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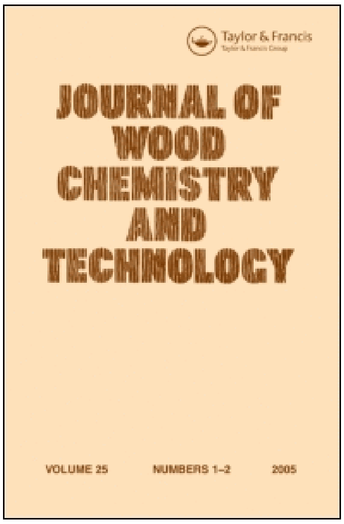

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Origin and Nature of Kraft Colour: 1 Role of Aromatics

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ORIGIN AND NATURE OF KRAFT COLOUR : 1
ROLE OF AROMATICS

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ABSTRACT

The chromophores responsible for kraft colour have been generally assumed to be derived from the aromatic portions of the lignin molecule. Analytical studies of the high molecular weight dissolved materials from kraft lignin, kraft cooked sugars, and extraction stage effluent by pyrolysis GC-MS, permanganate/periodate oxidation, and UV-visible spectroscopy showed that these materials had a wide variation in aromatic content but similar spectral properties. It is now proposed that carbohydrate degradation products produced by the kraft cooking of sugars are primarily responsible for the kraft colour.

INTRODUCTION

This paper reviews and examines the origin of colour in kraft black liquor, hereafter "kraft colour", and presents evidence to show that carbohydrates rather than lignin aromatics may be the chief source of colour progenitors, and assumes that the same chromophores are responsible for colour in black liquor, pulp, and extraction stage effluent (Eo). A subsequent paper will examine materials responsible for colour production in Eo effluent from multichlorination bleaching.

Pigman and Csellak[1] in their studies on the origin of kraft black liquor colour studied the resistance of black liquors, caramelised sugars, and tannins to calcium hypochlorite bleaching . They found that kraft black liquor was the most resistant to bleaching. On the basis of their studies, they proposed that

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lignin was the origin of kraft liquor colour. They supported their proposal by correlating residual lignin in pulp to the corresponding pulp brightness. They assumed that the lignin is the only compound being oxidized during the bleaching of the black liquors.

Gierer[2] assumed that the kraft liquor colour is caused by lignin degradation products and proposed a variety of leucochromophoric (colourless) groups which could be formed during pulping. Gierer also proposed that "auto-oxidation or dehydrogenation of such leucochromophoric systems should yield highly conjugated, potential chromophores". Several of these proposed leucochromophoric compounds have since been stated by a variety of authors[3, 4] to be the actual chromophores produced during kraft pulping. Although Hon and Glasser[5] have synthesized some of these compounds from model lignin compounds, their presence has not yet been demonstrated in kraft effluents.

Lignins are not the sole source of aromatic residues resulting from the kraft pulping of wood. Forsskahl *et al.*[6] studied the formation of aromatic structures from xylose and glucose under alkaline conditions. Among the compounds they isolated were 2-hydroxy-3-methyl-2-cyclopentene-1-one and pyrocatechol, which were previously isolated from kraft cooking liquors by Enkvist[7]. A variety of dihydroxyl- and trihydroxyl-, low molecular weight, phenolic compounds which showed antimicrobial activity were isolated by Suortti[8] from heated neutral glucose and fructose solutions. It has been proposed by Forsskahl *et al.*[6] that sugar degradation products formed under alkaline and kraft pulping conditions could be intermediates in colour formation. Furthermore Russell *et al.*[9] proposed that the aromatics could be formed from the reaction of ketoaldehydes with acetone.

The high molecular weight materials isolated from kraft black liquors and extraction liquors may also result from carbohydrate degradation products. Alen and Sjöström[10] have isolated various condensation products of glycolic, lactic, and 2-hydroxybutanoic acids from kraft black liquor. Among these products were trimers of lactic and 2-hydroxybutanoic acids. The endwise degradation of hydrocellulose to produce glycoaldehyde has been proposed by Johansson and Samuelson[11]. Glycoaldehyde is the key intermediate in the formation of formose sugars. During the production of formose sugars, greatest yield occurs at the "yellow point" of the reaction mixture[12]. Therefore the polymerization of glycoaldehyde with itself and other degradation products produced during the kraft cook may yield "pseudo" lignins.

