Studies on Lignin. III.[1] On the Lignin of *Paulownia imperialis*.

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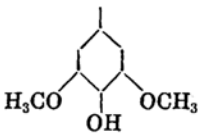
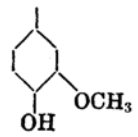
It was recently discovered that, according to the species of woods, lignins contained in them are classified into two series.[2][3] Namely, the one contains syringyl and guaiacyl radicals as building units, while the other consists mainly of guaiacyl radicals. Among the lignins of woods which have hitherto been studied, those of birch, maple, and beech contain both syringyl and guaiacyl radicals, and those of spruce and fir contain merely guaiacyl radicals. Japanese pine and cryptomeria belong to the latters. Thus, broad-leaved trees or hard woods contain syringyl radical, while needle-leaved trees or soft woods do not. The wood of Japanese paulownia, however, is very soft, but it belongs to broad-leaved trees. So it is not clear to which series the paulownia wood belongs. This communication concerns with this point.



Syringyl-radical



Guaiacyl-radical

The lignin content of paulownia wood is measured by sulphuric acid method.[4] That is, fine saw-dust (80 mesh) of paulownia is dried at 105°, and extracted with alcohol-benzene mixture for 4 hours. Then it is added to 72% sulphuric acid to remove cellulose, hemicellulose, and other materials by hydrolysis. Water is added to the mixture to make 3% sulphuric acid solution and the solution is boiled for 4 hours and filtered. The obtained lignin is weighed and the lignin content is found to be 19.3% of dried wood. While the lignin contents of soft woods as spruce or fir are 25 to 28%, and those of hard woods as maple or birch are about 20%.

Lignin is isolated from paulownia wood by method of Harris.[5] That is, fine saw-dusts of paulownia wood, extracted first with alcohol-benzene mixture, then with alcohol, and finally with hot water, are treated with 70% sulphuric acid for 20 hours at 10°. Then the mixture is diluted with water to make 3% sulphuric acid solution, boiled, and then filtered. The methoxyl-value of the lignin thus obtained is 20.7%, and is same as that of the lignin of maple wood obtained by Harris. As the methoxyl-contents of the lignin of needle-leaved trees such as spruce, fir, or cryptomeria are

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(1) K. Iwadare, *J. Chem. Soc. Japan*, **62** (1941), 186.

(2) K. Freudenberg and H. Fr. Müller, *Ber.*, **71** (1938), 1821.

(3) Hibbert et. al., *J. Am. Chem. Soc.*, **61** (1939), 509, 516, 868, 2198; **62** (1940), 986, 2149; **63** (1941), 312.

(4) C. J. Ritter, R. M. Seborg, and R. L. Mitchell, *Ind. Eng. Chem., Anal. Ed.*, **4** (1932), 202.

(5) E. C. Sherrard and E. E. Harris, *Ind. Eng. Chem.*, **24** (1932), 103; E. E. Harris, E. C. Sherrard, and R. L. Mitchell, *J. Am. Chem. Soc.*, **56** (1934), 889; E. E. Harris, *J. Am. Chem. Soc.*, **58** (1936), 894.

15–17%, the paulownia belongs apparently to the series of so-called hard-wood lignin.

Paulownia wood is ethanolised by usual method. Dry saw-dust, the resinous materials of which have been removed as mentioned above, is heated for 48 hours with absolute alcohol containing hydrogen chloride. The experimental data are as follows. (Table 1).

Table 1.[6]

		Weight (g.)	Percentage (%)	
			Calc. for wood-meal	Calc. for lignin
Starting substance	Paulownia wood-meal dried at 100-105°	70		
	Lignin content of the wood-meal (by 72% sulphuric acid method[4])	13.5	19.3	
Reaction products	Residual wood-meal	38	54	
	Lignin content of the residual wood-meal	2.8	7.4	21
	Lignin removed by ethanolysis	10.7		79
	Ethanol lignin	2.5		18
	Materials extracted with benzene: From aqueous solution	5.5		41
	Materials extracted with benzene: From ethanol lignin	3.5		26
	Materials extracted with benzene: Total	9.0		67

The methoxyl-content of the ethanol lignin is 26.9%, calculating ethoxyl as methoxyl.

