Structure of Alkali Lignins Fractionated from Ricinus communis and Bagasse. 2. Alkaline Nitrobenzene Oxidation

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ABSTRACT

Alkaline nitrobenzene oxidation of the different lignin fractions isolated from Ricinus communis and bagasse yielded mainly vanillin, followed by syringaldehyde and then p-hydroxybenzaldehyde. The number of the guaiacyl units is higher than the sum of both syringyl and p-hydroxyphenyl propane units in soda lignins and acetone-soluble sulfate lignins for both Ricinus communis and bagasse. For acetone-insoluble sulfate lignins, the number of guaiacyl units is less or equal to the sum of both syringyl and p-hydroxyphenyl propane units for both Ricinus communis and bagasse.

INTRODUCTION

Oxidation of lignins with nitrobenzene in the presence of sodium hydroxide has been carried out because this type of reaction yields products which still contain the benzene ring. Such oxidation has frequently been used in recent years for the characterization of lignin preparations.

The oxidation of lignin has been studied by several authors [1-4]. Hibbert et al. [5] applied the alkaline nitrobenzene method to the protolignins of many woods. They found that gymnosperms gave only vanillin whereas angiosperms gave a mixture of vanillin and syringaldehyde. Some conifers gave both vanillin and syringaldehyde.

Iwadare [6] found that the yield of aldehydes (vanillin and syringaldehyde) differs according to the method of isolation and the chemical treatment of the lignin. Alkali lignin was reported to produce the highest yield of vanillin.

The results obtained by Mansour et al. [7, 8], showed that alkali lignins of bagasse and cotton stalks isolated under the same conditions of cooking gave mainly vanillin on oxidation with alkaline nitrobenzene. In the case of bagasse, traces of p-hydroxybenzaldehyde were isolated. The oxidation of various alkali lignin isolated from rice straw (i.e., the whole plant and its leaves) with alkaline nitrobenzene yielded mainly vanillin in addition to traces of p-hydroxybenzaldehyde.

Hibbert et al. [5] and Leopold [9] applied alkaline nitrobenzene oxidation to dicotyledons including hardwoods, and they obtained mainly vanillin but no p-hydroxybenzaldehyde.

EXPERIMENTAL

Oxidation was achieved in closed ampules into which the samples to be analyzed had been introduced previously [10]. 0.2 g lignin, 10 mL of 2 N sodium hydroxide, and 0.6 mL of redistilled nitrobenzene were put in a small stainless steel autoclave at $180 \pm 2°C$ for 2 h. The autoclaves were shaken vigorously for 2 min every 15 min. After cooling, the reaction mixture was transferred to a liquid-liquid perculator and extracted with ether for about 2-3 d in order to remove the nitrobenzene and its reduced products. After acidification with dilute hydrochloric acid, the reaction mixture was reextracted with ether.

The etherial extract was evaporated and the remaining residue (acids and phenols) was treated with 50 mL sodium bicarbonate solution (10%) and extracted again with ether. The etherial solution of phenols and phenolic aldehydes was washed with water, dried over anhydrous sodium sulfate, concentrated to 2-3 mL, and quantitatively brought to 5 mL.

The identification of the products was achieved by gas-liquid chromatography. Authentic samples of 18 μg of each of p-hydroxybenzaldehyde, vanillin, and syringaldehyde were separated by gas-liquid chromatography (shown in Fig. 1). Retention times for these substituted aldehydes are 11, 17, and 43 min, respectively.
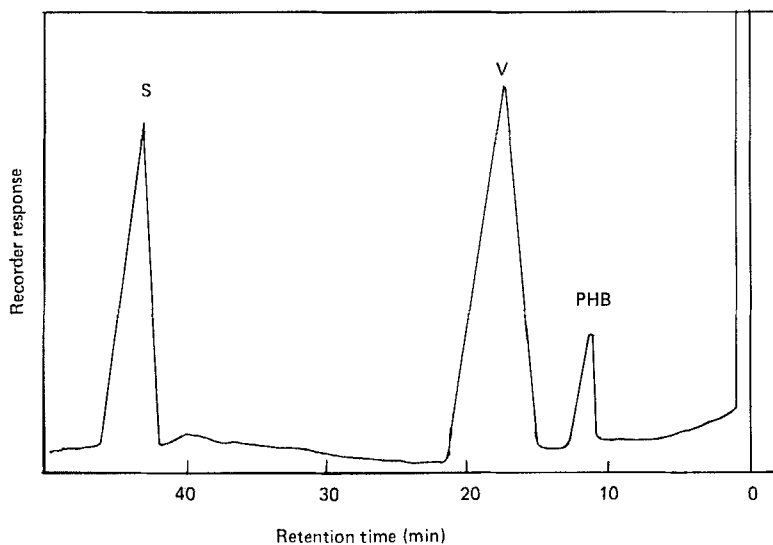
FIG. 1. Standard calibration curve of p-hydroxybenzaldehyde (PHB), vanillin (V), syringaldehyde (S) (18 mg of each).

