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The Investigation of Peracetic Acid-Oxidized Loblolly Pine by Pyrolysis-Gas Chromatography-Mass Spectrometry

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THE INVESTIGATION OF PERACETIC ACID-OXIDIZED LOBLOLLY PINE BY PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

A thesis submitted by

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SUMMARY

Peracetic acid (PAA) oxidized loblolly pine was investigated by pyrolysis-gas chromatography-mass spectrometry (PGCMS) using mainly a pyrolysis temperature of 400°C. Pyrolysis at 400°C was shown not to rearrange or degrade major lignin pyrolysis products among which are guaiacol, creosol, 4-ethylguaiacol, 4-propylguaiacol, 4-vinylguaiacol, eugenol, trans-isoeugenol, and vanillin.

Pyrolysis products were identified by mass spectrometry whenever possible and relative amounts of products were estimated by chromatogram peak areas. The pyrolysis products from lignin-model and oxidized-lignin-model compounds were used to interpret the pyrolysis products from dioxane lignin, loblolly pine, soluble PAA lignin and PAA oxidized loblolly pine.

The pyrolysis of pinoresinol gave a product distribution very similar to that found for lignin. The major pyrolysis product was creosol accompanied by substantial amounts of guaiacol and vanillin.

The pyrolyses of diisoeugenol and conidendrin both produced guaiacol as the main product without any detectable yield of creosol.

The pyrolyses of two β-aryl ethers, 2-(2-methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol and 2-(2-methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-one, both yielded creosol and propioveratrone as main products. The pyrolysis of the β-aryl ethers and 1-(3,4-dimethoxyphenyl)propan-1,2-diol produced tentatively identified unsaturated products such as the methyl ethers of cis- and trans-isoeugenol. No evidence was found for any aliphatic (phenylpropane side chain) hydroxyl products.

Coniferin yielded trans-isoeugenol as the major phenolic pyrolysis product along with substantial amounts of creosol and guaiacol.

Dehydrodivanillin pyrolyzed to give vanillin as the major product and guaiacol as a minor product.

Lignin-model compounds representing possible PAA oxidized lignin fragments were also pyrolyzed. Vanillic acid was relatively stable to pyrolysis yielding mainly the starting material, vanillic acid, with small amounts of guaiacol. 5-Methyl-2(5H)-furanone was also found to be relatively stable to pyrolysis yielding mainly the starting material with small amounts of an isomer. The pyrolysis of β-methylmuconic acid and 5-carboxymethyl-4-methyl-2(5H)-furanone both produced the same four major pyrolysis products which were tentatively identified as two pairs of lactone isomers. β-Methylmuconic acid apparently lactonizes on pyrolysis to form 5-carboxymethyl-4-methyl-2(5H)-furanone.

The pyrolysis of dioxane lignin and loblolly pine both produced guaiacol, creosol, 4-ethylguaiacol, 4-propylguaiacol, eugenol, 4-vinylguaiacol, cis-isoeugenol, trans-isoeugenol, vanillin, homovanillin and vanillyl methyl ketone. The major phenolic product from both was creosol along with substantial amounts of trans-isoeugenol.

Soluble PAA lignin produced a larger ratio of gaseous pyrolysis products to phenolic pyrolysis products than dioxane lignin. The main phenolic pyrolysis product of PAA lignin was guaiacol along with substantial amounts of vanillin, homovanillin, and vanillyl methyl ketone. Only very small amounts of other phenolic pyrolysis products were detected. The guaiacol was attributed to a lignin structure similar to conidendrin and diisoeugenol containing a benzyl carbon-to-carbon linkage with another phenylpropane structure. The vanillin, homovanillin, and vanillyl methyl ketone were attributed to a lignin structure containing a benzyl carbohydrate ether. The carbohydrate material associated with PAA lignin pyrolyzed to yield 2-furaldehyde.

Loblolly pinewood wafers delignified with PAA to various yield levels down to about 77% were analyzed by PGCMS. Carbonyl pyrolysis products, vanillin and homovanillin, increased during the first 1% loss in yield. The amounts of other phenolic pyrolysis products from loblolly pine decreased with yield at a rate proportional to the number of carbons on their side chains. Three carbon side-chain pyrolysis products (trans-isoeugenol, eugenol, and 4-propylguaiacol) decreased faster than 2-carbon side-chain pyrolysis products (4-vinyl guaiacol, 4-ethylguaiacol) which decreased faster than the one carbon side-chain compound (creosol). This was interpreted as a significant amount of the reaction occurring at the phenylpropane side chain of lignin rather than at the aromatic nucleus during the first 1% loss of the wood. One of the early reactions at the side chain was shown to involve coniferaldehyde-type groups. The stain intensity of phloroglucinol (a specific stain for coniferaldehyde-type groups in lignin) substantially decreased from 100 to 99% yield and disappeared by 97% yield. The initial increase in carbonyl pyrolysis products was attributed to PAA attack on α-aryl ethers and propenyl-type (such as coniferaldehyde types) side chains and subsequent formation of α-hydroxyls and carbonyls.

The rate of decrease for the 1, 2, and 3-carbon side-chain pyrolysis products became more nearly the same from 99 to 77% yield. This was interpreted as a loss in prominence of PAA attack on the side chain with the bulk of reaction involving the destruction of the aromatic ring.

INTRODUCTION

Peracetic acid (PAA) has been shown to be a selective delignifying agent in experimental pulping studies (1-7). Poljak (3) delignified spruce to 0.1% lignin content at 56-60% yield with PAA. Albrecht (6) found an apparent carbohydrate loss of only 1.4% at a 74% yield using loblolly pine. A detailed review of PAA reaction may be found in other sources (6,8-10).

PERACETIC ACID

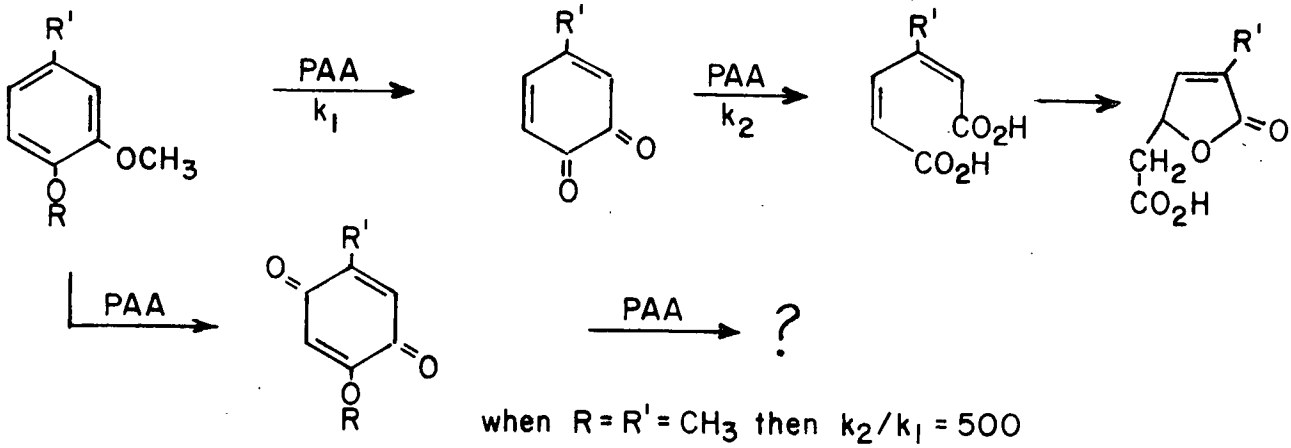
PAA is an oxidant which in aqueous media can donate the electrophilic hydroxylium ion, OH^+, to electron-rich centers (11-13). Lignin has unsaturated structures which are electron-rich sites that PAA may selectively attack. Some of these structures and their reactions with PAA are represented in Fig. 1.

After the substrate is oxidized by PAA, the initial product may be subject to further PAA oxidation possibly at an increased rate (8,9) as shown in Fig. 1 for ring oxidation. The PAA oxidation of an aromatic ring can produce a dicarboxylic acid (a muconic acid) or its lactone (8,9). Farrand (8) has identified approximately 40% of the PAA reaction products from creosol and from 4-methylveratrole. Most of the products were muconic acids and their corresponding lactones.

PERACETIC ACID WOOD STUDIES

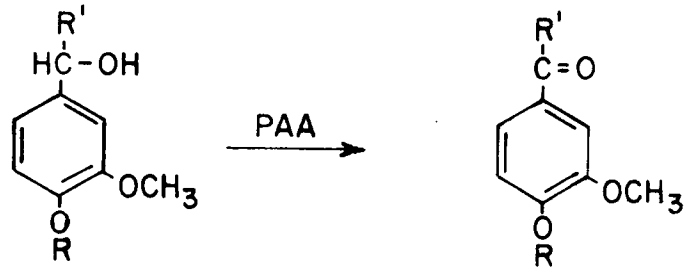
Albrecht (6) has investigated the solubilized PAA oxidized products from softwood. Specific details concerning the reactivity and transformation of the various phenylpropane units were not obtained due to the complexity of the polymeric product. However, these products were characterized by carboxylic acid, phenolic hydroxyl, and methoxyl contents, by molecular weight, and

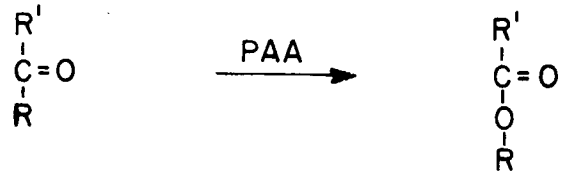
RING OXIDATION:

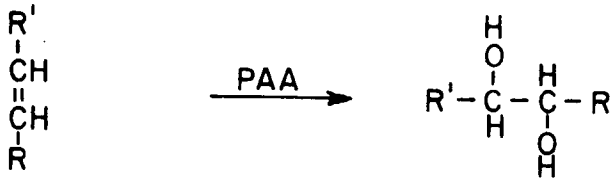


when $R = R' = CH_3$ then $k_2/k_1 = 500$

SIDE-CHAIN OXIDATION:







R, R' = Aliphatic or aromatic

Figure 1. Peracetic Acid Reactions (8)

by their UV and IR spectra (6). In general, these characterizations agree with anticipated results based on the model compound studies. The chemical changes in the PAA-oxidized wood itself have not been investigated and the solubilized products have not been as well defined as the model compound reaction products.

WOOD AND LIGNIN ANALYSIS BY PYROLYSIS-GAS CHROMATOGRAPHY

A gas chromatograph can be interfaced with a pyrolysis unit (PGC) to help separate and identify the pyrolysis products. The chromatogram obtained from pyrolysis (a pyrogram) may be used to "fingerprint" a polymer (14-25). Identification of the major products in a pyrogram can lead to determining functional groups (15) and monomer units of a polymer (14,16-25).

Wood is a complex structure consisting of, among other things, a variety of different polymers; cellulose, hemicelluloses, and lignin. The pyrolysis of wood may be described approximately as a pyrolysis of a simple mixture of cellulose, hemicelluloses, and lignin (26,27). The presence of any two components apparently has little if any effect on the other component. The pyrolysis or thermal degradation of wood and isolated lignin have been investigated (28-68). However, investigation of pyrolysis of PAA lignin has not previously been reported.

The pyrolysis products of lignin may be separated into fractions. Their approximate yields and descriptions are listed in Table I.

The methanol content in the aqueous distillate fraction does give an indication of the methoxyl content (58). The tar fraction, however, is the most descriptive in defining the original lignin structure. The coke fraction has been analyzed, but its molecular weight is too high and it is

too complex to be easily defined. The tar fraction contains many low molecular weight compounds such as guaiacol, 4-propylguaiacol, and eugenol (58), which are characteristic of structural moieties presumed present in lignin. Figure 2 is the tentative softwood lignin structure based on the formula by Freudenberg, et al. (71,72) and modified by Sarkanen (73). The pinoresinol structure (units 9-10) and biphenyl structures (units 16 and 26 and 8 and 9) in Fig. 2 may contribute only to a very limited extent to the structure of lignin (59-64). There is evidence that carbon-to-carbon bonds between side chains (such as α,β linkages) may be more prevalent than what is shown in Fig. 2 (59,64).

TABLE I

LIGNIN PYROLYSIS PRODUCTS (58)

Product	Approximate Yield, %
Coke (char)-condensed structure	55
Aqueous distillate-H_2O, MeOH, $(Me)_2CO$, AcOH	20
Tar-phenolics	15
Gaseous products — CO, CH_4, CO_2, C_2H_6	12

The pyrolysis conditions have varied greatly from one researcher to another so that it is difficult to compare results. Lignin pyrolysis products may vary from coniferyl alcohol (50) under mild conditions to vanillic acid (58,70) under harsh conditions. Some of the main variables involved in pyrolysis are the type of pyrolysis atmosphere (reactive, inert, vacuum, or pressurized), pyrolysis temperature, and time. The time at temperature is at least somewhat dependent on the particular design of the pyrolysis equipment (20). Many of the different pyrolysis product results are due to the different conditions or equipment used. Typically, lignin pyrolysis products

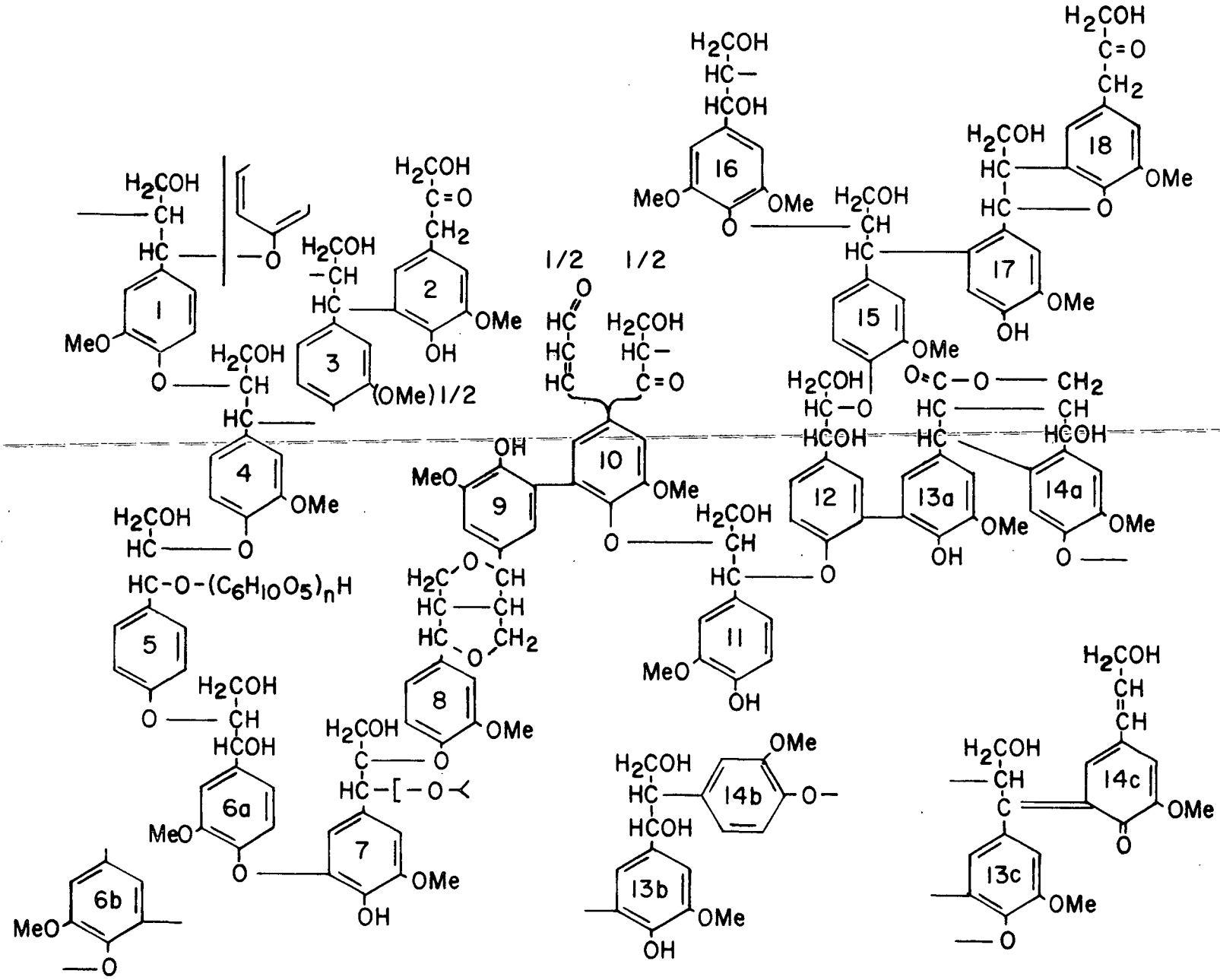


Figure 2. Tentative Softwood Lignin Structure Based on Formula by Freudenberg, et al. (71,72) and Modified by Sarkanen (73)

have been identified as guaiacol, creosol, 4-ethylguaiacol, 4-propylguaiacol, eugenol, 4-vinylguaiacol, cis-isoeugenol, trans-isoeugenol, vanillin, and acetovanillone (32,33,42,46,50,51,57,58). The method of identification in these studies has been comparison of GLC retention times to authentic samples. Very little NMR, IR, or MS has been carried out on lignin pyrolysis products to positively identify them. IR and GLC retention times have been used to identify hickory smoke components (47,48). Destructive distillation products of lignin have been identified by derivative melting points (65,68). A limited amount of mass spectrometry work has been done on wood pyrolysis products (69).

PYROLYSIS OF MODIFIED LIGNIN

Lignin pyrolysis products from wood or isolated lignin may be used to classify the sample as hardwood or softwood (50,51). Isolated lignins such as dioxane lignin, thiolignin, ethanol lignin, and hydrochloric acid lignin from the same wood give different pyrograms (32) indicating pyrolysis-gas chromatography (PGC) is sensitive to the method of isolation. Differential thermal analysis has already been used to characterize several different isolated lignins from the same wood (49).

PAA lignin should contain aromatic units and/or ring cleavage products (muconic acids) which probably can be identified by PGC. Aromatic units from the pyrolysis of lignin have been identified (mainly by GLC retention times). Conjugated carboxylic acids, lactones and their derivatives (which are similar to anticipated muconic acids) have been identified as pyrolysis products from man-made polymers and other materials (18,25,47,74-81). This indicates that PGC should be an excellent tool to characterize PAA lignin.

THESIS OBJECTIVE

The objective of this thesis was to gain a better understanding of the peracetic acid delignification process by studying the pyrolysis products of soluble peracetic acid lignin and peracetic acid-oxidized loblolly pine. Lignin-model compounds, oxidized-lignin-model compounds, dioxane lignin and loblolly pine pyrolysis products were used for a basis of comparison. Gas liquid chromatography was employed to separate pyrolysis products and mass spectrometry to identify them whenever possible.

RESULTS AND DISCUSSION

PYROLYSIS UNIT

The pyrolysis unit chosen for this work was a furnace-type unit, the Hamilton Multi-Purpose sampling system. The system is shown in the Experimental section (Fig. 45 and 46). A furnace-type pyrolysis unit is the most likely type of unit to give secondary reactions as compared to a Curie point or heated wire pyrolysis unit (20). The larger heated area and the larger sample size in the furnace unit increase the possibility of secondary reactions occurring during the pyrolysis. This possible disadvantage was not considered critical as it was felt that conditions could be optimized to minimize secondary reactions. The advantages of being able to handle almost any type of material (solids, liquids, tars, powders), and the ability to weigh samples before and after pyrolysis out weighed any apparent disadvantages in the furnace unit. The need to obtain pyrolysis products in large enough quantities to identify them by MS, NMR, or IR was the determining factor in choosing the furnace pyrolysis unit.

PYROLYSIS CONDITIONS

Due to the possibility of secondary reactions, mentioned above, it was necessary to check the thermal stability of anticipated pyrolysis products to determine acceptable working conditions. Creosol is reported as the major product from pyrolysis of softwood lignin (32,33,42,46,50,51,57,58). Model compound work has shown that creosol and guaiacol were both converted to cresols and xylenols at high (600°C) temperatures (82,83). Pyrolysis work done for this thesis, Table II, showed that creosol was not stable in the pyrolysis system at 600°C but was stable at 400°C. At 600°C dioxane lignin

produced only two main products, cresol(s) and xylenol(s), but at 400°C produced a variety of products described later. The maximum temperature at which secondary reactions were not significant (400°C), was used for the entire study to ensure a rapid pyrolysis. Guaiacol, creosol, 4-ethylguaiacol, 4-vinylguaiacol, vanillin, acetovanillone, and propiovanillone were shown to be stable to the 400°C pyrolysis conditions. Other lignin pyrolysis products such as 4-propylguaiacol, eugenol, cis-isoeugenol and trans-isoeugenol were pyrolyzed in mixtures at 400°C. Their appearance in pyrograms and their pyrolysis with other known compounds demonstrate that they are also stable at 400°C. Besides temperature, time at temperature may affect the stability of organic compounds. The time at temperature for pyrolysis products in the furnace pyrolysis unit (Fig. 46) is dependent on the carrier gas flow rate through the pyrolysis unit. Seventy-five milliliters of helium per minute was used throughout this study and was near the maximum flow possible for the system.

TABLE II

TEMPERATURE DEPENDENCE OF CREOSOL TO XYLENOL(S) CONVERSION IN FURNACE PYROLYSIS UNIT USED IN THIS THESIS WORK

Pyrolysis Temp., °C	Creosol/Xylenol(s) Ratio
600	no creosol
530	0.17
495	2.6
445	26
400	greater than 130

Most of the actual pyrolysis appears to occur in the first 2-5 sec after introduction of the sample into the 400°C zone. With most samples no further melting, boiling off and/or charring could be visibly detected after 5 sec.

There was essentially no difference between pyrograms for samples pyrolyzed at 400°C for 10 sec, 15 sec, and 3 hr. The peak resolution for all pyrograms run at 400°C was quite good (there was no peak spreading). This indicated that there was not a slow and/or continuous bleed of phenolic material which contributed to the pyrogram. This type of thermal degradation which releases all the pyrolysis products in the pyrogram essentially at the same time is termed flash pyrolysis. Undoubtedly, there are further reactions occurring to the char after 10 sec in the 400°C zone, but this degradation of the char material contributes little, if any, significance to the pyrogram.

Wood samples were left in the pyrolysis zone during the entire time (2-1/2 hr) for the GLC separation of all the pyrolysis products. This was to insure complete flushing of the less volatile carbohydrate pyrolysis products, especially levoglucosan, from the pyrolysis unit. After 10 sec at 400°C there was a 45-50% weight loss in the wood samples. After 2-1/2 hours there was a total weight loss of approximately 90%. This additional weight loss is considered to be in part a slow bleed of carbon dioxide and water from the further dehydration and degradation of the carbohydrate char (84) as shown in Fig. 3 and further condensation of the lignin char.

STRUCTURAL ANALYSIS BY PYROLYSIS-GAS CHROMATOGRAPHY

LIGNIN-MODEL COMPOUNDS

As mentioned previously the expected lignin pyrolysis products are stable to the pyrolysis conditions used for this work. Figures 4-14 represent the pyrograms of the model compounds studied. Each figure lists the pyrolysis products in order of increasing GLC retention time (see Appendix IX) with relative peak areas. The method of identification for each pyrolysis product

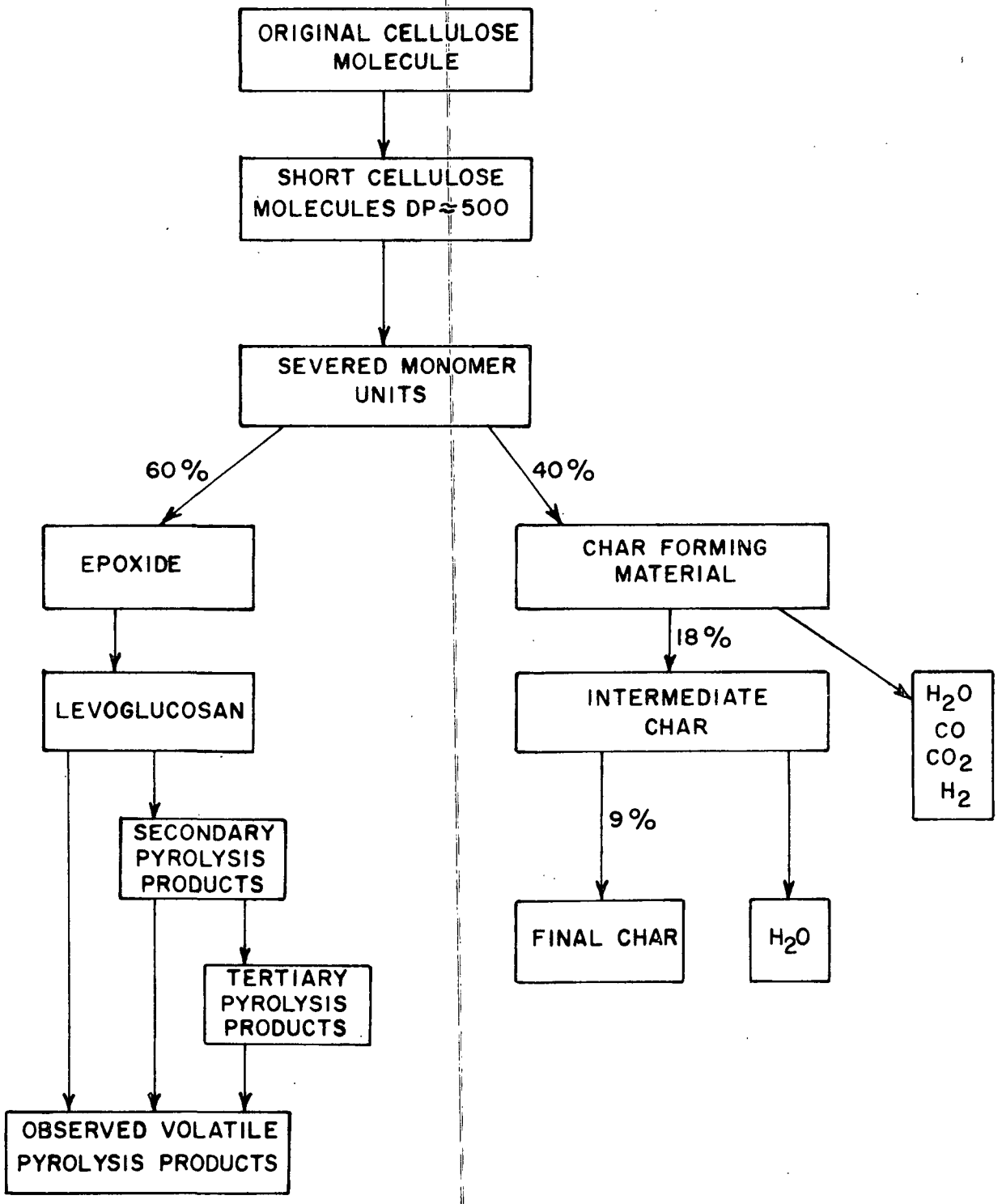


Figure 3. The Thermal Decomposition of Cellulose (84)

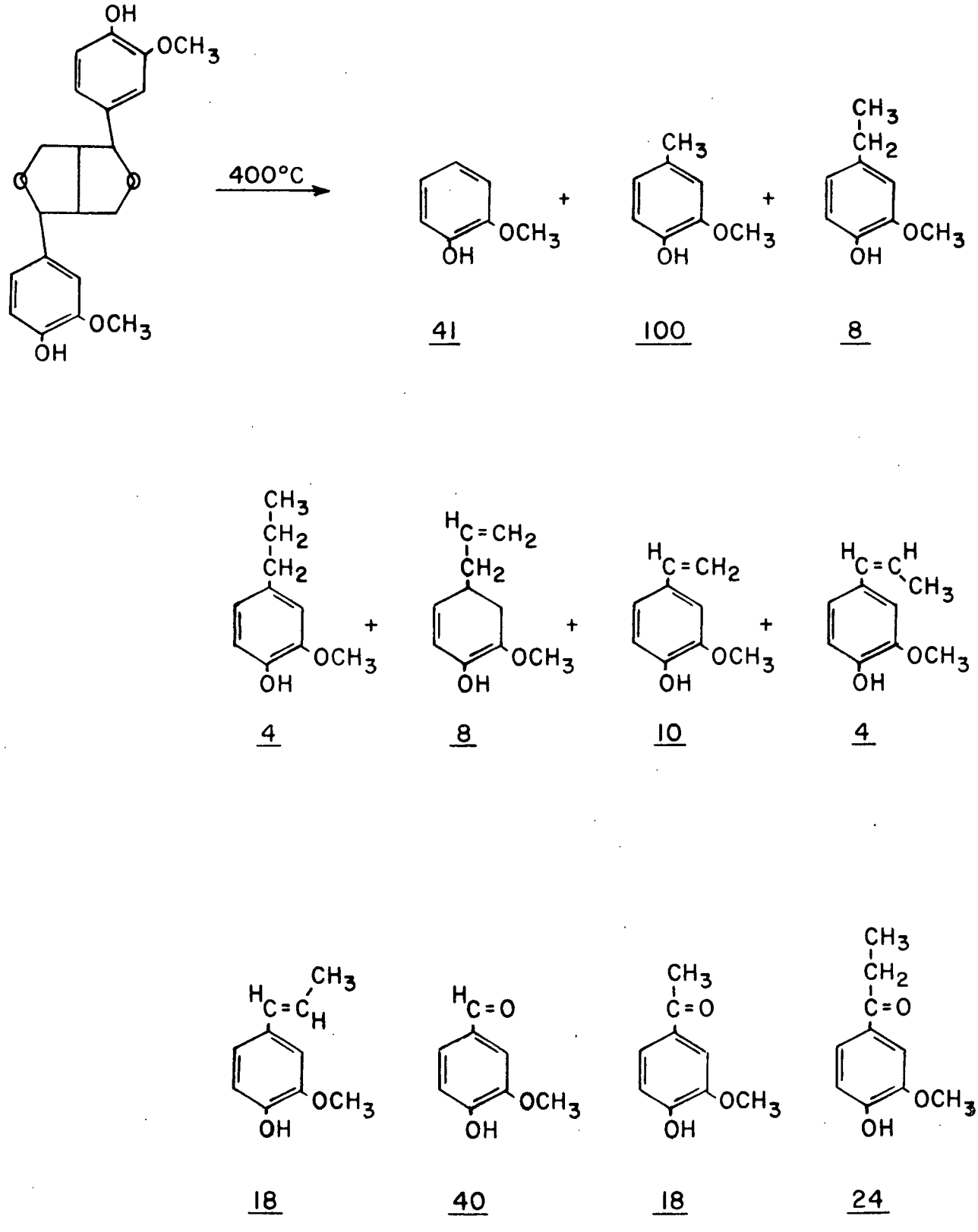


Figure 4. Pinoresinol Pyrogram Representation with Relative Peak Areas

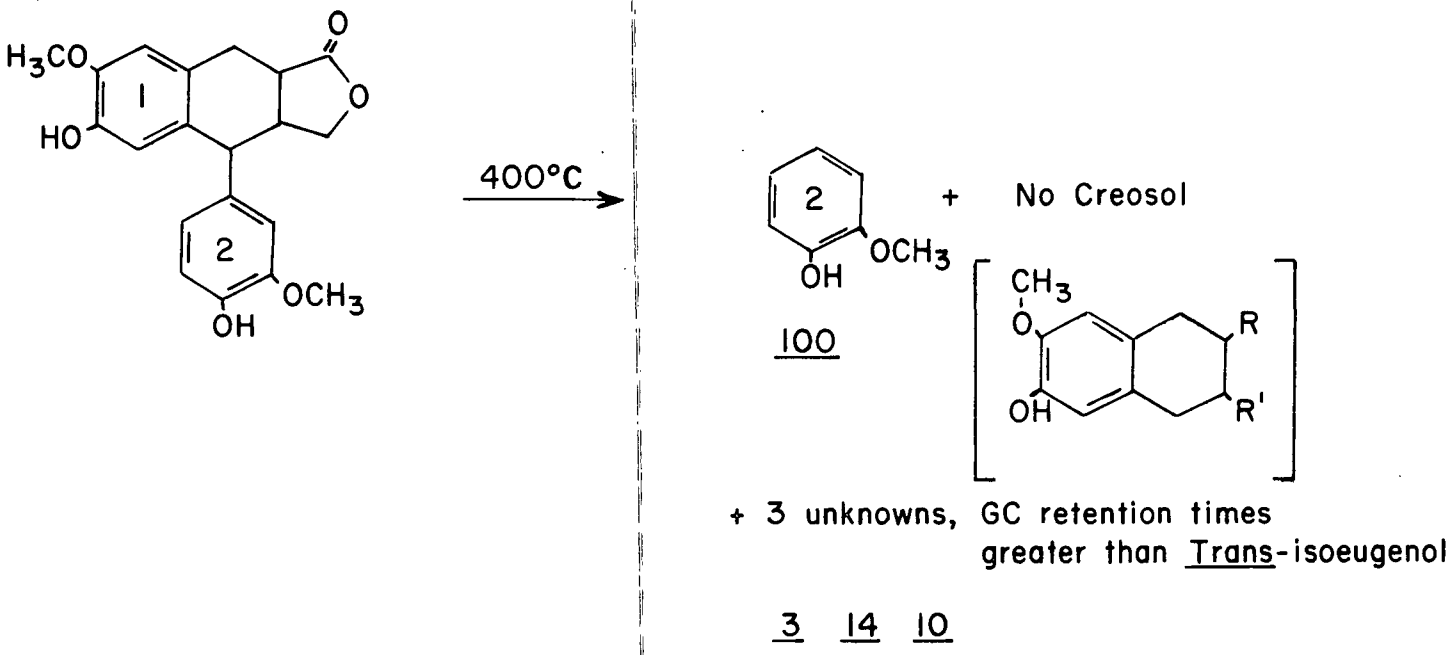


Figure 5. Conidendrin Pyrogram Representation with Relative Peak Areas

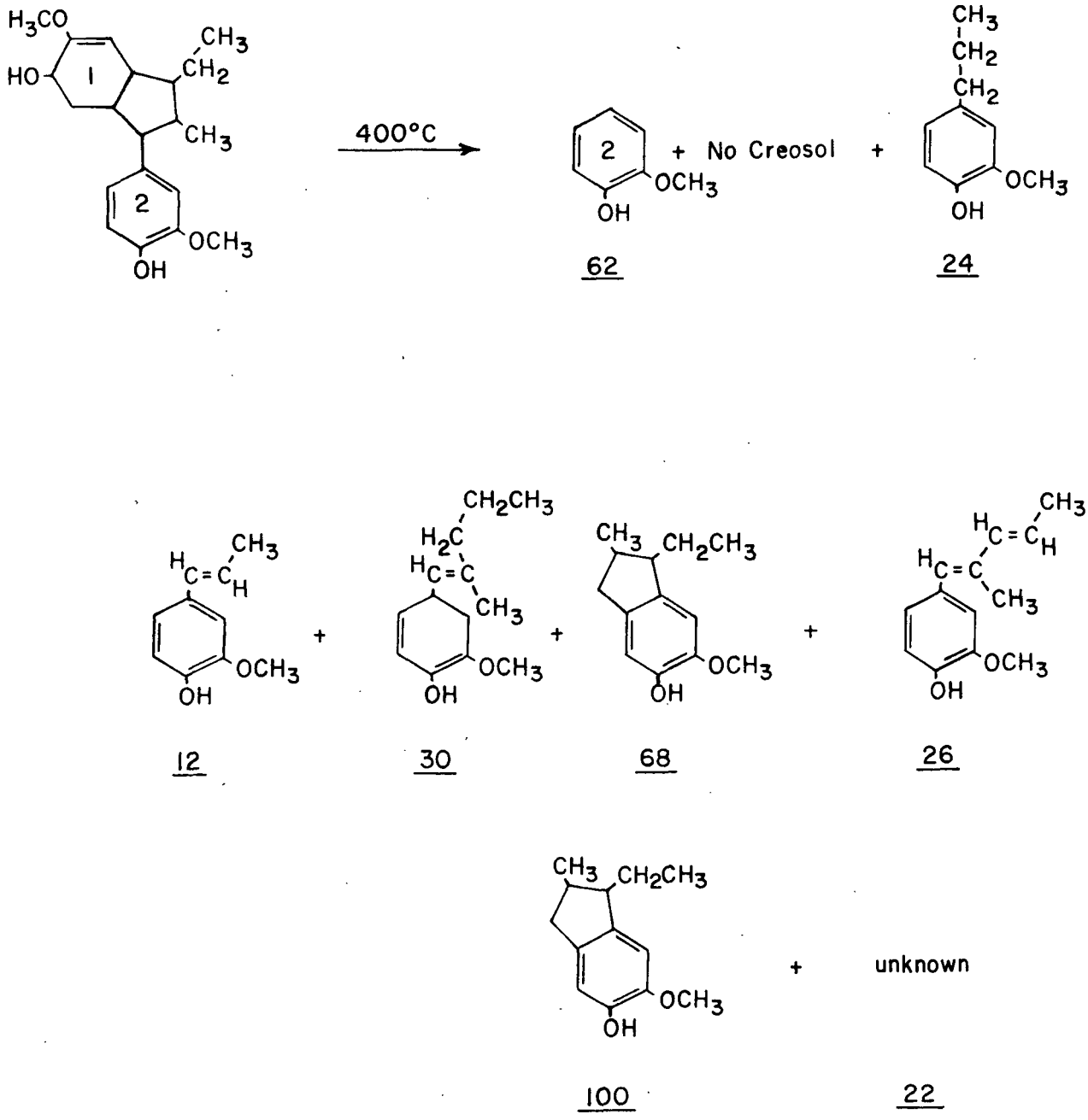


Figure 6. Diisoeugenol Pyrogram Representation with Relative Peak Areas

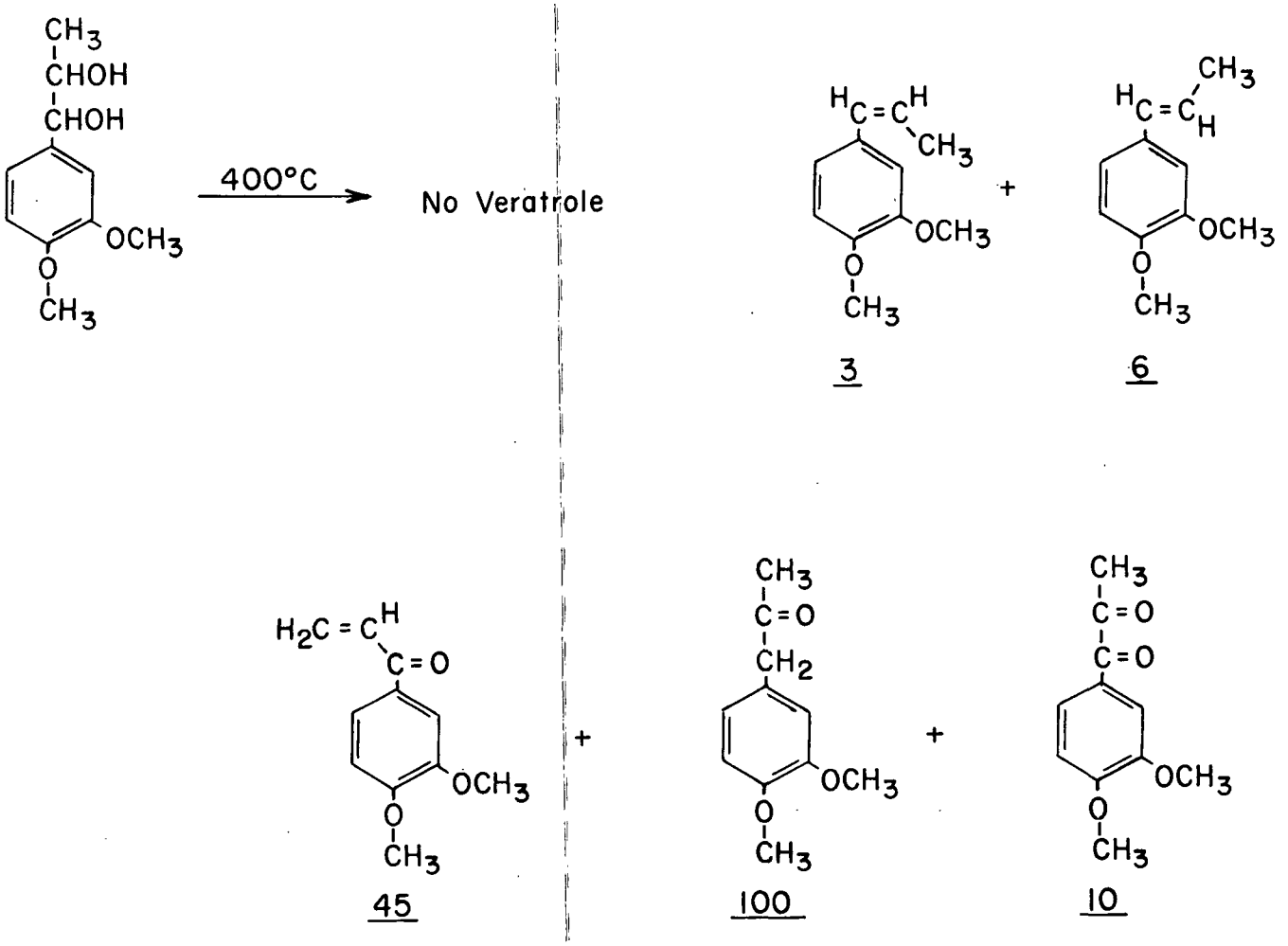


Figure 7. 1-(3,4-Dimethoxyphenyl)propan-1,2-diol
Pyrogram Representation with Relative Peak Areas

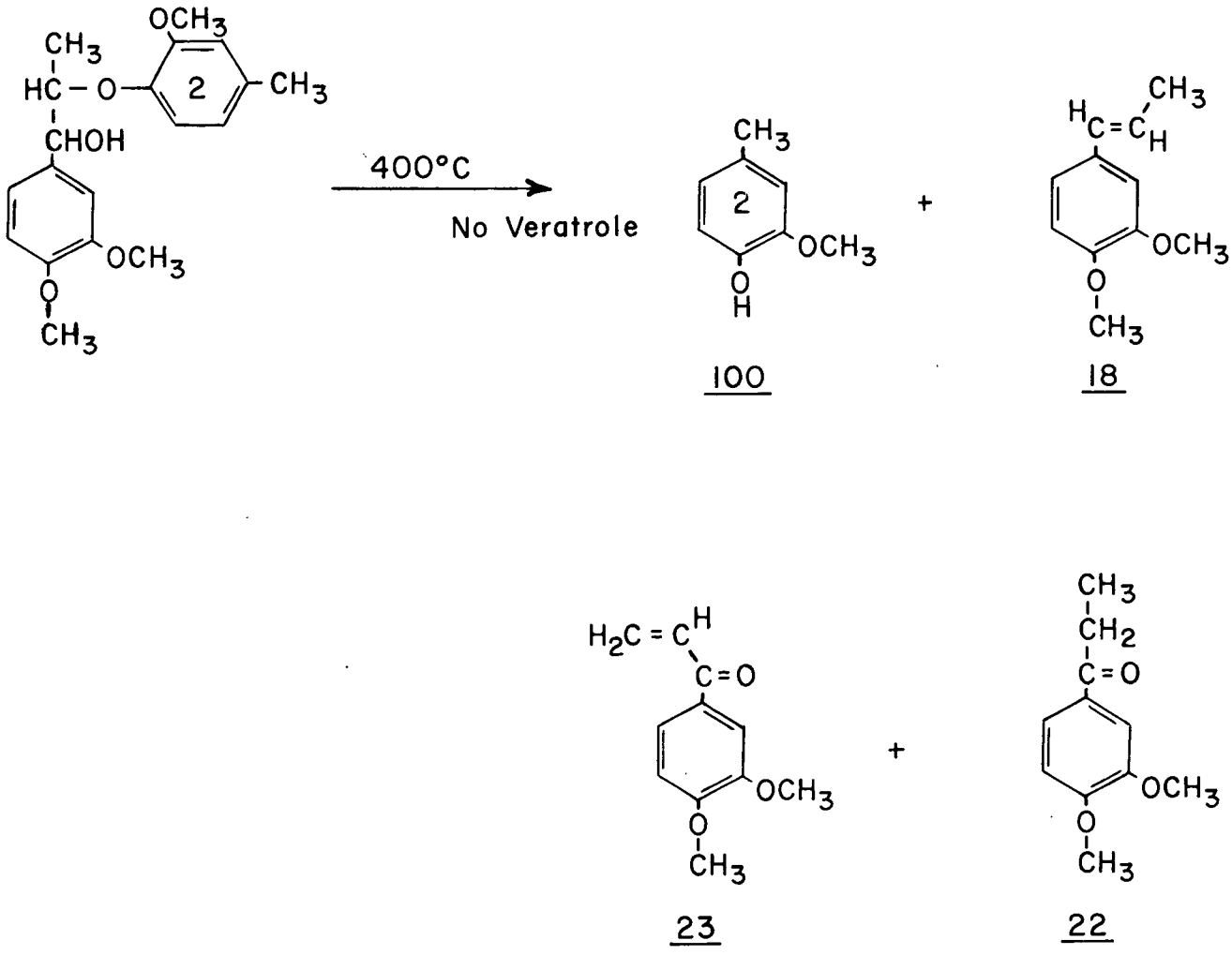


Figure 8. 2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)-propan-1-ol Pyrogram Representation with Relative Peak Areas

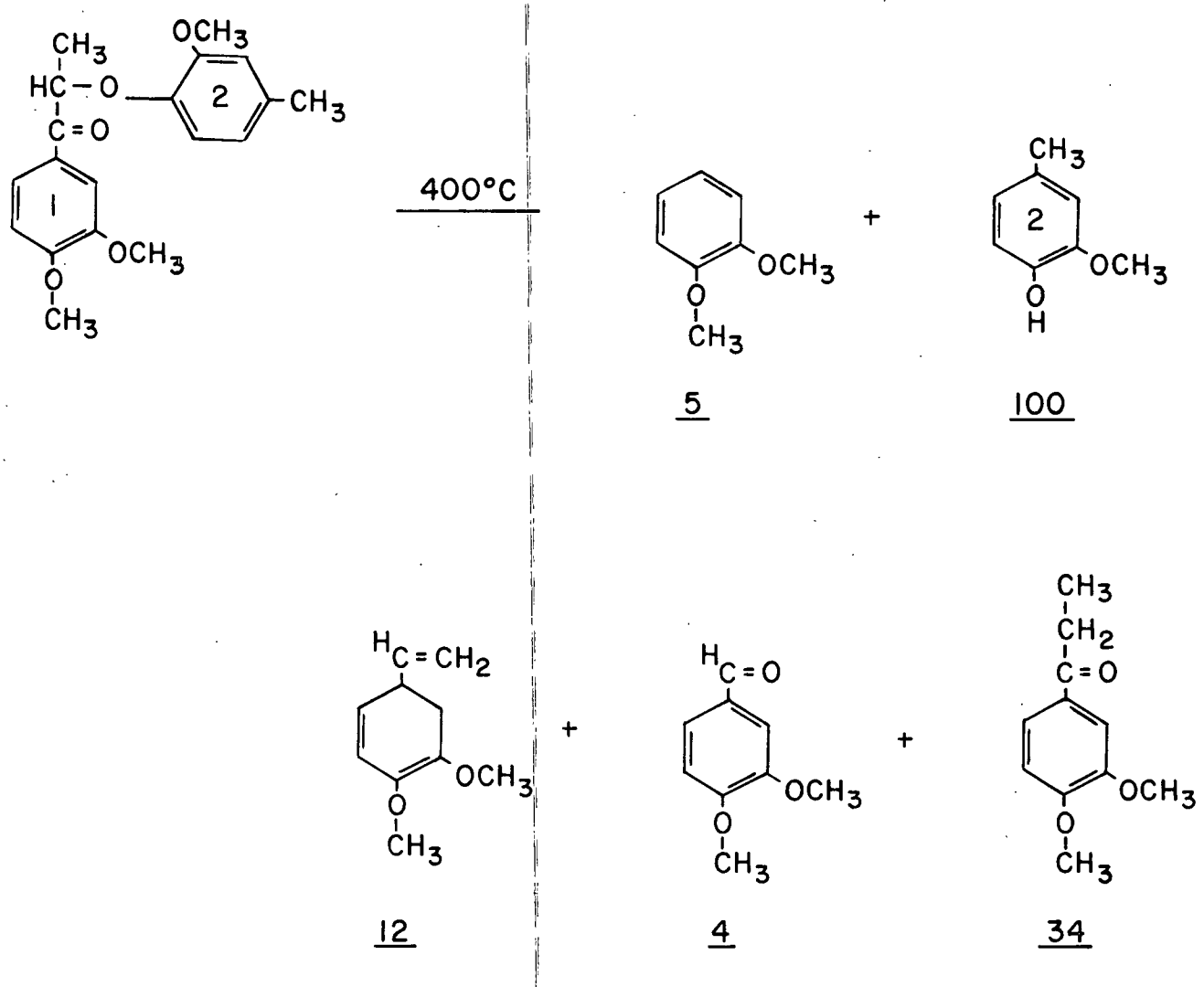


Figure 9. 2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)-propan-1-one Pyrogram Representation with Relative Peak Areas

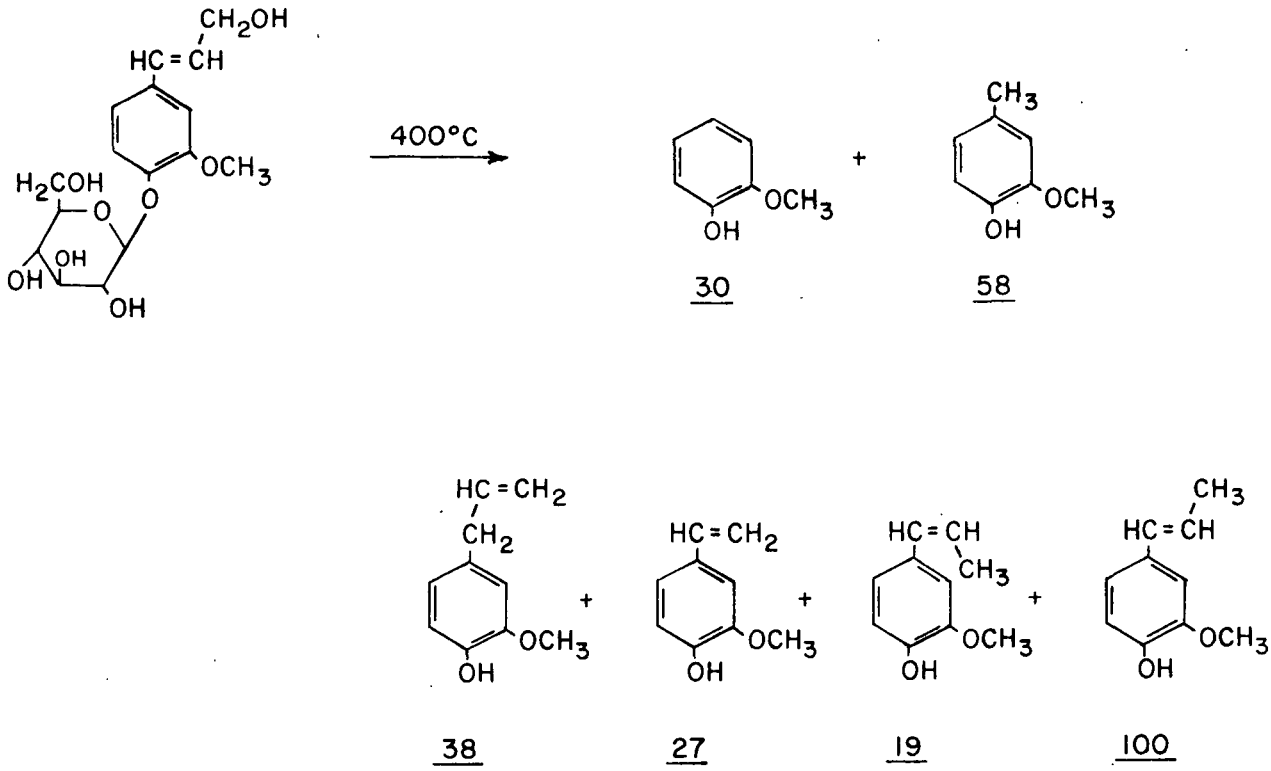


Figure 10. Coniferin Pyrogram Representation of Phenolic Products with Relative Peak Areas

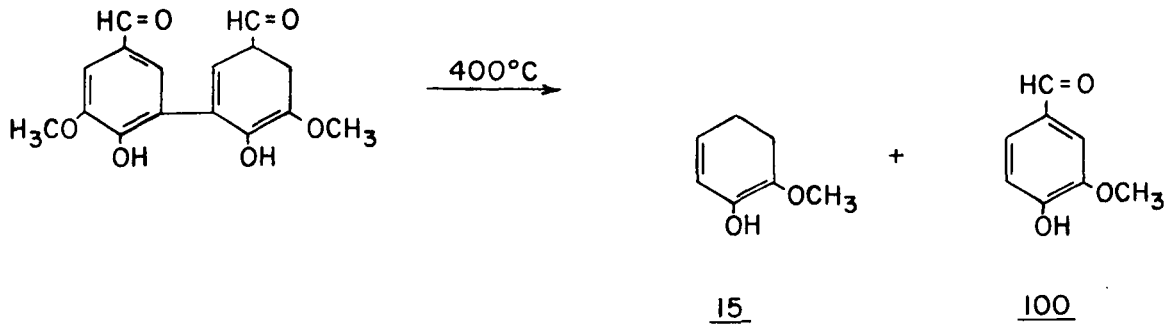


Figure 11. Dehydrodivanillin Pyrogram Representation with Relative Peak Areas

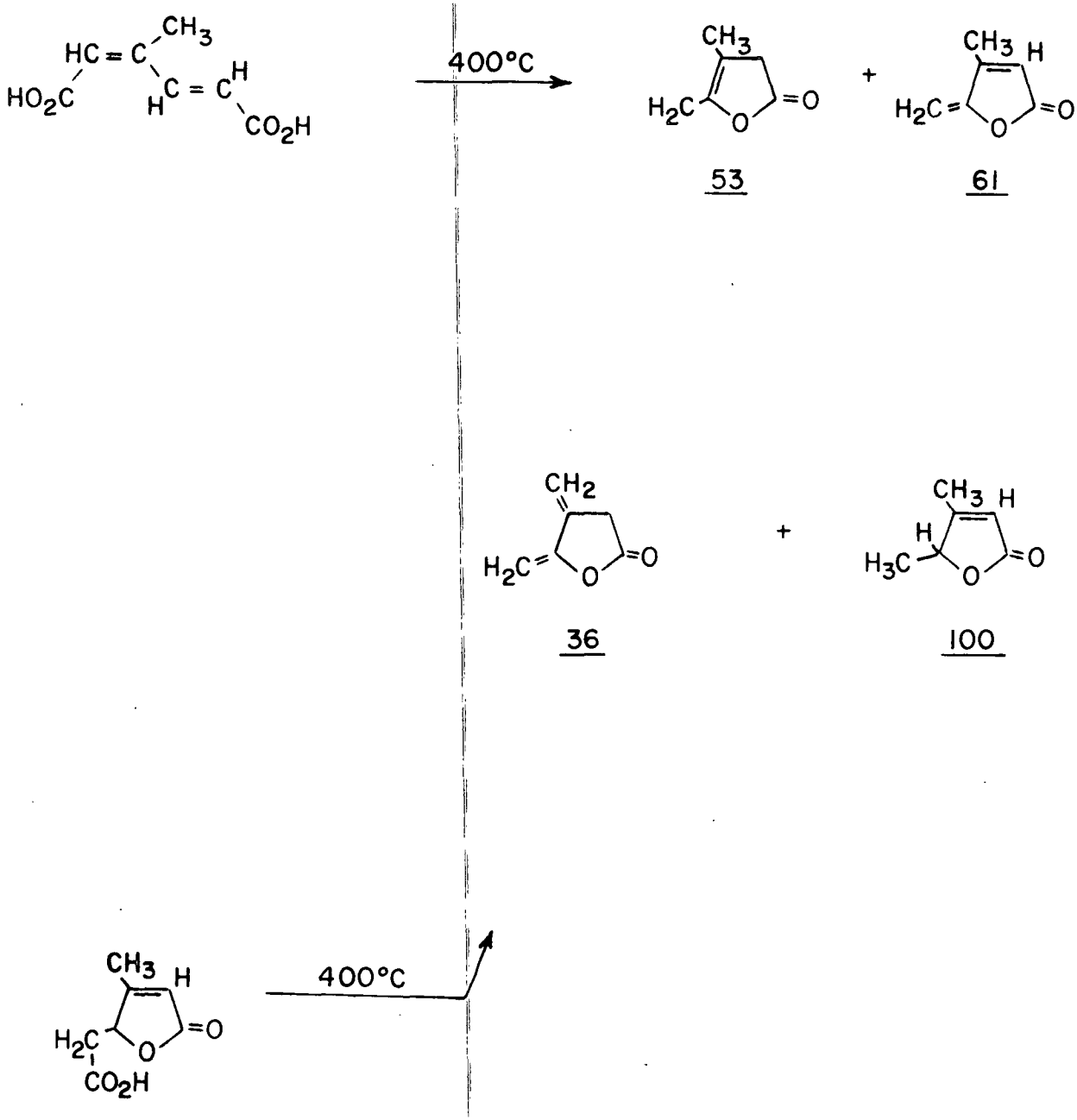


Figure 12. cis,trans-β-Methylmuconic Acid and its Lactone Pyrogram Representation with Relative Peak Areas

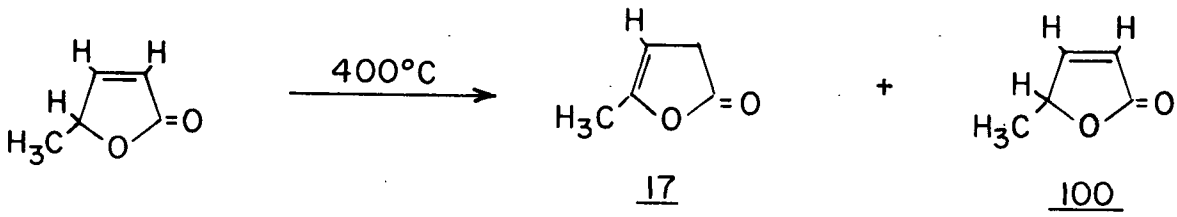


Figure 13. 5-Methyl-2(5H)-furanone Pyrogram Representation with Relative Peak Areas

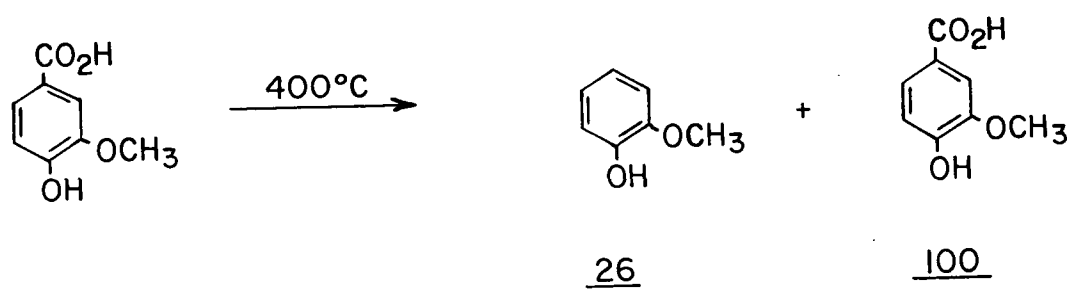


Figure 14. Vanillic Acid Pyrogram Representation with Relative Peak Areas

is listed in Table III. Many of the model compound pyrolysis products are the same as those cited in the previous section as lignin pyrolysis products. No single model compound completely represents lignin, but a suitable group of models can include almost all of the structures proposed to be present in lignin.

Pinoresinol

The pinoresinol structural unit appears in the proposed lignin structure between units 9 and 10 in Fig. 2. The pyrolysis of pinoresinol, represented in Fig. 4, yields many of the products in the same relative proportion as those found for the pyrolysis of lignin (32,33,42,46,50,51,57,58). All of the products in Fig. 4 except 4-propylguaiacol have been positively identified by GC and MS. The 4-propylguaiacol peak was identified by GC only (see Table III).

From the product distribution in Fig. 4, the relative thermal stability of certain bonds in the phenylpropane side chain may be proposed. The one carbon side-chain compounds (creosol and vanillin) predominate, indicating that the carbon-to-aromatic-ring bond is relatively stable. The large amount of guaiacol indicates that the aliphatic ring system competes with the aromatic ring for the α-carbon to a significant extent. The ether bonds appear to be the least stable and readily form α-carbonyls on pyrolysis.

Conidendrin

The pyrolysis of conidendrin is represented in Fig. 5. Conidendrin was used to partially represent carbon-to-carbon bonds between phenylpropane units which may be present in lignin (59,64,71-73). Conidendrin contains an α-aryl linkage (units 14 and 15, Fig. 2) and a β-β linkage (units 9 and 10, Fig. 2). These types of structures or linkages were considered as likely

TABLE III

PYROLYSIS PRODUCT IDENTIFICATION

Compound Pyrolyzed	Pyrolysis Product	Relative Peak Area	Molecular Weight by MS	Method of Identification[a]
Pinoresinol				
	guaiacol	41	124	GC,MS(A)
	creosol	100	138	GC,MS(A)
	4-ethylguaiacol	9	152	GC,MS(A)
	4-propylguaiacol	4		GC
	eugenol	7	164	GC,MS(A)
	4-vinylguaiacol	9	150	GC,MS(A)
	cis-isoeugenol	4	164	GC,MS(A)
	trans-isoeugenol	18	164	GC,MS(A)
	vanillin	40	152	GC,MS(A)
	acetovanillone	18	166	GC,MS(A)
	propiovanillone	24	180	GC,MS(A)
Conidendrin				
	guaiacol	100	124	GC,MS(A)
	unknown	3		
	unknown	14		
	unknown	10		
Diisoeugenol				
	guaiacol	62	124	GC,MS(A)
	4-propylguaiacol	24	166	
	trans-isoeugenol	12		GC
	4th peak	30	206	MS
	5th peak	68	206	MS
	6th peak	26	204	MS
	7th peak	100	204	MS
	unknown	22		
1-(3,4-Dimethoxyphenyl)propan-1,2-diol				
	1st peak	3	178	MS
	methylisoeugenol	6	178	MS(A)
	3rd peak	45	192	MS,VIV
	veratryl methyl ketone	100	194	MS,VIV
	5th peak	10	208	MS,VIV
2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol				
	creosol	100	138	GC,MS(A)
	methylisoeugenol	18	178	MS(A)
	3rd peak	23	192	MS,VIV
	propioveratrone	22	194	GC,MS,VIV

See end of table for footnote.

