STUDIES ON THE PULPING AND CHEMICAL CONSTITUENTS OF PINUS CARIBAEA

A THESIS
submitted in fulfilment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY

By

SHRI KANT GUPTA

INSTITUTE OF PAPER TECHNOLOGY
(UNIVERSITY OF ROORKEE)
SAHARANPUR-247001 INDIA

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CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in the thesis entitled '**Studies on the Pulping and Chemical Constituents of Pinus caribaea**' in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy, submitted in the Institute of Paper Technology, University of Roorkee, is an authentic record of my own work carried out during a period from May, 1982 to October 1987 under the supervision of Dr. M.C.Bansal, Reader in Chemical Engineering and Dr. R.N.Madan, Ex-Reader in Pulp Technology, Institute of Paper Technology (University of Roorkee), Saharanpur.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

Shrikant Gupta
CANDIDATE'S SIGNATURE

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

SIGNATURE(S) OF SUPERVISOR'S

M C Bansal

(DR.M.C. BANSAL)
Reader in Chemical Engg.
I.P.T. (U.O.R.)
Saharanpur - 247001

R

(DR. R.N.MADAN)
Ex-Reader in Pulp Tech.,
(S.R.O.) F.R.I.
Dehradun - 248 006

DATE: 28/12/87

The candidate has passed the Viva-Voce Examination held on _____ at _____.

The thesis is recommended for the award of the Ph.D.Degree

SIGNATURE OF GUIDES

SIGNATURE OF EXAMINERS

ABSTRACT

Pinus is genera of plants belonging to the family Pinaceae of the order coniferales and of class Gymnosperms. The genus pine, being a source of resins, turpenes and paper pulp is very important amongst the conifers in India.

Pinus caribaea grows in Bahama islands, Western Cuba and Nicaragua, it is mainly distributed in islands of Carribean and costal of Central America . The altitude range of Pinus caribaea is being taken from sea level to 300m.

Pinus caribaea is a fast growing exotic pine species in comparision to other pines species . Studies have thus been carried out to cover the pulping and chemical constituents of Pinus caribaea .

On reviewing the past literature ,it is evident that no systematic work is reported in literature on the chemistry of Pinus caribaea and the reactions occuring on the chemical constituents during pulping so far. This study will not only give the chemical composition of the wood but will also help in better under standing its reactic during pulping and bleaching for different grade of pulps

used for various types of papers. This study will also help in using alternative raw materials to the paper industry.

The subject matter of the thesis is broadly divided into six chapters. A summarised account of the results of above mentioned investigations are given as below:

SUMMATIVE ANALYSIS

Pinus caribaea logs were debarked. Splitted and chipped on chipper, the chips wereof 1.5 to 2.5 cm in size. For chemical analysis the chips were disintegrated into wood meal in a laboratory Willey Mill. The wood meal passing through 40 mesh but retained on 60 mesh was used for elemental and proximate analysis. P.caribaea wood was also examined for its bark content, fibre dimension, cell wall thickness, lumen diameter and density. The average bark content was 19.3 per cent by volume and 12.6 per cent by weight. The average fibre length (l) was 2.22 mm; diameter (d) 31 microns, lumen diameter (t) 29.6 microns and cell wall thickness (w) was 6 microns. The average density of the wood work was 480 kg per cubic metre. The Runkle's coefficient (2w/t) was 0.405 which is less than 1, therefore this species was considered for evaluation. All the results are comparable with other softwoods reported in the literature.

Pinus caribaea is of low ash (0.6 %) and acetyl content (1.1 %), it is of an average holocellulose(66.8 %)

pentosan contents (8.32 %) and slightly higher extractive contents (7.5 %). Generally pine species have higher extractive content (3-10 %). Summation may be accounted for the sum of all individual components. The chemical constitutents considered are holocellulose, lignin, extractives, ash and acetyl content. The sum of these constituents is 102.5 per cent, which is close to 100 per cent. The total of components in the range of 95-102 per cent is not uncommon. Elemental analysis of Pinus caribaea was carried out by combustion method. The ultimate analysis of wood consists of carbon 49.8 per cent, hydrogen 6.1 per cent and oxygen 43.3 per cent which is also comparable to the ultimate analysis of other pine species.

ISOLATION OF HEMICELLULOSE

For the study of hemicellulose of Pinus caribaea, wood meal was converted into holocellulose by reaction of sodium chlorite and acetic acid at 70°C and then holocellulose was treated with potassium hydroxide and boric acid (24 + 4 %) to prepare hemicellulose. Crude hemicellulose was purified by making its copper complex. The yield of holocellulose and hemicellulose was 66.8 per cent and 20.56 per cent respectively on the basis of o.d. wood. Holocellulose was examined for its ash content (1.10 %) pentosan content (11.75 %), acetyl value (0.72 %) and alpha - cellulose (72.06 %) etc.

Hemicelluloses are responsible for several important properties of pulp fibres. Their primary action is to

imbibe water and contribute to the fibre swelling and beating. Another effect of hemicellulose on the properties of pulp fibres occurs on drying and it improves the strength properties. However, the hemicellulose was also examined for ash content (1.05 %) pentosans (81.5 %), acetyl value (nil), uronic acid (15.8 %) methoxyl value (5.57 %), specific rotation (-72°C). The results of hemicellulose of Pinus caribaea shows that it is composed of high pentose, sugars and uronic acid which indicates the presence of acid sugars in hemicellulose, low ash content is due to isolation in purified form. Hemicellulose was hydrolysed with 72 % sulphuric acid, neutralized and reduced with sodium boro-hydride, treated with cation prepared and identified by GLC on Perkin Elmer Gas chromatograph. The composition is shown in Table I..

TABLE - 1 SUGAR COMPOSITION OF PINUS CARIBAEA

S.No.	Sugar compounds	Relative amount in percentage	Molar ratio
1.	Arabinose	3.5	1
2.	Xylose	13.0	4
3.	Glucose	65.0	16
4.	Mannose	12.5	3
5.	Galactose	6.0	2
6.	Uronic acid	15.8	4

GLC results indicate the high percentage of glucose, which proves that the polymer is mainly composed of glucose

building unit. The second building unit in hemicellulose may be considered as uronic acid. Infrared spectra of Pinus caribaea hemicellulose shows an absorption band at 895-900 cm^{-1} which is a characteristic of B-glycosidic linkage between different sugar units. The results of P. caribaea hemicellulose are comparable with other softwoods hemicelluloses reported in literature.

LIGNINS(ETHANOL AND THIO-LIGNIN)

Ethanol and thio-lignin were isolated using standard methods and the isolated lignins were examined for elemental analysis and functional groups. The results are recorded in Table 2 A,B. The results of elemental analysis shows that both ethanol and thiolignins consists of only carbon, hydrogen and oxygen. In both lignins the carbon content is high, which shows their aromatic nature. P. caribaea lignins have methoxyl value (13.96-14.05%) which is lower to hard-wood lignins methoxyl value (20.05-22.0 %) but comparable with softwood lignins methoxyl value (12-15 %). In comparing the two lignins, it is evident that ethanol lignin has high carbon content and high methoxyl content, a charact-eristics functional group of lignin. This is due to mild conditions used in isolation of ethanol lignin. However, the value of hydroxyl content of the lignins is higher due to splitting of methoxyl content during its isolation, on account of drastic conditions. As the lignin molecule is composed of basic building unit of phenyl-propane, C_9 formula of ethanol lignin and thiolignin was calculated

which are $C_9H_{9.4}O_{2.8}(OCH_3)_{.86}(OH)_{.91}$ and $C_9H_{9.2}O_{2.8}(OCH_3)_{.89}(OH)_{.90}$ respectively and comparable with C_9 formula of other softwood lignins given in the literature. Isolated lignins were oxidised by alkaline nitrobenzene in a small autoclave of about 10 ml capacity at 170°C for 3 hours. After this reaction, the mixture was acidified and oxidised and the products were extracted with ether and dried. The oxidation products were identified by paper chromatography. The identified products were vanillin (13.10-14.25 %) syringaldehyde (0.86-1,12 %) and para-hydroxy benzaldehyde (1.62-2,81 %). The value of vanillin is high, as P. caribaea is a softwood and softwoods are mainly built up of guaiacyl units and parahydroxy benzaldehyde in traces. Therefore, these lignins may be treated as co-polymers of guaiacyl and syringyl propane units only. Molecular weight of isolated lignins was determined. Ethanol lignin has molecular weight2511.

By the action of nitrous acid on ethanol lignin, 4,6-dinitroguaiacol (2.8 %) and 2,6-dimethoxy p-benzoquionone were recovered from the oxidation product. The recovery of 4,6-dinitroguaiacol indicates the electrophilic displacement reaction which contributes to the over all degradation. The ethanol lignin was methylated by dimethyl sulphate. The methoxyl of ethanol lignin increased from 14.85 per cent to 28.5 per cent. This increase of methoxyl content is due to the methylation of hydroxyl groups. By nitration of methylated ethanol lignin with nitric acid in alcoholic

process. The unbleached pulps were bleached by multistage bleaching using CEHD sequence. The yield of bleached pre-hydrolysed sulphate pulp was 32.8 per cent. The pulps were chemically analysed for alpha, beta and gamma - cellulose content, pentosan, ash, ether content, 1 per cent cupra-mmonium hydrozide, degree of polymerization (viscosity) and brightness according to standard procedures. The results have been given in Table 3.

TABLE - 3 ANALYSIS OF BLEACHED RGP PULP

Alpha-cellulose	%	92.6
Beta-cellulose	%	2.8
Gamma-cellulose	%	4.6
Pentosans	%	1.65
Ash	%	0.08
Ether solubility	%	0.29
Degree of polymerization		372
Brightness ISO	%	85.5

Pinus caribaea wood was chemically examined for its elemental and proximate chemical analysis. Summative and ultimate chemical analysis of wood species was carried out according to different TAPPI, (Technical Association of pulp and paper Industry), ISI and ISO Standard methods.

LIST OF PUBLICATIONS OF THE CANDIDATE

1. Gupta, S.K., Madan, R.N., Bansal, M.C., "Summative and Ultimate Analysis of Pinus caribaea," Pulp and Paper World, Vol. 12, No. 8, 19-21, (1983).

2. Gupta, S.K., Madan, R.N., Bansal, M.C., "Production of Semi-chemical Pulps for liner Board and Corrugating Medium", Holzforschung und Holzverwertung, 36(6), 120-122(1984).

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– *SHRIKANT GUPTA*

Institute of Paper Technology,
(University of Roorkee)
SAHARANPUR-247001

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CONTENTS

CHAPTER - I

GENERAL INTRODUCTION

The Indian Pulp and Paper Industry has made a significant strides in the past three decades and at present production statistics are about 20 lakh tonnes. Today there are 25 large, 15 medium and about 200 small mills and per capita consumption of paper is 2 kg.By the year 2000 A.D. the country would require about 45 lakh tonnes of paper due to increase of population and per capita consumption from 2kgto 5kg. In the World more than 90per cent of the paper making fibre comes from woods, gymnosperms (Coniferous Wood, soft wood) or Angiosperms (Broadleaved, hard wood).In India the major raw materials for pulping are bamboo, wood, agricultural residues, rags ,waste papers etc. To meet the resources of short fibred pulp, agricultural residues are available in the country while the resources of long fibres are limited and bamboo is being utilized to the fullest extent. The planning commission has fixed the target capacity of the forest raw material for paper making at 10 million tonnes towards the turn of century. To over-come this problem several field trials on fast growing pines are being under taken in various parts of the country.

Pinus caribaea is a fast growing species in comparison to other pine species. It is an exotic species and has been planted in various parts of the country. In Uttar Pradesh, Himachal Pradesh, Orissa, Madhya Pradesh and in Jammu and Kashmir and has given very promising results. It is a native of Mexico and has been widely planted in Australia and Africa and about 25 species of pines are even being tried in India too.

Wood is a heterogeneous material which, because of its complex biological nature, shows the anatomical variations. This is frequently in contrast to the condition of many of the homogeneous materials with which the chemist usually deals. Wood is formed during the growth of certain plants, and as such is composed of plant cells. The chemistry of the basic cell wall components as well as the extraneous materials deposited in certain individual cells and their walls, is considered in the chemistry of wood.

A. CHEMICAL COMPOSITION OF WOOD

Wood mainly consists of carbon, hydrogen, oxygen, small amounts of nitrogen and ash. The elementary composition of dry wood substance is about 50 per cent carbon, 6 per cent hydrogen and 44 per cent oxygen, with astonishingly small variations with species, including both soft woods and hard woods. This corresponds to an empirical formula of about $C_{1.5}H_{2.1}O_{1.0}$ [1].

The general chemical composition of wood is listed in Table 1.1.

TABLE - 1.1 SCHEMATIC CLASSIFICATION OF CHEMICAL COMPONENTS OF CELL WALL SUBSTANCE IN NORMAL WOOD

1. **Primary Components**	
a) Total Polysaccharide Fraction (Expressed as holocellulose)	60-80 %
i) Cellulose	40-50 %
ii) Hemicelluloses	20-30 %
b) Lignin	15-35 %
. **Secondary Components**	
a) Tannins	
b) Volatile Oils and Resin	
c) Gums, latex, alkaloids and other complex organic compounds including dyes and colouring materials	
d) Ash	

A brief introduction of the each class compound is as follows:

1. Polysaccharides

The polysaccharides portion of the whole wood comprises the bulk of cell walls of fibres and makes 60 to 80 per cent of the total wood. Polysaccharides of wood are high molecular weight carbohydrates yielding simple sugars such as glucose, mannose and xylose upon hydrolysis with dilute acids. The major polysaccharides component of wood is called cellulose and the rest is a mixture of shorter chain polysaccharides called hemicellulose. The components taken up together make up the fraction, termed holocellulose.

(a) Cellulose.- This is the major component of cell walls of the wood fibres and yields theoretically only the monosaccharide sugar D-glucose on hydrolysis. It is associated with closely related polymers of mannose and xylose. Cellulose is a high molecular weight and a highly crystalline material. The amount present is in the range of 40-50 per cent. It is a linear polysaccharide of sufficient chain length containing only anhydro-glucose units and possessing a well ordered structure. The structure of cellulose is shown in Fig. 1.1.

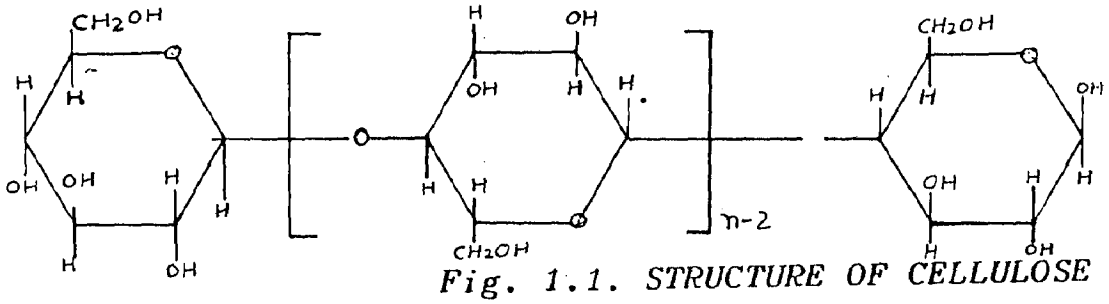


Fig. 1.1. STRUCTURE OF CELLULOSE

(b) Hemicellulose.- Cellulose is always accompanied by non-cellulosic polysaccharides called hemicellulose(20-30 %). These are alkali soluble and form a complex mixture of different polysaccharides of lower molecular weight and crystallinity than cellulose. These yield upon hydrolysis the hexoses, D-mannose, D-glucose and the pentoses D-xylose and L-arabinose.

2. Lignin

Lignin is an amorphous material of high molecular weight and is insoluble in common solvents. Lignin is an important component of all woods and represents what have been called the incrusting materials. Lignins are

probably the most complex and least well characterized group of substances in nature. They comprise of 15-35 per cent of the wood substances. It is distinguished from polysaccharides by its resistance to hydrolysis by acids and its greater reactivity with oxidizing agents. It is characterized by a considerable content of methoxyl groups and by the presence of hydroxyl groups, part of which are phenolic in nature. Lignin appears to be a polymer built up through condensation of structural units of a few similar types. Primarily these units are of phenylpropane (C_6C_3) type (a), but they may be combined in variety of ways. In woods of gymnosperms guaiacyl units (b) appears to be the basic building units, whereas in the angiosperms the lignin is made up of both guaiacyl and syringyl units (c). In some angiosperms and in the Gramineae the p-hydroxyl phenyl (d) unit is also an important constituent. These structural units are shown in Fig. 1.2.

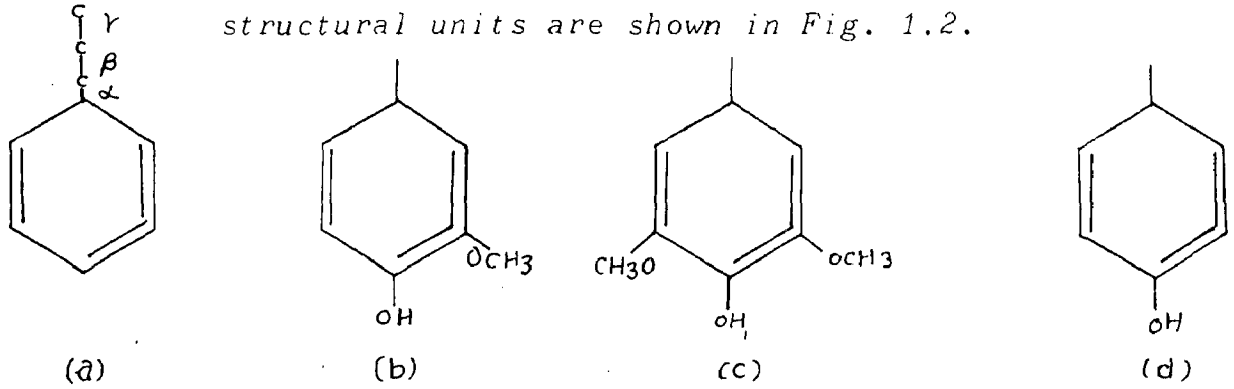


Fig. 1.2. STRUCTURAL UNITS OF LIGNIN

3. Extractives

Wood contains small amounts (generally 3-10 %) of some other substances as extractives, in addition to cellulose hemicellulose and lignin. The extractives

include resin, fatty acids and their esters, waxes, unsaponified substances and inorganic compounds which are partially or wholly insoluble in neutral solvents.

B. PAPER MAKING

Anatomy of Cell Wall[2]

Cell wall of wood fibre is made up of three layers (i) outer most layer or middle lamella, (ii) primary layer and (iii) secondary layer as shown in Fig. 1.3.

Cross Section of Wood Fibre Cell

M_L - Middle lamella.

