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

Studies on Lignin and Related Compounds. XXXIX. The Ethanolysis of Spruce and Maple Woods

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In a recent communication[1] a description was given of a method for the isolation of water-soluble ethanolysis products from spruce and maple wood. The present paper deals with a much improved process whereby higher yields and purer products are obtained. Instead of ether, benzene is used as the extraction medium and the entire operation is conducted in an atmosphere of carbon dioxide. Using these precautions practically no "acid constituent" is obtained, the presence of such in the earlier work evidently being due to oxidation of the aldehydic portion of the extract.

Method.—Both the spruce and the maple woodmeal (40-mesh) were first air-dried and then extracted for forty-eight hours with a 1:1 mixture (by volume) of absolute ethanol and benzene, then with absolute ethanol for twenty-four hours, and finally washed with hot running water for twelve hours. After air-drying, the woodmeal was dried in the vacuum oven (20 mm. pressure) for forty-eight hours at 50°.

Ethanolysis.—Woodmeal (1000 g.) and dry ethanol (8 liters) containing anhydrous hydrogen chloride (160 g.) were placed in a flask (12 liter capacity) fitted with a stirrer, gas inlet tube for carbon dioxide, and a water condenser. The contents were refluxed for forty-eight hours in carbon dioxide atmosphere, this inert atmosphere being maintained carefully in all subsequent operations. The mixture was cooled, filtered, and the residual woodmeal washed with hot anhydrous ethanol (2 liters). The combined ethanol liquors were concentrated to a small volume (1500 cc.) under reduced pressure in a carbon dioxide atmosphere at 50°. In some cases the ethanol liquors were neutralized with sodium bicarbonate or sodium ethylate before being concentrated and this resulted in higher yields in the case of maple wood. The ethanol concentrate was dropped in a very fine stream into vigorously stirred distilled water (9 to 10 liters). The precipitated ethanol lignin was filtered off and washed well with water. The aqueous solution and washings were concentrated to a small volume (2000 cc.) at 50° under reduced pressure (40–60 mm.) and the concentrated solution then extracted continuously for forty-eight hours with benzene.

The precipitated ethanol lignin was shaken with benzene (five 200-cc. portions) for at least two hours for each shaking in order to remove adsorbed oils. The benzene extract was treated separately. These results are shown in Table I.

TABLE I

SUMMARY OF DATA FOR ETHANOLYSIS OF SPRUCE AND MAPLE WOODS

		Spruce			Maple		
Starting material	Sample no.	1	2	3	1	2	3
	Oven dry wt., g.	1000	1000	1000	1000	1000	1000
	Klason lignin, %	28.6	28.6	28.6	21.4	21.4	21.4
	Klason lignin, g.	286	286	286	214	214	214
Reaction products[a]	Residual wood meal, Weight, g.	686	700	689	602	727	556
	Residual wood meal, Klason lignin, %	26.6	26.2	25.8	12.7	13.6	12.0
	Residual wood meal, Klason lignin, g.	183	183	178	76.3	99.0	67.0
	Residual wood meal, Klason lignin, Removed, g.	103	103	108	138	115	147
	Ethanol lignin	29.6	27.6	40.5	72.3	62.5	82.2
	Extracted oils, From aq. soln., g.	32.8	30.2	30.2	42.0	65.0	75.5
	Extracted oils, From EtOH lignin, g.	17.2	17.8	21.8	26.6	35.0	38.0
	Extracted oils, Total, g.	50.0	48.0	52.0	68.6	100.0	113.5
Lignin balance[a]	Lignin left in resid. woodmeal, %	64	64	62	36	46	31
	Lignin removed in process, %	36	36	38	64	54	69
	Lignin extracted, Oils from H_2O, %	12	11	11	20	30	35
	Lignin extracted, Oils from EtOH lignin, %	6.0	6.2	7.6	12	16	18
	Lignin extracted, Oils from Total, %	18	17	18	32	46	53
	Lignin extracted, Ethanol lignin, %	10	10	14	34	29	38
	Lignin extracted, Total, %	28	37	32	66	75	91
	Total lignin accounted for, %	92	91	94	102	121	122
	Neutralization reagent	$NaHCO_3$	None	Calcd. NaOEt	None	$NaHCO_3$	Calcd. NaOEt

[a] The percentages are given on the basis of the weight of Klason lignin in the starting material. Since an alkoxyl group has been added to the lignin left in the wood residue, to the ethanol lignin, and to some fractions of the isolated oils[2] the percentages given are subject to correction by the factor of $L/[L + (OC_2H_5)]$, where L equals the molecular weights of the lignin units.