This paper re-examines the proposition that lignin aromatic residues are the major source of colour. It examines and compares the following high molecular weight materials: milled wood lignin, kraft cooked milled wood lignin, the products obtained by treatment of sugars (monosaccharides and hemicelluloses) under kraft pulping conditions, and the high molecular products present in the

TABLE 1
Sample Abbreviations

KL	kraft lignin from laboratory cook
TKL	kraft lignin from a commercial kraft mill
MWL	milled wood lignin
KMWL	kraft cooked milled wood lignin
KG	kraft cooked glucose
KGX	kraft cooked glucose and xylose (1:1 mixture)
KCEL	kraft cooked cellobiose
E	extraction stage effluent from a commercial mill

extraction stage (E or Eo) of bleached kraft pulp production. The products were examined by the techniques of pyrolysis GC, permanganate/periodate oxidation, and UV-visible spectroscopy. The products examined, and the abbreviations used to describe them in text and diagrams, are given in Table 1.

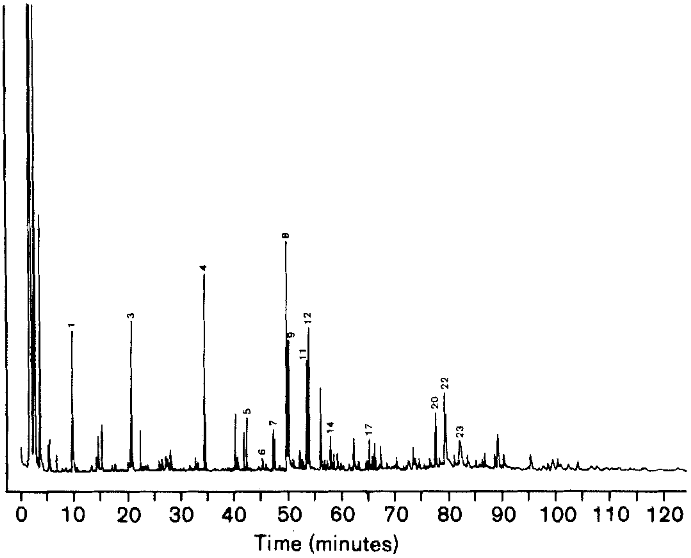
RESULTS AND DISCUSSION

Pyrolysis-gas Chromatography Studies

Pyrolysis-gas chromatography (PGC) mass spectrometry is a rapid method for the analysis of lignin and lignin degradation products. In this technique, the sample is rapidly heated in an inert atmosphere and is thermally degraded into a series of low molecular weight compounds. The resulting compounds are then separated and identified by gas chromatography and mass spectrometry. The resulting pyrogram gives a unique "fingerprint" of the sample. The technique has been used by a variety of authors[13, 14, 15, 16, 17] to study a wide range of wood and lignin related materials.

The pyrograms of milled wood lignin (MWL), kraft milled wood lignin (KMWL), kraft lignin (KL), commercial kraft lignin (TKL), and extraction stage effluent (Eo) effluent are shown in Fig. 1 and the products of pyrolysis are identified in Table 2. There is a significant difference between the types of compounds found in MWL and KMWL. This difference reflects the degradation of the native lignin structure during kraft cooking of the MWL, whereby some of the intramolecular linkages are broken. Pyrolysis of KMWL therefore gives rise to a greater quantity of volatile components than MWL, whereas the larger, less volatile components