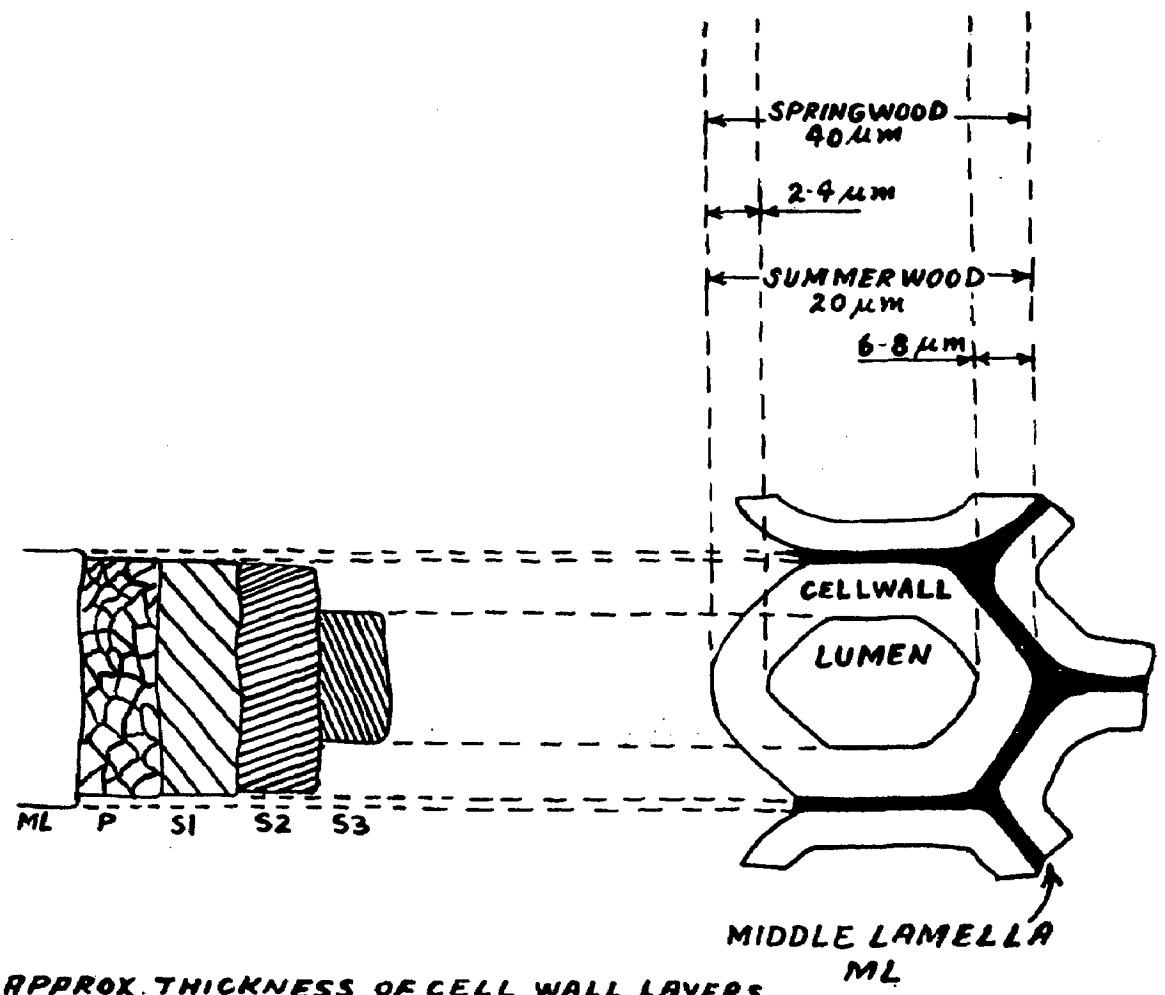
P - Primary wall.

S_1 - Outerlayer of the secondary wall.

S_2 - Middle layer of secondary wall.

S_3 - Inner layer of secondary wall(also called tertiary wall).

Outer layer or middle lamella is very thin in the beginning but becomes thicker later when the lignin is deposited. It has no fibrillar structure and consists mainly of lignin. The primary wall is very thin, probably only a few hundred angstrom units in thickness. In this layer the cellulose fibrils are highly individualised, somewhat irregularly dispersed and to some extent interwoven. They have a preferred orientation that is mainly longitudinal on the outside of the wall but transverse on the inside. The secondary wall is made up usually of three distinct layers : The outer layer of secondary wall(S_1), the middle layer (S_2) and inner layer (S_3).



APPROX. THICKNESS OF CELL WALL LAYERS
WALL. P. 50 μm.
SECONDARY WALL, S1. 75-200 μm.
SECONDARY WALL, S2, 2-8 μm
WALL. S3, 70-80 μm.

FIG. 1·3. CROSS SECTION OF WOOD FIBRE CELL INDICATING COMMONLY FOUND DIMENSIONS AND FIBRILLAR ARRANGEMENTS WITHIN THE WALL LAYERS (μm)
ONE MILLIONTH OF A MILLIMETRE.

Plant Fibres

Paper is a sheet or continuous web of material formed by decomposition of vegetable, mineral or synthetic fibres or their mixtures with or without the addition of other substances from a suspension in a liquid, in such a way that fibres are intermeshed and bounded together.

The basic material of paper is usually cellulose fibre that occurs naturally in many vegetable tissues, from which they may be extracted fairly easily by mechanical or chemical means. There are many possible sources of fibres, but the most important are tree wood, grass, straw, bagasse, cotton and rags. Of these, wood is by far the most important. About 65 per cent of paper and board is manufactured from wood pulp. Of the four main groups of plants, the Spermatophyta (seed plants) contain the trees and most sources of paper making fibre. Within the spermatophyta there are:

Gymnosperms (naked seed) conifers e.g. Pines, Spruce, Firs etc. All soft woods. Soft wood tissue contains 90-95 per cent by bulk of fibre, with individual fibres commonly between 2.0 mm and 3.5 mm long. They are comparatively thin walled.

Angiosperms (Encased seeds). Dicotyledous e.g. Oaks, Eucalyptus, Aspen, Poplar etc. All hard woods.

The hardwoods are of much recent origin than soft woods. Hardwood tissue varies in fibre content according

to the species. The individual fibre being commonly 1.00 to 1.5 mm long.

Pulping Process

Pulp preparation is the beginning phase of paper manufacture since it is impossible to produce paper without first reducing the raw material to the fibrous state. The first basic step in pulp preparation is pulping. This consist of cooking the raw material, usually wood in suitable chemicals in a digester under controlled conditions of temperature, pressure, time and liquor composition, or reducing the raw material to the fibrous state by mechanical or semi-mechanical means. The second basic step is pulp purification, whereby the pulp is subjected to bleaching and purifying agents to render the pulp more suitable for its intended use.

Pulping processes are of three principal type - mechanical, chemical and semi-chemical.

(a) **Mechanical Pulping**.- The mechanical process involves the reduction of wood or other raw material to the fibrous state by mechanical means. Logs of wood are held with pressure against the surface of stone, and as the stone grinds the wood into fibre, a stream of water is sprayed on the stone to carry the pulp away and to absorb the heat generated. The yield of pulp is high by this process (about 95 %), but the pulp is of low purity and there is considerable fibre damage and this pulp is mainly used for newsprint.

(b) ***Chemical Pulping***.- *Chemical pulping may be defined as the cooking of wood with chemical reagents to a point where the fibres can be easily separated from each other. Chemical process of pulping involves a cooking of the wood with chemicals which selectively remove lignin and other impurities, thereby isolating and partially purifying the individual fibres. The yield is, as would be expected much lower than in the mechanical pulping, but the purity is higher and there is relatively little fibre damage. There are three major chemical processes of commercial importance, namely soda, sulphate and sulphite.*

(i) ***Soda process***.- *The process of pulping wood under pressure in sodium hydroxide was patented in England in 1853 by both Watt and Burgass. The experiements were made on birch wood and the first commercial mill for alkaline and soda pulping was erected in America. Hardwoods are principally used in the soda process. Softwoods are used on occassion, but they constitute a minor source of supply.*

(ii) ***Kraft or Sulphate process***.- *The sulphate or kraft process is a newer process than the soda process, having been invented by Dahl, a German chemist in 1889. It differs from the soda process because sodium sulphide is used in the cooking liquor alongwith sodium hydroxide. The advantages of the sulphate process are (1) maximum flexibility with regard to species (any species can be used, even all woods), (2) cooking time is short, (3) the pulp can be bleached to high brightness level, (4) no pith problems*

(5) high pulp strength, (6) valuable products are produced in the form of tall oil and turpentine and (7) the recovery of spent liquor is easy.

(iii) **Sulphite process**.- Sulphite process is one of the oldest pulping processes, having been discovered in 1866 by Benjamin Tilghman, an American. For many decades following 1890, the sulphite process was the most important pulping process throughout the world because it yielded the brightest unbleached chemical pulp and could be easily bleached to high brightness. In this process the delignifying agent is sulphurous acid or its salts. The various salts used are of sodium, calcium, magnesium, ammonium.

(c) **Semi-Chemical process**.- Semi-chemical pulping is a two stage process involving chemical treatment of wood chips to obtain a softening and partial removal of the lignocellulose bonding material, followed by mechanical refining to complete the fibre separation. Recently semi-chemical process has been described as a three stage process consisting of (1) a pressure impragnation of wood chips with cooking liquor, (2) a mild digestion with chemicals which are practically neutral and which are capable of maintaining neutrality during cooking and (3) a mechanical reduction of softened chips to the fibrous state. Examples are (1) Cold Soda, neutral sulphite Semi-chemical (NSSC) Pulping.

Pulping processes classified according to yield are summarized in Table 1.2[3]

TABLE - 1.2 CLASSIFICATION OF PULPING PROCESSES

Class	Mechanical	Semi-Chemical	Chemical	Dissolving
Typical processes	Stone ground-wood chip refiner groundwood.	Neutral sulphite semi-chemical	Sulphite Magnefite sulphate (Kraft) Sivola Stora Kopparberg	Sulphite pre-hydrolyzed sulphate Sivola.
Yield of fibre %	90-95	60-85	43-55	33-43
Preferred species	Conifers Poplars, Eucalyptus other hard woods, wood residues.	Hardwoods (softwoods)	Almost any.	Almost any.
Pulping chemicals	None	Sodium sulphite or Ammonium sulphite	Calcium magnesium sodium or ammonium bisulphites plus sulphurous acid or sodium hydroxide plus sodium sulphide.	Bisulphites plus sulphurous acid or sodium hydroxide plus sodium sulphide.
Bleaching chemical	None or hydrosulphite or peroxide and hydro-sulphite	None or hypo-chlorite	Chlorine sodium hydroxide and hypo-chlorite with or without chlorine dioxide or peroxide.	Chlorine sodium hydroxide hypo-chlorite and chlorine oxide.
Uses	News-print printing papers. writing papers Tissue creped papers	Corrugating printing & writing papers coating base.	All papers and paper boards	Textile fibres chemicals plastics

C. REVIEW OF LIGNIN CHEMISTRY

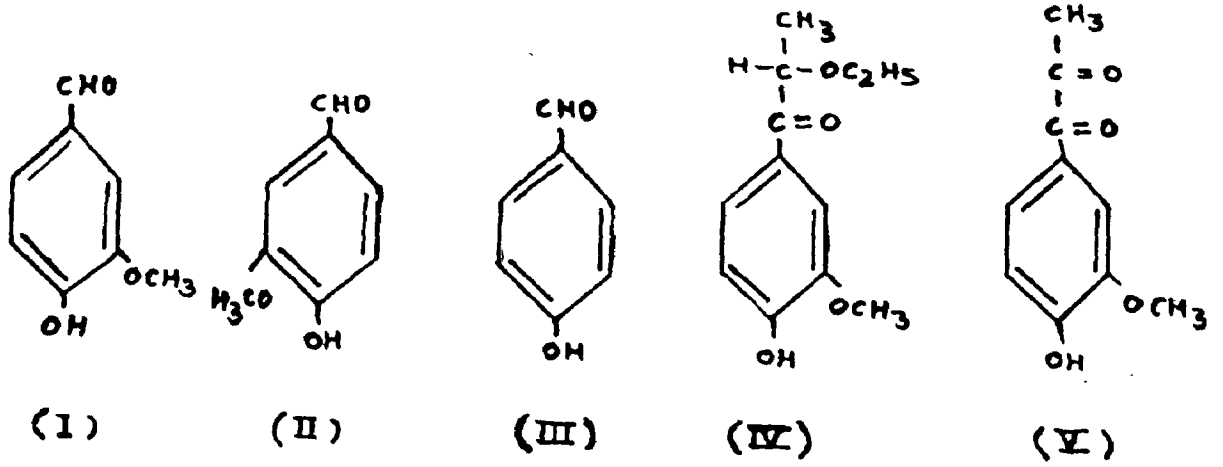
1. Definition of Lignin

Lignin cannot be considered the designation of a constitutionally defined compound. Various definitions based on their chemistry have been proposed by various workers[4]. Branus[5] suggested that the lignin is the incrusting material of the plant which is built up of mainly, if not entirely, of phenyl-propane units and carries the major part of the methoxyl content of wood. It is unhydrolysable with acids, readily oxidized and soluble in hot alkali and bisulphite. Lignins readily condense with phenol and thio compounds. On oxidation with nitrobenzene lignins yield vanillin (I) from conifers (softwoods), vanillin (I) and syringaldehyde(II) from deciduous (hardwoods) and p-hydroxybenzaldehyde (III) in addition to these two in case of perenial plant (monocots), and produces 'Hibbert's monomers' (Vanillin- -ethoxypropiorranillene (IV) and vanilleyl methyl ketone (V) upon subjection to ethanolysis. (I) to (IV) have been represented in Fig. 1.4.

Recently lignin has been defined as a polymeric natural product, arising from an enzyme initiated dehydrogenerative polymerization of three primary precursors:

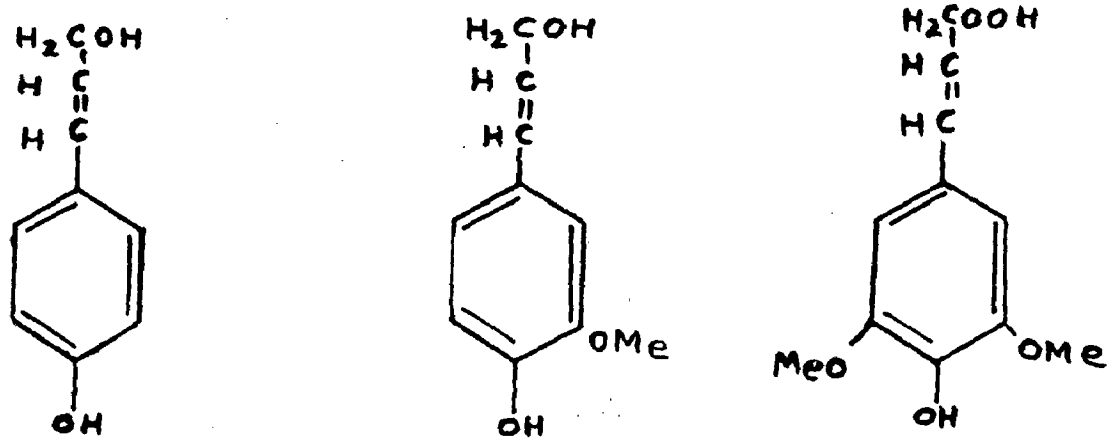
Trans-coniferyl (VI), Trans-sinapyl (VIII) and Trans-p-coumaryl alcohol (VIII).

VI to VIII have been represented in Fig. 1.5.



(I) (II) (III) (IV) (V)

FIG. 1.4. OXIDATION PRODUCTS OF LIGNIN.



(VI) (VII) (VIII)

P-COUMARYL ALCOHOL CONIFERYL ALCOHOL SINAPYL ALCOHOL

FIG. 1.5. PRECURSERS OF LIGNIN

Delignification i.e. the removal of lignin from wood or lignin-containing pulps, constitutes the main process involved in chemical pulping and lignin-degrading bleaching. It is primarily due to lignin fragmentation, resulting from the cleavage of particular inter unit bonds, and to lignin hydrophilization, brought about by the introduction of polar groups.

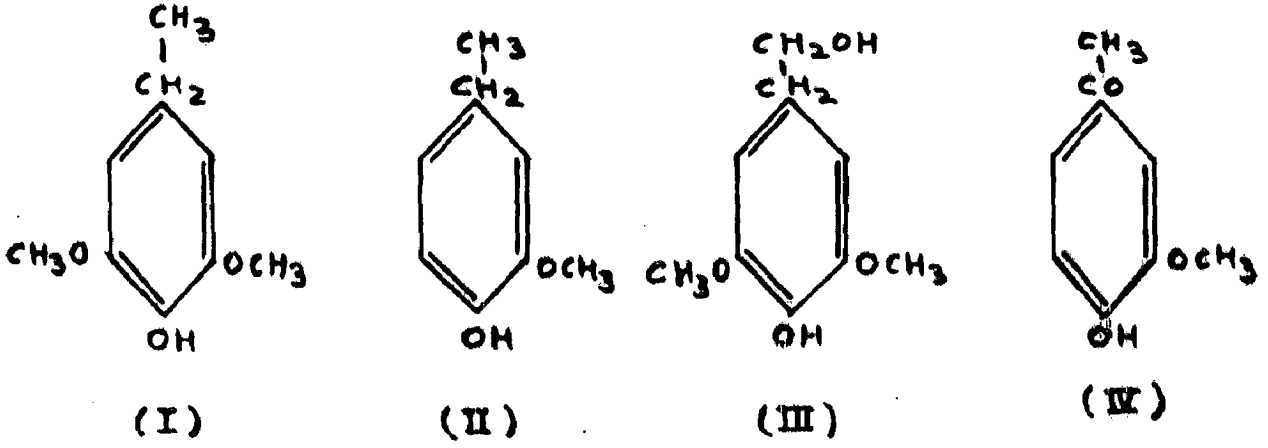
Pulping process is carried out under widely varying conditions with respect to structure and concentration of the substrate (lignin). pH, temperature as well as type and concentration of the delignifying reagent(s). Inspite of this great variety of conditions, the reaction responsible for delignification can be rationalized in terms of common mechanistic features and a general concept, covering the main lignin-degrading and lignin-modifying reactions of the pulping process currently used, can apply.

2. General Concept of the Reactions of Lignins during Pulping

The heating of lignin with alkaline solutions causes the splitting of alkyl-aryl ether linkages in the position 4, with the formation of phenolic hydroxyl groups. To liberate the phenolic groups in lignin, a temperature range between 160°C to 170°C has been used most frequently. The other linkage present in the methoxyl group is more stable and is degraded at temperature above 250°C, protocatecheuic acid and pyrocatechol have been isolated from such products. The carbon to carbon linkages in lignin are susceptible to alkaline media and there is a formation

of vanillin and acetaldehyde from coniferyl aldehyde groups. Indication also exists that linkages between B and carbon atoms of propyl side chains may likewise become partially degraded when a medium containing 3 per cent sodium hydroxide is used, only monomeric phenylethane derivatives (I, II, III) and (iv) are isolated (6) and shown in Fig. 1.6. It therefore appears probable that the alkaline medium causes a cleavage between B and r atoms. Further the existence of both acetoguaiacone(V) and formaldehyde among the alkaline hydrolysis products of lignin suggests a cleavage of B and r carbon linkages.