TABLE III (Continued)

PYROLYSIS PRODUCT IDENTIFICATION

Compound Pyrolyzed	Pyrolysis Product	Relative Peak Area	Molecular Weight by MS	Method of Identification
2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-one				
	veratrole	5	138	MS
	creosol	100	138	GC,MS(A)
	3rd peak	12	164	MS
	4th peak	4	166	MS
	propioveratrone	34	194	GC,MS(A)
Coniferin				
	guaiacol	30	124	GC,MS(A)
	creosol	58	138	GC,MS(A)
	eugenol	38	164	GC,MS(A)
	4-vinylguaiacol	27	150	GC,MS(A)
	cis-isoeugenol	19	164	GC,MS(A)
	trans-isoeugenol	100	164	GC,MS(A),VIV
Dehydrodivanillin				
	guaiacol	15		GC
	vanillin	100	152	GC,MS(A)
5-Carboxymethyl-4-methyl-2(5H)-furanone				
	1st peak	63	112	MS
	2nd peak	41	110	MS
	3rd peak	27	110	MS
	4th peak	100	112	MS
cis,trans-β-Methylmuconic acid				
	1st peak	61	products assumed to be the same as for 5-carboxymethyl-4-methyl-2(5H)-furanone. The two pyrograms are nearly identical and the starting materials are very similar	
	2nd peak	31		
	3rd peak	36		
	4th peak	100		
5-Methyl-2(5H)-furanone				
	5-methyl-2(3H)-furanone	17		GC
	5-methyl-2(5H)-furanone	100	96	GC,MS(A)
Vanillic acid				
	guaiacol	30		GC
	vanillic acid	100		GC

[a]Pyrolysis products were identified by their mass spectra (MS), comparison of their mass spectra to that of an authentic sample [MS(A)], decreasing the ionizing voltage for the mass spectra in order to identify the parent ion (VIV) and/or comparison of their GC retention time to that of an authentic sample (GC).

candidates responsible for the formation of guaiacol with negligible amounts of creosol during pyrolysis. This is discussed later in regard to interpretation of PAA lignin pyrolysis products. Only guaiacol was identified (see Table III) as a pyrolysis product from conidendrin. Creosol, the major lignin pyrolysis product (32,33,42,46,50,51,57,58) was absent from the conidendrin pyrogram. This is probably due to the stability of the tetrahydronapthalene-type structure which could cleave off aromatic ring 2 to produce guaiacol. Creosol could only be produced if the tetrahydronapthalene-type structure were destroyed.

Diisoeugenol

The pyrolysis of diisoeugenol in Fig. 6 is very similar to that of conidendrin in Fig. 5. Diisoeugenol contains an α-aryl linkage and an α,β side-chain linkage. It is proposed that all the guaiacol is formed from aromatic ring 2. The indane ring retains the α-carbon and thus prevents creosol formation from unit 2.

The finding of 4-propylguaiacol and trans-isoeugenol was not anticipated due to the α,β and α-aryl linkages (carbon-to-carbon bonds) in diisoeugenol similar to those in conidendrin and pinoresinol. In all cases, however, 4-propylguaiacol and trans-isoeugenol accounted for a relatively minor portion of the pyrogram.

These two products probably originate from both aromatic units in diisoeugenol. The indane-type structure is apparently not as stable as the tetrahydronapthalene-type structure in conidendrin.

The apparent molecular weights of the other products in Fig. 6 are too low to contain two aromatic units (123/guaiacyl unit). The proposed

products are based on their mass spectra, consideration of their relative retention times, and possible side-chain configurations based on the original structure (see Appendices VIII and IX).

1,2-Dihydroxy-1-(3,4-dimethoxyphenyl)propane and Two β-Aryl Ethers

Three compounds with a combination of α-hydroxy, α-carbonyl, β-hydroxy, and β-aryl ether were pyrolyzed, Fig. 7-9. The results were in part similar to the α-ether model compound, pinoresinol, Fig. 4. A limited amount of the oxygen on the side chain remains as a carbonyl. There was no evidence for an ether or a hydroxyl side-chain pyrolysis product from 1-(3,4-dimethoxyphenyl)-propan-1,2-diol or the two β-aryl ethers (Fig. 7-9). Except for the creosol, all the pyrolysis products from the two β-aryl ethers are considered to come from aromatic unit 1 (Fig. 8 and 9).

Creosol and propioveratrone were both positively identified as pyrolysis products of the two β-aryl ethers (Fig. 8 and 9). The other pyrolysis products were tentatively identified by their mass spectra. The mass spectra are interpreted in Appendix VIII.

The β-carbonyl isomer of propioveratrone, veratryl methyl ketone, was reported as a pyrolysis product from 2-(2-methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol by Russian researchers (85). Only the α-carbonyl isomer (propioveratrone) was found in this work (Fig. 8). The procedure used by the Russians (85) of pyrolyzing samples for 30 minutes in a sealed ampule may have permitted the benzyl alcohol to be dehydrated to the propenyl ether followed by hydrolysis to the β-carbonyl as shown in Fig. 15. This type of reaction is proposed to occur during the formation of Hibbert ketones under harsh or prolonged acidolysis conditions (86-98).

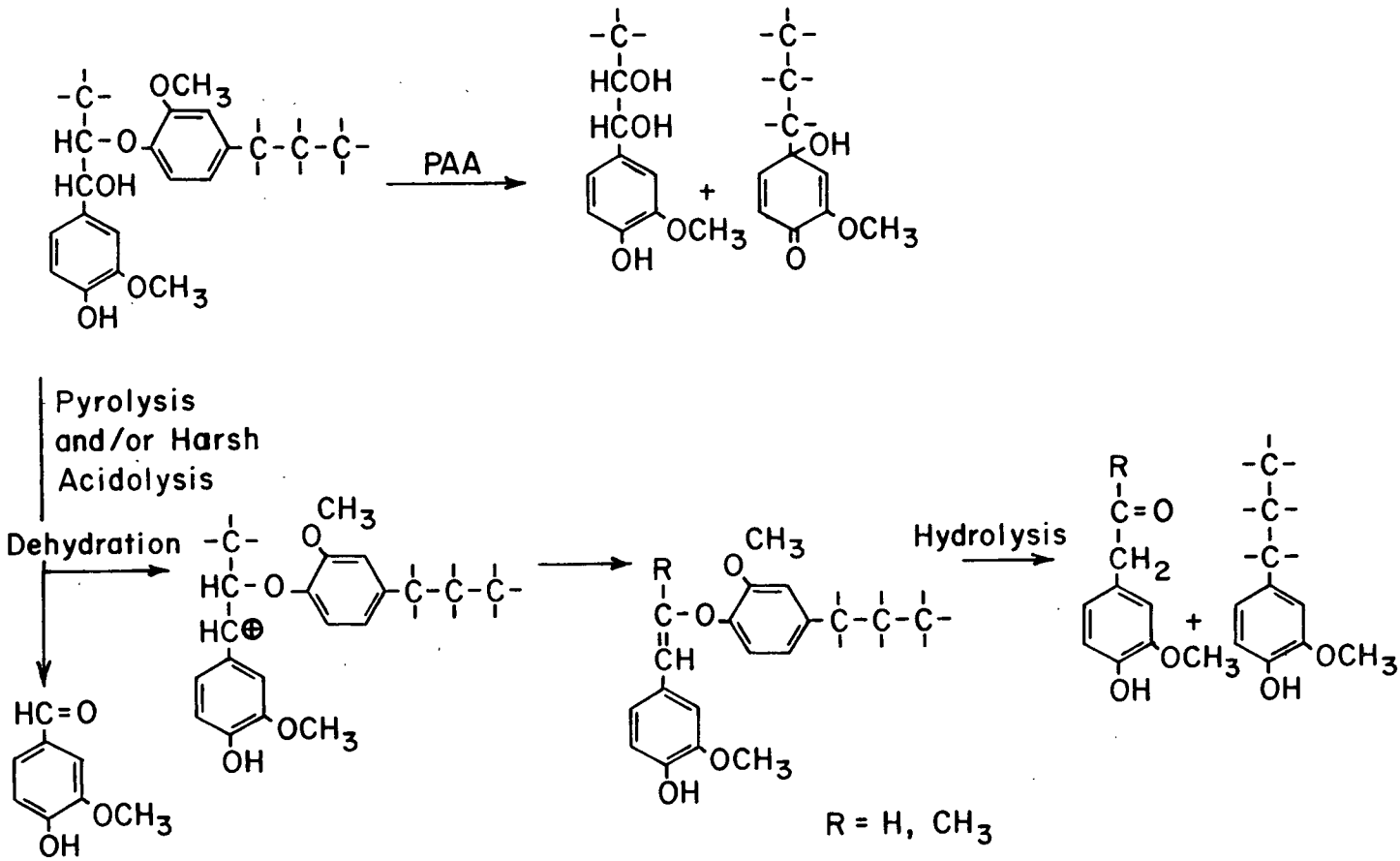


Figure 15. Possible Reactions with a β-Aryl Ether

Veratryl methyl ketone was identified (Appendix VIII) as a pyrolysis product of 1-(3,4-dimethoxyphenyl)propan-1,2-diol, Fig. 7. Dehydration of the benzyl alcohol to the enol and formation of the β-carbonyl is thought to occur during pyrolysis similar to the mechanism proposed during acidolysis as shown in Fig. 15. During the pyrolysis of wood, a considerable amount of water would be released which could promote conversion of β-aryl ether systems to β-carbonyl products.

The α-carbonyl, α-hydroxyl, and the α and β-ether structures are relatively common in the proposed lignin structure, Fig. 2. The β-hydroxyl structure represented by 1-(3,4-dimethoxyphenyl)propan-1,2-diol may be formed by PAA attack on a β-aryl ether (99-100) as shown in Fig. 15.

Coniferin

Coniferin generated a number of unsaturated side-chain compounds on pyrolysis, Fig. 10, as might be expected. Guaiacol and creosol were also positively identified as pyrolysis products (see Table III). Other pyrolysis products were also found for coniferin which were attributed to the carbohydrate portion. Products classified in a later section as carbohydrate 1, carbohydrate 4, and carbohydrate 5 are present based on their GLC retention times and mass spectrum for carbohydrate 1.

Dehydrodivanillin

Qualitatively, dehydrodivanillin gave more char and less products than any other model compound. Vanillin was the major pyrolysis product along with some guaiacol as shown in Fig. 11.

OXIDIZED-LIGNIN-MODEL COMPOUNDS

cis,trans-β-Methylmuconic Acid and its Lactone

The pyrolysis of compounds represented in Fig. 12-14 were used as models for PAA-oxidized lignin. The apparent molecular weight and GLC retention times (Appendix IX) of the four products from 5-carboxymethyl-4-methyl-2(5H)-furanone in Fig. 12 (β-methyl-lactone) are too low for the products to be the original acid. The lactone ring is considered to be relatively stable to pyrolysis. The four compounds are proposed to be two sets of lactone isomers. A pyrogram essentially identical to β-methyl-lactone was obtained from cis, trans-β-methylmuconic acid. It is proposed that the muconic acid lactonizes on heating to give the β-methyl-lactone which is then pyrolyzed.

5-Methyl-2(5H)-furanone

The angelicalactone 5-methyl-2(5H)-furanone was shown to be relatively stable to pyrolysis, Fig. 13. Some of the lactone probably isomerizes to the more volatile (shorter GC retention time) β,γ-unsaturated lactone. No identification work was done to substantiate this.

Vanillic Acid

Vanillic acid was also shown to be relatively stable to pyrolysis, Fig. 14. The carboxylic acids usually cleave on pyrolysis to give carbon dioxide. The conjugation of the acid with an aromatic ring greatly stabilizes it and minimizes decarboxylation.

DIOXANE LIGNIN AND WOOD

A dioxane lignin was obtained from acetone-extracted loblolly pine. The pyrogram obtained from the 400°C pyrolysis of the dioxane lignin is represented in Fig. 16. The products (peaks) are identified in Table IV. Separation of the lignin pyrolysis products was easily accomplished by running the GC column oven isothermally. All compounds represented in Fig. 16 have been identified by comparison of GLC retention times with known compounds. In addition, each compound except vanillyl methyl ketone has been identified by its mass spectrum and comparison of it to the mass spectrum of an authentic sample (see Table IV).

The relative areas and the diversity of pyrolysis products for dioxane lignin are very similar to that found for the model compounds pinoresinol and coniferin (Fig. 4, 10, 16, and Table V). Coniferin was chosen to represent an olefinic system which would result from dehydration (during pyrolysis) of the phenylpropane side chain. Suitable model compounds show this type of

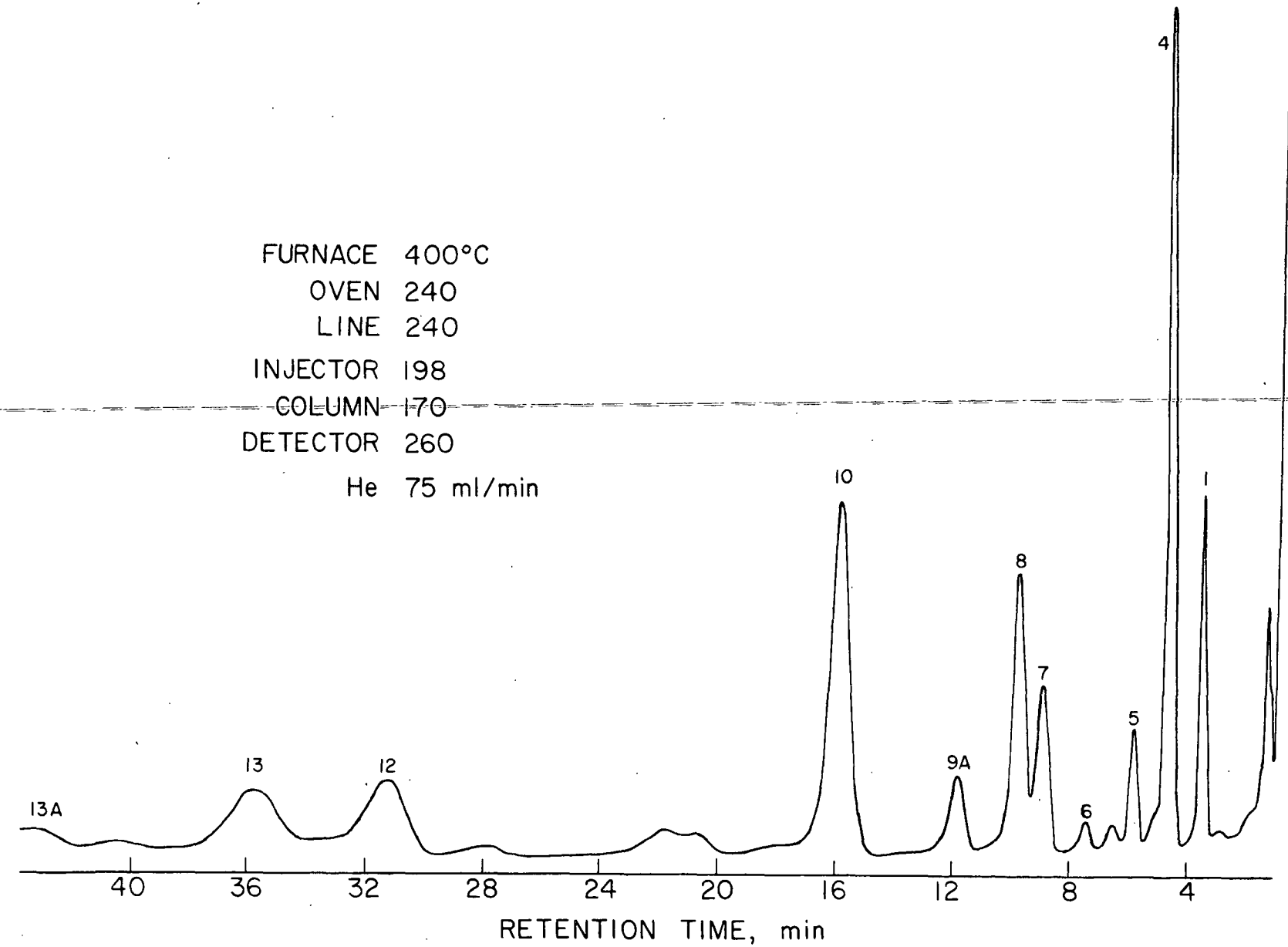


Figure 16. Dioxane Lignin Pyrogram

dehydration during pyrolysis (Fig. 7 and 8). The pinoresinol structure itself is present in the proposed lignin structure (units 9 and 10, Fig. 2).

TABLE IV

NUMBER CODE AND IDENTIFICATION FOR PYROGRAM PEAKS FROM PYROLYSIS OF WOOD AND LIGNIN

Code Number	Compound	Dioxane Lignin	Loblolly Pine	PAA Lignin
A1	2-furaldehyde		GC	GC,MS(A)
1	guaiacol	GC[a],MS(A)[b]	GC,MS(A)	GC,MS(A)
2	carbohydrate 1		UN[c]	
3	guaiacol and carbohydrate 1			
4	creosol	GC,MS(A)	GC,MS(A)	GC
5	4-ethylguaiacol	GC,MS(A)	GC,MS(A)	
6	4-propylguaiacol	GC,MS(A)	GC,MS(A)	
7	eugenol	GC,MS(A)	GC,MS(A)	GC
8	4-vinylguaiacol	GC,MS(A)	GC,MS(A)	GC
9	carbohydrate 2		UN	
9A	cis-isoeugenol	GC,MS(A)	GC,MS(A)	GC
10	trans-isoeugenol	GC,MS(A)	GC,MS(A)	GC
11	carbohydrate 3-HMF		GC,MS(A)	
12	vanillin	GC,MS(A)	GC,MS(A)	GC
13	homovanillin	GC,MS(A)	GC,MS(A)	GC
13A	vanillyl methyl ketone	GC	GC,MS(A)[d]	GC,MS(A)
13B	unknown		UN	
14	carbohydrate 4		UN	
15	carbohydrate 5-levo-glucosan		GC	

[a] Compound identified by GLC retention time comparison to authentic sample.

[b] Compound identified by comparison of its mass spectrum to that of an authentic sample.

[c] Compound unknown, no authentic sample matched its GLC retention time.

[d] This peak may also contain acetovanillone.

TABLE V

RELATIVE PYROGRAM PEAK AREAS

Peak	Coniferin	Pinoresinol	Loblolly Pine Dioxane Lignin	Loblolly Pinewood
Guaiacol	30	41	42	54
Creosol	58	100	100	100
4-Ethylguaiacol	AB[a]	8	22	25
4-Propylguaiacol	AB	4	8	44
Eugenol	38	8	18	31
4-Vinylguaiacol	27	10	34	61
cis-Isoeugenol	19	4	14	ND[b]
trans-Isoeugenol	100	18	61	72
Vanillin	AB	40	27	23
Homovanillin	AB	AB	26	27
Acetovanillone	AB	18	ND	ND
Vanillyl methyl ketone	AB	AB	21	14
Propiovanillone	AB	24	ND	ND

[a] Absent from pyrogram.

[b] Not determined but may be present.

The pyrolysis products from wood (loblolly pine) did not separate as well as the dioxane lignin pyrolysis products when the GC column oven was run isothermally. The satisfactory separation of these pyrolysis products was accomplished by temperature programming. The pyrolysis products from dioxane lignin were also separated by temperature programming the GC column oven for comparison to the wood pyrogram. All the identified peaks in the dioxane lignin pyrogram matched the retention times of prominent peaks in the wood pyrogram. The relative peak areas in the wood pyrogram were very similar to those found in the dioxane lignin pyrogram as shown in Table V. The peaks in the wood pyrogram which do not correspond to peaks in the dioxane lignin pyrogram were thought to be carbohydrate pyrolysis products. A suitable carbohydrate

material was pyrolyzed to compare the retention times of the pyrolysis products with those in the wood pyrogram. It is known that levoglucosan is the primary pyrolysis product of cellulose (84,99-106). The appearance of most of the other pyrolysis products from cellulose is due to the degradation of levoglucosan as shown in Fig. 3. Levoglucosan was pyrolyzed and its pyrogram compared to that of wood. Most of the peaks in the levoglucosan pyrogram match up with the peaks in the wood pyrogram thought to be carbohydrate pyrolysis products. However, the pyrogram for levoglucosan is not considered completely representative for cellulose and especially hemicelluloses. The three pyrograms of dioxane lignin, wood, and levoglucosan are represented together for comparison in Fig. 17-20. The wood sample used was PAA-treated loblolly pine, 99.51% yield. All of the compounds identified by MS in the pyrogram of dioxane lignin and also vanillyl methyl ketone have been identified in the wood pyrogram by MS (see Table IV).

Hydroxymethylfurfural (HMF) in the wood pyrogram was identified by MS (Table IV). The carbohydrate peak in close association with guaiacol in the wood pyrogram was investigated by MS, but its identity was not established. Based on the MS work it appears to have a molecular weight of 128. Levoglucosan and 2-furaldehyde were identified in the wood pyrogram by GLC retention times (Table IV). These three compounds identified in the wood pyrogram were also identified in the levoglucosan pyrogram by retention times.

Possible contamination of lignin peaks in the wood pyrogram was checked by comparing the mass spectrum for each peak with the spectrum of an authentic sample. Significant contamination would show up in the spectrum as additional ions. There was no indication of contamination in any of the spectra taken from the wood pyrolysis products except for the lignin peaks

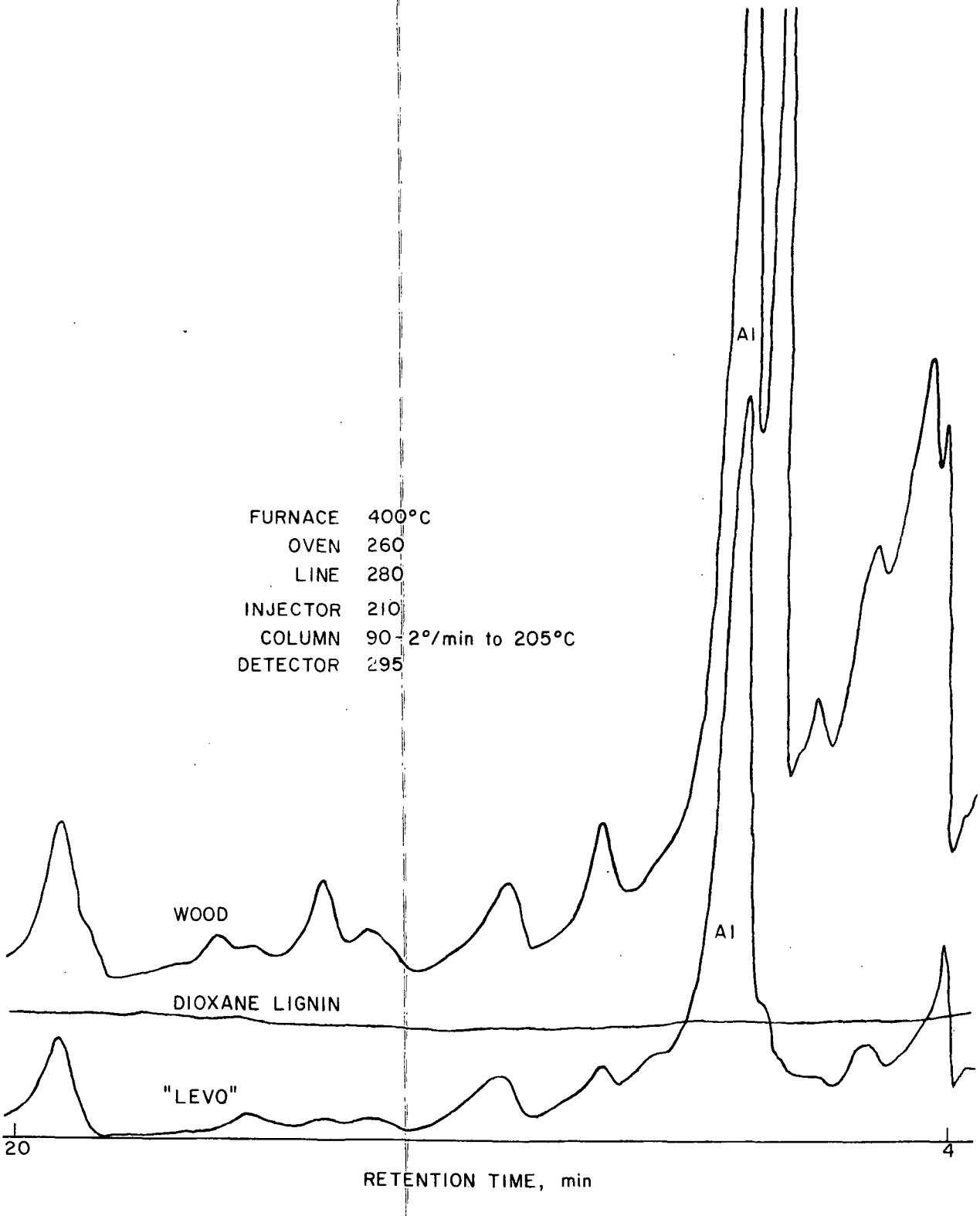


Figure 17. Comparison of Three Pyrograms from Wood, Dioxane Lignin and Levoglucosan from 4 to 20 Min

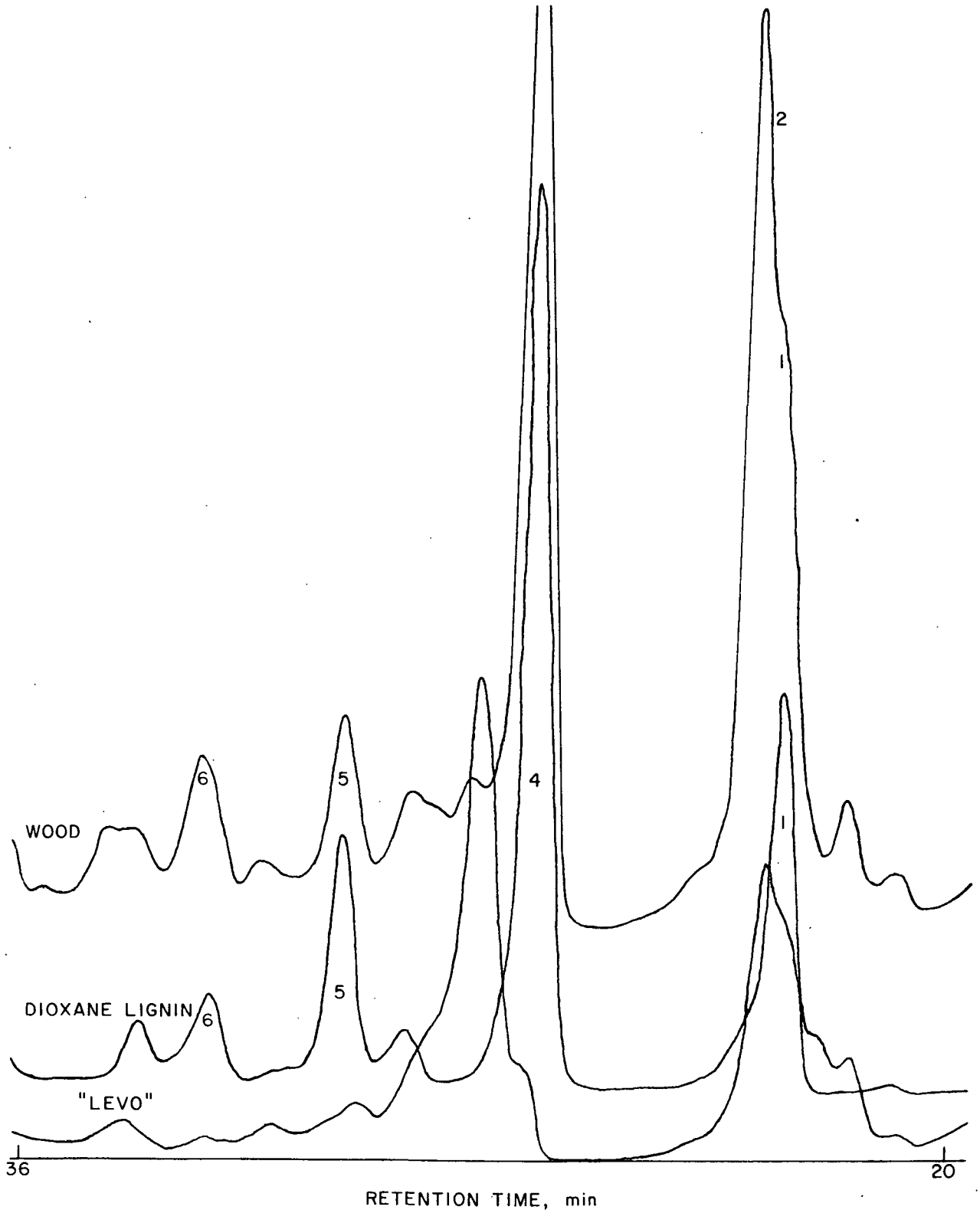


Figure 18. Comparison of Three Pyrograms from Wood, Dioxane Lignin and Levoglucosan from 20 to 36 Min

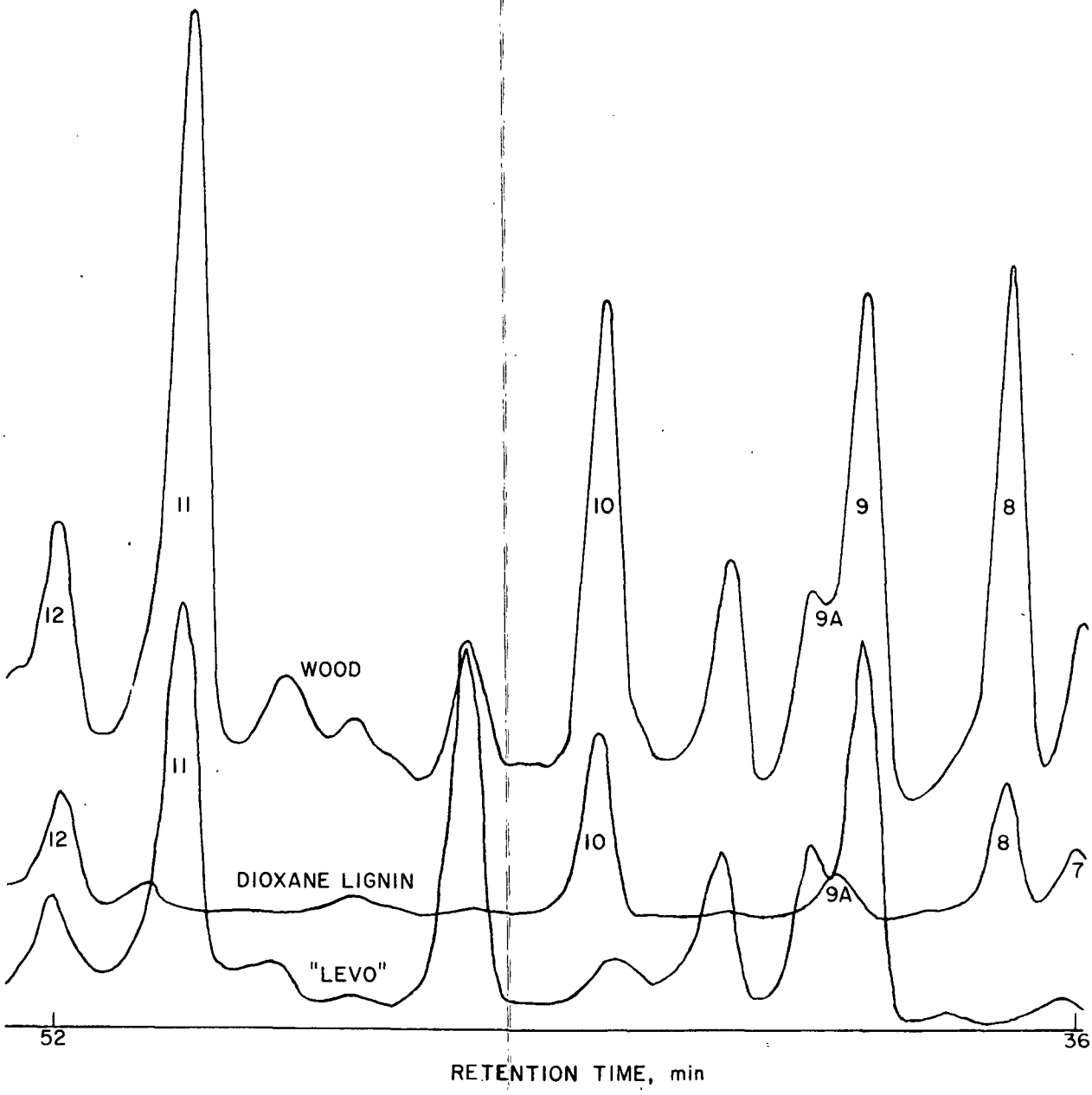


Figure 19. Comparison of Three Pyrograms from Wood, Dioxane Lignin and Levoglucosan from 36 to 52 Min

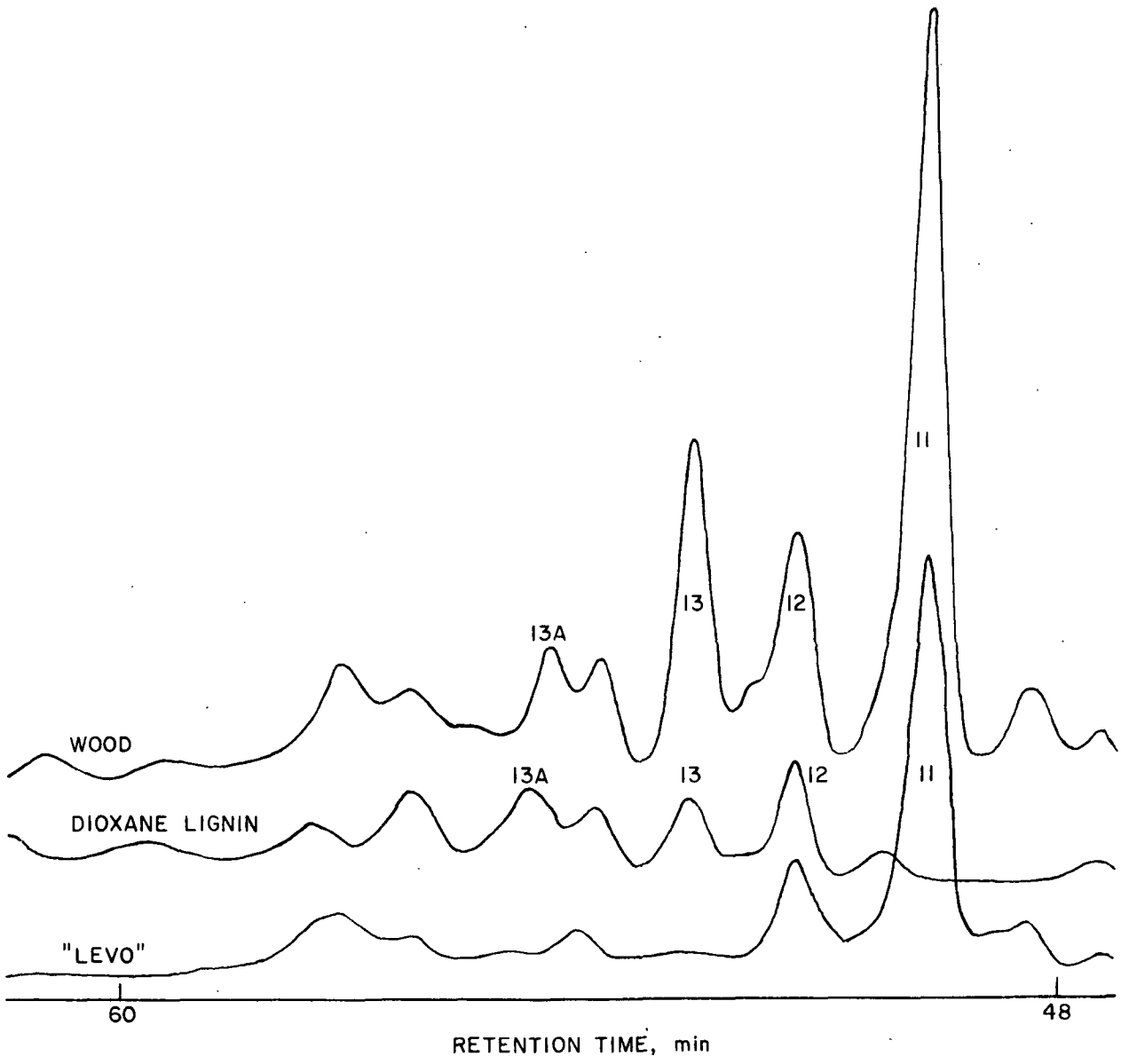


Figure 20. Comparison of Three Pyrograms from Wood, Dioxane Lignin and Levoglucosan from 48 to 60 Min

that came off the column at maximum temperature and guaiacol as mentioned above. Vanillin, homovanillin, and vanillyl methyl ketone have retention times which closely coincide with the end (maximum temperature) of the GC column oven temperature pyrogram. At this point the carbohydrate background bleed was at its highest. The contamination of these three peaks did not appear to be significant. There is evidence, however, that acetovanillone may partially comprise the vanillyl methyl ketone peak. The mass spectrum of vanillyl methyl ketone (Appendix VIII, Table XXXIII, 99.98% wood) contains certain ions (m/e 166, 151) characteristic of acetovanillone. The two compounds have similar GLC retention times.

SOLUBLE PERACETIC ACID LIGNIN

Lignin solubilized by the reaction of PAA (PAA lignin) with loblolly pine was obtained from Albrecht's work (6). Albrecht separated the PAA lignin on a GPC column and the various fractions were freeze-dried. The fractions used for this work were characterized by Albrecht (6) and are described in the Experimental section. Associated with the fractions (PAA lignin) was about 7% carbohydrate material, mainly arabinose and mannose. Figures 21 and 22 are pyrograms of PAA lignin recorded under different conditions and sensitivities. One of the major differences between the PAA lignin pyrogram (Fig. 22) and the dioxane lignin pyrogram (Fig. 23) is the greater ratio of gaseous products (short retention time products which are probably gases at 90°C) to other products in the PAA lignin pyrogram. This is shown in Table VI which contains the relative areas for both pyrograms. There appeared to be less char than for dioxane lignin indicating a less condensed structure. The guaiacol, vanillyl methyl ketone, and 2-furaldehyde peaks in the PAA lignin pyrogram were identified by MS (Table IV).

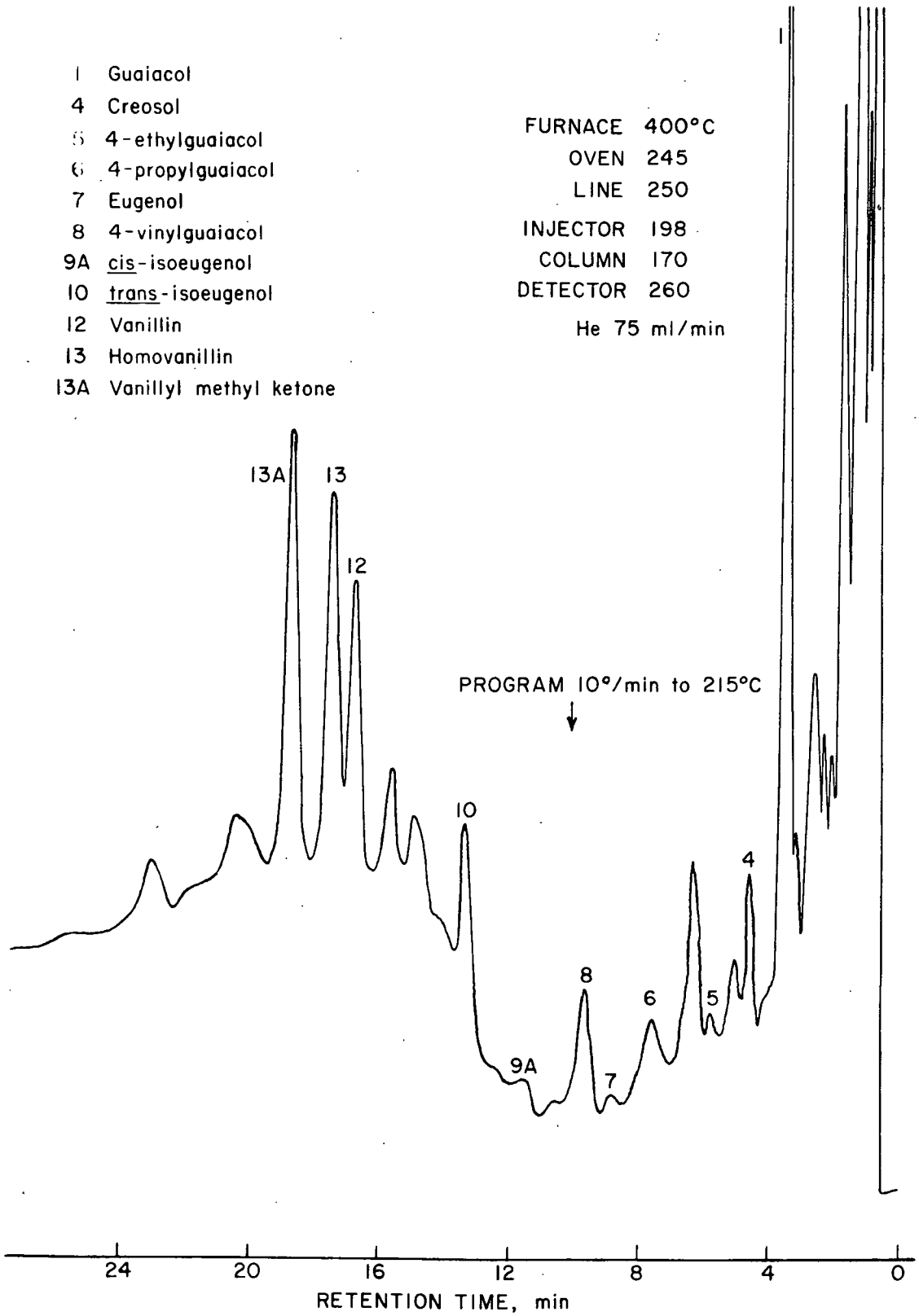


Figure 21. PAA Lignin Pyrogram, High Sensitivity

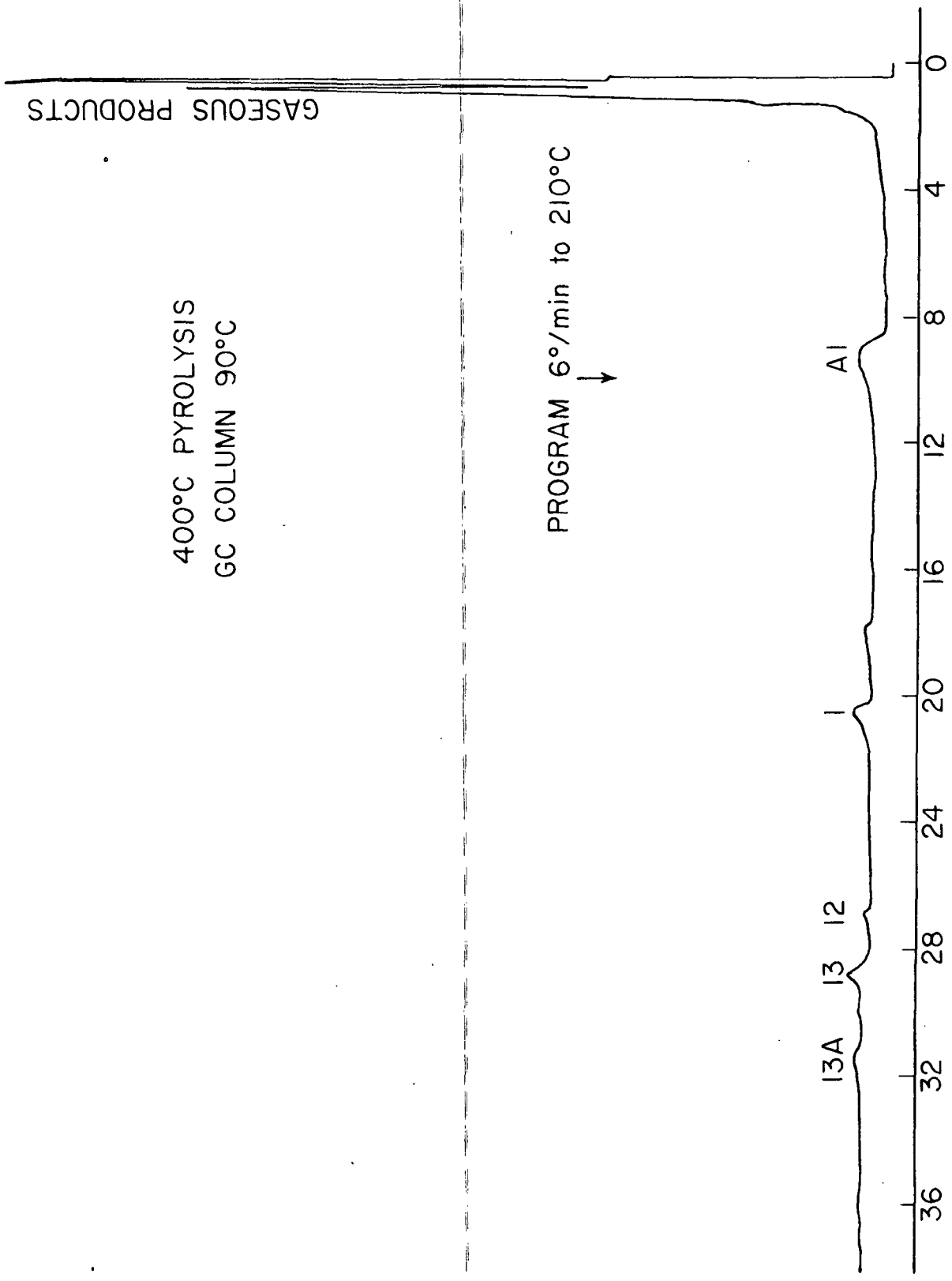


Figure 22. PAA Lignin Pyrogram, Low Sensitivity

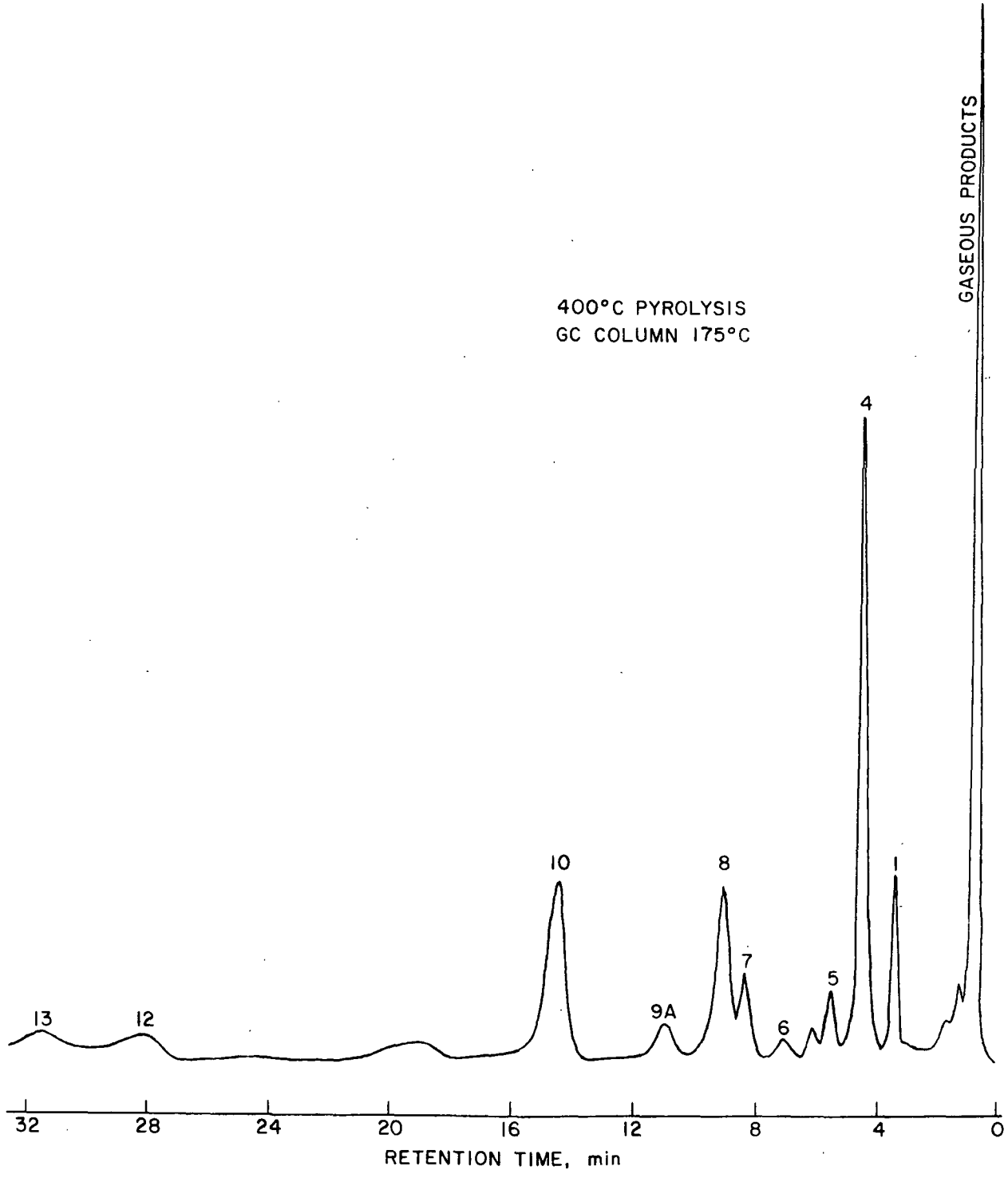


Figure 23. Dioxane Lignin Pyrogram

TABLE VI

RELATIVE PYROGRAM AREA COMPARISON

Total Area	Gaseous Products	All Other Peaks	Guaiacol	Creosol	Vanillin	Homo-vanillin	Vanillyl Methyl Ketone
			Dioxane lignin				
100	33	67	5(100)[a]	(238)	(64)	(62)	(50)
			PAA lignin				
100	90	10	4(100)	(9)	(45)	(57)	(64)

[a]Relative area calculated with guaiacol as base.

Vanillin and homovanillin, along with the other three compounds labelled in the PAA lignin pyrogram, were identified by GLC retention time.

The guaiacol peak makes up approximately the same relative portion of both the dioxane lignin and the PAA lignin pyrogram. The guaiacol, vanillin, homovanillin, and vanillyl methyl ketone peaks persist through PAA treatment and are the four main lignin peaks in the PAA lignin pyrogram. The structures which lead to these compounds on pyrolysis must be relatively stable to PAA. The other guaiacyl systems are almost completely absent from the PAA lignin pyrogram indicating a selective reaction(s) has occurred within the lignin structure.

Based on the model compound pyrolysis work presented earlier along with known PAA reactions, certain structural moieties for PAA solubilized lignin may be proposed and ethers eliminated. The carbonyl pyrolysis products (vanillin, homovanillin, and vanillyl methyl ketone) which persist through PAA treatment may come from structures having combinations of α and/or β-carbonyls, hydroxyls and ethers. Vanillin would not be produced from an α-aryl ether system as proposed in Fig. 24.

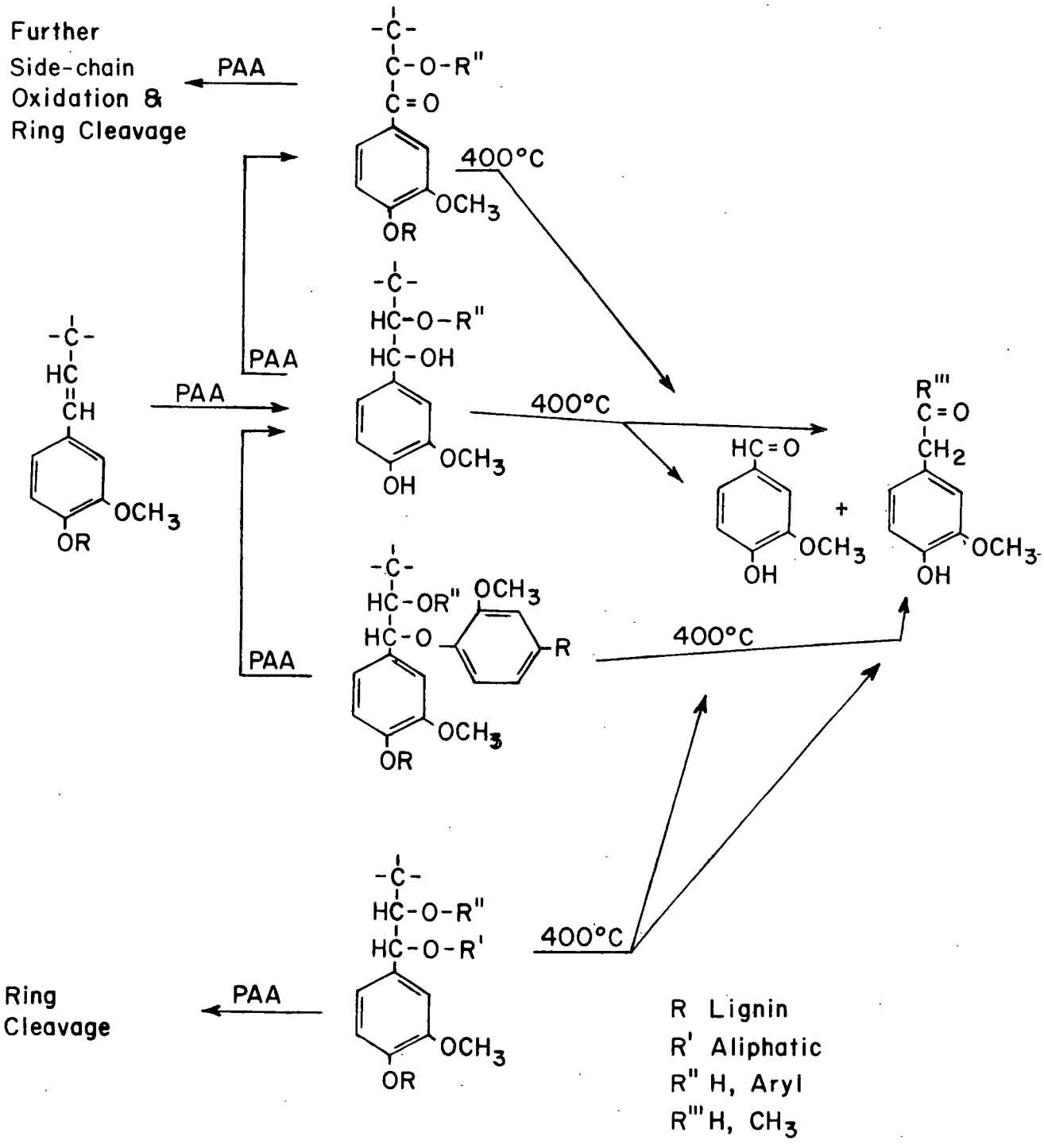


Figure 24. Interpretation of Carbonyl Pyrolysis Products from Lignin and PAA Lignin

However, β-aryl ethers as well as β-hydroxyls could be present prior to β-carbonyl formation (during pyrolysis) as shown in Fig. 15 and 24. The α-aryl ether structure was not considered a source of α-carbonyl products since the pyrolysis work on the aryl ether model compounds (Fig. 8 and 9) indicated aryl ether pyrolysis generates a phenolic compound but not a carbonyl on the side chain unless the propenyl ether is formed and hydrolyzed (Fig. 15). The α-hydroxyl and α-carbonyl structures were shown to give carbonyl compounds on pyrolysis (Fig. 7-9). These structures would, however, be expected to be diminished in PAA lignin due to their reactivity with PAA (99, 100,107-114).

α-Aryl ether cleavage (99,100,109) and attack on propenyl-type side chains (110) as shown in Fig. 24 would result in α-hydroxyl formation followed by α-carbonyl formation. The α-hydroxyls and α-carbonyls are apparently removed by further reaction. Albrecht (6) found that most of the α-carbonyls had been removed in soluble PAA lignin. Ishikawa, et al. (111) demonstrated that apocynol (1-guaiacyl ethanol) and acetovanillone have comparable half-lives of approximately 0.8 and 2.5 hr, respectively, in 3% PAA at 35°C. Acetovanillone is generated from PAA oxidation of apocynol and reaches a maximum concentration after 1-1/2 hr. This model compound work indicates that if Albrecht (6) found most of the α-carbonyls removed from PAA lignin it is very likely that most of the α-hydroxyls were also removed.

The only other possible structure that would yield α and β-carbonyls on pyrolysis is the α-aliphatic ether. The proposed aliphatic ether linkage may be either a lignin-to-lignin bond such as in pinoresinol or a lignin-to-carbohydrate bond such as proposed in the lignin structure in Fig. 2, unit 13. The pinoresinol structure would not be expected to be present to any

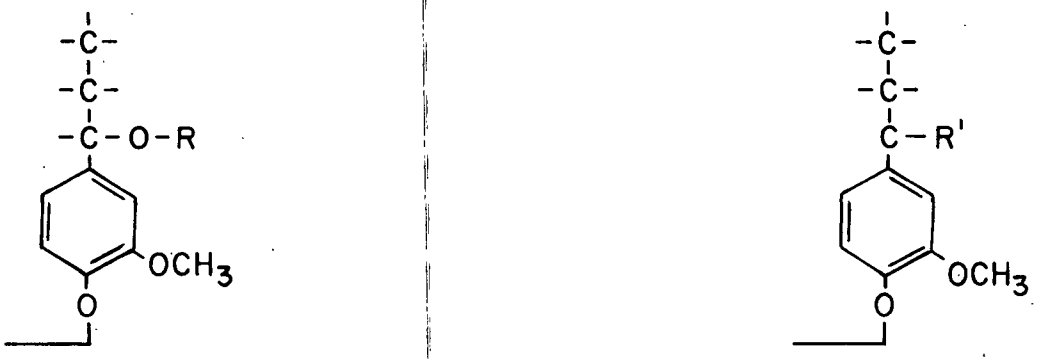
great extent in the PAA lignin since the compound yields relatively high proportions of creosol on pyrolysis and the PAA lignin does not. Based on the lignin structure put forth by Freudenberg, et al. (71-73) in Fig. 2, a significant amount of the PAA lignin structure which yields carbonyls on pyrolysis is proposed to contain a benzyl carbohydrate ether bond. This is the only structure which would be relatively stable to PAA but yield mostly carbonyl structures on pyrolysis. Albrecht (6) has shown by direct sugar analysis that the carbohydrate content in the PAA lignin is significant (7%).

The presence of guaiacol with little or no creosol in the PAA lignin pyrogram excluded most of the model compound structures. Only conidendrin and diisoeugenol produced large amounts of guaiacol on pyrolysis without yielding any creosol. The main contributing factor in yielding guaiacol without creosol is considered to be the phenyl α-carbon bond. A number of phenyl α-carbon linkages are proposed in Freudenberg's lignin structure, and these bonds would be expected to be relatively stable to PAA. There does not appear to be any other structure present in the proposed lignin structure that would yield guaiacol and not creosol. Oxidation of the "propane" side chain at the α-carbon by PAA would be detected in the pyrogram as a product other than guaiacol, such as vanillin or vanillic acid. Both vanillin and vanillic acid are relatively stable to pyrolysis. These structures would not account for the guaiacol found in the PAA lignin pyrogram. The PAA stable portion of a proposed PAA-oxidized lignin structure is represented in Fig. 25.

Carbohydrates

Arabinose and mannose both yield 2-furaldehyde when pyrolyzed. All of the 2-furaldehyde in the PAA lignin pyrogram can be accounted for as a

pyrolysis product of the carbohydrate present. Weighed samples of arabinose and PAA lignin were pyrolyzed individually, and both yielded amounts of 2-furaldehyde in equal proportion to the carbohydrate present. Formation of 2-furaldehyde from the pyrolysis of pentoses and hexoses has been established by other researchers (115-120) and is not considered to be a rearranged lactone from a muconic acid.



R = Carbohydrate

R' = Phenylpropane unit (carbon-to-carbon linkage)

Figure 25. Proposed PAA Stable Structural Moieties in Lignin

Muconic Acids

Besides the gaseous products in the PAA lignin pyrogram only 2-furaldehyde, guaiacol, and vanillyl methyl ketone were in large enough amounts to obtain mass spectra. The compounds in the gaseous products probably consist of less than 5-carbon atoms, such as carbon dioxide, methane, carbon monoxide, ethane, acetone and methanol (57). They were not investigated because their structures would not greatly aid in establishing structural units within PAA lignin. No muconic acid pyrolysis products could be detected by MS or by comparison of retention times to probable muconic acid pyrolysis products. It is possible that either there are no muconic acid structures present or they are present

in too low a concentration. If muconic acids are present, their structures may be greatly varied (lactones, isomeric acids) and pyrolysis of these structures would undoubtedly create several compounds from each structure as was seen with cis,trans-β-methylmuconic acid (Fig. 11). Generation of new compounds on pyrolysis may effectively reduce the concentration of any muconic acid pyrolysis product in the PAA lignin pyrogram to below detectable limits.

Artifacts

The later PAA lignin fractions from gel permeation chromatography (GPC, see Experimental section and Appendix II), which could not be freeze-dried (6), were investigated to determine if muconic acids were present. There was no difference in the chromatograms whether the sample was pyrolyzed or injected into the GC as shown in Appendix II. This indicated that nearly all of the material was relatively volatile. Acetic acid, crotonic acid, and 3-hydroxybutyric acid were positively identified from the PAA lignin fractions that could not be freeze-dried. Crotonic acid and 3-hydroxybutyric acid were identified by their mass spectra, NMR, and IR. Acrylic acid was also suspected to be present based on its mass spectrum. 3-Hydroxybutyric acid was shown to be an artifact presumably arising from aldol condensation of the acetaldehyde which is used to quench the PAA. Addition of acetaldehyde to a solution of PAA was shown to produce a significant amount of 3-hydroxybutyric acid. Crotonic acid could be a fragment from muconic acid but is considered to be a dehydration product of 3-hydroxybutyric acid. A muconic acid fragment of such a low molecular weight would not be expected to be detected without detection of other muconic acid structures, such as maleic or oxalic acid as found in other studies (121).

PERACETIC ACID WOOD

PAA-treated wood was investigated by PGC to determine the effect of PAA. Acetone-extracted loblolly pine was designated as 100% yield wood. Yield levels were corrected based on reaction time (Appendix VI). The pyrograms represented in Fig. 26-28 are of various yield levels of PAA-treated loblolly pine. The pyrograms show a decreasing trend in the lignin peaks (identified in Table IV) with decreasing yield. There also appears to be a dramatic change in the carbohydrate peaks. The more pronounced changes for both appear to occur at the high yield level. The wood pyrograms show no new peaks as a result of PAA oxidation. It is not surprising that new peaks are absent in the pyrogram of PAA-treated wood since they are also absent in the PAA lignin pyrogram. Persistence of guaiacol, vanillin, homovanillin, and vanillyl methyl ketone peaks would be expected on the basis of the PAA treatment relative to the other lignin peaks even to the 77% yield level.

THERMAL DEGRADATION IN TOLUENE

Since the flash pyrolysis technique used in this study did not produce the anticipated muconic acids, another technique was investigated following recent Russian work (85,122). PAA-treated wood and model compounds were heated in toluene for 25 minutes at 315°C in sealed glass tubes. No new products were found by GC as compared to the flash pyrolysis pyrograms of the same materials. Some shift in product distribution was noted. This was attributed to the long time at temperature which probably promoted degradation of the less stable compounds. A further discussion is presented in Appendix VII.