RESULTS AND DISCUSSION

Different lignin fractions were subjected to alkaline nitrobenzene oxidation. The separation of the different aldehydes was carried out by gas-liquid chromatography [11]. The results are shown in Figs. 2-4.

From these figures it is clear that vanillin represents the main aldehyde which resulted from the alkaline nitrobenzene oxidation of different lignin fractions followed by syringaldehyde and then p-hydroxybenzaldehyde. De Stevens et al. [12] found syringaldehyde in the native lignin of bagasse, whereas Mansour et al. [7] noted the absence of syringaldehyde in the hemilignin fractions isolated from cotton stalks and bagasse. However, the proportion of syringaldehyde in De Stevens et al.'s work is higher than that found in the present work. The absence of syringaldehyde in our previous work [7] may be attributed to the method of isolation of lignin, since the cooking temperature adopted in the previous work was 150°C and in this work it was 160-170°C. The difference between the proportions of syring-aldehyde found by De Stevens et al. and those presented in this work may be due to the difference in the proportion of aldehydes resulting from variations in the conditions of oxidation.

FIG. 2.   Chromatographic separation of oxidation products of lignins from soda cooking of bagasse (B) and Ricinus communis (Rc). (a) Lignin from one-step complete cooking of B.   (b) Lignin from 1st cooking stage of Rc.   PHB = p-hydroxybenzaldehyde.   V = vanillin. S = syringaldehyde.