In comparison with soda process, the rate of delignification in the Kraft process is more rapid and the obtained pulps contain less lignin. Both of these effects are believed to be due to less condensation in the latter process. It has been proposed that HS^- ions react with a part of condensing groups, thus inhibiting the condensation reaction. This view has gained support from studies of model compounds. These studies indicate that unetherified guaiacyl-propane units containing a hydroxyl or an alkyl ether group in the alpha position (V) may react with hydrosulphide anion forming mercaptan (VI) shown in Fig. 1.6. According to Enkvist[7] an increasing number of the above structures become available for reaction with hydrosulphide ions as the phenolic ether linkages are hydrolysed by the action of alkali. The protective action of the mercaptan groups appears to be only temporary, retarding rather than inhibiting the condensation reaction.



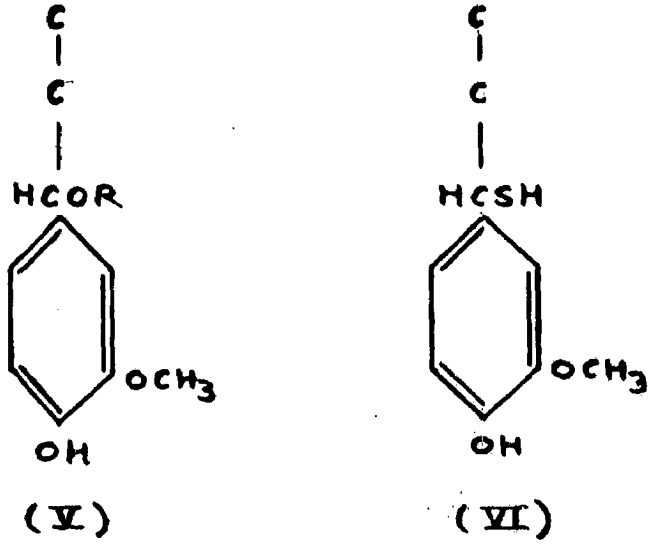


FIG. 1.6. PRODUCTS OBTAINED FROM LIGNIN DURING ALKALINE COOKING

D. OBJECT OF WORK

If the world demand for paper is going to increase as even close to the levels predicted by the FAO(256 million metric tons by 1990), much of the raw material must come from the developing world. In view of expansion of capacities and production target, the pulp and paper industry has to look into some other way to overcome the shortage of raw material, because the sources of bamboo which is the main commercial raw material are depleating and this fast growing species is the answer.

The growing industrialisation of India and planned rise in living standard of people are certain to result in considerable increase in the requirement of forest produce, particularly for purposes such as for the manufacture of pulp and paper. There is already a gap betweenthe requirement and supply of pulp wood which is likely to widen unless the low yielding mixed natural forests are replaced by fast growing trees mostly exotics producing highest possible yield per unit area with a view to produce long fibred material for pulp. The first priority must be given to confiers. Bamboo were being made use of for pulp wood has now become very scare. Silvilculturally concentrated bamboo plantations have not been of much success. The existence of forest land cannot be justified fully unless they are put to maximum use but in perpetuity. Tropical pines would help us to achieve this and to a great extent.

1. *Pinus roxburghii (Chir), 2. Pinus geradiana (Chilgosa)*
3. *Pinus kesiva (Khasi pine), 4. Pinus wallichiana(Kail).*

Under the scheme of short rotation forestry encouraging results have also been obtained from attempts to grow on man-made forestry basis for the following species:

Pinus brutia, Pinus caribaea, Pinusdouglasiana, Pinus elliottii, Pinus greggii, Pinus insularis, Pinus khasya, Pinus merkusii, Pinus montezumae, Pinus oocidentalis, Pinus oocarpa, Pinus patula, Pinus pseudostrobus, Pinus taeda and Pinus tropicalis.

The work so far has been done on indigenous pines and on exotic pines for suitability for pulp and paper. Furth work is required on production of mechanical and thermo nical pulps for newsprint and on production of prehyd sulphate pulps for rayon[10,11].

India by the year 2000 AD has to produce 4.5 million tonnes of paper as the per capita consum ion of paper will increase from 2 kg to 5 kg and the popula n will also increase. To produce 4.5 million tons of pa about 10 million tonnes of raw material will be requir By 2000 AD, the requirement of various cellulose raw materia s reported by National Commission on Agriculture are:

Bamboo	*14.8 %*
Hardwood	*49.4 %*
Softwood	*24.3 %*
Bagasse	*2.8 %*
Agricultural residue	*8.7 %*

Thus 1/4 of the cellulose raw material has to be of soft wood type. The National Commission on Agriculture has provisionally estimated that 30 hectares of forest has been brought under intensive management for desired products.(12)

Viewed from the stand-point of wood chemistry, the object of the sulphate process is to produce a maximum yield of non-degraded cellulose with partial complete removal of hemicelluloses and lignin. Varying amount of resistant cellulosans remain with the pulp being technically useful in the process of paper making, although if the pulp is to be used in the process of manufacture of cellulose derivatives further treatment is applied to remove them. In American and Canadian practise the wood most commonly used in the sulphite process are spruce, balsam and hemlock, because their forests are full of softwoods, although same hardwoods and some of the pines are also utilised commercially

To the pulp and paper maker, lignin is the unwanted component of wood that creates most problems encountered during pulping. In pulping our primary objectives is to isolate cellulosic fibres. Delignification is the formost goal of pulping as lignin undergoes more severe chemical changes during pulping than cellulose. Hemicellulose play a very important role in pulp and paper making and influence the chemical properties of pulp and paper.

As India is growing pine mainly for the pulp and paper industry, it is necessary to understand the chemistry of

different constituents of the wood. By understanding the reactions involved during pulping, it will be possible to modify the pulping and bleaching process.

On reviewing the past literature, it is evident that no work has been reported on the chemistry of the reactions occuring during pulping of Pinus caribaea. This study will not only help in optimising the pulping conditions for different grades of pulps but will also throw some light on the reactions involved during the delignification of wood. This study will be utilised for the production of rayon and paper grade pulps in a scientific manner and to control the losses during its processing.

B. SCHEME OF INVESTIGATION

1. **Chemical Composition of Pinus caribaea wood**
   - (a) Elemental composition of Pinus caribaea wood.
   - (b) Summative analysis of Pinus caribaea wood.
   - (c) Fibre dimensions of Pinus caribaea wood.
2. **Chemical Composition of Pinus caribaea hemicellulose**
   - (a) Isolation of holocellulose and hemicellulose from Pinus caribaea wood.
   - (b) Analysis of Pinus caribaea hemicellulose
   - (c) Indentification of sugar components in hemicellulose.
3. **Chemical Composition of Pinus caribaea Lignin**
   - (a) Isolation of Thiolignin and Ethanol lignin
   - (b) Elemental composition of lignins
   - (c) Determination of functional groups of lignins

(d) Nitrobenzene oxidation of lignins

(e) Methylation of dioxane lignin and its oxidation

(f) Spectroscopic studies of lignins.

4. ***Utilisation of Pinus caribaea wood***

(a) Paper Grade Pulp

(i) Sulphate pulping of Pinus caribaea

(ii) Bleaching of pulp

(iii) Analysis of pulp

(iv) Evaluation of Pinus caribaea Pulp.

(b) Rayon Grade Pulp

(i) Prehydrolysed sulphate pulping of Pinus caribaea

(ii) Systematic bleaching of pulp

(iii) Physical and chemical analysis of rayon grade pulp.

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CHAPTER - II

SUMMATIVE ANALYSIS AND ULTIMATE ANALYSIS OF PINUS CARIBAEA

a. introduction
A. INTRODUCTION

Knowledge of chemical composition of wood in terms of its principal components is very important from the view point of its use as raw material in pulp manufacture.

1. Chemical Components of Wood

Wood system is classified for convenience into four major chemical systems viz. Polysaccharides, lignins, extractives and inorganic constituents.

(a) **Polysaccharides**.- Polysaccharides roughly constitute three fourth of the wood substance. They include cellulose, the group of cold water insoluble non-cellulosic polysaccharides commonly designated as hemicellulose, starch, pectic substances and water soluble polysaccharides such as the arabinogalacton ...

(b) **Lignin**.- Lignin is probably the most complex and least well characterized group of substance in nature. This comprises 20-30 per cent of wood substance. Lignin is a highly reactive substance and it is generally insoluble in common solvents.

(c) **Extractives**.- Wood contains 3-10 per cent extractives. The compound present include terpenes, tannins, resins, fats, waxes etc.

(d) **Inorganic constituent**.- A number of mineral constituents are necessary for plant growth. The composition of mineral matter in wood depends somewhat on the environmental conditions under which the tree grows.

The mineral constituents are comprised chiefly of salt of Ca, K, Mg, but the salts of other elements are also present in smaller amounts. The acid radicals are carbonate phosphate, silicates, sulphates and in some cases oxlates.

In Table 2.1 average chemical composition of the two groups (softwoods and hardwoods) is given.

TABLE - 2.1 AVERAGE CHEMICAL COMPOSITION OF SOFTWOODS AND HARDWOODS*(1)

S.No.	Raw material	Cellulose %	Hemicellulose %	Lignin %
1.	Softwoods	43	28	29
2.	Hardwoods	45	34	21

*The values are mean percentage, extractive free wood basis.

The general composition of wood has been shown in Fig. 2.1.

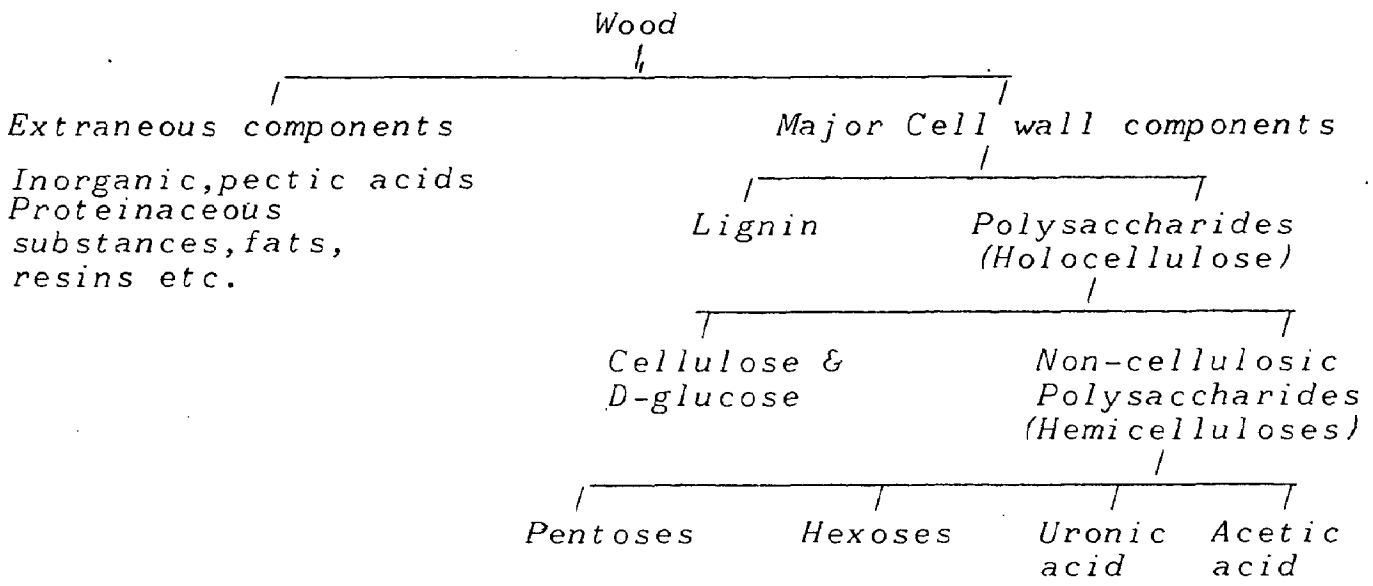

Fig. 2.1: The Composition of Wood

2. Summative Analysis

The summative analysis of wood is necessary for the technological utilization of different wood elements in research investigations relating to the changes which occur in wood and its constituents as they are subjected to alternations by chemical or physical processes and in the study of biological changes which accompany growth and decay.

In summative analysis the composition of a material is defined in terms of identifiable molecular or atomic species. The criterion of success in this direction is the achievement of a satisfactory summative analysis, in which the whole material is accounted for as the sum of all individual components. A summative analysis represent a rigorous evaluation of experimental data, and its interpretation can be of great value in judging the validity of analytical methods.

Summations may be taken in any of the two ways. The aim of each is to account for the whole wood[2].

A	B
Extractives	Extractives
Lignin	Lignin
Holocellulose	Glucan
	Mannan
	Galactan
	Xylan
	Arabinan
	Uronic Anhydride
	Acetyle groups

Ash is often not included in summative analysis since the ash content of most woods is small and the correction would be minimal. The results of summative analysis of some woods, by different ways, are recorded in Tables 2.2 and 2.3.

TABLE - 2.2. SUMMATIVE ANALYSIS OF WOODS (PERCENTAGE OF EXTRACTIVE-FREE DRY WOOD)[3]

Constituent	Dogulas fir	Loblolly pine	Black spruce	Nonterey pine
Ash	0.3	0.3	0.4	0.2
Acetyl	0.6	1.1	1.1	1.4
Lignin	28.4	29.5	28.0	26.5
		SUMMATION A		
Alpha-cellulose	57:2	55.0	51.5	54.8
Hemi-cellulose	14.1	15.3	17.4	16.4
Total	100.6	101.2	98.4	99.3

Constituent	Dogulas fir	Lobololly pine	Black spruce	Nonterey pine
		SUMMATION B		
Alpha-cellulose	48.3			45.3
Mannan	5.4			11.7
Xylan	6.2			9.3
Uronic anhydride	2.8			3.4
CH_2	0			0.1
Total	92.0			97.9

TABLE - 2.3 SUMMATIVE ANALYSIS OF CANADIAN WOODS (ALL VALUES IN PER CENT)(4)

S. No.	Species	Soluble in alcohol benzene	Soluble in hot water	Ash	Acetyl	Lignin	Alpha cellulose	Hemi cellulose	Total
1.	Pinus resinosa	9.7	1.8	0.2	1.9	23.4	47.8	15.1	99.9
2.	Fraxinus nigra	3.4	1.3	0.7	5.3	18.6	47.4	21.2	97.9
3.	Betula lutea	3.4	0.7	0.3	5.4	18.8	42.6	26.6	97.8
4.	Fagus grandifolia	2.0	0.7	0.4	5.3	22.2	43.6	23.6	97.8
5.	Acer saccharus	2.7	1.0	0.4	4.6	21.1	46.8	22.2	98.8

3. Ultimate Analysis

The greater part of wood is composed of carbon, hydrogen and oxygen. Nitrogen is present to the extent of about 0.2 per cent from proteinaceous residues originating during the early growth of the cells. If the wood contains alkaloids,

the nitrogen content may be significantly higher. Some typical values for ultimate analysis of woods are given in Table 2.4.

The essential requirement in preparing a wood sample for analysis are first that it should be representative of the whole of the material for which an analysis is required and secondary that it should be in a suitable form for manipulation and for reaction with the reagents employed. Wood for analysis must be reduced to a small particle size. It is desirable to grind or disintegrate the material so that it passes through a 40-mesh screen and in such a way as to produce the minimum of very fine material considering this (-40+60) fraction is taken for analysis. Fine material is undesirable because it renders filteration difficult and because it may be subjected to undue degradation in some of the analytical processes.

TABLE - 2.4 ULTIMATE ANALYSIS OF WOODS (ALL VALUES IN PER CENT)(5)

Constituent	Larch	Pine	Spruce	Oak	Beech
Carbon	49.6	50.2	50.0	49.2	48.9
Hydrogen	5.8	6.1	6.0	5.8	5.9
Nitrogen	0.2	0.2	0.2	0.4	0.2
Oxygen	44.2	43.4	43.5	44.2	44.5
Ash	0.2	0.2	0.3	0.4	0.5

4. Fibre Dimensions

A knowledge of the cellulose structure of wood is of value to the pulp chemist since anatomical structure of wood has an important influence on the penetration of liquids in pulping and affects the course of the pulping reactions. Variation in wood and fibre morphology can be statistically correlated with variation in paper properties. This has a great potential value for the paper industry and on account of fibre morphology paper made from softwoods is stronger than paper made from hardwoods. Typical fibre dimension and chemical composition of softwoods, hardwoods and grasses are recorded in Table 2.5.

TABLE- 2.5 TYPICAL FIBRE DIMENSION AND CHEMICAL COMPOSITION OF SOME RAW MATERIALS(6)

Raw material	Mean fibre length mm	Mean fibre diameter microns	Chemical constituents by wt.,%				
			Extraneous		Cell Wall		
			Mineral matter	Extractives (in water, alcohol)	Cellu-lose	Hemi-cellu-lose	Lignin
Softwoods	3-3.5	30-40	1-2	4-12	40-45	15-25	26-30
Hardwoods	1-2	20-40	4-2	4-12	38-49	22-34	16-25
Grasses	1-5	13	2-4	12	42	33	14-17

b. experiemntal

B. EXPERIMENTAL

1. Preparation of Pinus caribaea Wood Meal

Pinus caribaea logs collected from Forest Research Institute, Dehradun were first debarked manually and then were converted into chips in the Pilot Plant Chipper of the Cellulose and Paper Branch, Forest Research Institute,

Dehradun. The chips were milled to produce dust. Dust passed through 40 mesh but retained over 60 mesh sieve was used for elemental analysis and summative analysis.

All chemicals used during experiment were of analytical grade.

2. Fibre Dimensions

A small portion of chips was cooked by caustic soda in a digester. The unbleached pulp obtained was bleached with bleaching powder. A suspension of the fibres was made in water. A drop of suspension contains several fibres. A drop of suspension was taken on the glass slide and stained with 'Hertzberg stain' in order to give colour to fibre. The fibre dimensions were measured under the microscope having a standard scale in the eye piece by the usual procedure and also by projection microscope. Value of fibre length, diameter, cell wall thickness and lumen diameter are recorded in Table 2.6.

TABLE - 2.6 FIBRE DIMENSIONS AND THEIR DERIVED VALUES[7]

S.No.	Particulars	l mm	d μ	L μ	W μ	l/d	2W/L	l/d
1.	P.caribaea	2.22	41.5	29.6	6.00	54.34	0.4054	0.7099
2.	P.kesiya	2.32	38.5	22.75	7.87	60.36	0.6929	0.5909
3.	P. patula	2.27	44.0	22.6	10.70	57.68	0.9468	0.5130
4.	D.strictus	2.09	18.5	6.70	5.90	112.60	1.7610	0.3620
5.	E.tereticornis	0.83	17.1	9.94	4.06	45.88	0.820	0.550

l = stands for average fibre length; d = stands for fibre diameter
L = stands for lumen diameter W = stands for cell wall thickness
l/d=stands for felting coefficient 2W/L=stands for Runkle coefficient
l/d=stands for flexibility coefficient.

3. Determination of Carbon and Hydrogen Contents

The sample of Pinus caribaea dust was completely oxidised to carbon-dioxide and hydrogen to water, they were absorbed separately into absorption tubes and weighed. Carbon-di-oxide was absorbed in a tube filled with sodium hydroxide impregnated over asbestos and magnesium perchlorate absorbed water. From the amount of carbon dioxide and water so obtained, the percentage of carbon and hydrogen was calculated. Percentage of oxygen was determined by the difference.