The benzene solution of the extracted materials is shaked with aqueous solutions of sodium bisulphite, sodium bicarbonate and sodium hydroxide respectively and fractionated into aldehydic, acidic, phenolic, and neutral materials. (Table 2).

Table 2.[6]

	Weight (g.)	Percentage (Calc. for total lignin) (%)
Materials extracted with benzene	9	67
Aldehydic	0.8	6
Acidic	0.2	1.5
Phenolic	3.7	27
Neutral	0.4	3
Total	5.1	37.5%

(6) Some of the percentages in table 1 and 2 should be corrected by the factor $L/(L+OC_2H_5)$ owing to the ethoxyl group added to lignin. (L is the molecular weight of the building unit of lignin.)

The aldehydic fraction is dissolved in ethyl alcohol, and saturated ethyl alcohol solution of anhydrous potassium acetate and 2% potassium hydroxide-ethyl alcohol solution are added to it. Orange-yellow needles appear within half an hour. Adding semicarbazide hydrochloride to this precipitate, colourless crystals melting at 210.5–211.5° are obtained. This melting point agrees with that of monosemicarbazone of syringoylmethylketone (210–210.5°) obtained by Hibbert from maple wood, and so this compound obtained from paulownia lignin is identified as syringoylmethylketone. It is therefore established that paulownia lignin contains syringyl radicals, and belongs to so-called hard wood lignin.

Recently, it was reported by K. Freudenberg,[7] that vanilline was obtained by oxidation of spruce wood-meal with nitrobenzene, and now paulownia wood-meal was oxidized by the same method. That is, paulownia wood-meal is heated in an autoclave at 160° with nitrobenzene and aqueous alkaline solution. From the reaction mixture nitrobenzene is removed by water-distillation. The residual solution is filtered, made slightly alkaline with sodium bicarbonate, and extracted continuously with benzene for 72 hours. Benzene extract corresponds to about 14% of the initial wood-meal and therefore to 70% of the lignin contained in it. A small portion of the benzene extract is suspended in water and acidic aqueous solution of 2,4-dinitrophenylhydrazine is added. The precipitated 2,4-dinitrophenylhydrazone is weighed, and the whole quantity of the aldehydes in the benzene extract is calculated from it. It corresponds to about 38% (by weight) of the lignin existing in the initial wood-meal, assuming the aldehydes as vanilline, and to about 43%, assuming them as syringylaldehyde.

Another portion of the benzene extract is dissolved in alcohol, filtered if necessary, and alcohol which contains dry ammonia is added. Yellow crystals appear immediately on standing. 2,4-Dinitrophenylhydrazone melting at 234.5–235° is obtained from it, so it is identified as the syringaldehyde derivative.

Experimental.

Lignin content of paulownia wood-meal. Paulownia wood-meal (80 mesh) was dried at 105°, and 1.971 g. of it were extracted with benzene-alcohol mixture in Soxlet-apparatus for 4 hours. It was filtered, washed with alcohol, and heated with 400 c.c. of water in a boiling water bath for 3 hours. It was filtered, dried and mixed with 25 c.c. of 72% sulphuric acid. After 2 hours, it was diluted with water to make 3% sulphuric acid solution and boiled for 4 hours. Insoluble lignin was weighed by filtering the solution with a tared glass-filter. Brown lignin (0.380 g.) was obtained. This corresponds to 19.3% of the initial wood-meal.

The methoxyl-value of paulownia lignin. Paulownia wood-meal (24 g.) was mixed with 240 c.c. of 70% sulphuric acid, and stirred for 3 hours at 10°. After standing overnight in a refrigerator at 10°, it was poured in 9 l. of water and boiled for 4 hours. It was filtered and air-dried.

(7) K. Freudenberg, W. Lautsch, and K. Engler, *Ber.*, **73** (1940), 167.

Yield, 5 g. The methoxyl-value of the lignin dried at 100° in vacuo over phosphorous pentoxide is 20.7%.