FIG. 3. Chromatographic separation of oxidation products of lignins from kraft cooking of bagasse (B) and Ricinus communis (Rc). (a) Soluble lignin from one-step complete cooking of B. (b) Soluble lignin from 1st cooking stage of Rc.
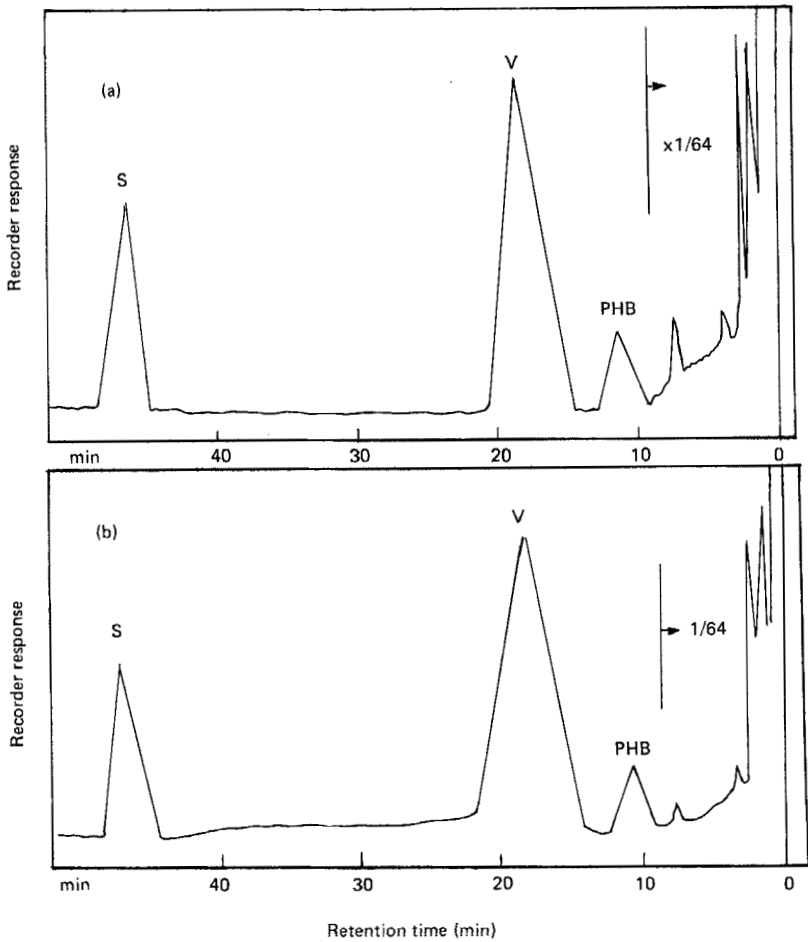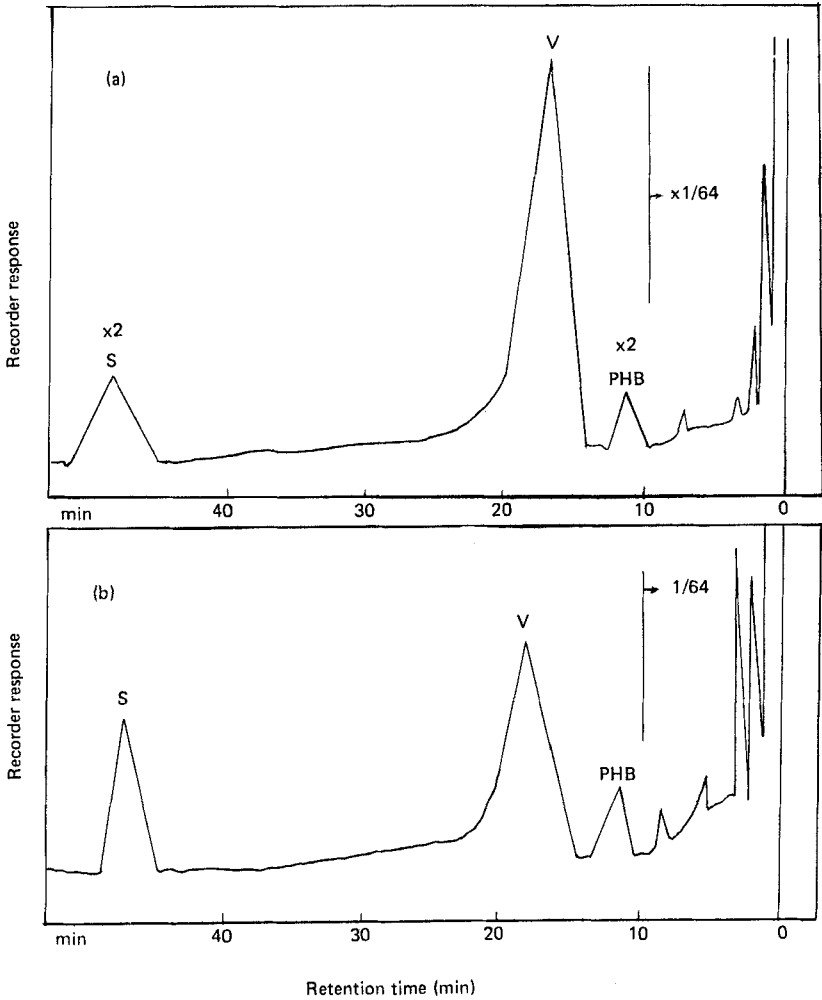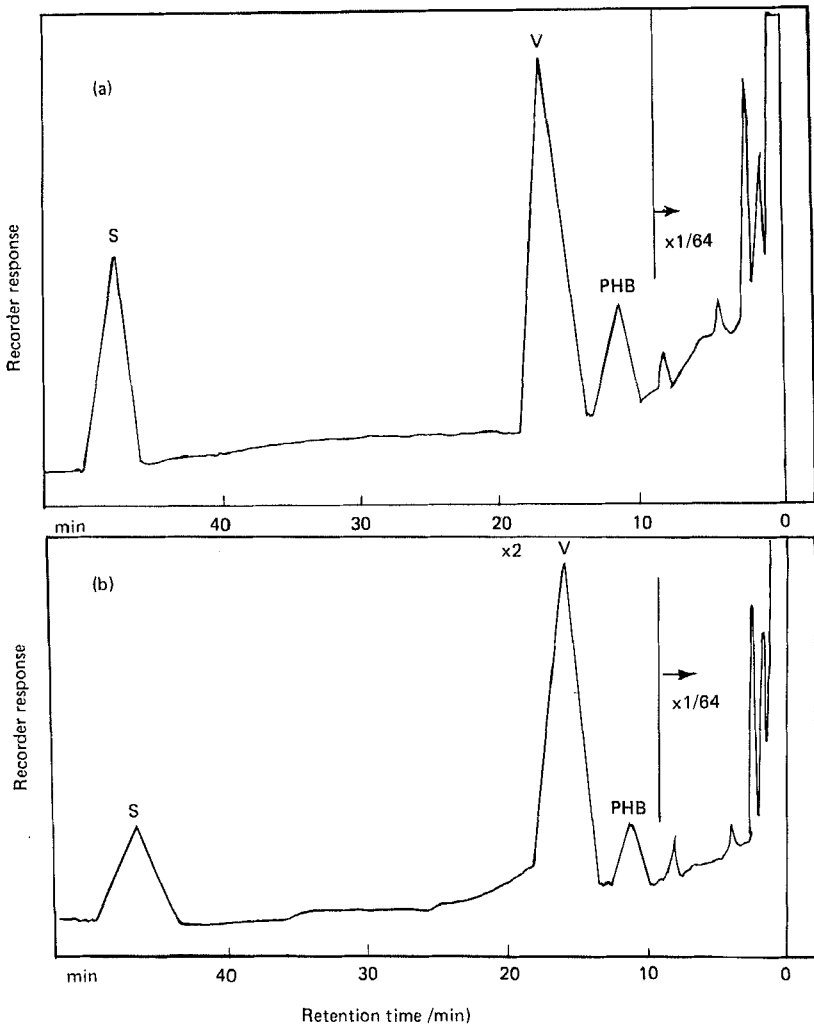
FIG. 4. Chromatographic separation of oxidation products of lignins from kraft cooking of bagasse (B) and Ricinus communis (Rc). (a) Insoluble lignin from one-step complete cooking of B.   (b) Insoluble lignin from 1st cooking stage of Rc.