Results are recorded in Table 2.7.

TABLE - 2.7 ULTIMATE ANALYSIS OF PINUS CARIBAEA

S.No.	Constituents	Wt. Percentage
1.	Carbon	49.8
2.	Hydrogen	6.1
3.	Nitrogen	0.2
4.	Oxygen	43.3
5.	Ash	0.6

4. Summative Analysis

For summative analysis, Pinus caribaea wood meal was analysed for ash content, Cold and hot water solubility, alcohol - benzene solubility, holocellulose and lignin content.

Standard methods of analysis were adopted as given in TAPPI Standards (Technical Association of Pulp and Paper Industry, U.S.A.) and the same are notified against each analysis.

(a) ***Ash content (T15-OS-58).***- *2.0 g wood dust was taken in silica crucible and ignited in a muffle furnace at 575 ± 25°C for 4 hours. After ignition, the silica crucible was allowed to cool in a desiccator and weighed. The ash content was calculated.*

$$\text{Ash contents, \%} = \frac{B \times 100}{A}$$

B = Stands for residues left after ignition.

A = Stands for o.d. weight of test specimen.

(b) ***Water solubility.***- *Tappi method T-207-OS-75 was used for the determination of water solubility.*

(i) ***Cold Water solubility (T 207-OS-75).***- *2 g wood dust was taken in a beaker (500 ml) and distilled water (300 ml) was added to it. The mixture was allowed to stand at room temperature for 48 hours with occasional stirring. The dust was filtered through G_1 crucible and washed thoroughly with cold distilled water. The residue was dried to constant weight in an oven at 105 ± 20°C. The cold water solubility was calculated as follows:*

$$\text{Cold water solubility, \%} = \frac{(A-B) \times 100}{A}$$

A = Stands for o.d. weight of the test specimen before extraction.

B = Stands for o.d. weight of the test specimen after extraction.

(ii) ***Hot water solubility (T207-OS-75).***- *Wood meal 2 g was taken in a Erlenmeyer flask (250 ml) fitted with a water condenser and distilled water (100 ml) was added to it. The flask was kept over a boiling water bath and*

refluxed for 3 hours. The contents of the flask were filtered through IG_1 crucible, washed with hot distilled water and dried to constant weight at 105 $\pm$ 2°C in an oven. Hot water solubility was calculated as follows:

$$\text{Hot water solubility, \%} = \frac{(A-B) \times 100}{A}$$

A = Stands for o.d. weight of the test specimen before extraction.

B = Stands for o.d. weight of the test specimen after extraction.

(c) **Alcohol-benzene solubility (T16m-OS-59).**- Wood dust 2 g was taken in a porous thimble and placed in the Soxhlet apparatus. The extraction was carried out with 250 ml alcohol-benzene mixture (1:2v/v) for 20 hours. After extraction, the material was removed from porous thimble and dried in an oven at 105 $\pm$2°C to constant weight. The alcohol-benzene solubility was calculated as follows:

$$\text{Alcohol-benzene solubility, \%} = \frac{(A - B) \times 100}{A}$$

A = Stands for o.d. weight of the test specimen before extraction.

B = Stands for o.d. weight of the test specimen after extraction.

(d) **Klason lignin content (T222-OS-74).**- 2 g extractive free wood meal was taken in a small beaker (100 ml) and treated with 72 per cent sulphuric acid (15 ml) for 2 hours at 20°C with occasional stirring. At the end of 2 hours the contents were transferred to one litre conical flask, acid concentration was brought down to 3 per cent by adding distilled water (560 ml) and refluxed for 4 hours. The

contents were then filtered through $1G_3$ crucible and washed thoroughly with hot distilled water until acid free. The crucible was dried to constant weight at 105 ±2°C in an oven. The lignin content was calculated as follows:

$$\text{Lignin content, \%} = \frac{A \times 100}{W}$$

A = Stands for o.d. weight of lignin.

W = Stands for o.d. weight of the test specimen.

(e) **Holocellulose**.- The total polysaccharides in the wood (alpha-cellulose + hemicellulose) are designated as holocellulose. To determine holocellulose, it is therefore, necessary to extract the lignin as completely as possible without removal or degradation of carbohydrate material.

The determination of holocellulose was done by chlorite method[8].

About 5 g (o.d. basis) dust of Pinus caribaea wood (40/60 mesh) mesh, (pre-extracted with alcohol-benzene 1:2, and with hot water) was taken in 1 litre flask and 160 ml of distilled water was added to it. The material was then treated with 1.5 g of sodium chlorite and 10 drops of acetic acid at 70-80°C for 1 hour. At the end of 1 hour, 1.5 g of sodium chlorite and 10 drops of acetic acid were again added and heated at the same temperature for 1 hour. In this way, the process was repeated 4 times till the dust became white, this was then filtered on a buchner funnel with suction and washed thoroughly with water and finally with acetone. The sample was air dried and the yield was determined.

(f) **Determination of acetyl value.**- Acetyl groups which are combined as O-acetyl groups with polysaccharide in wood, are hydroloysed by strong acids to acetic acid.

$$R\ COO\ \ CH_3 + HOH \longrightarrow R\ OH + CH_3COOH$$

Acetyl groups in wood and hemicelluloses can be determined by distilling and titrating the liberated acetic acid after acid hydrolysis or on alkaline saponification. Owing to the case of saponification, the acetyl groups are lost when hemicelluloses are isolated by extraction with alkaline solution.

(1 ml of 0.5N NaOH solution = 0.003 g AcOH)

The method described by Dore was used for the estimation of acetyl values[9].

2 g (o.d.) dust was boiled with 100 ml of 2.5 per cent sulphuric acid under reflux for 6 hours. After cooling, the contents of the flask were washed in 250 ml graduated flask and diluted to the mark with distilled water. After standing for 24 hours the liquid was filtered. 100 ml of the filterate was then taken in a distilled flask fitted with a dropping funnel. The distillation flask through a condensor was joined to 500 ml receiving flask, which was connected to a suction pump. The distillate was collected in the receiving flask.

When 20 ml was left in the distillation flask, distilled water was run into the flask from the dropping funnel.

Thus, 100 ml of the distillate was collected and then titrated against 0.05N sodium hydroxide solution using phenolphthalein as indicator and acetyl content was calculated as follows;

Volume of 0.01N NaOH solution used = A ml

A ml o.d. solution = .0039 acetic acid.

$$\text{Acetyl value \%} = \frac{.0039 \times A \times 100}{W}$$

A stands for volume of 0.01N NaOH used

W stands for o.d. weight of the test specimen.

The results of summative analysis are recorded in Table 2.8.

TABLE 2.8 SUMMATIVE ANALYSIS OF PINUS CARIBAEA

S.No.	Constituents	Percentage
1.	Holocellulose	66.8
2.	Lignin	26.5
3.	Extractives	7.5
4.	Ash contents	0.6
5.	Acetyl group	1.1

TABLE - 2.9 RESULTS OF PROXIMATE CHEMICAL ANALYSIS OF INDEGINEOUS PINE, TROPICAL PINE, BAMBOO AND EUCALYPTUS TERETICORNIS

S. No.	Name of species	Ash content %	Cold water solubility %	Hot water solubility %	1% NaOH solubility %	Alcohol benzene solubility %	Klason lignin %	Acetyl value %	Pentosans %	Holocellulose %
1.	P.roxburghii[10]	0.20	1.15	4.20	14.75	3.80	28.50	1.05	7.30	65.50
2.	P.kesiya	0.20	2.70	4.80	14.20	1.80	30.40	-	6.70	-
3.	P.patula	09.18	-	5.90	14.60	3.00	28.70	-	11.90	71.60
4.	D.strictus[11] (Bamboo)	1.90	9.60	11.20	29.70	-	26.7	-	17.5	61.0
5.	E.tereticornis[12]	0.46	1.27	3.22	20.56	1.69	25.46	2.05	16.72	70.70
6.	P.caribeae	0.6	1.18	3.80	13.56	7.5	26.05	1.1	7.38	66.80

C. RESULTS AND DISCUSSION

The results of fibre dimensions are recorded in Table 2.6. The average fibre length of Pinus caribaea is 2.22 mm and diameter is 29.6 microns. Generally the softwoods are of long fibre whereas hardwoods are of short fibre as shown in Table 2.5:

The fibre measurements of wood gives an idea about the quality of pulp and paper to be produced by the raw material. Results recorded in Table 2.6 give an idea about the fibre dimension and their derived values. The fibre length of Pinus caribaea is comparable among all the pine species and also higher than tropical hardwood, (Eucalyptus tereticornis) and Dendrocalamus strictus (Bamboo belongs to grasses). At the same time, the fibre diameter of P. caribaea is seems to be higher among the bamboo species, hardwoods and grasses. Since the nature of fibre of Pinus cariaea is more cylindrical, having greater length, obviously it gives the higher tearing strength to the paper produced than any of the other fibrous raw material under discussion. The properties are quite comparable as reported by other works[14].

The Runkle coefficient of Pinus caribaea is almost equal to the Runkle coefficient of any other good raw material which suggests that the bonding properties of paper produced from P. caribaea would be comparable to other raw materials. Obviously, P. caribaea is certainly

having advantage of tearing strength over any other raw material due to its higher fibre length and at the same time, paper produced from P. caribaea possess almost similar bonding strength. The paper machine runnability at commercial scale for the production of paper from P. caribaea would be better due to long fibre. It clearly indicates that P. caribaea is certainly better raw material for paper production and would improve the machine runnability when blended with short fibre pulps.

The results of elementary composition of Pinus caribaea wood meal are recorded in Table 2.7. Emperical formula was calculated on the basis of the elemental composition like carbon, hydrogen and oxygen. The empirical formula for P. caribaea wood meal is $C_{1.53}H_{2.25}O_{1.0}$ which is comparable with the normal empirical formula of softwood $C_{1.5}H_{2.1}O_{1.0}$.

The results of summative analysis of Pinus caribaea wood are recorded in Table 2.8.

All the calculations of summative analysis are based on the ash free basis. Therefore, ash content of P. caribaea wood meal was also determined. The ash content of wood corresponds to inorganics in the wood. These are the salts of Ca, K, Mg in the form of carbonate, phosphate, silicates and sulphates and in some cases oxalates. Generally the value of ash content in wood lies in the range of 0.1 to 1 per cent. The ash content in the wood should be low, otherwise it will create problems in the recovery of

chemicals from the spent liquor, which is obtained after cooking. The ash content of P.caribaea wood is 0.60 per cent which is comparable with the result of ash content in different species of softwoods shown in Tables 2.3 and 2.2. The results are quite comparable with other workers.(13)

There are different types of extractives which can be extracted by different solvents and with moisture of solvents. Generally sugars present in the wood are soluble in cold water and polyphenols are soluble in cold water and polyphenols are soluble in hot water. Alcohol: benzene(1:2) was used to determine the extractives in the wood like waxes, fats resins, starch, tannins, gums etc.

From Table 2.9, it is seen that extractives in Pinus caribaea wood meal are 7.5 per cent on the basis of raw material which shows that P.caribaea wood is of an average extractive content and the results are comparable with softwoods. Generally softwoods have higher extractive (4-12 %), content while hardwoods have an average or low extractive content. A fibrous raw material of average extractive is suitable for pulp and paper making, because the chemical consumption will not be more. A wood containing higher extractive content will consume more chemicals.

The Klason lignin content in P.caribaea wood is 26.5 per cent. The average lignin content of different woods is shown in Tables 2.3 and 2.2. Generally softwoods contain 26-30 per cent lignin and hardwood lignin lies in the range of 16-25 per cent. Lignin reduces the swelling

power of cell wall, so fibre with high lignin content reshaped slowly to healing and have ions bonding capacity and produces sheet of low strength. On the other hand reasonable amount of lignin content can be good for bulk, for dimensional stability and stiffness.

Holocellulose is the total carbohydrate fraction of the wood. It comprises of cellulose and hemicelluloses. The result of holocellulose is recorded in Table 2.9. Cellulose is the principal component of the cell walls of woods. Holocellulose from wood has found important industrial uses as a source of paper making and dissolving pulp. Cellulose makes up about 44 per cent of most paper making fibres. The hemicellulose of fibres are available in the pulp depending on the process used for pulping. Hemicelluloses help in beating process and improves the paper strength.

The Pinus caribaea contains 66.8 per cent of holocellulose content which of an average value and is good for pulp and paper.

Hardwoods have acetyl content in the range of 2.9 - 3.8 per cent, while softwood value lies in the range of 1.1 - 1.7 per cent. The results of acetyl value of P. caribaea are recorded in Table 2.8 and 2.9. The value is 1.1 per cent which is comparable to acetyl value of softwoods.

From the results, it is evident that Pinus caribaea is of low ash and acetyl content. It is of an average

cellulose and lignin content and of slightly higher extractives content. The values are in the range of chemical composition of other softwoods reported in literature. The sum of the constituents is 102.5 per cent which is close to 100 per cent. In practice the sum of summative analysis is in the range of 95-102 per cent is not uncommon.

From the above discussion, it can be concluded that Pinus caribaea 'a chemical composition is comparable to other softwoods and the species has been investigated for different types of pulps to be used for different purposes.

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CHAPTER - III

CHEMISTRY OF HEMICELLULOSES OF PINUS CARIBAEA

A. INTRODUCTION

1. HEMICELLULOSES

The hemicelluloses occur in close association with cellulose and lignin in the cell wall of higher plants. Hemicelluloses do not appear to be bounded chemically to cellulose but are closely associated with cellulose by physical intermixing and hydrogen bonding. Evidence shows that part of the hemicellulose may be linked chemically to lignin. Hemicelluloses are amorphus, soluble in dilute alkali and are hydrolysed readily by hot dilute mineral acids to simple sugars. However, the hemicellulose form a range of complex substances and a simplified picture will resemble the following:

Hemicelluloses

- Polyuronides
  - Pectic substances
- Cellulosan
  - Mannan (Specially softwoods)
  - Xylan (Mainly Hardwoods)

Before the extraction of hemicellulose from wood, the wood is made extractive-free and then whole carbohydrate portion 'holocellulose' is extracted from it. A minor portion of the hemicellulose can be removed before delignification. However, in most cases it is necessary to remove most of the lignin, before major portions of the hemicellulose of the cellulose can be isolated. Laboratory

exert in anhydride or lactone formation. The strong association between the polyuronides and the lignin is manifested by the fact, that it is impossible to remove all the lignin from wood without losing a considerable part of the hemicellulosic material, once wood has been delignified, the polyuronides become more readily soluble in dilute alkali. Table 3.1 gives a qualitative summary of the polymer composition of hemicellulose from hardwoods and softwoods.

TABLE – 3.1 MAJOR CARBOHYDRATE: POLYMER COMPONENTS OF HARDWOOD AND SOFTWOOD HEMICELLULOSES

S.No.	Polymer	Relative amount present	
		Softwoods	Hardwoods
1.	4-O-Methylglucuronoxylan (Acetate)	Small or none	Very large
2.	4-O-Methylglucuronic arabinoxylan	Medium	Trace
3.	Glucomannan	Nil	Small
4.	Galacto-glucomannan (Acetate)	Very large	Nil
5.	Arabinogalactan	Large for larch	Nil

The structural constituttion of hemicelluloses could largely be elucidated by X-ray, Infrared and Nuclear magnetic resonance techniques and three groups were recognised individually. Within each separate group there exists a series of polymers which differ with regards to their size, the relationship of their monomeric sugars participating in the structure, their branching and in other

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Cellulosan — *Mannan (Specially softwoods)*, *Xylan (Mainly Hardwoods)*

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processes of delignification are mostly based on the reaction of moist wood with chlorine gas or on digestion with an acidified solution of sodium chlorite. The classical method of Cross and Bevan[1] for isolation of cellulose preparations comprises alternate chlorination and extraction with a hot, aqueous sodium sulphite solution.

The procedure leads to removal of a considerable part of the hemicelluloses along with the lignin. Treatment that removes essentially all the lignin, while leaving the carbohydrate materials unattacked, lead to the preparation of holocellulose. Holocellulose can be prepared in the laboratory with a hot alcoholic solution of monoeth - anolamine[2]. Another method used for preparation of 'chlorite holocellulose' depends on digestion of wood meal with an acidified solution of sodium chlorite[3]. The temperature of treatment is varied from about 70 to 90°C. The extent of degradation of cellulose and holocellulose caused by these different methods of isolation has been compared and reviewed by several workers[4,5].

The hemicellulose can be extracted from holocellulose in a single step or in fraction by treating it with alkali. Fractionation by precipitation and extraction is based on the difference in solubility of the single component. With the hemicelluloses, difference in solubility occurs because of difference in the average molecular weights, difference in the distribution of the molecules. The configuration of the functional groups, the homogenity of the composition

exert in anhydride or lactone formation. The strong association between the polyuronides and the lignin is manifested by the fact, that it is impossible to remove all the lignin from wood without losing a considerable part of the hemicellulosic material, once wood has been delignified, the polyuronides become more readily soluble in dilute alkali. Table 3.1 gives a qualitative summary of the polymer composition of hemicellulose from hardwoods and softwoods.

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3.	Glucomannan	Nil	Small
4.	Galacto-glucomannan (Acetate)	Very large	Nil
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The structural constituttion of hemicelluloses could largely be elucidated by X-ray, Infrared and Nuclear magnetic resonance techniques and three groups were recognised individually. Within each separate group there exists a series of polymers which differ with regards to their size, the relationship of their monomeric sugars participating in the structure, their branching and in other

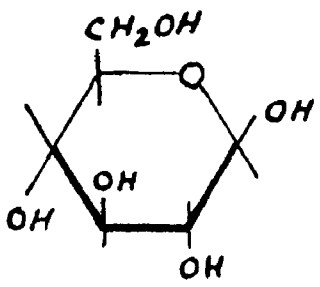
respects. Fig. 3.1 shows the structural formulae of the monomeric sugars that play a role in the structure of cellulose and hemicelluloses. In the softwood hemicelluloses, mannose are the most important monomers, whereas xylose, dominates in the hardwood hemicelluloses. Carbohydrate fraction of some species are recorded in Tables 3.2 and 3.3.

