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Structure of Alkali Lignins Fractionated from Ricinus communis and Bagasse. 3. IR Spectra

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ABSTRACT

The lignin fractions isolated by one- and multistage soda and sulfate cookings showed almost identical IR spectra, indicating the similarity of the lignin skeletal structure throughout the plant. However, the absorbances reveal some differences. Similarity of the spectra includes: 1) chelation and bonding of the hydroxyl groups. 2) Stretching vibration of C–H bonds in methyl, methoxyl, and methylene groups. 3) Stretching vibration of C≡N. 4) Carbonyl unconjugated β-ketone, conjugated acids, or esters at 1725 cm^{-1}. There is no change in the intensity of absorption at this band from that at 1515 cm^{-1} with the cooking stage. 5) Aromatic skeletal vibration at 1610 and 1515 cm^{-1}, affected by ring substituents at 1425 cm^{-1}. 6) The band at 1465 cm^{-1} showed a higher intensity for soda and soluble kraft lignins than for insoluble kraft ones. 7) The band at 1370 cm^{-1}, assigned to phenolic OH bending, is affected by the methoxyl group. 8) The absence of condensed guaiacyl and the presence of syringyl and uncondensed guaiacyl. Assignments for hardwood lignin are shown for soda and soluble kraft lignins of bagasse, while those for softwood lignin are shown for soda, soluble, and insoluble kraft lignins of Ricinus communis and for insoluble kraft lignin of bagasse. A relation exists between the carbohydrate's lignin and the band at 920 cm^{-1}. Lignins from Ricinus communis

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are of higher guaiacyl to syringyl ratios than those from bagasse. The presence of C–S vibration and the absence of thiol groups for kraft lignins are indicated.

INTRODUCTION

The absorption bands in the IR spectra of lignin are considered to be due to the presence of aromatic rings, saturated aliphatic groups, hydroxyl groups, and small amounts of carbonyl groups [1].

The hydroxyl groups in the lignin macromolecules appear to be involved in the hydrogen bonds and the phenolic hydroxyls are sterically hindered [2]. Jones [3] found that both aliphatic and aromatic hydroxyls, as well as aldehydic and ketonic carbonyl groups, are present in lignin. The different lignin fractions were found to be quite similar except in the carbonyl group intensity which changed from one fraction to another. Ekman [4] found that the stretching frequencies of the carbonyl groups are present in the 1720-1740 cm^{-1} region, which is of considerable interest. Bolker et al. [5, 6] and Lomova et al. [7] suggested that a band near 1710 cm^{-1} in the spectrum of isolated lignins arises as a result of the cleavage of a bond between lignin and carbohydrates. Sarkanen [8] found that in softwood lignin, the intensity of the band at 1660 cm^{-1} is significantly lower than that of the band at 1510 cm^{-1}, while in hardwood lignin these two bands are equal in intensity.

Structural studies of the lignins isolated by acidification of soda or kraft pulping liquors have been conducted to gain insight into the alkaline cooking process. The results indicate that the kraft process causes an increase in phenolic hydroxyl content through ether cleavage and loss of methoxyl group [9].

Kraft lignins have been fractionated by progressive acidification. The spectra of such fractions showed important differences, particularly in the carbonyl stretching region, providing evidence of the heterogeneity of this form of lignin.

Interesting results were obtained from the IR spectra of alkali lignins and their derivatives isolated from cotton stalks and bagasse under the same conditions of pulping [10]. Broadening of the bands was due to the inhomogeneity of the compound and to the fact that the bands are not from isolated monomer molecules but are from infinite polymer chain. Condensed and uncondensed guaiacyl units, as well as cross-linking, have been observed from broadening of the ether bonds. Finally, lignin undergoes keto-enol tautomerism during acetylation and methylation.

In this part of our series, successive fractionation of alkali lignins was carried out using 4 and 6 portions of alkaline reagents for both bagasse and Ricinus communis, respectively. The IR spectra of these lignin fractions were investigated and compared with lignin isolated by one step of cooking.

EXPERIMENTAL

Ricinus communis and bagasse were pulped by the soda and the sulfate processes; one with one stage and the other one with multistages. In one stage the amount of alkali used for pulping was added to the material in a rotating autoclave thermostatically heated and automatically controlled. The maximum temperature used was 160°C for 1 h. For the soda process 20% sodium hydroxide was used for cooking bagasse and 30% for cooking Ricinus communis. The sulfate or kraft pulping process was carried out at the same conditions but at 20% sulfidity for both bagasse and Ricinus communis. In the multistage cooking processes, the alkali concentrations used in the one-stage process were subdivided into four equal portions in the case of bagasse and into six equal portions in the case of Ricinus communis. Each portion was added to the material in the autoclave, heated to 160°C, and then left for 1 h. The material was then washed and used for the subsequent addition, and so on. For each cooking step, the black liquor was separated and lignin was isolated as follows.

At the end of the cooking time, the contents of the autoclave were filtered through a G_3 sintered glass funnel. The black liquor was acidified with concentrated hydrochloric acid to pH 1.5, heated to 90°C, and then left for 1 h to hydrolyze the residual carbohydrates. The crude alkali lignins (soda and kraft) were filtered, washed with water, and redissolved again in sodium hydroxide. Concentrated hydrochloric acid was added dropwise to pH 3, and the precipitate was then filtered through a G_3 sintered glass funnel and washed thoroughly with distilled water to neutrality. The pure alkali lignins were dried in air and then in a vacuum oven for 6 h. The dry products were brown in color and fine, containing less than 1% ash. For further purification, the soda lignins were dissolved in acetone, filtered, then the lignin was precipitated and filtered, dried in a vacuum oven for 8 h, and then used for IR investigation.

Kraft lignins were also dissolved into acetone. Two fractions were obtained: acetone-soluble and acetone-insoluble. The two fractions were dried in a vacuum oven for 8 h and then used for IR investigation.

RESULTS AND DISCUSSION

Several investigators have made efforts to establish assignments of the characteristic absorption bands of lignin [8, 11-13]. The aromatic nuclei in lignin represent mainly 1,2,4-tri- and 1,2,4,6-tetrasubstitution patterns. The former pattern exists in uncondensed guaiacyl nuclei; the latter in both syringyl and condensed guaiacyl nuclei.