As shown in Figs. 2-4, in addition to the aforementioned aldehydes there are other unidentified oxidation products which may be other aldehydes or ketones such as acetoguoiacone and acetosyringone, although they are present in small amounts. Areas under the peaks have been determined using a planimeter. Uncertainties in area are of the order of ± 5%. Figure 1 has been used to transform areas to weights. The amounts of vanillin, syringaldehyde, and p-hydroxy-benzaldehyde, as well as their molar proportions, are presented in Tables 1 and 2.

Calculations of the methoxyl group (MeO) per C_9 on the basis of the molar proportion of the aldehydes are listed in Tables 1 and 2. The values, which are higher than those determined by chemical analysis for all lignin preparations (cf. Tables 1 and 2 in Part 1 of this series), indicate the presence of condensed units.

From a study of the oxidation of model compounds, Wacek et al. [13] showed that the yield of the aldehydes is dependent not only on being uncondensed (i.e., from $>C-C<$) but also on having the right substituent on the α-carbon of the side chain. Thus, the yield of aldehydes can only give an upper possible limit of the percentage of condensed units [14]. It is worth mentioning that the yield of p-hydroxy-benzaldehyde from p-hydroxyphenyl propane elements is expected to be much lower than that of vanillin from the guaiacyl elements. Furthermore, the yield of syringaldehyde from syringyl elements is expected to be much higher than that of vanillin from guaiacyl elements [15]. This is because the p-hydroxyphenyl propane element may contain a large proportion of condensed elements, i.e., containing an extra carbon-carbon linkage in a position ortho to that hydroxyl group compared to the guaiacyl and syringyl elements, in addition to the steric hindrance effect [14].

Assuming that lignin is built of phenyl propane units, the aromatic nucleus is methoxyl free, such as in p-hydroxybenzaldehyde, guaiacyl (having one methoxyl) and syringyl elements (having two methoxyl). When p-hydroxybenzaldehyde is much lower in the aldehydic mixture than the p-hydroxyphenyl propane element in lignin, the calculated methoxyl per C_9 would be expected to be higher than the analytical one which has been found in this work. The following equation was used for calculating the methoxyl:

$$M_p + M_v + M_s = 1 \qquad\qquad\qquad (1)$$

then

$$M_v + 2M_2 = MeO \qquad\qquad\qquad (2)$$

where M_p, M_v, and M_s are the molar fractions of p-hydroxybenzalde-hyde, vanillin, and syringaldehyde, respectively, as present in lignin

TABLE 1. Nitrobenzene Oxidation Products of Lignins Isolated from Black Liquors of Kraft and Soda Cooking of Bagasse

Sample	Cooking stage	Area (cm²)			Weight (μg)			Molar proportion			Methoxyl group/C₉ expected from oxidation products
		pHB	V	S	pHB	V	S	pHB	V	S	
Lignins from soda cook	1	2.88	29.53	4.59	3.2	25.90	7.65	0.11	0.71	0.18	1.07
	4	4.2	32.26	12.8	4.66	28.3	21.33	0.11	0.55	0.34	1.23
	Cᵃ	2.38	17.25	6.75	2.64	15.13	11.25	0.10	0.55	0.34	1.23
Soluble lignins from kraft cook	1	1.43	33.05	6.6	1.59	28.9	11.0	0.05	0.72	0.23	1.18
	4	2.7	23.61	7.56	3.0	20.7	12.6	0.11	0.59	0.30	1.19
	Cᵃ	2.8	21.22	6.3	3.1	18.6	10.5	0.12	0.60	0.28	1.16
Insoluble lignins from kraft cook	1	2.38	23.44	5.4	2.64	20.56	9.0	0.11	0.66	0.24	1.13
	4	1.5	16.38	6.48	1.67	14.37	10.8	0.08	0.57	0.35	1.27
	Cᵃ	2.64	15.24	7.5	2.93	13.37	12.5	0.13	0.49	0.38	1.25

ᵃDenotes the one-step full cooking process.