TABLE - 3.2 CARBOHYDRATE COMPOSITION OF SPRUCE AND PINE, EARLY WOOD AND LATEWOOD(6)

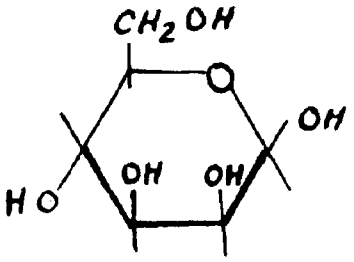
	Glucose %	Galactose %	Mannose %	Arabinose %	Xylose %
Piecea abies					
Earlywood	64.5	4.5	17.0	3.0	11.0
Latewood	62.0	8.0	19.5	2.0	8.5
Pinus Silvestris					
Earlywood	63.5	4.0	19.0	3.5	10.0
Latewood	64.5	5.5	17.5	3.0	9.5

TABLE - 3.3 APPROXIMATE CARBOHYDRATE COMPOSITION OF PINE, SPRUCE AND BIRCH CELLS(7)

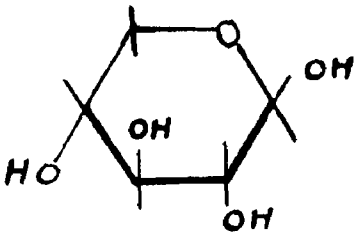
Wood species and Cells	Cellulose %	Glucomannan %	Glucurono-'arabino' xylan %	Galactan & arabinan %
Pinus silvestris				
Wood	56	26	14	4
Holocellulose	53	30	15	2
Picea abies				
Wood	59	22	16	2
Holocellulose	56	24	18	1
Betula verrucosa				
Wood	53	4	40	2
Holocellulose	54	4	41	1



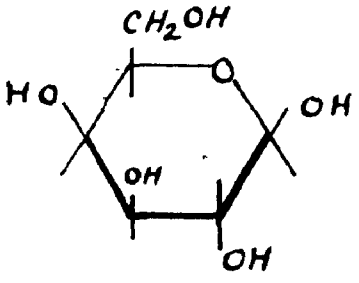
GLUCOSE



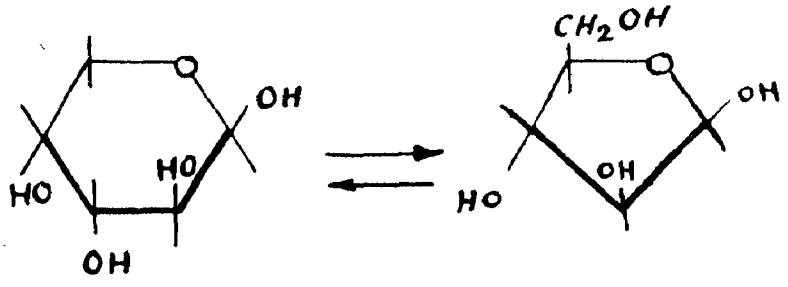
MANNOSE



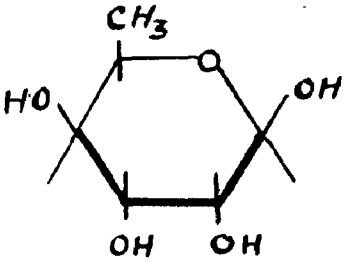
XYLOSE



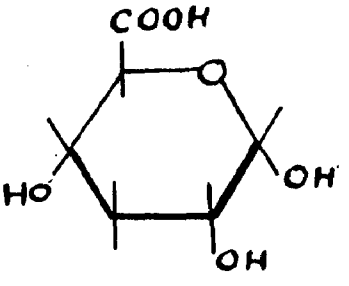
GALACTOSE



ARABINOSE



RHAMNOSE



GLUCURONIC ACID

FIG. 3.1. MONOMERIC SUGARS OF HEMICELLULOSE.

Hemicelluloses are responsible for several important properties of pulp fibres. Their primary action is to imbibe water and contribute to fibre swelling. This imbibing of water followed by swelling leads to internal lubrication of the fibre, and improves its flexibility and ease its beating to low freeness. Swelling causes an increase in the specific swollen volume and in the specific surface or bonding area of a fibre. Furthermore, the swelling pressure contributes in loosening the structure and fibrillation.

Another effect of hemicelluloses on the properties of a pulp fibre occurs on drying. The hemicellulose, being amorphous and adhesive in nature, tend to cement or hornify as the fibre shrinks and dries. The hornification reaction stiffens the fibres, and they swell and beat less readily than before drying.

B. EXPERIMENTAL

1. PREPARATION OF HEMICELLULOSE

In present investigations, the hemicelluloses were isolated by Timell method[8] and purified using barium hydroxide method[9]. Each purified hemicellulose was hydrolysed with sulphuric acid into monosugars and monosugars thus obtained, were identified by gas liquid chromatography. For preparation of hemicellulose from Pinus caribaea dust, weighed amount of extracted dust was converted into holocellulose by chlorite method given below:

About 100 g extractive-free dust was taken at a time in an Erlenmeyer flask of 4 litre capacity with distilled water containing 24 g of sodium chlorite and glacial acetic acid (50 ml). The contents were heated for one hour at 70°C. The treatment with sodium chlorite and acetic acid was again repeated two times. Finally the residue was filtered off and washed first with water thoroughly and finally with acetone. The sample was then air dried.

Now the holocellulose (50 g) was placed, in a 3 litre Erlenmeyer flask, fitted with a dropping funnel and two glass tubes, bending at right angles. One of which reached to the bottom of the flask. Nitrogen gas was then passed through the flask to replace the air for about 15 minutes. Subsequently 2 litres of potassium hydroxide and boric acid (24 + 4 %) were introduced into the flask slowly through the dropping funnel with shaking. The temperature of the reaction flask in water bath. The reaction was carried out for two hours with occassional shaking. After two hours the residue was filtered through fine cloth, kept in a Buchner funnel and washed first with potassium hydroxide solution (1 litre) and then with water thoroughly. Washings and the filterate were combined together. To the filterate and washings sufficient quantity of glacial acetic acid was added to bring the pH to about 5.5. Slight turbidity was obtained during this treatment. Absolute alcohol was then added in excess. Hemicellulose was precipitated completely. It was allowed to settle overnight. The supernatent

liquor was removed by siphon and the precipitate filtered and washed with increasing concentration of ethanol (50, 70, 90 per cent absolute alcohol). The final washing was done by ether and dried over calcium chloride under vaccum[8].

2. PURIFICATION OF HEMICELLULOSE

The hemicellulose was purified by the method of Chanda[9] et.al, by making its copper complex.

Hemicellulose (5g) was dissolved in 4 per cent sodium hydroxide solution (300 ml) and the solution was treated with freshly prepared Fehling solution (300 ml). The precipitate of the complex was removed by filtering through a Buchner funnel over a fine filter paper and washed with distilled water. The precipitate was vigorously stirred with water (200 ml) and then 2N hydrochloric acid was added slowly to decompose the copper complex. The acidity of the solution should be such that it should not hydrolyse the hemicellulose. Now the solution was poured into ethanol (600 ml). A white flocculent precipitate was obtained. The precipitate was filtered and washed with 0.1N hydrochloric acid in a mixture of acetone and water (6:4) to remove copper ions completely from the precipitate and then with solvent mixture to remove the acid. It was finally washed with ethanol and then with ether. The greenish white purified hemicellulose was dried in vacuum desicator over anhydrous calcium chloride.

3. PHYSICO-CHEMICAL ANALYSIS OF HOLOCELLULOSE

Holocellulose was chemically analysed for ash, lignin, pentosans, methoxyl value and alpha, beta and gamma - cellu-lose using standard TAPPI methods - T15-OS-58, T222-OS-74, T19m-50, T209-OS-72 and T203-OS-61 respectively. Acetyl value was determined by Dore method. These methods are described in detail in Chapter II. The results of physico-chemical analysis of holocellulose are recorded in Table 3.4.

TABLE - 3.4 RESULTS OF CHEMICAL ANALYSIS OF HOLOCELLULOSE OF P.CARIBAEA

S.No.	Chemical Analysis	Per cent
1.	Ash content	1.10
2.	Pentosans	11.7%
3.	Acetyl value	0.72
4.	Alpha-cellulose	72.06
5.	Beta-cellulose	1.23
6.	Gamma-cellulose	1.76
7.	Total hemicelluloses	26.56
8.	Yield of holocellulose	66.80
	All values are expressed on o.d. basis	

4. CHARACTERISTATION OF HEMICELLULOSE

Hemicellulose extracted from Pinus caribaea was examined for its ash content, pentosans, uronic acid and acetyl content equivalent weight and specific rotations. Sugar composition of the hydrolysate of hemicellulose was

determined by Gas liquid chromatography. Infrared spectrum of hemicellulose was also taken.

(a) Ash content.- Ash content of hemicellulose of Pinus caribaea was determined by Tappi method T-15-OS-58 described earlier.

(b) Determination of Pentosans.- Pentosans are those polysaccharides which are built up of pentose sugar residues containing five carbon atoms (principally xylose and arabinose). The determination of pentosans is based on their reaction with acids. Raw material with low pentosan value will be more suitable for paper grade pulp.

In the most commonly used method, the pentosans were obtained by distillation of the material with 12 per cent hydrochloric acid, which converts them into furfural with loss of water.

$$(C_5H_8O_4)_n \xrightarrow{H_2O} n\ C_5H_{10}O_5 \xrightarrow{-2n-H_2O} n\ C_5H_4O_2$$

Furfural was separated by distillation and determined either gravimetrically by precipitation with phloroglucinol, barbutaric acid or volumetrically by titration with potassium bromide-bromate solution. This solution liberates bromine, which brominates the furfural. The reactions taking place are as follows:

$$5K\,Br + KBrO_3 + 6HCl \longrightarrow 3\,Br_2 + 6KCl + 3H_2O$$

Furfural bromine reaction was carried out at 0-2°C The reaction was completed within 5 minutes and the excess

of bromine was determined by addition of potassium iodide with standard sodium thiosulphate using starch as indicator:

$$Br_2 + 2KI \longrightarrow 2\,KBr + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

However, materials other than pentosans, also produce furfural on distillation e.g. uronic acid and polyuronides yield furfural and carbon dioxide. In addition to furfural, the distillation of wood with hydrochloric acid may yield in the distillate hydroxy methyl furfural. Launer and Wilson had applied the method to the pulp and paper and their procedure forms the basis of the corresponding Tappi standard. The calculation is given below:

$$\%\ Pentosans = \frac{7.5 \times N \times (V_2 - V_1)}{W} - 1.1$$

Where

N = Normality of thiosulphate solution

$V_2 - V_1$ = Volume of the thiosulphate solution between blank and sample titrations.

W = Weight of the sample (o.d.) basis.

1.1 = Correction factor applied to compensate for hydroxyl methyl furfural arising from hexosans.

The factor 7.5 is the product of $\frac{100 \times 0.048}{0.727 \times 0.88}$

Where

0.048 = Milliequivalent of furfural

0.727 = Theoretical factor for converting furfural into pentosans.

0.88 = Yield of furfural from xylose as a fraction of theoretical yield.

Procedure

About 1 g of dust was placed in the 500 ml distillation flask and 12 per cent hydrochloric acid (100 ml) was added, washing all the fibres to the bottom. Hydrochloric acid (300 ml) was taken in a dropping funnel, and the dropping funnel was attached to distillation flask. The distillation flask was heated with a burner above which was placed one asbestos sheet to prevent over heating of the flask. The receiver was placed in an ice bath to prevent the escape of furfural. The distillation was carried out at a rate of 30 ml per 10 minute and a total of 300 ml of distillate was collected in a period of 100 minutes from the beginning of the distillation. During distillation the stop cork in the dropping funnel was so adjusted that the acid was added to maintain the original 100 ml level in the flask.

The distillate was transferred to 1 litre glass stoppered bottle and 50 ml of water was added. Crushed ice (250 g) was added to it. After the temperature has fallen to arround 0°C, bromate - bromide solution (20 ml, 0.2N) was added from pipette with minimum agitation. The bottle was stoppered promptly, shaken well, and allowed to stand for exactly 5 minutes. The stopper was removed, potassium iodide solution (10 ml, 10 %) was added and the stopper was allowed to absorb the bromine vapour and titrated with 1N sodium thiosulphate solution using starch as indicator.

A blank titration was made in similar way including all reagents except that 12 per cent hydrochloric acid

(270 ml) was diluted to 350 ml instead of 300 ml of distillate plus 50 ml of water.

(c) **Determination of Uronic acid**[10] .- Hemicellulose 0.5 g (o.d. basis) was weighed and transferred to a test tube and 72 per cent sulphuric acid (W/W) (5 ml) was added to it. The test tube was placed in water at 30°C and the mixture was stirred occasionaly with a glass rod to promote dissolution. After one hour, the hydrolystate was poured into a beaker (250 ml) and diluted with distilled water to 140 ml. The beaker was covered with a glass plate and autoclaved at 120°C for one hour. The hydrolystate was cooled and diluted to 400 ml. The resulting solution was neutralised with barium carbonate to pH 5.5. The precipitate formed due to barium sulphate was filtered off after thoroughly washing with distilled water. The filterate and the washings were combined and concentrated. The concentrated solution was poured dropwise into excess of methanol(1:10). The precipitate, thus formed, was filtered on Whatman No.42 and dried to constant weight. The filter paper with precipitate was ignited to burn the uronic acids The barium ions were left as residue. The uronic acids were calculated as follows:

(i)	Wt. of filter paper	= (A) g.
(ii)	Wt. of filter paper + Precipitate	= (B) g.
(iii)	Wt. of uronic acid as barium uranate	= (B)-(A)=(C) g.
(iv)	Wt. of residue left after ignition	=(D) g.

(v) Wt. of uronic acid = (C)-(D)=(C_1) g.

$$\text{Uronic acids \%} = \frac{C_1 \times 100}{W}$$

C_1 = Stands for the weight of uronic acid

W = Stands for the o.d. weight of the test specimen.

(d) Determination of Equivalent Weight of Hemicellulose.- Equivalent weight of each hemicellulose was determined by proposed method of Canary and Byrne[11].

0.10 g(o.d.) sample was dissolved in 0.01N sodium hydroxide solution (25 ml). The mixture was allowed to stand for 15 minutes. The excess of sodium hydroxide was titrated with 0.01N hydrochloric acid and equivalent weight was calculated as follows:

Strength of NaOH = 0.01N

Volume of HCl used = A ml.

Volume of NaOH consumed = 25-A = B ml.

1000 ml NaOH consumed = 0.4 g. NaOH

B ml. $= \frac{0.4 \times B}{1000}$

$= C$ g. NaOH

Equivalent weight $= \frac{0.10 \times 40}{C}$

$= 1425$

(e) Determination of Specific Rotation of Hemicelluloses.- Specific rotation of each hemicellulose fraction was determined by Perkin Elmer Polarimeter. Hemicellulose sample 0.001 g (o.d. basis) was dissolved in 10 per cent

potassium hydroxide solution (100 ml). Specific rotation was determined and calculated as follows:

$$t = \frac{100 \times A}{C \times 1}$$

A = Stands for reading observed by polarimeter

C = Stands for concentration of the test specimen.

1 = Stands for length of tube in decimeter.

t = Stands for temperature.

The results of these physico-chemical analysis of hemicelluloses are recorded in Table 3.5.

(f) **Determination of Neutral Sugars of Hemicellulose.**- Neutral sugars of hemicellulose were determined by Gas liquid chromatography.

General apparatus and requirement of GLC.- In gas liquid chromatography, the sample to be analysed is carried through the column by an inert carrier gas and the stationary phase selectively retards the sample components according to their distribution. Coefficient, which forms separate bands in carrier gas, the bands leave the column in the gas stream and are recorded. The essential components of gas chromatographic system have been described as follows.

(i) **Carrier Gas.**- It transports the sample components through the column and is inert gas like N_2, H_2, He, Ar etc depending upon the detector system.

(ii) **Sample Injection System.**- The sample should be introduced into the column as a sharp plug which should be vapourised

instananeously. The injector part usually provides for a gas tight self sealing rubber septum with an arrangement for heating the injector block.

(iii) **Column**.- Columns are made of copper, stainless steel, All or glass tubing of small bore and lengths varying from few feet to few hundreds.

In packed columns, the tubing is filled with solid support consisting of uniform, graded fine particles of diatomaceous earth. Solid support particles are coated with a proper stationary phase which is normally a nonvolatile organic compound.

(iv) Detector system. The detector responds and measures the load concentrations of the solutes emerging from the column. Most commonly used detector are thermal conductivity detector (T.C.D.), flame ionsation detector (F.I.D.), Electron conductive detector (E.C.D) A flame ionsation detector which is sensitive to all organic compounds was employed in the present set up.

(v) **Recorder**.- Signal generated by the detector is fed to the recorder which should be capable of measuring the signals of the order as 1 to 10 mμ. With full scale deflection.

The effluent leaving the column carries with it, the sample constitutents emerging at different times, and finally passes through the detector which indicates the

presence of the compound in the carrier gas. The response of the detector after amplification is fed to the strip chart recorders. This graphic representation is called a chromatogram. The time of emergence of a peak called retention time provides a means for identifying the components, the peak size (area), gives a measure of the concentration of the components.

Sampling.- A Perkin-Elmer gas chromatograph model 3920, equipped with a differential flame ionization detector and a Hitachi Perkin-Elmer recorder was employed.

Column	- The columns were constructed from 1/8th inch stainless steel tube 2 m each in length.
Solid	- Chromosorb WAW. DMCS, 80-100 mesh support.
Liquid phase	- ECNSS - M3 %
Carrier gas	- N_2, flow rate 40 ml/minute
Flame	- Hydrogen - air flame
	Hydrogen - 20 psi
	Air - 50psi
Column	- Oven temperature - 180°C

Calibration.- Since no integrator was available, peak areas were measured by triangulation method. The detector response for the mono-saccharides after reduction and acetylation was determined. Since some degradation of carbohydrates, during acid hydrolysis can not be avoided, conversion factors for pure monosaccharides were determined

by subjecting known amounts to complete analytical procedure and measuring peak areas.

Sampling

Total hydrolysis.- 0.1 g of moisture free hemicellulose was transferred to a test tube and 1 ml of 72 per cent (W/W) sulphuric acid was added. The tube was placed in water bath at 30°C and the mixture stirred occasionally to promote dissolution. After 1 hour the hydrolysate was poured into a 100 ml beaker and diluted to 28 ml of distilled water. The beaker was covered with a glass plate and autoclaved at 120°C for 1 hour. After complete hydrolysis, the resulting solution was cooled and diluted to 80 ml. This solution was neutralized by adding suitable quantity of anion exchange resin (IR - 45, 20-25 mesh) when the pH was reached to 4, the resin was separated from the solution of mesionisitol in water was added. The resulting solution was evaporated to dryness in a vaccum evaporator. Finally, water was added to give a volume of 5 ml.

Reduction and Acetylation.- To the above solution, 20 mg of sodium borohydride was added and the solution was allowed to stand for 4 hours. The sodium ions were removed by adding a small amount of cation-exchange resin (Dowe x 50 W - x B)H^+ from 50 - 100 mesh). After standing for 5 minutes, the solution was filtered through a sintered glass crucible (G-1) and the resin was washed with 1:1 ethanol - water mixture (15 ml). The filtrate and washings were collected in a small pear shaped flask and evaporated under vaccum

to dryness. The residual was refluxed for 4 hours with a mixture containing equal amount of acetic anhydride and pyridine (2 ml).

After cooling the mixture, the separation was carried out in the gas chromatography by injecting 0.4 micro litre of the sample.

Chromatogram of reference in sugars is shown in Fig. 3.2 and a typical chromatogram obtained of P.caribaea hemicellulose is shown in Fig. 3.3. The percentage composition were obtained by compairing the areas of the two chromatograms.

(g) Infra-red spectra of P.caribaea hemicellulose was taken by using Perkin-Elmer Infrared Spectrophotomer and a typical spectra is shown in Fig. 3.4.

TABLE - 3.5 ANALYSIS OF HEMICELLULOSE OF PINUS CARIBAEA

* Yield of holocellulose = 66.80 %

** Yield of Hemicellulose = 26.56 %

S.No.	Component	Percentage
1.	Ash content	1.050
2.	Pentosan	81.50
3.	Acetyl value	NIL
4.	Uronic acid	15.80
5.	Methoxyl value	5.57
6.	Specific rotation $[\alpha]_D^{t}$ (C=83 %) (-)	72°C

* Percentage based on oven dry weight of wood.
** Percentage based on oven dry weight of wood.