(a) MILLED WOOD LIGNIN



(b) KRAFT MILLED WOOD LIGNIN

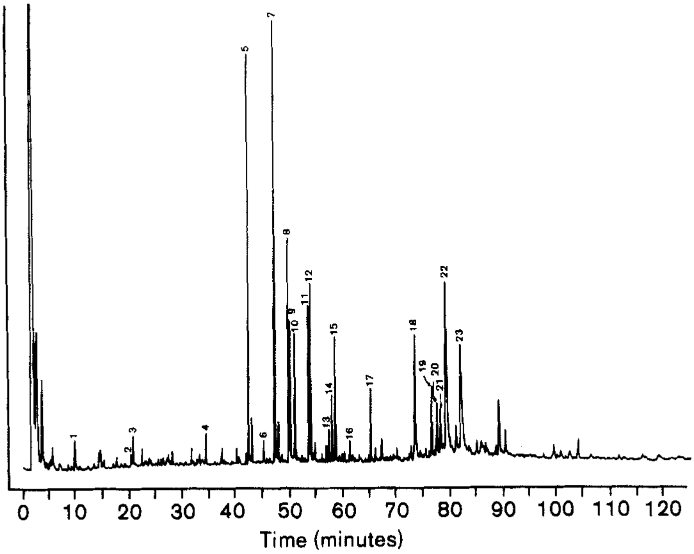
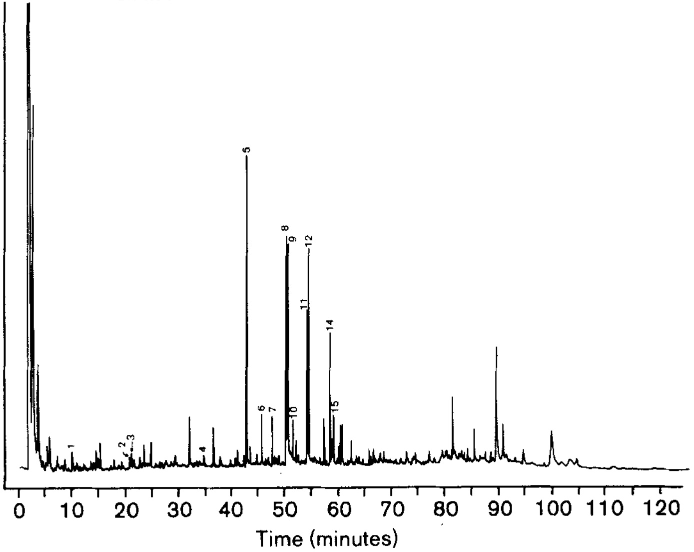
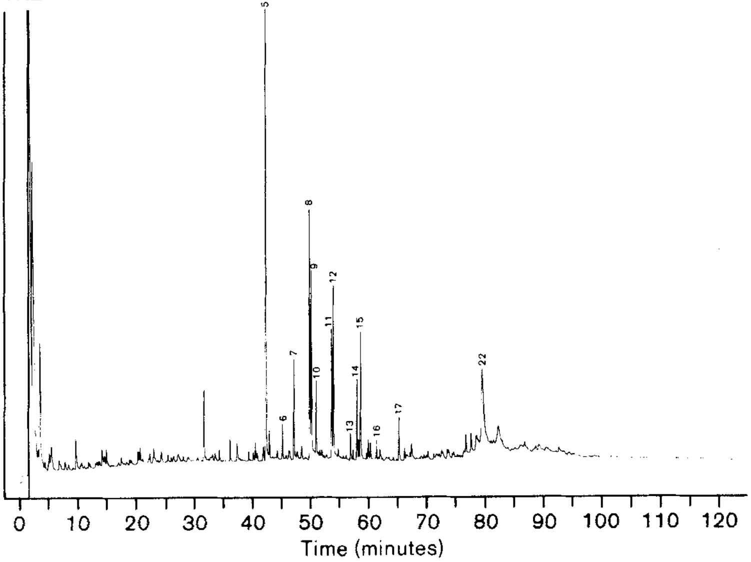


FIGURE 1. Comparison of pyrograms obtained from (a) milled wood lignin MWL (b) kraft cooked milled wood lignin KMWL, (c) kraft lignin from laboratory cook, (d) industrial kraft lignin TKL, and (e) industrial extraction effluent E. The numbered peaks are identified in Table 2.