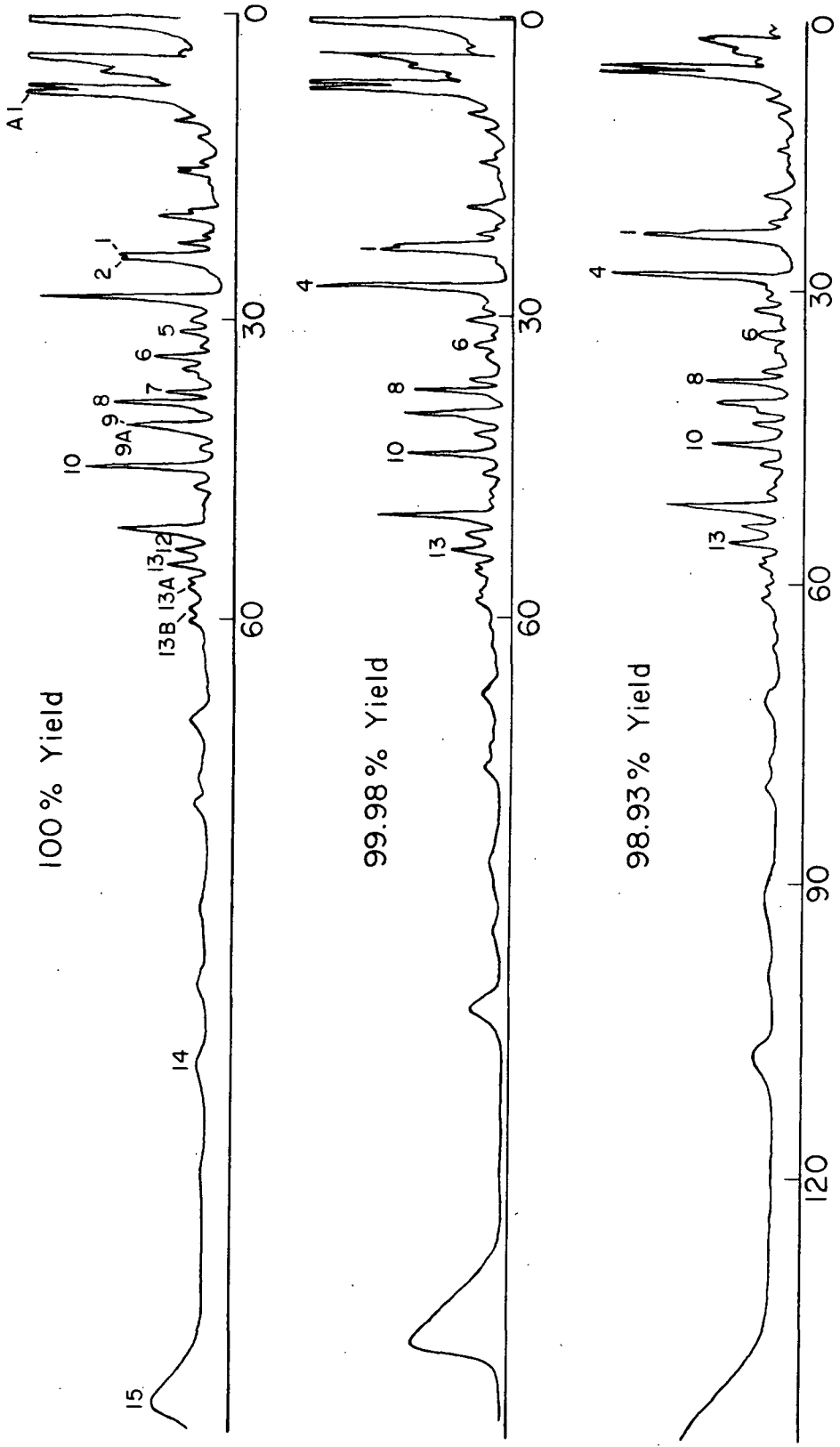


Figure 26. 100% Yield and PAA-Treated Loblolly Pine Pyrograms

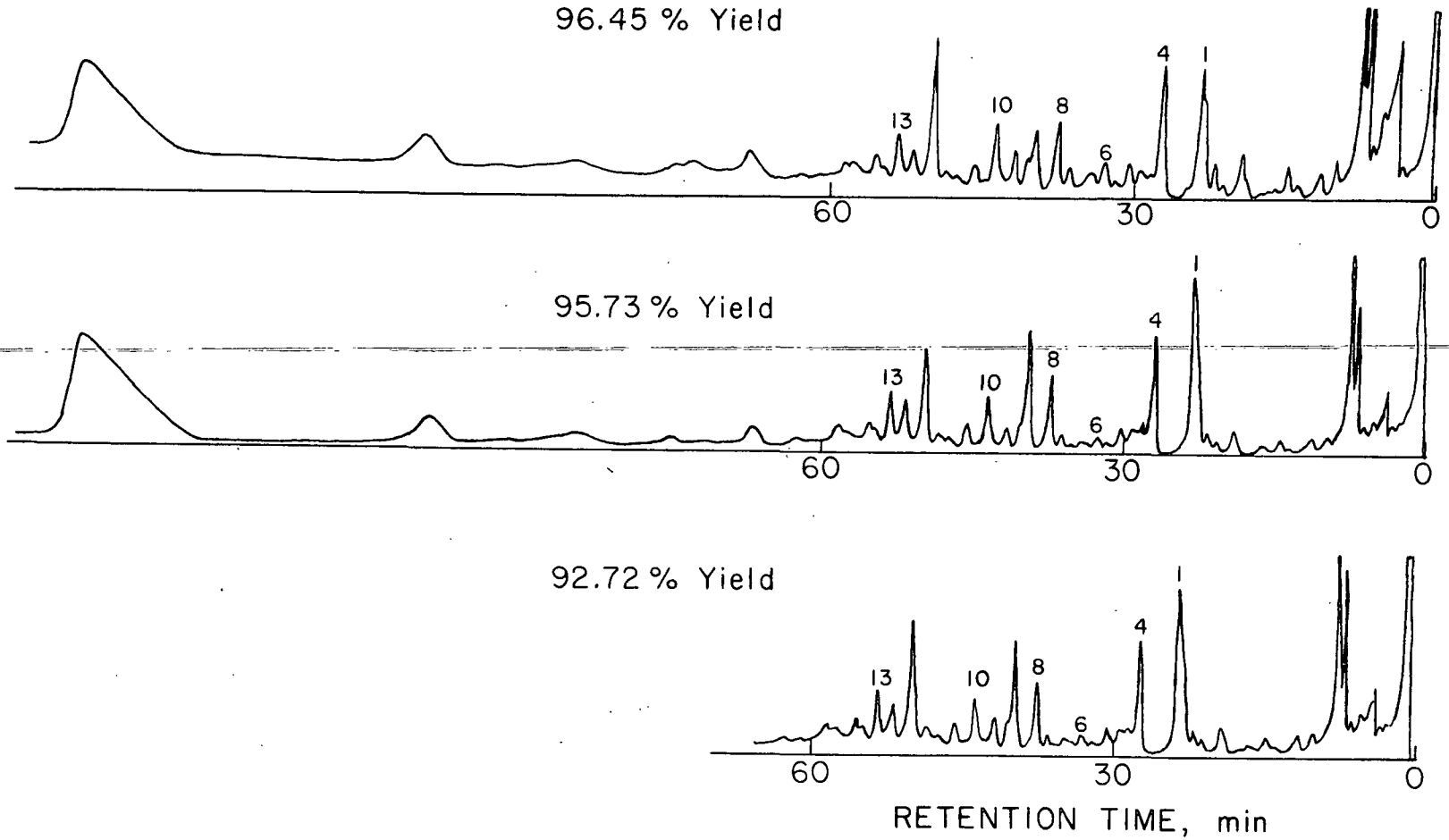


Figure 27. PAA-Treated Loblolly Pine Pyrograms

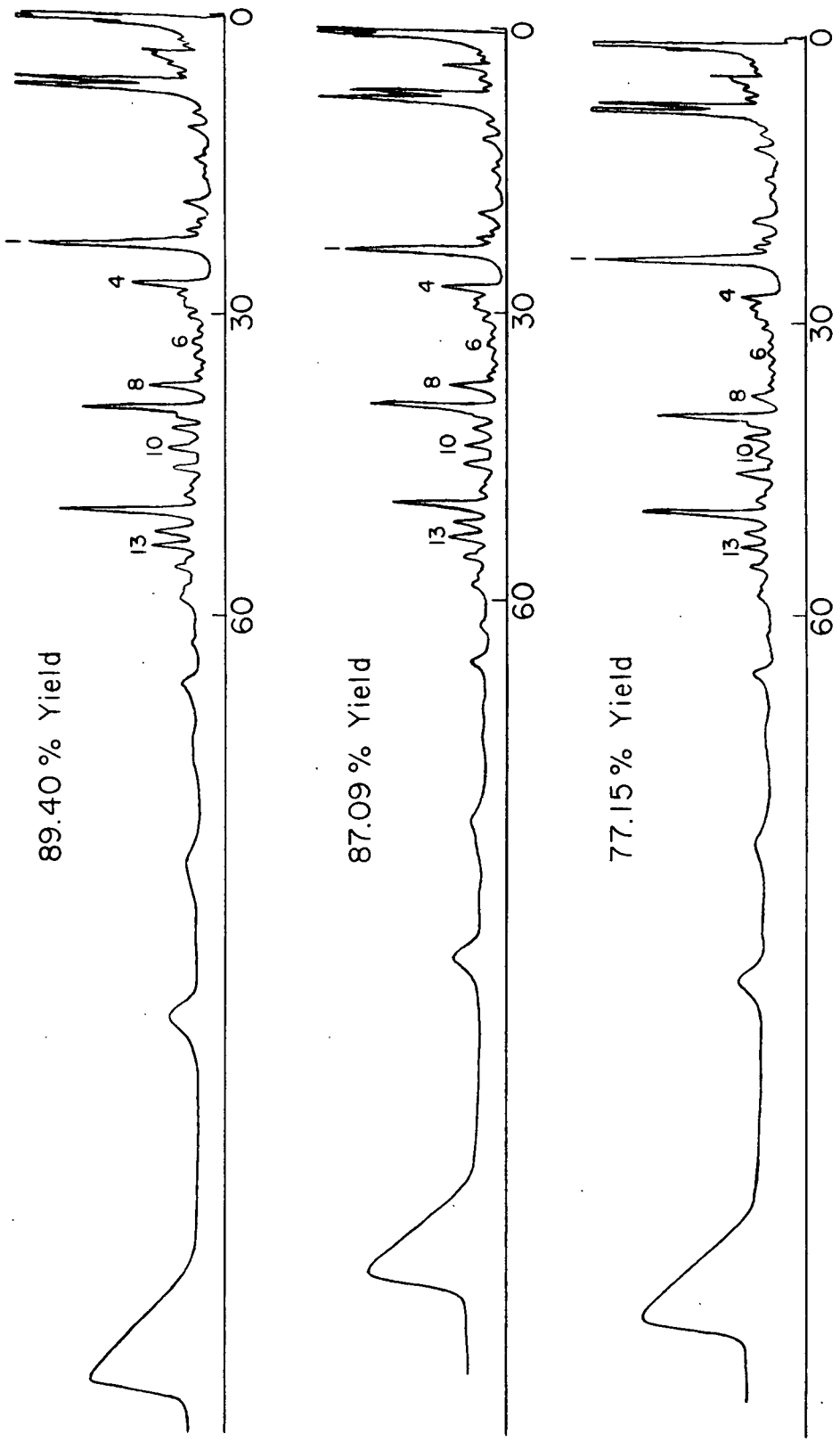


Figure 28. PAA-Treated Loblolly Pine Pyrogram

DETERMINATION OF PERACETIC ACID REACTIVITY WITH LIGNIN BY PYROLYSIS-GAS CHROMATOGRAPHY

ESTABLISHING THE IDENTITY OF WOOD PYROGRAM PEAKS

As shown previously in Fig. 17-20 the lignin peaks in the wood pyrogram had retention times very similar to the peaks in the dioxane lignin pyrogram. In addition, all the peaks were identified by MS. Table VII lists all the loblolly pine and PAA loblolly pine pyrogram peaks analyzed by MS. To be certain each peak contained mainly the compound indicated, each mass spectrum was compared to the spectrum of an authentic sample for extraneous ions.

TABLE VII

PGCMS OF LOBLOLLY PINE AND PAA LOBLOLLY PINE

GC Peak	Loblolly Pine[a]	77.2% Yield Loblolly Pine
Guaiacol	124[b]	124
Carbohydrate 1	128	ND[c]
Creosol	138	138
4-Ethylguaiacol	152	NH[d]
4-Propylguaiacol	166	NH
Eugenol	164	NH
4-Vinylguaiacol	150	NH
Carbohydrate 2	116	NH
cis-Isoeugenol	164	NH
trans-Isoeugenol	164	NH
Carbohydrate 3 (HMF)	126	126
Vanillin	152	152
Homovanillin	166	166
Vanillyl methyl ketone	180[e]	180

[a] PGCMS analysis run on 100 and 99.98% yield wood.

[b] Apparent molecular weight based on the mass spectrum for that peak.

[c] Present in the pyrogram but not analyzed by MS (ND).

[d] Not present in high enough concentration for MS analysis (NH).

[e] This peak may also contain acetovanillone.

The carbohydrate 1 mass spectrum indicates some contamination of guaiacol which is closely associated with it in the pyrogram (Fig. 26). Since the carbohydrate 1 peak is at a longer retention time than guaiacol, guaiacol probably tails into the carbohydrate 1 peak. The peak labeled as carbohydrate 2 appears to contain a great deal of cis-isoeugenol. The vanillin and homovanillin mass spectra show a few extraneous ions which probably arise from carbohydrate bleed. Vanillin and homovanillin come off the column near the end of the column oven temperature program, and the background bleed is greatest at this point. The peak area measurements for vanillin and homovanillin are not considered to be in error since the base line is adjusted for background bleed. As shown in Table VII only a few of the lignin peaks at the 77% yield level were present in high enough concentration to be identified.

The lignin peaks in the wood pyrograms are dependent on the relative thermal stability of the various types of structures present in lignin. Certain bonds are more easily broken than others. Pyrolysis may free or volatilize a relatively stable fragment such as an aromatic ring moiety. As was pointed out previously, only guaiacyl derivatives have been identified from lignin and from PAA-oxidized lignin. Aromatic ring cleavage products if present in PAA-oxidized lignin apparently can only be indirectly determined by the disappearance of aromatic compounds from the pyrogram and perhaps by the appearance of more gaseous products.

The proposed muconic acid products in PAA-oxidized lignin may be distributed among many isomers and derivatives due to pyrolysis as was found for the model compounds in Fig. 12. Although the PGC analysis cannot adequately detect all of the PAA lignin present in wood, it can detect the guaiacyl

moieties which have not been oxidized by ring cleavage. The relatively large amounts of guaiacol, vanillin, homovanillin, and vanillyl methyl ketone in PAA lignin pyrograms represent structures, such as those proposed in Fig. 25, which are relatively less reactive to PAA. Figures 29-31 are plots of the combined nine lignin peak areas versus yield over different yield ranges investigated in this work from PAA reacted loblolly pine (see Fig. 26). These plots describe the loss of guaiacyl moieties from the wood by both oxidation and solubilization.

TRENDS IN PERACETIC ACID-TREATED WOOD PYROGRAMS

PAA-treated loblolly pinewood wafers from yield levels ranging from 100.0 to 77.2% were pyrolyzed. Some of the representative pyrograms are included in Fig. 26-28. A regression analysis of individual and summed peaks (area/mg of wood) versus percentage yield of wood was run. The data analysis is explained in Appendix IV. Figures 29-31 are a result of such an analysis of all 9 lignin peaks summed together.

The least-squares line for the lignin peaks was calculated on the logarithm transform of the area, $\ln(\text{area}) = C + B(\text{yield})$. The logarithm transform was found to best describe the lignin peaks. Linear scale plots were obtained by taking the inverse-transform of the least-squares line. Figure 32 contains the regression lines for such a linear plot of all the individual lignin peaks. The first 1.4% loss of the wood by PAA action was analyzed separately from the next 22% loss of the wood, for better definition of the initial delignification process. Figures 33 and 34 represent the two separate regions.

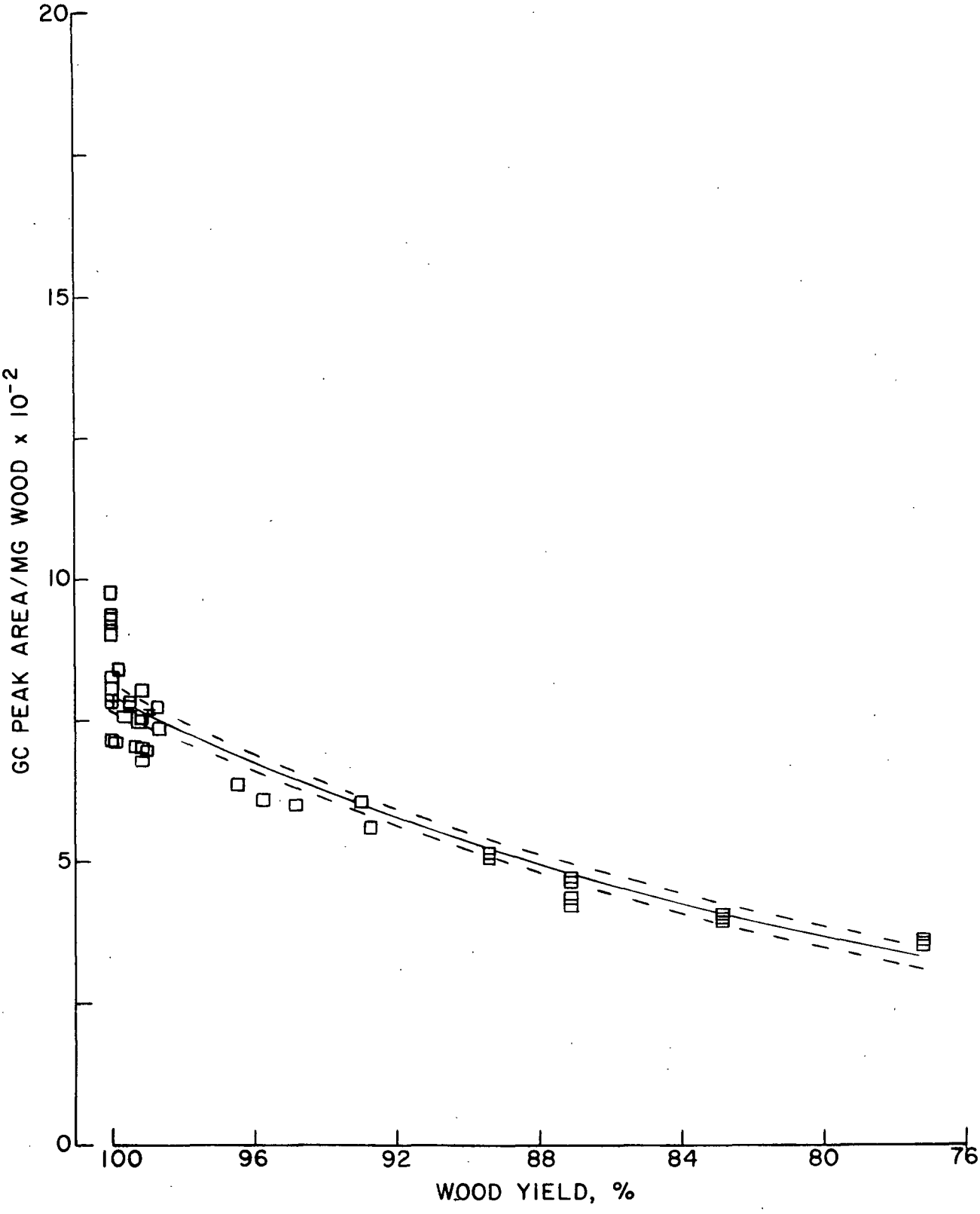


Figure 29. Lignin Peak Areas from Pyrograms of PAA Wood, 100-77.2% Yield

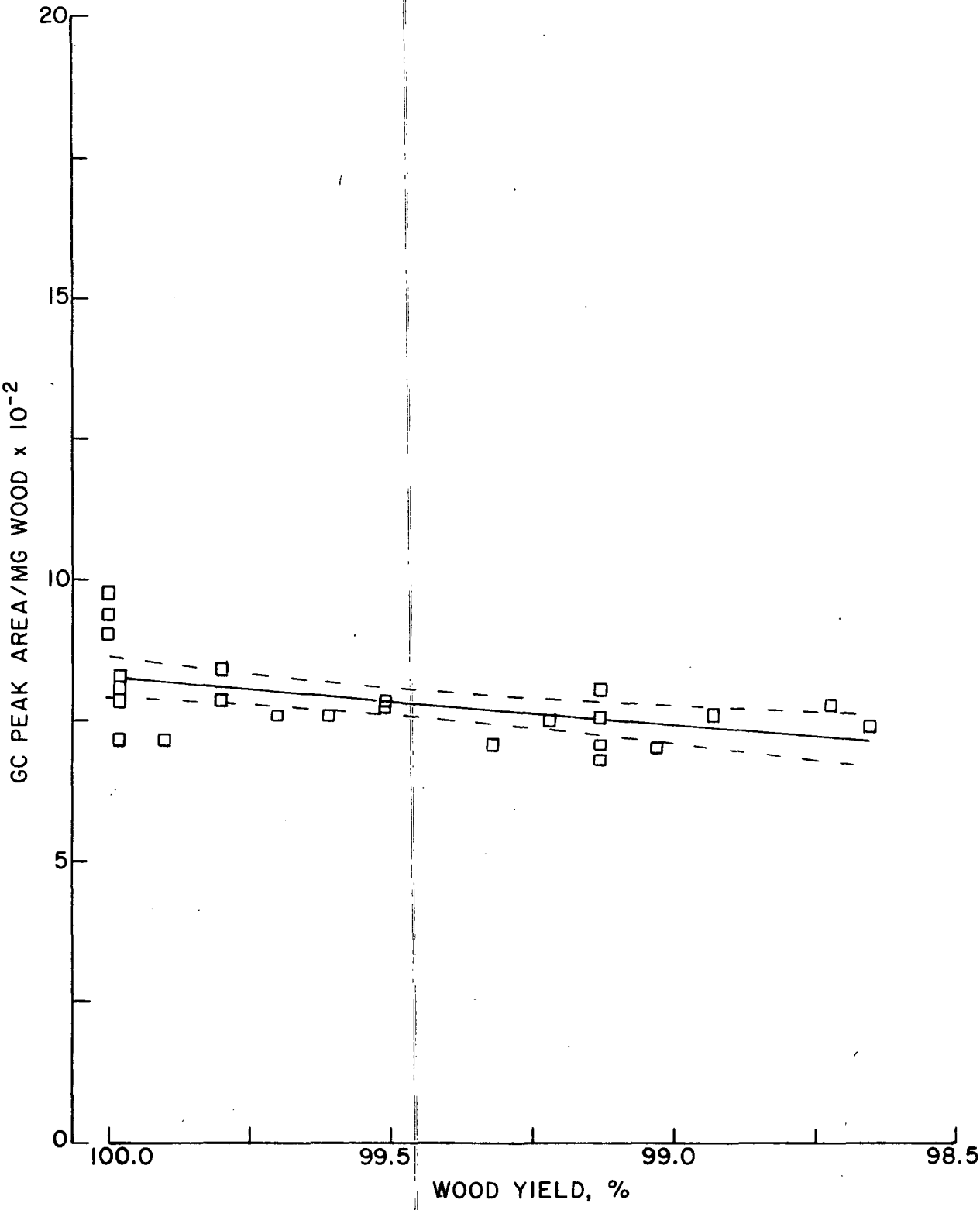


Figure 30. Lignin Peak Areas from Pyrograms of PAA Wood, 100-98.6% Yield

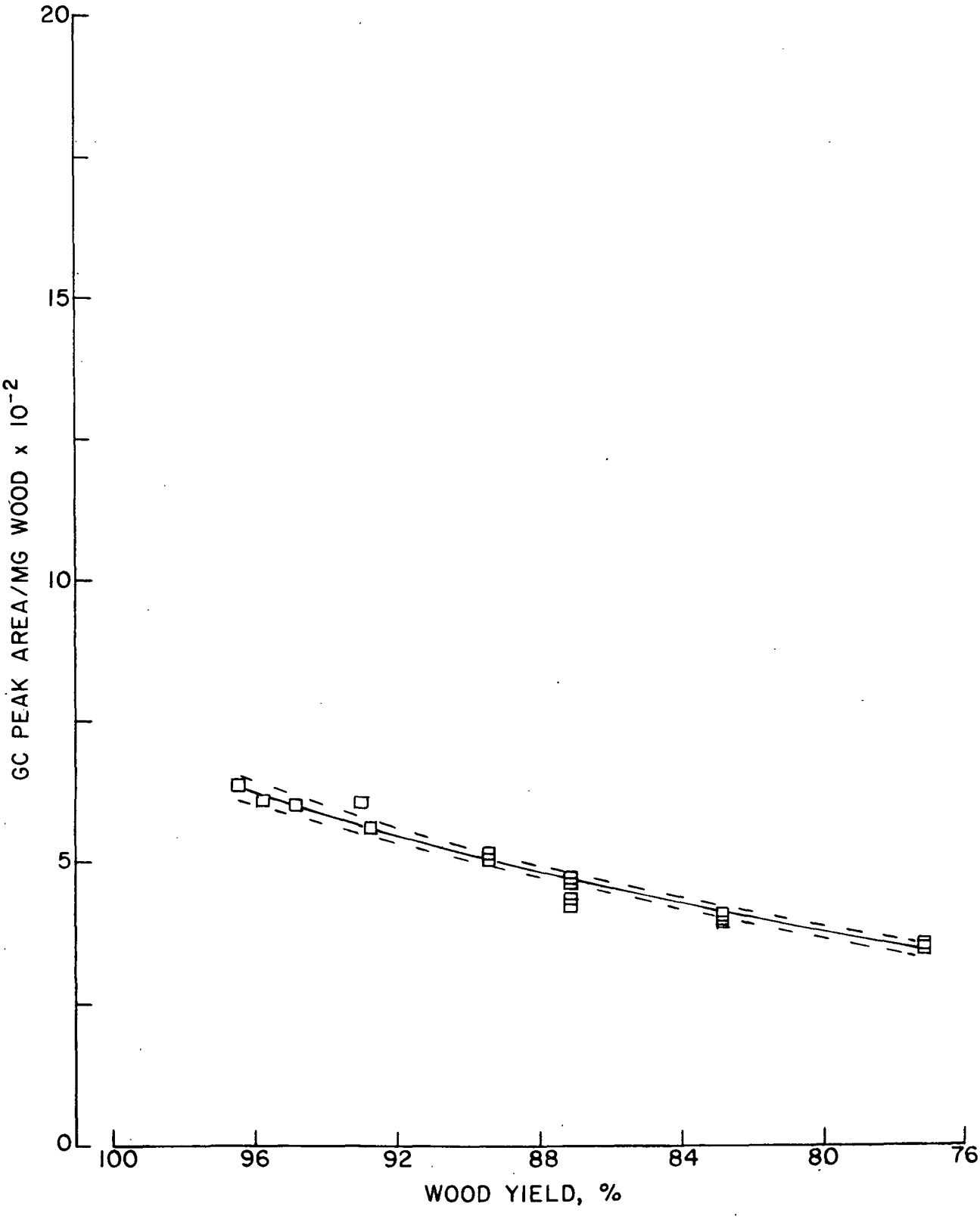


Figure 31. Lignin Peak Areas from Pyrograms of PAA Wood, 96.5-77.2% Yield

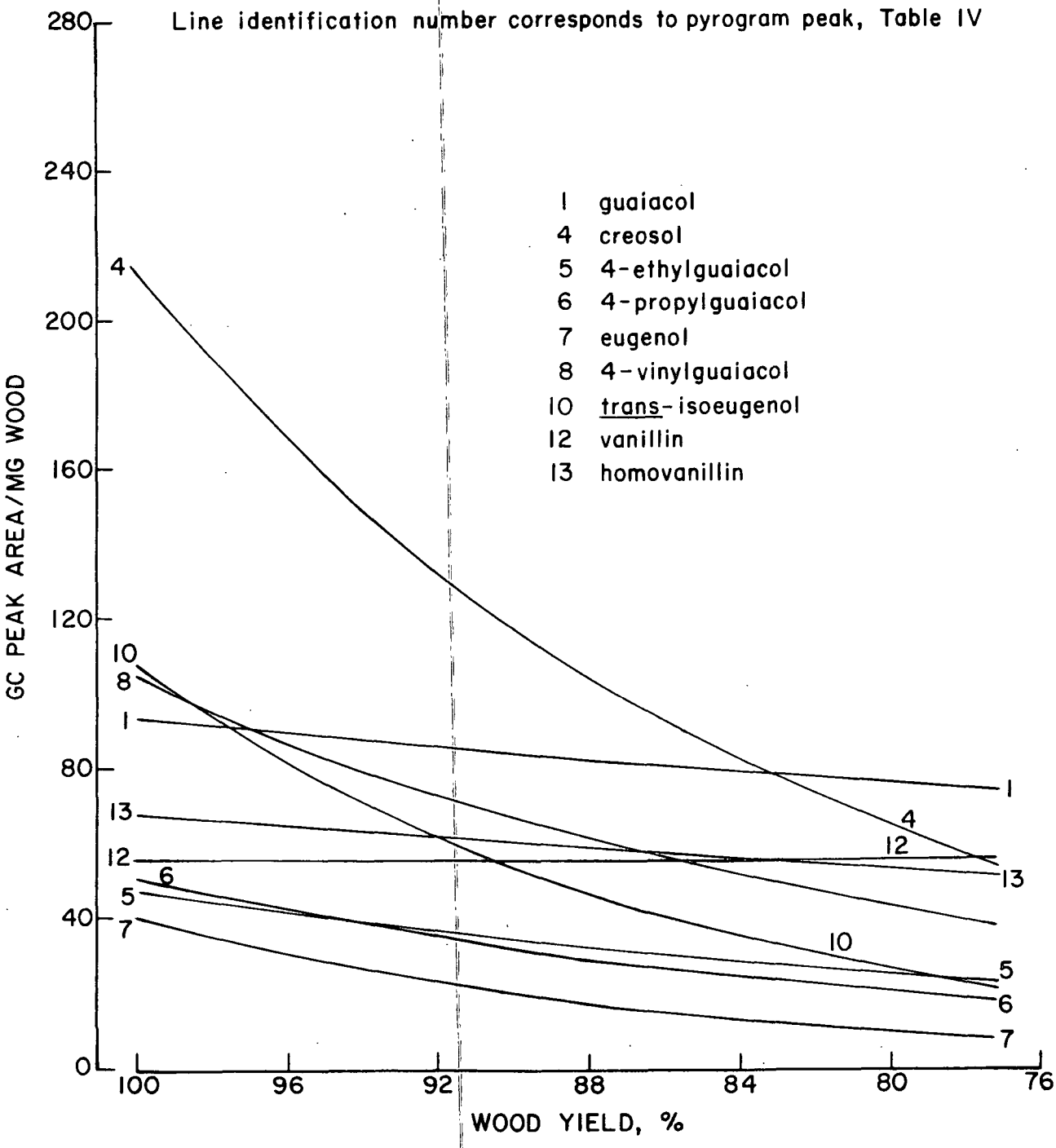


Figure 32. Inverse-Transform of the Least-Squares Line, ln(area) = $\underline{C}$ + $\underline{B}$(yield), for Lignin Peak Areas, 100.0-77.2% Yield

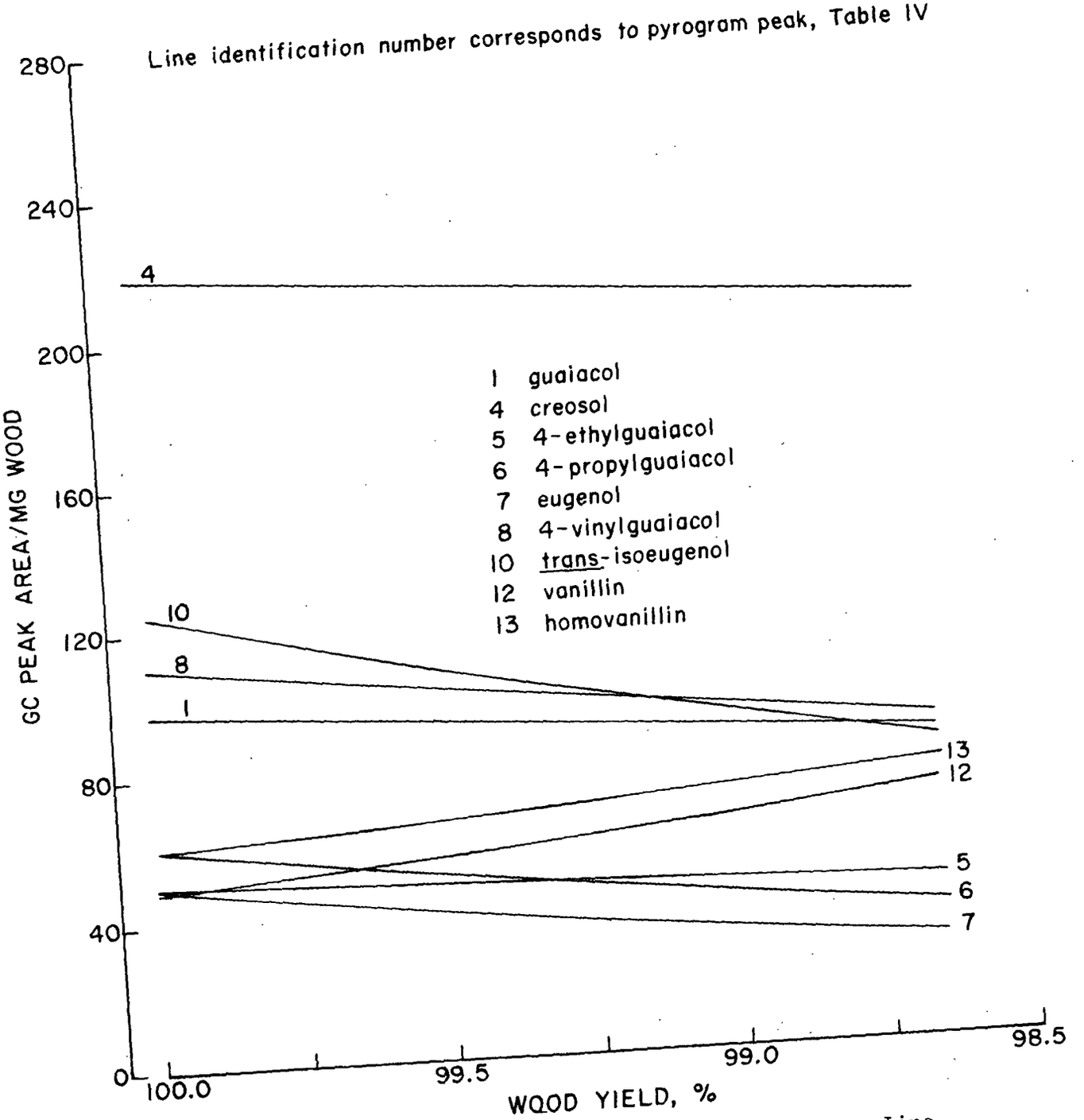


Figure 33. Inverse-Transform of the Least-Squares Line, $\ln(\text{area}) = C + B(\text{yield})$, for Lignin Peak Areas, 100.0-98.7% Yield

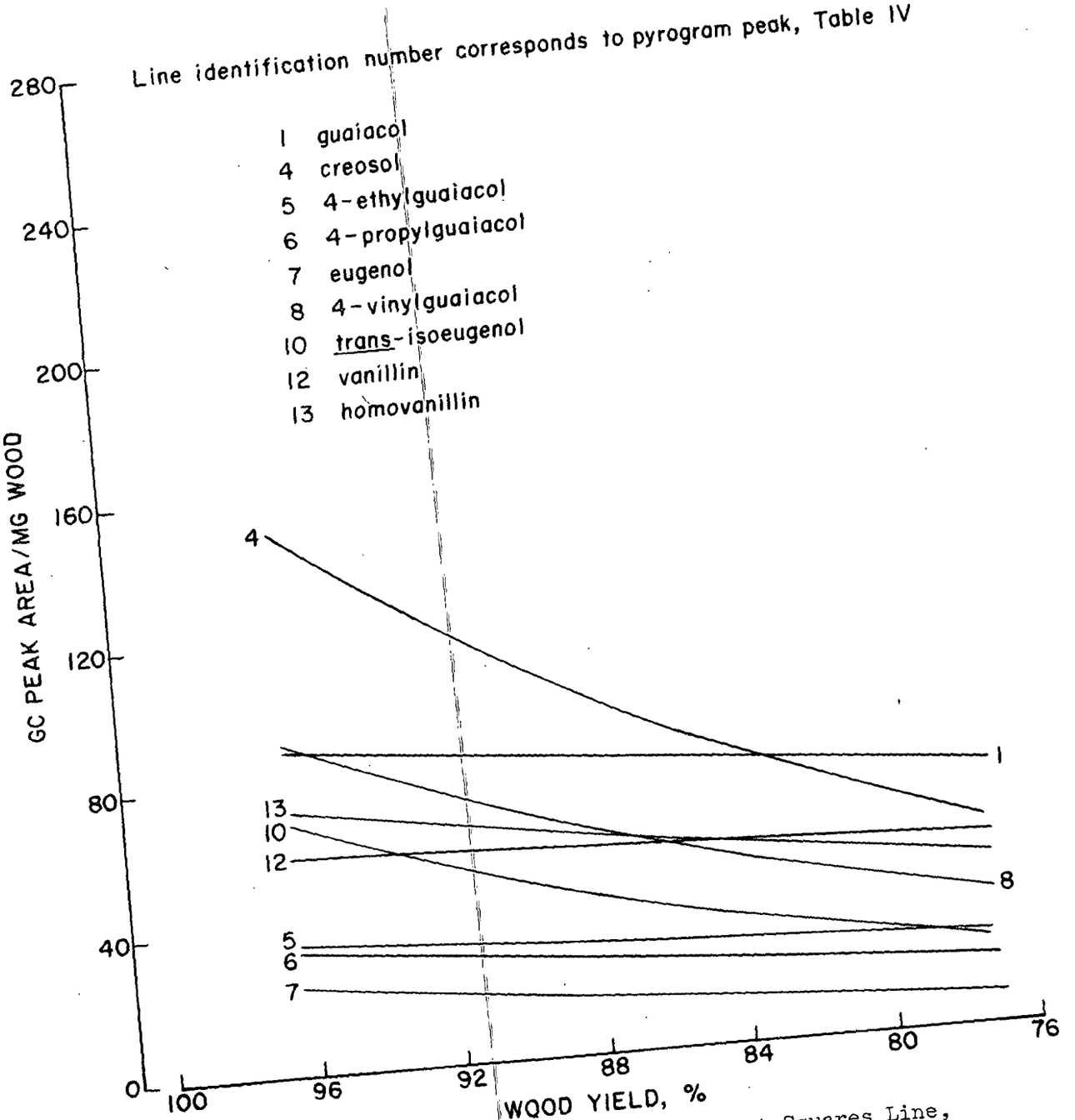


Figure 34. Inverse-Transform of the Least-Squares Line, $\ln(\text{area}) = \underline{C} + \underline{B}(\text{yield})$, for Lignin Peak Areas, 96.5-77.2% Yield

It is evident from these plots that certain lignin peaks disappear at a greater rate than other lignin peaks and during the first 1.4% loss of the wood most of the rates are highest. During the first 1% loss of the wood the lignin compounds with a 3-carbon side chain (4-propylguaiacol, eugenol, and trans-isoeugenol) disappear at the greatest rate. The compounds with a 2-carbon side chain (4-ethylguaiacol and 4-vinylguaiacol) disappear at a slower rate than the 3-carbon side-chain compounds but at a faster rate than for the 1-carbon side-chain compound (creosol). The vanillin and homovanillin peaks (carbonyl compounds) appear to be in a group by themselves and actually show a slight increase during the first 1.4% loss of the wood. This was interpreted as PAA cleavage of α-aryl ethers and attack on propenyl-type side chains (Fig. 24) as discussed earlier.

A summary of these plots is presented in Fig. 35-38 and in Table VIII. The group analyses were handled as for all nine lignin peaks in Fig. 29, summing the peak areas in each pyrogram and handling the sum as a single peak. The total area for all 9 lignin peaks at 100% yield (approximately 5.5 $in.^2$) corresponds to approximately 3% of the wood pyrolyzed.

Figure 38 shows that initially (100-98.6% yield) the longer the side chain the faster the disappearance. Throughout most of the reaction (96.5-77.2% yield) with PAA there is little difference in the rate of disappearance. This difference is interpreted as a major reaction occurring on the phenylpropane side chain during the first 1.4% loss of the wood. If most of the PAA oxidation were ring cleavage of the guaiacyl nucleus, the rate of disappearance for all compounds would be expected to be nearly the same during the majority of the reaction period (96.5-77.2% yield).

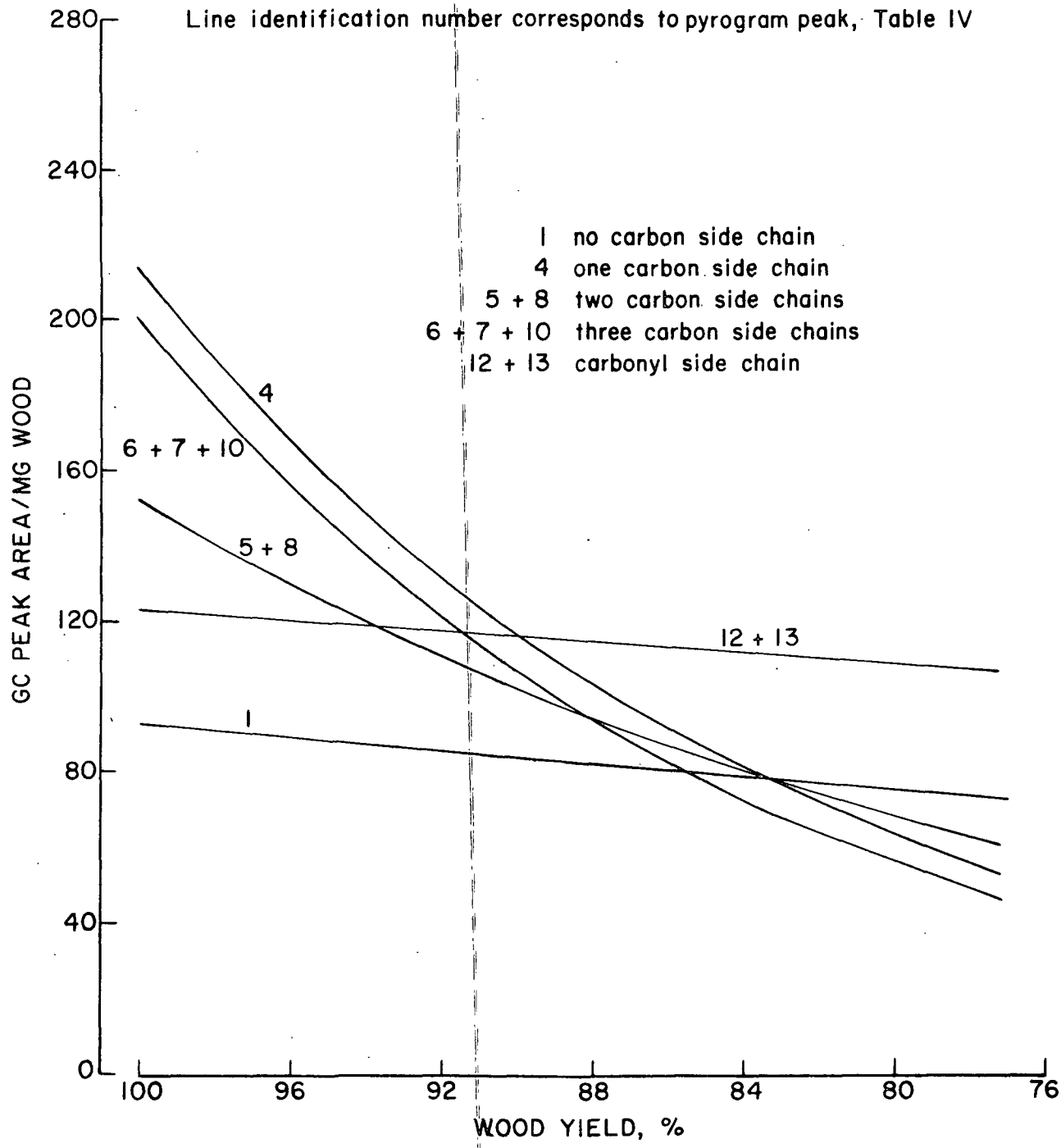


Figure 35. Inverse-Transform of the Least-Squares Line, $\ln(\text{area}) = \underline{C} + \underline{B}(\text{yield})$, for Combined Lignin Peak Areas, 100.0-77.2% Yield

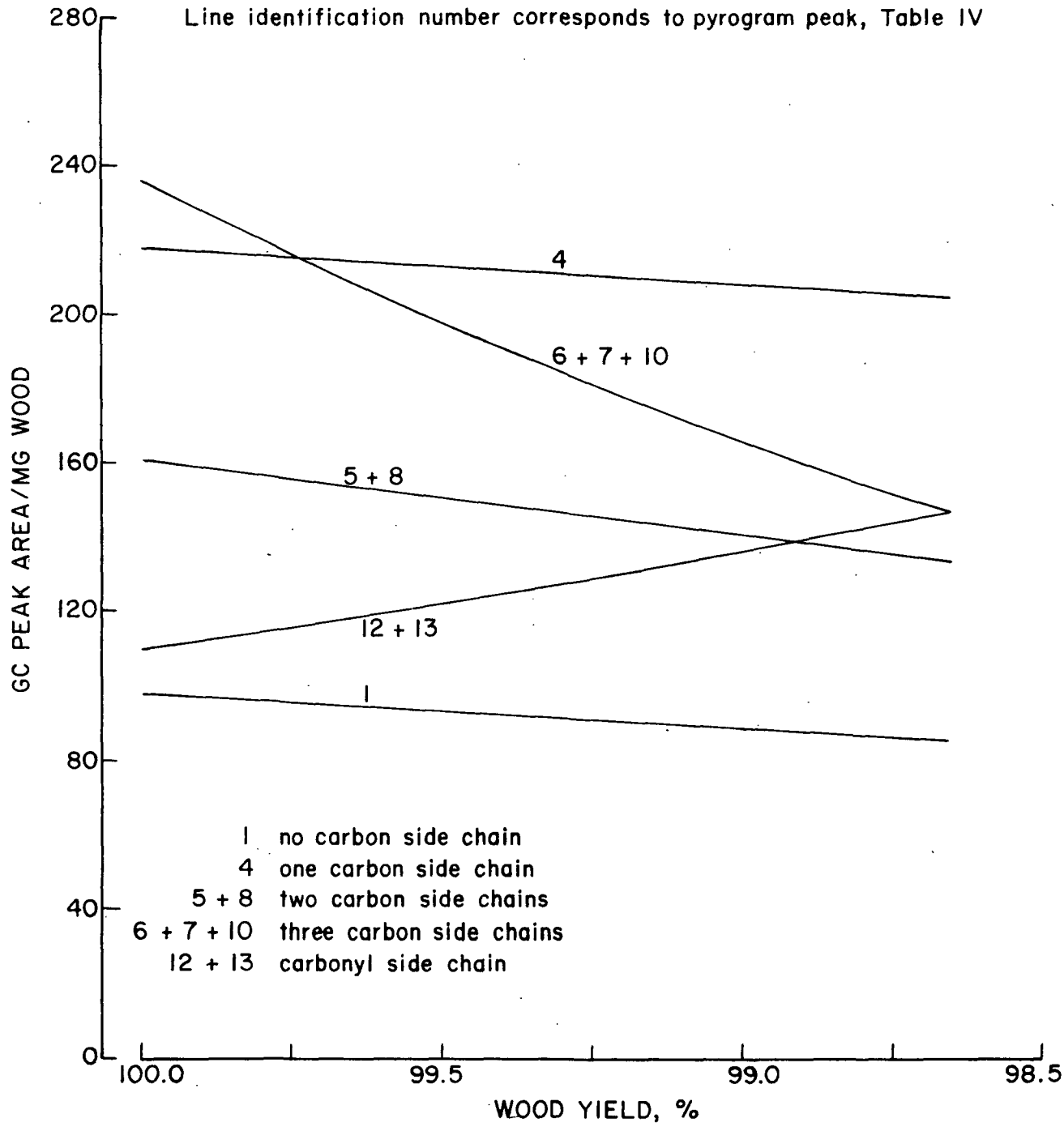


Figure 36. Inverse-Transform of the Least-Squares Line, $\ln(\text{area}) = \underline{C} + \underline{B}(\text{yield})$, for Combined Lignin Peak Areas, 100.0-98.7% Yield

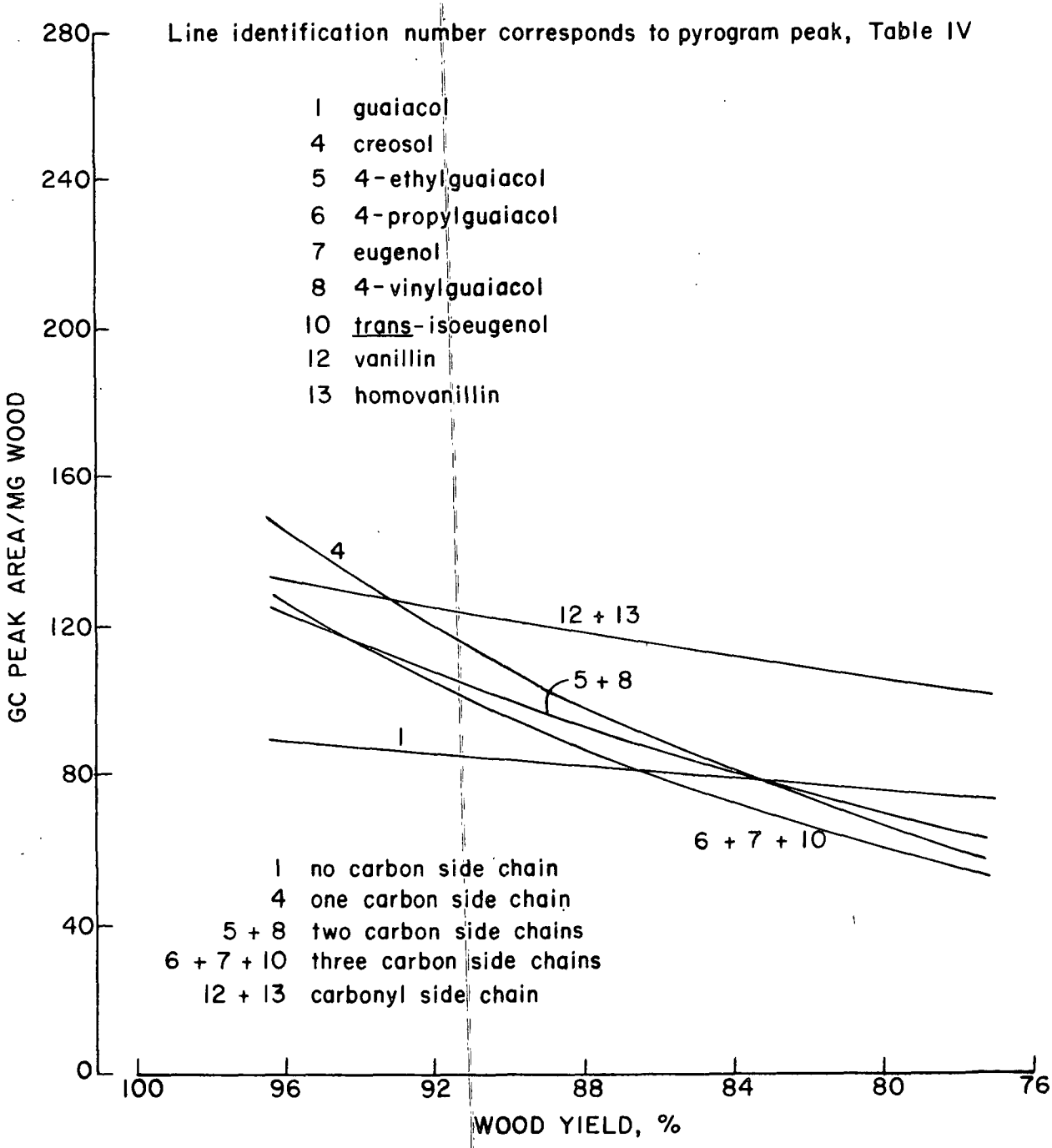


Figure 37. Inverse-Transform of the Least-Squares Line, $\ln(\text{area}) = \underline{C} + \underline{B}(\text{yield})$, for Combined Lignin Peak Areas, 96.5-77.2% Yield

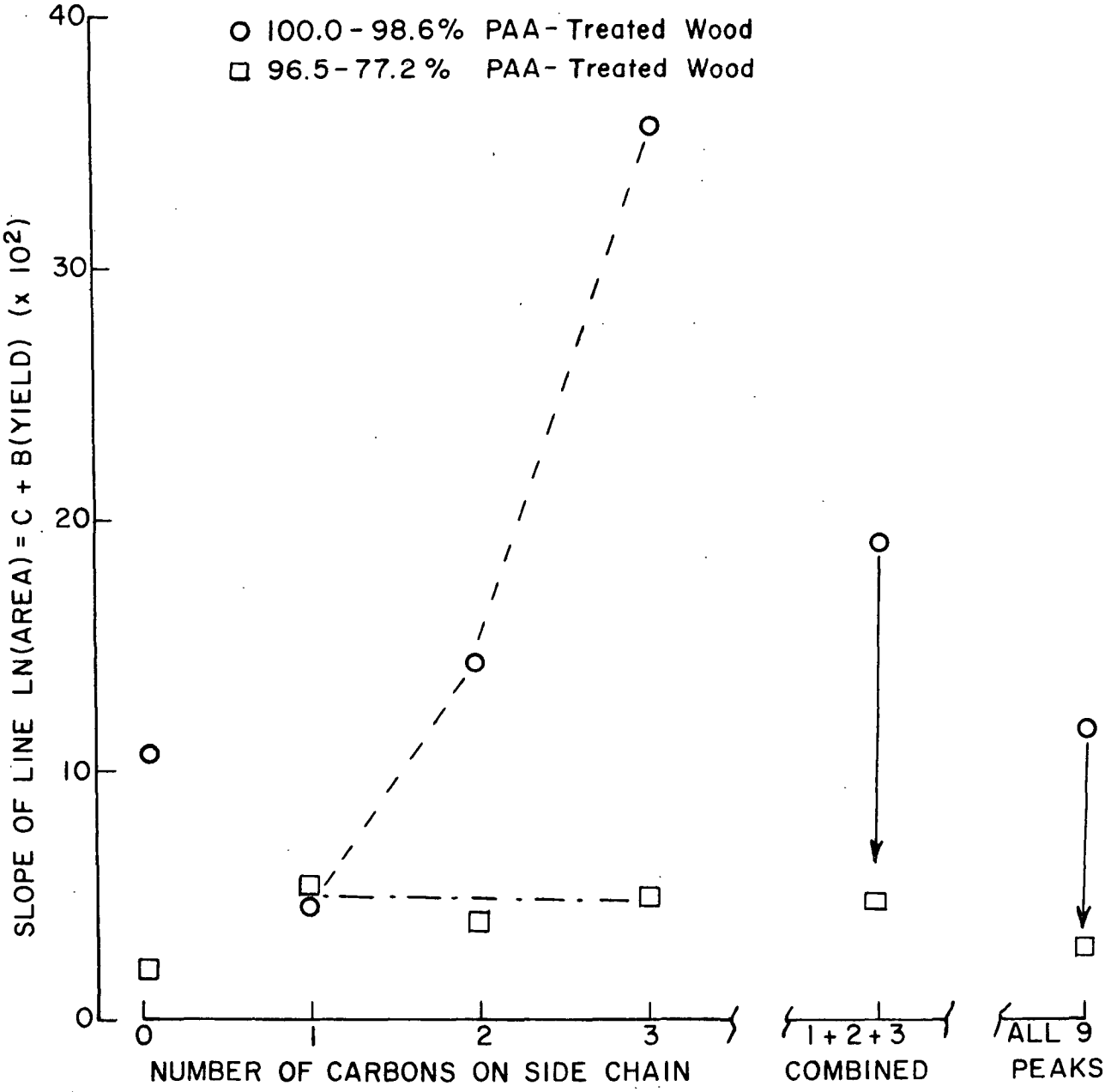


Figure 38. Slopes of the Least-Squares Line, ln(area) = C + B(yield), for Lignin Pyrogram Peaks

TABLE VIII

SLOPES OF THE LEAST-SQUARES LINE

$\ln(\text{area}) = \underline{C} + \underline{B}(\text{yield})$

PAA Wood Pyrogram Peak	Side Chain	100-98.0% Yield ($\times 10^{-2}$)	96.5-77.2% Yield ($\times 10^{-2}$)
Guaiacol	0	10.5	1.0
Creosol	1	4.6	5.1
4-Ethylguaiacol	2	8.9	1.8
4-Vinylguaiacol	2	16.7	4.7
4-Propylguaiacol	3	37.6	3.0
Eugenol	3	43.1	5.1
trans-Isoeugenol	3	31.5	5.7
Vanillin	Carbonyl	-27.0	0.6
Homovanillin	Carbonyl	-17.6	2.3
	Summary		
Guaiacol	0	10.5	1.0
Creosol	1	4.6	5.1
2-Carbon	2	14.0	3.7
3-Carbon	3	35.6	4.8
Carbonyl	Carbonyl	-22.0	1.5
1+2+3 Carbon	1,2+3	18.7	4.5
All 9	all	11.4	3.2

The slow disappearance of guaiacol, vanillin, and homovanillin indicate that their pyrolysis precursors are relatively unreactive to PAA. Some hydroxyl groups may be generated initially by aryl ether cleavage and attack on propenyl-type (such as coniferaldehyde types) side chains to increase the amounts of carbonyl pyrolysis products. At the 77% yield level after 10.5 hr of PAA (initially 3.0%) at 60°C it is likely that the carbonyl pyrolysis products represent only unreactive α-aliphatic ethers. This is in agreement with conclusions reached earlier on PAA solubilized lignin (Fig. 25). The slow disappearance compared to the other compounds can be readily seen in Fig. 32-37.

INITIAL PERACETIC ACID REACTION WITH WOOD

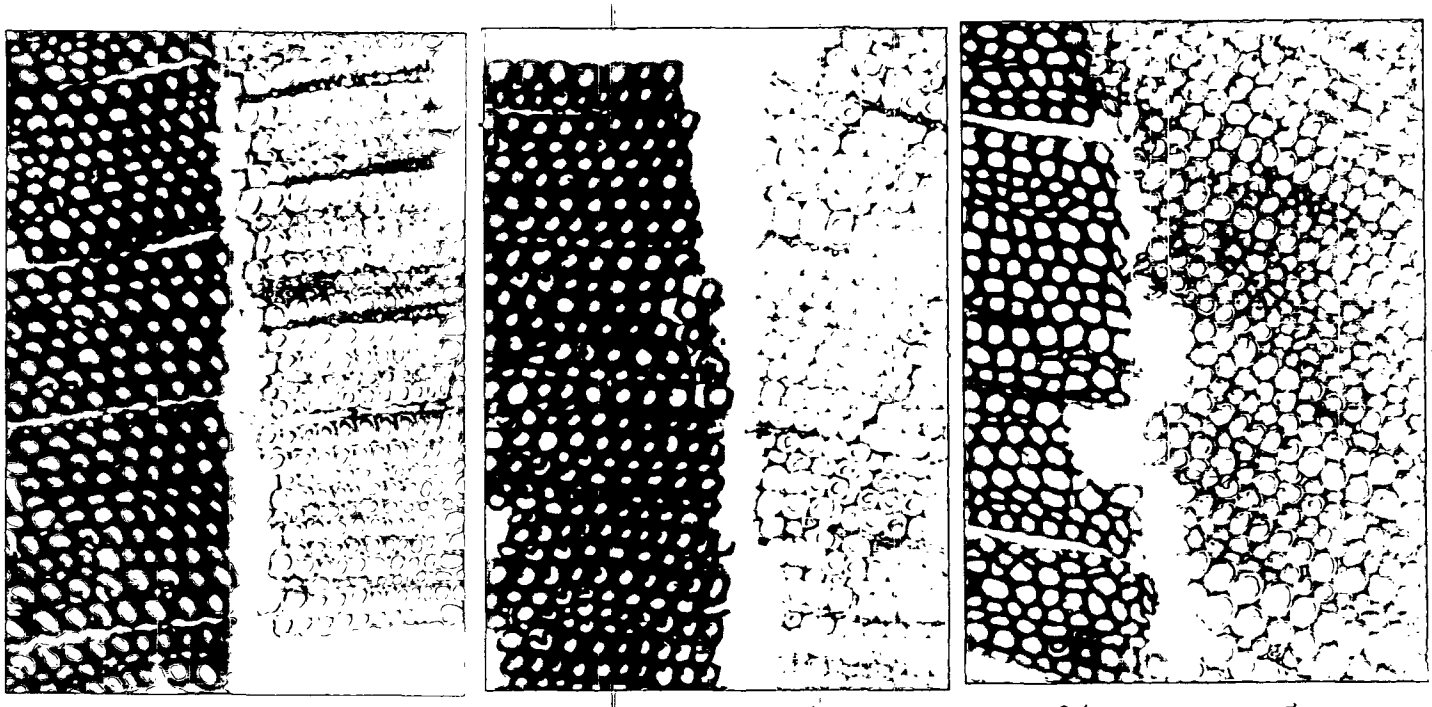
The selective reactivity of lignin moieties investigated by PGC is probably due to highly reactive structures or catalysis of PAA reactions. The faster initial PAA reaction as shown in Fig. 38 coincides with several other observations.

Reactive Structures

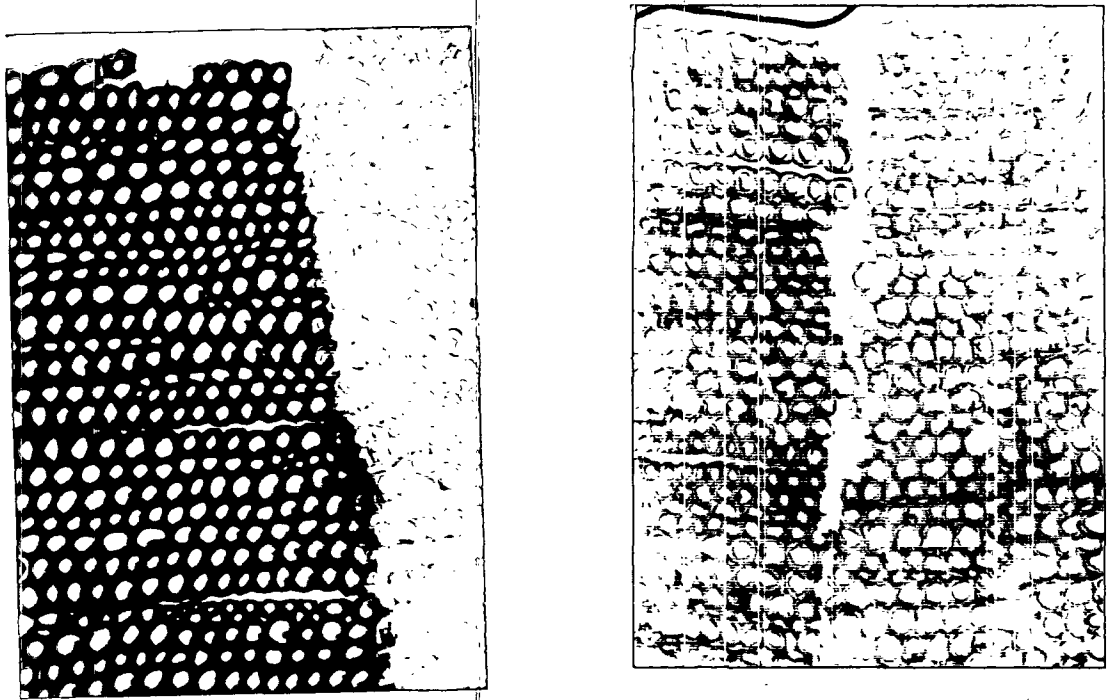
Baird (126) found that the warts (ligninlike material protruding on the lumen surface) are removed with PAA during the first 1% loss of loblolly pine. An attempt was made to document this further in this work. Warts were found only on a single fiber from the interior of the wood wafer at the 97% yield level while no warts were found in 99% yield level fiber. Only a half dozen photomicrographs were taken to investigate the warts, and it is not known whether the single appearance of warts is representative or not. It is assumed that the finding of warts at the 97% yield level is an isolated case due perhaps to aspirated pits and is not representative.

The phloroglucinol staining (selective lignin stain which reacts with coniferaldehyde-type side chains) of PAA-treated wood wafers is shown in Fig. 39. The phloroglucinol-stained specimens showed a marked decrease in stain intensity for the first 1% loss of the wood and a complete disappearance by the time the 96% yield level was reached.

Since the warts are the most accessible ligninlike material (126), it is likely that they are the first to react with PAA. The warts themselves may account for up to 1% of the cell-wall material (127,128) and therefore could account for a substantial part of the first 1% loss of the wood.



