and the resulting precipitate tested for bromine. No trace of bromine could be found with either flavylium salt.

Chemiluminescence of Flavylium Salts.—The reagents[7] used were the following: (A) hydrogen peroxide solution 0.4%; (B) a solution of 50 cc. of 5% sodium hypochlorite was added to 350 cc. of water in which had been dissolved 20 g. of sodium hydroxide; (C) acetone solution of the flavylium salt (1, 5 and 10 mg. per 4 cc. solvent). In each test carried out in a dark room, 2 cc. of solution A, was added to 4 cc. of solution C and then 2 cc. of solution B added with shaking. A perceptible flash of light occurred with as little as 1 mg. of the salts and bright flashes were observed when 5 to 10 mg. were used. The flashes of light lasted only a second since the alkaline reagents rapidly destroy the salt structure. Alcohol solutions likewise gave only a very dim flash due to a reaction with the solvent.[8]

Summary

Two flavylium salts, 3-methoxy-4'-bromoflavylium chloride and 3-methoxy-7-bromoflavylium chloride and their ferrichlorides have been prepared and the activity of the bromine atom tested. Molecular silver, silver nitrate, silver chloride or alcoholic sodium ethoxide did not remove the bromine from these salts which indicates that in these simple 3-methoxyflavylium salts no tautomerization to a quinoid structure takes place.

These flavylium salts were found to exhibit chemiluminescence when treated with dilute solutions of hydrogen peroxide and sodium hypochlorite.

URBANA, ILLINOIS RECEIVED MARCH 9, 1939

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY[1]]

Studies on Lignin and Related Compounds. XL. The Extraction of Birch Lignin with Formic Acid

BY MORRIS LIEFF,[2] GEORGE F. WRIGHT AND HAROLD HIBBERT

Conforming to the principle[3] that in the isolation of lignin the "extractant be considered as the first reagent in a series of reactions intended to prove structure," yellow birch wood was extracted with boiling formic acid in order to compare the properties of this birch lignin with others extracted by alternative methods.[4,5] The resulting extract was not so soluble as the corresponding acetic acid lignin[4] but it was comparatively free from hexoses and pentoses[4] and for this reason the conclusions to be drawn by comparison of the isolated and methylated lignins are of greater significance.

It was soon discovered that Grignard analyses *in dioxane* as a solvent were not reliable with the less soluble of these birch formic acid lignins and that *in pyridine* more satisfactory results were obtained. The lower values for active hydrogen and carbonyl obtained in dioxane are probably owing to incomplete reaction. This explains (Table I) the lower active hydrogen values obtained from the less soluble spruce formic acid lignin fraction better than the opinion previously offered,[3] namely, that the more insoluble fractions result from increasing aggregation of the lignin complex because of intermolecular dehydration.

TABLE I

GRIGNARD ANALYSES OF SPRUCE FORMIC ACID LIGNINS

Fraction		Chloroform-ether insoluble	Acetone-ether insoluble
OCH_3, %		13.4	13.4
Grignard analyses in dioxane	Act. H/kg.	4.6	3.5
	RMgX added/kg.	0.7	0.5
Grignard analyses in pyridine	Act. H/kg.	6.8	7.1
	RMgX added/kg.	3.1	3.3

Comparison of the Grignard analyses in dioxane and pyridine for birch formic acid lignin (Table IV) indicates in like manner that both active hydrogen and carbonyl values are much lower in the former solvent. Just as the lower carbonyl value determined in dioxane (*ca.* 0.8 group/kg.) for spruce formic[3] and birch acetic[5] acid lignin persisted throughout the methylation process, so the higher value (*ca.* 2.7 group/kg., Table V, Column 8) likewise persists as the more nearly true carbonyl value when measured in pyridine (subtracting effects of normal ester and lactone linkages, Table IV, Column 9). Part of this higher carbonyl value (*ca.* 0.6–1.0 group per kg.) is accounted for by the carboxyl group in lignin,[6,7] which is not indicated

(1) With financial assistance from the National Research Council of Canada and the Canadian Pulp and Paper Association.

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(3) Wright and Hibbert, THIS JOURNAL, **59**, 125 (1937).

(4) Hunter, Wright and Hibbert, *Ber.*, **71**, 734 (1938).

(5) Bell, Cramer, Wright and Hibbert, *ibid.*, **71**, 746 (1938).