The spectra of lignins obtained from soda and kraft cooks of bagasse and Ricinus communis are presented in Figs. 1-6. The spectra of the

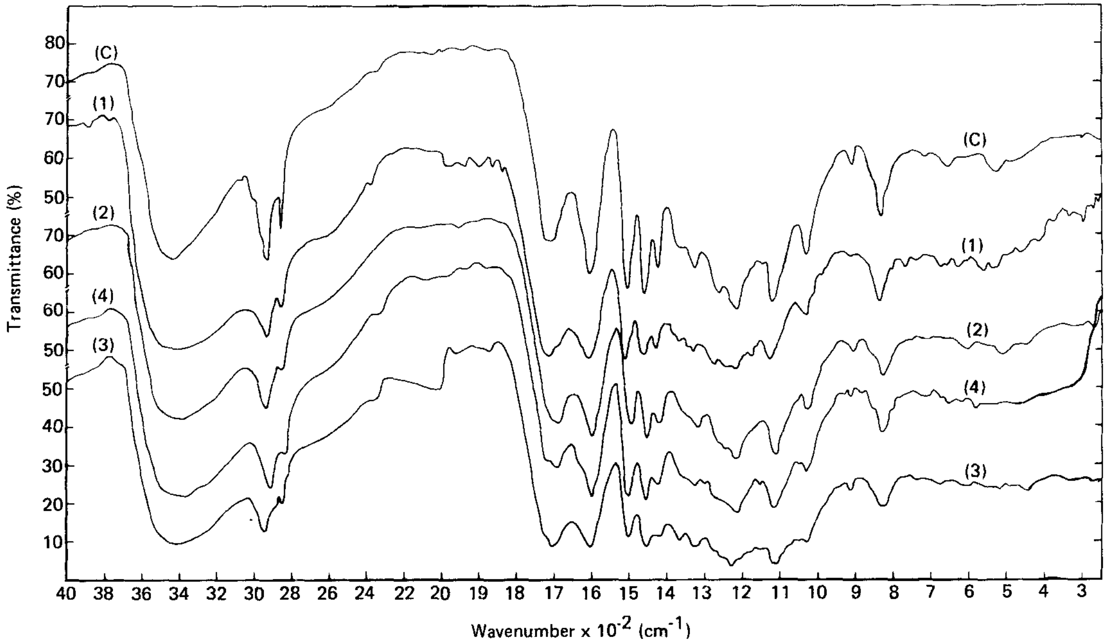

FIG. 1. IR spectra of lignin from multistage soda cooking of bagasse. The spectra are labeled by the number of successive cookings. (C) is a one-step complete cooking.

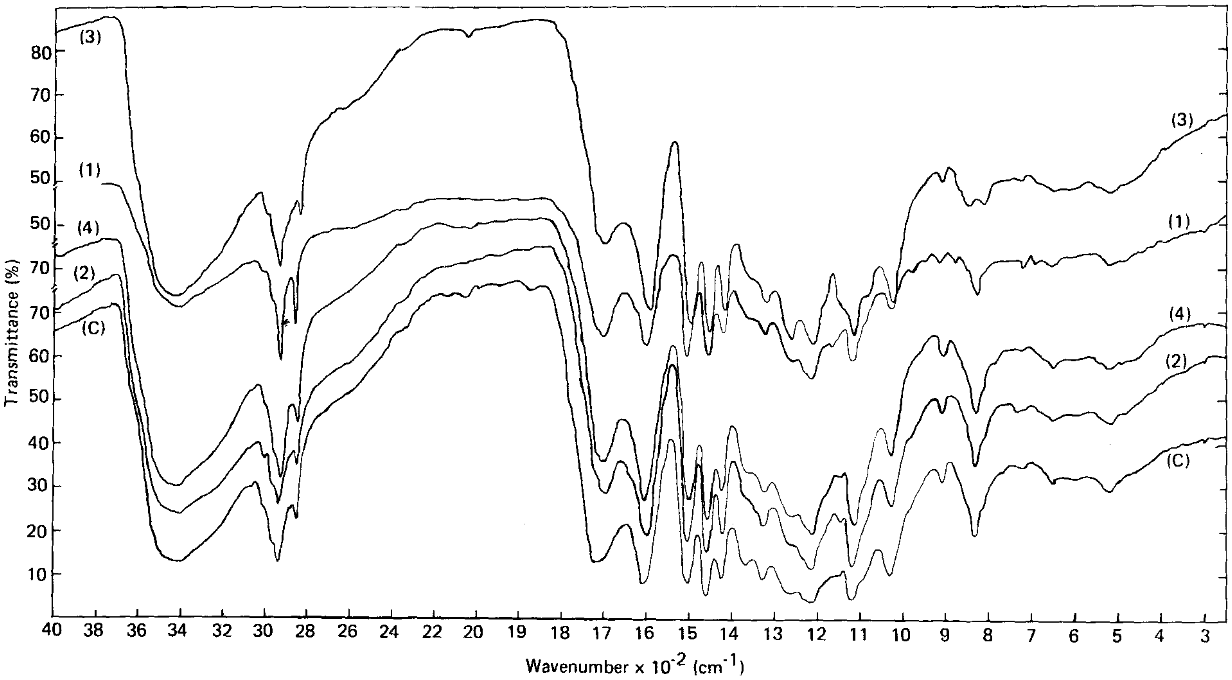

FIG. 2. IR spectra of soluble lignin from multistage kraft cooking of bagasse. The spectra are labeled by the number of successive cookings. (C) is a one-step complete cooking.

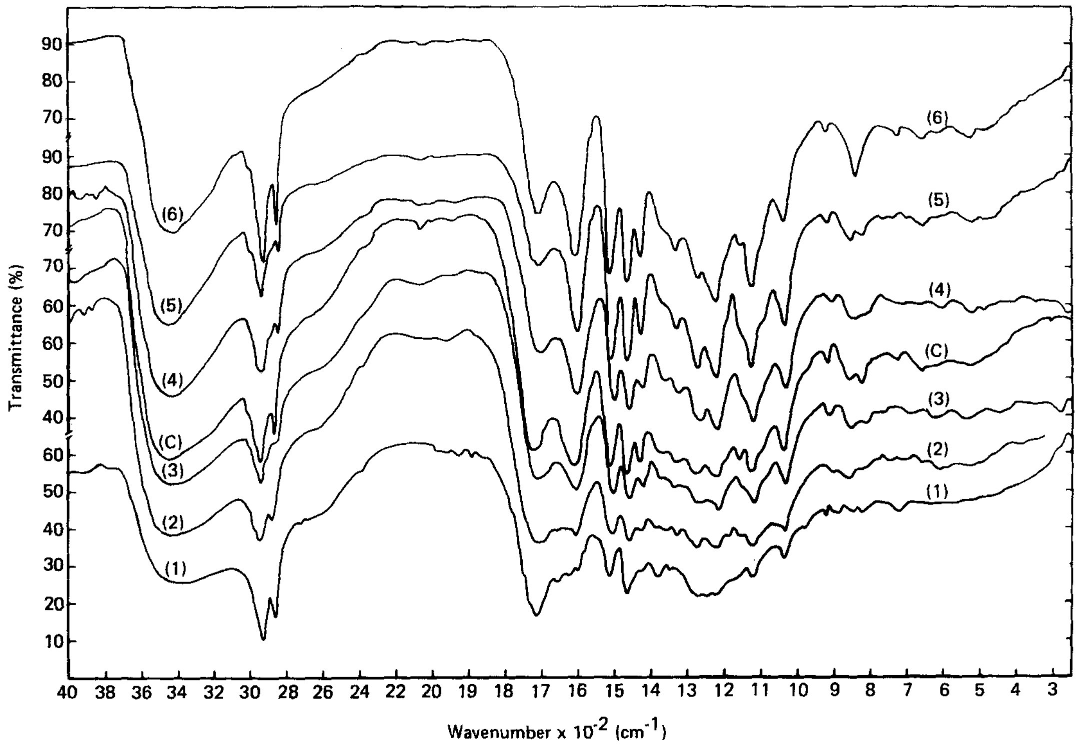

FIG. 3. IR spectra of lignin from multistage soda cooking of Ricinus communis. The spectra are labeled by the number of successive cookings. (C) is a one-step complete cooking.