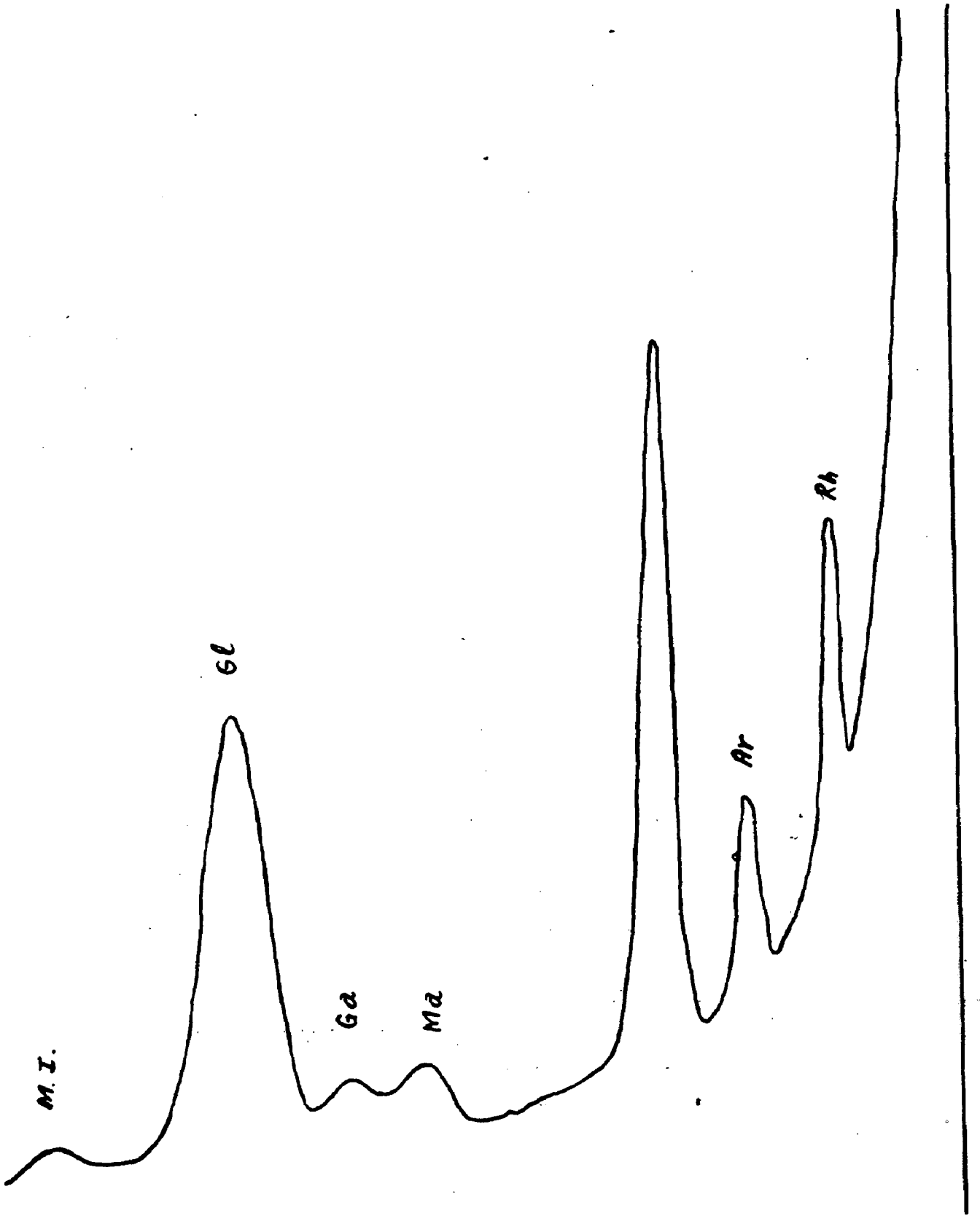


FIG. 3.2. GAS CHROMATOGRAM OF REFERENCE SUGARS

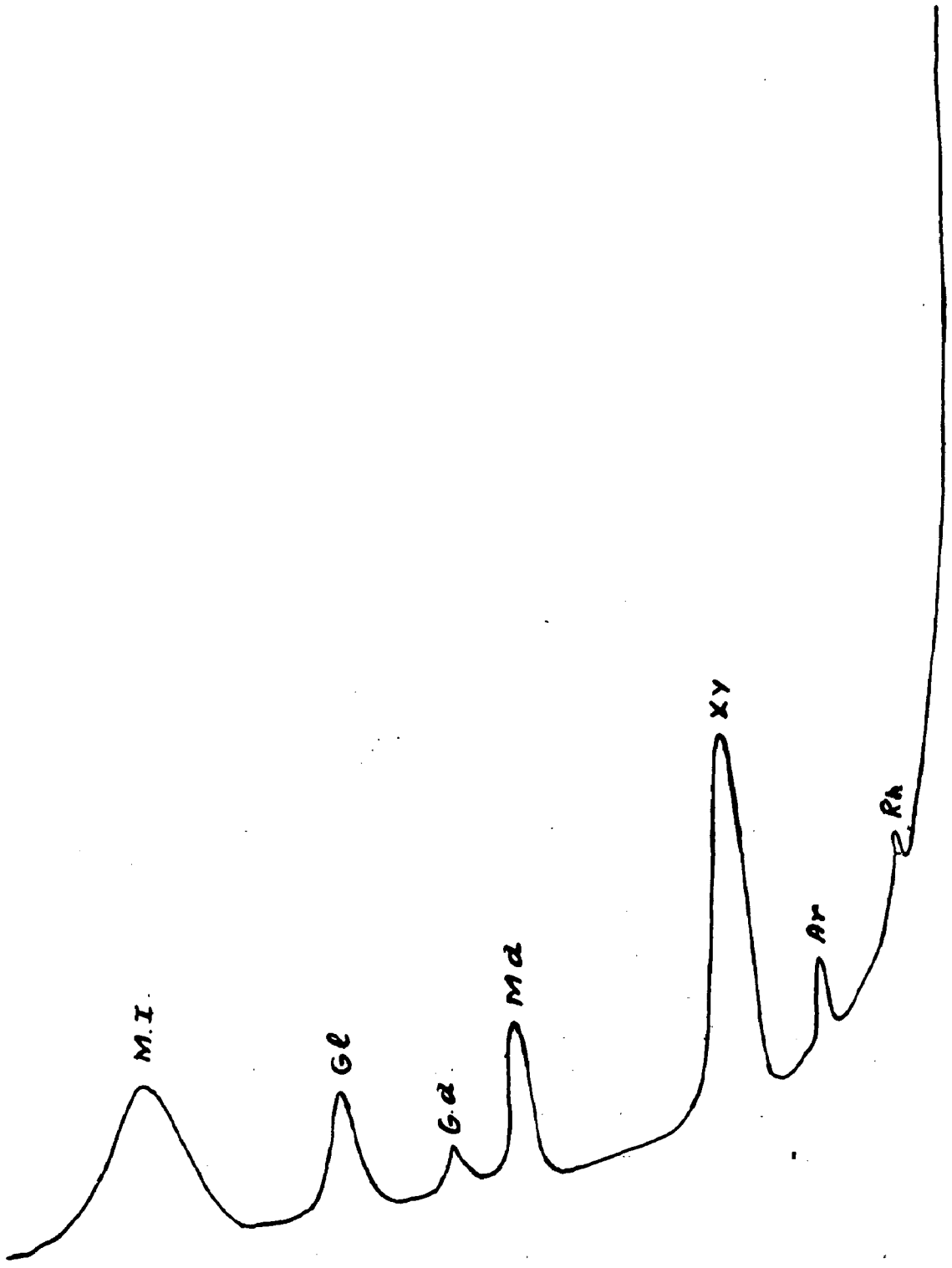


FIG. 3.3. GAS CHROMATOGRAM OF HEMICELLULOSE OF P. CARIBAEA

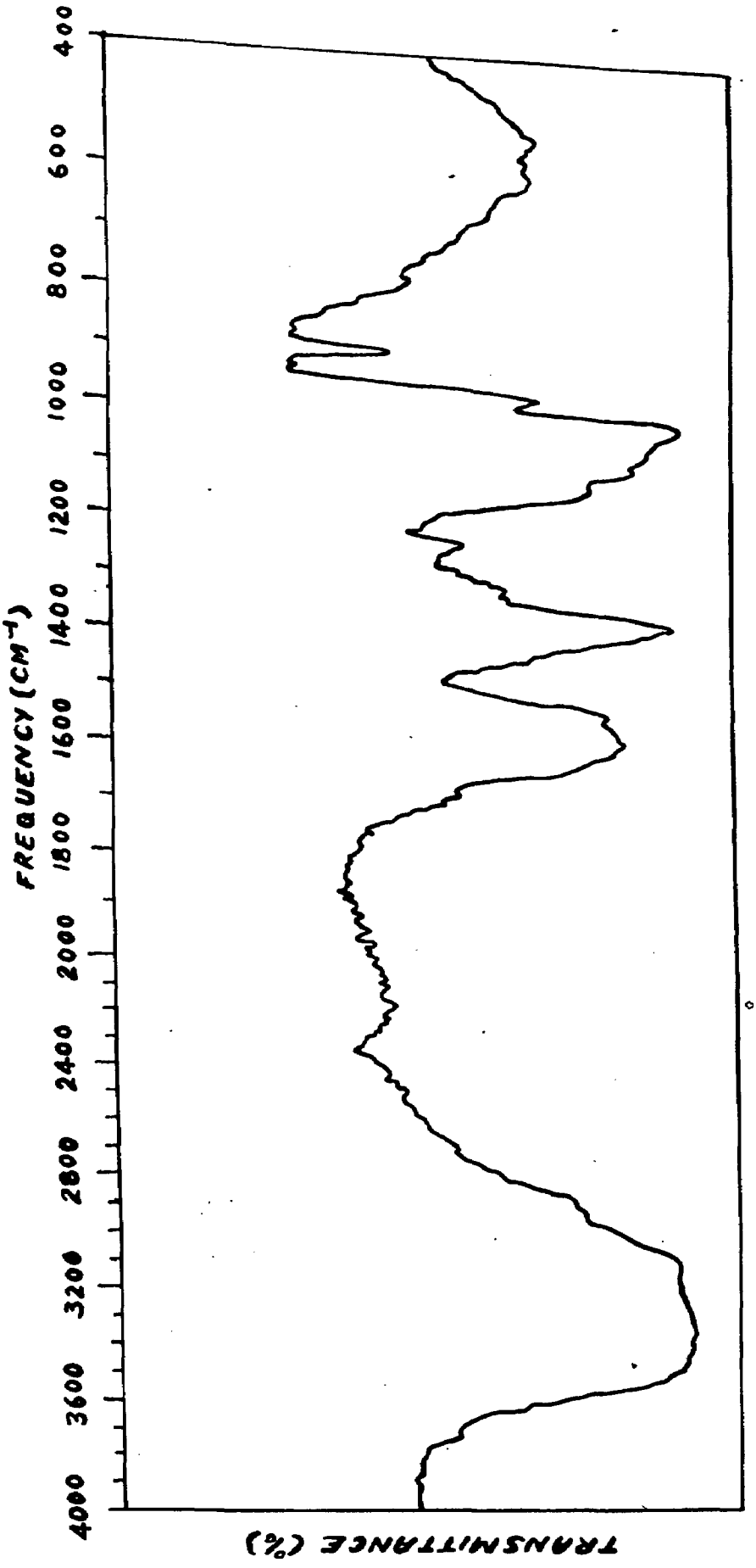


FIG. 3.4 INFRARED SPECTRA OF P. CARIBAEA HEMICELLULOSE.

TABLE - 3.6 SUGAR COMPOSITION OF HEMICELLULOSE OF PINUS CARIBAEA

S.No.	Sugar component	Relative amount %	Molar ratio
1.	Arabinose	3.5	1
2.	Xylose	13.0	4
3.	Glucose	65.0	16
4.	Mannose	12.5	3
5.	Galactose	6.0	2
6.	Uronic acid	15.80	4

TABLE - 3.7 CARBOHYDRATE COMPOSITION OF PICEA ABIES

S.No.	Sugar component	Relative amount %	Molar ratio
1.	Glucose	64.5	18
2.	Calactose	4.5	1
3.	Mannose	17.0	5
4.	Arabinose	3.0	1
5.	Xylose	11.0	4

C. RESULTS AND DISCUSSION

The results of analysis of Pinus caribaea holocellulose are recorded in Table 3.4. The yield of holocellulose is 66.8 per cent. Pinus caribaea holocellulose is of high alphacellulose (72.06 %), pentosans (11.75 %), and of low ash content (1.10 %) and acetyl content (0.72 %).

The yield of hemicellulose of Pinus caribaea is 30.7 per cent on the basis of holocellulose and 20.56 per cent on the basis of wood. The yield of holocellulose was 66.8 per cent on the basis of raw material (Table 3.5). Generally the yield of hemicellulose of hardwood lies in the range of 22.34 per cent, while it is 15-25 per cent in softwoods as shown in earlier chapter. From the above result it is seen that the yield of hemicellulose lies in the range of hemicellulose of softwoods.

The hemicelluloses were analysed for ash content, pentosan, acetyl value, uronic acid, methoxyl value, composition of sugar and specific rotation and infrared spectra was taken. The results of analysis of hemicellulose of Pinus caribaea are recorded in Table 3.5.

The value of pentosan content of hemicellulose of Pinus caribaea is 5.57 per cent. The pentosan content in hemicellulose indicate that pentoses are not dominent in Pinus caribaea. While these types of hemicelluloses are dominent in hardwoods. Methoxyl content (.83 %) may be attributed to the presence of hemi-cellulose and a very little amount of lignin. The optical rotation of hemi-cellulose is (-72°) which is comparable with the hemicellulose of other softwoods reported in literature. The hemicellulos of Pinus caribaea contains 15.80 per cent uronic acid content which indicates the presence of acidic sugars as glucuronic acid. The acetyl content of Pinus caribaea holocellulose was 0.72 per cent while it is absent in hemicellulose.

The absence of acetyl content in the polysaccharide indicates that they have been removed during alkaline extraction by saponification.

The results of quantitative estimation of individual sugars from the hydrolysate of hemicellulose are recorded in Table 3.6. Pinus caribaea hemicellulose consists of mainly glucose 65.0 per cent and uronic acid 15.80 per cent with relatively small amounts of xylose (13 %) and mannose (12.5 %). The percentage of glucose is very high indicating that the polymer is mainly composed of glucose building units. The second building unit in hemicellulose may be considered as uronic acid as its value is 15.80 per cent, next to glucose.

Molar ratio of sugars has been calculated as:

Glucose, mannose, Galactose, arabinose, xylose and uronic acids : 16, 3, 2, 1, 4 and 4 respectively. Therefore, the main building units of hemicellulose can be considered of glucose, uronic acid and xylose.

The average value of ratio of glucose to uronic acid have been found to be of 4:1 which is comparable with softwoods hemicellulose as shown in Table 3.7.

Infrared spectrum of purified hemicellulose (Fig. 3.4) shows an absorption band of 895-900 cm^{-1}, which is characteristics of B-glycosidic linkage between the different sugar units. This suggests that the glucose residues forming the back-bone of the macromolecule are linked by

B-glucosidic bonds.

The results of Pinus caribaea hemicellulose are comparable with other softwood hemicellulose as shown in Tables 3.2 and 3.3.

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CHAPTER - IV

CHEMISTRY OF PINUS CARIBAEA LIGNIN

A. INTRODUCTION

To study the properties and chemistry of lignin, it is desirable to isolate the lignin in high yields so that the chemical nature of lignin remains unchanged during isolation.

The major portion of the lignin can be isolated by the chemical reactions which solubilize either the lignin or the polysaccharides. For convenience, the isolation procedure may be classified into three types.

a) ISOLATION BY EXTRACTION

The lignin is dissolved by solvents which do not react with it, but which remove only a portion of the total lignin. A small fraction of wood lignin is soluble in some organic solvents and after purification is called 'native lignin'. The amount of soluble lignin can be increased by milling in a vibratory mill or by micro-biological attack on wood.

b) ISOLATION AS A RESIDUE

The polysaccharides were removed from the extractive free wood, leaving as a residue all or the major portion of the lignin, orginally present. The removal of the

polysaccharides is accomplished by acid hydrolysis, periodate oxidation, or solution in cuprammonium hydroxide.

c) ISOLATION AS DERIVATIVES

The wood is treated with reagents that react with the lignin to form soluble products, which can be separated from the polysaccharides or their reaction products through solubility or chemical behaviour.

The lignin in wood reacts with many reagents to form soluble lignin derivatives. Most of the reactions can be grouped into two classes; (i) those which are based on reaction with organic solvents, usually in the presence of an acid catalyst and which yield soluble products termed 'Organo-solvlignins', (ii) those which employ inorganic reagents such as sodium sulphide, sodium hydroxide and bisulphite solutions yielding thiolignin, alkali lignin, and ligno-sulphonate respectively.

1. Chemical Composition and Reactive Groups

Lignin is an aromatic, amorphous, material which forms a part of the cell wall and middle lamella in wood. Lignin contains only carbon, hydrogen and oxygen. The constitutional model of lignin is composed of many reactive groups such as others of various types, primary and secondary alcoholic-hydroxyl groups, phenolic hydroxyl groups, carbonyl groups, carboxyls and easter functions, methoxyl groups, ethylene linkages and aromatic sites of phenyl propanoid structures.

However methoxyl groups, total hydroxyl groups, phenolic hydroxyl and aliphatic hydroxyl content, carbonyl groups, carboxylic groups are important for studying the reaction of lignin from paper making point of view.

(i) **Methoxyl content**.- Methoxyl groups are characteristic function groups in lignin. The methoxyl content is an indispensable method of characterising lignin preparations. All methoxyl groups in lignin are aromatic in nature.

(ii) **Hydroxyl content**.- Lignin forms ethers on alkylation and esters, on acetylation indicating the presence of hydroxyl groups. Part of the hydroxyl groups are phenolic and the remaining are aliphatic in nature. Many of the common reactions of lignin result in the gain or loss of hydroxyl groups, and the determination of these groups is necessary in many lignin estimations. The total amount of hydroxyl groups (including both phenolic and aliphatic hydroxyl groups) has been determined by dimethyl-sulphate methylation and by acetylation. An extensive amount of work has been done lately on the determination of free phenolic groups in lignin and lignin derivatives. The methods used include potentiometric and conductometric titration techniques based on periodate oxidation, change in ultraviolet absorption due to the ionization of free phenolic groups. Different values for phenolic hydroxyl content for lignins of different woods were found by different lignin chemists.