100.0% 99.13% (94 min, 50°C) 100.0% 99.03% (104 min, 50°C) 99.98% (4 min, 50°C) 99.22% (84 min, 50°C)



100.0% 97.29% (94 min, 60°C) 97.29% (94 min, 60°C) 96.95% (109 min, 60°C)

Figure 39. Cross Sections of Various Yield Wood Wafers Stained with Phloroglucinol (Time of PAA Reaction and Temperature)

The early disappearance of the phloroglucinol stain indicates that a specific reaction has occurred with PAA and lignin. The structure in lignin which produces the staining reaction has been modified or removed. Phloroglucinol is proposed to be specific for cinnamaldehyde structures in lignin. Table X in the Experimental section contains a number of materials which were tested for color reactions with phloroglucinol. All the aldehydes tested reacted with phloroglucinol, but only the aldehydes conjugated to a guaiacyl nucleus gave the characteristic red color. If the PAA reaction were mainly ring cleavage of the guaiacyl nucleus, the stain intensity would be expected to slowly dissipate until most of the lignin was removed or reacted. The rapid disappearance of the staining agrees with the previous conclusion that a major PAA reaction initially occurs with the phenylpropane side chain of lignin.

Peracetic Acid Catalysis

The presence of metal ions is known to decompose peroxides and catalyze reactions with them (129-136). Hydrogen peroxide is present in PAA in small amounts (6,8) and it is known to decompose in the presence of metals through a free radical mechanism (129,130). The decomposition of peracids including PAA has not been studied in as much detail as hydrogen peroxide. Whether PAA itself decomposes to form a free radical or perhaps a more reactive metal peroxide in the presence of the inorganic material in loblolly pine is not known for sure. There is some evidence that PAA may form a free radical due to metal ion catalysis (136).

The ash content of the loblolly pine studied was 0.22 to 0.23% ovendry basis, Appendix III. This level of ash was reduced to 0.02-0.06% after a short treatment with PAA. Acetic acid of the strength present in the PAA

solution only reduced the ash level to 0.10%. Apparently, PAA is essential in removal of part of the inorganic material. It is possible to speculate that initially there is a fast free radical reaction mechanism that is catalyzed by the inorganic material present in the wood. This could account for the more rapid reaction or disappearance of some lignin peaks during the initial stage of the PAA reaction.

The larger increase in area (area/mg more than doubles) for the levoglucosan peak (Fig. 40 and 41) is apparently due to the loss of inorganic materials. It is possible that the inorganic material acts like a flame retardant and promotes the destruction of the levoglucosan ring structure (42,84,102,103,106,137-139). When the inorganic material is removed by the PAA solution, less levoglucosan is destroyed during pyrolysis and an increase in area is recorded for the levoglucosan peak.

To investigate if the removal of inorganic material had an effect on the lignin pyrolysis products, pyrograms were compared from 100% yield, 100% yield acetic acid extracted (to remove the inorganic material), 99.98% yield, and 99.98% yield with 0.22% ash added to loblolly pinewood. The results are presented in Table XVIII in Appendix III. The removal of the inorganic materials from the unreacted wood (100% yield) with acetic acid had no effect on the lignin peak areas. The addition of ash back into the wood also did not affect the lignin peak areas. These findings are in agreement with those of Ripley and Fung (42) and Tang (139). Lignin pyrolysis is affected little and pyrolysis products are not increased by the addition of cellulose flame retardants.

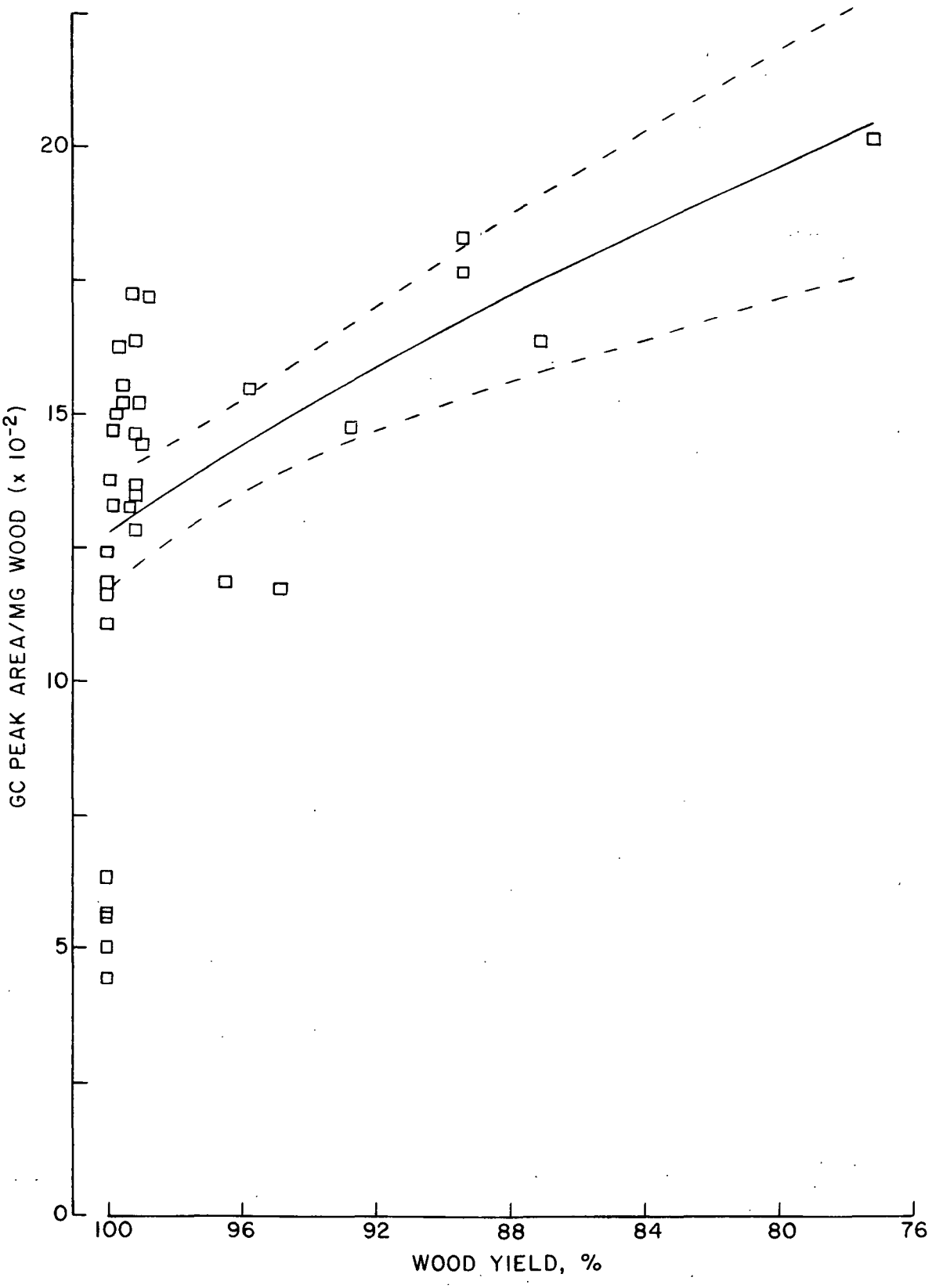


Figure 40. Levoglucosan (Carbohydrate 5) Peak Areas from Pyrograms of PAA Wood, 100-77.2% Yield

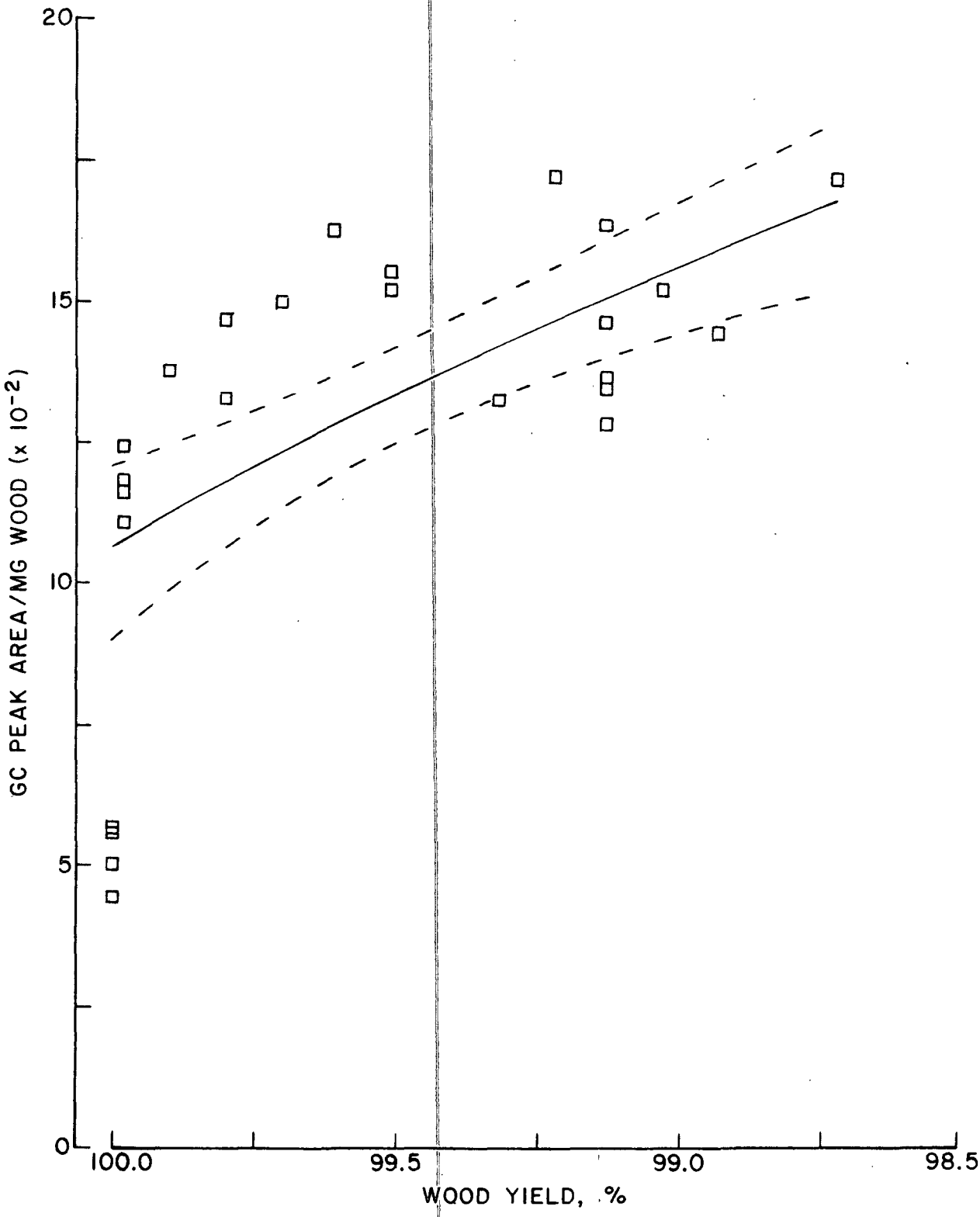


Figure 41. Levoglucosan (Carbohydrates) Peak Areas from Pyrograms of PAA Wood, 100.0-98.6% Yield

CARBOHYDRATE PYROLYSIS PRODUCTS

The carbohydrate portion of the wood pyrogram (see Fig. 17-20, 25-28) was investigated only to a limited extent. Carbohydrate 1 has an apparent molecular weight of 128 but no VIV MS work was conducted to confirm it. Its retention time between 2-furaldehyde and hydroxymethylfurfural (HMF, molecular weight 126) suggests a partially reduced form of HMF. Carbohydrate 2 was in close association with cis-isoeugenol and only cis-isoeugenol was positively identified by MS. Carbohydrate 3 was identified as HMF. It was the only carbohydrate in the wood pyrogram positively identified by MS. Carbohydrate 4 was not identified but carbohydrate 5 was identified as levoglucosan by its GLC retention time (as was peak A1,2-furaldehyde).

The carbohydrate peak areas showed a great deal more scatter than any of the lignin peak areas as can be seen in Fig. 40 and 41. The least-squares line was calculated with a power, $(\text{Area})^2$, transformation of the area/mg. All the carbohydrate peaks showed the best correlation with yield using this power transformation (Appendix IV). The nonreproducibility or scatter found for the carbohydrates was undoubtedly due, in part, to their relative thermal instability. Cellulose, starch, or glucose thermally degrade mainly through a levoglucosan pathway (37,84,102,103,106,137-139). Levoglucosan, the first pyrolysis product formed, in turn can thermally degrade to form other products. HMF is not formed directly from cellulose but by way of levoglucosan. The pyrogram for levoglucosan is very similar to the carbohydrate portion of a wood pyrogram as was seen in Fig. 17-20. This indicates that most of the carbohydrate peaks in the wood pyrogram are at least secondary wood pyrolysis products coming from levoglucosan. This unstable nature, apparently exhibited by most of the carbohydrate pyrolysis products, undoubtedly contributes to different product distributions for each pyrolysis.

EXPERIMENTAL

PREPARATION OF MATERIALS

CHEMICALS

Levulinic acid, methacrylic acid, and acrolein were obtained from Matheson Scientific, Incorporated. Crotonic, veratric, trans,trans-muconic, and 3-hydroxybutyric acid and benzaldehyde were obtained from Aldrich Chemical Company. Hydroquinone, veratrole, guaiacol, eugenol, isoeugenol, vanillin, D-xylose and D-mannose were obtained from Eastman Organic Chemicals. Phenol, creosol, o, m, and p-cresol, p-benzoquinone and 3,4-dihydroxytoluene were obtained from K & K Laboratories, Incorporated, and 2-furaldehyde was obtained from J. T. Baker Chemical Company. Samples of cis,trans-β-methylmuconic acid and 5-carboxymethyl-4-methyl-2-(5H)-furanone were obtained from J. C. Farrand's work (8) through Dr. D. C. Johnson along with propiovanillone. Samples of guaiacol, creosol, 4-ethylguaiacol, 4-propylguaiacol, ferulic acid, acetovanillone, vanillic acid, diisoeugenol, pinoresinol, conidendrin, dehydrodivanillin and vanillyl methyl ketone were obtained from the personal collection of Dr. I. A. Pearl. Coniferin was obtained from Mr. E. E. Dickey. Propioveratrone, 1-(3,4-dimethoxyphenyl)propan-1,2-diol, 2-(2-methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol, 2-(2-methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-one were obtained from W. Lawrence. Hydroxyacetylfuran and hydroxymethylfurfural were obtained from Dr. J. F. Harris, U.S.D.A. Forest Service. No further purification was carried out on any of these compounds. Metanephrine was obtained from Sigma Chemical Co.

5-METHYL-2(5H)-FURANONE

5-Methyl-2(5H)-furanone (angelicalactone) was prepared by a slow distillation of 125 g from levulinic acid (140-142) in a 250-ml round bottom flask for 2.5 hr. Three fractions were collected over the 2.5 hr: 1 — 25 ml, 90-145°C, 2 — 55 ml, 145-190°C, and 3 — 20 ml, 185-220°C. Fraction 2 was vacuum distilled and the fraction collected between 30 and 70°C (0.5-mm Hg) was redistilled. Two fractions were collected on redistilling, Fraction 2-1 — 2.0 ml, 25-30°C (1.75-mm Hg) and 2-2 — 2.0 ml, 54°C (160-mm Hg). The IR and NMR of Fraction 2-2 confirmed it as the α,β-unsaturated isomer [Lit. $b.p._3$ 73° (142)]. The NMR and IR spectra are represented in Table IX and Fig. 42 along with the IR of γ-butyrolactone and Fraction 2-1 suspected to be the lower boiling β,γ-unsaturated isomer [Lit. $b.p._{12}$ 53° (142)].

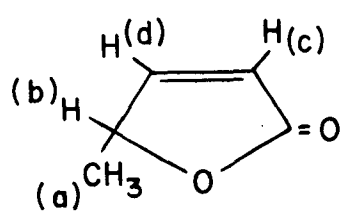
TABLE IX

SPECTRAL DATA FOR 5-METHYL-2(5H)-FURANONE (FRACTION 2-2)

NMR ($CDCl_3$)

δ, ppm	Multiplicity	J^a, Hz	Protons	Assignment
1.47	2	6.2	3	a
5.23	4 16	7.0 1.5	1	b
6.23	2 4	6.0 1.8	1	c
7.68	2 4	6.0 1.5	1	d

[a]Observed spacings.



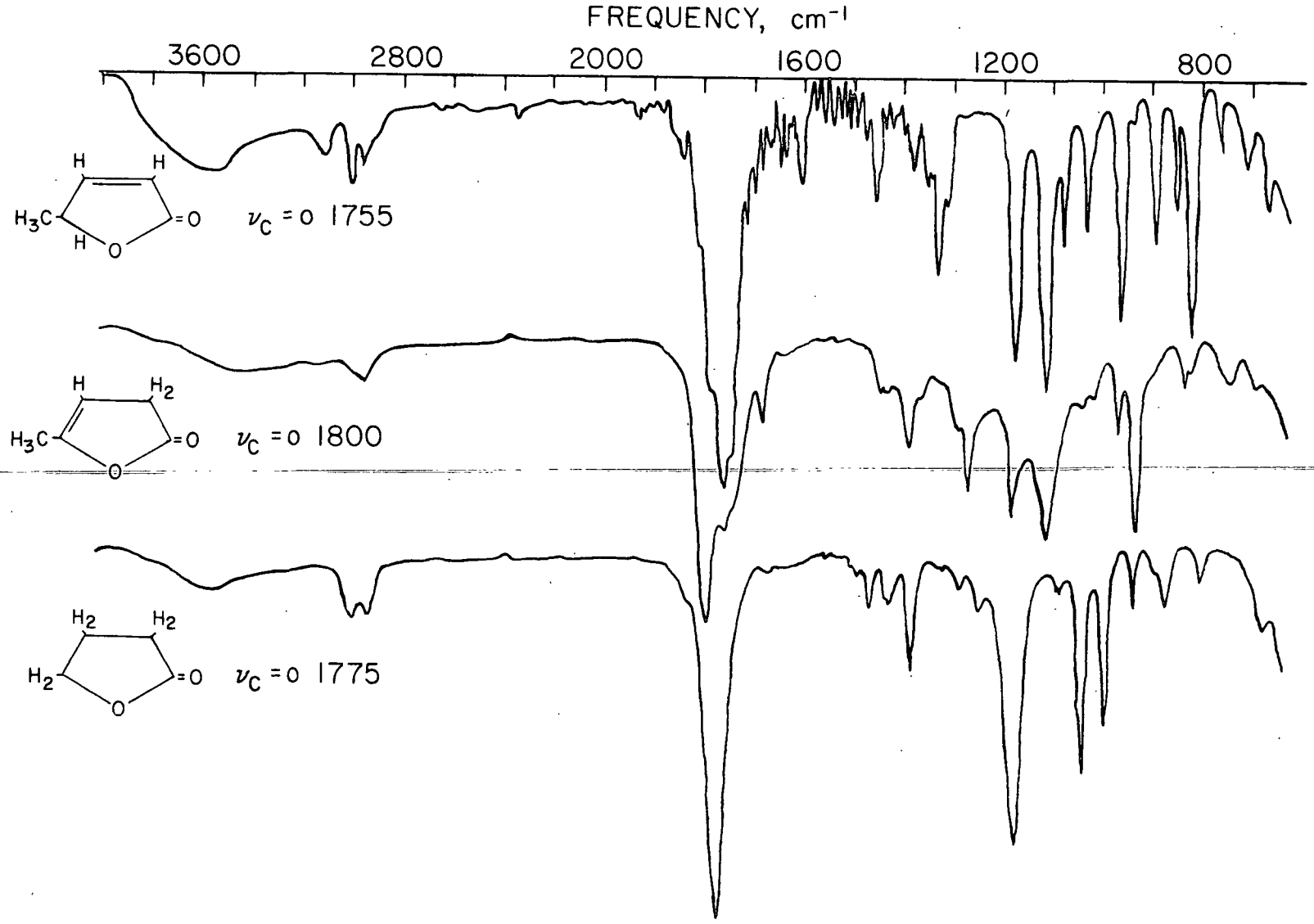


Figure 42. Infrared Spectra of Lactones

PREPARATION OF 4-VINYLGUAIACOL

Ferulic acid was pyrolyzed in order to obtain an authentic sample of 4-vinylguaiacol for GC and MS work. This method was considered to be a modification of a catalytic thermal decomposition of ferulic acid used to obtain 4-vinylguaiacol (143). The only pyrolysis product from ferulic acid had a GC retention time and mass spectrum expected for 4-vinylguaiacol. The product corresponded to the dioxane lignin pyrolysis product suspected to be 4-vinylguaiacol (GLC retention time) based on the literature (143) and its mass spectrum (Appendix VIII).

HOMOVANILLIN

Homovanillin was prepared from metanephrine as described by Robbins (144). Approximately 0.1 g of homovanillin was obtained from 0.3 g of metanephrine.

DIOXANE LIGNIN

Loblolly pine disks 6-9 inches in diameter with approximately 20 growth rings were ground on a macro-Wiley mill to pass through a 20-mesh screen. The bark and last growth ring and the center 2 inches of each disk were excluded from grinding and discarded. A total of 210 g of air-dried loblolly pinewood meal was extracted in two separate batches. Each batch was extracted with 1.0 liter of acetone in a 500-ml Soxhlet extractor for 6 hr. The wood meal was then vacuum dried.

The dioxane lignin was prepared similarly to that described in the literature (145-147). The vacuum-dried extracted wood meal (57 g) was refluxed with 1.0 liter of a 0.2N HCl solution of dioxane-water (9:1) for one hr.

After cooling, the wood meal was filtered and washed with neutral dioxane-water (9:1). The combined filtrate was neutralized with sodium bicarbonate and filtered again. The brown filtrate was concentrated to 100 ml on a rotary vacuum evaporator. One liter of 1% sodium sulfate was added to the concentrated filtrate and a brown precipitate formed. The precipitate was centrifuged, washed with 200 ml of distilled water, and centrifuged a total of 8 times. The precipitate was vacuum dried and weighed; 2.6 g was obtained. An IR spectrum taken from 2 mg of dioxane lignin in a 0.1 g KBr pellet is represented in Fig. 43.

The dioxane lignin was analyzed by Geller Laboratories and was found to contain: 63.38% carbon; 5.96% hydrogen; 0.26% ash; and 15.03% methoxyl.

The dioxane lignin was totally excluded on Sephadex G-25 coarse (exclusion limit molecular weight 5000) in DMSO. The exclusion chromatography was carried out by W. Baird on a 1-cm diameter × 75-cm column with a flow rate of 0.8 ml/min and continuous monitoring at 280 nm. A typical softwood dioxane lignin was reported to have a molecular weight of 15,000 and a methoxyl content of 15.4% (148,149).

PERACETIC ACID LIGNIN

PAA-oxidized loblolly pine lignin which had been solubilized from the wood by PAA and later fractionated on a GPC column (Porasil B) by J. Albrecht (6) was obtained from Dr. G. A. Nicholls. Fractions 1-65 (PAA lignin 1-65) from the GPC column were freeze-dried by Albrecht into a fluffy cream-colored material. Fractions above 65 (PAA lignin 66 and above) could not be freeze-dried satisfactorily and remained liquids or thick sirups. Freeze-dried Fractions 46 and 48 were analyzed by PGCMS. The IR of Fraction 46 is

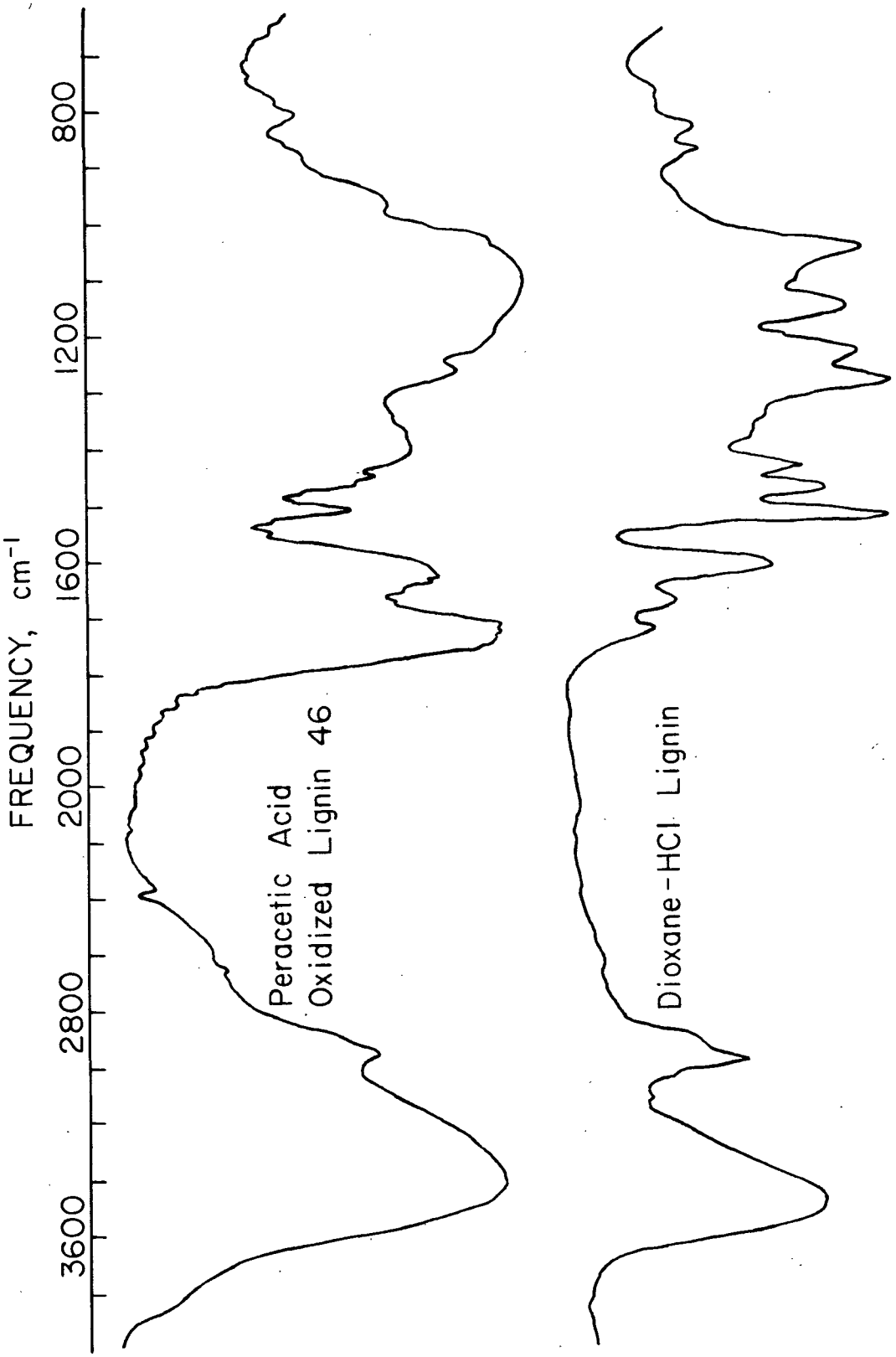


Figure 43. Infrared Spectra of Isolated Lignin

compared to that of dioxane lignin in Fig. 43. Fraction 48 was characterized by Albrecht as having 0.06 meq/100-mg phenolic hydroxyl, 0.28 meq/100-mg carboxyl content and 11,000-12,000 number average/molecular weight. Fractions 46 and 48 were considered essentially identical to each other and produced identical pyrograms. Fractions 72-109 were liquid samples and a limited number of their PGCMS, GCMS analyses appear in Appendix II.

PERACETIC ACID WOOD WAFERS

Loblolly pinewood wafers that had been treated with 3.0% PAA at 60°C for up to 11 hr were obtained from W. Baird (126). Yield levels down to 77.15% were obtained as shown in Appendix VI.

Two reaction groups were prepared from acetone-extracted wood wafers from Albrecht's work (6). For each group, twelve individual batches of approximately 1.160 g (o.d.) each were run in separate 250-ml Erlenmeyer flasks with 200 ml of PAA solution. Passivation of glassware and PAA preparation were carried out as described by Albrecht (6). All wood wafers were degassed in distilled water under vacuum. One reaction group was subjected to 2.8% PAA at 60.0 ± 0.1°C and the other group was subjected to 2.1% PAA at 50.0 ± 0.1°C. The PAA solution was heated in a controlled temperature bath to reaction temperature just prior to addition to the wood wafers. PAA addition and placement of all the flasks into the controlled temperature bath took approximately 4 min. The flasks were removed from the bath at 10 and 15-min intervals. The wood wafers were then filtered on a Buchner funnel, washed with 5.7% acetic acid, distilled water, and then stored in distilled water for 2 hr before drying to 6.9% moisture under a vacuum at room temperature. Yield levels were corrected based on time, Appendix VI. Yields down to 94.95%

were obtained with the 2.8% PAA-60.0°C group after 169 minutes and yields to 98.93% were obtained with the 2.1% PAA-50.0°C group after 114 minutes. The various yield levels are shown in Appendix VI.

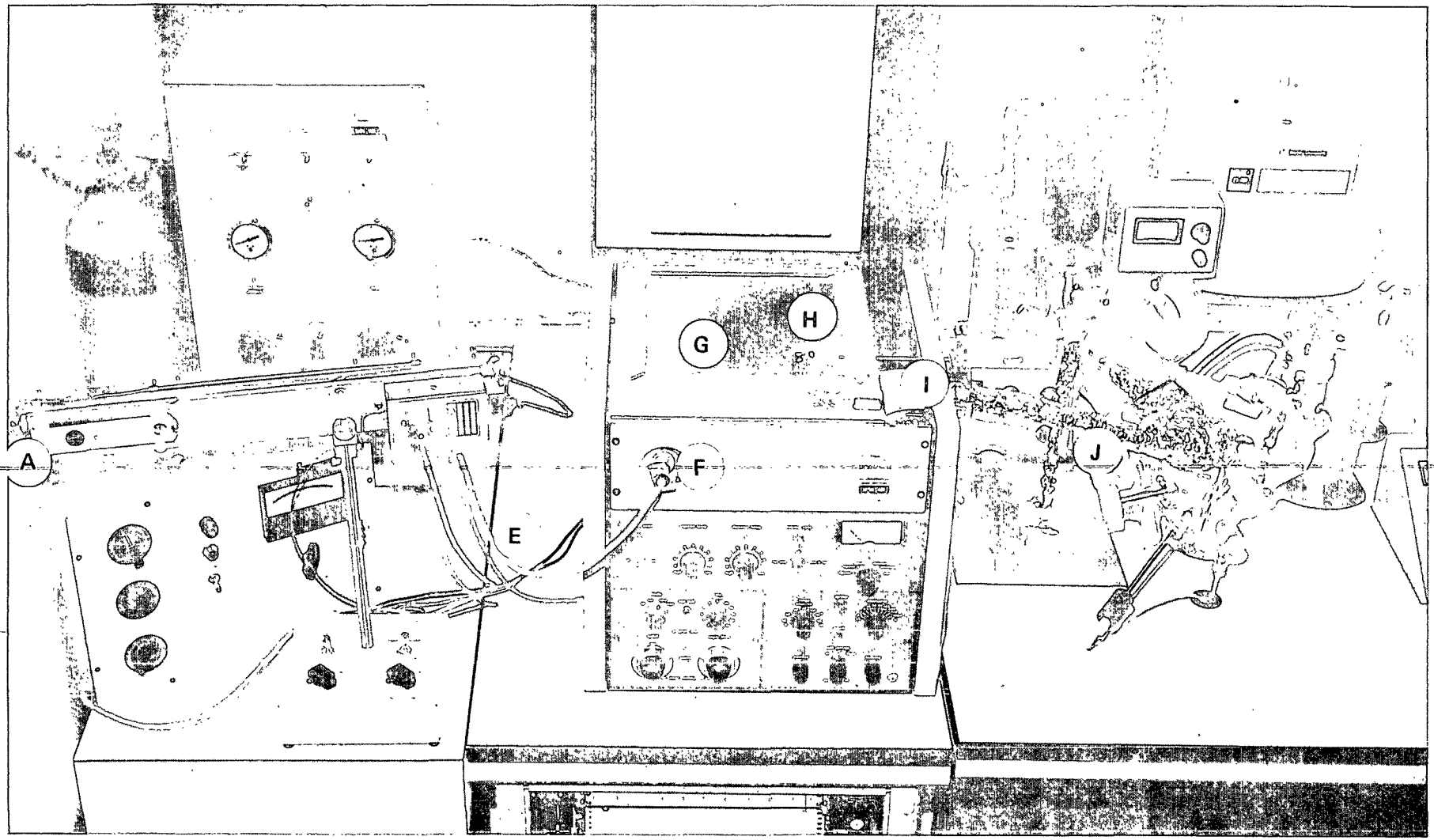
The last two 100% yield samples (4th and 5th line) for each peak in Table XIX, Appendix IV, were hot (50°C) water extracted for 10 minutes. There appeared to be no effect on lignin pyrolysis products as a result of the hot water extraction.

PROCEDURES FOR PRODUCT ANALYSIS

PYROLYSIS

A Hamilton multipurpose sampling system pictured in Fig. 44 and 45 was used for this work. A furnace temperature of 400°C was found to be the maximum temperature at which secondary reactions of lignin pyrolysis products were not significant. A flow rate of 75 ml/min of helium carrier gas and 400°C furnace temperature was used throughout this study. Initially, higher furnace temperatures were used to explore the temperature dependence of secondary reactions in this system. The oven temperature was maintained at 260°C and the heated line at 280°C.

For each sample pyrolyzed, the needle assembly was removed from the heated line for cleaning. Both the needle and the heated line were mechanically cleaned with a wire and drill bit to remove any possible buildup of tar. The oven teflon ferule seal and the rubber "O" ring seal at the access port were opened each time to introduce a new sample.



A - Sample port access

E - Heated line

F - Needle assembly in GC injector port

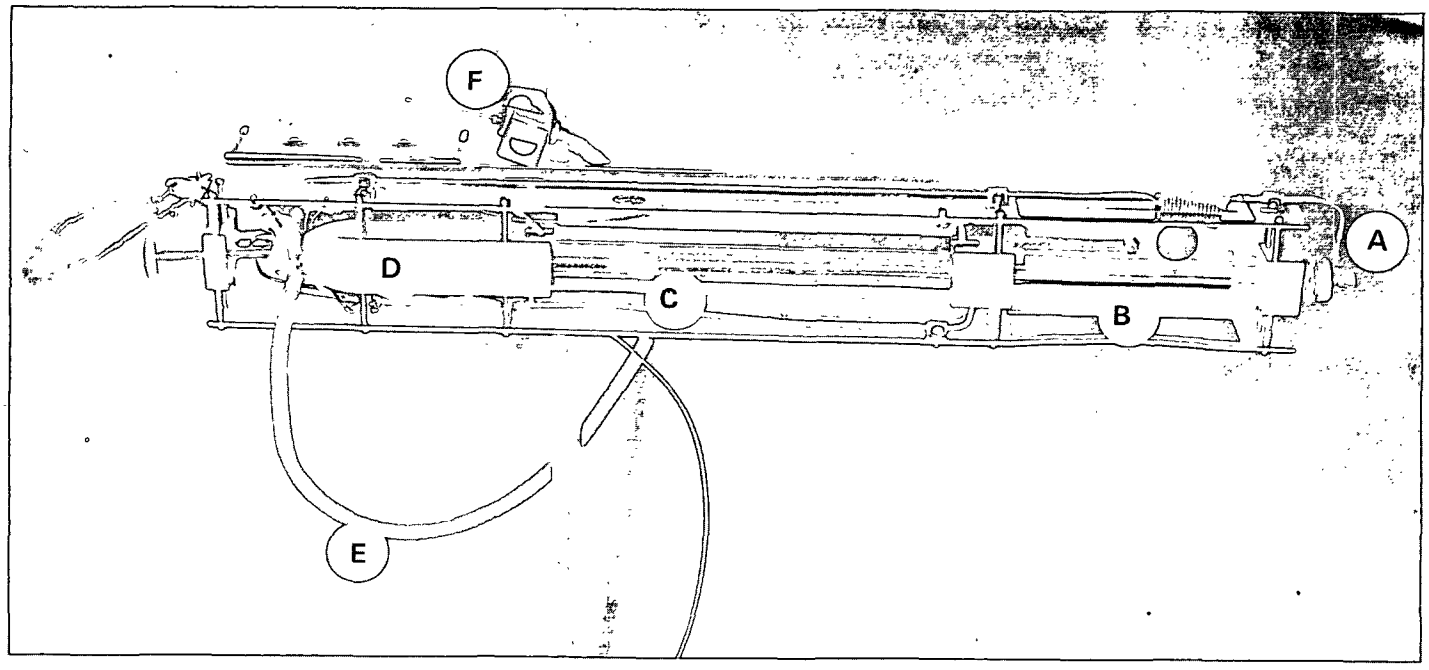
G - GC column furnace

H - GCMS splitter valve

I - Block heater, GCMS interface

J - Tape heater, GCMS interface line

Figure 44. Pyrolysis Gas Chromatography Mass Spectrometry System



A - Sample port access
B - Processing tube, room temperature zone
C - Furnace zone
D - Oven zone
E - Heated line
F - Needle assembly

Figure 45. Furnace and Heated Line Assembly

Each wood wafer sample was cut with a razor blade to a weight range of 1.90 to 2.00 mg and weighed on a semimicro balance in a conditioned room. All wood wafers were conditioned (50% RH, 72°F) in the weighing room at least 48 hr prior to weighing. The wood wafers weighed contained 8.18% moisture after conditioning. The ends of each wood wafer sliver were snugly fitted with short quartz capillary tubes about 3-mm × 2-mm diameter. The wood slivers were just over 10-mm long. The capillary tubes ensured sliding of the sample all the way down the quartz pyrolysis tube. All other samples, liquids or powders, were placed in a single quartz capillary tube about 10-mm long. After the sample was placed in the room temperature zone through the sample port access,

the system was sealed and the needle assembly (heated line) interfaced with the GC. The system was allowed to flush for at least 5 minutes (75 ml/min He) before pyrolysis. The sample was introduced into the furnace zone by pivoting the sample port access end up so that the sample would slide down into the heated zone. This was done with one quick movement. Afterwards the sample was removed by pivoting the sample port access end down and allowing the sample to slide out. Pyrolyzed samples were recovered in this manner to determine weight loss. All samples and capillary tubes were handled with tweezers to prevent contamination. All quartz items were cleaned prior to use in a gas-oxygen flame to remove organic material.

GAS CHROMATOGRAPHY

All GC work presented here was run using a 6 ft × 1/8 inch stainless steel column packed with 10% Carbowax 20 M on DMCS, A/W, 60/80 mesh Chromosorb W. The columns used were fitted for on column injection in the Varian 1400 GC used in this work. A Varian 200 GC with a thermal conductivity detector and a 5 ft × 0.25 inch 15% Carbowax column was used for preparative work (3-hydroxybutyric and crotonic acid from liquid PAA lignin). The Varian 1400 GC was equipped with a flame ionization detector.

A 10% SE-30 column and a 10% EGSS-X column were found not to be any better than the 10% Carbowax 20 M column in separating wood and dioxane lignin pyrolysis products. A 2°/min column oven program from 90 to 205°C was found to give the best separation for the most complex pyrogram, wood, and was used for the quantitative wood pyrograms. The quantitative pyrograms were recorded at an attenuation of 128×10^{-11} and 0.5 inch/min chart speed. The injector port and detector were run at 215 and 290°C, respectively.

Authentic samples listed in the chemicals section were used for GC retention times and/or MS spectra comparison for pyrolysis product identification. The isothermal mode and different programming conditions were used in certain instances to achieve a desirable pyrogram. For each particular pyrogram that utilized a different column condition, retention times of authentic samples were rechecked. The retention times for model compound pyrolysis products are listed in Appendix IX.

CHROMTOGRAM PEAK AREA DETERMINATION FROM PYROLYSIS PRODUCTS

All peak areas for the quantitative wood pyrograms were integrated on a Technicon Integrator/Calculator Model AAG. A base line was drawn for the wood pyrograms between guaiacol (23 minutes) and homovanillin (52 minutes). The area below this line to horizontal with guaiacol (the lowest point) was taken as the base-line area (see Fig. 46). The total area is all the pyrogram peak area between guaiacol and homovanillin minus the base-line area. Area measurements were taken which corresponded to 181 units per square inch. Peak height measurements were taken in centimeters from the drawn base line (P1) and from a second base line connecting the adjacent valley on either side for the next resolved peak (P2). The peak measurements were analyzed as described in Appendix IV.

There was no base-line drift for the column alone, 2°/min, 90 to 205°C and very little for the dioxane lignin pyrogram. All the base-line drift in the wood pyrogram is considered to be carbohydrate bleed.

The peak area determinations for the investigation of creosol pyrolysis over the range 400-600°C were done with a planimeter. Peak area determinations for the dioxane lignin and model compound pyrograms were done by cutting the peak out and weighing it.

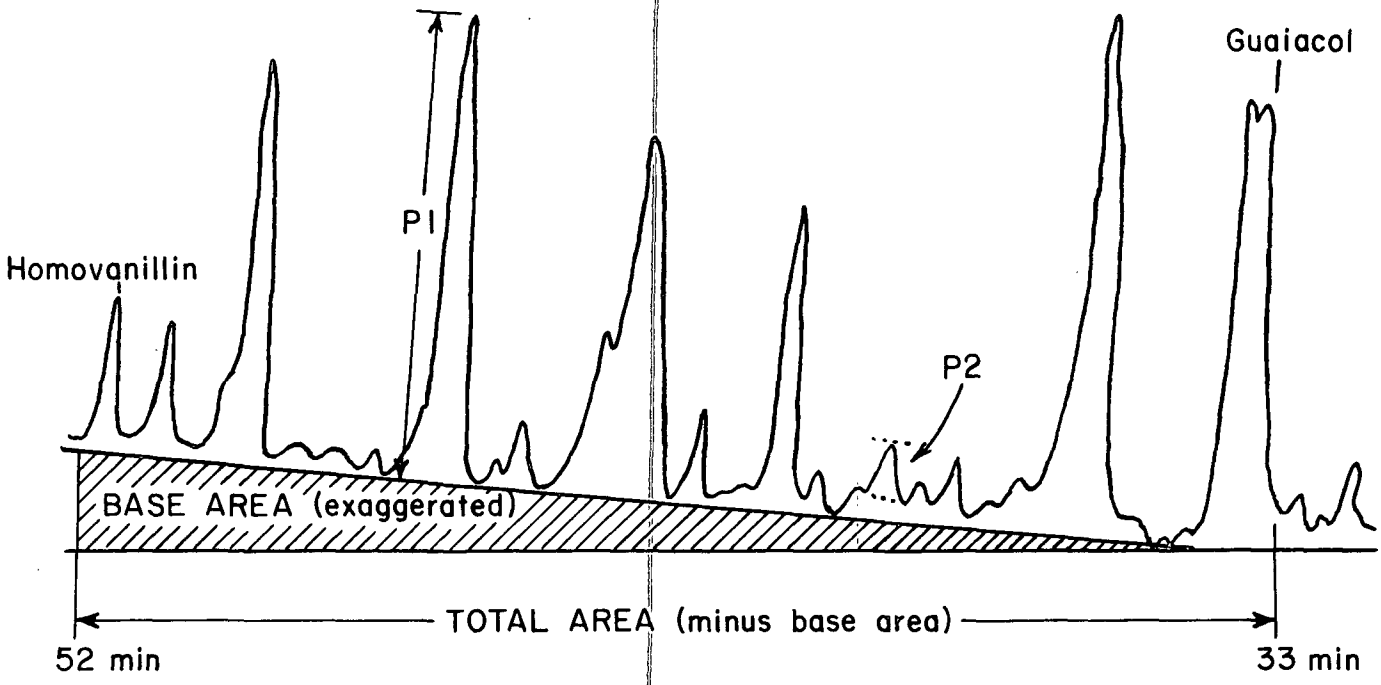


Figure 46. Representation of Quantitative Wood Pyrogram

Guaiacol, creosol, 4-ethylguaiacol, 4-propylguaiacol, and eugenol were injected onto the GC in weighed amounts of approximately 10^{-3} g. All compounds gave nearly the same response (relative peak area) with guaiacol giving the largest. Guaiacol samples in the range of 10^{-6} g (μg), 5×10^{-4} and 10^{-3} g were injected onto the GC. Peak area responses corresponding to an attenuation setting of 128×10^{-11} were calculated. The average value was approximately 10^{5} in.^{2} g or 10^{-5} g/in.^{2}

MASS SPECTROMETRY

A Dupont 21-491 mass spectrometer interfaced with the previously described Varian 1400 GC was used in this work and is partially shown in Fig. 45. The splitter block and interfacing tube were run at 300 to 310°C for all PGCMS and GCMS experiments. Normal operating temperatures for the oven and source were

105-115°C and 215-225°C, respectively. Operating pressures were 1.0-4.0 × 10^{-7} torr. Ultra high purity helium was used for all PGCMS and GCMS experiments. Perfluorotributylamine was used as a standard to confirm ion mass/charge ratios. Under optimum conditions a meaningful spectrum could be obtained via GC from 40-50-µg samples. All MS experiments via the GC were run with the filament in the GC mode. Variable ionizing voltage (VIV) experiments were run for some compounds to help to determine molecular weights using approximately 10-12 ev instead of 75 ev. All the mass spectra are tabulated in Appendix VIII.

INFRARED AND NMR SPECTRA

The IR spectra of the lignin samples (Fig. 43) were run in KBr pellets, 2.0 mg in 100 mg of KBr. The pellets were evacuated in the press for 5 minutes and then pressed to 22,000 psi for 3 minutes. All other samples were run neat between NaCl plates. All NMR spectra were run in the solvents listed with tetramethylsilane as internal standard on a Varian A-60A spectrometer. All J values are observed spacings.

PHLOROGLUCINOL STAINING

Microtome cross sections approximately 15 nm in thickness were prepared from the unreacted and the PAA-treated wood wafers. Two different yield levels were mounted on each slide and stained together with phloroglucinol (1-g phloroglucinol in 50-ml methyl alcohol, 50-ml concentrated HCl and 50-ml water — TAPPI Standard T 401 m-60). The purple, violet or red-purple reaction color (150) is attributed to coniferaldehyde-type carbonyl groups which are present in 3% or less of the phenylpropane units of lignin (151,152). The color reactions observed for phloroglucinol with various materials are recorded in Table X.

TABLE X

PHLOROGLUCINOL STAIN REACTIONS

Material	Reaction
Cinnamaldehyde	Deep golden (brown) red
Dioxane lignin	Dark red, magenta
Vanillin	Bright red
Benzaldehyde	Yellow-white cream
3-Hydroxybenzaldehyde	Yellow cream
2-Furaldehyde	Yellow dark brown, dark green
Hydroxymethylfurfural	Yellow, red-orange
Acrolein	White cream
Eugenol	Light (thin color) violet (impurity?)
Coniferin	Light (thin color) raspberry (impurity?)
Isoeugenol	None
Propiovanillone	None
Hydroquinone	None
D-Xylose	None
D-Arabinose	None
Crotonic acid	None
Methacrylic acid	None
trans,trans-Muconic acid	None
Styrene	None

CONCLUSIONS

Pyrolysis-gas chromatography is capable of detecting peracetic acid modifications in lignin. Aromatic ring cleavage products may be detected only indirectly by the disappearance of phenolic pyrolysis products. Muconic acid structures, if present, are dissipated on pyrolysis by formation of numerous compounds and isomers.

During the first 1% loss of wood, due to peracetic acid, oxidation at the phenylpropane side chain of lignin is more important than aromatic ring cleavage. Reactions at the side chain involve α-aryl ethers and coniferaldehyde-type structures. The subsequent peracetic acid delignification reaction from 99 to 77% yield is considered to be a combination of reaction at the side chain and aromatic ring cleavage with the latter predominating.

Two structures can be proposed to account for the aromatic systems which persist through peracetic acid treatment. The structures include a benzyl carbohydrate ether and a benzyl carbon-to-carbon linkage with another phenylpropane structure.

GLOSSARY

AcOH	acetic acid
angelicalactone	5-methyl-2(5H)-furanone
µg	micrograms
GC	gas chromatograph(y)
GLC	gas-liquid chromatography
GPC	gel-permeation chromatography
HMF	hydroxymethylfurfural
levo	levoglucosan, 1,6-anhydro-D-glucopyranose
MS	mass spectrometry
(MS)HIGH	the current to the source in the mass spectrometer has been increased above the GC or VIV modes
(MS)VIV	varied ionizing voltage, the ionizing voltage has been reduced in the source of the mass spectrometer
nm	nanometers
NMR	nuclear magnetic resonance
PAA	peracetic acid
PAA lignin	lignin solubilized by peracetic acid
PGC	pyrolysis gas chromatography
PGCMS	pyrolysis gas chromarography mass spectrometry

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APPENDIX I

INVESTIGATION OF CARBOHYDRATE PYROLYSIS PRODUCTS FROM PERACETIC ACID LIGNIN

The thermal degradation of cellulose and of levoglucosan both yield 2-furaldehyde as one of the major products (119). Shafizadeh, et al. (118) have shown that xylose yields 5.8% 2-furaldehyde at 500°C. In general, both hexose and pentose sugars apparently yield 2-furaldehyde as one of the major pyrolysis products (52,117-119). Weighed amounts of arabinose and PAA lignin no. 48 were pyrolyzed at 400°C and the 2-furaldehyde peak area in each pyrogram was measured. Based on the generation of 2-furaldehyde from the arabinose sample, the carbohydrate content of the PAA lignin no. 48 sample was calculated at 7%. The PAA lignin no. 48 sample was previously determined by Albrecht (6) to contain 7.8% carbohydrate material most of which is mannose (3.2%) and arabinose (2.6%). A sample of mannose was pyrolyzed, and a 2-furaldehyde peak comparable to that for arabinose was observed. It was concluded that most of the 2-furaldehyde peak in the PAA lignin pyrogram is generated from the carbohydrate material present. Little if any 2-furaldehyde is considered to come from the rearrangement of muconic acids.

APPENDIX II

DETERMINATION OF ACETALDEHYDE-QUENCHED PERACETIC ACID BY-PRODUCT, 3-HYDROXYBUTYRIC ACID

PAA lignin Fractions 68-69, 70, 74-76, 78-80, and 92-95 are all liquid samples that could not be freeze-dried to solids by Albrecht (6). Acetic, acrylic, crotonic and 3-hydroxybutyric acid appear to be the only major components in these samples as determined by PGCMS and GCMS as shown in Fig. 47 and 48. Crotonic acid was also identified by NMR and 3-hydroxybutyric acid by NMR and IR. These spectra are represented in Tables XI-XIV and Fig. 49. The mass spectra for the 4 compounds are presented in Appendix VIII.

PAA, 3.0%, was quenched with acetaldehyde as described by Albrecht (6). The concentrated residue was analyzed by GCMS. The major component was 3-hydroxybutyric acid. All the 3-hydroxybutyric acid in the liquid PAA lignin samples is considered to be an oxidized aldol condensation product from the acetaldehyde used to quench PAA and/or from a crossed aldol condensation of acetaldehyde and acetic acid. No crotonic acid was found in the quenched PAA. Its appearance in the liquid PAA lignin sample is considered to come from the dehydration of 3-hydroxybutyric acid on standing. Acrylic acid was only tentatively identified based on its mass spectrum; its origin is unknown.

The authentic sample and the compound identified as 3-hydroxybutyric acid both showed a prominent ion at m/e 116 in their mass spectra. This ion, 12 mass units above the molecular weight of 3-hydroxybutyric acid, was considered to come from the fragmentation of a dehydrodimer or other products from 3-hydroxybutyric acid molecules.

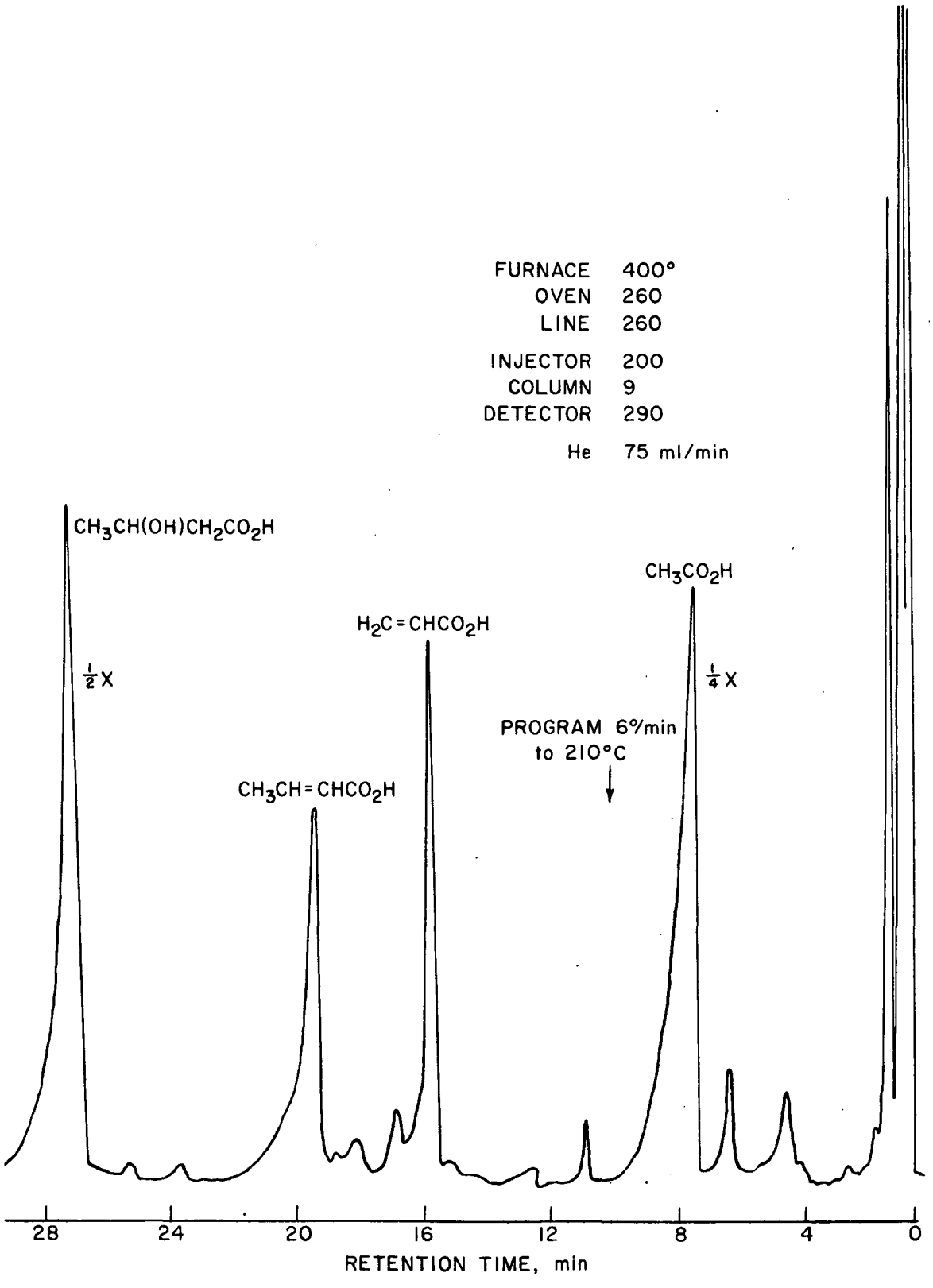


Figure 47. PGC of PAA Lignin No. 72

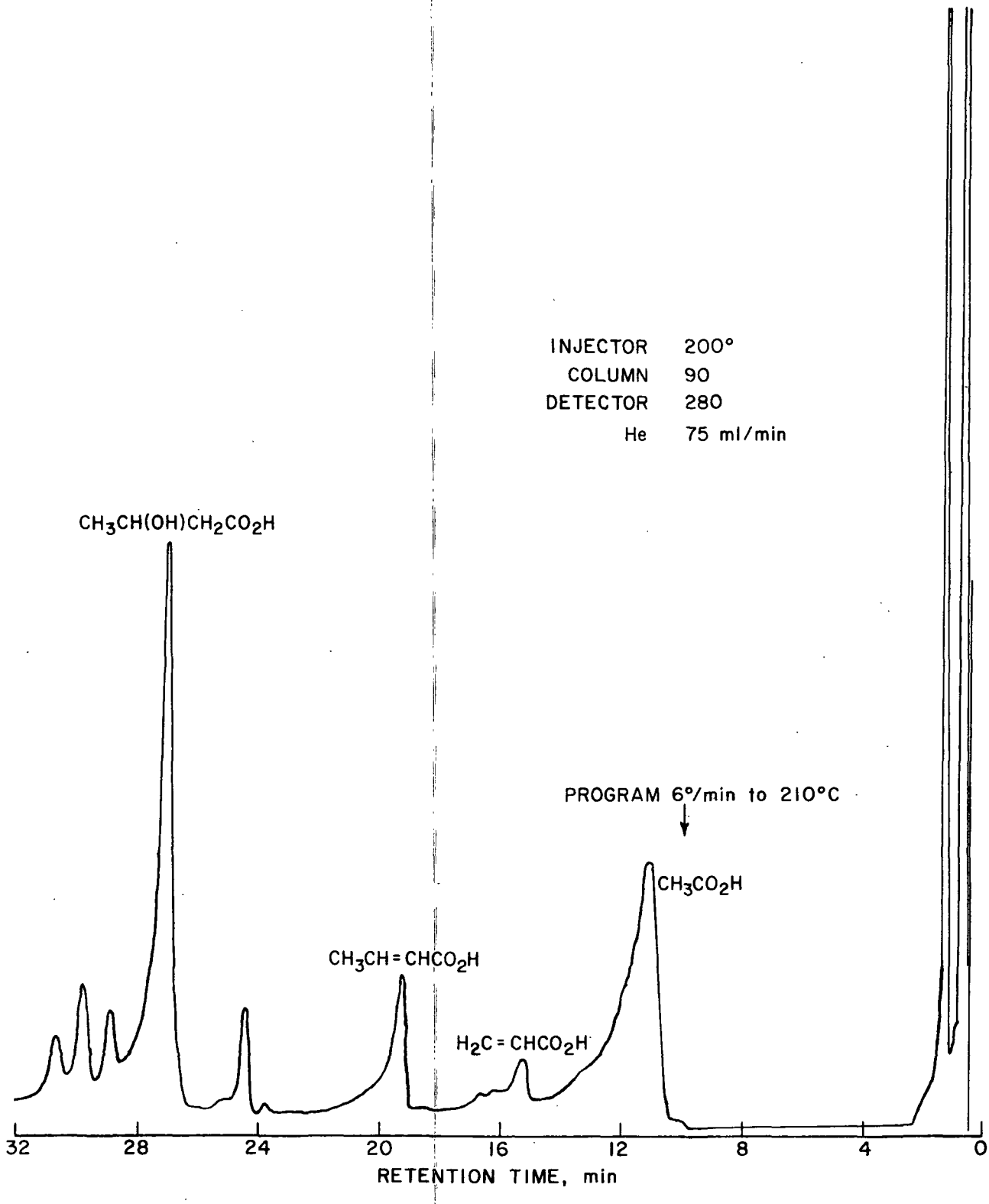


Figure 48. PAA Lignin No. 92-95 Injected Onto GC

TABLE XI

SPECTRAL DATA FOR CROTONIC ACID OBTAINED FROM PAA LIGNIN

NMR ($CDCl_3$)

δ, ppm	Multiplicity	J, Hz	Protons	Assignment
1.94	4		3	a
	2	1.5-2.0		
	2	7		
5.88	8		1	b
	2	15		
	4	1.5-2.0		
7.15	4		1	c
	2	7		
	2	15		
9.25	1		1	d

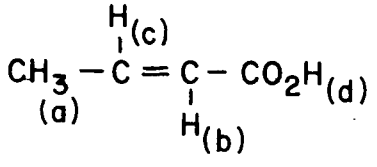


TABLE XII

SPECTRAL DATA OF CROTONIC ACID, AUTHENTIC SAMPLE

NMR ($CDCl_3$)

δ, ppm	Multiplicity	J, Hz	Protons	Assignment
1.90	4 (2 doublets)		3	a
	2	1-1.5		
	2	7		
5.85	8 (2 quartets)		1	b
	4	1.5		
	2	15		
7.11	8 (2 quartets)		1	c
	4	7		
	2	15		
12.00	1		1	d

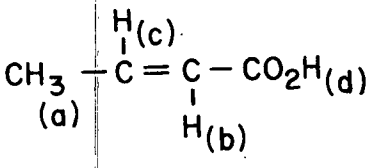


TABLE XIII

SPECTRAL DATA OF 3-HYDROXYBUTYRIC ACID OBTAINED FROM PAA LIGNIN

NMR ($CDCl_3$)

δ, ppm	Multiplicity	J, Hz	Protons	Assignment
1.25	2	6	3	a
2.51	2	6	2	b
4.28	6	6	1	c
7.11 (disappears with D_2O)	1		2	d

NMR (DMSO)

1.11	2	6	3	a
2.29	2	6	2	b
4.01	6	6	1	c

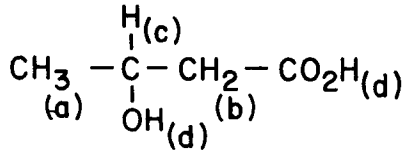


TABLE XIV

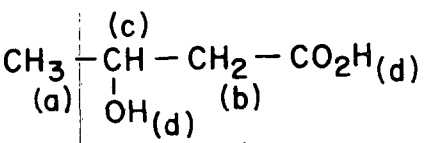
SPECTRAL DATA OF 3-HYDROXYBUTYRIC ACID, AUTHENTIC SAMPLE

NMR ($CDCl_3$)

δ, ppm	Multiplicity	J, Hz	Protons	Assignment
1.25	2	6	3	a
2.51	2	6	2	b
4.28	6	6	1	c
7.48	1		2	d

NMR (DMSO)

1.12	2	6	3	a
2.32	2	6	2	b
4.07	6	6	1	c



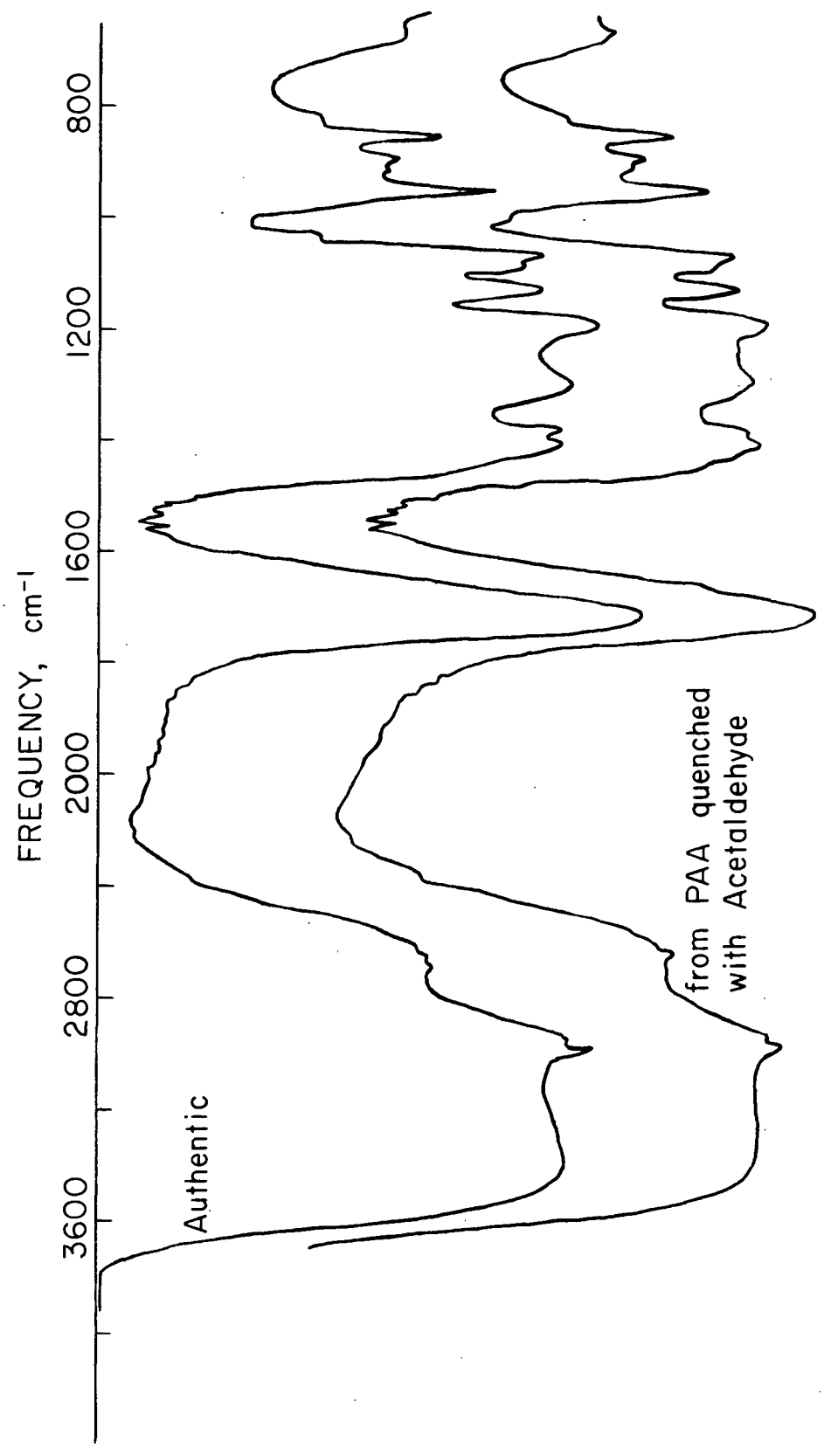


Figure 49. Infrared Spectra of 3-Hydroxybutyric Acid

APPENDIX III

THE REMOVAL OF INORGANIC MATERIAL FROM WOOD BY PERACETIC ACID AND ITS EFFECT ON PYROLYSIS PRODUCTS

The ash analyses were performed by the analytical department using emission spectroscopy. The ash content is based on ovendry sample weight. Ash was found by igniting for 2 hours at 600°C. Moisture content is based on sample weight in a conditioned atmosphere (50% RH, 72°F). Moisture is the weight loss after overnight drying at 105°C. The ash results are listed in Tables XV-XVII.