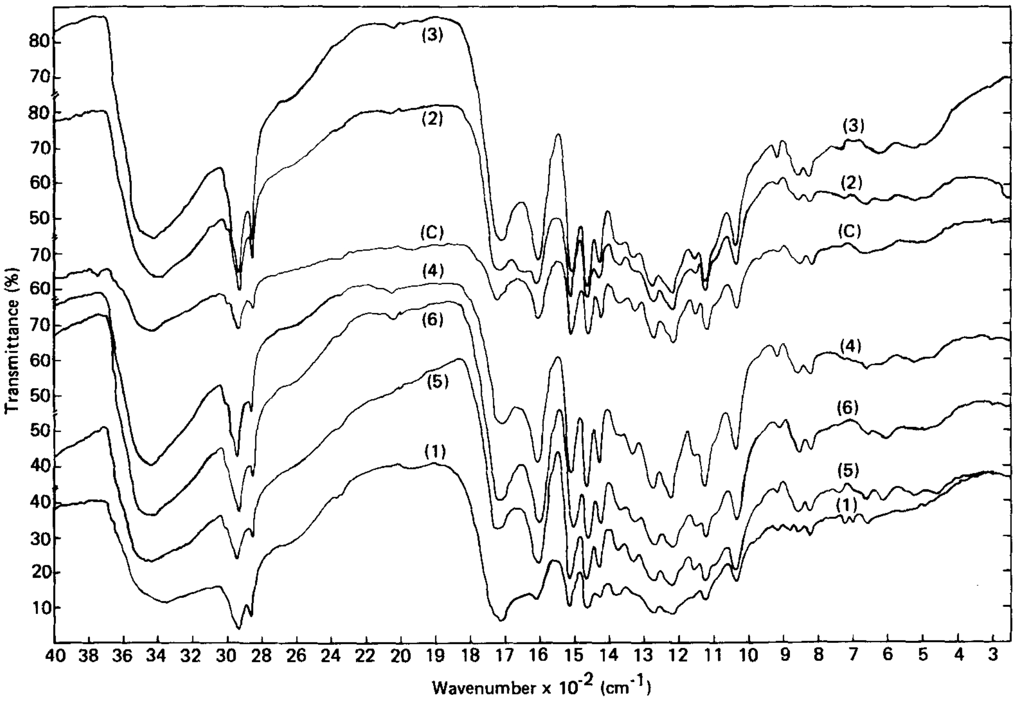

FIG. 4. IR spectra of soluble lignin from multistage kraft cooking of Ricinus communis. The spectra are labeled by the number of successive cookings. (C) is a one-step complete cooking.

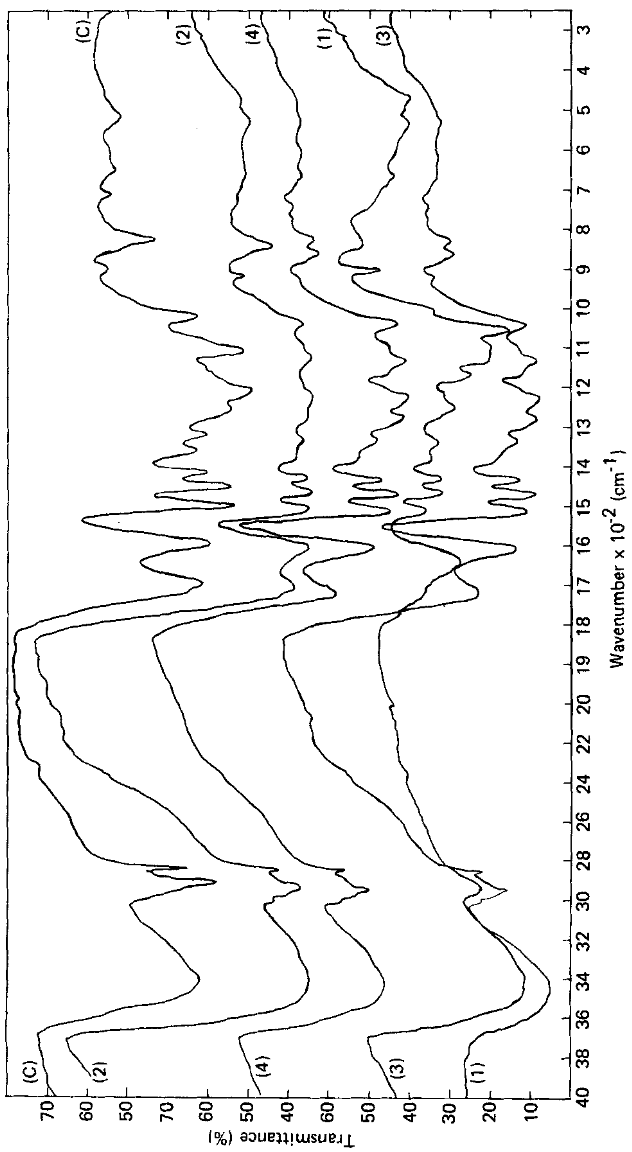

FIG. 5. IR spectra of insoluble lignin from multistage kraft cooking of bagasse. The spectra are labeled by the number of successive cookings. (C) is a one-step complete cooking.

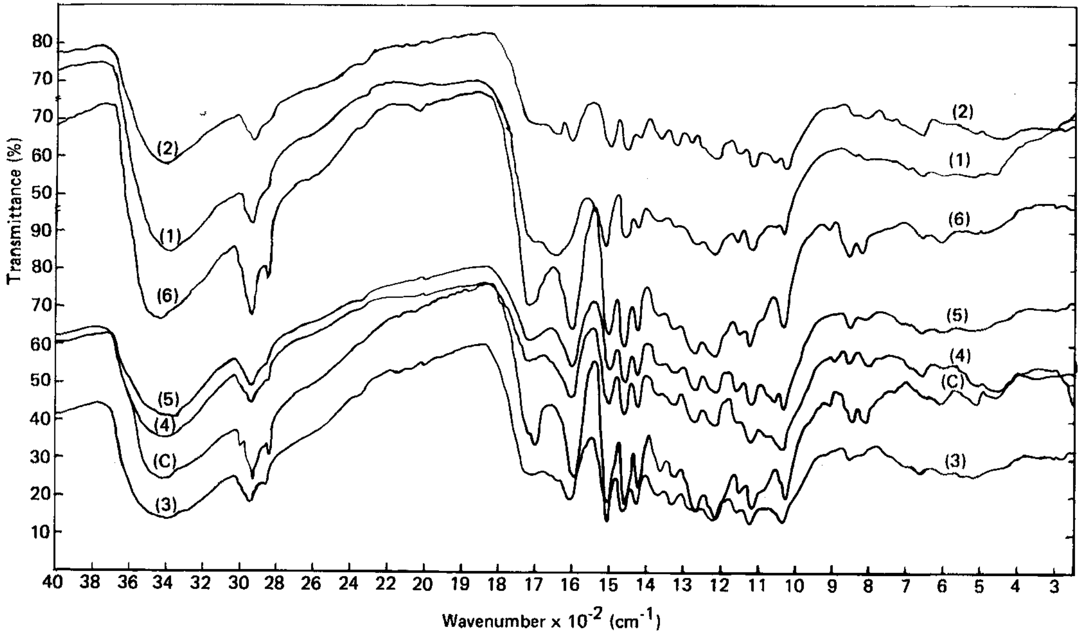

FIG. 6. IR spectra of insoluble lignin from multistage kraft cooking of Ricinus communis. The spectra are labeled by the number of successive cookings. (C) is a one-step complete cooking.