(c) KRAFT LIGNIN



(d) TKL



FIGURES 1C AND 1D

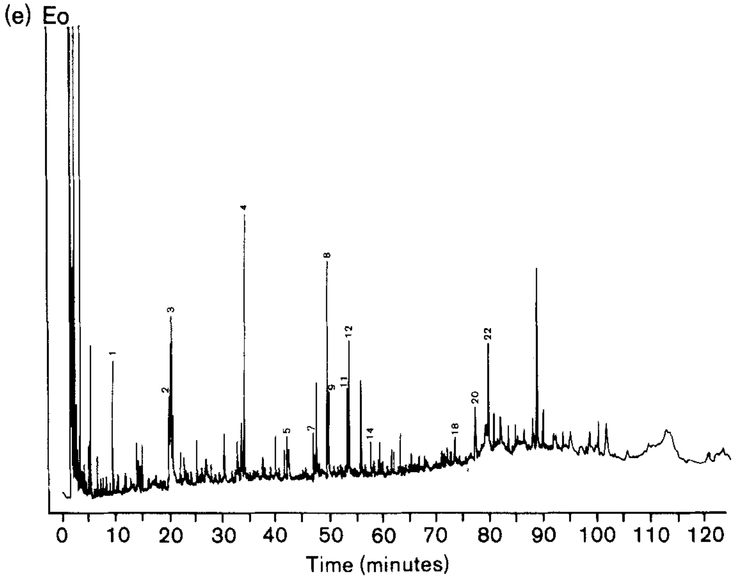


FIGURE 1E

from the pyrolysis of MWL, though volatile at 650°, may condense on the injector or first few centimetres of the column[15]. The pyrograms are drawn so that the phenol peak (Rt = 50 min) is set at 50%, owing to the lack of an appropriate internal standard.

There is very little difference in the types of compounds produced when the laboratory kraft lignin (KL) (Fig. 1c) and a sample of commercial kraft lignin (TKL) (Fig. 1d) were pyrolysed though they came from different sources. The predominant compound formed is guaiacol followed by phenol, cresols, and ethylphenol. The pyrolysis of the KL and TKL yields predominantly guaiacol and substituted phenols whereas the pyrolysis of KMWL yields a greater number of substituted guaiacols. The substituted phenols are readily seen in E effluent (Fig. 1e), while substituted guaiacols are barely detected. Styrene, indene, and napthalene are formed by the pyrolytic cracking of the materials and are present in the greatest amounts in the MWL and Eo sample.

The effect of kraft pulping on carbohydrates was studied by cooking various sugars and sugar polymers in white liquor. All of the carbohydrates tested

TABLE 2
Identification of Major Pyrolysis Peaks and Relative Amounts

Peak number	Rt	Compound	MWL	KMWL	TKL	KL	Eo
1	9.9	styrene	+	tr	-	tr	+
2	20	acetic acid	-	tr	-	tr	+
3	20.8	indene	+	tr	-	tr	++
4	34.4	naphthalene	+	tr	-	tr	++
5	42.8	guaiacol	tr	+++	+++	++	tr
6	43.4	dimethylphenol*	tr	tr	tr	tr	-
7	47.5	4 methylguaiacol	tr	+++	+	tr	tr
8	50.0	phenol	++	++	++	++	++
9	50.3	cresol*	+	++	++	++	+
10	51.1	4 ethylguaiacol	-	++	+	tr	-
11	53.8	4 ethylphenol	+	++	+	+	+
12	54.1	3 ethylphenol	+	++	++	++	+
13	57.5	eugenol	-	tr	tr	-	tr
14	58.1	phenol related	tr	+	+	+	-
15	58.8	4 vinylguaiacol	-	++	+	tr	-
16	61.5	cis-isoeugenol	-	tr	tr	-	-
17	65.4	trans-isoeugenol	tr	+	tr	-	-
18	73.8	unknown	-	++	-	-	tr
19	76.8	G-$CH_2CH_2CH_2OH$	-	++	-	-	-
20	77.8	G related	+	+	-	-	tr
21	78.9	P-$CHOH(CH_2)CH_3$	-	+	-	-	-
22	79.4	catechol	+	++	+	-	+
23	81.2	124MW	+	+	-	-	-

* substitution pattern could not be determined by mass spectrometry
tr trace
\+ low amount
+++ high amount
P = 4-hydroxyphenyl-
G = 4-hydroxy-3-methoxyphenyl-