(6) Moore, Wright and Hibbert, *Can. J. Research*, **B15**, 532 (1937).

(7) Bell, Wright and Hibbert, unpublished results.

in dioxane.[8] The remainder (*ca.* 1 group per kg.) is probably some hitherto unsuspected carbonyl group unreactive toward RMgX in quinoline or dioxane.[3]

Although the period of extraction with hot formic acid seemed to have but little effect on the yield of lignin (Table III), it was found, by retreating the lignin fractions with boiling formic acid, that the solubility decreased markedly. Since it has been shown[4] that these formic acid lignins contain little hydrolyzable hexose or pentose, it is evident that complexity of the lignin itself increases upon longer treatment with formic acid (bottom of Table IV), although, significantly, Grignard analyses and methoxyl values are practically unchanged.

The crude birch formic acid lignin has been separated by differential solubilities into four fractions (Table IV). The chloroform–petroleum ether (1) and chloroform–ether insoluble (2) fractions differ from the acetone–ether (3) and dioxane–ether insoluble (4a) or acetone–water–ether insoluble (4b) fractions by containing more methoxyl, more formyl and *less* active hydrogen (in pyridine) than the less soluble portions. Any significance which could be attached to the higher carbonyl value is masked by the higher formyl content. Otherwise it may be noted that the properties of the birch formic acid are quite similar to the spruce formic acid lignin (compare Tables I and IV) in that the more insoluble fractions in both cases react incompletely with methylmagnesium iodide in dioxane.

The diazomethane-methylated birch acetic acid lignins were analyzed for active hydrogen and carbonyl in dioxane and the results indicated that both the syringyl and guaiacyl fractions occurred as lactones in the isolated lignins.[5] Using the diazomethane-methylated birch formic acid lignins and analyzing in both pyridine and dioxane, comparison of the methoxyl increases (Tables IV and VI) shows that, while the syringyl fractions exist as lactones, the guaiacyl fractions are in the hydroxy acid form. For example, 0.6 group per kg. representing abnormal substitution (gain in methoxyl minus loss in active hydrogen (pyridine), Table VI, Columns 12 and 13) is found for the chloroform–petroleum ether insoluble (syringyl) fraction, while the dioxane–ether insoluble (guaiacyl) fraction shows no abnormal substitution. That this is weak evidence for the division of the lignin fractions into hydroxy acid and lactone forms is shown by the anomalous results obtained with the intermediate fractions (Table VI, Runs 2 and 3), although this discrepancy may be due to the fractionation of these products. To substantiate this admittedly weak evidence for the lactone linkage, comparison (Tables IV and VI) of the carbonyl values *in pyridine* shows that no increase has occurred upon diazomethane methylation of the syringyl fraction (in agreement with the fact that a lactone linkage consuming 2 moles RMgX has been converted to a methyl ester which likewise reacts with 2 moles). The guaiacyl fraction, on the other hand, consumes 0.3–0.9 mole more of Grignard reagent after diazomethane methylation, as would be expected if a carboxylic acid were converted to its methyl ester. While these results are undoubtedly more significant than those deduced from Grignard analyses *in dioxane*, it should be noted that the conclusions are dependent on the assumption that a lactone is hydrolyzed and methylated by the diazomethane solution[6] and that this reaction takes place with equal readiness with each lactone. Since this assumption has no experimental basis, the evidence for the lactone linkage should be accepted with reserve. It should be pointed out that lactone and hydroxy acid types refer to the predominating forms in equilibria, so that the slight bicarbonate solubilities of the isolated lignins (Table IV) are not surprising.

When these birch lignin fractions were methylated repeatedly with dimethyl sulfate and alkali using proportions such that the reaction system was finally neutral or acid, then the acidic hydroxyl groups were replaced by methoxyl. This was substantiated by further treating the dimethyl sulfate-methylated lignins with diazomethane. No increase in methoxyl was observed. All these methylated fractions of birch formic acid lignin increased in methoxyl by the same number of groups (5.3 per kg.) but the final methoxyl values differed among themselves by the same amounts as did the corresponding isolated lignin fractions (Tables IV and V), showing that the chloroform–ether and petroleum ether insoluble fractions contain the syringyl nucleus, while the acetone–ether and dioxane–ether fractions contain the guaiacyl nucleus. The difference between the increase in methoxyl and the decrease in active hydrogen (Table II, Line 5) is larger than the formyl content (Line 6) with all frac-

(8) Lieff, Wright and Hibbert, THIS JOURNAL, **61**, 865 (1939).