various lignin preparations have almost identical appearances. Similar results have been arrived at by Mansour et al. [10] in previous work regarding the lignins isolated from cotton stalks and bagasse by the soda cooking process. However, examination of the absorbances in the different IR regions revealed some differences. In the 3500-700 cm^{-1} range, the absorbances at the different wavenumbers related to that at 1515 cm^{-1}, i.e., A_{ν}/A_{1515}, for all lignin preparations are listed in Tables 1-3. For characterization of the IR charts, the IR range is classified into several regions.

Region 3500-2100 cm^{-1}

The broadening of the bands in the wavelength region 3500-3300 cm^{-1} reveals that the hydroxyl groups are not free but entering into different modes of hydrogen bonding [14]. It is also obvious that the OH groups are chelated since the bands are shifted to somewhat longer wavelength, namely, to 3400 cm^{-1}. In all lignin preparations the values $A_{\bar{\nu}}$ ranged between 0.66 and 3.8 (Tables 1-3). No relation was found between these values and the type of lignin.

In the absorption region 3000-2800 cm^{-1} the appearance of the two bands at 2940 and 2870 cm^{-1} may indicate the appearance of $-CH_3$ and $-CH_2$ groups [15]. Bands in the range 2832-2815 cm^{-1}, which are highly characteristic of the methoxy group [13, p. 16], may be shifted to a lower frequency; 2870-2850 cm^{-1} (Tables 1-3).

Bands in the range 2320-2295 cm^{-1} (Figs. 1-6) are characteristic of the $-C{\equiv}N$ stretching vibration [13, p. 263]. The origin of this group has been related to the linkage of lignin with protein in plants [16]. A band in the range 1420-1400 cm^{-1} for the $-C-N$ stretching absorption [13, p. 259] was taken as confirmation for such a linkage. As in organosolve lignins [16], treating of the isolated fractions of alkali lignins with 3 N HCl led to the disappearance of the bands above 2350 cm^{-1}, while the band at 2350-2320 cm^{-1} remained. The disappearance of the bands characteristic of $-CH_3$ and $-CH_2$ groups has been related to acyl-oxygen fission [17, p. 423] of an ester linkage containing these groups. The disappearance of the bands characteristic of methoxy groups has been similarly assigned to acyl-oxygen fission.

Region 1750-1600 cm^{-1}

In the region of carbonyl groups, bands in the range 1710-1695 cm^{-1} (Tables 1-3 and Figs. 1-6) may indicate the presence of aryl aldehyde which absorbs in the range 1715-1695 cm^{-1} [18] or saturated open chain ketone which absorbs in the range 1720-1705 cm^{-1} [13, pp. 134-136]. For the different lignin preparations, there is no increase or

TABLE 1. Ratio of A_ν/A_{1515} in Infrared Spectra for Soda Lignins of Bagasse (B) and Ricinus communis (Rc)

Wave-number (cm^{-1})	Lignins from soda cook											
	Cooking stage (B)					Cooking stage (Rc)						
	1	2	3	4	C[a]	1	2	3	4	5	6	C[a]
1515	0.57	0.24	0.301	0.365	0.46	0.122	0.361	0.365	0.222	0.256	0.331	0.628
3350	1.18	3.81	2.35	1.59	1.39	2.14	2.59	1.92	1.93	0.822	0.94	1.35
2940	0.339	1.50	0.759	0.674	0.748	2.99	1.19	0.8	0.73	0.787	0.779	0.73
2870-2850	0.192	0.659	0.322	0.191	0.274	1.64	0.525	0.276	0.278	0.187	0.143	0.358
1695-1710	1.36	1.89	2.5	1.17	0.85	2.85	2.0	1.09	0.775	0.34	0.511	0.89
1680-1660	vw	vw	-	-	-	vw	vw	-	-	-	-	-
1610	1.22	1.92	2.13	1.59	1.06	0.134	0.698	0.992	1.12	0.797	0.85	0.88
1465	0.55	0.98	0.85	0.75	0.83	0.72	0.88	0.75	0.67	0.62	0.66	0.83
1425	0.41	0.60	0.34	0.51	0.50	0.178	0.212	0.37	0.297	0.395	0.399	0.432
1370	0.17	0.138	0.349	0.298	0.218	0.486	0.145	0.125	0.219	0.046	0.154	0.232
1330	0.26	0.44	0.475	0.342	0.268	0.121	0.152	0.198	0.214	0.171	0.163	0.247
1270	0.43	0.59	0.74	0.27	0.47	0.309	0.638	0.36	0.54	0.38	0.223	0.435
1220	0.529	1.18	1.086	0.578	0.759	0.309	0.638	0.559	0.81	0.612	0.604	0.479
1160	0.208	vw	0.0823	0.149	0.041	0.254	0.262	0.152	0.111	0.135	0.054	0.220
1130	0.48	0.87	0.68	0.559	0.541	0.491	0.678	0.59	0.76	0.607	0.549	0.605
1030	0.209	0.41	0.415	0.223	0.370	0.465	0.914	0.721	0.685	0.471	0.329	0.511
920	0.035	0.129	0.143	0.09	0.085	0.238	0.057	0.113	0.095	0.064	0.058	0.077
860-820	0.293	0.244	0.329	0.244	0.279	0.276	0.12	0.145	0.124	0.161	0.302	0.098

[a] C denotes the one-step full cooking process.