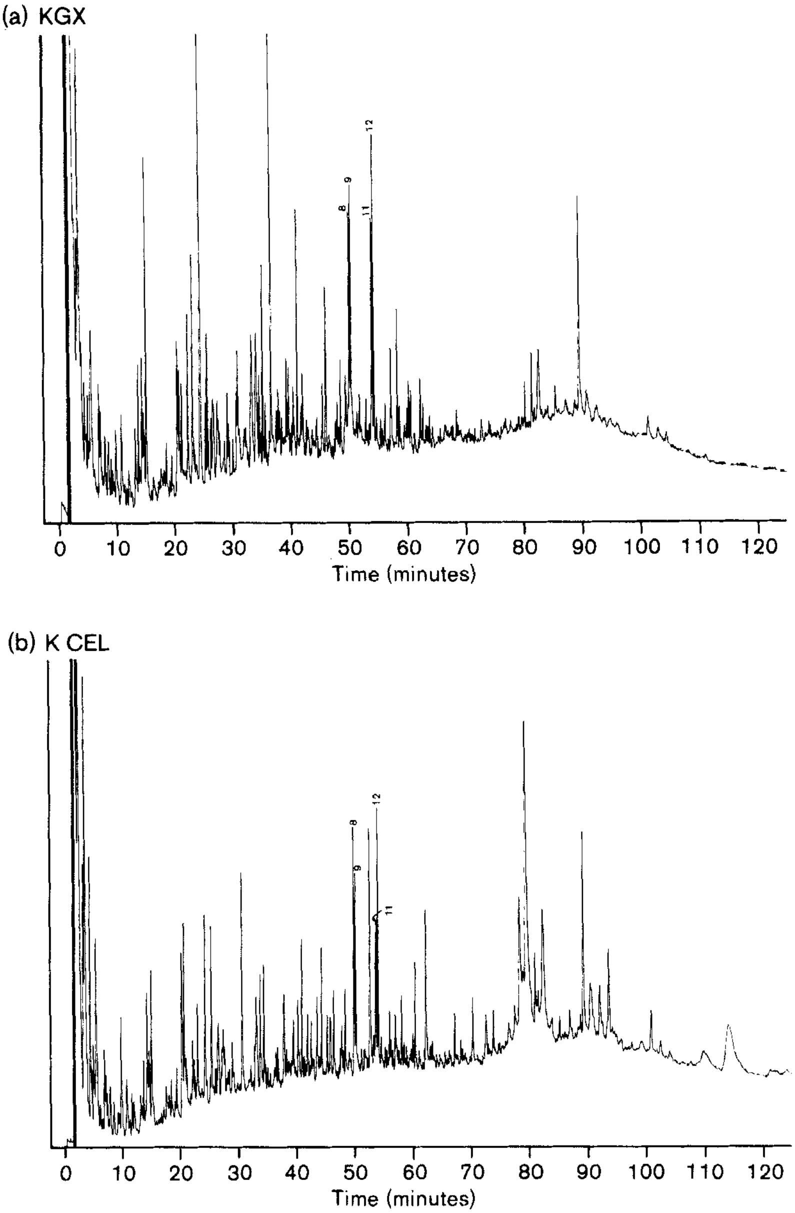


FIGURE 2. Comparison of pyrograms obtained from (a) kraft cooked glucose plus xylose KGX and (b) kraft cooked cellobiose KCEL.

TABLE 3
Reproducibility of Pyrolysis

Compound	FID Area/mg Initial wt	Standard Deviation	% Coefficient of Variance
styrene	59 330	31 144	52.49
acetic acid	130 716	24 446	18.70
indene	89 848	16 803	18.70
napthalene	41 277	25 672	62.19
phenol	119 207	24 953	20.93
cresol	68 699	36 638	53.33
3-ethylphenol	58 736	9 850	16.77
4-ethylphenol	77 716	12 847	16.53
phenol related	31 571	24 465	77.49
P-CHOH$(CH_2)_3CH_3$	55 439	7 205	13.00
unknown	115 365	60 535	52.47
average CV			38.8

produced dark brown liquors and dark brown precipitates after pH adjustment to 3. The yield of precipitates ranged from 1.4% from bleached kraft pulp to 6.5% for glucose or xylose. The pyrograms obtained from KGX and KCEL are compared in Fig. 2. The types of compounds produced by pyrolysis of the high molecular weight materials from KGX and KCEL are very similar, but differ in the amounts produced. The identification of phenol, (Rt=50), cresol (Rt=50.4), and ethylphenols (Rt 53.8 and 54.2) by GC/MS confirm the presence of aromatics in the original high molecular weight material.

Though pyrolysis has shown qualitative differences between the different high molecular weight fractions, quantification of the peaks is difficult owing to the lack of an appropriate internal standard. To measure the variability of the system the E effluent was analysed seven times and area per milligram of initial weight, standard deviation, and coefficient of variance were calculated for the most prominent peaks. As shown in Table 3, the variance ranged from 15% to 80% with an average of 39% based on initial weight. Greater variance was observed when the peak area from the FID was correlated to the weight lost during pyrolysis.