The ethanolysis of paulownia wood-meal. Paulownia wood-meal (70 g.), freed from resinous materials by extracting with alcohol-benzene mixture, alcohol, and then with hot water, was boiled for 48 hours with 850 c.c. of absolute ethyl alcohol containing 2% of hydrogen chloride. It was filtered, washed well with alcohol, and the combined filtrate and washings were neutralized with sodium ethylate, and evaporated under reduced pressure to 150 c.c. It was poured into 1.2 l. of water, and filtered. The precipitate was dried and extracted ten times by shaking mechanically with benzene (50 c.c.). The filtrate was evaporated to 200 c.c. and extracted continuously with benzene for 48 hours. Both benzene extracts were evaporated, and 3.5 g. and 5.5 g. of sirups were obtained respectively. The sirups were dissolved in benzene and the combined benzene solution was extracted many times with aqueous solution of sodium bisulphite, sodium bicarbonate and sodium hydroxide to fractionate it into aldehydic, acidic, phenolic and neutral materials. The sodium bisulphite extract was made acidic by sulphuric acid, isolated sulphurous acid being removed under diminished pressure, and extracted continuously with benzene. The benzene extract was evaporated to sirup (0.8 g.) and dissolved in absolute ethanol (25 c.c.). The ethyl alcoholic solution of sodium acetate was added to it, and 2% alcoholic solution of sodium hydroxide was added to the mixture to make it slightly alkaline. Orange-yellow needles precipitated within half an hour. It was filtered, and 20 mg. of the precipitate were dissolved in 1 c.c. of water, and 14 mg. of semicarbazide hydrochloride and 20 mg. of potassium acetate were added. It was filtered after 2 hours. Melting point, 210.5–211.5° (corrected). This corresponds to monosemicarbazone of syringoylmethylketone.

The methoxyl-value of ethanol lignin is 26.9%, and that of the lignin isolated from the residual wood-meal by 70% sulphuric acid method is 21.0%, which is almost equal to the methoxyl-value of the lignin from initial wood-meal. Other experimental data are given in tables 1 and 2.

The oxidation of paulownia wood-meal with nitrobenzene. Paulownia wood-meal (35 g.) was heated for five hours in an autoclave with 400 c.c. of 10% sodium hydroxide solution and 20 c.c. of nitrobenzene. The mixture was water-distilled, and remaining solution was filtered. The filtrate was made slightly acidic by adding hydrochloric acid, and then made slightly alkaline by sodium bicarbonate. It was continuously extracted with benzene for 72 hours, and the benzene solution was evaporated in vacuo. The residual sirup was 5.0 g. It was dissolved in 100 c.c. of benzene, and 1 c.c. of it was evaporated and acidic aqueous solution of 2,4-dinitrophenylhydrazine was added to it. Calculating from the weight (58.2 mg.) of 2,4-dinitrophenylhydrazone obtained, 2.66 g. or 2.92 g. of aldehydes should exist in the benzene extract, if the aldehydes are assumed to consist only of vanilline or syringaldehyde respectively. They correspond to about 38% or 43% (by weight) of the lignin existing in the initial wood-meal.

Benzene extract (0.7 g.) was dissolved in 5 c.c. of alcohol, filtered, and alcohol which contained dry ammonia was added. Yellow crystals

were obtained. It was dissolved in ethanol containing a few drops of concentrated hydrochloric acid, and 2,4-dinitrophenylhydrozine was added. Red crystals melting at 234.5–235° were obtained. This melting point agrees with that of 2,4-dinitrophenylhydrazone of syringaldehyde.

The residual aqueous solution, which had been extracted with benzene, was made acidic by adding hydrochloric acid and extracted continuously with benzene. Thus, 1.2 g. of acidic fraction were obtained.

Summary.

Although paulownia wood is very soft, its lignin belongs to so-called hard-wood lignin, and it contains both syringyl and guaiacyl radicals. These facts are established by the measurements of the lignin content and of the methoxyl value of the paulownia wood lignin, and by the ethanolysis and oxidation with nitrobenzene.

In conclusion, the author wishes to express his hearty thanks to Prof. B. Kubota for his kind advice for this experiment.

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