Samples 99.80 + 99.70% and 96.95 + 96.45 are combined yield levels of PAA-reacted wood wafers. The 100% samples had only been acetone extracted (6), and acetone and hot (50°C) water extracted and are used as a base reference. Samples 1, 2, and 12 were obtained in a similar manner as the PAA- (2.1% PAA, 50°C) treated wood wafers. The difference was that instead of 2.1% PAA, 0.24% acetic acid was used. The 2.1% PAA solution was calculated to contain approximately 0.24% acetic acid based on Albrecht's results (6). Sample 1 was only soaked in 0.24% acetic acid (50°C) for 5 minutes. Sample 2 was only washed with 5.7% acetic acid while Sample 12 was soaked and then washed with 5.7% acetic acid. The ash results show that washing removes some of the inorganic material but soaking is more efficient. It appears necessary to have PAA present to obtain the lowest ash level of 0.02-0.06%.

Acetone-extracted untreated wood wafers (0.22% ash) were cut into thin strips weighing 2.00 mg and ashed at 600°C for 2 hours. Wood wafers from the 99.98% yield group were cut and weighed to a range of 1.90 to 2.00 mg

TABLE XV

ANALYSIS OF WOOD SAMPLES

	100% Yield Acetone Ext.			100% Yield Acetone and H_2O Ext.			98.93% Yield		
	Test 1	Test 2	Av.	Test 1	Test 2	Av.	Test 1	Test 2	Av.
Moisture, %	7.99	8.08	8.04	8.19	8.12	8.16	8.10	8.19	8.14
Ash (600°C), %	0.21	0.22	0.22	0.23	0.23	0.23	0.03	0.02	0.02
Barium, ppm	1.3	1.4	1.4	1.3	1.4	1.4	0.38	0.38	0.38
Boron, ppm	16	14	15	9.0	9.8	9.4	6.1	7.1	6.6
Silicon, ppm	3.4	2.3	2.8	2.2	3.2	2.7	2.0	2.6	2.3
Phosphorus, ppm	25	23	24	14	16	15	4.9	5.9	5.4
Manganese, ppm	29	25	27	26	20	23	9.4	10.7	10
Aluminum, ppm	7.2	7.1	7.2	4.4	4.7	4.6	1.0	1.1	1.0
Iron, ppm	7.6	7.0	7.3	2.9	4.1	3.5	3.2	3.5	3.4
Magnesium, ppm	259	278	268	198	189	194	5.0	5.5	5.2
Lead, ppm	1.1	0.9	1.0	0.49	0.53	0.51	0.34	0.37	0.36
Calcium, ppm	664	799	732	534	460	497	34	34	34
Copper, ppm	0.61	0.46	0.54	0.50	0.54	0.52	0.68	0.64	0.66
Zinc, ppm	5.7	4.4	5.0	4.6	5.4	5.0	0.80	1.0	0.90
Sodium, ppm	94	81	88	110	129	120	1.0	1.2	1.1
Potassium, ppm	275	243	259	Nickel present			37	50	44
Nickel, ppm	--	--	--	1.4	1.5	1.4	--	--	--
Titanium, ppm	--	--	--	--	--	--	0.10	0.10	0.10

TABLE XVI

ANALYSIS OF WOOD SAMPLES

	99.80 + 99.70% Yield			96.95 + 96.45% Yield			94.95% Yield		
	Test 1	Test 2	Av.	Test 1	Test 2	Av.	Test 1	Test 2	Av.
Moisture, %	8.36	8.26	8.31	8.64	8.63	8.64	8.53	8.48	8.50
Ash (600°C), %	0.06	0.06	0.06	0.10	0.08	0.09	0.04	0.05	0.04
Barium, ppm	1.7	1.7	1.7	1.5	1.7	1.6	0.35	0.35	0.35
Boron, ppm	63	67	65	74	72	73	13	10	12
Silicon, ppm	22	21	22	21	20	20	8.7	8.7	8.7
Phosphorus, ppm	17	16	16	14	16	15	6.7	6.3	6.5
Manganese, ppm	3.0	3.6	3.3	4.4	4.5	4.4	3.5	3.0	3.2
Aluminum, ppm	4.2	4.2	4.2	3.4	3.4	3.4	1.2	1.0	1.1
Iron, ppm	7.7	7.9	7.8	9.6	9.0	9.3	4.0	3.3	3.6
Magnesium, ppm	28	30	29	18	18	18	21	17	19
Lead, ppm	1.4	1.8	1.6	3.0	3.1	3.0	0.54	0.52	0.53
Calcium, ppm	151	176	164	285	262	274	126	136	131
Copper, ppm	2.2	2.4	2.3	1.3	1.2	1.2	0.88	0.92	0.90
Zinc, ppm	6.4	7.0	6.7	4.5	4.8	4.6	2.5	2.8	2.6
Sodium, ppm	19	19	19	112	127	120	18	19	18
Potassium, ppm	Nickel present			Nickel present			Nickel present		
Nickel, ppm	2.1	2.2	2.2	1.7	1.8	1.8	0.43	0.43	0.43
Titanium, ppm	0.69	0.62	0.66	0.75	0.70	0.72	0.30	0.30	0.30

Basis of report: Moisture content is based on sample weight in a conditioned atmosphere (50% RH, 72°F).
Ash content is based on ovendry weight.
Metals are based on ovendry sample weight.

Methods: Moisture is the weight loss upon overnight drying at 105°C.
Ash was found by igniting for two hours at 600°C.
Metals by emission spectroscopy — potassium could not be determined when nickel was present.

TABLE XVII

ANALYSIS OF WOOD SAMPLES

	Sample 1			Sample 2			Sample 12		
	Test 1	Test 2	Av.	Test 1	Test 2	Av.	Test 1	Test 2	Av.
Ash, %			0.098			0.17			0.091
Aluminum, ppm	4.6	5.0	4.8	6.2	6.6	6.4	5.4	6.2	5.8
Barium, ppm	1.4	1.5	1.4	1.9	2.1	2.0	1.4	1.5	1.4
Boron, ppm	2.4	2.5	2.4	3.0	2.9	3.0	2.1	2.4	2.2
Calcium, ppm	274	301	288	466	520	493	267	267	267
Copper, ppm	1.0	1.1	1.0	1.7	1.8	1.8	1.2	1.2	1.2
Iron, ppm	3.1	3.8	3.4	4.8	5.1	5.0	3.7	4.0	3.8
Lead, ppm	0.62	0.69	0.66	0.86	0.90	0.88	0.81	0.86	0.84
Magnesium, ppm	69	70	70	154	149	152	63	68	66
Manganese, ppm	9.6	10.1	9.8	16	18	17	9.5	9.0	9.2
Phosphorus, ppm	14.1	16.1	15	21	19	20	15	16	16
Potassium, ppm	165	180	172	249	244	246	160	164	162
Silicon, ppm	5.8	6.7	6.2	11	10	10	7.4	6.7	7.0
Sodium, ppm	10.0	12.0	11	34	39	36	15	18	16

as was done with previous quantitative samples. The 99.98% weighed wood samples were moistened with distilled water and the ash from a 2.00-mg 100% yield wood sample was placed on the moist wood. The ash appeared to move into the wood structure with the water. No ash could be seen on the surface of the wood. The 99.98% yield wood with the ash added was dried in a vacuum, conditioned, and then pyrolyzed. The pyrogram areas are compared with other samples including Sample 12 (acetic-acid-extracted 100% yield wood) in Table XVIII.

TABLE XVIII

PYROGRAM AREAS FROM TREATED WOOD

No.	Peak	100%[a] AcOH Extracted	100%[b]	99.98%[b]	99.98% +0.22% Ash[c]
1	Guaiacol	112	116	89	91
4	Creosol	198	213	217	217
5	4-Ethylguaiacol	57	54	45	44
6	4-Propylguaiacol	85	93	46	43
7	Eugenol	64	66	44	47
8	4-Vinylguaiacol	147	130	105	109
10	trans-Isoeugenol	158	153	114	116
12	Vanillin	67	49	48	56
13	Homovanillin	48	57	60	64

[a] Sample 12, single determination.

[b] Average from five pyrograms.

[c] Average from three pyrograms.

APPENDIX IV

DATA HANDLING FOR QUANTITATIVE ANALYSIS OF 9 WOOD PYROGRAM PEAK AREAS

Table XIX contains the area measurements from the 46 PAA wood pyrograms used in this study. The first column is the peak identification number corresponding to the list below:

Peak Identification No.	Description
1	Guaiacol
2	Carbohydrate 1
3	Guaiacol + Carbohydrate 1
4	Creosol
5	4-Ethylguaiacol
6	4-Propylguaiacol
7	Eugenol
8	4-Vinylguaiacol
9	Carbohydrate 2
10	trans-Isoeugenol
11	Carbohydrate 3 — HMF
12	Vanillin
13	Homovanillin
14	Carbohydrate 4
15	Carbohydrate 5 — levo
16	Base area
17	Total area

The second column is the measured peak area per milligram of sample (10th column) pyrolyzed. Column 3 is the peak area divided by the total area (Column 9) and multiplied by 1000. Columns, 4, 5, 6, and 7 are the two peak height measurements P1 (Columns 4 and 6) and P2 (Columns 5 and 7) divided by the weight of the sample (Columns 4 and 5) and divided by the total area (Columns 6 and 7) and multiplied by 10,000. Column 8 is the precentage

TABLE XIX

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
1	127.24	71.45	7.31	6.55	41.04	36.77	100.00	1780.96	1.97	256.35	
1	119.80	67.32	6.65	5.99	37.37	33.66	100.00	1779.44	1.97	195.43	
1	119.34	68.19	7.15	6.48	40.85	37.00	100.00	1750.26	1.93	210.36	
1	107.31	59.58	6.63	5.97	36.82	33.14	100.00	1801.28	1.96	259.18	7
1	107.07	57.34	7.02	6.36	37.60	34.08	100.00	1867.17	1.98	231.31	1
1	85.37	47.73	7.14	6.48	39.94	36.23	99.98	1788.52	1.96	204.08	4
1	82.64	47.33	6.98	6.35	39.98	36.40	99.98	1745.83	1.92	255.73	4
1	81.17	50.68	6.68	6.06	41.73	37.85	99.98	1601.55	1.93	251.30	2
1	88.66	56.59	6.24	5.62	39.81	35.86	99.98	1566.75	1.94	239.18	2
1	107.71	62.82	7.04	6.33	41.03	36.93	99.98	1714.57	1.99	245.23	9
1	79.06	50.18	6.34	5.71	40.21	36.22	99.90	1575.39	1.91	143.46	8
1	87.93	52.08	6.99	6.38	41.40	37.78	99.80	1688.27	1.96	168.37	6
1	94.10	50.95	6.61	5.99	35.81	32.43	99.80	1846.88	1.92	188.54	6
1	81.46	49.23	6.63	5.97	40.09	36.08	99.70	1654.59	1.96	178.57	9
1	93.47	56.94	6.29	5.57	38.31	33.91	99.61	1641.50	1.94	173.20	10
1	86.46	50.02	6.40	5.69	37.00	32.89	99.51	1728.43	1.97	203.05	5
1	94.47	53.10	6.48	5.83	36.44	32.76	99.51	1779.15	1.99	217.09	5
1	99.15	63.59	5.97	5.31	38.29	34.03	99.32	1559.18	1.96	166.84	8
1	84.79	51.40	6.05	5.33	36.69	32.33	99.22	1649.49	1.95	160.00	9
1	96.24	61.21	6.10	5.49	38.81	34.90	99.13	1572.31	1.95	176.92	5
1	84.97	49.31	6.53	5.80	37.88	33.67	99.13	1723.32	1.93	237.31	4
1	82.30	45.38	6.08	5.41	33.54	29.84	99.13	1813.66	1.94	213.92	5
1	90.28	58.19	5.83	5.16	37.60	33.24	99.13	1551.30	1.92	97.40	11
1	80.48	47.99	5.91	5.23	35.22	31.20	99.13	1677.20	1.93	237.31	5
1	76.88	47.66	5.93	5.23	36.75	32.39	99.03	1613.32	1.99	174.37	8
1	88.61	53.98	6.68	6.02	40.71	36.67	98.93	1641.58	1.96	178.57	3
1	103.59	61.09	6.77	6.05	39.92	35.69	98.93	1695.64	1.95	182.56	2
1	85.02	48.28	7.32	6.67	41.59	37.86	98.72	1760.86	1.98	176.77	7
1	93.00	52.00					98.65	1779.00	1.99	448.00	
1	93.43	61.36	6.16	5.45	40.46	35.82	96.45	1522.73	1.98	232.83	7
1	99.65	66.62	6.81	6.07	45.50	40.60	95.73	1495.81	1.91	175.92	10
1	68.07	42.88	6.05	5.32	38.12	33.48	94.82	1587.63	1.90	170.53	7
1	89.00	50.00					92.97	1785.00	1.91	297.00	
1	85.81	56.73	6.36	5.59	42.04	36.96	92.72	1512.56	1.95	287.69	10
1	86.29	55.42	6.35	5.58	40.75	35.86	89.40	1557.11	1.97	185.28	7
1	97.75	62.43	6.63	5.91	42.36	37.72	89.40	1565.80	1.93	186.01	7
1	74.78	56.24	6.17	5.34	46.37	40.13	87.09	1329.79	1.93	219.17	11
1	81.00	56.00					87.09	1442.00	1.97	254.00	
1	83.00	54.00					87.09	1528.00	2.00	168.00	
1	83.00	51.00					87.09	1628.00	1.96	647.00	
1	76.00	49.00					82.84	1537.00	2.00	281.00	
1	73.00	46.00					82.84	1568.00	1.94	139.00	
1	77.00	49.00					82.84	1568.00	1.93	308.00	
1	71.88	50.36	5.52	4.64	38.69	32.48	77.15	1427.08	1.92	155.21	8
1	74.00	48.00					77.15	1535.00	1.97	126.00	
1	77.00	52.00					77.15	1470.00	1.93	280.00	

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
2	81.73	45.89	4.82	4.26	27.08	23.94	100.00	1780.96	1.97	256.35	9
2	101.86	57.24	5.94	5.63	33.38	31.66	100.00	1779.44	1.97	195.43	7
2	73.40	41.94	4.35	3.78	24.87	21.61	100.00	1750.26	1.93	210.36	9
2	118.20	65.62	6.48	5.92	35.97	32.86	100.00	1801.28	1.96	259.18	7
2	130.47	69.88	7.47	6.92	40.03	37.06	100.00	1867.17	1.98	231.31	1
2	177.89	99.46	8.98	8.42	50.21	47.07	99.98	1788.52	1.96	204.08	4
2	178.47	102.23	8.65	8.13	49.52	46.54	99.98	1745.83	1.92	255.73	4
2	192.75	120.35	10.00	9.48	62.44	59.20	99.98	1601.55	1.93	251.30	2
2	181.27	115.70	9.28	8.76	59.22	55.93	99.98	1566.75	1.94	239.18	2
2	150.42	87.73	7.84	7.24	45.72	42.20	99.98	1714.57	1.99	245.23	9
2	160.38	101.81	7.91	7.38	50.18	46.86	99.90	1575.39	1.91	143.46	8
2	177.21	104.97	9.03	8.52	53.49	50.47	99.80	1688.27	1.96	168.37	6
2	188.54	102.09	9.53	9.01	51.61	48.79	99.80	1846.88	1.92	188.54	6
2	189.80	114.71	9.08	8.52	54.89	51.50	99.70	1654.59	1.96	178.57	9
2	156.19	95.15	8.04	7.42	48.99	45.22	99.61	1641.50	1.94	173.20	10
2	196.62	113.75	10.30	9.70	59.62	56.09	99.51	1728.43	1.97	203.05	5
2	207.04	116.37	10.55	10.00	59.31	56.21	99.51	1779.15	1.99	217.09	5
2	134.35	86.17	7.35	6.73	47.12	43.19	99.32	1559.18	1.96	166.84	8
2	164.96	100.01	8.41	7.85	50.99	47.57	99.22	1649.49	1.95	160.00	9
2	166.15	105.68	9.08	8.56	57.73	54.47	99.13	1572.31	1.95	176.92	5
2	194.47	112.85	8.86	8.29	51.41	48.11	99.13	1723.32	1.93	237.31	4
2	191.75	105.73	9.48	8.92	52.29	49.17	99.13	1813.66	1.94	213.92	5
2	154.86	99.83	7.92	7.34	51.03	47.34	99.13	1551.30	1.92	97.40	11
2	169.08	100.81	9.95	9.38	59.31	55.92	99.13	1677.20	1.93	237.31	5
2	187.27	116.08	9.45	8.84	58.56	54.82	99.03	1613.32	1.99	174.37	8
2	181.97	110.85	9.34	8.83	56.88	53.77	98.93	1641.58	1.96	178.57	3
2	181.03	106.76	9.64	9.13	56.86	53.83	98.93	1695.64	1.95	182.56	2
2	241.41	137.10	12.32	11.77	69.98	66.83	98.72	1760.86	1.98	176.77	7
2	151.18	99.28	8.08	7.47	53.07	49.09	96.45	1522.73	1.98	232.83	7
2	213.79	142.92	11.47	10.89	76.65	72.80	95.73	1495.81	1.91	175.92	10
2	176.84	111.39	9.11	8.53	57.35	53.70	94.82	1587.63	1.90	170.53	7
2	216.58	143.19	10.51	9.90	69.50	65.43	92.72	1512.56	1.95	287.69	10
2	225.55	144.85	11.37	10.71	73.02	68.79	89.40	1557.11	1.97	185.28	7
2	223.14	142.51	11.97	11.35	76.44	72.47	89.40	1565.80	1.93	186.01	7
2	209.67	157.67	6.17	5.34	46.37	40.13	87.09	1329.79	1.93	219.17	11
2	232.99	163.26	12.66	11.98	88.69	83.94	77.15	1427.08	1.92	155.21	8
3	199.31	113.87	4.35	3.78	24.87	21.61	100.00	1750.26	1.93	210.36	9
3	209.64	117.71	4.82	4.26	27.08	23.94	100.00	1780.96	1.97	256.35	9
3	218.95	123.04	5.94	5.63	33.38	31.66	100.00	1779.44	1.97	195.43	7
3	222.45	123.50	6.48	5.92	35.97	32.86	100.00	1801.28	1.96	259.18	7
3	237.71	127.31	7.47	6.92	40.03	37.06	100.00	1867.17	1.98	231.31	1
3	269.73	150.81	8.98	8.42	50.21	47.07	99.98	1788.52	1.96	204.08	4
3	263.72	151.05	8.65	8.13	49.52	46.54	99.98	1745.83	1.92	255.73	4
3	272.19	169.96	10.00	9.48	62.44	59.20	99.98	1601.55	1.93	251.30	2
3	271.82	173.49	9.28	8.76	59.22	55.93	99.98	1566.75	1.94	239.18	2
3	250.42	146.05	7.84	7.24	45.72	42.20	99.98	1714.57	1.99	245.23	9
3	240.84	152.87	7.91	7.38	50.18	46.86	99.90	1575.39	1.91	143.46	8
3	265.99	157.55	9.03	8.52	53.49	50.47	99.80	1688.27	1.96	168.37	6
3	276.91	149.93	9.53	9.01	51.61	48.79	99.80	1846.88	1.92	188.54	6
3	269.05	162.61	9.08	8.52	54.89	51.50	99.70	1654.59	1.96	178.57	9
3	245.19	149.37	8.04	7.42	48.99	45.22	99.61	1641.50	1.94	173.20	10
3	290.86	168.28	10.30	9.70	59.62	56.09	99.51	1728.43	1.97	203.05	5
3	297.82	167.40	10.55	10.00	59.31	56.21	99.51	1779.15	1.99	217.09	5
3	240.14	154.01	7.35	6.73	47.12	43.19	99.32	1559.18	1.96	166.84	8
3	248.38	150.58	8.41	7.85	50.99	47.57	99.22	1649.49	1.95	160.00	9
3	258.63	164.49	9.08	8.56	57.73	54.47	99.13	1572.31	1.95	176.92	5
3	278.24	161.46	8.86	8.29	51.41	48.11	99.13	1723.32	1.93	237.31	4
3	275.60	151.96	9.48	8.92	52.29	49.17	99.13	1813.66	1.94	213.92	5
3	240.63	155.11	7.92	7.34	51.03	47.34	99.13	1551.30	1.92	97.40	11
3	250.26	149.21	9.95	9.38	59.31	55.92	99.13	1677.20	1.93	237.31	5
3	264.99	164.25	9.45	8.84	58.56	54.82	99.03	1613.32	1.99	174.37	8
3	271.43	165.35	9.34	8.83	56.88	53.77	98.93	1641.58	1.96	178.57	3
3	282.56	166.64	9.64	9.13	56.86	53.83	98.93	1695.64	1.95	182.56	2
3	329.12	186.91	12.32	11.77	69.98	66.83	98.72	1760.86	1.98	176.77	7
3	240.91	158.21	8.08	7.47	53.07	49.09	96.45	1522.73	1.98	232.83	7
3	305.06	203.94	11.47	10.89	76.65	72.80	95.73	1495.81	1.91	175.92	10
3	245.61	154.70	9.11	8.53	57.35	53.70	94.82	1587.63	1.90	170.53	7
3	301.88	199.58	10.51	9.90	69.50	65.43	92.72	1512.56	1.95	287.69	10
3	309.98	199.08	11.37	10.71	73.02	68.79	89.40	1557.11	1.97	185.28	7
3	314.33	200.75	11.97	11.35	76.44	72.47	89.40	1565.80	1.93	186.01	7
3	285.49	214.69	6.17	5.34	46.37	40.13	87.09	1329.79	1.93	219.17	11
3	305.38	213.99	12.66	11.98	88.69	83.94	77.15	1427.08	1.92	155.21	8

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
4	222.50	124.93	11.62	11.37	65.27	63.84	100.00	1780.96	1.97	256.35	
4	204.23	114.77	11.32	10.96	63.61	61.62	100.00	1779.44	1.97	195.43	
4	200.86	114.76	11.24	10.98	64.24	62.76	100.00	1750.26	1.93	210.36	
4	210.37	116.79	11.53	11.22	64.01	62.31	100.00	1801.28	1.96	259.18	7
4	226.43	121.27	12.02	11.72	64.38	62.75	100.00	1867.17	1.98	231.31	1
4	230.78	129.04	12.40	12.04	69.32	67.32	99.98	1788.52	1.96	204.08	4
4	230.21	131.86	12.29	11.93	70.41	68.32	99.98	1745.83	1.92	255.73	4
4	192.57	120.24	11.35	11.04	70.85	68.91	99.98	1601.55	1.93	251.30	2
4	203.61	129.96	10.26	9.95	65.47	63.50	99.98	1566.75	1.94	239.18	2
4	228.31	133.16	11.96	11.56	69.75	67.41	99.98	1714.57	1.99	245.23	9
4	205.06	130.16	11.47	11.15	72.78	70.79	99.90	1575.39	1.91	143.46	8
4	227.55	134.78	12.55	12.14	74.34	71.92	99.80	1688.27	1.96	168.37	6
4	229.51	124.27	12.19	11.87	65.99	64.30	99.80	1846.88	1.92	188.54	6
4	228.74	138.25	12.35	12.04	74.62	72.77	99.70	1654.59	1.96	178.57	9
4	227.15	138.38	11.91	11.55	72.54	70.34	99.61	1641.50	1.94	173.20	10
4	222.17	128.54	11.98	11.57	69.31	66.96	99.51	1728.43	1.97	203.05	5
4	221.44	124.46	11.91	11.56	66.94	64.96	99.51	1779.15	1.99	217.09	5
4	191.50	122.82	10.20	9.85	65.44	63.15	99.32	1559.18	1.96	166.84	8
4	211.79	128.40	11.74	11.38	71.20	69.02	99.22	1649.49	1.95	160.00	9
4	188.21	119.70	10.72	10.10	68.17	64.25	99.13	1572.31	1.95	176.92	5
4	208.29	120.87	11.14	10.73	64.64	62.24	99.13	1723.32	1.93	237.31	4
4	212.20	117.00	11.24	10.93	61.96	60.25	99.13	1813.66	1.94	213.92	5
4	192.53	124.11	10.31	9.79	66.48	63.12	99.13	1551.30	1.92	97.40	11
4	204.15	121.72	10.88	10.31	64.87	61.48	99.13	1677.20	1.93	237.31	5
4	201.68	125.01	10.95	10.65	67.90	66.03	99.03	1613.32	1.99	174.37	8
4	219.39	133.64	11.89	11.28	72.42	68.69	98.93	1641.58	1.96	178.57	3
4	215.73	127.22	11.64	11.28	68.65	66.54	98.93	1695.64	1.95	182.56	2
4	213.30	121.13	11.26	10.66	63.96	60.52	98.72	1760.86	1.98	176.77	7
4	200.00	112.00					98.65	1779.00	1.99	448.00	
4	156.40	102.71	8.33	7.98	54.73	52.40	96.45	1522.73	1.98	232.83	7
4	143.28	95.79	7.64	7.17	51.10	47.95	95.73	1495.81	1.91	175.92	10
4	147.54	92.93	7.68	7.32	48.40	46.08	94.82	1587.63	1.90	170.53	7
4	143.00	80.00					92.97	1785.00	1.91	297.00	
4	133.68	88.38	7.08	6.56	46.79	43.40	92.72	1512.56	1.95	287.69	10
4	100.00	64.22	4.87	4.21	31.30	27.06	89.40	1557.11	1.97	185.28	7
4	101.73	64.97	5.03	4.35	32.10	27.80	89.40	1565.80	1.93	186.01	7
4	79.62	59.87	3.99	3.52	30.00	26.50	87.09	1329.79	1.93	219.17	11
4	95.00	62.00					87.09	1528.00	2.00	168.00	
4	86.00	53.00					87.09	1628.00	1.96	647.00	
4	83.00	58.00					87.09	1442.00	1.97	254.00	
4	70.00	45.00					82.84	1537.00	2.00	281.00	
4	81.00	52.00					82.84	1568.00	1.93	308.00	
4	71.00	45.00					82.84	1568.00	1.94	139.00	
4	59.38	41.61	2.50	1.93	17.52	13.50	77.15	1427.08	1.92	155.21	8
4	61.00	42.00					77.15	1470.00	1.93	280.00	
4	61.00	40.00					77.15	1535.00	1.97	126.00	

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
5	54.82	30.78	2.84	1.93	15.96	10.83	100.00	1780.96	1.97	256.35	
5	52.62	29.57	2.54	1.88	14.26	10.55	100.00	1779.44	1.97	195.43	
5	54.23	30.98	2.80	2.12	15.99	12.14	100.00	1750.26	1.93	210.36	
5	52.04	28.89	2.50	1.84	13.88	10.20	100.00	1801.28	1.96	259.18	7
5	54.21	29.03	2.47	1.77	13.25	9.47	100.00	1867.17	1.98	231.31	1
5	45.92	25.67	2.30	1.73	12.84	9.70	99.98	1788.52	1.96	204.08	4
5	46.53	26.65	2.19	1.61	12.53	9.25	99.98	1745.83	1.92	255.73	4
5	44.21	27.61	2.07	1.61	12.94	10.03	99.98	1601.55	1.93	251.30	2
5	41.58	26.54	2.01	1.55	12.83	9.87	99.98	1566.75	1.94	239.18	2
5	47.57	27.75	2.41	1.86	14.07	10.84	99.98	1714.57	1.99	245.23	9
5	48.34	30.69	2.25	1.73	14.29	10.97	99.90	1575.39	1.91	143.46	8
5	49.32	29.21	2.40	1.89	14.20	11.18	99.80	1688.27	1.96	168.37	6
5	48.61	26.32	2.34	1.77	12.69	9.59	99.80	1846.88	1.92	188.54	6
5	51.53	31.14	2.60	2.09	15.73	12.64	99.70	1654.59	1.96	178.57	9
5	56.53	34.44	2.73	2.22	16.64	13.50	99.61	1641.50	1.94	173.20	10
5	49.58	28.68	2.28	1.73	13.22	9.99	99.51	1728.43	1.97	203.05	5
5	47.57	26.74	2.46	1.91	13.84	10.73	99.51	1779.15	1.99	217.09	5
5	47.96	30.76	2.14	1.58	13.74	10.14	99.32	1559.18	1.96	166.84	8
5	53.16	32.23	2.62	2.10	15.86	12.75	99.22	1649.49	1.95	160.00	9
5	43.76	27.83	1.95	1.44	12.39	9.13	99.13	1572.31	1.95	176.92	5
5	42.83	24.85	2.02	1.45	11.73	8.42	99.13	1723.32	1.93	237.31	4
5	46.39	25.58	2.06	1.44	11.37	7.96	99.13	1813.66	1.94	213.92	5
5	46.70	30.10	2.24	1.77	14.44	11.42	99.13	1551.30	1.92	97.40	11
5	43.52	25.95	1.97	1.45	11.74	8.65	99.13	1677.20	1.93	237.31	5
5	45.56	28.24	2.26	1.76	14.02	10.90	99.03	1613.32	1.99	174.37	8
5	48.30	29.42	2.35	1.84	14.30	11.19	98.93	1641.58	1.96	178.57	3
5	47.52	28.03	2.31	1.74	13.61	10.28	98.93	1695.64	1.95	182.56	2
5	39.56	22.47	1.82	1.31	10.33	7.46	98.72	1760.86	1.98	176.77	7
5	45.00	25.00					98.65	1779.00	1.99	448.00	
5	40.74	26.76	1.82	1.26	11.94	8.29	96.45	1522.73	1.98	232.83	7
5	32.29	21.58	1.52	1.05	10.15	7.00	95.73	1495.81	1.91	175.92	10
5	35.79	22.54	2.05	1.11	12.93	6.96	94.82	1587.63	1.90	170.53	7
5	36.00	20.00					92.97	1785.00	1.91	297.00	
5	32.82	21.70	1.49	1.03	9.83	6.78	92.72	1512.56	1.95	287.69	10
5	31.30	20.10	1.32	0.76	8.48	4.89	89.40	1557.11	1.97	185.28	7
5	31.95	20.41	1.30	0.78	8.27	4.96	89.40	1565.80	1.93	186.01	7
5	27.63	20.78	1.19	0.62	8.96	4.68	87.09	1329.79	1.93	219.17	11
5	30.00	20.00					87.09	1528.00	2.00	168.00	
5	29.00	18.00					87.09	1628.00	1.96	647.00	
5	29.00	20.00					87.09	1442.00	1.97	254.00	
5	29.00	19.00					82.84	1537.00	2.00	281.00	
5	26.00	17.00					82.84	1568.00	1.93	308.00	
5	29.00	18.00					82.84	1568.00	1.94	139.00	
5	25.87	18.13	1.04	0.57	7.30	4.01	77.15	1427.08	1.92	155.21	8
5	26.00	18.00					77.15	1470.00	1.93	280.00	
5	27.00	18.00					77.15	1535.00	1.97	126.00	

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
6	107.61	60.42	4.67	3.76	26.22	21.09	100.00	1780.96	1.97	256.35	
6	86.29	48.50	3.96	3.20	22.25	17.97	100.00	1779.44	1.97	195.43	
6	106.22	60.69	3.26	2.38	18.65	13.62	100.00	1750.26	1.93	210.36	
6	87.07	48.34	4.08	3.32	22.66	18.41	100.00	1801.28	1.96	259.18	7
6	77.78	41.66	3.54	2.78	18.93	14.88	100.00	1867.17	1.98	231.31	1
6	50.68	28.34	1.99	1.48	11.13	8.27	99.98	1788.52	1.96	204.08	4
6	48.26	27.65	1.88	1.41	10.74	8.05	99.98	1745.83	1.92	255.73	4
6	44.39	27.71	1.87	1.45	11.65	9.06	99.98	1601.55	1.93	251.30	2
6	42.44	27.09	1.65	1.24	10.53	7.90	99.98	1566.75	1.94	239.18	2
6	47.40	27.65	1.91	1.41	11.14	8.21	99.98	1714.57	1.99	245.23	9
6	43.80	27.81	1.68	1.20	10.63	7.64	99.90	1575.39	1.91	143.46	8
6	43.20	25.59	1.68	1.28	9.97	7.56	99.80	1688.27	1.96	168.37	6
6	51.91	28.11	1.98	1.51	10.72	8.18	99.80	1846.88	1.92	188.54	6
6	43.37	26.21	1.63	1.22	9.87	7.40	99.70	1654.59	1.96	178.57	9
6	44.85	27.32	1.60	1.19	9.73	7.22	99.61	1641.50	1.94	173.20	10
6	48.05	27.80	1.83	1.42	10.57	8.22	99.51	1728.43	1.97	203.05	5
6	50.42	28.34	2.01	1.56	11.30	8.76	99.51	1779.15	1.99	217.09	5
6	44.22	28.36	1.63	1.22	10.47	7.85	99.32	1559.18	1.96	166.84	8
6	46.67	28.29	1.74	1.33	10.57	8.08	99.22	1649.49	1.95	160.00	9
6	38.63	24.57	1.49	1.08	9.46	6.85	99.13	1572.31	1.95	176.92	5
6	43.52	25.26	1.92	1.45	11.12	8.42	99.13	1723.32	1.93	237.31	4
6	51.72	28.52	2.06	1.60	11.37	8.81	99.13	1813.66	1.94	213.92	5
6	33.16	21.38	1.25	0.94	8.06	6.04	99.13	1551.30	1.92	97.40	11
6	49.22	29.35	1.66	1.30	9.89	7.72	99.13	1677.20	1.93	237.31	5
6	44.89	27.83	1.71	1.31	10.59	8.10	99.03	1613.32	1.99	174.37	8
6	43.54	26.52	1.68	1.33	10.26	8.08	98.93	1641.58	1.96	178.57	3
6	47.69	28.13	2.05	1.64	12.10	9.68	98.93	1695.64	1.95	182.56	2
6	31.65	17.97	1.21	0.86	6.88	4.88	98.72	1760.86	1.98	176.77	7
6	45.00	25.00					98.65	1779.00	1.99	448.00	
6	46.30	30.40	1.87	1.41	12.27	9.29	96.45	1522.73	1.98	232.83	7
6	23.21	15.52	0.89	0.63	5.95	4.20	95.73	1495.81	1.91	175.92	10
6	48.60	30.61	2.05	1.58	12.93	9.95	94.82	1587.63	1.90	170.53	7
6	31.00	17.00					92.97	1785.00	1.91	297.00	
6	24.79	16.39	0.97	0.67	6.44	4.41	92.72	1512.56	1.95	287.69	10
6	24.37	15.65	0.96	0.66	6.19	4.24	89.40	1557.11	1.97	185.28	7
6	28.32	18.09	1.04	0.73	6.62	4.63	89.40	1565.80	1.93	186.01	7
6	22.28	16.75	0.83	0.57	6.23	4.29	87.09	1329.79	1.93	219.17	11
6	27.00	17.00					87.09	1528.00	2.00	168.00	
6	23.00	14.00					87.09	1628.00	1.96	647.00	
6	22.00	15.00					87.09	1442.00	1.97	254.00	
6	22.00	14.00					82.84	1537.00	2.00	281.00	
6	25.00	16.00					82.84	1568.00	1.93	308.00	
6	22.00	14.00					82.84	1568.00	1.94	139.00	
6	19.97	13.99	0.68	0.47	4.74	3.28	77.15	1427.08	1.92	155.21	8
6	21.00	14.00					77.15	1470.00	1.93	280.00	
6	19.00	13.00					77.15	1535.00	1.97	126.00	

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
7	68.36	38.38	3.25	2.64	18.24	14.82	100.00	1780.96	1.97	256.35	
7	65.99	37.08	3.25	2.84	18.26	15.97	100.00	1779.44	1.97	195.43	
7	65.63	37.50	3.21	2.64	18.35	15.10	100.00	1750.26	1.93	210.36	
7	63.95	35.50	3.27	2.81	18.13	15.58	100.00	1801.28	1.96	259.18	7
7	64.48	34.53	3.33	2.88	17.85	15.42	100.00	1867.17	1.98	231.31	1
7	49.32	27.58	2.55	2.24	14.26	12.55	99.98	1788.52	1.96	204.08	4
7	47.92	27.45	2.50	2.14	14.32	12.23	99.98	1745.83	1.92	255.73	4
7	39.90	24.91	2.12	1.87	13.26	11.65	99.98	1601.55	1.93	251.30	2
7	38.66	24.68	1.91	1.65	12.17	10.53	99.98	1566.75	1.94	239.18	2
7	43.05	25.11	2.16	1.81	12.60	10.55	99.98	1714.57	1.99	245.23	9
7	40.49	25.70	1.94	1.62	12.30	10.30	99.90	1575.39	1.91	143.46	8
7	40.99	24.28	2.09	1.79	12.39	10.58	99.80	1688.27	1.96	168.37	6
7	43.23	23.41	2.19	1.88	11.84	10.15	99.80	1846.88	1.92	188.54	6
7	38.44	23.23	1.84	1.53	11.10	9.25	99.70	1654.59	1.96	178.57	9
7	38.32	23.34	1.75	1.44	10.68	8.79	99.61	1641.50	1.94	173.20	10
7	35.03	20.26	1.78	1.47	10.28	8.52	99.51	1728.43	1.97	203.05	5
7	33.84	19.02	1.76	1.51	9.89	8.47	99.51	1779.15	1.99	217.09	5
7	34.52	22.14	1.63	1.33	10.47	8.51	99.32	1559.18	1.96	166.84	8
7	36.41	22.07	1.74	1.44	10.57	8.71	99.22	1649.49	1.95	160.00	9
7	31.79	20.22	1.59	1.33	10.11	8.48	99.13	1572.31	1.95	176.92	5
7	31.95	18.54	1.87	1.61	10.82	9.32	99.13	1723.32	1.93	237.31	4
7	39.00	21.51	1.96	1.65	10.80	9.09	99.13	1813.66	1.94	213.92	5
7	29.69	19.14	1.46	1.15	9.40	7.39	99.13	1551.30	1.92	97.40	11
7	37.31	22.24	1.66	1.40	9.89	8.34	99.13	1677.20	1.93	237.31	5
7	31.66	19.62	1.56	1.26	9.66	7.79	99.03	1613.32	1.99	174.37	8
7	32.31	19.68	1.68	1.43	10.26	8.70	98.93	1641.58	1.96	178.57	3
7	33.68	19.86	1.69	1.44	9.98	8.47	98.93	1695.64	1.95	182.56	2
7	29.46	16.73	1.57	1.36	8.89	7.74	98.72	1760.86	1.98	176.77	7
7	36.00	20.00					98.65	1779.00	1.99	448.00	
7	31.82	20.90	1.52	1.21	9.95	7.96	96.45	1522.73	1.98	232.83	7
7	20.42	13.65	1.05	0.84	7.00	5.60	95.73	1495.81	1.91	175.92	10
7	30.35	19.12	1.47	1.16	9.28	7.29	94.82	1587.63	1.90	170.53	7
7	21.00	12.00					92.97	1785.00	1.91	297.00	
7	18.63	12.32	0.97	0.77	6.44	5.09	92.72	1512.56	1.95	287.69	10
7	15.40	9.89	0.76	0.56	4.89	3.59	89.40	1557.11	1.97	185.28	7
7	15.37	9.82	0.78	0.47	4.96	2.98	89.40	1565.80	1.93	186.01	7
7	15.37	11.56	0.67	0.36	5.07	2.73	87.09	1329.79	1.93	219.17	11
7	15.00	10.00					87.09	1528.00	2.00	168.00	
7	14.00	8.00					87.09	1628.00	1.96	647.00	
7	15.00	11.00					87.09	1442.00	1.97	254.00	
7	12.00	7.00					82.84	1537.00	2.00	281.00	
7	12.00	8.00					82.84	1568.00	1.93	308.00	
7	11.00	7.00					82.84	1568.00	1.94	139.00	
7	10.94	7.66	0.52	0.31	3.65	2.19	77.15	1427.08	1.92	155.21	8
7	9.00	6.00					77.15	1470.00	1.93	280.00	
7	11.00	7.00					77.15	1535.00	1.97	126.00	

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
8	136.55	76.67	7.26	6.19	40.76	34.77	100.00	1780.96	1.97	256.35	
8	120.98	67.99	6.65	6.04	37.37	33.95	100.00	1779.44	1.97	195.43	
8	130.22	74.40	7.05	6.48	40.26	37.00	100.00	1750.26	1.93	210.36	
8	126.02	69.96	6.58	6.12	36.54	33.99	100.00	1801.28	1.96	259.18	7
8	133.84	71.68	6.87	6.41	36.79	34.35	100.00	1867.17	1.98	231.31	1
8	117.69	65.80	6.22	5.92	34.80	33.09	99.98	1788.52	1.96	204.08	4
8	116.49	66.73	6.20	5.89	35.50	33.71	99.98	1745.83	1.92	255.73	4
8	99.48	62.12	5.49	5.23	34.29	32.68	99.98	1601.55	1.93	251.30	2
8	93.64	59.77	5.10	4.85	32.57	30.93	99.98	1566.75	1.94	239.18	2
8	100.00	58.32	5.53	5.23	32.24	30.48	99.98	1714.57	1.99	245.23	9
8	91.10	57.83	4.97	4.71	31.57	29.91	99.90	1575.39	1.91	143.46	8
8	106.12	62.86	5.66	5.41	33.54	32.03	99.80	1688.27	1.96	168.37	6
8	113.54	61.48	5.89	5.57	31.87	30.17	99.80	1846.88	1.92	188.54	6
8	90.82	54.89	4.95	4.64	29.91	28.06	99.70	1654.59	1.96	178.57	9
8	79.90	48.67	4.28	4.02	26.06	24.49	99.61	1641.50	1.94	173.20	10
8	95.77	55.41	5.28	5.03	30.54	29.07	99.51	1728.43	1.97	203.05	5
8	102.85	57.81	5.53	5.28	31.07	29.66	99.51	1779.15	1.99	217.09	5
8	84.35	54.10	4.44	4.18	28.47	26.83	99.32	1559.18	1.96	166.84	8
8	81.03	49.12	4.51	4.26	27.36	25.80	99.22	1649.49	1.95	160.00	9
8	95.21	60.56	5.08	4.87	32.29	30.98	99.13	1572.31	1.95	176.92	5
8	100.35	58.23	5.60	5.34	32.47	30.97	99.13	1723.32	1.93	237.31	4
8	109.97	60.63	5.77	5.52	31.83	30.41	99.13	1813.66	1.94	213.92	5
8	73.78	47.56	4.06	3.80	26.19	24.51	99.13	1551.30	1.92	97.40	11
8	105.70	63.02	5.18	4.97	30.89	29.66	99.13	1677.20	1.93	237.31	5
8	84.59	52.43	4.67	4.42	28.97	27.41	99.03	1613.32	1.99	174.37	8
8	95.92	58.43	5.15	4.95	31.39	30.15	98.93	1641.58	1.96	178.57	3
8	92.82	54.74	5.18	4.92	30.55	29.03	98.93	1695.64	1.95	182.56	2
8	114.48	65.01	6.41	6.26	36.43	35.57	98.72	1760.86	1.98	176.77	7
8	96.00	54.00					98.65	1779.00	1.99	448.00	
8	79.80	52.40	4.24	3.99	27.86	26.20	96.45	1522.73	1.98	232.83	7
8	88.48	59.15	4.76	4.55	31.85	30.45	95.73	1495.81	1.91	175.92	10
8	78.77	49.62	4.42	4.16	27.85	26.19	94.82	1587.63	1.90	170.53	7
8	87.00	49.00					92.97	1785.00	1.91	297.00	
8	77.09	50.97	4.21	4.00	27.80	26.45	92.72	1512.56	1.95	287.69	10
8	69.20	44.44	3.65	3.50	23.47	22.49	89.40	1557.11	1.97	185.28	7
8	67.01	42.80	3.58	3.42	22.83	21.84	89.40	1565.80	1.93	186.01	7
8	56.82	42.73	3.06	2.90	22.99	21.82	87.09	1329.79	1.93	219.17	11
8	63.00	41.00					87.09	1528.00	2.00	168.00	
8	60.00	37.00					87.09	1628.00	1.96	647.00	
8	60.00	42.00					87.09	1442.00	1.97	254.00	
8	47.00	30.00					82.84	1537.00	2.00	281.00	
8	52.00	33.00					82.84	1568.00	1.93	308.00	
8	47.00	30.00					82.84	1568.00	1.94	139.00	
8	32.29	22.63	1.67	1.51	11.68	10.58	77.15	1427.08	1.92	155.21	8
8	39.00	27.00					77.15	1470.00	1.93	280.00	
8	35.00	22.00					77.15	1535.00	1.97	126.00	

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
9	116.07	65.17	4.47	4.31	25.08	24.23	100.00	1780.96	1.97	256.35	9
9	137.73	77.40	6.04	5.94	33.95	33.38	100.00	1779.44	1.97	195.43	7
9	120.55	68.88	4.25	4.09	24.27	23.39	100.00	1750.26	1.93	210.36	9
9	139.29	77.33	5.77	5.66	32.01	31.44	100.00	1801.28	1.96	259.18	7
9	165.99	88.90	6.77	6.67	36.25	35.70	100.00	1867.17	1.98	231.31	1
9	142.86	79.87	6.38	6.33	35.66	35.37	99.98	1788.52	1.96	204.08	4
9	140.45	80.45	6.41	6.35	36.69	36.40	99.98	1745.83	1.92	255.73	4
9	125.73	78.51	5.75	5.70	35.91	35.59	99.98	1601.55	1.93	251.30	2
9	124.74	79.62	5.52	5.46	35.20	34.87	99.98	1566.75	1.94	239.18	2
9	137.69	80.30	6.08	6.03	35.46	35.17	99.98	1714.57	1.99	245.23	9
9	119.72	75.99	5.34	5.29	33.90	33.57	99.90	1575.39	1.91	143.46	8
9	122.11	72.33	5.26	5.20	31.13	30.83	99.80	1688.27	1.96	168.37	6
9	132.47	71.72	5.47	5.42	29.61	29.33	99.80	1846.88	1.92	188.54	6
9	109.69	66.30	4.85	4.80	29.29	28.99	99.70	1654.59	1.96	178.57	9
9	101.37	61.76	4.74	4.69	28.89	28.58	99.61	1641.50	1.94	173.20	10
9	110.83	64.12	5.03	4.97	29.07	28.78	99.51	1728.43	1.97	203.05	5
9	111.06	62.42	5.08	5.03	28.53	28.24	99.51	1779.15	1.99	217.09	5
9	91.67	58.79	3.83	3.78	24.54	24.21	99.32	1559.18	1.96	166.84	8
9	98.29	59.59	4.10	4.05	24.87	24.56	99.22	1649.49	1.95	160.00	9
9	95.38	60.67	4.26	4.15	27.07	26.42	99.13	1572.31	1.95	176.92	5
9	96.20	55.82	3.99	3.89	23.15	22.55	99.13	1723.32	1.93	237.31	4
9	101.20	55.80	4.12	4.07	22.74	22.45	99.13	1813.66	1.94	213.92	5
9	85.42	55.06	3.91	3.85	25.18	24.84	99.13	1551.30	1.92	97.40	11
9	89.81	53.55	3.89	3.83	23.17	22.86	99.13	1677.20	1.93	237.31	5
9	90.62	56.17	4.07	4.02	25.23	24.92	99.03	1613.32	1.99	174.37	8
9	98.81	60.19	4.18	4.13	25.49	25.17	98.93	1641.58	1.96	178.57	3
9	101.71	59.98	4.41	4.36	26.01	25.71	98.93	1695.64	1.95	182.56	2
9	143.60	81.55	6.97	6.92	39.58	39.29	98.72	1760.86	1.98	176.77	7
9	81.14	53.29	3.69	3.64	24.21	23.88	96.45	1522.73	1.98	232.83	7
9	161.26	107.81	7.70	7.64	51.45	51.10	95.73	1495.81	1.91	175.92	10
9	82.81	52.16	3.53	3.47	22.21	21.88	94.82	1587.63	1.90	170.53	7
9	138.63	91.65	6.87	6.82	45.43	45.09	92.72	1512.56	1.95	287.69	10
9	162.44	104.32	8.07	8.02	51.83	51.51	89.40	1557.11	1.97	185.28	7
9	154.40	98.61	7.98	7.93	50.96	50.63	89.40	1565.80	1.93	186.01	7
9	162.35	122.09	8.55	8.39	64.29	63.12	87.09	1329.79	1.93	219.17	11
9	169.27	118.61	8.13	8.02	56.93	56.20	77.15	1427.08	1.92	155.21	8

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
10	160.91	90.35	8.12	7.87	45.60	44.18	100.00	1780.96	1.97	256.35	
10	148.05	83.20	8.02	7.77	45.07	43.65	100.00	1779.44	1.97	195.43	
10	159.41	91.08	8.19	7.98	46.77	45.59	100.00	1750.26	1.93	210.36	
10	147.45	81.86	8.16	7.96	45.32	44.19	100.00	1801.28	1.96	259.18	7
10	147.98	79.25	8.18	8.03	43.82	43.01	100.00	1867.17	1.98	231.31	1
10	130.61	73.03	6.94	6.73	38.80	37.66	99.98	1788.52	1.96	204.08	4
10	123.78	70.90	6.88	6.67	39.38	38.19	99.98	1745.83	1.92	255.73	4
10	108.29	67.62	5.80	5.60	36.23	34.94	99.98	1601.55	1.93	251.30	2
10	99.14	63.28	5.26	5.05	33.56	32.24	99.98	1566.75	1.94	239.18	2
10	106.87	62.33	5.78	5.48	33.70	31.95	99.98	1714.57	1.99	245.23	9
10	98.25	62.37	5.18	4.97	32.90	31.57	99.90	1575.39	1.91	143.46	8
10	111.90	66.28	5.87	5.61	34.75	33.24	99.80	1688.27	1.96	168.37	6
10	126.74	68.62	6.20	5.89	33.56	31.87	99.80	1846.88	1.92	188.54	6
10	102.04	61.67	5.26	4.95	31.76	29.91	99.70	1654.59	1.96	178.57	9
10	93.30	56.84	4.79	4.48	29.20	27.32	99.61	1641.50	1.94	173.20	10
10	97.46	56.39	4.87	4.57	28.19	26.43	99.51	1728.43	1.97	203.05	5
10	96.65	54.32	5.08	4.77	28.53	26.83	99.51	1779.15	1.99	217.09	5
10	88.27	56.61	4.39	4.13	28.14	26.51	99.32	1559.18	1.96	166.84	8
10	97.26	58.97	5.08	4.77	30.78	28.91	99.22	1649.49	1.95	160.00	9
10	90.43	57.51	4.62	4.41	29.35	28.05	99.13	1572.31	1.95	176.92	5
10	101.73	59.03	5.44	5.18	31.57	30.07	99.13	1723.32	1.93	237.31	4
10	112.20	61.86	5.77	5.41	31.83	29.84	99.13	1813.66	1.94	213.92	5
10	76.22	49.13	3.85	3.49	24.84	22.49	99.13	1551.30	1.92	97.40	11
10	101.38	60.45	5.13	4.51	30.58	26.88	99.13	1677.20	1.93	237.31	5
10	85.76	53.16	4.47	4.17	27.72	25.85	99.03	1613.32	1.99	174.37	8
10	93.54	56.98	4.69	4.39	28.59	26.73	98.93	1641.58	1.96	178.57	3
10	85.30	50.30	4.67	4.36	27.52	25.71	98.93	1695.64	1.95	182.56	2
10	93.27	52.97	5.00	4.80	28.40	27.25	98.72	1760.86	1.98	176.77	7
10	95.00	53.00					98.65	1779.00	1.99	448.00	
10	77.44	50.86	3.94	3.64	25.87	23.88	96.45	1522.73	1.98	232.83	7
10	63.87	42.70	3.25	3.09	21.70	20.65	95.73	1495.81	1.91	175.92	10
10	68.25	42.99	3.89	3.58	24.53	22.54	94.82	1587.63	1.90	170.53	7
10	64.00	36.00					92.97	1785.00	1.91	297.00	
10	58.46	38.65	3.03	2.77	20.00	18.31	92.72	1512.56	1.95	287.69	10
10	46.02	29.56	2.34	2.08	15.00	13.37	89.40	1557.11	1.97	185.28	7
10	46.29	29.56	2.28	2.02	14.56	12.91	89.40	1565.80	1.93	186.01	7
10	37.65	28.31	1.81	1.61	13.64	12.08	87.09	1329.79	1.93	219.17	11
10	39.00	26.00					87.09	1528.00	2.00	168.00	
10	40.00	24.00					87.09	1628.00	1.96	647.00	
10	38.00	26.00					87.09	1442.00	1.97	254.00	
10	29.00	19.00					82.84	1537.00	2.00	281.00	
10	30.00	19.00					82.84	1568.00	1.93	308.00	
10	30.00	19.00					82.84	1568.00	1.94	139.00	
10	27.08	18.98	1.25	0.99	8.76	6.93	77.15	1427.08	1.92	155.21	8
10	25.00	17.00					77.15	1470.00	1.93	280.00	
10	25.00	17.00					77.15	1535.00	1.97	126.00	

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
11	97.63	54.82	4.31	4.01	24.23	22.52	100.00	1780.96	1.97	256.35	9
11	121.49	68.27	5.89	5.58	33.09	31.38	100.00	1779.44	1.97	195.43	7
11	97.93	55.95	4.61	4.30	26.35	24.57	100.00	1750.26	1.93	210.36	9
11	121.77	67.60	5.92	5.61	32.86	31.16	100.00	1801.28	1.96	259.18	7
11	123.74	66.27	5.76	5.51	30.84	29.48	100.00	1867.17	1.98	231.31	1
11	150.34	84.06	7.60	7.30	42.50	40.79	99.98	1788.52	1.96	204.08	4
11	148.09	84.82	7.03	6.72	40.27	38.48	99.98	1745.83	1.92	255.73	4
11	129.53	80.88	6.27	6.01	39.15	37.53	99.98	1601.55	1.93	251.30	2
11	127.84	81.59	6.29	6.03	40.14	38.49	99.98	1566.75	1.94	239.18	2
11	153.43	89.49	7.69	7.39	44.84	43.08	99.98	1714.57	1.99	245.23	9
11	142.23	90.28	6.54	6.23	41.54	39.55	99.90	1575.39	1.91	143.46	8
11	136.56	80.89	6.84	6.48	40.50	38.38	99.80	1688.27	1.96	168.37	6
11	173.09	93.72	7.81	7.34	42.30	39.76	99.80	1846.88	1.92	188.54	6
11	147.79	89.32	6.79	6.33	41.01	38.24	99.70	1654.59	1.96	178.57	9
11	145.02	88.34	6.70	6.29	40.82	38.31	99.61	1641.50	1.94	173.20	10
11	167.01	96.62	7.66	7.21	44.35	41.70	99.51	1728.43	1.97	203.05	5
11	166.50	93.58	7.94	7.54	44.63	42.37	99.51	1779.15	1.99	217.09	5
11	173.64	111.37	7.76	7.35	49.74	47.12	99.32	1559.18	1.96	166.84	8
11	150.09	90.99	7.38	6.97	44.77	42.28	99.22	1649.49	1.95	160.00	9
11	154.36	98.17	7.23	6.87	45.99	43.71	99.13	1572.31	1.95	176.92	5
11	173.58	100.72	8.96	8.50	52.01	49.31	99.13	1723.32	1.93	237.31	4
11	189.52	104.50	9.43	8.92	52.01	49.17	99.13	1813.66	1.94	213.92	5
11	150.00	96.69	6.82	6.41	43.98	41.30	99.13	1551.30	1.92	97.40	11
11	183.94	109.67	8.29	7.82	49.43	46.65	99.13	1677.20	1.93	237.31	5
11	153.77	95.31	7.59	7.19	47.03	44.54	99.03	1613.32	1.99	174.37	8
11	142.18	86.61	6.94	6.53	42.27	39.78	98.93	1641.58	1.96	178.57	3
11	152.82	90.13	7.44	7.03	43.85	41.43	98.93	1695.64	1.95	182.56	2
11	146.97	83.46	7.68	7.32	43.60	41.59	98.72	1760.86	1.98	176.77	7
11	191.58	125.82	9.29	8.89	61.03	58.37	96.45	1522.73	1.98	232.83	7
11	129.32	86.45	6.34	6.02	42.35	40.25	95.73	1495.81	1.91	175.92	10
11	193.16	121.66	9.74	9.32	61.33	58.68	94.82	1587.63	1.90	170.53	7
11	160.51	106.12	8.00	7.59	52.89	50.18	92.72	1512.56	1.95	287.69	10
11	190.86	122.58	9.04	8.63	58.03	55.42	89.40	1557.11	1.97	185.28	7
11	182.90	116.81	9.22	8.81	58.90	56.25	89.40	1565.80	1.93	186.01	7
11	134.89	101.44	6.48	6.17	48.70	46.37	87.09	1329.79	1.93	219.17	11
11	190.10	133.21	9.01	8.54	63.14	59.85	77.15	1427.08	1.92	155.21	8

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
12	46.53	26.13	2.18	1.88	12.26	10.55	100.00	1780.96	1.97	256.35	
12	46.19	25.96	2.18	1.83	12.27	10.27	100.00	1779.44	1.97	195.43	
12	49.40	28.22	2.28	1.97	13.03	11.25	100.00	1750.26	1.93	210.36	
12	47.96	26.63	2.19	1.79	12.18	9.91	100.00	1801.28	1.96	259.18	7
12	54.71	29.30	2.42	2.02	12.98	10.82	100.00	1867.17	1.98	231.31	1
12	53.74	30.05	2.35	1.89	13.12	10.55	99.98	1788.52	1.96	204.08	4
12	50.17	28.74	2.29	1.88	13.13	10.74	99.98	1745.83	1.92	255.73	4
12	45.60	28.47	2.02	1.61	12.62	10.03	99.98	1601.55	1.93	251.30	2
12	46.91	29.94	1.96	1.49	12.50	9.54	99.98	1566.75	1.94	239.18	2
12	44.89	26.18	2.01	1.61	11.72	9.38	99.98	1714.57	1.99	245.23	9
12	46.07	29.25	2.04	1.62	12.96	10.30	99.90	1575.39	1.91	143.46	8
12	52.72	31.23	2.35	1.84	13.90	10.88	99.80	1688.27	1.96	168.37	6
12	59.03	31.96	2.50	1.93	13.54	10.43	99.80	1846.88	1.92	188.54	6
12	54.42	32.89	2.30	1.99	13.88	12.03	99.70	1654.59	1.96	178.57	9
12	53.09	32.34	2.11	1.55	12.87	9.42	99.61	1641.50	1.94	173.20	10
12	63.96	37.00	2.59	1.98	14.98	11.45	99.51	1728.43	1.97	203.05	5
12	61.31	34.46	2.61	2.01	14.69	11.30	99.51	1779.15	1.99	217.09	5
12	51.70	33.16	2.09	1.58	13.42	10.14	99.32	1559.18	1.96	166.84	8
12	65.98	40.00	2.67	2.10	16.17	12.75	99.22	1649.49	1.95	160.00	9
12	56.75	36.09	2.62	2.05	16.63	13.05	99.13	1572.31	1.95	176.92	5
12	65.98	38.28	2.69	2.07	15.63	12.03	99.13	1723.32	1.93	237.31	4
12	68.21	37.61	2.84	2.22	15.63	12.22	99.13	1813.66	1.94	213.92	5
12	63.02	40.62	2.50	1.88	16.12	12.09	99.13	1551.30	1.92	97.40	11
12	60.97	36.35	2.80	2.18	16.68	12.97	99.13	1677.20	1.93	237.31	5
12	57.96	35.92	2.51	1.91	15.57	11.84	99.03	1613.32	1.99	174.37	8
12	62.07	37.81	2.60	2.04	15.85	12.43	98.93	1641.58	1.96	178.57	3
12	57.09	33.67	2.51	1.95	14.82	11.49	98.93	1695.64	1.95	182.56	2
12	87.88	49.91	3.94	3.38	22.37	19.22	98.72	1760.86	1.98	176.77	7
12	61.00	34.00					98.65	1779.00	1.99	448.00	
12	44.95	29.52	1.92	1.46	12.60	9.62	96.45	1522.73	1.98	232.83	7
12	65.45	43.75	2.93	2.46	19.60	16.45	95.73	1495.81	1.91	175.92	10
12	48.25	30.39	2.11	1.58	13.26	9.95	94.82	1587.63	1.90	170.53	7
12	70.00	39.00					92.97	1785.00	1.91	297.00	
12	59.32	39.22	2.56	2.05	16.95	13.56	92.72	1512.56	1.95	287.69	10
12	65.99	42.38	2.84	2.34	18.26	15.00	89.40	1557.11	1.97	185.28	7
12	64.94	41.47	2.90	2.38	18.53	15.22	89.40	1565.80	1.93	186.01	7
12	54.23	40.78	2.44	2.02	18.31	15.20	87.09	1329.79	1.93	219.17	11
12	62.00	41.00					87.09	1528.00	2.00	168.00	
12	63.00	39.00					87.09	1628.00	1.96	647.00	
12	52.00	36.00					87.09	1442.00	1.97	254.00	
12	55.00	35.00					82.84	1537.00	2.00	281.00	
12	52.00	33.00					82.84	1568.00	1.93	308.00	
12	57.00	36.00					82.84	1568.00	1.94	139.00	
12	50.00	35.04	1.93	1.46	13.50	10.22	77.15	1427.08	1.92	155.21	8
12	51.00	35.00					77.15	1470.00	1.93	280.00	
12	50.00	33.00					77.15	1535.00	1.97	126.00	