Pyrolysis has identified qualitative changes in the nature of the high molecular weight materials. Lignin-derived materials generate substituted guaiacols and phenols while pyrolysis of E effluents yields predominantly phenols.

Permanganate/Periodate Oxidation Studies

Another commonly used technique for the analysis of lignin samples is permanganate/periodate oxidation of lignin samples. This technique degrades the samples into their respective methylated benzoic acids[18, 19]. Erickson and Dence[20], Lindström and Österberg[21], and Österberg and Lindström[22] have applied this technique to study kraft mill effluents.

The resulting GC traces for the permanganate/periodate oxidation products of KL, and Eo effluent are seen in Fig. 3. The traces are plotted so that the internal standard (Rt = 35.0) is set at 75% full scale. Oxidation yielded a series of organic acids with the structures shown in Table 4. The three peaks (Rt 73.6, 90.0, and 97.5; Fig. 3a) are compounds A,B,C and are present in a ratio of 16.5:2.5:1. These three compounds account for a third of the FID response for the kraft lignin sample. These lignin degradation products have previously been identified in unbleached kraft lignin from *Pinus mugo*[18] in a ratio of 20.9:5.6:1. These compounds have also been identified in unbleached kraft pulps from *Pinus sylvestris* in unspecified quantities by Gellerstedt and Lindfors[23].

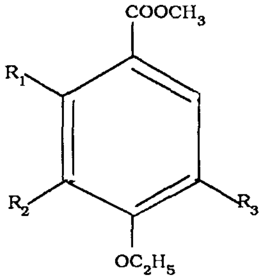
p-Hydroxybenzoic acid (compound D) was isolated from both KL and Eo effluent but the isohemipinic acids were isolated from KL. The lack of guaiacol derivatives in E effluent indicates that a CE bleaching sequence destroys the guaiacyl nature of the dissolved lignin. Assuming that the chromophores responsible for the kraft colour are the same for both KL and Eo, then guaiacol-derived compounds are not responsible for the kraft colour as proposed by Gierer[2].

In addition to the aromatic lignin degradation products, a series of methyl esters of linear acids of varying chain lengths were also isolated as shown in Fig. 3. The difference in intensities of the peaks between Fig. 3a and 3b reflects the degradation of the kraft lignin structure by the bleaching processes. However, it is not possible to speculate at this time what structures in the high molecular weight materials would give rise to these acids.

Ultraviolet and Visible Spectroscopy

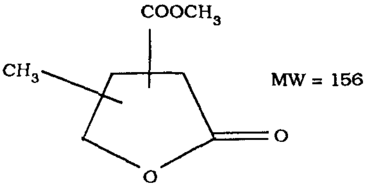
UV-vis spectroscopy was used to further investigate the relationship between colour and the aromatic nature of the high molecular weight materials. The absorptivities at 465 nm (colour), 280 nm (phenolics), and 254 nm (aromatics) were determined for TKL, KL, KG, and E. The results are given in Table 5 and

TABLE 4
Identification of Oxidation Acids



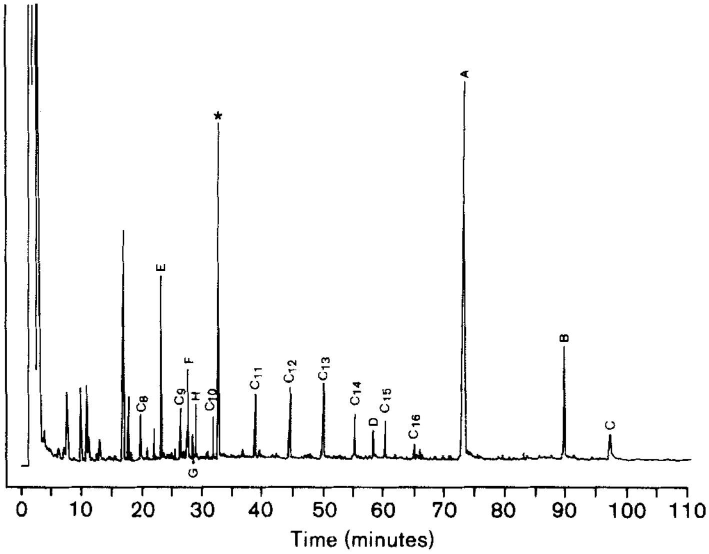
	COMPOUND	Rt
A	$R_1 = H$, $R_2 = H$, $R_3 = OCH_3$	73.6
B	$R_1 = COOCH_3$, $R_2 = H$, $R_3 = OCH_3$	90.0
C	$R_1 = H$, $R_2 = COOCH_3$, $R_3 = OCH_3$	97.5
D	$R_1 = H$, $R_2 = H$, $R_3 = H$	58.5

C_X Methyl ester of linear acid of chain length



E, F, G, and H
Exact position of the functional groups and double bond cannot be determined by mass spectrometry.