TABLE 2. Ratio of A_{ν}/A_{1515} in Infrared Spectra for Kraft Soluble Lignins of Bagasse (B) and Ricinus communis (Rc)

Wave-number (cm^{-1})	Soluble lignins from kraft cooks											
	Cooking stage (B)					Cooking stage (Rc)						
	1	2	3	4	C[a]	1	2	3	4	5	6	C[a]
1515	0.165	0.379	0.389	0.393	0.523	0.342	0.310	0.447	0.269	0.665	0.447	0.127
3400	0.884	1.106	1.20	1.25	1.25	1.20	0.989	1.0	1.32	0.765	1.25	1.19
2940	1.134	0.472	0.470	0.664	0.652	1.45	0.628	0.935	0.777	0.352	0.633	0.551
2870-2850	0.636	0.377	0.190	0.247	0.219	0.968	0.338	0.447	0.257	0.146	0.217	0.268
1695-1710	1.213	0.627	0.794	1.074	1.25	1.59	0.825	0.805	0.576	0.522	0.846	0.551
1680-1660	vw	vw	-	-	-	vw	vw	-	-	-	-	-
1610	1.167	1.027	0.812	1.36	1.42	0.515	0.335	0.89	0.922	0.708	0.944	0.819
1465	0.797	0.829	1.22	0.765	1.0	0.746	1.20	0.881	0.937	0.565	0.226	0.75
1425	0.489	0.693	0.596	0.409	0.616	0.182	0.371	0.42	0.517	0.328	0.438	0.433
1370	0.229	0.222	0.208	0.237	0.337	0.264	0.146	0.213	0.181	0.391	0.195	0.268
1330	0.283	0.345	0.254	0.154	0.390	0.03	0.115	0.143	0.185	0.158	0.15	0.185
1270	0.431	0.243	0.463	0.259	0.449	0.374	0.264	0.423	0.446	0.359	0.434	0.484
1220	0.616	0.567	0.637	0.628	0.488	0.404	1.16	0.67	0.717	0.40	0.602	0.661
1160	0.051	0.10	0.143	0.061	0.111	0.196	0.079	0.123	0.186	0.157	0.139	0.188
1130	0.479	0.602	0.477	0.649	0.654	0.442	0.391	0.543	0.596	0.334	0.394	0.465
1030	0.287	0.361	0.563	0.374	0.576	0.488	0.596	0.483	0.654	0.483	0.636	0.581
920	0.123	0.092	0.077	0.093	0.096	0.078	0.084	0.069	0.104	0.02	0.046	0.072
860-820	0.315	0.399	0.121	0.347	0.465	0.140	0.238	0.108	0.126	0.131	0.158	0.197

[a] C denotes the one-step full cooking process.

TABLE 3. Ratio of A_ν/A_{1515} in Infrared Spectra for Kraft Insoluble Lignins of Bagasse (B) and Ricinus communis (Rc)

Wave-number (cm^{-1})	Insoluble lignins from kraft cook											
	Cooking stage (B)					Cooking stage (Rc)						
	1	2	3	4	C^a	1	2	3	4	5	6	C^a
1515	0.077	0.653	0.510	0.38	0.776	0.182	0.075	0.195	0.103	0.071	0.155	0.40
3400	0.938	1.461	1.109	1.12	0.776	2.14	2.28	2.12	2.13	2.48	1.2	0.658
2940	1.56	0.507	0.42	0.46	0.63	0.53	0.51	0.64	0.80	0.76	0.43	0.348
2870-2850	-	0.231	0.162	0.201	0.43	0.196	0.24	1.54	0.204	0.27	0.134	0.193
1695-1710	1.42	1.28	0.843	0.95	0.99	0.817	0.473	0.828	0.602	0.97	0.491	0.471
1680-1660	vw	-	-	-	-	vw	vw	-	-	-	-	-
1610	2.96	1.48	1.13	1.23	0.95	vw	0.708	0.902	1.19	1.41	1.01	0.639
1465	1.403	0.864	0.771	0.574	0.695	0.624	0.685	0.948	0.874	0.908	0.69	0.558
1425	1.13	0.169	0.519	0.589	0.494	0.29	0.258	0.593	0.67	0.72	0.474	0.352
1370	0.623	0.269	0.171	0.183	0.281	0.177	0.462	0.256	0.223	0.325	0.194	0.202
1330	0.0719	0.352	0.265	0.248	0.233	0.113	0.372	0.343	0.233	0.227	0.208	0.103
1270	1.06	0.730	0.543	0.603	0.425	0.297	0.265	0.314	0.495	0.832	0.414	0.363
1220	0.506	0.894	0.671	0.732	0.639	0.369	0.565	0.466	0.612	0.841	0.455	0.425
1160	0.079	-	0.226	0.170	0.038	0.252	0.27	0.262	0.408	0.370	0.213	0.160
1130	0.78	0.339	0.345	0.377	0.254	0.479	0.475	0.582	0.492	0.660	0.348	0.258
1030	1.17	0.528	0.551	0.702	0.389	0.45	1.17	1.03	0.98	0.85	0.703	0.433
920	0.96	0.093	0.061	0.029	0.07	-	-	-	0.117	-	-	0.050
860-820	0.17	0.261	0.135	0.146	0.119	0.094	0.19	0.343	0.223	0.276	0.128	0.108

[a] C denotes the one-step full cooking process.

decrease with the cooking stage for the intensity ratio of these bands to that at 1515 cm^{-1} due to C–H stretching vibration in the benzene ring (Tables 1-3 and Figs. 1-6).

Compounds consisting of two quinonoid carbonyls in the same ring absorb in the range 1680-1660 cm^{-1} [13, pp. 134-136]. According to Sarkanen [8], the absorption at 1660 cm^{-1} is characteristic for the stretching of conjugated aryl-carbonyl. In our opinion, as has been indicated in our previous work [16], this band absorption relates to two quinonoid carbonyls in the same ring. In some lignin preparations this band is either overlapped with the neighboring one or present as shoulders (Figs. 1-6).

It is also claimed that in compounds which contain only an isolated double bond, the absorption peak normally occurs within the range 1680-1620 cm^{-1}, with the majority absorbing in the 1660-1640 cm^{-1} region [13, p. 35]. The assignments of C–O and C–C stretching also occur in this region. From Tables 1-3 and Figs. 1-6, if the assignments in this region are considered as an indication for the presence of an isolated double bond, the result can be taken to favor the absence of a conjugated double bond with the aromatic ring.

Region 1650-700 cm^{-1}

Considering the general pattern of band structure of the aromatic type, as illustrated in the IR charts, and the ratio of absorption of each band to the absorption of the substituted benzene ring at 1515 cm^{-1} (Tables 1-3), the following was noted.

The presence of bands in the region 1600-1500 cm^{-1} confirmed the aromatic structure of the different alkali lignin fractions [13, pp. 69-71]. However, fundamental studies on benzene vibrations have shown that the characteristic skeletal stretching modes of semi-unsaturated carbon-carbon bonds lead to the appearance of four bands between 1650-and 1450 cm^{-1}, of which those near 1600 and 1500 cm^{-1} are highly characteristic of the aromatic ring itself [13, p. 69-71].

The actual position of the bands are influenced to some extent by the nature of substituted groups, but depend to a rather greater degree on the way in which the latter are arranged around the ring. In some cases it is possible to obtain a certain amount of confirmatory evidence as to the type of substitution. Thus, in softwoods and unconjugated guaiacyl model compounds, the intensity of 1600 cm^{-1} is significantly lower than that of 1510 cm^{-1} [8, pp. 273-284]. In other words, the intensity ratio of A_{1610}/A_{1515} cm^{-1} is less than 1, which is the case for the lignins of Ricinus communis (Tables 1 and 2 and Figs. 3 and 4). Exceptions are the lignins of the 4th step of the multistage soda cook and the insoluble kraft lignins of the 4th, 5th, and 6th steps of the multistage cooking. Insoluble kraft lignins are those which are insoluble in acetone, dimethylformamide (DMF), dioxane, dimethylsulfoxide (DMS), and alcohols (refer to the Experimental section).