(iii) ***Carbonyl group***.- *The presence of carbonyl groups in lignin is indicated by the infrared spectra and by the formation of carbonyl derivatives such as phenyl hydrazones and oximes. Quantitiative determinations based on the oxime formation have given 0.12 and 0.10 carbonyl groups per methoxyl for spruce BNL (Braun's native lignin) and lignosulphonic acids respectively.*

(iv) ***Carboxylic group***.- *The content of carboxyl groups in protolignin appears to be very low. Recently spectroscopic studies have shown the presence of small amounts of carboxyl groups in different lignin preparations of different woods.*

(v) ***Oxidation of lignin***.- *Being phenolic in nature, the lignin macromolecule is prone to oxidation by either homo or heterolytic pathway*[1] *depending on the oxidant and the reaction conditions used.*

Since the lignin macromolecule is susceptible to a wide variety of oxidants, the oxidation reactions have been arbitrarily classified into three categories according to the degree of lignin degradation achieved. These comprise (a) degrading lignin to aromatic carbonyl compounds and carboxylic acids, (b) degrading aromatic rings and (c) limited to specific groups.

The first category include oxidations using nitrobenzene, molecular oxygen or metal oxides, all in alkaline medium, as well as permangnate degradation of methylated

lignin. This type of oxidation is of special importance in the characterization of lignin as well as in the commercial production of aromatic compounds from pulping wastes.

Among all of the oxidation of the above type, the most illuminating has been the alkaline. Two electron transfer process of nitrobenzene degradation which over the years has become a main stay of lignin investigations. This procedure was introduced as a diagnostic device by the Heidelberg group around 1940 being an adaptation of a long known technique for the conversion of isoeugenol 1 to vanillin 2[2]. The mechanics of alkaline nitrobenzene reaction have been explained in Fig. 4.1.

SPECTROCHEMISTRY OF LIGNIN

(a) Infrared spectra.- Infrared spectra have played an important role in establishing structural relationships between lignin preparations. The first comprehensive study of lignin infrared spectra was made at the Institute of Paper Chemistry. The infrared spectra of lignin preparations contains many absorption bands, not all of which can be assigned unequivocally to structural groups. Comparison of spectra with those of model compounds permits many assignments, but the structure of lignin can not be deducted with certainity from spectral evidence. Indeed the structure of lignins appear to vary with genera and in a single species native lignin is not identical with that of the whole wood. Although no lignin can be selected to represent protolignin, spectral studies can be of service

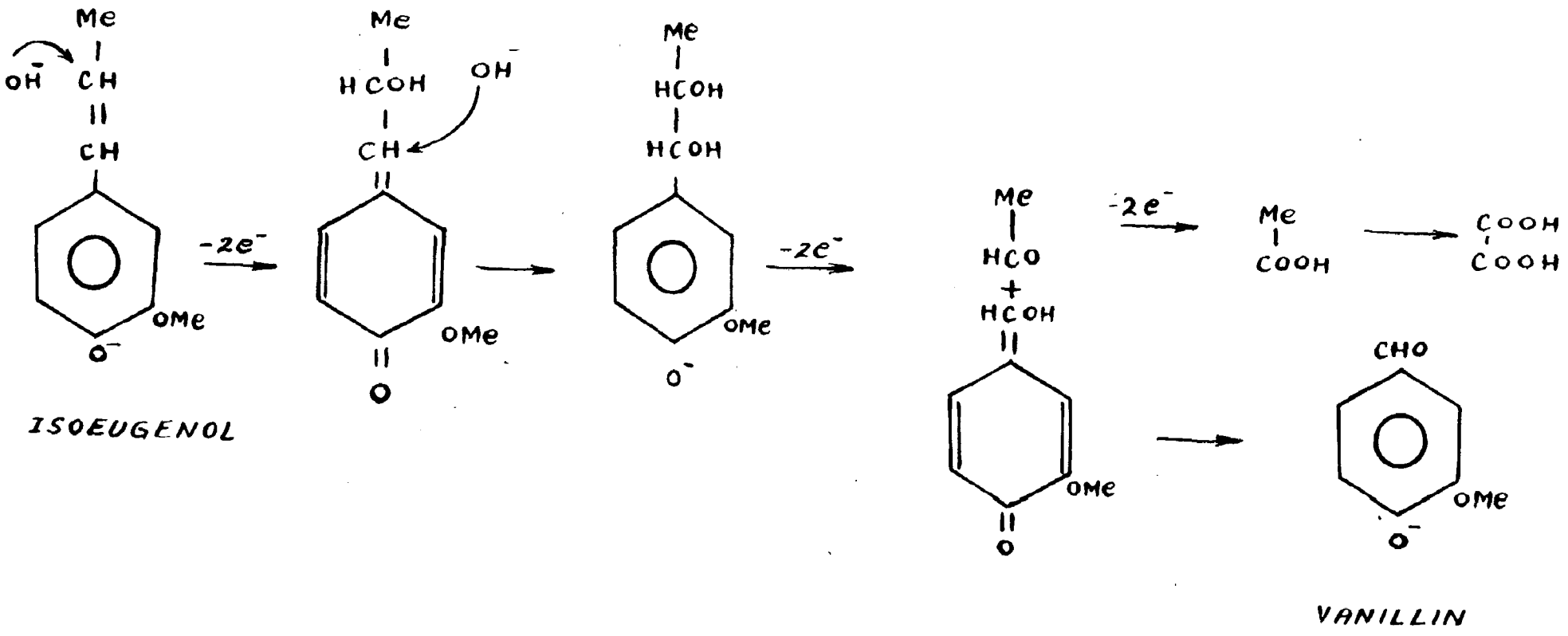


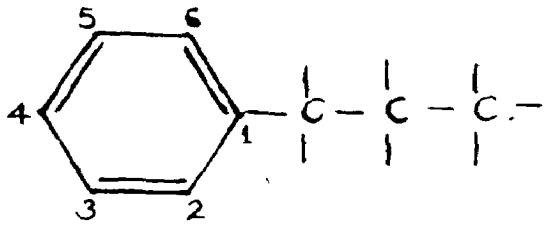
FIG. 4.1. MECHANISM OF NITROBENZENE OXIDATION OF ISOEUGENOL.

in assessing changes in structural incident to chemical reactions. The absorption bands in infrared spectra of lignins are considered to be due to the presence of aromatic rings, saturated aliphatic groups, hydroxyl groups and small amount of carbonyl groups[3].

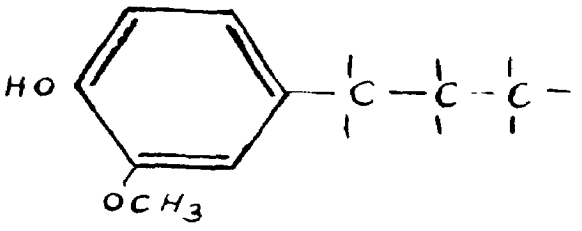
(b) **Ultraviolet spectra**.- Lignin, due to its aromatic nature, absorbs strongly in the ultraviolet range of the spectrum. In ultraviolet absorption spectra of lignin and its derivatives the absorptivities of the various structural elements are superimposed on each other. Although UV spectral studies are all in general less informative regarding special structural features than those in the IR region, some intensity observations may be made when used as a means of comparing the isolated lignins and provide a valuable tool in the identification of unsaturated organic compounds and in elucidation of structure[4].

2. Previous work done on Isolated Lignins

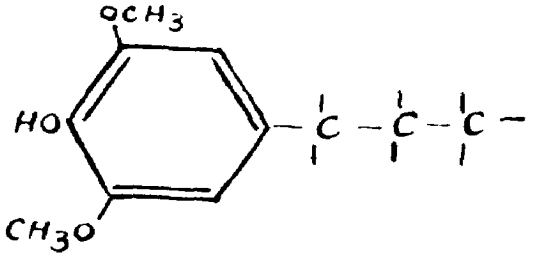
A large variety of so called organosolv lignin has been prepared by treating plant materials (generally in the presence of small amount of mineral acid, but also in slightly alkaline of even neutral solutions) with different solvents, such as ethylene glycol, dioxane, ethanol, glycol-chlorohydrin, aqueous butanol, phenol, thiophenol, acetic and formic acids. The chemistry of lignin is extremely complex. The lignin molecules are composed of building blocks having general structure of a 6-carbon ring with three carbons attached to one



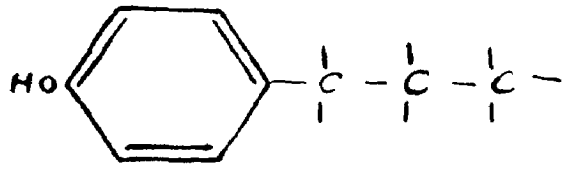
PROPYL BENZENE STRUCTURE



PROPYL GUAICOL STRUCTURE



PROPYL SYRINGOL STRUCTURE



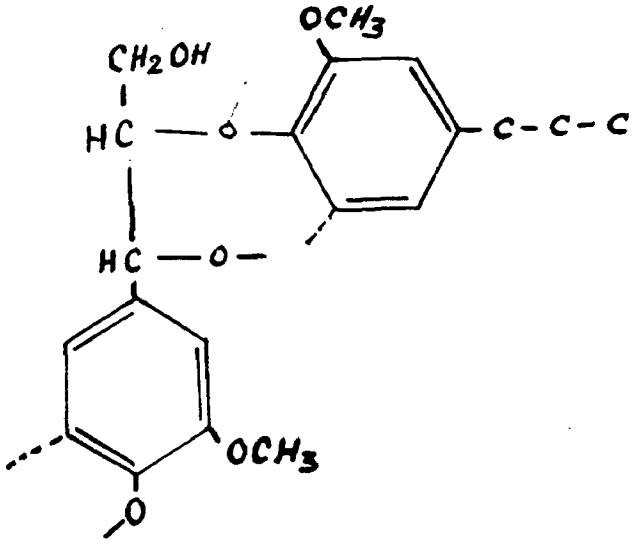
PROPYL PHENOL STRUCTURE

FIG. 4.2. BUILDING UNITS OF LIGNIN.

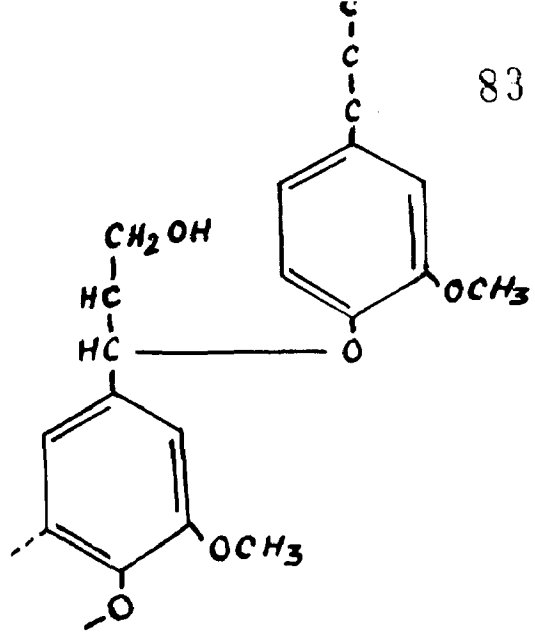
end, called a phenylpropane or propylbenzene structure. Fig. 4.2 shows the basic units of lignin molecule. The combination of these building units can occur either through ether and/or by carbon to carbon linkages as shown in Fig. 4.3 and 4.4. respectively.

(i) **Ethanol lignin**.- The amount of native lignin that can be extracted by organic reagents without the use of catalyst is relatively small. Brauns isolated lignin with pure ethanol and obtained the formula $C_9H_{8.7}O_{2.6}(OCH_3)_{0.9}$ [5]. A small amount of mineral acid is added to the alcohol as a catalyst, a considerably large amount of lignin is dissolved out. Klason[6] discovered that ethanol in the presence of a small amount of hydrochloric acid dissolved a part of lignin. By pouring a concentrated extract into water, he separated the lignin as a light brown flocculent precipitate in a yield of 6 to 7 per cent. It has 64.86 per cent carbon, 5.66 per cent hydrogen and 15.2 per cent methoxyl.

Schuerch et al[7] isolated about 80 per cent of the total lignin in spruce wood meal. Approximately 35 per cent of the isolated lignin was obtained as an oil containing ethanolysis products. He gave formula $C_9H_{7.6}O_{2.6}(OCH_3)_{0.95}$ to his lignin. Gruss[8] applied similar experiments by treating preextracted and degummed pine wood meal with 17 per cent hydrochloric acid for a short time and subsequently cooked within alcohol. The lignin was then fractionally precipitated with water. This lignin contained



A



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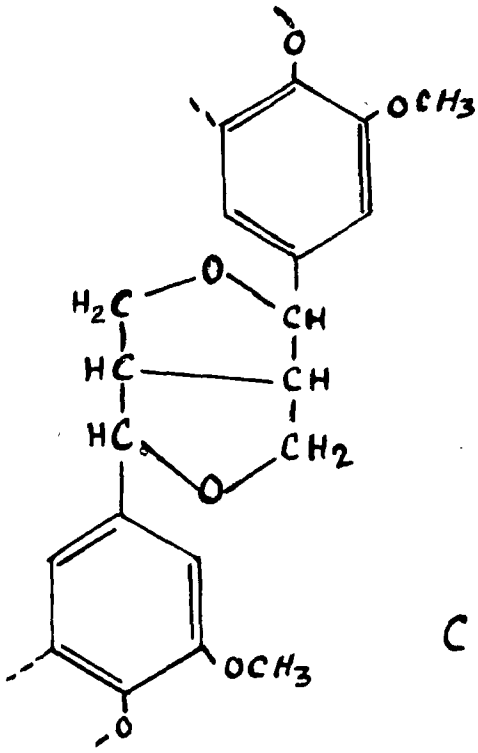

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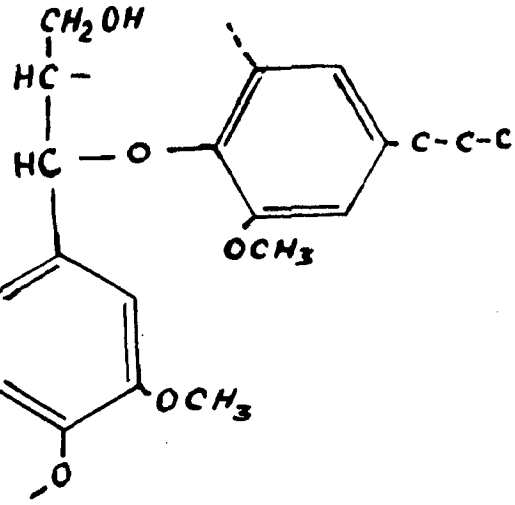

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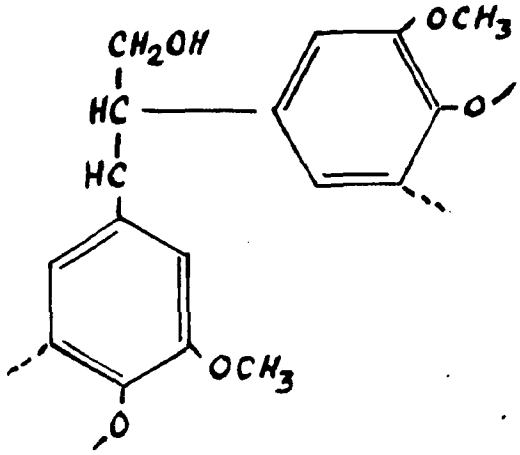

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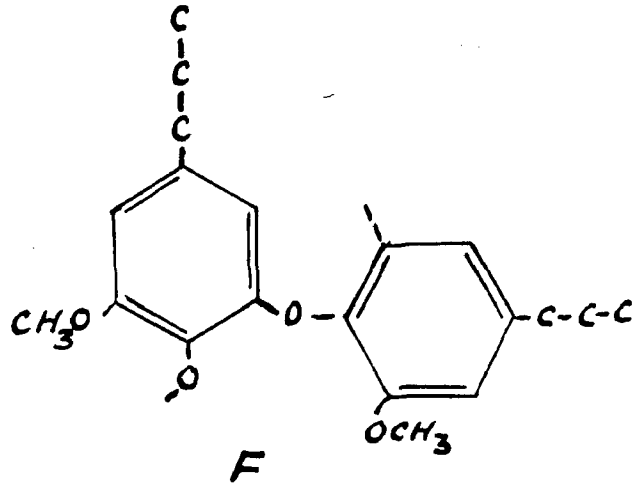


F

FIG. 4·3. DIFFERENT TYPES OF ETHER LINKAGES IN LIGNIN.

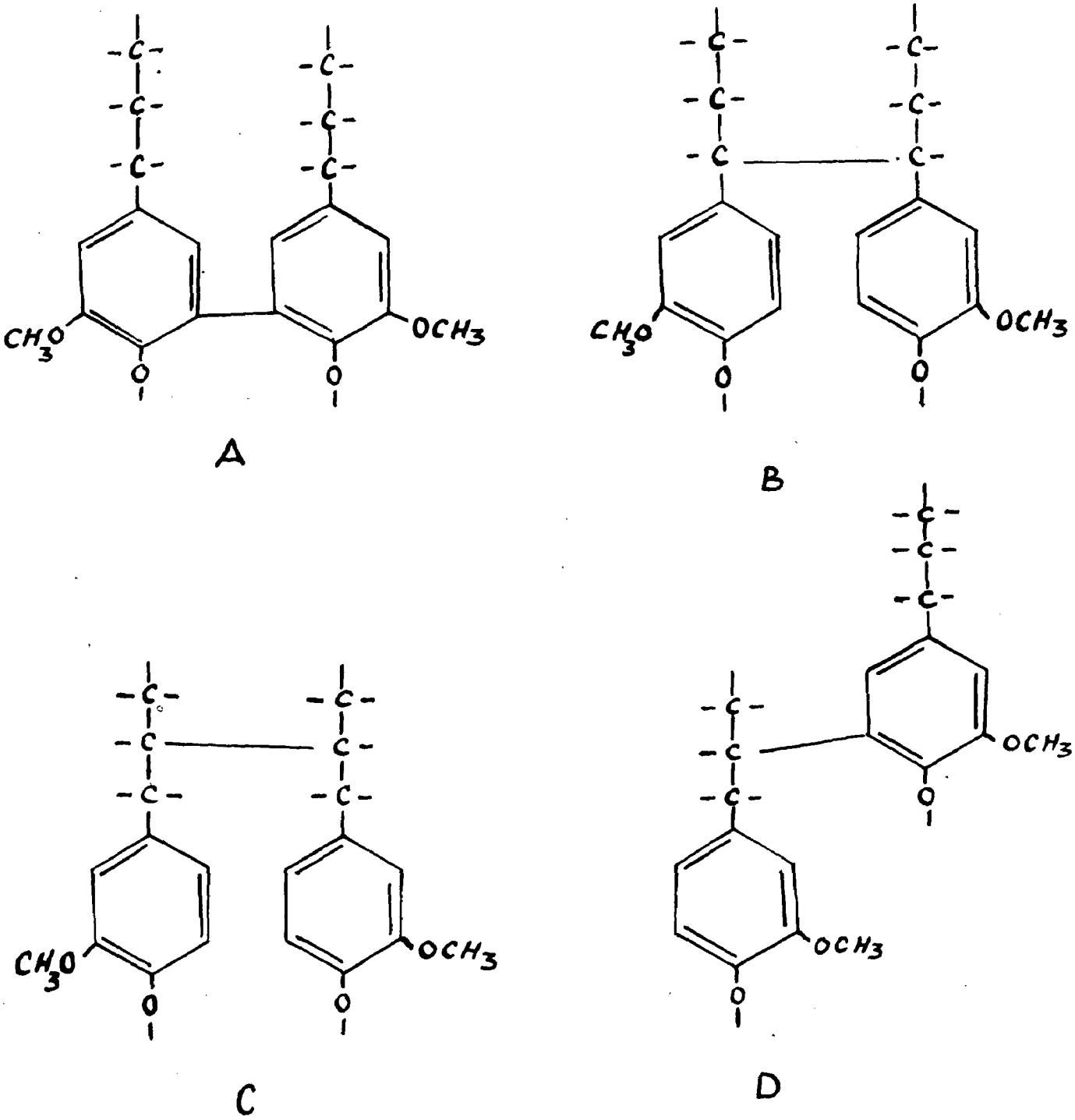


FIG. 4.4. DIFFERENT TYPES OF CARBON-CARBON LINKAGES IN LIGNIN.