TABLE II

COMPARISON OF METHOXYL INCREASE TO ACTIVE HYDROGEN[a] DECREASE

Lignin fraction	Syringyl fraction			Guaiacyl fraction	
	$CHCl_3$–pet. ether insol.	$CHCl_3$–ether insoluble		Acetone–ether insol. methylated at	
				25°	60°
Solvent for Grignard reagent	Dioxane	Dioxane	Pyridine	Pyridine	Pyridine
(1) Isolated lignin act. H/kg.	4.8	4.4	5.7	6.7	6.7
(2) "Completely" meth. lignin, act. H/kg.	2.6	1.7	3.3	3.8	3.6
(3) Decr. in act. H on methylation, (1)–(2)	2.2	2.7	2.4	2.9	3.1
(4) Incr. in OCH_3 on methylation, group/kg.	5.3	5.3	5.3	5.3	5.5
(5) Abnormal substn., (4)–(3)	3.1	2.6	2.9	2.4	2.4
(6) Formyl group/kg.	1.2	1.1	1.1	0.8	0.8

[a] All values for active hydrogen are reduced to the basis of the isolated lignin.

tions, showing that the abnormal substitution cannot be accounted for entirely by hydrolysis and methylation of these esterified hydroxyls. The remainder of this abnormal substitution (hidden hydroxyl) amounting to 1.5–1.9 per kg. (Table II, Line 5 minus Line 6) may be involved in the lactone linkage.

When the products are recovered from the Grignard machine and re-analyzed, a notable methoxyl loss is observed (Table VIII). In each instance the loss is greater in pyridine than in dioxane. This indicates that methoxyl is lost during a reaction that is incomplete in dioxane, but it cannot be simple fission of a methylated acidic hydroxyl group[9]

$$ROR' + R''MgI \longrightarrow ROMgI + [R', R'']$$

because when the demethylated product was treated with diazomethane no methoxyl increase was observed. Inspection of Table VIII shows that a certain basal methoxyl loss occurring during Grignard analysis is characteristic of all lignins, while an increasing loss is observed as the lignin becomes methylated more completely. It is suggested that these phenomena may be explained by: (1) a loss of "apparent ethoxyl" caused by alteration of the ethyl iodide-producing group[5] and (2) the loss of methoxyl because a carbomethoxyl linkage is converted to a tertiary carbinol.

Alkaline saponification of these birch formic acid lignins with 5% sodium hydroxide increased the methoxyl value more than would be expected as a result of hydrolysis of the formate group (Table VII). All fractions analyzed increased in active hydrogen content but decreased in carbonyl (compare Tables IV and VII). The saponification failed to remove completely the formate group. The stability of these ester linkages is evidence for the presence of the 2-hydroxy-1,3-dioxole group in formic acid lignin. When these saponified products were treated with diazomethane the newly created acidic hydroxyl groups[5] were methylated to give lignins containing 24.6–34.5% OCH_3. Part of this newly introduced methoxyl can be saponified with alkali (Table VII, Run 4) but it is restored on retreatment with diazomethane. Grignard analysis of one of the most completely methylated products (Table VII, Run 2) shows that the carbonyl decrease persists after methylation. Since the normal carbonyl value for similarly diazomethane-methylated lignins, not saponified (Table VI, Column 11), is about 3.2 group per kg. (in pyridine), the difference between this value and that found for the methylated saponified lignin (Table VII, 1.4 group per kg. in pyridine) evidently represents loss of carbonyl. This recalls the observation[10] that carbonyl disappears when spruce formic acid lignin is treated with alkali. The fact that methoxyl increases while carbonyl decreases suggests that part of the lignin complex (containing a carbonyl group) has been split off during the alkaline treatment.

Experimental

Extraction with Formic Acid.—The same birch woodmeal, similarly extracted, was used for the preparation of both acetic[5] and formic acid lignins. A coarser woodmeal (*ca.* 60 mesh) is more suitable for formic acid extraction. The extraction and fractionation were similar to those reported for spruce formic acid lignin[3] except that dioxane and acetone-water were used interchangeably and the chloroform and acetone extractions were effected by Soxhlet in Expt. 2 (Table IV). Diagram 1 illustrates this fractionation into chloroform soluble and insoluble and repre-

(9) Späth, *Monatsh.*, **35**, 319 (1914).