In hardwoods, lignins, and unconjugated syringyl model compounds, the intensity of the two bands 1600 and 1510 cm^{-1} is approximately equal. The intensity ratio of these two bands may be affected by the presence of p-hydroxyphenyl esters, carboxylate ions in carbohydrate impurities, or condensed tannin impurities, all of which tend to increase the relative intensity of the 1600 cm^{-1} band with respect to the 1510 cm^{-1} band [8, pp. 273-293]. This applies for the lignins of bagasse, with the exception of the one-stage insoluble kraft lignin and the soluble lignin of the 3rd step of multistage kraft cook (Tables 1-3 and Figs. 1-6).

On hydrolyzing some of the lignin fractions which showed ratios higher than 1 for 1610/1515 with 0.1 N HCl, the band at 1610 cm^{-1} became comparably equal or less than that at 1515 cm^{-1} (Figs. 7-9). The equality of the band at 1610 cm^{-1} to that at 1515 cm^{-1} may relate to insufficient hydrolysis, probably due to higher resistance of some of the carbohydrate residues. Bolker [5, 6] and Lomova et al. [7] suggested that the band at 1710 cm^{-1} arises as a result of the cleavage of a bond between lignin and a carbohydrate. Figures 7-9 showed sharper bands for the lignin fractions showing ratios higher than 1 on hydrolyzing with 0.1 N HCl due to removal of residual carbohydrates, comparable with the unhydrolyzed samples (Figs. 1-6). In conclusion, one may say that lignins from both Ricinus communis and bagasse consist mainly of unconjugated guaiacyl nuclei.

For most aromatic materials with p-substitution, there is a small shift toward higher frequencies, 1650-1585 cm^{-1} [13, p. 71], and this also applies to a lesser extent to unsymmetrically trisubstituted material. With vicinal trisubstituted materials, on the other hand, the shift is toward lower frequencies, 1610-1560 cm^{-1}. Based on these assignments, the lignins under investigation showed bands in the range 1610-1600 cm^{-1} (Tables 1-3 and Figs. 7-9) and accordingly may indicate vicinal trisubstituted aromatic structure.

It is claimed that the band at 1580 cm^{-1} is used to recognize the conjugation with the aromatic ring [13, p. 72]. The absence of this band for all the lignins considered here may indicate the absence of such conjugation, a result that has been previously achieved above. Another indication for the absence of conjugation of the ring with any double bond, such as CO, C=C, and NO_2, is the lower intensity of the bands in the region 1600-1500 cm^{-1} [13, p. 73].

Absorption at 1465 cm^{-1} is attributed to aromatic C–H deformation in methyl or methylene groups considerably affected by methoxyl groups [19]. Gol'man et al. [20] assigned this band to asymmetric vibration of the C–H in MeO. The intensity of the band differs in different lignin preparations, both for bagasse and Ricinus communis. The intensity of the absorption of this band for lignins obtained from soda cook and kraft-soluble lignin is slightly higher than that for kraft-insoluble lignins (Tables 1-3). Determination of OCH_3/C_9 showed higher values (1.2-0.9) for the former two than those for the latter (0.7-0.6).

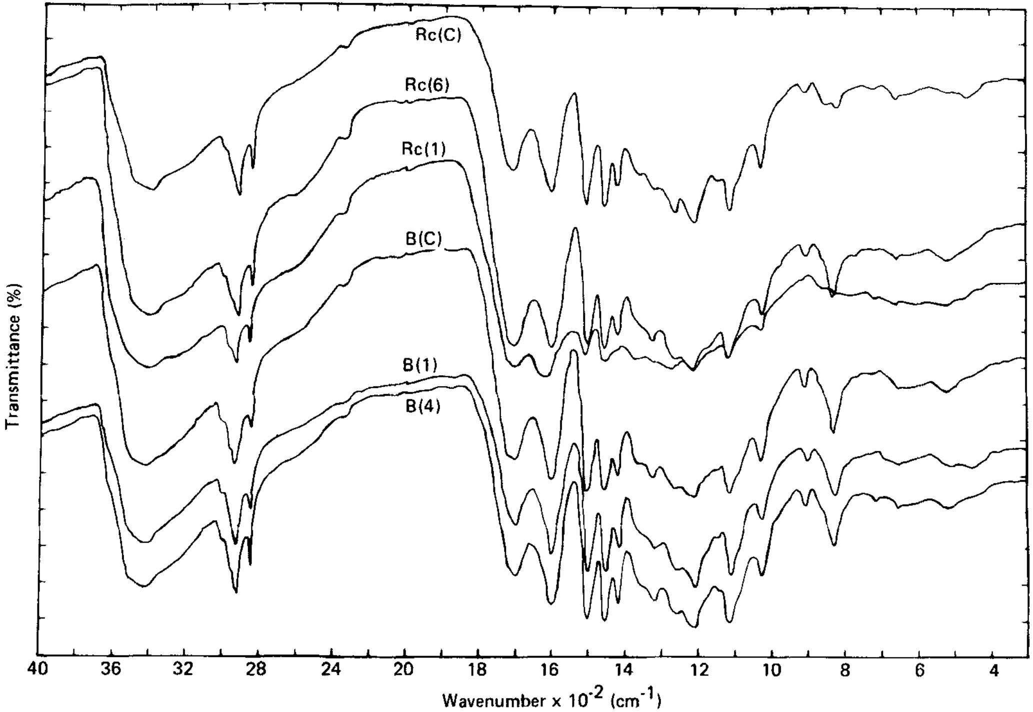

FIG. 7. IR spectra of hydrolyzed lignins from multistage soda cooking of bagasse (B) and Ricinus communis (Rc). The numbers in parentheses indicate the cooking stage. (C) is a one-step complete cooking.

