and R. Schmitt, *Cellulosechemie*, **1**, 49–58 (1920); **2**, 81 (1921).

[9] Recent work at this Laboratory has shown definitely that these products are mixtures.