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
13	51.27	28.79	2.39	2.03	13.40	11.40	100.00	1780.96	1.97	256.35	
13	56.01	31.47	2.59	2.23	14.55	12.55	100.00	1779.44	1.97	195.43	
13	52.33	29.90	2.38	2.02	13.62	11.55	100.00	1750.26	1.93	210.36	
13	61.22	33.99	2.65	2.19	14.73	12.18	100.00	1801.28	1.96	259.18	7
13	63.97	34.26	2.73	2.32	14.61	12.44	100.00	1867.17	1.98	231.31	1
13	63.44	35.47	2.91	2.45	16.26	13.69	99.98	1788.52	1.96	204.08	4
13	60.59	34.71	2.81	2.34	16.11	13.42	99.98	1745.83	1.92	255.73	4
13	58.72	36.67	2.69	2.23	16.82	13.91	99.98	1601.55	1.93	251.30	2
13	58.76	37.51	2.68	2.22	17.11	14.15	99.98	1566.75	1.94	239.18	2
13	58.63	34.19	2.81	2.36	16.41	13.77	99.98	1714.57	1.99	245.23	9
13	60.56	38.44	2.83	2.36	17.95	14.96	99.90	1575.39	1.91	143.46	8
13	64.80	38.38	3.06	2.60	18.13	15.41	99.80	1688.27	1.96	168.37	6
13	74.65	40.42	3.39	2.76	18.33	14.95	99.80	1846.88	1.92	188.54	6
13	67.01	40.50	3.21	2.65	19.43	16.03	99.70	1654.59	1.96	178.57	9
13	69.59	42.39	3.25	2.68	19.78	16.33	99.61	1641.50	1.94	173.20	10
13	74.96	43.37	3.45	2.74	19.97	15.86	99.51	1728.43	1.97	203.05	5
13	73.87	41.52	3.47	2.81	19.49	15.82	99.51	1779.15	1.99	217.09	5
13	61.39	39.38	2.76	2.30	17.67	14.73	99.32	1559.18	1.96	166.84	8
13	71.97	43.63	3.28	2.72	19.90	16.48	99.22	1649.49	1.95	160.00	9
13	61.37	39.03	2.87	2.41	18.26	15.33	99.13	1572.31	1.95	176.92	5
13	73.23	42.49	3.26	2.75	18.94	15.94	99.13	1723.32	1.93	237.31	4
13	81.27	44.81	3.45	2.78	19.04	15.35	99.13	1813.66	1.94	213.92	5
13	71.85	42.84	3.21	2.54	19.15	15.14	99.13	1677.20	1.93	237.31	5
13	70.66	45.55	3.07	2.40	19.81	15.44	99.13	1551.30	1.92	97.40	11
13	68.51	42.46	3.32	2.66	20.56	16.51	99.03	1613.32	1.99	174.37	8
13	74.49	45.38	3.42	2.86	20.82	17.40	98.93	1641.58	1.96	178.57	3
13	69.57	41.03	3.23	2.67	19.05	15.73	98.93	1695.64	1.95	182.56	2
13	80.13	45.51	3.89	3.28	22.09	18.64	98.72	1760.86	1.98	176.77	7
13	65.00	36.00					98.65	1779.00	1.99	448.00	
13	65.15	42.79	2.93	2.42	19.24	15.92	96.45	1522.73	1.98	232.83	7
13	72.77	48.65	3.35	2.83	22.40	18.90	95.73	1495.81	1.91	175.92	10
13	74.39	46.85	3.42	2.89	21.55	18.23	94.82	1587.63	1.90	170.53	7
13	64.00	36.00					92.97	1785.00	1.91	297.00	
13	71.28	47.13	3.33	2.77	22.04	18.31	92.72	1512.56	1.95	287.69	10
13	66.84	42.92	2.99	2.49	19.23	15.97	89.40	1557.11	1.97	185.28	7
13	63.21	40.37	3.06	2.54	19.52	16.21	89.40	1565.80	1.93	186.01	7
13	53.54	40.26	2.54	2.18	19.09	16.36	87.09	1329.79	1.93	219.17	11
13	60.00	39.00					87.09	1528.00	2.00	168.00	
13	65.00	40.00					87.09	1628.00	1.96	647.00	
13	54.00	38.00					87.09	1442.00	1.97	254.00	
13	54.00	35.00					82.84	1537.00	2.00	281.00	
13	56.00	36.00					82.84	1568.00	1.93	308.00	
13	56.00	36.00					82.84	1568.00	1.94	139.00	
13	45.83	32.12	1.98	1.56	13.87	10.95	77.15	1427.08	1.92	155.21	8
13	48.00	32.00					77.15	1470.00	1.93	280.00	
13	45.00	29.00					77.15	1535.00	1.97	126.00	

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
14	80.20	45.03	0.0	0.0	0.0	0.0	100.00	1780.96	1.97	256.35	9
14	58.88	33.09	0.0	0.0	0.0	0.0	100.00	1779.44	1.97	195.43	7
14	89.12	50.92	0.0	0.0	0.0	0.0	100.00	1750.26	1.93	210.36	9
14	56.89	31.58	0.0	0.0	0.0	0.0	100.00	1801.28	1.96	259.18	7
14	47.47	25.43	0.0	0.0	0.0	0.0	100.00	1867.17	1.98	231.31	1
14	119.39	66.75	0.0	0.0	0.0	0.0	99.98	1788.52	1.96	204.08	4
14	118.75	68.02	0.0	0.0	0.0	0.0	99.98	1745.83	1.92	255.73	4
14	142.75	89.13	0.0	0.0	0.0	0.0	99.98	1601.55	1.93	251.30	2
14	130.15	83.07	0.0	0.0	0.0	0.0	99.98	1566.75	1.94	239.18	2
14	178.64	104.19	0.0	0.0	0.0	0.0	99.98	1714.57	1.99	245.23	9
14	148.17	94.05	0.0	0.0	0.0	0.0	99.90	1575.39	1.91	143.46	8
14	142.09	84.16	0.0	0.0	0.0	0.0	99.80	1688.27	1.96	168.37	6
14	166.41	90.10	0.0	0.0	0.0	0.0	99.80	1846.88	1.92	188.54	6
14	158.93	96.05	0.0	0.0	0.0	0.0	99.70	1654.59	1.96	178.57	9
14	186.60	113.68	0.0	0.0	0.0	0.0	99.61	1641.50	1.94	173.20	10
14	179.95	104.11	0.0	0.0	0.0	0.0	99.51	1728.43	1.97	203.05	5
14	176.63	99.28	0.0	0.0	0.0	0.0	99.51	1779.15	1.99	217.09	5
14	176.02	112.89	0.0	0.0	0.0	0.0	99.32	1559.18	1.96	166.84	8
14	191.03	115.81	0.0	0.0	0.0	0.0	99.22	1649.49	1.95	160.00	9
14	139.49	88.71	0.0	0.0	0.0	0.0	99.13	1572.31	1.95	176.92	5
14	151.30	87.79	0.0	0.0	0.0	0.0	99.13	1723.32	1.93	237.31	4
14	146.65	80.86	0.0	0.0	0.0	0.0	99.13	1813.66	1.94	213.92	5
14	233.59	150.58	0.0	0.0	0.0	0.0	99.13	1551.30	1.92	97.40	11
14	142.75	85.11	0.0	0.0	0.0	0.0	99.13	1677.20	1.93	237.31	5
14	178.14	110.42	0.0	0.0	0.0	0.0	99.03	1613.32	1.99	174.37	8
14	126.53	77.08	0.0	0.0	0.0	0.0	98.93	1641.58	1.96	178.57	3
14	138.21	81.51	0.0	0.0	0.0	0.0	98.93	1695.64	1.95	182.56	2
14	157.32	89.34	0.0	0.0	0.0	0.0	98.72	1760.86	1.98	176.77	7
14	182.83	120.07	0.0	0.0	0.0	0.0	96.45	1522.73	1.98	232.83	7
14	168.59	112.71	0.0	0.0	0.0	0.0	95.73	1495.81	1.91	175.92	10
14	163.16	102.77	0.0	0.0	0.0	0.0	94.82	1587.63	1.90	170.53	7
14	179.95	115.57	0.0	0.0	0.0	0.0	89.40	1557.11	1.97	185.28	7
14	182.12	116.31	0.0	0.0	0.0	0.0	89.40	1565.80	1.93	186.01	7
14	167.88	126.24	0.0	0.0	0.0	0.0	87.09	1329.79	1.93	219.17	11
14	166.41	116.61	0.0	0.0	0.0	0.0	77.15	1427.08	1.92	155.21	8
15	445.43	250.11	0.0	0.0	0.0	0.0	100.00	1780.96	1.97	256.35	9
15	557.87	313.51	0.0	0.0	0.0	0.0	100.00	1779.44	1.97	195.43	7
15	501.04	286.26	0.0	0.0	0.0	0.0	100.00	1750.26	1.93	210.36	9
15	566.58	314.54	0.0	0.0	0.0	0.0	100.00	1801.28	1.96	259.18	7
15	633.84	339.46	0.0	0.0	0.0	0.0	100.00	1867.17	1.98	231.31	1
151	107.65	619.31	0.0	0.0	0.0	0.0	99.98	1788.52	1.96	204.08	4
151	161.20	665.13	0.0	0.0	0.0	0.0	99.98	1745.83	1.92	255.73	4
151	242.75	775.96	0.0	0.0	0.0	0.0	99.98	1601.55	1.93	251.30	2
151	181.44	754.07	0.0	0.0	0.0	0.0	99.98	1566.75	1.94	239.18	2
151	184.17	690.65	0.0	0.0	0.0	0.0	99.98	1714.57	1.99	245.23	9
151	377.49	874.38	0.0	0.0	0.0	0.0	99.90	1575.39	1.91	143.46	8
151	329.08	787.25	0.0	0.0	0.0	0.0	99.80	1688.27	1.96	168.37	6
151	468.49	795.12	0.0	0.0	0.0	0.0	99.80	1846.88	1.92	188.54	6
151	500.26	906.72	0.0	0.0	0.0	0.0	99.70	1654.59	1.96	178.57	9
151	626.29	990.74	0.0	0.0	0.0	0.0	99.61	1641.50	1.94	173.20	10
151	554.06	899.12	0.0	0.0	0.0	0.0	99.51	1728.43	1.97	203.05	5
151	520.85	854.82	0.0	0.0	0.0	0.0	99.51	1779.15	1.99	217.09	5
151	325.26	849.97	0.0	0.0	0.0	0.0	99.32	1559.18	1.96	166.84	8
151	724.36	1045.39	0.0	0.0	0.0	0.0	99.22	1649.49	1.95	160.00	9
151	367.44	869.70	0.0	0.0	0.0	0.0	99.13	1572.31	1.95	176.92	5
151	463.99	849.52	0.0	0.0	0.0	0.0	99.13	1723.32	1.93	237.31	4
151	346.65	742.50	0.0	0.0	0.0	0.0	99.13	1813.66	1.94	213.92	5
151	638.02	1055.90	0.0	0.0	0.0	0.0	99.13	1551.30	1.92	97.40	11
151	284.46	765.83	0.0	0.0	0.0	0.0	99.13	1677.20	1.93	237.31	5
151	521.61	943.16	0.0	0.0	0.0	0.0	99.03	1613.32	1.99	174.37	8
151	443.37	879.25	0.0	0.0	0.0	0.0	98.93	1641.58	1.96	178.57	3
151	444.10	851.66	0.0	0.0	0.0	0.0	98.93	1695.64	1.95	182.56	2
151	719.44	976.48	0.0	0.0	0.0	0.0	98.72	1760.86	1.98	176.77	7
151	185.10	778.28	0.0	0.0	0.0	0.0	96.45	1522.73	1.98	232.83	7
151	547.12	1034.30	0.0	0.0	0.0	0.0	95.73	1495.81	1.91	175.92	10
151	172.63	738.60	0.0	0.0	0.0	0.0	94.82	1587.63	1.90	170.53	7
151	829.70	1175.06	0.0	0.0	0.0	0.0	89.40	1557.11	1.97	185.28	7
151	764.51	1126.90	0.0	0.0	0.0	0.0	89.40	1565.80	1.93	186.01	7
151	637.31	1231.25	0.0	0.0	0.0	0.0	87.09	1329.79	1.93	219.17	11
152	018.23	1414.23	0.0	0.0	0.0	0.0	77.15	1427.08	1.92	155.21	8

TABLE XIX (Continued)

AREA MEASUREMENTS OF PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9	10	11	12
161780.	961000.	00	0.0	0.0	0.0	0.0	100.00	1780.96	1.97	256.35	9
161779.	441000.	00	0.0	0.0	0.0	0.0	100.00	1779.44	1.97	195.43	7
161750.	261000.	00	0.0	0.0	0.0	0.0	100.00	1750.26	1.93	210.36	9
161801.	281000.	00	0.0	0.0	0.0	0.0	100.00	1801.28	1.96	259.18	7
161867.	171000.	00	0.0	0.0	0.0	0.0	100.00	1867.17	1.98	231.31	1
161788.	521000.	00	0.0	0.0	0.0	0.0	99.98	1788.52	1.96	204.08	4
161745.	831000.	00	0.0	0.0	0.0	0.0	99.98	1745.83	1.92	255.73	4
161601.	551000.	00	0.0	0.0	0.0	0.0	99.98	1601.55	1.93	251.30	2
161566.	751000.	00	0.0	0.0	0.0	0.0	99.98	1566.75	1.94	239.18	2
161714.	571000.	00	0.0	0.0	0.0	0.0	99.98	1714.57	1.99	245.23	9
161575.	391000.	00	0.0	0.0	0.0	0.0	99.90	1575.39	1.91	143.46	8
161688.	271000.	00	0.0	0.0	0.0	0.0	99.80	1688.27	1.96	168.37	6
161846.	881000.	00	0.0	0.0	0.0	0.0	99.80	1846.88	1.92	188.54	6
161654.	591000.	00	0.0	0.0	0.0	0.0	99.70	1654.59	1.96	178.57	9
161641.	501000.	00	0.0	0.0	0.0	0.0	99.61	1641.50	1.94	173.20	10
161728.	431000.	00	0.0	0.0	0.0	0.0	99.51	1728.43	1.97	203.05	5
161779.	151000.	00	0.0	0.0	0.0	0.0	99.51	1779.15	1.99	217.09	5
161559.	181000.	00	0.0	0.0	0.0	0.0	99.32	1559.18	1.96	166.84	8
161649.	491000.	00	0.0	0.0	0.0	0.0	99.22	1649.49	1.95	160.00	9
161572.	311000.	00	0.0	0.0	0.0	0.0	99.13	1572.31	1.95	176.92	5
161723.	321000.	00	0.0	0.0	0.0	0.0	99.13	1723.32	1.93	237.31	4
161813.	661000.	00	0.0	0.0	0.0	0.0	99.13	1813.66	1.94	213.92	5
161551.	301000.	00	0.0	0.0	0.0	0.0	99.13	1551.30	1.92	97.40	11
161677.	201000.	00	0.0	0.0	0.0	0.0	99.13	1677.20	1.93	237.31	5
161613.	321000.	00	0.0	0.0	0.0	0.0	99.03	1613.32	1.99	174.37	8
161641.	581000.	00	0.0	0.0	0.0	0.0	98.93	1641.58	1.96	178.57	3
161695.	641000.	00	0.0	0.0	0.0	0.0	98.93	1695.64	1.95	182.56	2
161760.	861000.	00	0.0	0.0	0.0	0.0	98.72	1760.86	1.98	176.77	7
161522.	731000.	00	0.0	0.0	0.0	0.0	96.45	1522.73	1.98	232.83	7
161495.	811000.	00	0.0	0.0	0.0	0.0	95.73	1495.81	1.91	175.92	10
161587.	631000.	00	0.0	0.0	0.0	0.0	94.82	1587.63	1.90	170.53	7
161512.	561000.	00	0.0	0.0	0.0	0.0	92.72	1512.56	1.95	287.69	10
161557.	111000.	00	0.0	0.0	0.0	0.0	89.40	1557.11	1.97	185.28	7
161565.	801000.	00	0.0	0.0	0.0	0.0	89.40	1565.80	1.93	186.01	7
161329.	791000.	00	0.0	0.0	0.0	0.0	87.09	1329.79	1.93	219.17	11
161434.	901005.	47	0.0	0.0	0.0	0.0	77.15	1427.08	1.92	155.21	8
17	256.35	143.94	0.0	0.0	0.0	0.0	100.00	1780.96	1.97	256.35	9
17	195.43	109.83	0.0	0.0	0.0	0.0	100.00	1779.44	1.97	195.43	7
17	210.36	120.19	0.0	0.0	0.0	0.0	100.00	1750.26	1.93	210.36	9
17	259.18	143.89	0.0	0.0	0.0	0.0	100.00	1801.28	1.96	259.18	7
17	231.31	123.88	0.0	0.0	0.0	0.0	100.00	1867.17	1.98	231.31	1
17	204.08	114.11	0.0	0.0	0.0	0.0	99.98	1788.52	1.96	204.08	4
17	255.73	146.48	0.0	0.0	0.0	0.0	99.98	1745.83	1.92	255.73	4
17	251.30	156.91	0.0	0.0	0.0	0.0	99.98	1601.55	1.93	251.30	2
17	239.18	152.66	0.0	0.0	0.0	0.0	99.98	1566.75	1.94	239.18	2
17	245.23	143.02	0.0	0.0	0.0	0.0	99.98	1714.57	1.99	245.23	9
17	143.46	91.06	0.0	0.0	0.0	0.0	99.90	1575.39	1.91	143.46	8
17	168.37	99.73	0.0	0.0	0.0	0.0	99.80	1688.27	1.96	168.37	6
17	188.54	102.09	0.0	0.0	0.0	0.0	99.80	1846.88	1.92	188.54	6
17	178.57	107.92	0.0	0.0	0.0	0.0	99.70	1654.59	1.96	178.57	9
17	173.20	105.51	0.0	0.0	0.0	0.0	99.61	1641.50	1.94	173.20	10
17	203.05	117.47	0.0	0.0	0.0	0.0	99.51	1728.43	1.97	203.05	5
17	217.09	122.02	0.0	0.0	0.0	0.0	99.51	1779.15	1.99	217.09	5
17	166.84	107.00	0.0	0.0	0.0	0.0	99.32	1559.18	1.96	166.84	8
17	160.00	97.00	0.0	0.0	0.0	0.0	99.22	1649.49	1.95	160.00	9
17	176.92	112.52	0.0	0.0	0.0	0.0	99.13	1572.31	1.95	176.92	5
17	237.31	137.70	0.0	0.0	0.0	0.0	99.13	1723.32	1.93	237.31	4
17	213.92	117.95	0.0	0.0	0.0	0.0	99.13	1813.66	1.94	213.92	5
17	97.40	62.78	0.0	0.0	0.0	0.0	99.13	1551.30	1.92	97.40	11
17	237.31	141.49	0.0	0.0	0.0	0.0	99.13	1677.20	1.93	237.31	5
17	174.37	108.08	0.0	0.0	0.0	0.0	99.03	1613.32	1.99	174.37	8
17	178.57	108.78	0.0	0.0	0.0	0.0	98.93	1641.58	1.96	178.57	3
17	182.56	107.67	0.0	0.0	0.0	0.0	98.93	1695.64	1.95	182.56	2
17	176.77	100.39	0.0	0.0	0.0	0.0	98.72	1760.86	1.98	176.77	7
17	232.83	152.90	0.0	0.0	0.0	0.0	96.45	1522.73	1.98	232.83	7
17	175.92	117.61	0.0	0.0	0.0	0.0	95.73	1495.81	1.91	175.92	10
17	170.53	107.41	0.0	0.0	0.0	0.0	94.82	1587.63	1.90	170.53	7
17	287.69	190.20	0.0	0.0	0.0	0.0	92.72	1512.56	1.95	287.69	10
17	185.28	118.99	0.0	0.0	0.0	0.0	89.40	1557.11	1.97	185.28	7
17	186.01	118.80	0.0	0.0	0.0	0.0	89.40	1565.80	1.93	186.01	7
17	219.17	164.82	0.0	0.0	0.0	0.0	87.09	1329.79	1.93	219.17	11
17	155.21	108.76	0.0	0.0	0.0	0.0	77.15	1427.08	1.92	155.21	8

yield of the wood wafer pyrolyzed. The 4th and 5th entry for each peak (last two 100% yield samples) were hot- (50°C) water extracted for 10 minutes. Column 9 is the total area (all the area from guaiacol to homovanillin) per milligram of sample and Column 10 is the weight in milligrams of the sample pyrolyzed. The base-line area/mg of sample as in Column 11 and Column 12 contains the data identification numbers taken in sequential order of the day pyrolyzed.

The date, sample weight, base-line area, total area, and percentage yield were analyzed as independent variables by the multiple regression program listed in Table XX. The six area measurements (Columns 2-7) were each taken as the dependent variable. Column 7 showed the least correlation and Column 2 showed slightly better correlation with the independent variables than any of the other dependent variables. Column 2 was used as the dependent variable for all the following analyses.

Percentage yield (Column 8) showed the highest average correlation ($\underline{T}$ = 3.26) with Column 2 (area/mg of sample). Weight and date showed very little correlation with average $\underline{T}$ = 0.96 and 1.09, respectively. The basic working equation was then defined as shown below:

$$\text{peak area/mg of sample} = \text{constant} + \underline{B}(\text{percentage yield of wood})$$

$$\text{simplified:} \quad \text{area} = \underline{C} + \underline{B}(\text{yield}).$$

Several transforms of the data were used in an attempt to increase the correlation between area and yield. Logarithm, exponential, power, trigonometric functions and various combinations were used. The best correlation came from using a logarithm transform for the lignin peaks and a power (square) of the carbohydrate peaks.

$$\text{Lignin:} \quad LN\ (\text{area}) = \underline{C} + \underline{B}(\text{yield})$$

$$\text{Carbohydrate:} \quad (\text{area})^2 = \underline{C} + \underline{B}(\text{yield})$$

The plots drawn for the data were done on the computer using the Calcomp Plotter. The plotting program for the data, least-squares line, and 95% confidence limits is also listed in Table XX. All the graphs were plotted on a linear scale. Those analyses which utilized transforms were plotted using the inverse-transform.

The lignin peak areas were summed into various groups for analysis. These included groups of all 9 lignin peaks, 2 carbon side-chain peaks (4-ethylguaiacol and 4-vinylguaiacol), 3 carbon side-chain peaks (4-propylguaiacol, eugenol, trans-isoeugenol) and carbonyl systems (vanillin and homovanillin) are listed in Table XXI with the same coding as in Table XIX. These sums of peak areas were analyzed as one peak.

The least-squares line was used to determine the trend for the peak(s) analyzed. The carbohydrate peak areas generally increased with lower percentage yield, the lignin peaks generally decreased with vanillin, homovanillin, and guaiacol showing the slowest decrease. The total area decreased with yield and extrapolating to 2.0% yield at zero area. The analysis for all 9 lignin peaks showed lignin decreasing with yield and extrapolating to 70.9% yield at zero area.

TABLE XX

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
C*****************************************************************
C              MULTIPLE REGRESSION ANALYSIS PROGRAM
C                    FOR UP TO 20 VARIABLES
C                    AND 300 OBSERVATIONS
C*****************************************************************
      DIMENSION D(300,20),X(40),R(400),ID(20),SSX(40),CNST(20),Z(40)
      DIMENSION IA(20)
      INTEGER OUT
      DOUBLE PRECISION R
      EQUIVALENCE (SSX(1),Z(1))
      IN = 5
      OUT = 6
C******  ISN NO. OF CARDS AT BEGINNING TO BE IGNORED
C******  LLN NO. OF CARDS AT END TO BE IGNORED
      ISN = 5
      LLN = 1
      LAN = ISN + LLN
    1 READ(5,9001) NR,NV,IPR
 9001 FORMAT(20I3)
      CALL INPUT (ID,CNST,NX,20)
      DO 9991  I = 1,ISN
 9991 READ(5,9002)
      NR = NR-LAN
      ITT = 1
      DO 3 I = ITT,NR
      READ(IN,9002)   (Z(J),J=1,NV)
 9002 FORMAT(F3.0,7F7.2,F9.2,F5.2,F7.2      )
      CALL DATA   (Z,X,ID,CNST,NX)
      D(I,1) = 1.
      DO 2 J = 1,NX
    2 D(I,J+1) = X(J)
    3 CONTINUE
      DO 9993  I = 1,LLN
 9993 READ(5,9002)
    9 READ(5,9001) IA
      IF(IA(1)) 90,1,90
   90 N = 0
      DO 10 I = 1,20
      IF(IA(I)) 10,11,10
   10 N = I
   11 DO 12 I = 1,N
      L = N - I + 1
   12 IA(L+1) = IA(L) + 1
      IA(1) = 1
      L = N + 1
      CALL MATRIX (D,R,300,20,NR,N+1,X,IA)
      DO 4 I = 2,N
      K = I - 1
      AV = R(I)/R(1)
      J = L*(I - 1) + I
    4 SSX(I) = R(J) - R(I)**2/R(1)
      CALL INVERT (R,N+1)
      CALL SOLN (R,X,N+1)
      CALL ANOVA (R,N+1,NR,SSY,SSB,SSW,F)
      RSQ = SSB/SSY
      NDF1 = N - 1
      NDF2 = NR - N
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
      VAR = SSW/NDF2
      IANLYZ = IA(L) - 1
      DO 5 I = 2,N
      M = L*(I-1) + L
      J = L*(I-1) + I
      SE = SQRT(DABS(VAR*R(J)))
      T = SQRT(R(M)**2)/SE
      CX = (SSX(I) - 1./R(J))/SSX(I)
      SSX(I) = R(M)
      J = IA(I) - 1
    5 CONTINUE
      SSX(1) = R(L)
      IND = 0
      CALL TEST (SSY,IND)
      CALL TEST (SSW,IND)
      IF (IND)  52,51,52
   51 GO TO 53
   52 CONTINUE
   53 IF(IPR) 6,9,6
    6 CONTINUE
      IY = IA(L)
      WRITE(10,655) NR,K
  655 FORMAT('0OBS=',I2,' VAR=',I1)
      XINT = -R(L)/R(M)
      WRITE(10,955) RSQ,XINT
  955 FORMAT('0RSQ=',F4.2,' XINT=',F4.1)
      WRITE(10,444)
  444 FORMAT('PERCENT YIELD OF WOOD')
      WRITE(10,449)
  449 FORMAT('GC PEAK AREA/MG WOOD')
      WRITE(10,8080)NR
 8080 FORMAT(I2)
      DO 8 I = 1,NR
      DO 7 J = 1,N
      L = IA(J)
    7 X(J) = D(I,L)
      CALL PRED (SSX,X,P,N,R,VP)
C     VP = SQRT(VP*VAR)
      VP = SQRT(ABS(VP*VAR))
      CON=1.96*VP
      UCON = P+CON
      DCON = P - CON
      DIF = P - D(I,IY)
    8 WRITE(10,9994)D(I,2),D(I,IY),P,UCON,DCON,D(I,9),I
 9994 FORMAT(F3.0,5F8.2,I4)
      GO TO 9
      END
      SUBROUTINE TEST (SSQ,IND)
      IF(SSQ - 1.E+7) 2,2,1
    1 IND = 1
      RETURN
    2 IF(SSQ - 1.E-6)  3,3,4
    3 IND = 1
    4 RETURN
      END
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
      SUBROUTINE PRED (C,D,P,K,R,VP)
      DIMENSION C(1),D(1),R(1),TVP(20)
      DOUBLE PRECISION R
      P = 0.
      VP = 0.
      KP1 = K + 1
      DO 1 I = 1,K
    1 P = P + C(I)*D(I)
      DO 2 I = 1,K
      TVP(I) = 0.
      DO 2 J = 1,K
      IJ = KP1*(J-1) + I
    2 TVP(I) = TVP(I) + D(J)*R(IJ)
      DO 3 I = 1,K
    3 VP = VP + TVP(I)*D(I)
      RETURN
      END

      SUBROUTINE ANOVA(R,K,N,SSY,SSB,SSW,F)
      DIMENSION R(1)
      DOUBLE PRECISION R
      I = K*(K - 1) + 1
      M = K*K
      SSY = R(M) - R(I)**2/N
      SSB = 0.
      M = K - 1
      DO 1 I = 2,M
      IN = K*(I - 1) + K
      NI = K*(K - 1) + I
    1 SSB = SSB + R(IN)*R(NI)
      SSW = SSY - SSB
      F = (SSB*(N - K + 1))/(SSW*(K - 2))
      RETURN
      END

      SUBROUTINE SOLN (X,Z,N)
      DIMENSION X(1),Z(1),B(50)
      DOUBLE PRECISION X
      LIM = N - 1
      DO 2 I = 1,LIM
      B(I) = 0.
      DO 1 J = 2,LIM
      IJ = N*(I - 1) + J
      NJ = N*(N - 1) + J
    1 B(I) = B(I) + X(IJ)*X(NJ)
    2 CONTINUE
      C = Z(N)
      DO 3 I = 2,LIM
      C = C - B(I)*Z(I)
      NJ = N*(I - 1) + N
    3 X(NJ) = B(I)
      X(N) = C/Z(1)
      RETURN
      END
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
      SUBROUTINE INVERT (A,N)
      DIMENSION A(1)
      DOUBLE PRECISION A
      LIM = N - 1
      DO 6 I = 1,LIM
      II = N*(I - 1) + I
      X = A(II)
      IF (ABS(X) - 1.E-9)  1,1,2
    1 WRITE(6,9001) I
 9001 FORMAT(' MATRIX NON-INVERTABLE ON THE ',I2,'TH ROW' )
      CALL EXIT
    2 A(II) = 1.
      DO 3 J = 1,LIM
      IJ = N*(I - 1) + J
    3 A(IJ) = A(IJ)/X
      DO 6 K = 1,LIM
      IF(K - I) 4,6,4
    4 KI = N*(K - 1) + I
      X = A(KI)
      A(KI) = 0.
      DO 5 J = 1,LIM
      KJ = N*(K - 1) + J
      IJ = N*(I - 1) + J
    5 A(KJ) = A(KJ) - X*A(IJ)
    6 CONTINUE
      RETURN
      END

      SUBROUTINE MATRIX (X,R,NRX,NCX,N,K,Z,IA)
      DIMENSION X(1),R(1),Z(1),IA(1)
      DOUBLE PRECISION R
      L = K*K
      DO 1 I = 1,L
    1 R(I) = 0.
      DO 2 I = 1,N
      DO 2 J = 1,K
      DO 2 L = 1,K
      IR = K*(  J   - 1) + L
      JX = NRX*(IA(J) - 1) + I
      LX = NRX*(IA(L) - 1) + I
    2 R(IR) = R(IR) + X(JX)*X(LX)
      M = K - 1
      DO 3 I = 2,M
      IR = K*(K - 1) + I
      Z(I) = R(I)
    3 R(IR) = R(IR) - R(K)*R(I)/N
      Z(1) = R(1)
      Z(K) = R(K)
      RETURN
      END
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
      SUBROUTINE DATA (Z,X,ID,CNST,NX)
      DIMENSION X(1),ID(1),CNST(1),Z(1)
      DO 10 I = 1,NX
      CALL DECODE (ID(I),J,K,L)
      IF(K - 3) 1,7,8
    1 IF(L - 50) 2,3,4
    2 WRITE(6,9001) ID(I)
 9001 FORMAT(' INCORRECT SPECIFICATION CARD-',I10)
      CALL EXIT
    3 X(I) = Z(J) + CNST(I)
      GO TO 10
    4 IF(L - 51) 2,5,6
    5 X(I) = ALOG(Z(J) + CNST(I))
      GO TO 10
    6 X(I) = EXP(Z(J) + CNST(I))
      GO TO 10
    7 X(I) = X(J)*X(L) + CNST(I)
      GO TO 10
    8 IF(K - 4) 2,9,2
    9 X(I) = X(J)/X(L) + CNST(I)
   10 CONTINUE
      RETURN
      END

      SUBROUTINE DECODE (ID,J,K,L)
      J = ID/1000
      K = ID/100 - 10*J
      L = ID - 1000*J - 100*K
      RETURN
      END

      SUBROUTINE INPUT (ID,CNST,NX,LIM)
C     THE GENERAL FORMAT OF THE DEFINITION CARDS IS
C                   XX T VV  CC.CC
C                   12 3 45  6-15
C     IF VV IS A NUMBER GREATER THAN 50 THE FOLLOWING MEANING HOLDS
C          XX = THE POSITION NUMBER OF THE VARIABLE ON THE CARD
C          T = 1 FOR '+', 2 FOR '-', 3 FOR '*', 4 FOR '/'
C          VV = 50 FOR NO TRANSFORMATION OF THE VARIABLE ON THE CARD
C               51 FOR A LOG TRANSFORMATION OF THE VARIABLE ON THE CARD
C               52 FOR AN EXP TRANSFORMATION OF THE VARIABLE ON THE CARD
C
C     IF VV IS LESS THAN 50 (FORM A VARIABLE FROM PREVIOUSLY DEFINED
C     VARIABLES.)
C          XX = THE REGRESSION VARIABLE IDENT. NUMBER I
C          T = THE SAME AS ABOVE
C          VV = THE REGRESSION VARIABLE IDENT. NUMBER J
C     A BLANK CARD ENDS INPUT OF DEFINITION CARDS
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
C
      DIMENSION ID(1),CNST(1)
      NX = 0
      DO 13 I = 1,9999
      READ(5,9001) ID(I),CNST(I)
 9001 FORMAT(I5,F10.0)
      IF(ID(I)) 1,14,1
    1 NX = I
  100 CALL DECODE (ID(I),J,K,L)
      IF(K - 3) 2,8,9
    2 IF(L - 50) 3,4,5
    3 WRITE(6,9002) ID(I)
 9002 FORMAT(' INCORRECT SPECIFICATION CARD-',I10)
      CALL EXIT
    4 WRITE(6,9003) I,J,CNST(I)
      GO TO 13
    5 IF(L - 51) 3,6,7
    6 WRITE(6,9004) I,J,CNST(I)
      GO TO 13
    7 WRITE(6,9005) I,J,CNST(I)
      GO TO 13
    8 WRITE(6,9006) I,J,L,CNST(I)
      GO TO 13
    9 IF(K - 4) 3,10,3
   10 WRITE(6,9007) I,J,L,CNST(I)
   13 CONTINUE
   14 IF(NX - LIM)  15,15,16
   15 RETURN
   16 WRITE(6,9008) NX,LIM
 9008 FORMAT('OTHE ',I3,' TERMS IN THE EQUATION EXCEED THE LIMIT OF',I3)
      CALL EXIT
 9003 FORMAT(' X(',I2,') = INPUT(',I2,') PLUS',F10.4)
 9004 FORMAT(' X(',I2,') = LOG(INPUT',I2,') PLUS',F10.4,')')
 9005 FORMAT(' X(',I2,') = EXP(INPUT',I2,') PLUS',F10.4,')')
 9006 FORMAT(' X(',I2,') = X(',I2,') * X(',I2,') PLUS',F10.4)
 9007 FORMAT(' X(',I2,') = X(',I2,') / X(',I2,') PLUS',F10.4)
      END
/DATA
 36 11  1
01150
02150
03150
04150
05150
06150
07150
08150
09150
10150
11150
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
/JOB GO,TIME=10
C*****************************************************************
C                DATA PLOT, LEAST SQRS.LINE AND DASHED
C                     LINE CONFIDENCE LIMITS.  J.A.FLECK
C*****************************************************************
C*****************************************************************
      DIMENSION PKN(50),YOB(50),YPR(50),YUCL(50),YLCL(50),XYD(50)
      DIMENSION PYRN(50)
      DIMENSION XDOT(50),YDOT(50),XDAT(50),YDAT(50),XLIN(50),YLIN(50)
      DIMENSION XCONU(50),YCONU(50),XCONL(50),YCONL(50)
      DIMENSION XMDT(50),YMDT(50),LX(20),LY(20)
      DIMENSION XDAS(10),YDAS(10)
      COMMON   XDEL,XFSTV,YDEL,YFSTV,DLEH,DLIH
      INTEGER TITL(20),PYRN,TINF(20),TLINF(20)
      CALL ITLZ
      CALL DPT(1,4)
      CALL PLOT(0.,-11.,2)
      CALL PLOT(1.0,-10.5,-3)
C***********
      IET = 5
      READ(IET,100) TITL
      READ(IET,100) TINF
      READ(IET,100) TLINF
      READ(IET,100) LX
      READ(IET,100) LY
  100 FORMAT(20A4)
C*************
C**** READ IN TITLE OF GRAPH AND AXES ANNOTATIONS ********
      READ(IET,105) N
  105 FORMAT(I2)
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
C***  N = NUMBER OF DATA CARDS PER GRAPH (36)      *******
    5 READ(IET,110)(PKN(I),YOB(I),YPR(I),YUCL(I),YLCL(I),XYD(I),PYRN(I),
     1I=1,N)
  110 FORMAT(F3.0,5F8.2,I4)
C***  READ IN THE FIRST N (36) DATA CARDS AND STORE    ******
      DLEH = 0.11
      DLIH = 0.15
      XFSTV = 100.
      XDEL = -4.
      YFSTV = 0.
      YDEL = 40.
      SDLEH = DLEH
      XYD(N+1) = XFSTV
      XYD(N+2) = XDEL
      YOB(N+1) = YFSTV
      YOB(N+2) = YDEL
C************************
      CALL AXIS(0.25,0.,LX,-40,6.,0.,XYD(N+1),XYD(N+2))
      CALL AXIS(0.,0.,LY,40,9.,90.,YOB(N+1),YOB(N+2))
      CALL PLOT(0.25,0.,-3)
      M1 = 1
      M2 = 3
      M3 = M2-M1+1
      DO 200  M = M1,M2
      MS = M
      XDOT(MS) = XYD(M)
      XDOT(MS) = 100.0
      YDOT(MS) = YOB(M)
  200 CONTINUE
      XDOT(M3+1) = XFSTV
      XDOT(M3+2) = XDEL
      YDOT(M3+1) = YFSTV
      YDOT(M3+2) = YDEL
      CALL LINE (XDOT,YDOT,M3,1,-1,7)
      MM1 = 4
      MM2 = 5
      MM3 = MM2-MM1+1
      DO 280 MM = MM1,MM2
      MMS = MM-MM1+1
      XMDT(MMS) = XYD(MM)
      YMDT(MMS) = YOB(MM)
  280 CONTINUE
      NS = 1
      MM4 = MM3+NS
      NM = N
      XMDT(MM4) = XYD(NM)
      YMDT(MM4) = YOB(NM)
      XMDT(MM4+1) = XFSTV
      XMDT(MM4+2) = XDEL
      YMDT(MM4+1) = YFSTV
      YMDT(MM4+2) = YDEL
      XO =  (XMDT(1)-XFSTV)/XDEL
      YO =  (YMDT(1)-YFSTV)/YDEL
      CALL PLOT(XO,YO,3)
      CALL LINE (XMDT,YMDT,MM4,1,-1,4)
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
      L1 = 6
      L2 = N - NS
      L3 = L2-L1+1
      DO 300  L = L1,L2
      LS = L-L1+1
      XDAT(LS) = XYD(L)
      YDAT(LS) = YOB(L)
  300 CONTINUE
      XDAT(L3+1) = XFSTV
      XDAT(L3+2) = XDEL
      YDAT(L3+1)  = YFSTV
      YDAT(L3+2) = YDEL
      CALL LINE (XDAT,YDAT,L3,1,-1,3)
C*******
C******
C     DO  977   NKL = 1,3
      XYD(N+1) = XFSTV
      XYD(N+2) = XDEL
      YPR(N+1) = YFSTV
      YPR(N+2) = YDEL
      CALL LINE (XYD,YPR,N,1,0,2)
      DO 490  I = 1,2
      IF (I-1)  410,410,450
  410 DO 415  J = 1,N
      YLIN(J) = YUCL(J)
  415 CONTINUE
      GO TO 470
  450 DO 455  J = 1,N
      YLIN(J) = YLCL(J)
  455 CONTINUE
      GO TO 470
  470 CALL FLEKDS (XYD,YLIN,N,2)
  490 CONTINUE
C     READ (IET,105) N
C     READ(IET,110)(PKN(I),YOB(I),YPR(I),YUCL(I),YLCL(I),XYD(I),PYRN(I),
C    1I=1,N)
C     DLEH = SDLEH + ((SDLEH/2)*NKL)
C 977 CONTINUE
      CALL SYMBOL(0.5,9.3,.28,TITL,0.,25)
      CALL SYMBOL(0.5,8.95,.14,TINF,0.,25)
      CALL SYMBOL(0.5,8.7,.14,TLINF,0.,25)
      CALL PLOT (0.5,0.,-3)
      CALL FINAL
      CALL EXIT
      END
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
      SUBROUTINE FLEKDS (XQ,YQ,KZ,LC)
      COMMON    XDEL,XFSTV,YDEL,YFSTV,DLEH,DLIH
      DIMENSION  XP(50),YP(50),XX(50),YY(50),XQ(50),YQ(50)
C*****************************************************
C       DLEH = DASH LENGTH, DLIH = SPACE LENGTH
C                 J.A. FLECK
C*****************************************************
      KK = KZ+1
      M = -1
      KM = -1
      L = 1
      KL   = 1
      D = 0.0
      DO 3  I = 1,KK
      XP(I) = XQ(I)
      YP(I) = YQ(I)
    3 CONTINUE
    4 LL = L+1
      IF (LC-1)   1,1,8
    1 AL =(3*DLEH)/4
      KM = KM*M
      AL = AL*KM
      DLEH = DLEH + AL
    8 CONTINUE
      IF (YP(LL)-0.0)  2,5,5
    2 IF (XP(LL)-XP(L))  22,21,22
   21 SLP =  9999.
      GO TO 23
```

TABLE XX (Continued)

MULTIPLE REGRESSION AND PLOTTING PROGRAMS