(10) Wright and Hibbert, THIS JOURNAL, **59**, 125 (1937). In this communication it was stated (p. 128, see also Table II, Expt. 13) that the hydroxyl increase to 12.5 group/kg. was incorrect. This value has been found to be 7.8 group/kg., the carbonyl value 0.0 group per kg.

sents roughly a separation into syringyl and guaiacyl fractions. When the effluent gases from the extraction (reflux condenser at 40°) were passed through 20% sodium hydroxide, this solution gave a positive test for methanol. The gases were analyzed: CO_2, 14.2; CO, 75.8; O_2, 2.6; N_2, 7.2.

TABLE III

EXTRACTION OF LIGNIN WITH FORMIC ACID (95%)

		Expt. 1	Expt. 2	Expt. 3
Wt. woodmeal, g.		200	400	200
Moisture content, %		19	7	19
Extraction period, hr.		20	12	12
Yield of crude lignin	g.	43.2	86.8	44.0
	%	26.6	23.4	
Residual woodmeal	g.	43.9	110.0	47.4
	%	26.9	33.8	..
Soluble carbohydrates	g.	70.0	..	..
	%	42.2	..	..
CO_2 liberated, g.		..	2.06	..

When the lignin fractions were boiled with formic acid for twenty hours and precipitated into water, the aqueous solution gave a positive aniline acetate test for furfural. The composition of the lignin was essentially unchanged as shown by analysis but the lignins were now only soluble in dioxane and in acetone (Table IV). A solution of 0.1 g. of chloroform–ether insoluble fraction (OCH_3, 20.5%; OCOH, 4.9%) in 12 cc. of dioxane and 7 cc. of concentrated hydrochloric acid was diluted with 18 cc. of 4% hydrochloric acid after one day and allowed to react for eighteen days. The product, recovered by dilution with water, was now only slightly soluble in chloroform. Its dioxane solution, precipitated into ether, contained 19.8% OCH_3 and 0.1% OCOH, wt. 0.06 g. When the chloroform–petroleum ether insoluble fraction was refluxed for two hours with pyridine, no change could be found in solubility, methoxyl content or Grignard analysis in dioxane.

Methylation with Dimethyl Sulfate.—The procedure previously outlined[5] was used except that 0.04 mole of dimethyl sulfate and 0.05 mole of 30% sodium hydroxide per g. of lignin were used. Under these conditions methylation of acidic hydroxyl groups was complete after four repetitions as shown by the fact that diazomethane treatment failed to increase the methoxyl value. The products were precipitated from chloroform into petroleum ether (b. p. 30–50°), Skellysolve F.