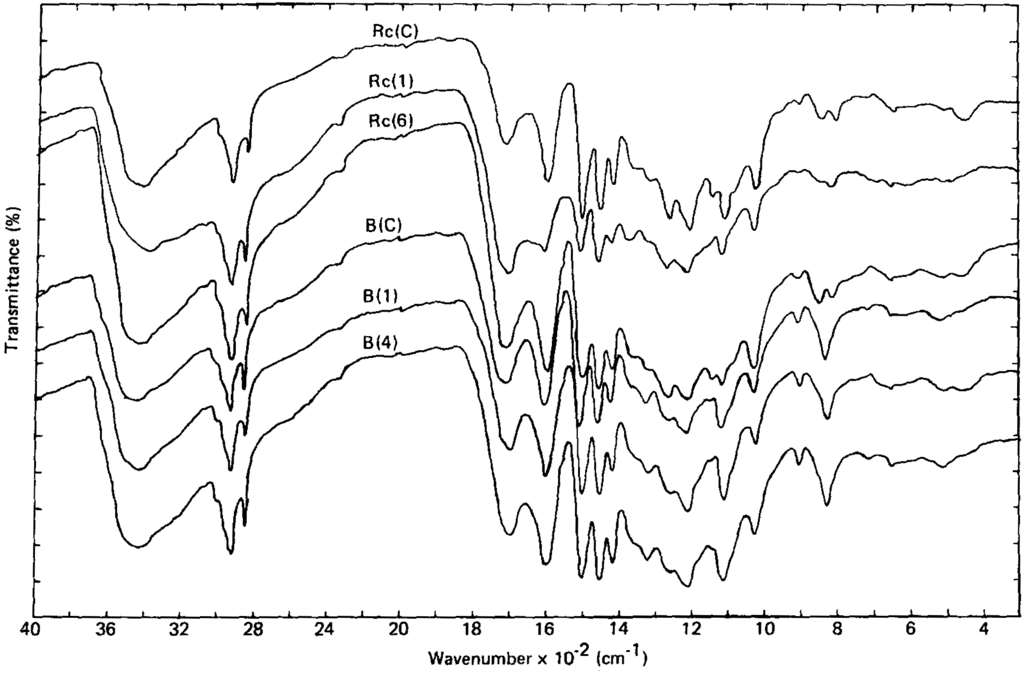

FIG. 8. IR spectra of hydrolyzed soluble lignins from multistage kraft cooking of bagasse (B) and Ricinus communis (Rc). The numbers in parentheses indicate the cooking stage. (C) is a one-step complete cooking.

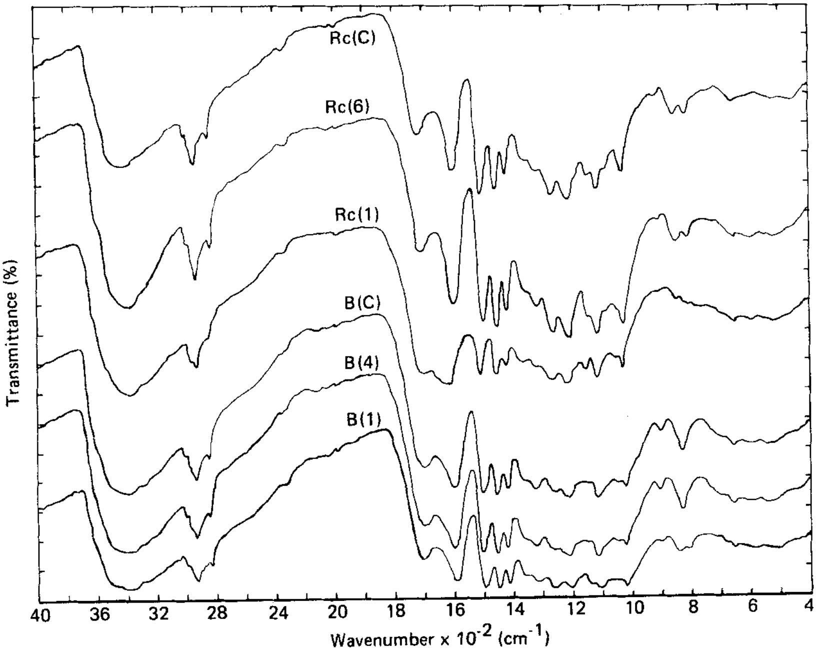

FIG. 9. IR spectra of hydrolyzed insoluble lignins from multistage kraft cooking of bagasse (B) and Ricinus communis (Rc). The numbers in parentheses indicate the cooking stage. (C) is a one-step complete cooking.

Although the bands in the region 1450-1420 cm^{-1} are assigned for both guaiacyl and syringyl models, as stated by Sarkanen [21], their assignment remains uncertain. He found in his studies, and was supported by Mansour et al. [10], that this band is actually associated with the ring-stretching modes similar to the 1500 cm^{-1}. However, this band, as suggested by Lecomite [13, p. 73], is assigned to a fourth skeletal C–C frequency. For monosubstituted aromatics, this band fell in the range 1470-1439 cm^{-1}. It is frequently overlaid by CH_2 deformation [13, p. 73] which reduces its usefulness for identification, though it can be identified in polynuclear compounds. Thus, the presence of such a band in the lignins considered here may support their polynuclear nature.

The absorption at 1425 cm^{-1} is due to aromatic skeletal vibration, strongly coupled by C–H in-plane deformation and sensitive to the nature of ring substituents [14]. The intensity of the absorption of this band is the same (~0.4) for all lignin preparations except for soluble-kraft lignin which is slightly high. The variation in the intensity of lignins from the different steps is of the order 20-30% (Tables 1-3 and Figs. 7-9).

The absorption at 1370 cm^{-1} was assigned by Sarkanen [21] to phenolic OH bending character. Gol'man et al. [20] and Pilipechuk et al. [22] assigned the region 1330-1380 cm^{-1} to symmetric vibration of the C–H groups in MeO. From Part 1 of this work (Tables 1 and 2 [23]) there is overall agreement between the intensity of the 1370 cm^{-1} band and the phenolic OH content/C_9. In the meantime, there is an increase in the intensity of the 1370 cm^{-1} band accompanying the decrease of the methoxyl content/C_9. It is therefore obvious that this band, assigned to phenolic OH bending as stated by Sarkanen [21], is affected by the methoxyl group; it increases with a decrease in the methoxyl content.

With reference to the work done by Sarkanen on lignin model compounds, the maximum at 1275 cm^{-1}, characteristic for uncondensed guaiacyl nuclei, is shifted to 1300 cm^{-1} in condensed ones and to 1335 cm^{-1} in syringyl compounds [21].

The intensity of absorption at 1330 cm^{-1} ranged from 0.2-0.4 for lignins isolated from bagasse and from 0.1-0.25 for lignins isolated from Ricinus communis (Tables 1-3).

The band at 1300 cm^{-1} is absent or very weak in most lignin preparations, which may favor the absence of the condensed guaiacyl nuclei in these lignins (Figs. 7-9).

On the other hand, both bands at 1335 and 1235 cm^{-1} are assignable to ring breathing with C–O stretching for syringyl and guaiacyl units [8]. In this work these two bands are shifted to 1330 and 1220 cm^{-1}. According to Sarkanen, the absorption at 1220 cm^{-1} is due to ring breathing with C–O stretching in guaiacyl and syringyl units [21]. This assignment, together with the assignment of the band at 1270 cm^{-1} and that at 1130 cm^{-1}, is probably due to the guaiacyl compounds [8]. The intensity of the absorption of the bands increased on going from 1330 to 1220 cm^{-1} in most lignins (Tables 1-3).

The intensity of the bands at 1220 cm^{-1} are higher than those at 1270 cm^{-1}, except for insoluble- kraft lignins obtained from the 1st step kraft cook of bagasse (Table 3). The IR spectrum of this latter lignin, as shown in Fig. 5, is different from all other insoluble lignins in the region 1600-1700 cm^{-1}. The greater intensity of the band at 1220 cm^{-1} than at 1270 cm^{-1} in hardwood lignins is a function of the syringyl and p-hydroxyphenyl content [8].