(1) Cramer, Hunter and Hibbert, THIS JOURNAL, **61**, 523 (1939).

(2) Cramer, Hunter and Hibbert, *ibid.*, **61**, 509 (1939).

TABLE II

SUMMARY OF DATA FOR FRACTIONATION OF "CRUDE OILS" FROM SPRUCE AND MAPLE WOODS

Sample	Wt. of "crude oil," g.	Bisulfite soluble Wt., g.	Bisulfite soluble %	Bicarbonate soluble Wt., g.	Bicarbonate soluble %[a]	Alkali soluble Wt., g.	Alkali soluble %[a]	"Neutral" Wt., g.	"Neutral" %[a]	Total accounted for Wt., g.	Total accounted for %[a]
Spruce, Experiment 1											
Oils from aqueous soln.	32.8	5.1	1.8	1.03	0.36	11.5	4.0	2.13	0.8	19.76	6.9
Oils from ethanol lignin	17.2	0.68	0.2	0.22	.07	7.0	2.5	3.60	1.2	11.50	4.0
Total oils	50.0	5.78	2.0	1.25	.4	18.5	6.5	5.73	2.0	31.26	10.9
Experiment 3											
Oils from aqueous soln.	30.2	5.8	2.0	0.62	.2	14.4	5.0	3.2	1.1	24.02	8.4
Oils from ethanol lignin	21.8	0.42	0.2	0.63	.2	10.0	3.5	5.6	2.0	16.65	5.8
Total oils	52.0	6.22	2.2	1.25	.4	24.2	8.5	8.8	3.1	40.67	14.2
Maple, Experiment 2											
Oils from aqueous soln.	65.0	14.2	6.6	0.86	.3	27.4	13.0	4.1	1.9	46.56	21.7
Oils from ethanol lignin	35.0	1.7	0.8	0.22	.01	17.8	8.3	5.5	2.6	25.22	11.8
Total oils	100.0	15.9	7.4	1.08	.3	45.2	21.3	9.6	4.5	71.78	33.5
Experiment 3											
Oils from aqueous soln.	75.5	15.7	7.3	0.80	.4	29.7	14.0	7.9	3.7	54.1	25.2
Oils from ethanol lignin	38.0	1.8	0.4	0.40	.2	14.6	6.8	5.6	2.6	22.4	10.5
Total oils	113.5	17.5	7.7	1.20	.6	44.3	20.8	13.5	6.3	76.5	35.4

[a] The percentages given are based on the weight of Klason lignin in the starting material. Since an alkoxyl group has been added to some of the constituents (without doubt in the case of the alkali soluble fraction), the percentages given are subject to correction by the factor $M/[M + (OC_2H_5)]$, where "M" represents the average molecular weights.

Fractionation of the Oils.—The oils isolated from the aqueous solution and from the precipitated ethanol lignin were fractionated separately, using an identical treatment in both cases, as follows.

The benzene solution was extracted successively with: (a) eight 50 cc. portions of 20% sodium bisulfite; (b) three 50 cc. portions of 8% sodium bicarbonate; (c) six 50 cc. portions of 5% sodium hydroxide, a neutral fraction remaining in the benzene.

Extract (a) was acidified with dilute sulfuric acid (10%), the liberated sulfur dioxide removed under reduced pressure, and the solution then extracted for forty-eight hours with benzene. Extracts (b) and (c) were acidified separately with dilute sulfuric acid (10%) and thoroughly hand-extracted with benzene. The results are shown in Table II.

Similar results have been obtained with other plant materials, as for example the following:

	Yield of "Crude Oils,"[a] %[b] From the aq. soln.	From ethanol lignin	Total
Douglas fir	9.0	5.6	14.6
Redwood	7.7	6.2	13.9
Red oak	31.5	19.4	50.9
Bamboo	29.7	20.4	50.1
Jute	42.9	31.1	74.0
Corn (stalks)	22.5	37.1	59.6
Rye (straw)	14.9	25.7	40.6

[a] Results obtained by Messrs. MacInnes and West. [b] The percentages are given on the basis of the weight of Klason lignin in the starting materials.

Investigation and characterization of these several ethanolysis products is being carried out and the results will be reported in a later communication.

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Summary

1. A description is given of an improved method for the extraction and isolation of water-soluble ethanolysis products from spruce and maple woods.

2. Preliminary results are included showing that ethanolysis "oils" can be obtained from all types of ligneous plant materials as yet investigated.

3. These preliminary results indicate that the ethanolysis method is broadly applicable as a means of isolating in high yield the building units from the lignin of a wide variety of plant types.

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