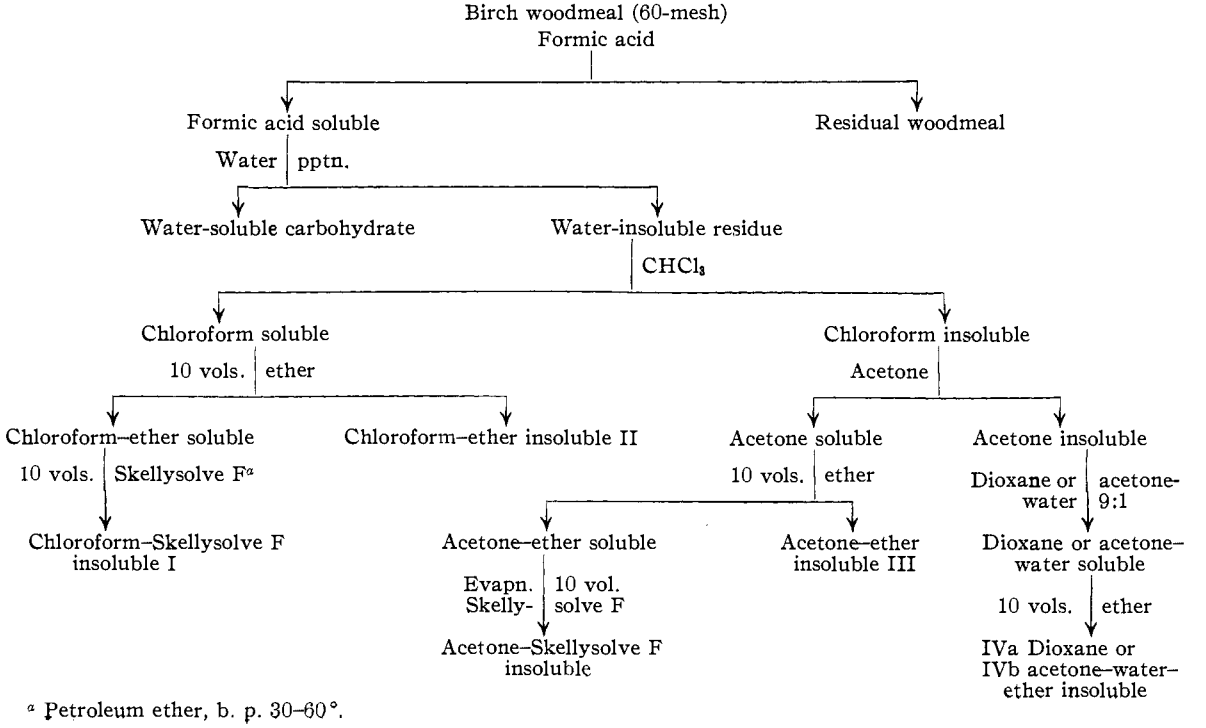
Methylation with Diazomethane.—No change was made in the prescribed[5] procedure. The products were precipitated from acetone into 10 volumes of ether. The material remaining in the precipitating liquors was recovered after evaporation by solution in chloroform and precipitation into 10 volumes of Skellysolve F.

Saponification and Diazomethane Treatment.—Saponification was effected by solution in 5% sodium hydroxide, adding dioxane if necessary for homogeneity, for a certain reaction period. The saponified product, recovered by acidification with dilute hydrochloric acid, was precipitated for analysis from dioxane–water (9:1) into ether. The same dioxane–water solution was then treated with diazomethane and the product obtained in the usual manner (see Table VII).

Recovery of Lignins Analyzed in Grignard Machine.—After analysis the products were acidified with acetic acid,

DIAGRAM 1

EXTRACTION AND FRACTIONATION OF BIRCH FORMIC ACID LIGNIN



[a] Petroleum ether, b. p. 30–60°.

TABLE IV

FRACTIONATION OF BIRCH FORMIC ACID LIGNIN

	Fraction	Experiment 1 Wt., g.	OCH_3, %	OCOH, %	Solubility in $NaHCO_3$	Grignard analysis In dioxane Act. H/kg.	In dioxane RMgX added/kg.	In pyridine Act. H/kg.	In pyridine RMgX added/kg.	Expt. 2 Wt., g.	Expt. 2 OCH_3, %	Expt. 3 Wt., g.	Expt. 3 OCH_3, %
1	Chloroform–pet. ether insol.	4.5	20.7	5.2	Slly. sol.	4.8	1.8	5.7	3.5	5.6	21.3	3.7	21.1
2	Chloroform–ether insol.	6.0	20.5	4.9	Slly. sol.	4.4	1.8	5.7	3.2	12.0	19.9	12.3	20.2
3	Acetone–ether insol.	14.6	17.7	3.8	Almost insol.	2.3	0.8	6.7	2.5	26.7	19.1	14.8	21.1
4	Acetone–pet. ether insol.									4.0	20.0		
4a	Dioxane–ether insol.	14.9	16.3	3.7	Almost insol.	2.2	.8	6.7	2.9				
4b	Acetone–water–ether insol.									29.6	17.2	5.1	17.3
	RETREATMENT WITH FORMIC ACID												
5	Chloroform–pet. ether insol.		19.1	4.9		4.6	1.3	5.9	3.5				
6	Chloroform–ether insol.		19.7	5.2		4.5	1.8	5.6	3.1				
7	Acetone–ether insol.		17.9			2.4	1.0						

TABLE V

DIMETHYL SULFATE–METHYLATED BIRCH FORMIC ACID LIGNINS

Quantity used in each case, 1 g.