(a) KRAFT LIGNIN



(b) Eo

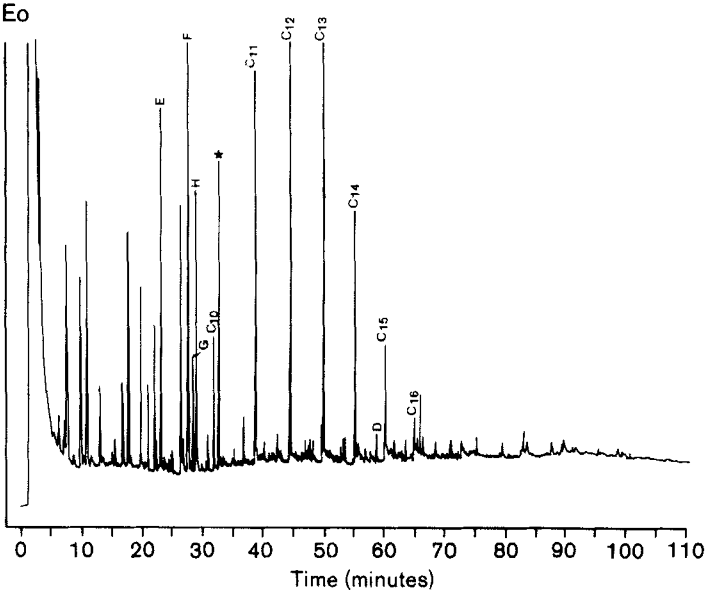


FIGURE 3. Gas chromatogram of the products resulting from the permanganate/periodate oxidation of (a) kraft lignin KL and (b) extraction effluent E.

TABLE 5
Absorptivities at Selected Wavelengths

	465 nm	280 nm	254 nm
TKL	1.37	21.4	23.2
KG	2.84	20.0	23.7
E	1.67	15.6	19.8
KL	0.517	11.6	12.5

TABLE 6
Ratio of Absorptivities

	465/280 • 10^{-2}	465/245 • 10^{-2}	280/254
KL	4.46	4.13	0.928
TKL	6.41	5.92	0.923
KG	14.2	12.0	0.844
E	10.6	8.4	0.788

the ratios of the absorptivities in Table 6. Sundman *et al.*[24] reported that kraft E effluent has an absorptivity of 1.8 Lg^{-1} cm^{-1} at pH 7.6 and 465 nm compared to 1.67 Lg^{-1} cm^{-1} found in this report.

Discussion

As shown by the pyrograms the aromatic components of TKL (commercial kraft lignin) and KL (laboratory kraft lignin) are very similar. Their phenolic/ aromatic absorptivities (0.928 and 0.923 respectively) are also similar. However, there is a major difference in their colour with TKL having an absorbance of 1.37 Lg^{-1} cm^{-1} (465 nm) and KL of 0.517 Lg^{-1} cm^{-1} (465 nm). This reflects the effect of the cook and the origin of the samples. KL was produced from *Pinus radiata* chips in a controlled batch laboratory cook whereas TKL is from a commercial mill which operates both continuous and batch digesters using *P. radiata*.

The analytical data for E effluent (pyrolysis, permanganate/periodate oxidation, and UV-visible spectroscopy) shows that few, if any, guaiacol residues are present. Therefore it is doubtful if the leucochromophores responsible for kraft colour are guaiacol based, as proposed by Gierer. Instead the chromophores may be sugar degradation products attached to lignin molecules.

CONCLUSIONS

The commonly held view is that the chromophores responsible for kraft colour are lignin derived. Though guaiacol and related compounds were readily detected in KL and TKL, these compounds were not present in E effluents. Furthermore, there is a dramatic shift in the ratio of absorptivities of colour to either phenolic or aromatic residues between KL and E effluents. This evidence indicates that their colour is independent of the guaiacol content and that the leucochromophores responsible for kraft colour, as proposed by Gierer, are not related to the actual chromophores.