```
   22 SLP =(YP(LL)-YP(L))/(XP(LL)-XP(L))
   23 CN = YP(L)-(XP(L)*SLP)
      XP(LL) = -CN/SLP
      YP(LL) = 0.0
    5 XDIS =(XP(LL) - XP(L))/XDEL
      YDIS =(YP(LL) - YP(L))/YDEL
      XYLEN = ABS(SQRT(XDIS**2 + YDIS**2))
      DK = XYLEN
      D =DK + D
      XYLEN = D
      IF (XYLEN - DLEH)  999,30,30
   30 KL = KL+1
      DO 35   IT = 1,KL
      IL = (LL-KL ) + IT
      XX(IT) = XP(IL)
      YY(IT) = YP(IL)
   35 CONTINUE
      XX(KL) = XP(LL)-((XDIS)*((XYLEN-DLEH)/DK))*XDEL
      XX(KL+1) = XFSTV
      XX(KL+2) = XDEL
      YY(KL) = YP(LL)-((YDIS)*((XYLEN-DLEH)/DK))*YDEL
      YY(KL+1) = YFSTV
      YY(KL+2) = YDEL
      CALL  LINE (XX,YY,KL,1,0,2)
      XP(L) = XX(KL)
      YP(L) = YY(KL)
      D = 0.0
      KL   = 1
      IF(LL-KK) 500,1010,1010
C****
  500 XDIS =(XP(LL) - XP(L))/XDEL
      YDIS =(YP(LL) -YP(L))/YDEL
      XYLEN = ABS(SQRT(XDIS**2 + YDIS**2))
      DK= XYLEN
      D =DK + D
      XYLEN = D
      IF (XYLEN - DLIH)   600,800,800
  800 XP(L) = XP(LL)-((XDIS)*((XYLEN-DLIH)/DK))*XDEL
      YP(L) = YP(LL)-((YDIS)*((XYLEN-DLIH)/DK))*YDEL
      D = 0.0
      GO TO 4
C****
  600 L = LL
      LL = LL+ 1
      IF(LL-KK)  500,1010,1010
  999 L = L+1
      KL = KL+1
      IF (LL-KK) 4,1010,1010
 1010 RETURN
      END
/DATA
```

TABLE XXI

LIGNIN PEAK AREA SUMMATIONS FROM PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9
ALL 9 LIGNIN PEAKS								
0.	975.79	547.90	49.64	44.22	278.75	248.25	100.00	16028.62
0.	900.16	505.86	47.16	42.74	265.01	240.19	100.00	16014.94
0.	937.64	535.72	47.56	43.05	271.76	246.01	100.00	15752.32
0.	903.39	501.54	47.59	43.22	264.27	239.91	100.00	16211.50
0.	930.47	498.32	48.58	44.29	260.21	237.22	100.00	16804.52
0.	827.55	462.71	44.80	40.96	250.47	229.06	99.98	16096.68
0.	806.59	462.02	44.02	40.22	252.10	230.31	99.98	15712.46
0.	714.33	446.03	40.09	36.70	250.39	229.06	99.98	14413.93
0.	713.40	455.36	37.07	33.62	236.55	214.52	99.98	14100.75
0.	784.43	457.51	41.61	37.65	242.66	219.52	99.98	15431.11
0.	712.73	452.43	38.70	35.07	245.59	222.66	99.90	14178.49
0.	784.53	464.69	42.65	38.94	252.62	230.58	99.80	15194.43
0.	841.32	455.54	43.29	39.17	234.35	212.07	99.80	16621.91
0.	757.83	458.01	40.77	37.08	246.39	224.17	99.70	14891.31
0.	756.20	460.66	38.71	34.70	235.81	211.32	99.61	14773.50
0.	773.44	447.47	40.46	36.20	234.06	209.39	99.51	15555.87
0.	782.42	439.77	41.31	37.24	232.19	209.29	99.51	16012.34
0.	703.06	450.92	35.25	31.48	226.11	201.89	99.32	14032.62
0.	749.06	454.11	39.43	35.43	239.10	214.83	99.22	14845.40
0.	702.39	446.72	37.04	33.18	235.47	211.02	99.13	14150.78
0.	752.85	436.86	40.47	36.38	234.80	211.08	99.13	15509.86
0.	803.26	442.90	41.23	36.96	227.37	203.77	99.13	16322.91
0.	677.23	433.07	34.71	30.52	222.28	195.44	99.13	14087.58
0.	753.39	452.62	38.26	33.75	229.57	202.34	99.13	14968.89
0.	697.49	432.33	37.38	33.37	231.74	206.82	99.03	14519.86
0.	758.17	461.84	40.14	36.14	244.60	220.04	98.93	14774.21
0.	752.99	444.07	40.05	36.05	236.20	212.62	98.93	15260.74
0.	774.75	439.98	42.42	38.58	240.94	219.14	98.72	15847.73
0.	736.00	411.00	0.0	0.0	0.0	0.0	98.65	16011.00
0.	636.03	417.70	32.73	28.82	214.92	189.38	96.45	13704.55
0.	609.42	407.41	32.20	28.69	215.25	191.80	95.73	13462.28
0.	600.01	377.93	33.14	28.70	208.85	180.67	94.82	14288.66
0.	605.00	339.00	0.0	0.0	0.0	0.0	92.97	16065.00
0.	561.88	371.49	30.00	26.21	198.33	173.27	92.72	13613.03
0.	505.41	324.58	26.08	22.18	167.57	142.47	89.40	14013.98
0.	516.57	329.92	26.60	22.60	169.75	144.27	89.40	14092.18
0.	421.92	317.28	22.70	19.12	170.66	143.79	87.09	11968.10
0.	472.00	312.00	0.0	0.0	0.0	0.0	87.09	13666.00
0.	463.00	287.00	0.0	0.0	0.0	0.0	87.09	14552.00
0.	436.00	297.00	0.0	0.0	0.0	0.0	87.09	13164.00
0.	394.00	253.00	0.0	0.0	0.0	0.0	82.84	13833.00
0.	407.00	260.00	0.0	0.0	0.0	0.0	82.84	14112.00
0.	400.00	254.00	0.0	0.0	0.0	0.0	82.84	14112.00
0.	343.24	240.52	17.09	13.44	119.71	94.14	77.15	12843.71
0.	354.00	239.00	0.0	0.0	0.0	0.0	77.15	13295.00
0.	350.00	231.00	0.0	0.0	0.0	0.0	77.15	13750.00

TABLE XXI (Continued)

LIGNIN PEAK AREA SUMMATIONS FROM PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9
2 CARBON SIDE CHAIN								
0.	191.37	107.45	10.10	8.12	56.72	45.60	100.00	3561.92
0.	173.60	97.56	9.19	7.92	51.63	44.50	100.00	3558.88
0.	184.45	105.38	9.85	8.60	56.25	49.14	100.00	3500.52
0.	178.06	98.85	9.08	7.96	50.42	44.19	100.00	3602.56
0.	188.05	100.71	9.34	8.18	50.04	43.82	100.00	3734.34
0.	163.61	91.47	8.52	7.65	47.64	42.79	99.98	3577.04
0.	163.02	93.38	8.39	7.50	48.03	42.96	99.98	3491.66
0.	143.69	89.73	7.56	6.84	47.23	42.71	99.98	3203.10
0.	135.22	86.31	7.11	6.40	45.40	40.80	99.98	3133.50
0.	147.57	86.07	7.94	7.09	46.31	41.32	99.98	3429.14
0.	139.44	88.52	7.22	6.44	45.86	40.88	99.90	3150.78
0.	155.44	92.07	8.06	7.30	47.74	43.21	99.80	3376.54
0.	162.15	87.80	8.23	7.34	44.56	39.76	99.80	3693.76
0.	142.35	86.03	7.55	6.73	45.64	40.70	99.70	3309.18
0.	136.43	83.11	7.01	6.24	42.70	37.99	99.61	3283.00
0.	145.35	84.09	7.56	6.76	43.76	39.06	99.51	3456.86
0.	150.42	84.55	7.99	7.19	44.91	40.39	99.51	3558.30
0.	132.31	84.86	6.58	5.76	42.21	36.97	99.32	3118.36
0.	134.19	81.35	7.13	6.36	43.22	38.55	99.22	3298.98
0.	138.97	88.39	7.03	6.31	44.68	40.11	99.13	3144.62
0.	143.18	83.08	7.62	6.79	44.20	39.39	99.13	3446.64
0.	156.36	86.21	7.83	6.96	43.20	38.37	99.13	3627.32
0.	120.48	77.66	6.30	5.57	40.63	35.93	99.13	3102.60
0.	149.22	88.97	7.15	6.42	42.63	38.31	99.13	3354.40
0.	130.15	80.67	6.93	6.18	42.99	38.31	99.03	3226.64
0.	144.22	87.85	7.50	6.79	45.69	41.34	98.93	3283.16
0.	140.34	82.77	7.49	6.66	44.16	39.31	98.93	3391.28
0.	154.04	87.48	8.23	7.57	46.76	43.03	98.72	3521.72
0.	141.00	79.00	0.0	0.0	0.0	0.0	98.65	3558.00
0.	120.54	79.16	6.06	5.25	39.80	34.49	96.45	3045.46
0.	120.77	80.73	6.28	5.60	42.00	37.45	95.73	2991.62
0.	114.56	72.16	6.47	5.27	40.78	33.15	94.82	3175.26
0.	123.00	69.00	0.0	0.0	0.0	0.0	92.97	3570.00
0.	109.91	72.67	5.70	5.03	37.63	33.23	92.72	3025.12
0.	100.50	64.54	4.97	4.26	31.95	27.38	89.40	3114.22
0.	98.96	63.21	4.88	4.20	31.10	26.80	89.40	3131.60
0.	84.45	63.51	4.25	3.52	31.95	26.50	87.09	2659.58
0.	93.00	61.00	0.0	0.0	0.0	0.0	87.09	3056.00
0.	89.00	55.00	0.0	0.0	0.0	0.0	87.09	3256.00
0.	89.00	62.00	0.0	0.0	0.0	0.0	87.09	2884.00
0.	76.00	49.00	0.0	0.0	0.0	0.0	82.84	3074.00
0.	78.00	50.00	0.0	0.0	0.0	0.0	82.84	3136.00
0.	76.00	48.00	0.0	0.0	0.0	0.0	82.84	3136.00
0.	58.16	40.76	2.71	2.08	18.98	14.59	77.15	2854.16
0.	65.00	45.00	0.0	0.0	0.0	0.0	77.15	2940.00
0.	62.00	40.00	0.0	0.0	0.0	0.0	77.15	3070.00

TABLE XXI (Continued)

LIGNIN PEAK AREA SUMMATIONS FROM PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9
3 CARBON SIDE CHAIN								
0.	336.88	189.15	16.04	14.27	90.06	80.09	100.00	5342.88
0.	300.33	168.78	15.23	13.81	85.58	77.59	100.00	5338.32
0.	331.26	189.27	14.66	13.00	83.77	74.31	100.00	5250.78
0.	298.47	165.70	15.51	14.09	86.11	78.18	100.00	5403.84
0.	290.24	155.44	15.05	13.69	80.60	73.31	100.00	5601.51
0.	230.61	128.95	11.48	10.45	64.19	58.48	99.98	5365.56
0.	219.96	126.00	11.26	10.22	64.44	58.47	99.98	5237.49
0.	192.58	120.24	9.79	8.92	61.14	55.65	99.98	4804.65
0.	180.24	115.05	8.82	7.94	56.26	50.67	99.98	4700.25
0.	197.32	115.09	9.85	8.70	57.44	50.71	99.98	5143.71
0.	182.54	115.88	8.80	7.79	55.83	49.51	99.90	4726.17
0.	196.09	116.15	9.64	8.68	57.11	51.38	99.80	5064.81
0.	221.88	120.14	10.37	9.28	56.12	50.20	99.80	5540.64
0.	183.85	111.11	8.73	7.70	52.73	46.56	99.70	4963.77
0.	176.47	107.50	8.14	7.11	49.61	43.33	99.61	4924.50
0.	180.54	104.45	8.48	7.46	49.04	43.17	99.51	5185.29
0.	180.91	101.68	8.85	7.84	49.72	44.06	99.51	5337.45
0.	167.01	107.11	7.65	6.68	49.08	42.87	99.32	4677.54
0.	180.34	109.33	8.56	7.54	51.92	45.70	99.22	4948.47
0.	160.85	102.30	7.70	6.82	48.92	43.38	99.13	4716.93
0.	177.20	102.83	9.23	8.24	53.51	47.81	99.13	5169.96
0.	202.92	111.89	9.79	8.66	54.00	47.74	99.13	5440.98
0.	139.07	89.65	6.56	5.58	42.30	35.92	99.13	4653.90
0.	187.91	112.04	8.45	7.21	50.36	42.94	99.13	5031.60
0.	162.31	100.61	7.74	6.74	47.97	41.74	99.03	4839.96
0.	169.39	103.18	8.05	7.15	49.11	43.51	98.93	4924.74
0.	166.67	98.29	8.41	7.44	49.60	43.86	98.93	5086.92
0.	154.38	87.67	7.78	7.02	44.17	39.87	98.72	5282.58
0.	176.00	98.00	0.0	0.0	0.0	0.0	98.65	5337.00
0.	155.56	102.16	7.33	6.26	48.09	41.13	96.45	4568.19
0.	107.50	71.87	5.19	4.56	34.65	30.45	95.73	4487.43
0.	147.20	92.72	7.41	6.32	46.74	39.78	94.82	4762.89
0.	116.00	65.00	0.0	0.0	0.0	0.0	92.97	5355.00
0.	101.88	67.36	4.97	4.21	32.88	27.81	92.72	4537.68
0.	85.79	55.10	4.06	3.30	26.08	21.20	89.40	4671.33
0.	89.98	57.47	4.10	3.22	26.14	20.52	89.40	4697.40
0.	75.30	56.62	3.31	2.54	24.94	19.10	87.09	3989.37
0.	81.00	53.00	0.0	0.0	0.0	0.0	87.09	4584.00
0.	77.00	46.00	0.0	0.0	0.0	0.0	87.09	4884.00
0.	75.00	52.00	0.0	0.0	0.0	0.0	87.09	4326.00
0.	63.00	40.00	0.0	0.0	0.0	0.0	82.84	4611.00
0.	67.00	43.00	0.0	0.0	0.0	0.0	82.84	4704.00
0.	63.00	40.00	0.0	0.0	0.0	0.0	82.84	4704.00
0.	57.99	40.63	2.45	1.77	17.15	12.40	77.15	4281.24
0.	55.00	37.00	0.0	0.0	0.0	0.0	77.15	4410.00
0.	55.00	37.00	0.0	0.0	0.0	0.0	77.15	4605.00

TABLE XXI (Continued)

LIGNIN PEAK AREA SUMMATIONS FROM PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9
1,2 + 3 CARBON SIDE CHAIN								
0.	750.75	421.53	37.76	33.76	212.05	189.53	100.00	10685.75
0.	678.16	381.11	35.74	32.69	200.82	183.71	100.00	10676.63
0.	716.57	409.41	35.75	32.58	204.26	186.21	100.00	10501.55
0.	686.90	381.34	36.12	33.27	200.54	184.68	100.00	10807.67
0.	704.72	377.42	36.41	33.59	195.02	179.88	100.00	11203.01
0.	625.00	349.46	32.40	30.14	181.15	168.59	99.98	10731.12
0.	613.19	351.24	31.94	29.65	182.88	169.75	99.98	10474.97
0.	528.84	330.21	28.70	26.80	179.22	167.27	99.98	9609.29
0.	519.07	331.32	26.19	24.29	167.13	154.97	99.98	9400.50
0.	573.20	334.32	29.75	27.35	173.50	159.44	99.98	10287.41
0.	527.04	334.56	27.49	25.38	174.47	161.18	99.90	9452.33
0.	579.08	343.00	30.25	28.12	179.19	166.51	99.80	10129.62
0.	613.54	332.21	30.79	28.49	166.67	154.26	99.80	11081.27
0.	554.94	335.39	28.63	26.47	172.99	160.03	99.70	9927.54
0.	540.05	328.99	27.06	24.90	164.85	151.66	99.61	9849.00
0.	548.06	317.08	28.02	25.79	162.11	149.19	99.51	10370.58
0.	552.77	310.69	28.75	26.59	161.57	149.41	99.51	10674.89
0.	490.82	314.79	24.43	22.29	156.73	142.99	99.32	9355.08
0.	526.32	319.08	27.43	25.28	166.34	153.27	99.22	9896.93
0.	488.03	310.39	25.45	23.23	161.77	147.74	99.13	9433.85
0.	528.67	306.78	27.99	25.76	162.35	149.44	99.13	10339.91
0.	571.48	315.10	28.86	26.55	159.16	146.36	99.13	10881.95
0.	452.08	291.42	23.17	20.94	149.41	134.97	99.13	9307.79
0.	541.28	322.73	26.48	23.94	157.86	142.73	99.13	10063.20
0.	494.14	306.29	25.62	23.57	158.86	146.08	99.03	9679.91
0.	533.00	324.67	27.44	25.22	167.22	153.54	98.93	9849.47
0.	522.74	308.28	27.54	25.38	162.41	149.71	98.93	10173.83
0.	521.72	296.28	27.27	25.25	154.89	143.42	98.72	10565.16
0.	517.00	289.00	0.0	0.0	0.0	0.0	98.65	10674.00
0.	432.50	284.03	21.72	19.49	142.62	128.02	96.45	9136.37
0.	371.55	248.39	19.11	17.33	127.75	115.85	95.73	8974.85
0.	409.30	257.81	21.56	18.91	135.92	119.01	94.82	9525.77
0.	382.00	214.00	0.0	0.0	0.0	0.0	92.97	10710.00
0.	345.47	228.41	17.75	15.80	117.30	104.44	92.72	9075.35
0.	286.29	183.86	13.90	11.77	89.33	75.64	89.40	9342.66
0.	290.67	185.65	14.01	11.77	89.34	75.12	89.40	9394.79
0.	239.37	180.00	11.55	9.58	86.89	72.10	87.09	7978.73
0.	269.00	176.00	0.0	0.0	0.0	0.0	87.09	9168.00
0.	252.00	154.00	0.0	0.0	0.0	0.0	87.09	9768.00
0.	247.00	172.00	0.0	0.0	0.0	0.0	87.09	8652.00
0.	209.00	134.00	0.0	0.0	0.0	0.0	82.84	9222.00
0.	226.00	145.00	0.0	0.0	0.0	0.0	82.84	9408.00
0.	210.00	133.00	0.0	0.0	0.0	0.0	82.84	9408.00
0.	175.53	123.00	7.66	5.78	53.65	40.49	77.15	8562.47
0.	181.00	124.00	0.0	0.0	0.0	0.0	77.15	8820.00
0.	178.00	117.00	0.0	0.0	0.0	0.0	77.15	9210.00

TABLE XXI (Continued)

LIGNIN PEAK AREA SUMMATIONS FROM PAA WOOD PYROGRAMS

1	2	3	4	5	6	7	8	9
VANILLIN AND ACETOVANILLONE								
0.	97.80	54.92	4.57	3.91	25.66	21.95	100.00	3561.92
0.	102.20	57.43	4.77	4.06	26.82	22.82	100.00	3558.88
0.	101.73	58.12	4.66	3.99	26.65	22.80	100.00	3500.52
0.	109.18	60.62	4.84	3.98	26.91	22.09	100.00	3602.56
0.	118.68	63.56	5.15	4.34	27.59	23.26	100.00	3734.34
0.	117.18	65.52	5.26	4.34	29.38	24.24	99.98	3577.04
0.	110.76	63.45	5.10	4.22	29.24	24.16	99.98	3491.66
0.	104.32	65.14	4.71	3.84	29.44	23.94	99.98	3203.10
0.	105.67	67.45	4.64	3.71	29.61	23.69	99.98	3133.50
0.	103.52	60.37	4.82	3.97	28.13	23.15	99.98	3429.14
0.	106.63	67.69	4.87	3.98	30.91	25.26	99.90	3150.78
0.	117.52	69.61	5.41	4.44	32.03	26.29	99.80	3376.54
0.	133.68	72.38	5.89	4.69	31.87	25.38	99.80	3693.76
0.	121.43	73.39	5.51	4.64	33.31	28.06	99.70	3309.18
0.	122.68	74.73	5.36	4.23	32.65	25.75	99.61	3283.00
0.	138.92	80.37	6.04	4.72	34.95	27.31	99.51	3456.86
0.	135.18	75.98	6.08	4.82	34.18	27.12	99.51	3558.30
0.	113.09	72.54	4.85	3.88	31.09	24.87	99.32	3118.36
0.	137.95	83.63	5.95	4.82	36.07	29.23	99.22	3298.98
0.	118.12	75.12	5.49	4.46	34.89	28.38	99.13	3144.62
0.	139.21	80.77	5.95	4.82	34.57	27.97	99.13	3446.64
0.	149.48	82.42	6.29	5.00	34.67	27.57	99.13	3627.32
0.	134.87	83.46	5.71	4.42	35.27	27.23	99.13	3228.50
0.	131.63	81.90	5.87	4.58	36.49	28.41	99.13	3228.50
0.	126.47	78.38	5.83	4.57	36.13	28.35	99.03	3226.64
0.	136.56	83.19	6.02	4.90	36.67	29.83	98.93	3283.16
0.	126.66	74.70	5.74	4.62	33.87	27.22	98.93	3391.28
0.	168.01	95.42	7.83	6.66	44.46	37.86	98.72	3521.72
0.	126.00	70.00	0.0	0.0	0.0	0.0	98.65	3558.00
0.	110.10	72.31	4.85	3.88	31.84	25.54	96.45	3045.46
0.	138.22	92.40	6.28	5.29	42.00	35.35	95.73	2991.62
0.	122.64	77.24	5.53	4.47	34.81	28.18	94.82	3175.26
0.	134.00	75.00	0.0	0.0	0.0	0.0	92.97	3570.00
0.	130.60	86.35	5.89	4.82	38.99	31.87	92.72	3025.12
0.	132.83	85.30	5.83	4.83	37.49	30.97	89.40	3114.22
0.	128.15	81.84	5.96	4.92	38.05	31.43	89.40	3131.60
0.	107.77	81.04	4.98	4.20	37.40	31.56	87.09	2659.58
0.	122.00	80.00	0.0	0.0	0.0	0.0	87.09	3056.00
0.	128.00	79.00	0.0	0.0	0.0	0.0	87.09	3256.00
0.	106.00	74.00	0.0	0.0	0.0	0.0	87.09	2884.00
0.	109.00	70.00	0.0	0.0	0.0	0.0	82.84	3074.00
0.	108.00	69.00	0.0	0.0	0.0	0.0	82.84	3136.00
0.	113.00	72.00	0.0	0.0	0.0	0.0	82.84	3136.00
0.	95.83	67.16	3.91	3.02	27.37	21.17	77.15	2854.16
0.	99.00	67.00	0.0	0.0	0.0	0.0	77.15	2940.00
0.	95.00	62.00	0.0	0.0	0.0	0.0	77.15	3070.00

APPENDIX V

TRENDS FROM PERACETIC ACID WOOD PYROGRAMS FOR SEVERAL YIELD RANGES

Tables XXII-XXVII contain the slope of the least-squares line for the equation LN(area) = C + B(yield) and the T values. When T is greater than 2.0 the area can be predicted at a given yield level (95% confidence limits). Below 2.0 the area cannot be predicted because the slope of the least-squares line is no different from zero. In Table XXII peak 12 (vanillin) has a low T value and the slope is essentially zero. This is interpreted to mean there is no change in peak area for no. 12 even though there is loss in yield.

The yield range from 100.0 to 77.15% was analyzed. In addition, this yield range was subdivided into several smaller ranges which were analyzed separately to investigate the trends peculiar to that range. Yield ranges of 100.0-98.65%, 96.45-77.15%, 99.98-98.72%, 96.45-87.09%, and 82.82-77.15% were examined.

TABLE XXII

PYROGRAM TRENDS 100.00-77.15% YIELD

LN(area) = C + B(yield)

Peak No.	Slope ($\times 10^{-2}$)	T
1	1.06	4.35
4	6.16	35.00
5	3.16	15.70
6	4.88	8.68
7	7.13	15.58
8	4.55	17.14
10	7.21	21.07
12	0.04	0.14
13	1.20	5.09
5+8	4.05	21.72
6+7+10	6.50	15.92
12+13	0.65	2.58
all 9	3.90	23.40

TABLE XXIII

PYROGRAM TRENDS 100.00-98.65% YIELD

LN(area) = C + B(yield)

Peak No.	Slope ($\times 10^{-2}$)	T
1	10.5	1.97
4	4.64	1.84
5	8.87	2.68
6	37.6	3.50
7	43.1	6.61
8	16.7	2.80
10	31.5	5.23
12	-27.0	6.78
13	-17.6	4.69
5+8	14.0	3.43
6+7+10	35.6	4.97
12+13	-22.0	6.09
all 9	11.39	3.31

TABLE XXIV

PYROGRAM TRENDS 96.45-77.15% YIELD

LN(area) = C + B(yield)

Peak No.	Slope ($\times 10^{-2}$)	T
1	1.04	2.91
4	5.07	15.32
5	1.78	7.39
6	3.00	4.08
7	5.08	9.32
8	4.24	16.85
10	5.69	17.65
12	0.62	1.23
13	2.25	8.90
5+8	3.68	22.03
6+7+10	4.76	11.41
12+13	1.49	4.81
all 9	3.20	19.84

TABLE XXV

PYROGRAM TRENDS 99.98-98.72% YIELD

LN(area) = C + B(yield)

Peak No.	Slope ($\times 10^{-2}$)	T
1	-0.10	0.03
4	5.80	1.76
5	4.20	1.04
6	11.7	1.92
7	28.9	7.11
8	7.00	1.07
10	20.3	3.81
12	-30.0	5.91
13	-16.6	4.18

TABLE XXVI

PYROGRAM TRENDS 96.45-87.09% YIELD

$LN(area) = \underline{C} + \underline{B}(yield)$

Peak No.	Slope ($\times 10^{-2}$)	$\underline{T}$
1	0.83	0.86
4	6.69	11.91
5	2.65	5.22
6	4.94	2.62
7	6.89	5.92
8	3.87	7.17
10	7.01	16.21
12	-0.99	-0.66
13	2.13	3.22

TABLE XXVII

PYROGRAM TRENDS 82.84-77.15% YIELD

$LN(area) = \underline{C} + \underline{B}(yield)$

Peak No.	Slope ($\times 10^{-2}$)	$\underline{T}$
1	0.25	0.55
4	3.51	4.23
5	1.09	1.59
6	2.45	2.70
7	2.23	1.76
8	5.61	4.96
10	2.54	4.98
12	1.44	2.97
13	3.14	7.85

APPENDIX VI

WOOD YIELD AS A FUNCTION OF REACTION TIME

Reaction time was plotted against the observed percentage yield from the weighed samples. Due to the uncertainties of correctly measuring high yields, percentage yield was determined as a linear function of time for the two high-yield groups generated for this work. The corrected yield levels used in this study are listed in Table XXVIII. Baird's (126) samples are graphed for comparison along with both high-yield groups in Fig. 50-52.

TABLE XXVIII

WOOD YIELD LEVELS OF THREE PAA REACTION GROUPS

2.1% PAA 50°C			2.8% PAA 60°C			3.0% PAA 60°C (126)	
Corrected Yield, %	Time of Reaction, min	Observed Yield, %	Corrected Yield, %	Time of Reaction, min	Observed Yield, %	Time of Reaction, min	Observed Yield, %
99.98	4	99.98	99.73	14	99.60	80	98.72
99.90	14	99.91	99.42	24		160	95.73
99.80	24	101.38	99.19	34	99.48	240	92.72
99.70	34	98.05	98.65	49	98.45	320	89.40
99.61	44	99.84	98.25	64	98.38	400	87.09
99.51	54	99.53	97.75	79	97.68	480	86.18
99.41	64	99.38	97.29	94		560	82.84
99.32	74	99.27	96.95	109	97.32	640	77.15
99.22	84	99.24	96.45	124	96.45		
99.13	94	99.32	95.92	139	95.92		
99.03	104	99.19	95.38	154	94.82		
98.93	114	98.54	94.95	169	94.71		

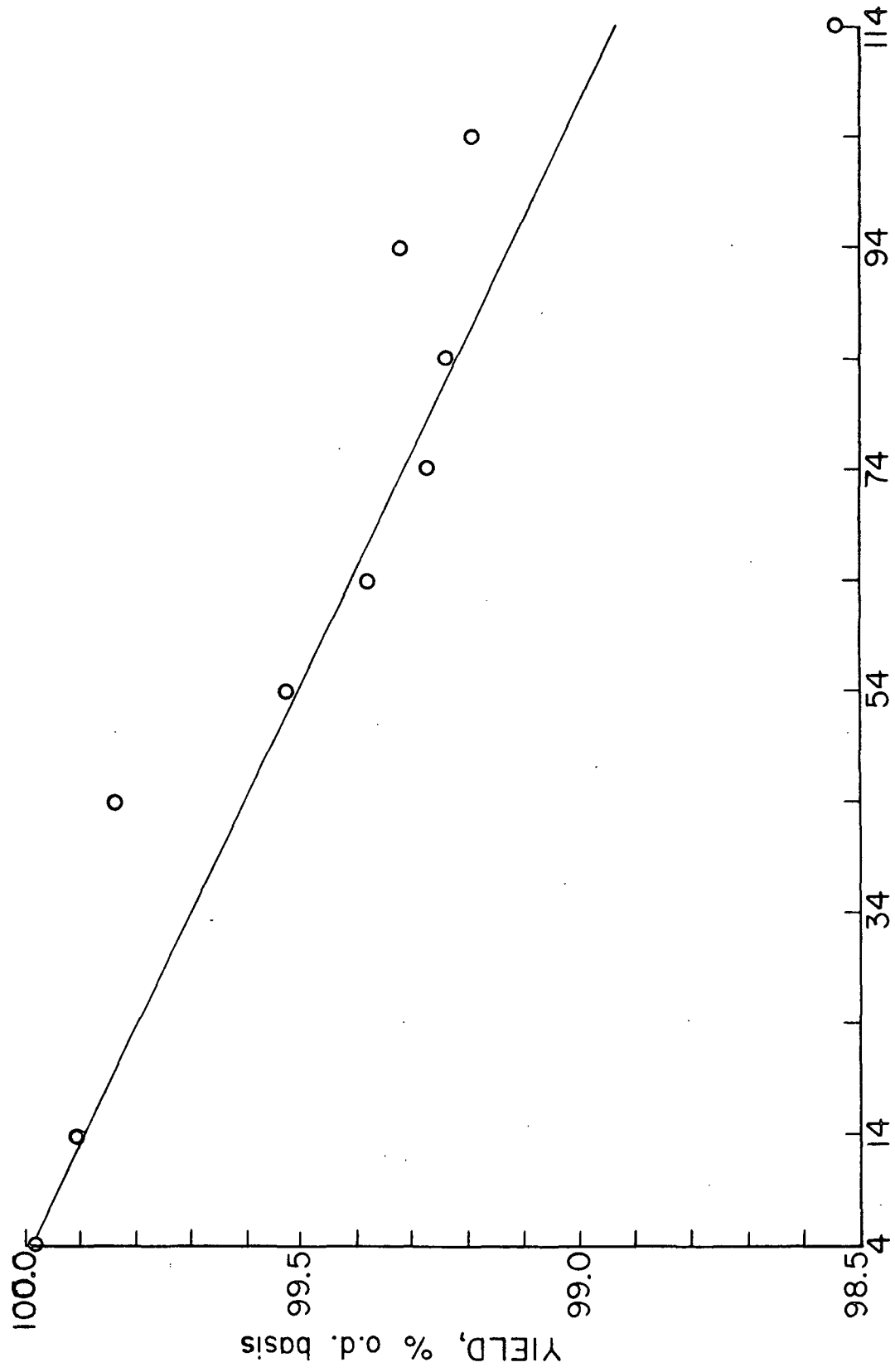


Figure 50. Percentage Yield-Time Dependence of 50°C, 2.1% PAA-Treated Loblolly Pine

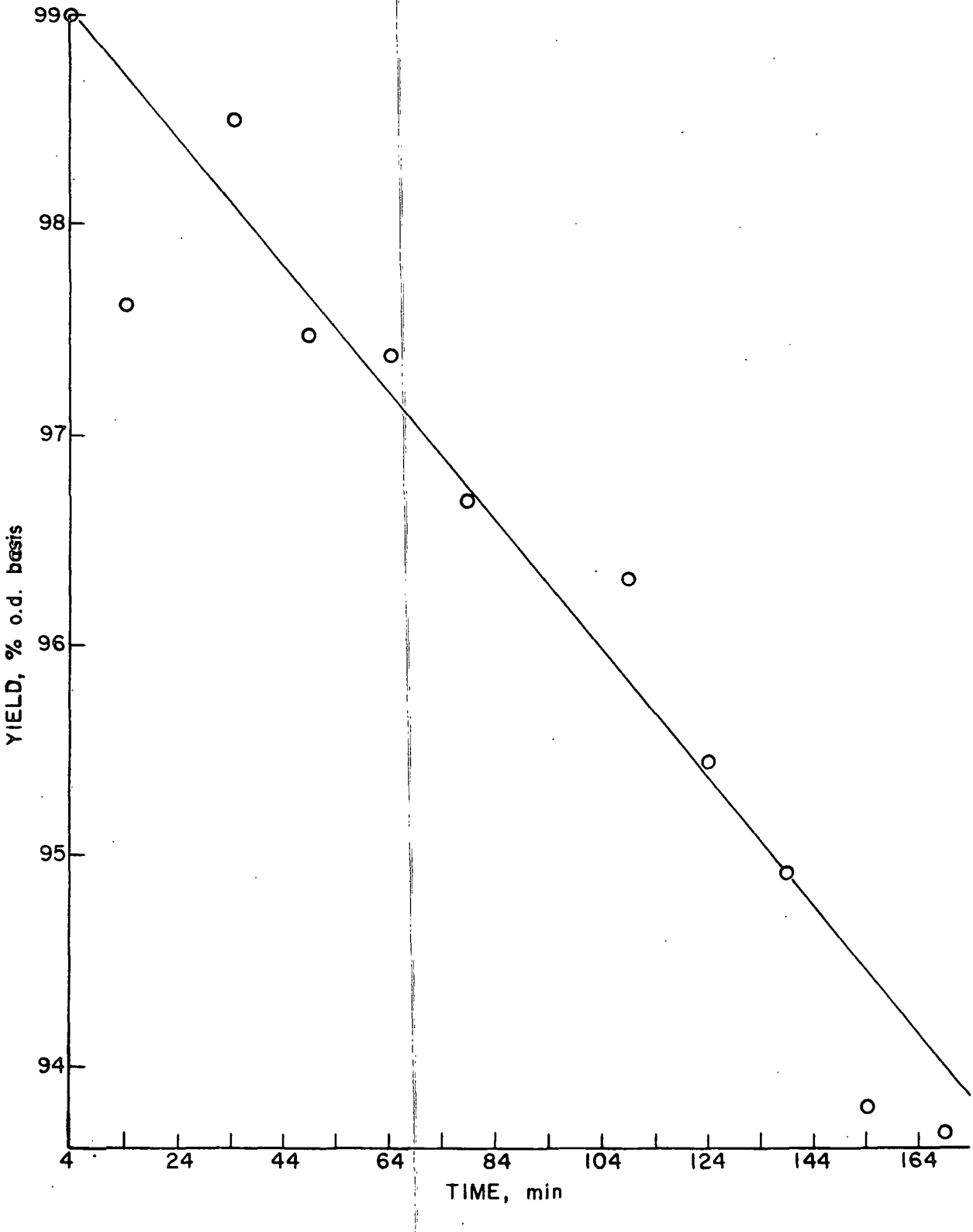


Figure 51. Percentage Yield-Time Dependence of 60°C, 2.8% PAA-Treated Loblolly Pine

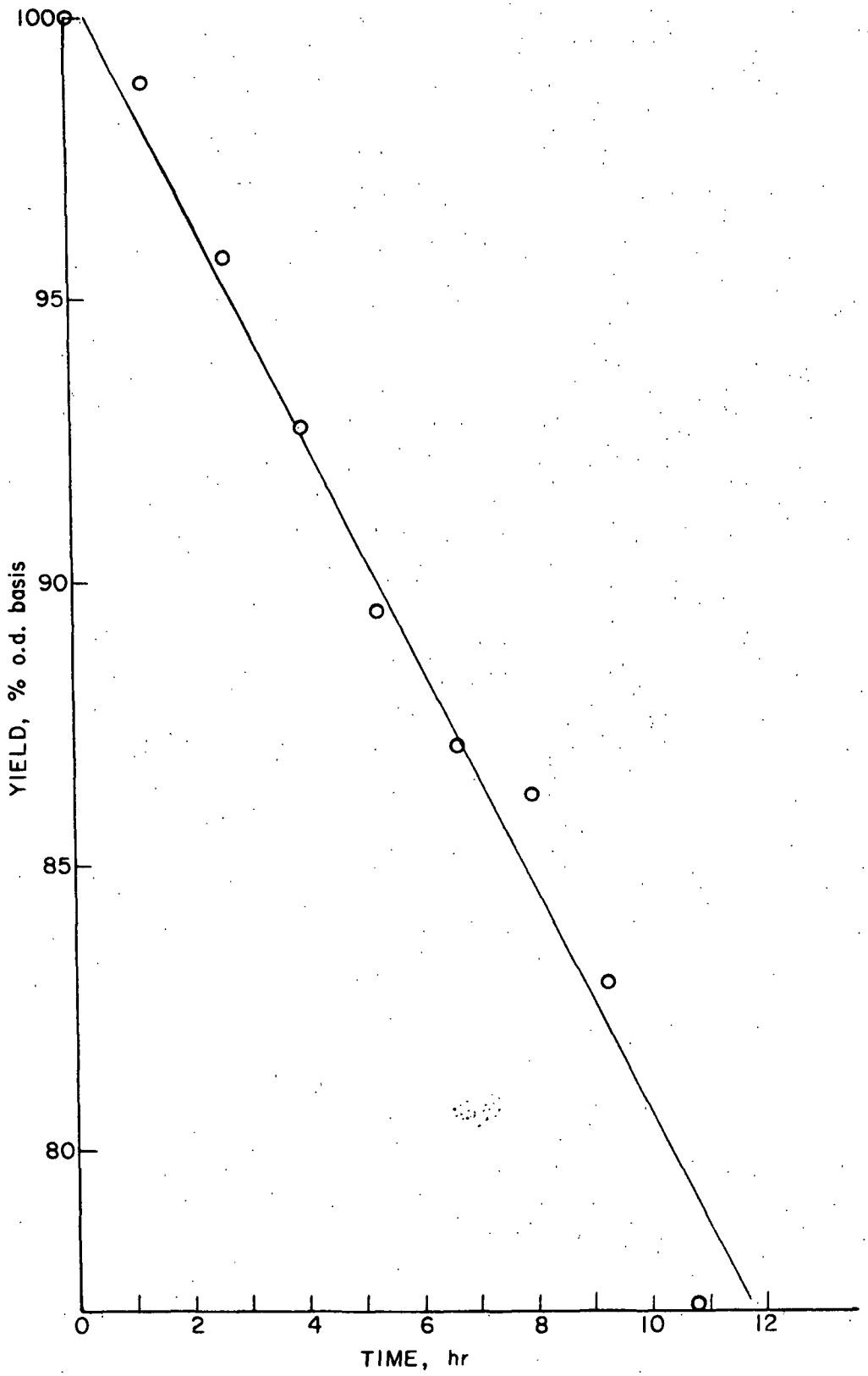


Figure 52. Percentage Yield-Time Dependence of 60°C, 3.0% PAA-Treated Loblolly Pine (126)

APPENDIX VII

THERMAL DEGRADATION IN TOLUENE

The Autoclave designed and manufactured by Autoclave Engineers, Inc. (Erie, PA, 1958), Serial Number AC-4376, was used for this work. A 1000-psi safety rupture disk was used as operating pressures below 900 psi were anticipated. Six glass tubes containing samples were run simultaneously in the Autoclave. Each sample tube was 14-cm long, 9-mm OD, 3-mm ID. Each tube contained 0.23-ml AR-grade toluene and 0.01 g of sample. The samples were 5-carboxymethyl-4-methyl-2(5H)-furanone, dioxane lignin, 100% yield loblolly pinewood, 98.93% yield loblolly pinewood, 2-(2-methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol and a blank with only 0.23 ml of toluene. After one end of the glass tube was melted shut, the samples and toluene were placed in the cooled tubes. A vacuum (15-mm Hg) was placed on the open end of the tube to remove the air and facilitate sealing the tube. While under vacuum the tube was heated near the open end until the tube collapsed and sealed. Approximate sealed volume was 1.0 cc.

The sealed tubes were then placed in the Autoclave and sealed. The chamber was more than half filled with 300 ml of water. The temperature rise was about 5°C/minute. At 300°C the pressure reached 800 psi and steam was bled off to maintain 750 psi. The temperature was held at 315°C for 25 minutes and then the Autoclave was rapidly cooled down.

The samples were analyzed by draining aliquots (toluene solution) out of the opened tubes with a syringe and injecting them on the GC. The chromatograms showed no degradation of the toluene.

All 5 materials used in this study were insoluble in toluene before heating. After heating, the toluene solutions (except the toluene only tube) were colored indicating some material was in solution. The chromatograms from the toluene solutions were similar to the pyrograms of the original material. Some product distributions were different but no new products were detected. The carbohydrate peaks for the wood chromatograms were eliminated probably due to their thermal instability and/or insolubility in toluene. The long time at temperature increases the possibility of secondary reactions. For this reason and possible product insolubility, this method was not pursued further.

APPENDIX VIII

MASS SPECTRA

Table XXIX contains an index to the mass spectra in this appendix. Table XXX contains the mass spectra of authentic samples, Table XXXI contains the mass spectra of lignin-model compound pyrolysis products, Table XXXII contains the mass spectra of dioxane lignin pyrolysis products, Table XXXIII contains the mass spectra of wood and PAA wood pyrolysis products and Table XXXIV contains the mass spectra of PAA lignin pyrolysis products. The last section in this appendix contains the mass spectra interpretations of some of the tentatively identified lignin-model compound pyrolysis products. The base ion was taken as the most abundant ion above 44 m/e due to air contamination contributing to 28 (N_2), 32(O_2), 40 (Ar), and 44(CO_2). In a limited number of spectra, higher base ions were taken as base to compensate for the inbalance of intensities at low m/e compared to high m/e due to nonuniformities in GCMS operations (153).

The data listed in the following tables describe the method of analysis (which includes the method used to introduce the sample into the mass spectrometer, either PGC, GC, or direct injection) and the compound which was analyzed by MS. PGCMS pinoresinol, guaiacol means that pinoresinol was pyrolyzed and separated by GLC, the mass spectrum is of the guaiacol peak.

TABLE XXIX

INDEX TO MASS SPECTRA

TABLE XXIX (Continued)

INDEX TO MASS SPECTRA

TABLE XIX (Continued)

INDEX TO MASS SPECTRA

TABLE XIX (Continued)

INDEX TO MASS SPECTRA

TABLE XIX (Continued)

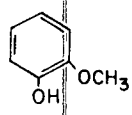
INDEX TO MASS SPECTRA

TABLE XXX

MASS SPECTRA OF AUTHENTIC SAMPLES

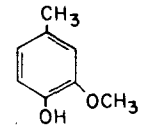
GCMS Guaiacol

m/e	Base, %	m/e	Base, %
125	14	54	7
124	75	53	36
123	4	52	25
122	11	51	26
121	10	50	17
110	10	49	3
109	100(Base)	45	4
107	4	44	61
104	6	43	13
100	3	42	3
97	3	41	10
96	5	40	66
95	8	39	50
94	6	38	20
93	4		
87	3		
83	3		
82	12		
81	59		
80	4		
79	3		
78	3		
77	7		
76	3		
70	3		
69	3		
66	6		
65	23		
64	3		
63	9		
62	4		
61	3		
58	3		
57	4		
56	3		
55	9		



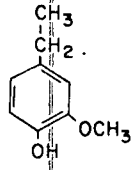
GCMS Creosol

m/e	Base, %	m/e	Base, %
139	12	58	4
138	100(Base)	57	4
137	11	56	6
136	19	55	60
135	11	54	6
124	13	53	33
123	100	52	22
122	6	51	57
121	3	50	26
120	3	49	3
118	3	45	7
109	4	44	62
108	4	43	28
107	11	42	8
106	7	41	62
105	4	40	65
96	3	39	119
95	41	38	21
94	9	37	7
91	7	33	6
89	3	31	13
81	5	30	4
79	9		
78	20		
77	44		
74	6		
71	3		
69	10		
68	4		
67	50		
66	18		
65	22		
64	3		
63	18		
62	5		
61	3		



MS High 4-Ethylguaiacol

154	8	77	39
153	45	76	4
152	92	71	7
151	24	69	6
139	11	67	13
138	58	66	13
137	100(Base)	65	29
136	14	64	4
135	21	63	13
133	4	62	6
131	3	57	12
129	4	56	3
124	4	55	24
123	10	54	5
122	58	53	34
121	26	52	12
120	19	51	14
119	19	50	7
111	6	43	17
110	3	41	22
109	24	40	5
108	5	39	34
107	14	38	6
105	7	37	5
96	1		
95	14	29	19
94	34		
93	13	27	26
92	6		
91	42		
89	8		
82	5		
81	20		
80	4		
79	16		
78	7		



GCMS 4-Ethylguaiacol

153	6	62	4
152	53	55	24
151	5	54	4
150	11	53	33
138	18	52	22
137	100(Base)	51	27
136	4	50	14
135	15	45	6
123	7	44	44
122	19	43	34
121	3	42	5
120	3	41	35
119	4	40	39
109	8	39	64
108	3	38	20
107	6		
105	6	31	13
103	3	29	38
95	7		
94	16	27	52
92	5		
91	27		
81	12		
80	4		
79	16		
78	4		
77	25		
76	4		
75	4		
69	5		
68	3		
67	6		
66	9		
65	25		
64	3		
63	8		

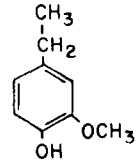
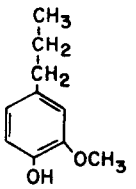


TABLE XXX (Continued)

MASS SPECTRA OF AUTHENTIC SAMPLES

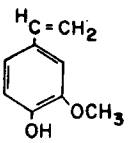
GCMS 4-Propylguaiacol

m/e	Base, %	m/e	Base, %
167	6	56	3
166	41	55	12
165	3	52	7
164	5	51	8
162	3	46	12
151	6	45	22
150	14	44	87
149	3	43	16
147	4	42	4
137	100(Base)	40	37
136	8	39	24
135	8	38	4
134	3		
133	5		
123	9		
122	22		
121	3		
120	3		
114	7		
109	10		
108	23		
107	29		
103	28		
95	5		
94	12		
93	3		
92	3		
91	18		
86	7		
81	8		
79	19		
77	20		
69	11		
65	3		
63	3		
57	10		



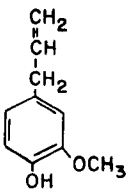
PGCMS Ferulic Acid 4-Vinylguaiacol

m/e	Base, %	m/e	Base, %
152	9	80	4
151	65	79	67
150	100(Base)	78	55
149	16	77	84
148	9	76	9
147	10	75	36
137	10	74	12
136	58	69	3
135	96	67	8
134	8	66	8
133	7	65	38
132	3	64	12
124	4	63	42
123	3	62	17
122	6	61	4
121	11	60	3
120	5	57	3
119	6	55	42
118	9	54	9
117	6	53	58
108	36	52	54
107	84	51	68
106	10	50	36
105	14	44	8
103	12	43	7
102	8	42	4
94	4	41	10
93	4	40	7
92	7	39	74
91	43	38	19
90	6	37	9
89	35		
88	3	29	22
87	3		
85	4		
81	10		



MS High Eugenol

m/e	Base, %	m/e	Base, %	m/e	Base, %
166	17	110	5	65	45
165	52	109	15	64	15
164	100(Base)	108	6	63	32
163	42	107	26	62	15
162	7	106	15	61	8
161	4	105	61	60	4
157	3	104	53	59	4
152	3	103	61	58	7
151	6	102	27	57	11
150	38	98	4	56	15
149	64	96	6	55	61
148	12	95	14	54	9
147	42	94	39	53	58
146	4	93	45	52	42
138	23	92	23	51	56
137	55	91	50	50	36
136	7	90	12	49	10
135	30	89	27	46	6
134	35	88	3	45	12
133	52	87	8	44	9
132	48	86	45	43	50
131	65	85	5	42	10
130	7	81	20	41	64
128	4	80	12	40	38
124	3	79	58	39	62
123	11	78	38	38	39
122	59	77	55	37	6
121	64	76	14		
120	12	75	14		
119	26	74	15	31	29
118	8	73	4	29	30
117	12	71	7		
116	6	70	6	27	55
115	29	69	33		
114	4	68	14		
112	3	67	7		
111	3	66	48		



GCMS cis-Isoeugenol

m/e	Base, %	m/e	Base, %
165	40	71	5
164	100(Base)	70	4
163	15	69	6
150	7	68	4
149	62	67	7
147	5	66	13
138	3	65	27
137	27	64	11
134	9	63	11
133	44	62	4
132	18	55	60
131	44	54	3
122	10	53	13
121	29	52	16
120	7	51	29
119	9	50	13
116	4	44	3
115	9	43	22
107	16	42	4
105	18	41	13
104	27	40	5
103	47	39	40
102	7	38	7
95	3		
94	3	31	5
93	17	29	8
92	12		
91	44	27	20
88	4		
82	8		
81	6		
79	20		
78	31		
77	56		
75	8		
74	4		

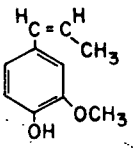
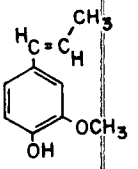


TABLE XXX (Continued)

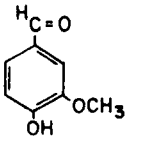
MASS SPECTRA OF AUTHENTIC SAMPLES

GCMS trans-Isoeugenol



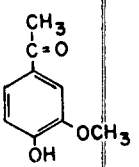
m/e	Base, %	m/e	Base, %
166	8	93	3
165	30	92	7
164	100(Base)	91	19
163	11	89	4
162	44	85	6
161	8	83	6
150	8	81	4
149	52	79	10
148	7	77	33
147	18	76	3
137	9	75	3
135	9	70	5
134	15	68	3
133	52	67	3
132	23	65	6
131	55	64	6
130	5	63	3
123	4	57	3
122	6	56	4
121	19	55	14
120	6	53	6
119	11	52	5
117	4	51	5
116	4	50	14
115	9	44	88
112	4	43	5
109	12	41	7
107	9	40	67
105	7		
104	24		
103	33		
102	4		
101	3		
96	4		
95	3		
94	6		

PGCMS Vanillin



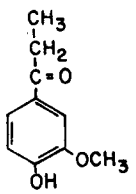
m/e	Base, %	m/e	Base, %
153	51	57	3
152	100(Base)	55	11
151	97	53	21
150	27	52	30
149	16	51	23
147	6	50	19
138	3	49	3
137	32	44	40
136	11	41	8
135	3	40	26
125	3	39	19
124	3	38	11
123	53	37	4
122	3		
121	8	31	3
110	6	30	6
109	45	29	11
108	23		
95	12	27	6
93	11		
92	3		
81	4		
80	9		
79	10		
78	6		
77	18		
75	3		
74	6		
69	8		
67	8		
66	8		
65	30		
64	3		
63	19		
62	8		
61	4		

PGCMS Acetovanillone



m/e	Base, %	m/e	Base, %
167	17	53	17
166	63	52	24
164	6	51	26
152	35	50	24
151	100(Base)	45	4
150	6	44	39
149	11	43	58
137	3	42	6
136	6	41	14
124	7	40	29
123	63	39	17
122	8	38	8
121	6	37	6
119	4		
109	9	29	8
108	17		
105	3	27	6
95	8		
94	3		
93	12		
92	7		
91	3		
81	8		
80	10		
79	8		
77	15		
74	3		
73	3		
67	13		
66	3		
65	31		
64	4		
63	11		
62	7		
61	3		
55	17		

PGCMS Propiovanillone



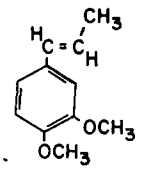
m/e	Base, %	m/e	Base, %
181	27	75	6
180	71	74	3
178	10	73	3
177	3	70	3
166	6	69	6
165	4	68	7
153	8	67	25
152	47	66	8
151	100(Base)	65	61
150	10	64	4
149	51	63	25
137	7	62	18
136	11	61	4
135	3	57	12
124	11	56	6
123	63	55	3
122	12	54	7
121	12	53	35
120	6	52	59
119	3	51	41
109	12	50	25
108	51	49	7
107	5	44	63
105	4	43	9
103	4	42	7
95	10	41	4
94	12	40	13
93	18	39	41
92	11	38	20
91	24	37	4
86	3	32	57
81	4	31	18
80	22	30	5
79	27	29	65
77	31		
76	5	27	47

TABLE XXX (Continued)

MASS SPECTRA OF AUTHENTIC SAMPLES

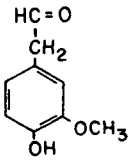
MS Methylisoeugenol

m/e	Base, %
179	12
178	100(Base)
164	5
163	23
162	5
161	4
147	7
135	12
117	4
115	9
107	27
105	6
104	3
103	7
93	7
92	7
91	21
82	4
80	4
79	4
78	4
77	5
76	5
70	11
65	8
63	5
55	7
51	8
50	8



GCMS Homovanillin

m/e	Base, %
167	4
166	29
138	11
137	100(Base)
122	23
94	8
77	12
68	4
65	4
63	5
58	8
39	12



GCMS Vanillyl Methyl Ketone

m/e	Base, %
181	7
180	44
138	15
137	100(Base)
123	4
122	16
94	8
91	4
77	6
66	4
65	6
55	3
53	4
51	4
43	21
40	4
39	5

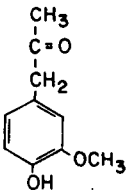
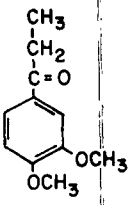


TABLE XXX (Continued)

MASS SPECTRA OF AUTHENTIC SAMPLES

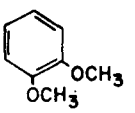
GCMS Propioveratrone

m/e	Base, %	m/e	Base, %
196	3	69	4
195	25	68	3
194	65	67	6
192	7	66	22
167	3	65	14
166	42	64	12
165	100(Base)	63	18
149	5	62	8
138	12	57	26
137	46	55	23
134	5	54	4
123	3	53	20
122	32	52	10
121	12	51	48
120	8	50	26
119	12	49	3
109	6	45	9
108	6	44	7
107	34	43	7
105	14	42	3
104	9	41	23
103	3	40	7
94	28	39	20
93	5	38	17
92	28		
91	15	31	3
89	3	29	51
81	6		
80	8	27	37
79	66		
78	17		
77	54		
76	22		
75	11		
74	5		
71	3		



GCMS Veratrole

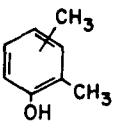
m/e	Base, %	m/e	Base, %
139	15	52	44
138	100(Base)	51	49
137	4	50	3
132	3	49	8
131	6	48	4
126	5	44	93
124	7	41	27
123	47	40	18
122	4	39	27
121	3	38	3
117	3		
113	5		
112	10		
111	4		
110	8		
108	11		
96	3		
95	25		
93	6		
91	3		
86	5		
81	4		
80	4		
78	7		
77	59		
73	7		
67	22		
66	5		
65	61		
64	10		
63	8		
57	3		
56	5		
55	4		
54	9		
53	13		



600°C PGCMS Creosol

VIV Xylenol

124	3	57	6
123	51	55	20
122	100(Base)	53	35
121	69	52	11
120	19	51	11
119	8	44	31
114	3	43	29
112	3	42	22
110	3	40	35
109	45	39	25
108	96		
107	92		
106	22		
105	24		
104	20		
103	22		
97	8		
95	9		
94	10		
93	12		
92	9		
91	37		
90	31		
89	8		
83	4		
81	11		
80	27		
79	61		
78	33		
77	63		
71	5		
70	3		
67	7		
66	5		
65	18		
63	7		



Xylenol

124	2	63	18
123	47	62	13
122	100(Base)	61	15
121	84	60	31
120	24	59	6
119	8	57	4
109	31	55	31
108	80	54	15
107	100	53	47
106	5	52	37
105	33	51	45
104	27	50	27
103	36	49	7
102	7	48	5
95	8	45	5
94	12	44	50
92	29	43	31
91	55	41	24
90	33	40	45
89	13	39	61
87	5	38	7
86	6	37	5
82	7		
81	11		
80	33		
79	63		
78	45		
77	69		
76	7		
75	12		
74	9		
69	7		
68	4		
67	9		
65	37		
64	15		

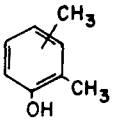
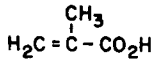


TABLE XXX (Continued)

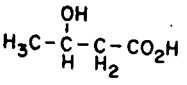
MASS SPECTRA OF AUTHENTIC SAMPLES

MS Methacrylic Acid



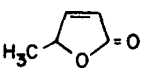
m/e	Base, %	m/e	Base, %
89	6	37	62
88	23	36	23
87	74	34	4
86	100(Base)		
85	62	31	38
84	3	30	23
83	3	29	68
81	3		
77	9	27	79
71	49		
70	32		
69	74		
68	69		
67	6		
60	28		
59	10		
58	64		
57	49		
56	14		
55	36		
54	4		
53	43		
52	4		
51	15		
50	12		
49	6		
47	14		
46	19		
45	77		
44	53		
43	77		
42	96		
41	109		
40	98		
39	102		
38	75		

GCMS 3-Hydroxybutyric Acid



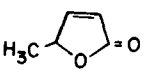
m/e	Base, %
116	54
101	30
89	12
86	100(Base)
80	15
75	33
73	12
71	12
69	23
60	22
58	20
57	14
45	101
44	143
43	141
42	76
41	107
40	19
39	36
38	16
36	18
31	18

PGCMS 5-Methyl-2(5H)-furanone



98	27
83	8
68	6
56	27
55	83
54	71
53	27
52	8
51	15
50	27
49	14
48	4
45	15
44	33
43	100(Base)
42	48
41	58
39	77
38	25
37	25
36	4
29	69
27	121
26	71
25	17

MS 5-Methyl-2(5H)-furanone

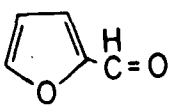


99	12
98	68
97	5
96	4
95	4
84	6
83	68
81	4
71	6
70	8
69	24
60	4
57	13
56	14
55	100(Base)
54	50
53	7
50	3
45	5
44	14
43	59
42	7
41	15
40	11
39	12
38	5
29	29
27	74
26	35
25	4

TABLE XXX (Continued)

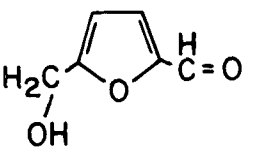
MASS SPECTRA OF AUTHENTIC SAMPLES

GCMS 2-Furaldehyde



m/e	Base, %
98	6
97	29
96	100(Base)
95	100
94	4
71	4
69	3
67	21
66	5
61	4
57	4
53	9
51	9
50	4
49	4
44	84
42	7
41	4
40	7
39	66
38	24
37	14
34	3
29	24

MS Hydroxymethylfurfural



m/e	Base, %
155	5
154	16
138	6
128	4
127	40
126	100(Base)
125	67
124	51
123	35
111	8
109	49
108	4
99	11
98	42
97	100
96	18
95	28
93	7
82	6
81	26
80	18
79	33
75	5
74	3
71	6
70	19
69	81
68	23
67	19
66	14
62	3
61	5

m/e	Base, %
59	4
57	8
55	23
54	14
53	72
52	23
51	60
50	47
49	4
48	3
46	5
45	6
44	8
43	33
42	49
41	126
40	26
39	116
38	72
37	49
36	14
35	4
34	14

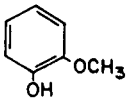
TABLE XXXI

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS Pinoresinol

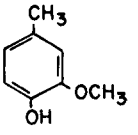
Guaiacol

m/e	Base, %
125	21
124	100(Base)
123	4
110	21
109	92
95	3
93	4
82	10
81	63
80	8
79	5
77	5
76	5
71	3
65	17
63	15
62	4
61	3
57	3
55	7
54	4
53	12
52	12
51	17
50	8
44	46
40	4
39	10
38	5
37	4



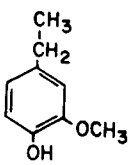
Creosol

m/e	Base, %	m/e	Base, %
140	6	52	8
139	34	51	25
138	100(Base)	50	14
137	30	44	25
136	14	42	3
135	9	41	17
125	5	40	6
124	30	39	30
123	92	38	5
122	8		
110	4		
109	9		
108	3		
107	20		
106	11		
105	6		
96	6		
95	63		
94	17		
91	6		
90	5		
81	6		
79	12		
78	14		
77	28		
69	6		
68	4		
67	28		
66	19		
65	17		
64	3		
63	9		
62	3		
61	5		
55	31		
53	14		



4-Ethylguaiacol

m/e	Base, %	m/e	Base, %
153	3	51	9
152	44	50	3
151	13	46	4
149	3	44	56
139	7	43	8
138	25	41	3
137	100(Base)	39	9
136	3	38	3
135	4		
124	5		
123	16		
122	12		
121	6		
120	4		
110	4		
109	7		
108	4		
107	6		
105	4		
98	3		
97	4		
95	3		
94	5		
92	4		
91	10		
82	5		
81	3		
79	4		
77	5		
70	6		
69	3		
65	6		
64	3		
55	12		
53	8		
52	4		



Eugenol

m/e	Base, %	m/e	Base, %
165	30	57	16
164	100(Base)	55	5
163	5	44	498
162	22	40	15
161	15	38	13
153	12		
152	9		
149	20		
148	22		
138	25		
137	22		
136	8		
132	6		
125	8		
124	22		
122	31		
121	17		
119	13		
111	11		
109	21		
108	8		
106	17		
105	15		
104	7		
103	18		
97	18		
96	11		
95	17		
94	15		
91	14		
84	10		
83	19		
79	8		
78	6		
77	18		
69	19		

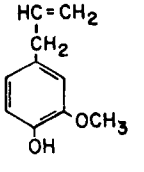


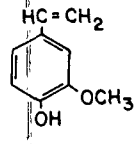
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS Pinoresinol

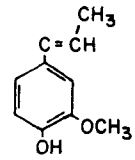
4-Vinylguaiacol

m/e	Base, %	m/e	Base, %
150	18	51	123
149	18	44	584
143	22	43	15
139	11	42	34
138	14	40	92
136	8		
135	14		
130	12		
122	16		
120	13		
119	18		
116	11		
114	18		
113	7		
109	18		
107	14		
96	34		
95	17		
93	22		
91	100(Base)		
89	39		
86	23		
85	23		
81	10		
80	10		
79	22		
78	8		
77	48		
71	25		
70	34		
65	45		
63	25		
58	17		
56	19		
55	36		
53	50		



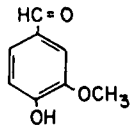
trans-Isoeugenol

m/e	Base, %
164	100(Base)
163	14
162	11
150	17
149	62
148	6
147	20
137	18
133	31
132	13
131	41
122	4
121	23
120	3
119	3
115	4
109	6
107	5
105	15
104	29
103	29
102	3
93	7
92	5
91	40
77	48



Vanillin

m/e	Base, %
153	19
152	100(Base)
151	73
150	6
149	9
137	10
123	35
93	6
87	5
83	5
81	13
79	9
77	11
68	5
65	16
60	6
57	9
56	6
53	18
52	8
51	20
50	5
44	87
40	38
39	37



Acetovanillone

m/e	Base, %
167	25
166	100(Base)
161	11
153	10
152	18
151	29
150	6
122	9
109	8
108	13
93	9
91	6
83	7
80	6
71	11
70	7
67	9
57	7
56	8
55	11
51	16
44	180
43	11
40	110

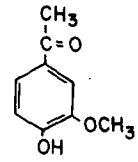


TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS Pinoresinol

Propiovanillone

m/e	Base, %	m/e	Base, %
181	4	55	7
180	21	51	7
178	4	45	4
173	3	44	96
164	6	41	4
160	4	40	40
153	3		
152	24		
151	100(Base)		
150	6		
149	7		
138	4		
137	6		
133	4		
124	3		
123	4		
122	4		
113	3		
110	4		
108	5		
98	6		
94	2		
91	5		
86	2		
85	3		
83	4		
80	3		
79	3		
77	4		
70	4		
69	6		
68	3		
63	11		
61	3		
57	6		

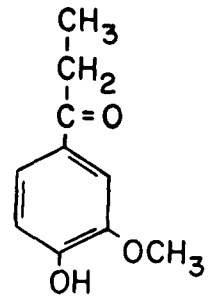


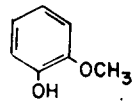
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS Diisoeugenol

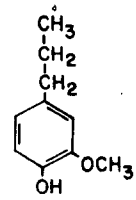
Guaiacol

m/e	Base, %
125	22
124	88
123	3
122	6
121	3
112	3
110	16
109	100(Base)
95	5
83	5
82	5
81	82
79	3
77	5
67	4
66	5
65	22
64	9
63	5
62	4
61	3
55	4
54	6
53	43
52	27
51	29
50	11
49	6
46	3
44	22
43	5
41	9
40	4
39	22
38	14
37	7



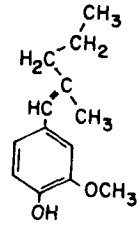
4-Propylguaiacol

m/e	Base, %	m/e	Base, %
167	11	62	4
166	53	57	6
165	2	55	9
164	3	53	2
163	2	52	3
162	2	51	9
151	2	50	3
150	2	49	2
149	3	44	63
147	2	43	3
138	21	40	4
137	100(Base)	39	9
136	3	38	2
135	7		
134	4		
131	4		
123	9		
122	15		
109	2		
108	2		
107	4		
106	3		
105	2		
94	7		
93	2		
83	2		
81	5		
79	4		
78	5		
77	6		
75	2		
69	2		
67	2		
66	3		
65	9		
63	7		



3rd Peak

m/e	Base, %	m/e	Base, %
207	12	55	3
206	60	51	7
205	3	44	25
192	3	43	5
190	3	41	8
178	19	39	10
177	100(Base)	38	3
164	4		
162	11		
161	9		
160	3		
159	5		
148	3		
147	13		
146	13		
145	70		
141	3		
133	4		
131	7		
117	13		
115	3		
105	8		
104	5		
103	11		
91	14		
83	3		
79	6		
78	5		
77	20		
76	6		
75	4		
72	3		
66	6		
65	7		
63	5		
57	3		



4th Peak

m/e	Base, %	m/e	Base, %
207	13	104	4
206	57	103	6
205	4	102	3
204	6	99	3
203	5	93	3
202	9	92	6
189	5	91	18
187	3	89	6
178	26	87	5
177	100(Base)	85	3
176	6	79	3
175	19	78	6
172	3	77	9
164	4	74	3
162	8	69	5
161	6	66	3
160	3	65	10
159	4	64	3
149	3	63	4
147	10	62	3
146	24	55	8
145	71	53	7
137	3	52	5
132	3	51	6
131	8	50	6
130	5	45	3
128	5	44	26
127	3	43	7
124	8	41	21
119	4	39	12
118	3	38	4
117	31		
116	4		
115	12		
107	5		
105	10		

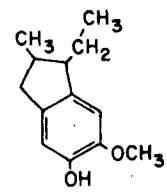


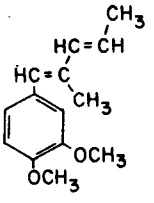
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS Diisoeugenol

5th Peak

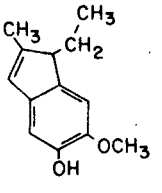
m/e	Base, %
204	51
203	13
202	82
190	18
189	28
187	100(Base)
185	4
175	6
174	20
173	12
163	5
162	11
161	20
160	15
159	28
152	10
150	5
147	45
146	8
145	20
144	13
142	10
139	9
134	12
133	11
131	7
128	5
104	15
64	20
56	6
55	19
44	18
41	7
40	11



6th Peak

m/e	Base, %
206	3
205	32
204	100(Base)
203	16
202	48
201	11
192	4
191	3
190	23
189	86
188	5
187	39
186	5
185	5
180	3
176	9
175	48
174	10
173	10
172	23
171	10
169	4
165	3
164	5
161	25
160	41
159	6
158	16
157	20
148	3
147	5
146	4
145	8
144	17
143	17
142	3

m/e	Base, %
141	5
133	5
132	6
131	14
130	3
129	20
128	13
124	11
123	3
117	5
116	11
115	34
114	3
109	3
107	5
106	4
105	13
104	4
103	7
102	12
101	5
94	4
91	7
89	3
87	4
79	3
78	10
77	20
76	3
71	3
70	3
69	3
66	4
65	5
63	10
62	5



m/e	Base, %
58	3
55	13
53	3
52	9
51	9
50	5
44	45
43	4
41	7
39	17

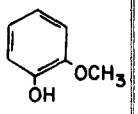
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS Coniferin

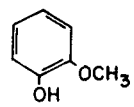
Guaiacol & Carbohydrate 1

m/e	Base, %	m/e	Base, %
143	5	55	37
137	5	54	6
129	6	53	27
128	20	52	13
126	6	51	12
125	6	45	11
124	96	44	89
122	4	43	67
115	4	42	17
114	28	41	17
110	17	40	8
109	100(Base)	39	33
100	6		
96	4		
95	7		
91	3		
86	3		
85	3		
84	3		
83	6		
82	8		
81	56		
77	10		
74	3		
72	4		
71	5		
70	5		
69	10		
66	4		
65	14		
64	5		
63	7		
62	13		
61	5		
58	11		
57	17		



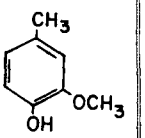
Guaiacol

m/e	Base, %
125	11
124	77
123	3
110	5
109	100(Base)
100	4
98	3
96	3
95	4
93	3
82	7
81	46
70	5
69	3
68	8
67	3
65	4
63	6
57	6
55	6
54	4
52	3
50	6
44	119
43	4
42	4
41	12
40	3
38	4



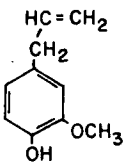
Creosol

m/e	Base, %	m/e	Base, %
140	5	61	4
139	55	58	4
138	100(Base)	56	6
137	49	55	79
136	14	53	32
135	15	52	32
126	5	51	32
125	17	50	34
124	74	47	4
123	96	45	4
122	14	44	32
112	10	43	32
110	10	41	45
109	70	40	28
107	15	39	79
106	16	38	17
105	6	37	8
96	10		
95	55		
94	21		
93	6		
91	14		
83	5		
82	5		
81	55		
79	13		
78	23		
77	47		
69	13		
68	5		
67	60		
66	28		
65	21		
64	7		
63	21		
62	6		



Eugenol

m/e	Base, %	m/e	Base, %
166	8	107	25
165	22	106	10
164	100(Base)	105	47
163	4	104	83
162	3	103	90
152	4	102	5
151	10	99	9
150	10	97	4
149	60	95	15
148	5	94	37
147	12	93	33
146	5	92	15
145	4	91	73
138	16	90	6
137	63	89	18
135	5	85	7
134	13	83	4
133	40	81	12
132	15	80	4
131	67	79	37
130	4	78	47
126	5	77	110
124	8	76	5
123	17	75	10
122	50	74	10
121	83	73	3
120	5	70	3
119	15	69	5
118	6	67	14
117	7	66	23
116	5	65	47
115	9	64	15
113	5	63	40
110	4	62	4
109	23	58	4
108	5	57	4



m/e	Base, %
56	3
55	107
53	47
52	22
51	70
50	33
46	6
45	5
44	83
43	40
42	7
41	57
40	21
39	73
38	11
37	9

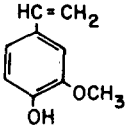
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS Coniferin

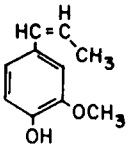
4-Vinylguaiacol

m/e	Base, %	m/e	Base, %
151	35	78	14
150	100(Base)	77	73
149	11	75	6
148	4	70	5
147	9	68	3
136	25	67	6
135	100	66	6
134	3	65	16
133	4	64	10
132	9	63	23
131	6	62	4
123	5	55	13
122	7	54	5
119	4	53	25
118	4	52	14
117	3	51	20
108	8	50	10
107	43	49	3
105	8	44	40
104	3	43	12
103	4	42	4
102	4	41	3
99	4	40	5
94	6	39	25
93	4	38	3
92	3	37	4
91	11		
90	6		
89	17		
87	3		
86	3		
85	5		
84	3		
83	3		
81	5		
79	23		



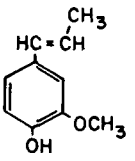
cis-Isoeugenol

m/e	Base, %	m/e	Base, %
165	26	85	8
164	100(Base)	84	6
163	7	82	8
162	6	80	3
161	5	79	11
160	6	78	11
152	5	77	43
151	4	71	3
150	16	70	6
149	61	69	17
147	8	68	4
139	3	67	3
138	5	66	5
137	19	65	15
135	10	64	5
134	4	63	5
133	20	62	3
132	13	60	4
131	36	59	4
124	3	58	10
121	27	57	15
120	6	56	8
119	4	55	43
109	4	53	14
108	6	51	12
107	4	50	5
106	5	49	5
105	9	45	15
104	16	44	96
103	21	43	19
102	4	42	8
97	5	41	29
95	6	40	8
94	8	39	17
92	9	38	5
91	29		



trans-Isoeugenol

m/e	Base, %	m/e	Base, %
166	11	105	35
165	71	104	56
164	100(Base)	103	54
163	29	102	10
162	29	101	3
161	5	99	3
150	23	95	3
149	83	94	8
148	11	93	21
147	38	92	14
146	4	91	67
145	3	90	5
139	6	89	13
137	38	83	7
136	3	82	21
135	9	81	15
134	4	80	6
133	56	79	25
132	25	78	29
131	67	77	81
130	3	76	8
129	5	75	13
124	6	74	13
123	5	69	7
122	16	68	3
121	54	67	6
120	11	66	6
119	10	65	44
118	4	64	7
117	3	63	23
116	6	62	7
115	10	60	5
109	14	56	8
108	5	55	77
107	16	54	5
106	4	53	17



m/e	Base, %
52	21
51	42
50	23
45	8
44	52
43	25
41	19
40	5
39	44
38	5

trans-Isoeugenol Filament VIV

m/e	Base, %
166	11
165	52
164	100(Base)
163	22
162	12
151	3
150	17
149	58
148	8
147	14
138	5
137	20
136	3
135	5
134	6
133	38
132	18
131	43
122	4
121	37
107	9
106	3
105	7
104	34
103	26
98	3
93	8
92	4
91	10
81	3
78	5
77	17
55	35
44	3
43	6

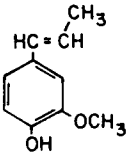


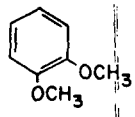
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS 2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-one

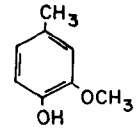
Veratrole

m/e	Base, %	m/e	Base, %
139	17	40	16
138	100(Base)	39	22
131	6	38	11
124	9	37	7
123	39		
121	5	30	18
112	9	29	47
110	7		
108	7	27	8
95	29		
93	5		
92	3		
80	4		
78	6		
77	67		
75	7		
74	4		
73	7		
71	6		
67	19		
66	4		
65	73		
64	12		
63	14		
62	8		
56	6		
55	5		
54	9		
53	10		
52	38		
51	50		
49	10		
46	7		
44	133		
43	7		
41	49		



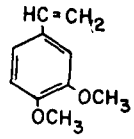
Creosol

m/e	Base, %	m/e	Base, %
139	21	54	5
138	100(Base)	53	39
137	22	52	26
136	7	51	65
135	14	50	35
124	14	47	4
123	100	45	5
122	13	44	5
110	4	43	14
109	9	42	5
107	21	41	68
106	16	40	39
96	11	39	84
95	77	38	18
94	16		
93	4	29	26
91	18		
89	3	27	39
81	11		
80	6		
79	18		
78	29		
77	71		
75	4		
74	4		
73	4		
69	5		
68	8		
67	87		
66	39		
65	48		
64	5		
63	29		
62	15		
61	12		
55	87		



3rd Peak

m/e	Base, %
165	9
164	100(Base)
150	34
149	79
147	11
146	8
135	5
134	13
132	5
122	7
119	7
118	7
107	3
106	11
105	4
93	4
92	11
91	45
90	5
89	12
87	3
78	11
77	18
70	22
65	13
63	11
53	4
51	7
44	39
40	62
39	3
36	3
31	37
29	7



Veratrolaldehyde

m/e	Base, %
168	3
166	100(Base)
165	37
164	5
151	12
109	7
105	10
95	26
94	9
77	11
66	5
65	8
44	200
40	15
30	9
29	67

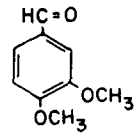


TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS 2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-one

Propioveratrone

m/e	Base, %
195	7
194	63
166	31
165	100(Base)
149	4
138	3
137	26
122	22
121	4
120	8
109	4
107	7
105	7
103	4
94	10
93	3
92	9
91	8
79	22
78	10
77	23
76	4
75	3
69	4
66	4
65	9
57	14
53	6
51	12
50	6
44	6
39	5
29	7
27	12

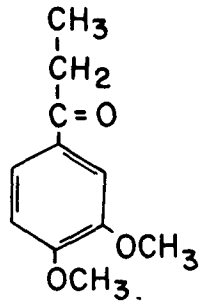


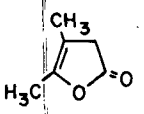
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS β-Methyl Lactone

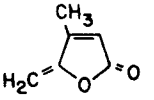
1st Peak

m/e	Base, %	m/e	Base, %
113	14	30	4
112	100(Base)	29	30
111	8		
110	36		
104	7		
100	7		
98	8		
97	30		
85	10		
84	30		
83	8		
82	7		
81	9		
79	11		
78	7		
77	3		
70	6		
69	38		
68	25		
67	6		
65	13		
59	6		
57	27		
56	25		
55	10		
54	6		
46	11		
44	320		
43	12		
42	82		
41	18		
40	111		
39	7		
38	10		
34	3		



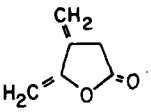
2nd Peak

m/e	Base, %
111	1
110	100(Base)
107	3
97	6
83	6
82	19
81	3
76	4
70	4
69	23
68	45
67	4
65	4
62	3
57	3
55	31
54	24
53	31
52	4
50	4
45	4
44	110
43	13
42	34
41	15
40	115
39	28
38	6
37	6
33	3
30	3
29	20



3rd Peak

m/e	Base, %
111	3
110	100(Base)
97	3
87	5
82	11
68	42
57	3
55	3
54	14
53	10
52	3
51	6
49	3
45	6
44	104
43	6
42	67
41	10
40	96
39	67
38	24
37	5
34	7
30	3
29	20
26	3



4th Peak

m/e	Base, %
113	14
112	40
111	9
110	100(Base)
97	30
95	7
93	5
84	5
83	5
82	33
70	13
69	90
68	63
67	16
57	4
55	8
54	19
53	4
52	4
51	3
50	15
44	73
43	9
42	26
41	10
40	80
39	70
38	13
37	3
36	4
31	3
29	21

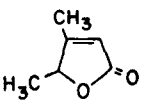


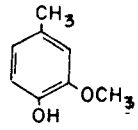
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS 2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol

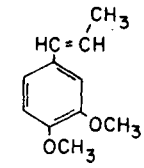
Creosol

m/e	Base, %	m/e	Base, %
139	15	62	6
138	100(Base)	57	6
137	10	55	45
136	14	54	3
135	16	53	21
124	9	52	15
123	88	51	33
122	6	50	16
118	3	44	35
113	4	43	15
109	5	42	3
108	3	41	23
107	14	40	18
106	6	39	55
97	3	38	6
96	10	37	4
95	35		
94	5	31	6
91	8	30	4
90	5	29	13
85	4		
83	5		
81	5		
79	6		
78	13		
77	30		
75	4		
74	4		
71	4		
69	4		
68	6		
67	35		
66	12		