	Methylations	Yield, g.	OCH_3, %	Grignard analysis In dioxane Active H/kg.	In dioxane RMgX added/kg.	In pyridine Active H/kg.	In pyridine RMgX added/kg.
Chloroform–petroleum ether insoluble	4	0.31	34.9	2.6	1.3	...	...
Chloroform–ether insoluble	4	.64	34.7	1.7	1.4	3.3	2.9
Acetone–ether insoluble	5	.64	31.9	2.7	1.5	3.7	2.5
Acetone–ether insoluble (at 60°)	4	.66	32.4	2.4	1.2	3.5	2.2
Dioxane[a]–ether insoluble	5	.2	32.2	2.3	1.2	...	...

[a] Dioxane-insoluble material formed during methylation: 0.38 g. (OCH_3, 28.0%) after third methylation; 0.22 g. after fourth methylation.

TABLE VI

DIAZOMETHANE METHYLATION OF BIRCH FORMIC ACID LIGNIN

(Quantity used in each case, 1 g.)

	Before methylation		After methylation				Grignard analysis In dioxane		In pyridine			
Run	Fraction	OCH_3, %	Soly. of prod.	Wt., g.	OCH_3, %	OCOH, %	Act. H/kg.	RMgX added/kg.	Act. H/kg.	RMgX added/kg.	Gain in methoxyl group/kg.	Loss in active H (pyridine) group/kg.
1	$CHCl_3$–pet. ether insol. (syringyl)	20.7	$CHCl_3$–pet. ether insol.	0.77	27.8	4.5	3.4	1.5	3.8	3.6	2.6	2.0
2	$CHCl_3$–ether-insol. (syringyl)	20.5	Acetone–ether insol.	.65	26.0	4.7	3.2	1.9	3.4	3.3	2.0	2.4
			$CHCl_3$–pet. ether insol.	.30	27.3				4.2	3.2		
									Only one analysis			
3	Acetone–ether insol. (guaiacyl)	17.7	Acetone–ether insol.	.90	21.8	3.6	3.7	1.6	4.6	3.4	1.5	2.2
			$CHCl_3$–pet. ether insol.	.06								
4	Dioxane–ether insol. (guaiacyl)	16.3	Acetone–ether insol.	.56[a]	22.2	3.5	3.5	1.5	4.6	3.2	2.1	2.2

[a] Part of reaction product lost because of insolubility in dioxane.

diluted with water, filtered and washed with ether to remove isoamyl ether. The residue on the filter was dissolved in either chloroform or dioxane and precipitated into Skellysolve F. Treatment of two such products with diazomethane (Table VIII) did not increase the methoxyl value.

Reduction and Methylation.—A solution of 5 g. of chloroform–ether insoluble fraction (OCH_3, 19.6%) was saponified with a solution of 55 cc. of 1% sodium hydroxide and 10 cc. of methanol (under nitrogen) over a twelve-hour period; 250 g. of 5% sodium amalgam was then added to the stirred solution over a twenty-four hour period. After removal of the mercury, together with a test sample (precipitated from dioxane into ether, OCH_3, 19.8%), the stirred solution was methylated under nitrogen over a three-day period with three portions of 19.4 cc. (0.2 mole) of dimethyl sulfate and 66.5 cc. (0.5 mole) of 30% sodium hydroxide, 300 cc. of dioxane being added gradually in order to keep the lignin in solution. The reaction mixture was then acidified with hydrochloric acid and extracted with chloroform. Two-fifths of this evaporated chloroform solution was treated for two days in 100 cc. of dioxane with two 10-cc. portions of diazomethane–ether solution from 5 cc. of nitrosomethylurethan. After evaporation to dryness the methylated lignin was entirely dissolved in benzene (30 cc.) and precipitated into Skellysolve F (400 cc.): wt., 1.68 g.; OCH_3, 34.4%; $[\alpha]^{26}_{6563} = -1.25°$. Titration at 0° with 0.065 molar perbenzoic acid in chloroform over an eighty-three day period indicated that this product still contained 5.9 double bonds per kg. The evaporated precipitating liquors were dissolved in ether and precipitated into Skellysolve F: wt. 30 g.; OCH_3, 37.8%. The remaining three-fifths of the evaporated chloroform