TABLE 2. Nitrobenzene Oxidation Products of Lignins Isolated from Black Liquors of Soda and Kraft Cooks of Ricinus communis

Sample	Cooking stage	Area (cm)^2			Weight (μg)			Molar proportion			Methoxy group/C_9 expected from oxidation products
		PHB	V	S	PHB	V	S	PHB	V	S	
Lignins from soda cook	1	1.87	19.38	5.89	2.07	17.0	9.82	0.09	0.61	0.30	1.20
	4	1.53	16.43	6.93	1.73	14.4	11.55	0.08	0.56	0.37	1.29
	6	1.36	9.72	4.84	1.5	8.07	8.07	0.11	0.48	0.41	1.29
	C[a]	1.62	18.04	6.3	1.8	16.15	10.5	0.08	0.59	0.33	1.24
Soluble lignins from kraft cook	1	1.8	13.56	4.86	2.0	11.89	8.1	0.11	0.56	0.33	1.22
	4	1.8	20.3	6.76	2.0	17.8	11.25	0.09	0.45	0.50	1.24
	6	1.92	21.84	6.24	2.13	19.16	10.4	0.08	0.56	0.36	1.20
	C[a]	1.54	21.58	6.75	1.71	18.93	11.25	0.07	0.62	0.31	1.24
Insoluble lignins from kraft cook	1	1.47	28.29	4.78	1.63	24.82	7.96	0.06	0.74	0.20	1.14
	6	1.3	24.22	6.11	1.44	21.25	10.18	0.06	0.68	0.27	1.21
	C[a]	1.47	29.31	8.39	1.63	25.71	13.98	0.05	0.65	1.30	1.24

[a]Denotes the one-step full cooking process.

itself, and MeO is the number of methoxyl groups per C_9. From Eqs. (1) and (2), one can deduce:

$$M_p = M_s + (1 - MeO) \tag{3}$$

From this equation the proportion of MeO free elements should be approximately equal to the syringyl elements in lignin when MeO/C_9 is equal to 1.

However, as seen from Tables 1 and 2, the molar ratio of p-hydroxybenzaldehyde to syringaldehyde for soda lignin is less than 1. On the other hand, the MeO/C_9 (Tables 1 and 2) is equal to or approaches 1, indicating the equality of the p-hydroxyphenyl and syringyl elements. This result indicates that the number of p-hydroxyphenyl propane units condensed is more than the syringyl units.

For kraft lignins of bagasse, the values of MeO/C_9 are much lower than those of soda lignins, which mean that the methoxy-free elements should be higher than syringyl units, but still the molar ratio of p-hydroxybenzaldehyde to syringaldehyde is low and less than those of soda lignin. This reveals that a much higher proportion of methoxy-free elements are condensed in draft lignins than in the soda lignin of bagasse.

Soda lignins isolated from the black liquor of soda cooking of Ricinus communis showed MeO/C_9 values larger than 1 (Tables 1 and 2). This means that the proportion of methoxy-free elements in the lignin itself is less than that in syringyl elements, but the yield of p-hydroxybenzaldehyde and syringaldehyde is still too small. This suggests that the proportion of condensed methoxy-free elements in lignin from the soda cook of Ricinus communis is less than that from lignins from the soda cook of bagasse. As for lignins from the kraft cook of Ricinus communis, similar conclusions for condensation as for those of bagasse can be applied.

Summing up, the number of guaiacyl elements is higher than the sum of both syringaldehyde and methoxy-free elements in lignins from soda cooks and soluble lignins from kraft cooks of both bagasse and Ricinus communis.

On the other hand, for the insoluble lignins from kraft cooks of both bagasse and Ricinus communis, the number of guaiacyl units in these is expected to be less than or equal to the sum of both methoxy-free and syringyl elements, since the values of MeO/C_9 are significantly lower than the others.

However, these deductions are for the case in which relative and absolute yields of aldehydes mainly depend on the nitrobenzene oxidation, the conditions of time and temperature [11], and also on the place of cleavage of the bond.

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