65	30		
64	4		
63	6		



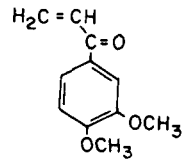
Methylisoeugenol

m/e	Base, %	m/e	Base, %
179	26	53	5
178	100(Base)	52	5
177	3	50	9
164	6	48	3
163	57	44	28
149	4	41	4
147	17	39	4
146	4		
135	15		
133	4		
131	6		
120	4		
119	8		
118	7		
117	12		
116	3		
115	22		
110	6		
108	8		
107	54		
105	13		
104	7		
103	24		
95	3		
91	11		
89	4		
79	15		
77	15		
70	5		
69	8		
66	5		
65	19		
64	7		
63	13		
56	4		
55	4		



VIV 3rd Peak

197	4		
194	4		
193	23		
192	100(Base)		
183	4		
178	7		
177	7		
167	15		
166	84		
165	58		
164	19		
163	58		
151	12		
149	14		
137	4		
134	7		
133	10		
132	8		
125	3		
121	8		
106	3		
95	11		
79	4		
77	7		
67	4		
65	4		
44	15		



3rd Peak

193	5	69	6
192	50	65	6
178	3	63	16
177	4	62	4
167	3	57	7
166	41	56	3
165	25	55	9
164	35	53	6
163	100(Base)	52	8
149	3	51	22
148	3	50	11
137	4	44	77
135	3	43	4
134	4	41	11
133	22	40	18
132	14		
121	10	29	28
120	5		
119	10		
118	5		
117	4		
109	5		
108	5		
107	6		
105	6		
103	7		
102	4		
95	13		
92	4		
91	16		
89	9		
80	3		
79	5		
78	6		
77	32		
76	3		

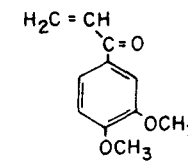


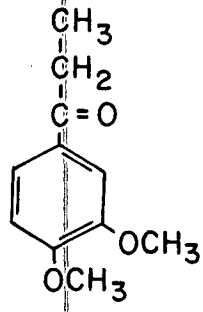
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS 2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol

Propioveratrone

m/e	Base, %	m/e	Base, %
195	16	41	3
194	65	40	4
193	4	39	3
192	23		
167	6	29	6
166	45		
165	100(Base)		
162	6		
151	5		
149	5		
137	25		
123	5		
122	16		
121	3		
120	4		
107	5		
95	4		
94	9		
92	10		
80	3		
79	23		
78	4		
77	30		
76	6		
69	3		
66	5		
65	3		
64	3		
57	8		
55	8		
53	3		
51	13		
50	4		
45	4		
44	50		
43	4		



VIV Propioveratrone

m/e	Base, %
195	10
194	76
192	27
170	4
167	7
166	24
165	100(Base)
164	4
163	4
161	3
151	3
139	3
137	14
125	5
123	5
122	4
121	3
119	3
110	3
109	3
92	3
83	4
77	6
57	3
55	7
44	6
30	4

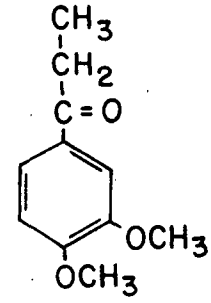


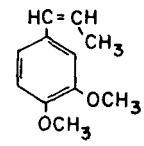
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS 1-(3,4-Dimethoxyphenyl)propan-1,2-diol

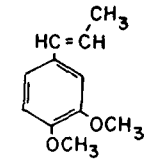
1st Peak

m/e	Base, %	m/e	Base, %
179	15	95	16
178	100(Base)	94	4
177	5	93	3
176	4	92	16
175	3	91	67
164	10	90	10
163	57	89	13
162	6	88	4
161	4	80	3
151	3	79	22
150	3	78	10
149	4	77	18
148	4	75	3
147	24	74	5
146	12	65	9
145	3	64	3
136	5	63	6
135	35	60	3
134	3	57	11
133	7	55	16
132	7	53	9
131	13	52	10
121	6	51	24
120	14	50	11
119	6	44	41
118	11	41	7
117	18	39	8
116	8		
115	35		
108	12		
107	90		
106	6		
105	22		
104	13		
103	57		
102	9		



Methylisoeugenol

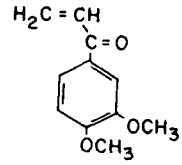
m/e	Base, %	m/e	Base, %
179	54	94	6
178	100(Base)	93	4
177	9	92	13
176	8	91	54
165	4	90	5
164	11	89	21
163	84	85	3
162	7	79	37
161	8	78	11
151	5	77	43
148	3	76	5
147	37	74	4
146	13	70	6
145	4	69	5
136	4	67	5
135	32	66	8
134	3	65	35
133	8	64	10
132	6	63	19
131	14	62	7
122	3	60	6
121	5	59	7
120	10	57	11
119	6	56	4
118	4	55	24
117	19	53	13
116	10	52	18
115	22	51	41
108	14	50	16
107	65	46	7
106	4	45	13
105	27	44	22
104	13	43	12
103	46	42	4
102	3	41	54
95	13	40	8



m/e	Base, %
39	41
38	8
37	5

3rd Peak

m/e	Base, %	m/e	Base, %
193	2	75	7
192	24	74	5
178	2	71	3
168	7	69	3
167	33	67	14
166	100(Base)	66	7
165	81	65	20
164	11	64	3
163	30	63	28
152	9	62	11
151	56	61	3
150	4	57	4
149	4	54	3
137	31	53	10
133	9	52	13
132	4	51	39
123	5	50	24
122	15	49	5
121	10	45	3
120	4	44	70
119	17	43	3
109	8	41	33
108	3	39	12
107	9	38	17
106	4		
105	28		
104	3		
96	8		
95	65		
94	7		
92	20		
91	15		
80	15		
79	54		
78	14		
77	65		



3rd Peak Filament VIV

m/e	Base, %	m/e	Base, %
194	2	44	5
193	9	41	7
192	62		
178	2		
177	5		
168	3		
167	51		
166	100(Base)		
165	81		
164	17		
163	39		
152	5		
151	43		
149	3		
137	14		
135	3		
133	9		
123	3		
122	4		
121	5		
119	3		
109	5		
108	4		
107	3		
106	3		
105	11		
96	4		
95	36		
93	5		
91	3		
80	6		
79	5		
78	6		
77	28		
67	8		
65	9		

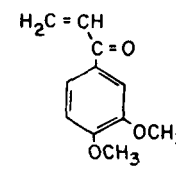


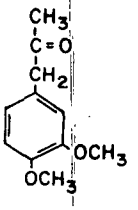
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS 1-(3,4-Dimethoxyphenyl)propan-1,2-diol

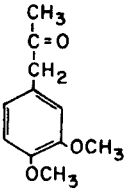
Veratryl Methyl Ketone

m/e	Base, %	m/e	Base, %
195	21	69	3
194	66	66	6
193	5	65	20
192	13	64	4
178	3	63	9
177	10	61	3
166	7	57	3
165	8	55	3
163	3	53	6
153	7	52	5
152	50	51	14
151	100(Base)	44	33
137	13	43	49
136	5	42	3
135	23	41	6
122	8	40	3
121	6	39	14
118	8		
117	3		
109	3		
108	23		
107	33		
106	26		
105	20		
103	4		
94	3		
93	4		
92	4		
91	21		
90	24		
81	6		
80	8		
79	14		
78	21		
77	23		
71	3		



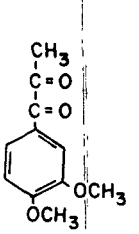
Veratryl Methyl Ketone Filament VIV

m/e	Base, %
196	8
195	35
194	81
193	3
192	12
178	4
177	7
166	3
165	4
153	11
152	58
151	100(Base)
150	3
137	12
135	4
122	3
117	3
108	9
107	23
106	16
91	7
90	5
43	19



5th Peak

209	1	64	6
208	12	63	9
194	2	62	6
192	2	59	4
178	3	53	8
168	2	51	22
167	6	50	5
166	33	44	40
165	100(Base)	43	22
164	4	42	3
163	3	41	8
152	4	40	3
151	14	39	4
149	4	38	3
138	3		
137	46		
136	3		
123	3		
122	24		
121	4		
120	3		
109	5		
108	4		
107	9		
104	3		
95	3		
94	11		
93	3		
92	22		
91	5		
79	27		
78	6		
77	43		
76	9		
66	3		
65	6		



5th Peak Filament VIV

m/e	Base, %
209	3
208	7
194	3
167	5
166	41
165	100(Base)
152	4
151	17
137	27
122	6
109	3
94	5
77	19
55	4
45	3

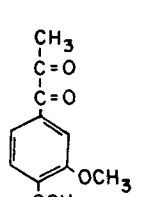


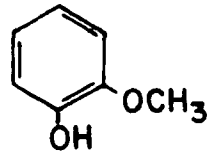
TABLE XXXI (Continued)

MASS SPECTRA OF LIGNIN-MODEL PYROLYSIS PRODUCTS

PGCMS Conidendrin

Guaiacol

m/e	Base, %	m/e	Base, %
125	33	50	33
124	90	49	9
123	4	44	29
122	17	43	3
121	11	41	14
114	3	40	17
111	5	39	67
110	23	38	27
109	100(Base)	37	12
108	5	36	6
96	5		
95	10		
94	4		
93	7		
92	5		
83	3		
82	11		
81	83		
80	11		
79	8		
78	4		
77	14		
76	4		
67	7		
66	9		
65	31		
64	8		
63	23		
62	15		
61	6		
56	3		
55	29		
54	13		
53	73		
52	44		
51	52		



PGCMS Dehydrodivanillin

Vanillin

m/e	Base, %
153	12
152	100(Base)
151	81
150	18
149	6
137	8
123	10
81	44

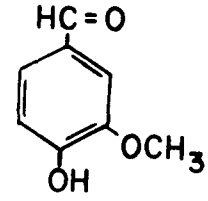


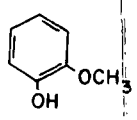
TABLE XXXII

MASS SPECTRA OF DIOXANE LIGNIN PYROLYSIS PRODUCTS

PGCMS Dioxane Lignin

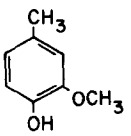
Guaiacol

m/e	Base, %	m/e	Base, %
127	9	41	39
125	10	40	237
124	39	39	21
123	14	38	7
113	13	37	11
108	30	35	10
98	3	34	18
96	11	33	8
93	9		
91	14	31	13
86	11	30	28
85	10	29	70
84	10		
83	9	27	25
81	76		
80	19		
78	9		
77	30		
76	6		
71	100(Base)		
70	16		
69	12		
68	8		
66	20		
65	13		
64	10		
63	10		
55	21		
54	21		
53	25		
52	46		
51	39		
50	7		
44	195		
43	19		
42	7		



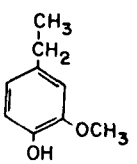
Creosol

m/e	Base, %	m/e	Base, %	m/e	Base, %
139	13	74	4	31	8
138	71	72	5	30	6
137	29	71	12	29	88
136	34	69	6		
135	18	68	4	27	100
133	3	67	100(Base)		
132	4	66	22		
125	12	65	53		
124	13	64	6		
123	94	63	13		
122	6	62	13		
120	5	61	17		
118	4	60	4		
113	3	59	4		
112	4	58	5		
111	3	57	16		
110	3	56	22		
109	6	55	100		
107	12	54	4		
106	8	53	47		
103	3	52	25		
97	3	51	47		
96	5	50	47		
95	76	49	5		
94	17	45	6		
91	16	44	100		
90	7	43	25		
89	18	42	6		
85	7	41	76		
83	9	40	118		
82	6	39	129		
81	9	38	44		
80	5	37	13		
79	23	34	14		
78	33	33	3		
77	40				



4-Ethylguaiacol

152	78	76	9
151	20	69	4
150	17	67	3
149	3	66	4
139	8	65	25
138	40	64	4
137	100(Base)	63	7
136	5	60	3
135	42	58	4
134	3	57	5
133	5	55	17
127	3	53	11
126	3	52	10
123	6	51	23
122	48	50	17
121	13	49	6
120	7	46	6
119	12	45	16
114	3	44	80
110	3	43	7
109	15	42	3
108	6	41	25
107	11	40	20
105	4	39	33
103	5	38	11
95	12	37	3
94	20	36	3
93	5		
92	12	31	17
91	38	30	5
85	4	29	25
81	3		
80	8	27	5
79	25		
78	9		
77	35		



4-Propylguaiacol

167	5	69	9
166	32	64	4
164	5	63	4
162	5	62	4
150	10	57	7
149	5	56	4
147	3	55	10
138	7	53	7
137	100(Base)	52	7
136	7	51	6
135	9	46	10
133	6	45	19
129	3	44	128
127	3	43	15
124	3	42	6
123	7	41	4
122	12	40	32
120	4	39	16
117	3	38	7
114	7	34	5
109	6		
108	19	31	32
107	26	30	7
103	30	29	21
101	4		
97	4		
95	5		
94	11		
91	11		
90	3		
86	5		
81	4		
79	10		
78	3		
77	15		
73	3		

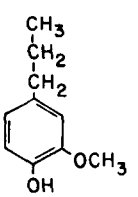


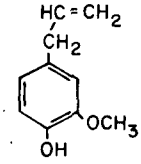
TABLE XXXII (Continued)

MASS SPECTRA OF DIOXANE LIGNIN PYROLYSIS PRODUCTS

PGCMS Dioxane Lignin

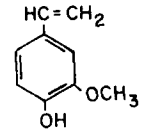
Eugenol

m/e	Base, %	m/e	Base, %
165	11	81	11
164	100(Base)	79	3
163	13	78	9
162	18	77	32
160	7	73	3
149	52	71	6
147	20	70	3
144	3	69	7
139	3	67	4
137	36	65	17
136	3	64	6
134	8	63	5
133	36	62	5
132	23	57	4
131	40	55	32
122	29	53	6
121	23	52	8
119	8	51	17
115	6	50	5
108	7	45	15
107	56	44	120
106	6	43	14
105	4	42	3
104	24	41	21
103	40	40	30
101	4	39	29
97	3		
95	7	31	31
94	10	30	10
93	9	29	27
92	13		
91	27	27	26
90	8		
89	6		
86	7		
82	6		



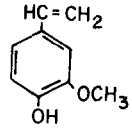
4-Vinylguaiacol

m/e	Base, %	m/e	Base, %
152	7	70	9
151	4	69	17
150	100(Base)	68	6
149	9	67	9
148	18	66	5
147	5	57	29
145	4	56	14
137	5	55	9
135	58	51	24
134	4	44	245
129	7	43	17
126	5	42	4
125	5	41	24
124	6	40	236
123	5	39	11
119	22	38	5
111	7	36	7
107	8	34	29
106	6		
105	10	30	6
104	7	29	182
98	8		
94	18	27	27
91	6		
90	7		
89	4		
85	4		
83	17		
82	6		
81	17		
79	6		
78	5		
77	17		
74	3		
72	6		
71	21		



4-Vinylguaiacol

150	43		
148	45		
135	100(Base)		
123	43		
107	75		
99	36		
89	132		
85	25		
79	54		
78	35		
77	28		
72	37		
71	33		
69	38		
67	34		
55	82		
51	79		
44	546		
41	40		
40	400		
39	239		
29	329		
27	75		



cis-Isoeugenol

m/e	Base, %	m/e	Base, %
166	8	77	22
164	100(Base)	65	4
163	10	63	5
162	21	58	6
160	5	57	11
152	3	56	6
151	4	55	3
150	5	52	8
149	44	50	4
147	8	45	19
144	4	44	156
137	11	43	3
135	11	41	9
134	8	40	33
133	15	37	5
132	5		
131	7	31	41
122	4	30	22
121	10	29	50
116	8		
112	5	27	9
111	5		
107	11		
104	10		
103	22		
102	7		
98	3		
97	7		
96	4		
95	4		
91	21		
89	6		
87	8		
86	7		
83	5		
78	4		

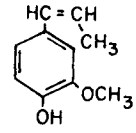


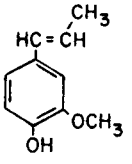
TABLE XXXII (Continued)

MASS SPECTRA OF DIOXANE LIGNIN PYROLYSIS PRODUCTS

PGCMS Dioxane Lignin

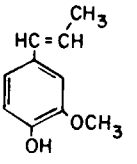
trans-Isoeugenol

m/e	Base, %	m/e	Base, %
166	8	65	10
164	100(Base)	60	11
163	18	57	65
162	14	56	30
161	9	55	56
151	10	53	10
150	9	51	14
149	17	50	7
147	7	46	6
145	10	44	326
144	9	43	41
134	14	41	26
131	27	40	367
130	23	39	21
128	7	36	26
127	13	34	63
121	12		
119	10	31	86
117	7	30	14
111	9	29	272
109	7		
105	15	27	23
104	10		
103	12		
99	13		
97	55		
86	14		
83	10		
82	7		
81	32		
79	10		
76	26		
73	36		
70	30		
69	16		
67	10		



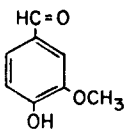
trans-Isoeugenol

m/e	Base, %	m/e	Base, %
164	98	43	23
163	19	41	44
162	91	40	593
160	22	39	65
156	23	38	24
151	17	36	17
149	31		
144	22	30	30
133	100(Base)	29	356
131	26		
129	28	27	49
128	28		
123	22		
113	25		
111	28		
110	27		
107	49		
104	15		
103	65		
102	11		
93	21		
91	53		
89	30		
83	16		
81	72		
79	79		
77	42		
74	53		
71	21		
69	31		
65	28		
62	29		
55	37		
53	18		
51	81		
44	553		



Vanillin

153	15		
152	100(Base)		
151	86		
150	8		
149	6		
145	3		
137	9		
132	12		
129	3		
124	5		
123	17		
121	5		
117	3		
110	11		
109	25		
108	13		
96	3		
95	7		
94	3		
93	10		
81	28		
80	8		
79	8		
67	6		
65	21		
64	5		
63	5		
53	6		
52	6		
51	8		
50	12		
44	89		
40	43		



Homovanillin

166	52	46	14
165	15	45	23
164	24	44	300
163	9	40	93
162	8	39	30
155	24		
152	9		
150	9		
149	9		
147	15		
145	12		
138	12		
137	100(Base)		
132	26		
126	7		
124	22		
122	31		
120	21		
116	14		
101	10		
94	18		
93	33		
91	15		
84	12		
83	9		
79	12		
78	15		
77	19		
66	8		
65	17		
64	15		
62	11		
58	15		
55	10		
51	12		
50	66		

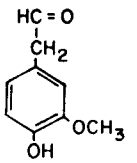
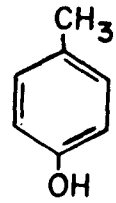


TABLE XXXII (Continued)

MASS SPECTRA OF DIOXANE LIGNIN PYROLYSIS PRODUCTS

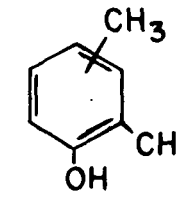
600°C PGCMS Dioxane Lignin

Cresol



m/e	Base, %
109	9
108	96
107	81
106	3
105	4
94	100(Base)
92	4
91	10
90	44
89	25
80	9
79	70
78	15
77	52
66	44
65	70
63	19
50	21
49	9
39	44

Xylenol



m/e	Base, %
123	10
122	88
121	19
120	8
118	3
108	42
107	100(Base)
105	3
104	4
97	5
94	7
93	3
91	20
90	3
81	8
80	7
79	29
78	5
77	31
76	4
67	8
65	16
64	4
62	6
58	5
56	5
54	3
53	30
52	8
50	4
41	7
39	30
38	7
34	4
29	37
27	13
26	12

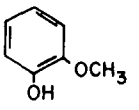
TABLE XXXIII

MASS SPECTRA OF WOOD AND PERACETIC ACID WOOD PYROLYSIS PRODUCTS

PGCMS 99.98% Loblolly Pine

Guaiacol

m/e	Base, %	m/e	Base, %
125	29	51	27
124	100(Base)	50	22
112	4	44	46
111	5	43	27
110	22	42	10
109	98	41	13
108	4	40	10
98	5	39	54
97	5	38	10
96	5	37	11
95	13		
94	4	31	6
93	4	30	5
84	7	29	18
82	12		
81	88		
79	7		
78	6		
77	7		
75	4		
74	3		
73	3		
70	3		
69	8		
68	9		
65	22		
64	4		
63	17		
62	5		
61	3		
58	3		
56	4		
55	20		
54	16		
53	63		
52	34		



PGCMS 99.98% Loblolly Pine

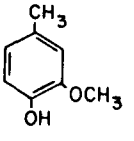
Carbohydrate M. . .

m/e	Base, %	m/e	Base, %
144	4	73	7
139	3	72	33
138	9	71	6
137	3	70	8
129	12	69	3
128	71	68	12
127	4	67	9
126	11	65	10
125	8	64	6
124	67	63	7
123	19	59	7
116	7	58	67
115	11	57	64
114	100(Base)	56	24
113	6	55	55
112	5	54	11
110	11	53	29
109	64	52	7
106	3	51	6
102	4	50	7
100	8	49	5
97	4	46	4
96	5	45	11
95	6	44	98
94	3	43	88
93	4	42	38
87	4	41	21
86	15	40	9
85	17	39	40
84	3	38	13
83	9	37	16
82	11		
81	50	31	33
80	4	30	79
77	14	29	55
74	4		

PGCMS 99.98% Loblolly Pine

Creosol

m/e	Base, %	m/e	Base, %
140	6	65	32
139	52	64	3
138	100(Base)	63	16
137	48	62	4
136	20	61	5
135	13	60	4
125	5	58	3
124	46	57	7
123	96	56	6
122	14	55	60
115	4	54	13
114	4	53	30
112	4	52	26
109	20	51	40
108	6	50	22
107	38	44	22
106	30	43	26
105	7	42	4
97	7	41	36
96	18	40	15
95	72	39	50
94	26	38	11
93	7	37	6
91	12	33	3
81	15		
80	4	31	9
79	9	30	6
78	28	29	34
77	54		
76	3		
75	4		
72	4		
69	18		
68	10		
67	60		
66	22		



PGCMS 100% Loblolly Pine

4-Ethylguaiacol

m/e	Base, %
154	3
153	16
152	100(Base)
151	3
150	16
147	3
144	2
139	2
138	16
137	71
136	3
135	13
124	2
122	4
120	2
119	4
117	4
107	8
106	3
95	3
91	3
79	2
69	4
65	7
55	2
44	12
43	5
40	3
39	3

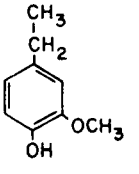


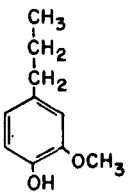
TABLE XXXIII (Continued)

MASS SPECTRA OF WOOD AND PERACETIC ACID WOOD PYROLYSIS PRODUCTS

PGCMS 100% Loblolly Pine

4-Propylguaiacol

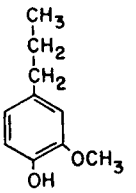
m/e	Base, %	m/e	Base, %
167	5	94	6
166	39	93	9
165	3	91	16
151	7	90	12
150	10	89	9
140	6	87	7
139	9	86	24
138	7	85	11
137	30	84	11
136	5	83	15
132	8	82	7
131	4	77	5
130	3	71	10
129	8	70	7
128	4	69	18
126	4	67	3
124	14	64	7
123	21	60	5
122	51	58	24
117	26	57	84
116	5	55	40
114	17	54	10
112	6	53	7
111	8	51	23
110	6	49	5
109	23	45	14
108	100(Base)	44	125
107	90	43	91
106	8	42	55
103	12	41	58
102	7	40	8
101	17	39	93
99	16	38	13
98	21		
96	5		
95	23		



PGCMS 99.98% Loblolly Pine

4-Propylguaiacol

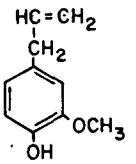
m/e	Base, %	m/e	Base, %
166	31	79	13
165	3	78	9
162	3	77	29
151	5	73	3
147	3	72	5
138	5	69	8
128	7	68	3
126	3	67	6
124	3	65	8
123	4	64	7
122	33	63	3
121	17	62	6
118	4	60	4
117	3	59	8
116	3	58	7
111	5	57	12
110	4	56	3
109	9	55	23
108	74	54	10
107	100(Base)	53	19
106	5	52	12
104	3	51	23
103	6	50	17
97	11	45	6
96	5	44	84
95	9	43	53
94	13	42	8
93	5	41	15
92	4	40	15
91	16	39	25
90	11	38	10
88	3		
87	3	31	7
85	10	30	9
81	12	29	24
80	9		



PGCMS 100% Loblolly Pine

Eugenol

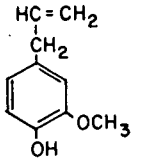
m/e	Base, %	m/e	Base, %
165	6	83	6
164	100(Base)	81	7
162	7	79	11
152	8	77	30
150	14	70	11
149	29	69	14
147	10	66	9
140	6	65	7
138	11	64	11
137	14	63	9
135	7	58	22
133	11	57	33
132	8	56	10
131	25	55	32
123	4	53	7
122	40	52	7
121	14	51	63
119	13	50	22
117	7	45	25
115	8	44	113
112	11	43	113
109	20	42	26
108	14	41	29
107	26	39	39
105	17	38	9
103	23		
101	9		
96	5		
95	4		
94	9		
93	21		
92	11		
90	13		
89	9		
86	12		
85	7		



PGCMS 99.98% Loblolly Pine

Eugenol

m/e	Base, %	m/e	Base, %
166	3	95	39
165	8	94	4
164	100(Base)	93	5
163	6	92	3
162	15	91	39
161	6	88	4
160	3	89	5
149	19	87	4
147	11	86	8
138	6	85	27
137	18	83	7
136	6	81	15
135	6	79	9
133	17	78	9
132	12	77	43
131	20	76	8
124	8	75	6
123	7	74	7
122	9	73	10
121	35	71	7
120	4	70	9
119	8	69	15
114	5	67	3
113	3	66	5
112	4	65	4
111	3	63	6
110	3	59	9
109	4	58	9
108	11	57	22
107	20	56	3
105	13	55	39
104	13	54	4
103	18	53	11
98	5	52	14
97	4	51	20
96	6	50	8



m/e	Base, %
49	4
45	8
44	81
43	57
42	9
41	18
40	6
39	31
38	11
31	6
29	17

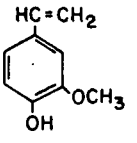
TABLE XXXIII (Continued)

MASS SPECTRA OF WOOD AND PERACETIC ACID WOOD PYROLYSIS PRODUCTS

PGCMS 99.98% Loblolly Pine

4-Vinylguaiacol

m/e	Base, %	m/e	Base, %
152	11	79	49
151	49	78	49
150	100(Base)	77	77
149	12	75	13
148	8	74	9
147	5	71	5
137	8	70	6
136	33	69	7
135	85	68	6
133	3	67	7
132	3	66	7
126	18	65	26
121	5	64	17
120	5	63	26
119	7	62	17
118	6	61	13
117	3	60	3
115	3	59	4
109	6	58	5
108	17	57	16
107	79	56	9
106	3	55	21
105	8	54	6
103	8	53	21
101	5	52	31
95	6	51	31
91	28	50	31
90	3	49	6
89	19	45	8
87	3	44	38
85	5	43	44
84	5	42	10
82	3	41	10
81	12	40	8
80	4	39	59

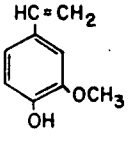


m/e	Base, %
38	18
37	9
31	8
30	7
29	26

PGCMS 100% Loblolly Pine

4-Vinylguaiacol

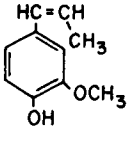
m/e	Base, %	m/e	Base, %
152	2	65	12
151	33	64	12
150	100(Base)	63	19
149	9	62	8
147	7	61	3
138	7	57	9
136	31	56	3
135	83	55	15
123	3	54	3
121	3	53	25
117	3	52	22
108	5	51	33
107	81	50	19
105	8	44	25
103	3	43	20
102	3	42	3
98	3	41	9
95	4	39	31
91	23	38	15
90	5	37	5
89	12		
86	14		
85	4		
84	4		
81	9		
80	3		
79	42		
78	22		
77	75		
75	6		
74	10		
72	4		
71	4		
69	5		
68	5		
67	5		



PGCMS 99.98% Loblolly Pine

cis-Isoeugenol & Carbohydrate

m/e	Base, %	m/e	Base, %
165	4	104	4
164	29	103	12
163	1	99	7
162	3	98	11
161	1	97	7
159	3	96	17
152	1	95	3
151	2	94	7
150	9	93	7
149	15	92	5
147	8	91	9
145	3	90	5
143	3	89	5
142	1	87	5
138	5	86	16
135	3	85	52
134	2	84	12
133	2	83	3
132	2	82	42
131	5	81	8
129	4	80	2
126	7	79	7
122	5	78	7
121	12	77	15
119	3	76	2
117	6	75	8
116	14	74	4
115	7	73	2
114	5	72	9
112	3	71	29
110	4	70	65
109	3	69	100(Base)
108	4	68	12
107	8	67	7
106	3	66	1
105	4	65	6

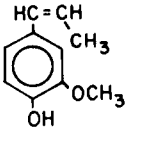


m/e	Base, %
64	2
63	5
62	1
61	2
60	22
59	3
58	65
57	65
56	6
55	29
54	7
53	9
52	3
51	7
50	12
46	1
45	29
44	84
43	106
42	42
41	94
40	45
39	48
38	10
37	5
31	71
30	8
29	55

PGCMS 100% Loblolly Pine

Carbohydrate No. 2 — cis-Isoeugenol

m/e	Base, %	m/e	Base, %
165	6	91	14
164	100(Base).	87	11
163	4	86	22
162	4	85	53
150	10	84	5
149	27	83	8
147	3	82	42
140	5	79	12
137	6	78	7
136	3	77	35
135	3	75	3
133	10	74	4
132	5	73	6
131	3	72	6
129	4	71	40
128	4	70	106
126	3	69	94
125	3	68	16
121	31	67	6
119	3	65	3
118	4	64	4
117	6	62	7
116	7	61	4
114	13	60	18
109	9	59	13
107	25	58	53
105	7	57	82
104	19	56	23
103	18	55	34
102	8	54	3
100	6	53	14
99	4	52	3
97	8	51	20
96	10	50	13
94	4	45	35
93	12	44	82



m/e	Base, %
43	141
42	59
41	165
40	46
39	65
38	19
37	8

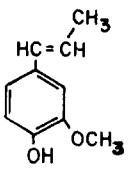
TABLE XXXIII (Continued)

MASS SPECTRA OF WOOD AND PERACETIC ACID WOOD PYROLYSIS PRODUCTS

PGCMS 100% Loblolly Pine

trans-Isoeugenol

m/e	Base, %	m/e	Base, %
166	4	92	7
165	38	91	53
164	100(Base)	90	5
163	8	89	3
162	5	88	3
161	3	87	4
150	8	85	3
149	75	81	6
148	6	79	11
147	7	78	12
137	16	77	59
135	3	76	3
134	5	71	3
133	41	70	4
132	11	69	9
131	41	68	3
122	4	67	5
121	50	66	25
120	4	65	69
119	4	64	16
118	3	63	50
117	6	62	8
115	6	61	7
112	3	60	4
109	3	58	5
108	5	57	18
107	15	56	6
106	3	55	97
105	14	54	9
104	19	53	56
103	38	52	19
102	9	51	75
101	3	50	34
95	3	49	6
94	6	45	25
93	8	44	47

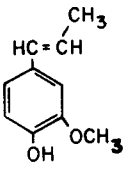


m/e	Base, %
43	59
42	4
41	59
40	19
39	88
38	21
37	10

PGCMS 99.98% Loblolly Pine

trans-Isoeugenol

m/e	Base, %	m/e	Base, %
166	4	106	5
165	51	105	17
164	100(Base)	104	41
163	26	103	59
162	16	102	7
161	14	101	8
151	6	100	3
150	17	99	3
149	72	98	9
147	23	97	5
144	3	95	10
138	8	94	4
137	28	93	20
135	5	92	7
134	7	91	49
133	49	90	15
132	33	89	2
131	62	86	3
130	3	84	2
128	3	82	6
126	5	81	8
124	5	79	28
123	3	78	18
122	13	77	64
121	49	76	7
120	11	75	8
119	17	74	4
118	6	73	3
117	4	72	6
116	5	71	9
115	3	70	4
114	3	69	8
112	4	67	5
109	7	66	12
108	3	65	31
107	8	63	17



m/e	Base, %
62	5
61	6
60	3
59	3
57	8
56	10
55	49
54	7
53	26
52	11
51	26
50	7
44	46
43	38
42	5
41	14
40	3
39	28
38	5
37	5
31	4
29	23

PGCMS 100% Loblolly Pine

Carbohydrate No. 3, Hydroxymethylfurfural

128	5	54	3
127	7	53	25
126	53	52	13
125	1	51	50
124	52	50	22
123	26	49	37
118	4	48	3
112	3	45	18
111	3	44	100
110	4	43	107
109	10	42	54
108	4	41	233
100	4	40	30
99	4	39	200
98	4	38	120
97	100(Base)	37	87
96	2		
95	10		
93	5		
91	5		
85	3		
83	8		
81	13		
80	4		
77	11		
71	7		
69	46		
68	9		
67	10		
61	4		
60	4		
59	4		
58	3		
57	20		
56	5		
55	21		

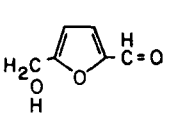


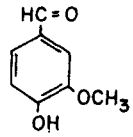
TABLE XXXIII (Continued)

MASS SPECTRA OF WOOD AND PERACETIC ACID WOOD PYROLYSIS PRODUCTS

PGCMS 100% Loblolly Pine

Vanillin

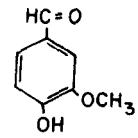
m/e	Base, %	m/e	Base, %
154	4	69	9
153	11	67	8
152	92	66	4
151	100(Base)	65	14
150	7	63	16
149	9	62	8
148	4	60	15
147	4	58	5
141	4	57	20
138	3	56	7
137	12	55	15
131	4	54	4
125	5	53	28
123	26	52	15
122	5	51	36
121	9	50	9
119	4	45	11
111	4	44	52
110	4	43	30
109	36	42	13
108	6	41	32
100	3	40	5
98	3	39	40
95	8	38	10
93	5		
91	14		
87	8		
85	10		
82	8		
81	36		
80	6		
79	10		
77	7		
73	4		
71	8		
70	4		



PGCMS 99.98% Loblolly Pine

Vanillin

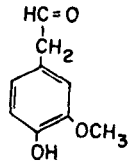
m/e	Base, %	m/e	Base, %
153	12	68	4
152	100(Base)	67	6
151	97	65	19
150	7	64	11
148	10	63	10
147	11	62	3
138	6	60	5
137	14	59	7
136	4	57	17
135	3	55	11
126	5	54	6
125	3	53	13
124	8	52	20
123	41	51	11
119	6	50	12
110	6	46	3
109	19	45	8
108	15	44	44
103	3	43	26
102	3	41	19
97	11	40	4
96	4	39	38
95	5	38	12
91	7	37	7
90	3		
85	5	29	12
83	4		
82	3		
81	32		
80	6		
79	13		
77	8		
75	8		
74	4		
73	3		
69	11		



PGCMS 99.98% Loblolly Pine

Homovanillin

m/e	Base, %	m/e	Base, %
168	4	96	3
167	7	95	10
166	38	94	16
165	13	93	3
164	15	92	5
163	3	91	9
161	4	90	4
153	4	86	4
152	11	85	7
151	24	84	11
149	16	83	7
146	5	82	6
145	5	81	5
139	5	80	9
138	16	79	10
137	100(Base)	78	12
136	3	77	8
135	6	76	9
134	5	74	14
132	4	72	4
131	5	71	4
128	6	70	12
124	10	69	13
123	16	68	7
122	22	67	7
121	6	66	16
120	5	65	17
113	4	64	4
112	10	63	11
111	3	62	4
109	4	61	5
108	9	60	4
107	3	59	14
106	3	58	3
105	9	57	15
97	5	56	5

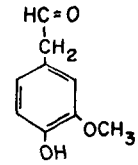


m/e	Base, %
55	12
54	3
53	14
52	4
51	15
45	7
44	66
43	18
42	21
41	15
40	6
39	41
38	4
31	5
30	15
29	17

PGCMS 100% Loblolly Pine

Homovanillin

m/e	Base, %	m/e	Base, %
167	12	99	10
166	42	98	4
165	8	97	5
164	3	96	3
161	5	95	5
158	4	94	18
152	13	87	5
151	23	86	3
150	3	85	3
149	5	84	3
147	5	82	4
144	4	81	6
142	3	80	3
140	5	79	4
139	3	77	6
138	13	74	13
137	100(Base)	71	4
136	2	69	11
133	5	68	5
129	3	67	5
128	7	65	5
127	3	63	4
126	3	57	6
123	13	56	4
122	24	55	11
121	4	53	10
116	6	52	7
115	4	51	8
114	3	50	7
113	4	45	20
112	6	44	158
109	6	43	104
106	5	42	38
105	9	41	38
103	3	40	12
102	3	39	54



m/e	Base, %
38	7
37	9

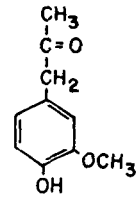
TABLE XXXIII (Continued)

MASS SPECTRA OF WOOD AND PERACETIC ACID WOOD PYROLYSIS PRODUCTS

PGCMS 100% Loblolly Pine

Vanillyl Methyl Ketone

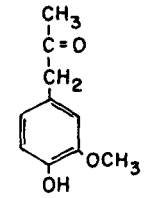
m/e	Base, %	m/e	Base, %
181	9	69	9
180	47	68	4
179	3	67	8
164	3	66	4
151	6	63	9
148	3	62	5
140	3	61	5
139	5	58	5
138	16	57	23
137	100(Base)	56	9
135	17	55	7
133	4	54	3
128	3	53	6
124	19	52	9
123	7	51	10
122	13	45	3
120	4	44	47
112	5	43	37
109	5	42	7
108	3	41	14
105	7	40	4
97	4	39	22
96	5	38	4
95	6		
94	10		
93	3		
91	11		
87	3		
85	6		
84	5		
81	4		
78	4		
77	12		
76	8		
74	6		
73	4		



PGCMS 99.98% Loblolly Pine

Vanillyl Methyl Ketone & Acetovanillone

m/e	Base, %	m/e	Base, %
181	4	89	5
180	33	87	6
179	9	85	6
168	5	82	9
167	5	80	7
166	46	79	14
165	29	78	14
163	4	77	17
162	9	74	3
160	4	72	4
159	5	71	8
153	7	69	7
152	13	68	5
151	100(Base)	67	11
149	14	66	3
139	6	65	16
137	38	63	8
136	6	62	3
131	7	61	5
126	7	59	7
125	4	58	3
124	19	57	18
123	38	56	3
122	6	55	13
121	10	54	6
120	3	53	7
112	3	52	19
110	4	51	18
108	11	50	11
107	10	45	3
105	8	44	46
97	5	43	50
95	7	41	14
94	15	40	8
93	7	39	22
92	4	38	6



m/e	Base, %
31	14
30	8
29	15

TABLE XXXIII (Continued)

MASS SPECTRA OF WOOD AND PERACETIC ACID WOOD PYROLYSIS PRODUCTS

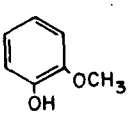
PGCMS 77% Loblolly Pine

Guaiacol + Carbohydrate No. 1

m/e	Base, %	m/e	Base, %
128	3	43	56
127	6	42	10
124	4	41	4
122	5	40	11
115	10	39	10
114	100(Base)	38	18
113	4		
112	4		
109	11		
98	17		
97	6		
96	11		
95	11		
92	9		
89	6		
86	5		
85	11		
81	5		
79	6		
74	3		
73	7		
71	14		
70	11		
69	5		
68	23		
61	5		
59	4		
58	35		
57	29		
56	12		
55	82		
54	12		
53	4		
51	4		
45	3		
44	173		

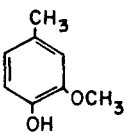
Guaiacol

m/e	Base, %
125	15
124	91
123	16
121	30
112	25
111	23
110	24
109	100(Base)
100	17
98	20
96	18
95	17
94	37
93	22
86	19
83	24
82	37
81	9
79	35
70	19
69	23
66	20
57	18
56	28
55	12
45	21
44	480
43	67
41	23
40	52
39	20



Creosol

m/e	Base, %	m/e	Base, %
139	18	57	6
138	100(Base)	56	2
137	6	55	9
136	8	52	5
135	3	51	5
124	3	50	3
123	76	44	119
122	25	43	6
121	1	41	4
114	2	40	3
113	2		
112	3		
110	3		
109	2		
108	3		
107	2		
106	7		
105	5		
104	2		
103	3		
101	7		
98	2		
97	2		
96	5		
95	30		
91	3		
85	3		
83	6		
81	2		
79	4		
78	6		
77	14		
72	3		
71	8		
68	3		
67	3		



Carbohydrate No. 3 — HMF

m/e	Base, %	m/e	Base, %
129	3	40	15
128	5	39	57
127	7	38	48
126	81	37	27
125	19		
124	86		
123	43		
122	4		
111	3		
110	20		
109	37		
108	4		
99	6		
98	15		
97	100(Base)		
96	14		
95	25		
85	10		
84	4		
83	6		
82	5		
81	13		
71	11		
69	8		
67	10		
66	6		
57	13		
53	11		
51	10		
50	6		
46	4		
45	8		
44	105		
43	3		
42	15		
41	81		

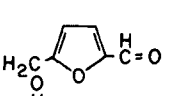


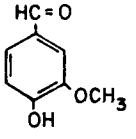
TABLE XXXIII (Continued)

MASS SPECTRA OF WOOD AND PERACETIC ACID WOOD PYROLYSIS PRODUCTS

PGCMS 77% Loblolly Pine

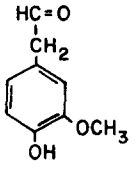
Vanillin

m/e	Base, %	m/e	Base, %
154	3	62	10
153	22	60	5
152	100(Base)	57	34
151	69	56	12
149	6	55	24
148	50	53	13
147	6	51	11
144	4	50	5
140	11	45	8
139	9	44	211
138	10	43	144
133	6	42	37
131	6	41	68
128	11	40	21
125	5	39	111
124	10	38	38
123	23		
121	5		
112	4		
111	8		
110	4		
109	12		
108	4		
105	8		
95	24		
94	5		
87	5		
84	10		
83	13		
82	6		
81	14		
77	8		
72	6		
70	8		
69	9		
67	14		



Homovanillin

m/e	Base, %	m/e	Base, %
167	12	99	4
166	41	98	5
164	7	96	6
161	3	95	23
160	4	94	14
152	9	93	11
151	20	91	10
150	4	88	4
149	7	87	3
148	6	86	6
147	4	85	16
146	3	83	14
138	13	82	16
137	100(Base)	81	18
136	6	79	9
135	9	78	7
134	8	77	31
133	4	76	6
126	11	75	5
124	9	74	11
123	13	73	8
122	28	72	14
121	5	71	15
120	4	69	19
115	7	68	4
114	4	67	5
112	3	66	4
111	11	65	14
110	5	63	7
109	6	62	6
108	5	59	10
107	3	58	4
106	11	57	23
105	9	56	17
104	3	55	23
103	14	54	6



m/e	Base, %
53	6
51	14
50	7
47	6
44	155
43	9
40	8

Vanillyl Methyl Ketone

181	12	71	5
180	48	69	11
166	4	68	5
163	3	67	3
152	3	66	7
151	8	65	6
150	4	64	3
149	3	63	8
148	3	58	3
147	4	57	15
145	3	56	36
142	3	55	15
138	30	54	4
137	100(Base)	53	3
133	3	52	5
131	7	51	18
125	3	50	4
124	5	47	3
123	8	45	8
122	30	44	38
120	4	43	60
110	6	42	9
109	4	41	16
107	3	40	3
105	4	39	16
102	4	38	5
94	8		
91	4		
90	3		
83	3		
82	6		
81	5		
79	4		
78	5		
77	13		
73	7		

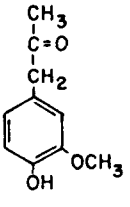
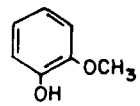


TABLE XXXIV

MASS SPECTRA OF PERACETIC ACID LIGNIN PYROLYSIS PRODUCTS AND BY-PRODUCTS

PGCMS PAA Lignin No. 46

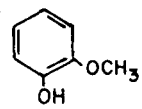
Guaiacol



m/e	Base, %	m/e	Base, %
127	2	65	9
126	2	64	4
125	17	63	16
124	88	62	7
122	13	57	17
121	7	56	3
115	9	55	38
114	3	54	17
112	3	53	53
111	3	52	23
110	18	51	13
109	100(Base)	50	8
108	7	49	5
106	3	46	4
101	3	45	7
100	3	44	82
96	4	43	19
95	6	42	13
94	11	41	30
93	3	40	65
90	3	39	65
85	6	38	46
84	3	37	16
83	13	34	4
82	9		
81	76	31	3
80	7	30	4
79	12	29	44
78	3		
77	10	27	53
71	20		
70	5		
69	8		
68	6		
67	12		
66	8		

PGCMS PAA Lignin No. 46

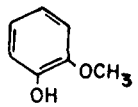
Guaiacol



m/e	Base, %	m/e	Base, %
124	80	68	15
123	13	67	13
122	6	66	23
121	4	65	26
120	4	64	10
119	11	63	18
112	5	62	7
111	12	60	9
110	11	58	9
109	100(Base)	57	18
107	10	56	6
106	8	55	65
102	5	54	28
99	4	53	6
98	6	52	56
96	12	51	26
95	10	50	41
94	7	49	21
90	11	45	47
89	7	44	11
88	6	43	120
87	5	42	9
86	7	41	56
85	9	40	58
84	21	39	160
83	18	38	61
82	13	37	26
81	60	36	7
80	7	35	7
77	14		
75	7	31	3
73	6	29	90
72	3		
71	6	27	170
70	11	26	82
69	17	25	4

PGCMS PAA Lignin No. 46

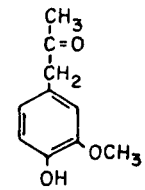
Guaiacol



125	12	49	4
124	94	45	3
123	4	44	94
122	8	43	21
121	12	42	19
110	31	41	26
109	100(Base)	40	25
108	5	39	78
98	7	38	34
95	18		
94	6	31	15
93	6	29	28
92	5		
83	5	27	63
82	19		
81	78		
80	12		
79	8		
77	11		
71	6		
69	6		
68	7		
67	8		
66	11		
65	28		
64	5		
63	18		
62	11		
59	7		
57	15		
55	22		
54	19		
53	66		
52	50		
51	31		
50	5		

PGCMS PAA Lignin No. 46

Vanillyl Methyl Ketone



180	40	81	17
179	6	78	5
178	7	77	7
176	6	74	6
166	11	73	4
165	4	71	3
164	3	70	11
163	5	69	14
160	5	68	5
150	9	67	4
149	5	66	7
147	4	62	9
146	9	61	3
142	4	56	5
140	4	54	9
138	23	51	7
137	100(Base)	50	13
136	3	45	15
135	12	44	133
130	6	43	16
126	5	42	15
123	4	41	18
122	10	40	83
119	7	39	10
115	3	38	6
107	8	37	5
105	3	34	14
103	10		
98	6	31	5
97	12	30	7
96	13	29	28
94	5		
92	3	26	16
91	6		
89	4		
83	6		

TABLE XXXIV (Continued)

MASS SPECTRA OF PERACETIC ACID LIGNIN PYROLYSIS PRODUCTS AND BY-PRODUCTS

PGCMS PAA Lignin No. 46

2-Furaldehyde

m/e	Base, %
99	3
98	3
97	12
96	98
95	100(Base)
84	3
83	5
82	3
71	3
70	5
69	4
68	7
67	9
64	4
60	23
57	6
51	6
50	7
48	3
45	25
44	64
43	41
42	22
41	10
40	27
39	75
38	11
37	8
36	4
34	5
30	4
29	41
27	5
26	3

PGCMS PAA Lignin No. 48

2-Furaldehyde

m/e	Base, %
96	95
95	100(Base)
85	3
82	3
66	6
67	9
65	4
57	4
55	5
53	6
50	4
49	12
48	4
45	24
44	181
43	8
42	14
41	11
40	67
39	100
38	71
37	33
36	12
35	5
34	9
30	4
29	76

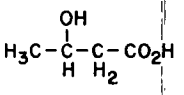
TABLE XXXIV (Continued)

MASS SPECTRA OF PERACETIC ACID LIGNIN PYROLYSIS PRODUCTS AND BY-PRODUCTS

PGCMS PAA Lignin No. 72

3-Hydroxybutyric Acid

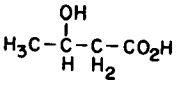
m/e	Base, %	m/e	Base, %
185	10	61	7
160	10	60	38
147	2	59	23
145	30	58	129
143	2	57	7
131	4	55	3
121	2	51	6
118	4	50	3
117	9	47	19
116	100(Base)	46	10
115	5	45	81
112	3	44	171
107	4	43	181
105	4	42	69
103	15	41	43
102	10	40	11
101	62	39	29
99	3	38	14
89	3	37	8
88	7	34	5
87	13		
86	2	31	2
85	7	30	4
84	13	29	110
79	12		
78	5	27	28
77	38	26	13
76	13		
75	105		
74	4		
73	4		
72	17		
71	9		
70	3		
69	24		
68	4		



GCMS PAA Lignin No. 74-76

3-Hydroxybutyric Acid

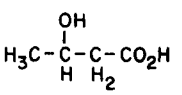
m/e	Base, %	m/e	Base, %
119	4	45	157
117	5	44	195
116	38	43	138
115	7	42	146
103	7	41	124
102	3	40	59
101	24	39	100
100	3	38	32
99	3	37	32
89	7		
88	7	31	19
87	32	30	11
86	92	29	149
85	5		
84	7	27	70
78	3		
77	14		
75	41		
74	6		
73	10		
72	11		
71	43		
70	5		
69	70		
68	30		
62	3		
61	24		
60	97		
59	11		
58	100(Base)		
57	17		
55	17		
53	5		
50	4		
47	10		
46	8		



PGCMS PAA Lignin No. 74-76

3-Hydroxybutyric Acid

117	4		
116	100(Base)		
115	4		
109	11		
102	7		
101	32		
95	14		
84	8		
78	7		
77	47		
75	58		
72	36		
71	15		
69	16		
66	4		
61	22		
60	26		
59	13		
58	54		
57	7		
55	5		
53	7		
51	9		
50	9		
47	5		
45	45		
44	340		
43	220		
42	120		
41	74		
40	46		
39	65		
38	19		



PGCMS VIV PAA Lignin No. 74-76

3-Hydroxybutyric Acid

117	5	36	7
116	58		
101	11	31	7
97	3	30	5
96	6	29	137
95	6		
86	6		
84	5		
82	6		
79	5		
77	11		
76	4		
75	12		
73	3		
72	5		
70	7		
69	18		
68	8		
67	3		
60	84		
59	12		
58	100(Base)		
57	3		
56	3		
55	21		
54	4		
50	3		
46	6		
45	63		
44	237		
43	189		
42	132		
41	53		
40	23		
39	22		
37	5		

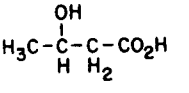


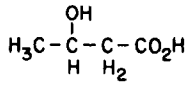
TABLE XXXIV (Continued)

MASS SPECTRA OF PERACETIC ACID LIGNIN PYROLYSIS PRODUCTS AND BY-PRODUCTS

GCMS VIV PAA Lignin No. 92-95

3-Hydroxybutyric Acid

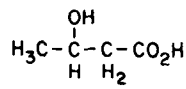
m/e	Base, %	m/e	Base, %
118	3	40	16
117	4	39	22
116	8	38	3
115	7	36	4
113	3		
101	15	31	4
99	3	30	6
89	14	29	11
88	3		
87	20		
86	76		
85	12		
84	5		
77	7		
76	4		
75	15		
73	3		
71	51		
70	11		
69	56		
68	42		
61	15		
60	100(Base)		
59	15		
58	91		
57	5		
56	4		
55	3		
54	3		
47	4		
46	4		
45	140		
44	138		
43	120		
42	102		
41	64		



PGCMS PAA Lignin No. 92-95

3-Hydroxybutyric Acid

m/e	Base, %	m/e	Base, %
118	5	55	6
117	10	53	4
116	100(Base)	50	4
115	6	47	13
114	2	46	6
103	7	45	43
102	15	44	94
101	86	43	87
100	3	42	40
97	3	41	26
96	5	40	20
95	3	39	19
91	4	38	11
89	3	36	5
86	12		
85	6	31	7
84	8	29	46
81	3		
79	4		
78	3		
77	42		
76	8		
75	71		
74	6		
73	16		
72	36		
71	6		
70	3		
69	43		
68	8		
62	4		
61	15		
60	11		
59	20		
58	57		
57	9		



GCMS PAA + Ac H Quenched

3-Hydroxybutyric Acid

117	2	45	125
116	11	44	150
115	2	43	119
103	5	42	97
102	1	41	94
101	8	40	36
99	3	39	69
97	1	38	17
91	2	37	16
90	1	36	7
89	14		
88	2	31	19
87	10	29	114
86	56		
85	2	27	78
84	3	26	42
83	1		
82	3		
77	5		
75	9		
74	3		
73	2		
72	1		
71	44		
69	42		
68	19		
65	1		
61	6		
60	100(Base)		
59	7		
58	78		
57	12		
55	8		
53	1		
47	4		
46	7		

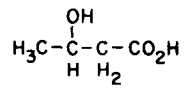
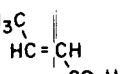


TABLE XXXIV (Continued)

MASS SPECTRA OF PERACETIC ACID LIGNIN PYROLYSIS PRODUCTS AND BY-PRODUCTS

PGCMS PAA Lignin No. 74-76

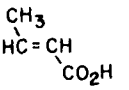
Crotonic Acid



m/e	Base, %
87	9
86	100(Base)
85	13
84	5
80	4
78	3
72	4
71	25
70	3
69	41
68	77
67	6
60	7
58	11
57	14
55	5
54	3
53	6
51	4
50	9
46	10
45	41
44	155
43	64
42	33
41	95
40	50
39	123
38	32
37	9
36	10
31	7
30	6
29	55

PGCMS PAA Lignin No. 92-95

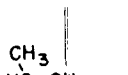
Crotonic Acid



m/e	Base, %	m/e	Base, %
124	2	31	8
122	3	30	3
87	7	29	23
86	100(Base)		
85	6	27	49
84	5	26	36
81	5		
77	6		
73	3		
71	44		
69	69		
68	74		
67	4		
65	4		
60	16		
58	4		
57	13		
56	5		
55	15		
54	3		
53	8		
50	5		
47	3		
46	7		
45	69		
44	54		
43	36		
42	41		
41	95		
40	69		
39	103		
38	46		
37	33		
36	11		
34	3		

PGCMS PAA Lignin No. 72

Crotonic Acid



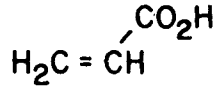
122	6
86	100(Base)
85	10
84	2
72	3
71	14
70	10
69	54
68	36
67	2
60	21
58	10
57	12
55	7
54	3
53	4
49	3
45	58
44	73
43	51
42	23
41	94
40	16
39	76
38	11
37	18
31	3
29	33
27	12
26	15
25	2

TABLE XXXIV (Continued)

MASS SPECTRA OF PERACETIC ACID LIGNIN PYROLYSIS PRODUCTS AND BY-PRODUCTS

PGCMS PAA Lignin No. 72

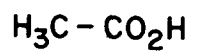
Acrylic Acid



m/e	Base, %
72	20
71	3
61	3
59	15
58	9
57	5
56	3
54	4
45	3
44	77
43	100(Base)
42	29
41	8
40	15
39	66

PGCMS PAA Lignin No. 72

Acetic Acid



m/e	Base, %
61	42
60	88
50	3
46	17
45	92
44	63
43	100(Base)
42	62
41	42
40	17
39	3

MASS SPECTRA INTERPRETATION OF PROPOSED PYROLYSIS PRODUCTS

2-(2-METHOXY-4-METHYLPHENOXY)-1-(3,4-DIMETHOXYPHENYL)PROPAN-1-OL

The mass spectra for the second and third peaks in the 2-(2-methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol pyrogram (Fig. 8) are represented in Table XXVI. The prominent ions and their proposed interpretation are listed in Table XXXV along with those for the authentic sample of propioveratrone. The parent ion (P) was assigned to the highest even-numbered ion of significant relative abundance.

The proposed structure (Fig. 8) for the second peak (Table XXXV) and isoeugenol, the guaiacyl analog, have very similar mass spectra. Both have major ions at P-15 (parent minus 15 mass units), P-27, P-31, P-33, P-43, P-61, P-71, P-73, and P-75. The apparent molecular weight of 14 more than isoeugenol suggests they differ only by a methyl group. The spectrum for the third peak (Table XXXV) is one of the few in this series that contain a P-27 ion. This P-27 peak is interpreted as a loss of the vinyl group on the proposed structure (Fig. 8).

1-(3,4-DIMETHOXYPHENYL)PROPAN-1,2-DIOL

The prominent ions and their proposed interpretation from the mass spectra of 1-(3,4-dimethoxyphenyl)propan-1,2-diol pyrolysis products are listed in Table XXXVI. The first and second peaks have nearly identical spectra and are considered to be isomers. The spectra for Peaks 1 and 2 are essentially the same as the spectrum of the second peak for the propan-1-ol compound in Table XXXV. The first two peaks for the 1,2-diol compound were assigned structures as cis- and trans-isomers (see Fig. 7). The third peak for the 1,2-diol compound had the same mass spectrum and GC retention

TABLE XXXV

MASS SPECTRA INTERPRETATION

m/e	2-(2-Methoxy-4-methyl-phenoxy)-1-(3,4-dimethoxy-phenyl)propan-1-ol	Pyrolysis Products	Propioveratrone Authentic Sample
	2nd Peak (Methyl Isoeugenol)	3rd Peak	
194			P
192		P	P-2(H_2)
178	P		
167		P-25($C{\equiv}CH$)	
166		P-26($CH{\equiv}CH$)	P-28(CO or CH_2CH_2)
165		P-27($CH_2{=}CH$)	P-29(CH_3CH_2)
163	P-15(CH_3)	P-29(CH_3,CH_2)	
151		P-41($CH_2{=}CH_1CH_2$)	
149		P-43(CO,CH_3)	
147	P-31(OCH_3)		
137		P-55($CH_2{=}CHCO$)	P-57(CH_3CH_2CO)
136			
135	P-43(CO,CH_3)		
133		P-59(CH_3OH,$CH_2{=}CH$) or (CO,OCH_3)	
131	P-47		
122			P-72(CH_3CH_2CO,CH_3)
119			P-75(CH_3CH_2,OCH_3,CH_3)
117	P-61(OCH_3,OCH_2)		
115	P-63(OCH_3,$HOCH_3$)		
107	P-71($CH{=}CHCH_3$,CH_3,CH_3)		P-87(CH_3CH_2CO,CH_3,CH_3)
105	P-73		P-89(CH_3CH_2,OCH_2,OCH_2)
103	P-75		
95		P-97	
94			P-100
92			P-102
91	P-87($CH{=}CHCH_3$,OCH_3,CH_3)		P-103
77	P-101($CH{=}CHCH_3$,OCH_2,OCH_2)		P-117

TABLE XXXVI

MASS SPECTRA INTERPRETATION OF 1-(3,4-DIMETHOXYPHENYL)PROPAN-1,2-DIOL PYROLYSIS PRODUCTS

m/e	1st Peak	2nd Peak	3rd Peak	5th Peak
208				P
192			P	
178	P	P		
167			P-25($C\equiv CH$)	
166			P-26($CH\equiv CH$)	
165			P-27($CH_2=CH$)	P-43(CO,CH_3)
163	P-15(CH_3)	P-15(CH_3)	P-29(CH_3,CH_2)	
151			P-41($CH_2=CH,CH_2$)	P-57(CH_3CO,CH_2)
147	P-31(OCH_3)	P-31(OCH_3)		
137			P-55($CH_2=CHCO$)	P-71(CH_3COCO)
135	P-43(CO,CH_3)	P-43(CO,CH_3)		
131	P-47	P-47		
122				P-86(CH_3COCO,CH_3)
117	P-61(OCH_3OCH_2)	P-61(OCH_3,OCH_2)		
115	P-63($OCH_3,HOCH_3$)	P-63($OCH_3,HOCH_3$)		
107	P-71($CH=CHCH_3,CH_3,CH_3$)	P-71($CH=CHCH_3,CH_3,CH_3$)		
95			P-97	
94				P-114
92				P-116
91	P-87	P-87		
79				P-131
77				

time as the third peak for the propan-1-ol compound. The fifth peak was assigned a molecular weight of 208 based on the VIV MS experiment. The greater retention time and the higher molecular weight of the fifth peak as compared to propioveratrone suggests one more oxygen than propioveratrone. The ions at 165 and 137 for the fifth peak are also characteristic of propioveratrone and suggest that both have a similar structure (dicarbonyls).

2-(2-METHOXY-4-METHYLPHENOXY)-1-(3,4-DIMETHOXYPHENYL)PROPAN-1-ONE

The third peak in the 2-(2-methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-one pyrogram is considered to be a veratryl derivative (see Fig. 9). The mass spectrum, interpretation Table XXXVII, shows loss of 2 methyl groups (P-15 and P-30) which is consistent with the proposed dimethoxy compound. The fourth peak (Fig. 9) is proposed to be veratryl aldehyde. The loss of 73 (P-73) is also found in the other proposed unsaturated side-chain veratryl compounds [second peak for 2-(2-methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol and the first and second peaks of the 1-(3,4-dimethoxyphenyl)propan-1,2-diol as well as for isoeugenol, Table XXX]. The ion at 91 is also found to result from other unsaturated side-chain aromatics such as the proposed pyrolysis products of the propan-1-ol compound, the 1,2-diol compound, isoeugenol, and 4-vinylguaiacol. The ion at 91 is considered to be the tropylium ion. Propioveratrone, an α-carbonyl compound, apparently does not form this ion, based on the proposed parent ion (164), the 4-vinyl veratrole compound (Fig. 9) is the best fit for the data.

TABLE XXXVII

MASS SPECTRA INTERPRETATION OF PYROLYSIS PRODUCTS FROM 2-(2-METHOXY-4-METHYLPHENOXY)-1-(3,4-DIMETHOXYPHENYL)PROPAN-1-ONE

m/e	1st Peak Veratrole	3rd Peak	4th Peak
166			P
164		P	
151			P-15(CH_3)
149		P-15(CH_3)	
138	P		
134		P-30(CH_3,CH_3)	
123	P-15(CH_3)		
105			P-61(OCH_3,OCH_2)
95			P-71(CO,CO,CH_3)
91	P-43(CO,CH_3)	P-73	
77	P-61(OCH_3,OCH_2)		

DIISOEUGENOL

The structures proposed for the fourth, fifth, sixth, and seventh peaks from the PGC of diisoeugenol (Fig. 6) are based on the apparent molecular weights from the mass spectra. Molecular weights of 204 and 206 are greater than 4-propylguaiacol (166) but too small for two guaiacol units (246 or 248). The products must have a complex side chain left from the diisoeugenol structure. The mass spectra interpretation in Table XXXVIII show loss of CH_3CH_2 (P-29) and CH_3,CH_3 (P-30) which is consistent with the proposed side chains. The sixth peak structure has two methyl groups, and its mass spectrum is the only one to show a P-30 ion and not a P-29 ion. The other three spectra show a P-29 ion which corresponds to the ethyl groups found in each proposed structure.

TABLE XXXVIII

MASS SPECTRA INTERPRETATION FOR DIISOEUGENOL PYROLYSIS PRODUCTS

m/e	3rd Peak (20 min) Diisoeugenol	5th Peak (22 min)	6th Peak	7th Peak
206	P	P		
204			P	P
202			P-2(H,H)	P-2(H,H)
189				P-15(CH_3)
187			P-17(H_3,H,H)	P-17(CH_3,H,H)
177	P-29(CH_3CH_2)	P-29(CH_3CH_2)		
175		P-31(OCH_3)		P-29(CH_3CH_2)
174			P-30(CH_3,CH_3)	
172				P-32(CH_3OH)
161			P-43(CO,CH_3)	P-43(CO,CH_3)
160			P-44	P-44
159			P-45	
157				P-47
147			P-57	
145	P-63(OH,OCH_3,CH_3)	P-63	P-61	
144				P-62
143				P-63
129				P-75
117	P-89	P-89		
115				P-89
91	P-115	P-115		
77	P-129	P-129		P-127

CIS,TRANS-β-METHYL MUCONIC ACID AND ITS LACTONE

The four pyrolysis products from 5-carboxymethyl-4-methyl-2(5H)-furanone and the muconic acid are apparently two sets of two isomers each. The mass spectra interpretations in Table XXXIX agree with the proposed structures in Fig. 11. The two isomers with apparent molecular weights of 112 are the only mass spectra to show P-15 ions, loss of methyl. The fourth peak even shows loss of two methyl groups, P-30. The two isomer structures with apparent molecular weights of 110 have one or both their methyl groups unsaturated (methylene) and, therefore, less likely to lose CH_3. The low molecular weight and GC retention times (Table XL, Appendix IX) agree with a lactone structure as opposed to a free acid. The lactone ring apparently remains intact on pyrolysis and forms four major products.

TABLE XXXIX

MASS SPECTRA INTERPRETATIONS FOR CIS,TRANS-β-METHYL MUCONIC ACID AND ITS LACTONE

m/e	1st Peak	2nd Peak	3rd Peak	4th Peak
112	P			P
110	P-2(H,H)	P	P	
97	P-15(CH_3)			P-15(CH_3)
84	P-28(CO)			
82		P-28(CO)	P-28(CO)	P-30(CH_3,CH_3)
70				P-42(C_3H_6)
69	P-43(CO,CH_3)	P-41(C_3H_5)		P-43(CO,CH_3)
68	P-44(CO_2)	P-42(C_2H_2O)	P-42(C_2H_2O)	P-44(CO_2)

APPENDIX IX

GAS LIQUID CHROMATOGRAPHY RETENTION TIMES OF MODEL COMPOUND PYROLYSIS PRODUCTS

Table XL contains the retention times of pyrolysis products from lignin model compounds in Fig. 4-14. As listed in Table XL, many of the products were identified by GLC and MS comparison to an authentic sample. For each column condition, an authentic sample was run the same day the pyrogram was recorded. This was to ensure against misleading results due to possible column deterioration over several months.

TABLE XL

MAJOR PYROLYSIS PRODUCTS FROM MODEL COMPOUNDS

Pyrolyzed Compound	Pyrolysis Product	Relative Peak Area	Retention Time[a], min 170°	170-1°/min	170-2°/min	90-2°/min
Pinoresinol	Guaiacol[b]	41	3.8			22.9
	Creosol	100	4.6			27.2
	4-Ethylguaiacol	9	5.9			30.6
	4-Propylguaiacol	4	7.8			32.8
	Eugenol	7	9.1			36.2
	4-Vinylguaiacol	9	9.8			37.3
	cis-Isoeugenol	4	11.9			39.9
	trans-Isoeugenol	18	16.2			43.8
	Vanillin	40	31.4			52.0
	Acetovanillone	18	35.7			53.6
	Propiovanillone	24	43.3			55.9
Conidendrin	Guaiacol	100		3.8		
	Unknown[c]	3		28.0		
	Unknown	14		29.6		
	Unknown	10		52.4		
2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-ol						
	Creosol	100	4.7		4.2	28.1
	2nd Peak[d]	18	10.3		7.7	40.0
	3rd Peak	23	21.2		12.1	45.2
	Propioveratrone	22	35.3		16.3	52.5

[a] There are four column conditions for which retention times are listed: 170° isothermal (170°), 170° initially with 1°/min program to 205°C (170-1°/min), 170° initially with 2°/min program to 205°C (170-2°/min), and 90° initially with 2°/min program to 205°C (90-2°/min).

[b] Authentic samples were run for all products listed by name.

[c] Compound was not investigated by MS and its retention time did not correspond to an authentic sample.

[d] Compound was investigated by MS and a structure proposed but no authentic sample was available for comparison.

TABLE XL (Continued)

MAJOR PYROLYSIS PRODUCTS FROM MODEL COMPOUNDS

Pyrolyzed Compound	Pyrolysis Product	Relative Peak Area	Retention Time, min			
			170°	170-1°/min	170-2°/min	90-2°/min
1-(3,4-Dimethoxyphenyl)propan-1,2-diol						
	1st Peak	3	10.4	9.3		
	2nd Peak	6	14.2	11.2		
	3rd Peak	45	27.9	20.3		
	Veratryl Methyl Ketone	100	32.4	24.4		
	5th Peak	10	44.8	32.7		
2-(2-Methoxy-4-methylphenoxy)-1-(3,4-dimethoxyphenyl)propan-1-one						
	Veratrole	5			2.4	
	Creosol	100			4.3	
	3rd Peak	12			8.0	
	4th Peak	4			12.2	
	Propioveratrone	34			16.1	
Dehydrodivanillin	Guaiacol			3.9		22.1
	Vanillin			27.1		51.6
Diisoeugenol	Guaiacol	62		3.8		
	4-Propylguaiacol	24		7.7		
	trans-Isoeugenol	12		16.4		
	4th Peak	30		19.3		
	5th Peak	68		21.9		
	6th Peak	26		26.6		
	7th Peak	100		30.3		
	Unknown	22		32.5		

TABLE XL (Continued)

MAJOR PYROLYSIS PRODUCTS FROM MODEL COMPOUNDS

Pyrolyzed Compound	Pyrolysis Product	Relative Peak Area	Retention Time, min			
			170°	170-1°/min	170-2°/min	90-2°/min
Coniferin	Guaiacol	30		4.0		
	Creosol	58		4.6		
	Eugenol	38		8.9		
	4-Vinylguaiacol	27		9.6		
	cis-Isoeugenol	19		11.6		
	trans-Isoeugenol	100		15.8		
5-Carboxymethyl-4-methyl-2(5H)-furanone						
	1st Peak	63	1.9			13.3
	2nd Peak	41	2.1			14.6
	3rd Peak	27	3.4			21.1
	4th Peak	100	4.9			27.8
cis,trans-β-Methylmuconic Acid						
	Unknown	61	1.9			
	Unknown	31	2.1			
	Unknown	36	3.4			
	Unknown	100	4.9			
Vanillic Acid	Guaiacol	30			4.0	
	Vanillic Acid	100			76.0	
5-Methyl-2(5H)-furanone	Unknown	17	2.0			
	5-Methyl-2(5H)-furanone	100	2.6			