TABLE VII

SAPONIFICATION AND DIAZOMETHANE METHYLATION OF BIRCH FORMIC ACID LIGNINS

Run number		1	2	3	4	5
Weight used, g.		0.8	3.0	2.0	0.8	1.5
Lignin		Chloroform–petroleum ether insoluble		$CHCl_3$–Et_2O insoluble	Diazomethane methylated prod. 3	Acetone–ether insoluble
OCH_3, %		20.3	21.3	19.9	28.7	17.8
HCOO, %		..	5.0	4.9	..	3.8
Reaction period, hours		45	24	48	72	45
		With 5% sodium hydroxide				
Solubility of product		Dioxane–water–ether 1a insoluble	Dioxane–water–ether 1b soluble	Dioxane–water–ether 2a insoluble	Dioxane–water–ether 2b soluble	Dioxane soluble	Alkali insoluble	Dioxane–water–ether insoluble
Yield, g.		0.28	0.30	1.20	0.92	1.77	0.8	0.55
HCOO, %		...	...	...	...	1.2	...	...
OCH_3, %		19.9	23.4	19.4	25.8	18.9	25.9	20.4
Grignard analysis	In dioxane: Act. H/kg.	...	6.9	...	6.3	5.4	...	...
	In dioxane: RMgX added/kg.	...	0.6	...	0.3	0.5	...	...
	In pyridine: Act. H/kg.	6.9	7.3	8.0	7.2	7.7	...	...
	In pyridine: RMgX added/kg.	1.5	2.3	0.8	2.2	1.1	...	...
		With diazomethane						
Solubility of product		...	...	Insoluble in pet. ether and $CHCl_3$	Et_2O	Sol. in $CHCl_3$ Insol. in NaOH	Benzene soluble	...
Yield, g.		...	...	...	...	1.71	0.56	0.48
HCOO, %		...	...	0.7	...	...	...	.3
OCH_3, %		...	...	33.3	34.5	28.7	29.5	24.6
Grignard analysis	In dioxane: Act. H/kg.	...	...	3.3	...	...	...	...
	In dioxane: RMgX added/kg.	...	...	0.8	...	...	...	...
	In pyridine: Act. H/kg.	...	...	3.8	...	...	...	...
	In pyridine: RMgX added/kg.	...	...	1.4	...	...	...	...

TABLE VIII

PRODUCTS RECOVERED FROM GRIGNARD ANALYSIS OF BIRCH FORMIC ACID LIGNINS

	Analysis				After analysis							
			Grignard anal.						Grignard analysis			
							OCH_3 after		In dioxane		In pyridine	
Material	OCH_3, %	Solvent for Grignard	Act. H/kg.	RMgX added /kg.	OCH_3, %	Soly. in alkali	treat. with CH_2N_2, %	Loss in OCH_3, %	Act. H/kg.	RMgX added /kg.	Act. H/kg.	RMgX added /kg.
Chloroform–pet. ether insol.												
Isolated	20.0	Dioxane	4.6	1.3	16.2	+		2.9				
Diazomethane methylated	27.8	Dioxane	3.4	1.5	24.2	−		3.6				
	27.8	Pyridine	3.8	3.9	23.6	−		4.2				
Dimethylsulfate meth.	34.9	Dioxane	2.6	1.3	29.8	−	29.3	5.1				
Acetone–ether insoluble												
Isolated	17.7	Dioxane	2.3	0.9	16.7	+		1.0	4.0	0.1		
Isolated	17.7	Pyridine	6.7	2.5	15.1	+		2.6				
Diazomethane methylated	21.8	Dioxane	3.7	1.8	18.4	+[a]		3.4				
	21.8	Pyridine	4.6	3.4	17.0	+[a]		4.8			6.0	0.5
Dimethyl sulfate methylated	32.4	Dioxane	2.4	1.2	27.6	−		4.8				
	32.4	Pyridine	3.5	2.2	26.3	−	26.6	6.1				

[a] Incompletely methylated.

solution (2.42 g.) was separated into the following fractions: (1) chloroform–Skellysolve F insoluble (wt. 0.71 g.; OCH_3, 28.4%; Grignard analysis in pyridine: active H, 3.8; RMgX added, 1.3 per kg.); (2) benzene–Skellysolve F insoluble (wt. 1.49 g.; OCH_3, 30.6%); (3) ether–Skellysolve F insoluble (wt. 0.18 g.; OCH_3, 38.1%).

Summary

1. Birch formic acid lignins have been prepared, fractionated and their properties compared with the corresponding fractions from birch acetic acid lignin.

2. The evidence submitted provides further confirmation of the presence of the guaiacyl and syringyl groups in birch lignin.

MONTREAL, CANADA RECEIVED MARCH 16, 1939