Pilipchuk et al. [22] found that the intensity of the band at 1270 cm^{-1} has no relation with the methoxy content. They also reported that the band at 1270 cm^{-1} relates well with the intensity of the band at 2900 cm^{-1} assigned to the stretching vibration of methylene groups. In this work the band at 1270 cm^{-1} correlates for all the steps of the multistage cooking of the insoluble-kraft lignins (Table 3), while for other lignins the correlation holds only for some of the steps. The intensity of absorbance of the band at 1270 cm^{-1} is almost the same, being 0.40-0.45, for all lignins isolated from bagasse and Ricinus communis by one-step cooking (Tables 1-3).

It can be seen from the figures that the different lignins under investigation show weak bands at 1220-1225 cm^{-1} and at 1115-1125 cm^{-1}, together with an additional weak band in the range 1025-1050 cm^{-1}. These band assignments refer to the presence of 1:2, 1:4, or 1:2:4-aromatics. The latter can be differentiated from the others in simple molecules by the presence of an additional band in the range 1175-1125 cm^{-1} [13, p. 81].

The absorption at 1160 cm^{-1} is characteristic of aromatic skeletal vibration [21] or to a single band or unresolved bands [8]. This band, which appeared to be of low intensity, ranged between 0.04 to 0.26 for most lignins under investigation, while it was very weak in the others (Tables 1-3, Figs. 7-9).

Summing up, the results obtained from these IR spectra revealed the presence of both guaiacyl and syringyl nuclei in the lignins isolated from both multi- and one-stage cooks with kraft and soda processes, and the absence of condensed guaiacyl.

The disappearance of the band at 1085 cm^{-1} [8, p. 271] means the absence of C–O deformation of secondary alcohol and aliphatic ether (Figs. 7-9). The band at 1030 cm^{-1} is assigned to C–O–C symmetric stretching in dialkyl ether linkages [6]. However, according to Sarkanen [21], the absorption at 1030 cm^{-1} is assigned to the aromatic C–H in-plane deformation characteristic of uncondensed guaiacyl and C–O deformation of primary alcohol (Figs. 7-9).

From Tables 1-3 it is clear that the intensity of the band at 1030 cm^{-1} is greater than or nearly equal to that of the band at 1130 cm^{-1} for soda lignins isolated from Ricinus communis, while it is always lower for soda lignins isolated from bagasse. For the soluble-kraft lignin of bagasse, the intensity of the band at 1030 cm^{-1} is almost lower than that at 1130 cm^{-1} (Table 2), while it is higher for insoluble-kraft lignin for both Ricinus communis and bagasse, and almost higher for soluble-kraft lignin from Ricinus communis (Table 3). According to Sarkanen [8], softwood lignins showed a higher or equal intensity for the band at 1035 cm^{-1} than that at 1140 cm^{-1}, while the reverse was true for the hardwood lignins [8]. Accordingly, it may be concluded that soda and soluble-kraft lignins of bagasse resemble hardwood lignin, while soda, soluble-, and insoluble-kraft lignins of Ricinus communis and insoluble-kraft lignin of bagasse resemble softwood lignins.

The absorption at 920 cm^{-1} has been assigned by Miranda et al. [19] to aromatic CH out-of-plane deformation of syringyl units. Hergert [12] left this peak unassigned. The relative absorbance of this peak for insoluble lignin from the first step of kraft cook of bagasse is too large, being 1 (Table 3), compared with an average of almost 0.1 for all lignin preparations (Tables 1 and 2). This result, together with the OH and methoxyl contents per C_9 listed in Tables 1 and 2 of Part 1 of this work [23], suggests that the peak is not due to either OH or methoxyl groups vibration. On hydrolysis of the different lignins with

0.1 N hydrochloric acid, the intensity of this band becomes about the same for all lignins (Figs. 7-9). This suggests that there is a relation between the presence of carbohydrate and the position of the groups assigning for their bands (Figs. 7-9).

The absorption at 860-820 cm^{-1} appeared as one broad band for all lignins of soda cooking of bagasse and about half of the latter lignins of the kraft cooks. The other kraft lignins of bagasse and all lignins from Ricinus communis showed almost two peaks of approximately equal intensity in this region (Figs. 7-9). The intensities of absorption in this region for lignins from Ricinus communis are, in general, lower than those from bagasse, a result that may favor higher guaiacyl to syringyl nuclei ratios in lignins from the former than those from the latter, in analogy to the achievement of Sarkanen [8]. He found that temperate hardwood lignins show a medium intensity at 835 cm^{-1}, characteristic of the syringyl nucleus, while tropical hardwood lignins show a somewhat weaker 835 cm^{-1} band with shoulders at 855 and 815 cm^{-1}, indicating a higher guaiacyl to syringyl nuclei ratio than in the former.

However, the presence of the two bands, one in the range 865-810 cm^{-1} and the other band in the range 765-730 cm^{-1}, are characteristic of the 1,3,5-trisubstituted aromatic [13, p. 79]. Colthup proposed the range 770-730 cm^{-1} for the position of the out-of-plane C–H bending absorption of monosubstituted aromatics. Ortho-disubstituted materials absorbed in approximately the same range of frequencies. However, the absence of a band within the range 700 ± 10 cm^{-1} is strong evidence for the absence of a monosubstituted product, but the converse is not necessarily true, and confirmation must be sought from the 750 cm^{-1} region. The meta-disubstituted aromatic structure shows two bands, one in the range 810-750 cm^{-1} and the other in the range 710-690 cm^{-1}. The absence of bands in the range 910-700 cm^{-1} may indicate that the aromatic ring is hexa-substituted [13 (pp. 76-78), 23].

Based on these assignments, one or more of the above-mentioned substitutions may be found in one of the lignins considered, taking into consideration that some of the bands may undergo some shift in their positions due to the complex nature of the lignin (Figs. 7-9). However, some of the lignins showed the absence of bands in the range 910-700 cm^{-1}, which indicates the absence of hexa-substitution in these lignins.

Region 700-600 cm^{-1}

The absorption in the region 600-700 cm^{-1} has been assigned by Hergert [12] to be due to the C–S vibrations. Bolker and Somerville [6] reported a very weak band at 630 cm^{-1} in softwood thiolignin which they assigned to C–S stretching. In the region 600-700 cm^{-1}, no band appeared in the spectra of soda lignin of Ricinus communis (Fig. 3). For soda cooking of bagasse, very weak bands or shoulders are shown near 600 cm^{-1} region. For kraft lignin, soluble and insoluble, from both Ricinus communis and bagasse, either sharper and more intense bands or more than one band are shown in this region (Figs. 7-9), indicating the presence of C–S in these thiolignins. No absorption band was observed at 2600 cm^{-1} in the spectra of these thiolognins (Figs. 7-9), indicating the absence of the thiol (S–H) group [8].

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