Furthermore, this work has shown that high molecular weight coloured materials can be produced by kraft pulping of sugars and that these polymers contain aromatic residues.

EXPERIMENTAL

Sources of Materials

Kraft black liquor and E stage effluent were collected from a commercial kraft pulp mill operating predominantly on *Pinus radiata*, and stored at 4°C until used. The bleaching sequence of the mill is (C+D)EoDED. Precipitated kraft lignin was prepared from a kraft cook of *Pinus radiata* chips. The cook had a sulphidity of 27.1, 17% AA, 1900 H factor, and the pulp had a kappa number of 27.1. The kraft lignin was precipitated by adjusting the pH to 3 with 3 M sulphuric acid. Milled wood lignin from *Pinus radiata* was prepared according to the method of Bjorkman[25]. Kraft milled wood lignin was prepared by cooking MWL in white liquor (3.5 g NaOH and 3.1 g $Na_2S.9H_2O$/100 ml H_2O). Abbreviations for the various samples tested are listed in Table 1.

Kraft Cooked Sugars

Kraft cooked sugars were produced by dissolving 10 g of either glucose (Sigma G-5000), xylose (Sigma X-2000), 5 g glucose + 5 g xylose, microcrystalline cellulose (Sigma S-5504), bleached *Pinus radiata* pulp, or *Pinus radiata* holocellulose in 3.5 g NaOH and 3.1 g $Na_2S{\bullet}9H_2O$/100 ml distilled water in a teflon-lined bomb. The reaction bombs were purged with nitrogen before being sealed. The samples were then submerged in a preheated oil bath at 80°C. The temperature was raised to 170°C over 70 minutes and maintained at 170°C for 95 minutes. During cooking the vessels were agitated every half hour. The reaction was stopped by rapidly chilling the vessels in cold water.

Precipitated kraft sugars were isolated by adjusting the pH of the black liquor to 3 with 10% sulphuric acid. The yield ranged from 1.5% for cooked bleached pulps, to 7% for cooked xylose and cooked glucose. The precipitated kraft sugars were then dissolved in 50 ml 0.1 N NaOH and extracted three times with chloroform. The aqueous phase was then ultrafiltered (see below) against MilliQ water until the conductivity of the permeate was less than 3.0 µs/cm.

Ultrafiltration

Ultrafiltration was carried out according to the method of Alen *et al.*[26], using either an Amicon model 52 stirred well (working volume of 75 ml) with a YM2 membrane, or an Amicon DC2A hollow fibre system with an H1P3 cartridge. The retentate from the ultrafiltration was freeze dried and stored as a freeze dried powder at room temperature.

Pyrolysis Gas Chromatography

Weighted samples of approximately 1 mg of the freeze dried material were pyrolyzed using a Hewlett Packard pyroprobe attached to an HP 5890 gas chromatograph. The sample was flushed with helium and heated at 200°C for 2.5 minutes before being pyrolyzed at 650°C for 20 sec. Pyrolysis fragments were analysed on a 25 m carbowax 20 M column using a purged split injection (1:25). The helium flow through the column was 1 ml/min. Injector and detector temperatures were maintained at 250°C. The column was maintained at 30°C for 2 minutes after pyrolysis and then ramped at 2°C/min to 200°C and held at that temperature for 38 minutes and the peaks detected by flame ionization with either an HP 3393a integrator or Delta software integration package operating on an IBM clone for peak quantification. Pyrolysis products were identified using a similar GC attached to an HP 5985 mass spectrophotometer operated in the EI mode at 70eV, with a scan rate of 3 scans per second.

Permanganate/Periodate Oxidation

Oxidation of the various samples was carried out according to the method of Erickson and Dence[20], as modified by Lindström and Österberg[21], using α-bromotoluene as an internal standard. The resulting products were analysed by gas chromatography using the same column and temperature program as the pyrolyzed samples.

Spectral Analysis

Known amounts of freeze dried samples were dissolved in 0.05 M phosphate buffer at pH 7.6 and absorbances at selected wavelengths were determined using a Pye Unicam SP6-550 UV-visible spectrophotometer.

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