60.2 per cent carbon, 9 per cent hydrogen and 20.9 per cent methoxyl corresponding to the formula $C_{26}H_{46}O_{10}$.

Merewether[9] isolated lignin comprised of refluxing the pre-extracted wood meal with absolute alcohol containing anhydrous hydrogen chloride for 48 hours. The alcoholic filtrate was neutralised with sodium bicarbonate and the filtrate was added drop-wise to distilled water. The crude ethanol lignin was purified twice from acetone water and finally dissolveing in dioxane and precipitating into the solution of ether and petroleum ether(1:1).

The elementary composition of some milled wood lignin preparations form are recorded in Table 4.1 and 4.2.

TABLE – 4.1 ELEMENTARY COMPOSITION OF SOME MILLED WOOD LIGNIN PREPARATIONS FROM VARIOUS SPECIES(10)

Sl.No.	Wood species	C %	H %	O %	OCH_3 %
1.	*Picea abies*	63.8	6.0	29.7	15.8
2.	*Pinus silvestris*	64.0	6.1	29.8	15.7
3.	*Tsuga heterophylla*	63.4	6.3	29.8	13.7
4.	*Thuja plicata*	63.8	6.1	30.1	16.1
5.	*Betula verrucose*	58.8	6.5	34.0	21.5
6.	*Populus tremula*	60.4	6.2	33.0	21.4

TABLE - 4.2 COMPOSITION OF MILLED WOOD LIGNIN FROM VARIOUS WOOD SPECIES(11)

Sl. No.	Wood species	Carbon %	Hydrogen %	Oxygen %	Methoxyl %	Methoxyl / C_9
1.	Birch	58.80	6.50	34.00	21.50	1.58
2.	Beech	60.30	6.30	33.40	21.40	1.43
3.	Aspen	60.40	6.20	33.00	21.40	1.43

*(ii) **Thio-lignin**.- The main aspect of pulping is the fibrization of the structure which can be achieved by mechanical chemical and semi-mechanical methods. Chemical methods are either acidic or alkaline in nature. The alkalines used are caustic soda, or a combination of caustic soda and sodium sulphide. The lignin can be precipitated from the alkaline black liquor by mild acidification or by addition of neutral salts of divalentions, such as barium chloride. The lignin from a cook in which only caustic soda is used, is called soda lignin, and that from a cook which makes use of a mixture of sodium hydroxide and sodium sulphide(Kraft process) is called 'thiolignin', because it contains sulphur. The thiolignin is heterogenous in nature and is in degraded form.*

The isolation of thiolignin was first carried out by Klason and Segerfelt[12]. The precipitated lignin by passing carbon-dioxide and purified by extracting with chloroform. The lignin contained 63.3 per cent carbon, 5.24 per cent hydrogen and 12-12.8 per cent methoxyl content.

A thorough investigation of thiolignin was carried by Ahlm[13]. He obtained thiolignin by acidifying the black liquor of pre-extracted black spruce dust. The res of analysis is recorded in Table 4.3. On the basis of methylation and acetylation studies he advanced a sugges regarding the formation of thiolignin which is represent as follows:

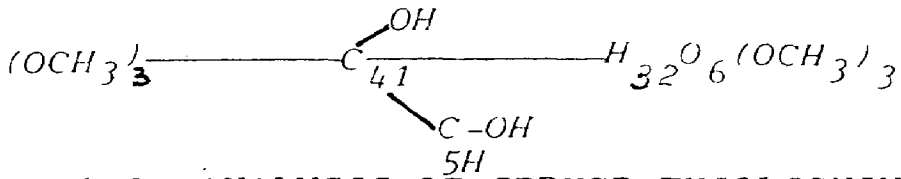


TABLE - 4.3 ANALYSIS OF SPRUCE THIOLIGNIN ACCORDING TO AHLM(13)

Cook No.	Carbon %	Hydrogen %	Methoxyl %	Sulphur %	Ash %
1	64.2	5.6	14.6	3.2	1.9
2	64.2	5.6	14.2	3.1	1.3
3	63.8	5.5	14.3	3.2	0.3
4	63.5	5.5	13.7	3.4	0.3

Studies on this acidolysis on lignin and its compa ison acidolysis was carried out by catherine. et al.[26 have indicated the monomer yields for lignin thioacidol were higher then for acidolysis.

B. EXPERIMENTAL

1. ISOLATION OF ETHANOL LIGNIN

For the preparation of ethanol lignin from pine, t method of Holmberg and Runius[14] was followed with few modifications.

200 g of extractive-free pine dust was placed in a five litre three-necked round bottom flask, fitted with stirrer, nitrogen bubbler and reflux condensor and a dropping funnel. Ethanol(3L) containing HCl to a solution to acid concentration 0.2N was added to the flask slowly from the dropping funnel. The contents of the flask were gradually heated to 85 ± 2°C on a water bath for 2 hours. A slow stream of nitrogen gas at the rate of about 60 bubbles per minute was maintained throughout the experiment. The reaction mixture was cooled to 35°C and was filtered on a buchner funnel. The dust was washed with pure ethyl alcohol until the washings were colourless. The filterate and washings were combined and concentrated under reduced pressure at 35°C. The lignin was precipitated by pouring the concentrated extract in a thin stream over a large excess of vigorously stirred distilled water and separated by centrifugation. The crude ethanol lignin was dissolved in pure dioxane and precipitating into ether washed with fresh ether and twice with petroleum ether and finally dried in vacuum.

2. ISOLATION OF THIOLIGNIN

Thiolignin was isolated by digestion of pre-extracted pine wood dust (dust which had been pre-extracted with ethanol : benzene (1:2 V/V) in a Soxhlet extractor) is again extracted with acetone for 6 hours to free of lignins and with low boiling petroleum ether(boiling range 60-80°C for 6 hours to free of volatile oils etc.) by

cooking 100 g (o.d. basis) in 2.5 litre stainless autoclave under the following conditions:

Active alkali, %	= 20
Sulphidity (% as Na_2O)	= 25
Initial temperature, °C	= 50
Time to reach maximum temperature (min.)	= 90
Maximum temperature, °C	= 153
Precipitant - Dilute sulphuric acid	
pH at precipitation	= 3

The black liquor was separated by filtration on a muslin cloth and acidified with dilute sulphuric acid in two steps firstly upto pH 9(while gently stirring to promote the release of hydrogen sulphide and carbondioxide) and secondly to pH 3 after heating the suspension to 80°C. A heavy precipitate separated immediately which was filtered and washed successively with dilute hydrochloric acid and water since in an acidified water the precipitate is colloidal. Finally, the precipitate was washed with distilled water, until free of chloride ions and freeze dried.

The crude thiolignin was purified according to the method described by Brauns. The crude thiolginin was dissolved in anhydrous dioxane and concentrated under reduced pressure. The dioxane solution was centrifuged to separate precipitated sulphur and carbohydrates and the clear solution was diluted with dioxane to give a 10 per cent solution. The thiolignin was precipitated by adding the dioxane solution dropwise to vigorously stirred

anhydrous ether. The precipitate was washed twice with fresh ether and then twice with pure benzene and finally twice with low boiling petroleum ether by centrifugation. The suspension of lignin in petroleum ether was kept over night and centrifuged, dried in vaccum desiccator over phosphorous pentaoxide. The thiolignin was exhaustively extracted in a Soxhlet for 4 hours with carbon disulphide, for the removalof any elemental sulphur. Finally repeatedly precipitated from dioxane into ether until the methoxyl content remained constant.

3. CHEMICAL CHARACTERIZATION : STRUCTURAL FEATURES OF LIGNIN

A series of experiments were carried out in order to study the chemical constitution of lignins. It includes determination of carbon and hydrogen content, methoxyl content, hydroxyl content, carbonyl contentand carboxyl content. The lignins were oxidised by alkaline nitro-benzene and nitrous acid and the oxidation products were identified by paper chromatography. The ethanol lignin was methylated and the methylated lignin was oxidised by nitric acid and the oxidised products were indentified. In addition to these studies ultraviolet spectra and infrared spectra of these lignins was also taken and molecular weight of lignins was determined by vapour pressure osmometer.

(a) ***Carbon, Hydrogen and Oxygen.***- *Percentage of carbon and hydrogen were determined by combustion method detailed in Chapter II. The results are recorded in Table 4.4.*

(b) ***Methoxyl content:***- *Tappi method T-209-SU-69 was applied for the determination of methoxyl content. About 0.05 g dust weighed in a gelatinous capsule, was introduced in reaction flask. Phosphorous slurry was added through the condenser about half filled. 7 ml of bromine was added in receiver. Few glass beads or clay chips were added in flask. 0.5 ml of hydroiodic acid was added to the reaction flask and the ground glass joints were moisten with a few drops of hydro-iodic acid. Side arm of the reaction flask was connected to the nitrogen cylinder. N_2 was passed in the apparatus at the rate of about 2 bubbles per second. The flask was immersed in the oil bath to maintain the temperature of 145 to 150°C for 40 minutes.*

At the end of the reaction the contents of the receiver were transferred to 500 ml Erlenmeyer flask. The receiver was first washed with 10 ml of sodium acetate solution followed by 125 ml distilled water. The excess of bromine was destroyed by adding formic acid dropwise. A total of 12 to 15 drops are usually required. After keeping for 3 minutes, 15 ml of 10 per cent KI solution and 15 ml of 10 per cent sulphuric acid solution was added to flask. The liberated iodine was titrated against 0.1N sodium thiosulphate solution to a light straw colour. Then starch was added as an indicator to flask and again titrated with hypo, the appearance of blue colour was its end point.

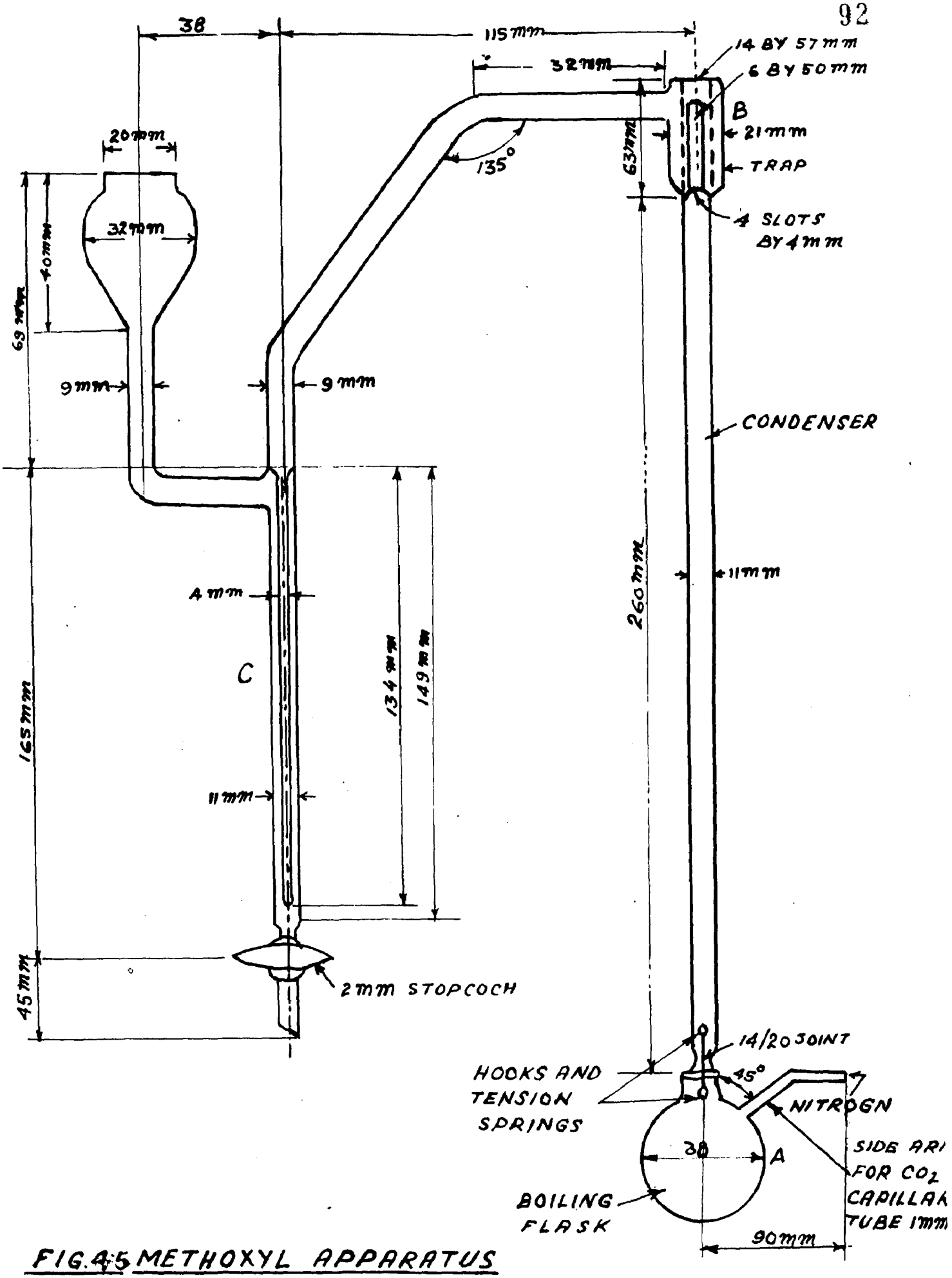


FIG. 4.5 METHOXYL APPARATUS

A blank determination with empty gelatin capsule was carried out in a similar way.

Calculation

$$\% \text{ of methoxyl content} = \frac{(A-B)N \times 0.00517 \times 100}{W}$$

Where

A = Ml. of sodium thiosulphate solution required for specimen.

B = Ml of sodium thiosulphate solution required for blanks.

N = Normality of sodium thiosulphate solution.

W = Moisture free weight of the specimen in gm.

0.00517 = Methoxyl in gm. equivalent to 1 ml of normal sodium thiosulphate solution.

The apparatus used has been shown in Fig. 4.5.

(c) **Total hydroxyl content**.- A number of methods have been applied for the determination of total hydroxyl content and these have been summarized by Brauns. In the present investigation, the total hydroxyl content (both aliphatic and aromatic) was conveniently determined by acetylation. The method involves two steps (a) Acetylation of lignin and (b) estimation of acetyl content.

(a) Ethanol, lignin (0.1 g) was acetylated to constant acetyl content by dissolving it in a mixture of 2 ml pyridine and 2 ml acetic anhydride. The solution was allowed to stand for 24 hours at 20°C and then poured into 200 ml distilled water. The acetylated product was collected by filtration, washed and dried in vacuum.

(b) The acetyl content was determined by the method of Whistler and Jeans[14].

Acetylated lignin (0.1 g) was introduced into 250 ml round bottom flask. The flask was attached to a glass distillation apparatus. The solution of sodium methoxide (0.2N, 50 ml prepared by dissolving metallic sodium in anhydrous methanol) was introduced followed by 50 ml of anhydrous methanol. The flask was heated in a water bath at 75 - 80°C and distillation was allowed to take place. The distillate was collected in 500 ml flask provided with a drying tube containing calcium chloride and soda lime. The flask was immersed in ice water. When most of the liquid in reaction flask had distilled, then an additional 50 ml of methanol was added and distillation continued. The distillate (200-250 ml) was boiled under reflux for 20 minutes with 50 ml of 0.1N sodium hydroxide The solution was cooled to room temperature and the excess of alkali was determined by titration with 0.1N hydrochloric acid (Phenol phthalein indicator). A blank withmethanol (200 ml) was carried out by the same procedure. The percentage of total hydroxyl content was calculated as follows:

$$\% \text{ of total hydroxyl content} = \frac{(A-B) \times N \times 0.043 \times 100}{W}$$

Where

A = ml of acid in blank

B = ml of acid in sample

N = Normality of acid

D = Dry weight of the sample

(d) ***Phenolic hydroxyl content.-*** *Phenolic hydroxyl content was determined by ultraviolet Spectroscopic method which has been developed by Aulin Erdtman and has been simplified further by Goldschimd*[15].

The details of the method are as follows:

Solutions containing 0.1 to 0.3 g lignin per 100 ml in pH 12 buffer solution was prepared (stock solution). As soon as the sample was completely dissolved. 2 ml portion of the solution were diluted to 50 ml with pH 12 buffer solution (alkaline solution) and 2 ml of 0.1N sulphuric acid and diluted to 50 ml with pH 6 buffer solution (neutralized solution). The difference spectrum was recorded by placing alkaline solution in sample beam and neutral solution in reference beam.

The phenolic hydroxyl content of the lignin was calculated as follows:

Moles of phenolic hydroxyl per gram $= a_{max.}/4100$

OR *% Phenolic hydroxyl* $= a_{max.} \times 17/41$

Where

$a_{max.}$ *is the absorptivity in the difference spectra at the wave length of maximum absorbance.*

4100 is the a_{max} *value for model compounds (i.e. eugenol and comidendrin) and 17 is the molar weight of hydroxyl*

(e) ***Carbonyl group.-*** *In the present investigation,*

carbonyl groups were determined by hydroxyl-amine-hydrochloride method of Gierer and Sodenberg[16].

Ethanol lignin (200 mg) was accurately weighed and dissolved in 95 per cent ethanol (10 ml) with addition of a little water if necessary. The solution was adjusted to pH 4 and at zero time added to a solution of hydroxyl-amine hydrochloride (138.2 milimole) in 95 per cent ethanol (4.0 ml) at pH 4 in a titration vessel maintained at 25°C. After standing for 18 hours along side a blank containing no lignin, the pH of the blank was observed (usually pH 4.0 $\pm$ 0.1) and the lignin solution titration to the same pH with 0.1N sodium hydroxide solution and carbonyl groups were calculated using the formula -

$$\text{Carbonyl}/C_9 = \frac{(A-B) \times N \times M}{W \times 100}$$

Where

A = ml of sodium hydroxide required for blank.

B = ml of sodium hydroxide required for sample.

N = Normality of sodium hydroxide solution.

M = C_9 formula weight of lignin unit

W = Weight of lignin in gms.

(f) **Carboxylic group**.- Carboxylic groups were determined by titrating a lignin solution in alcohol against standard sodium hydroxide using pH meter. The point of inflection of the curve obtained on plotting the amount of sodium hydroxide added against pH of the system was taken as end point. The amount per C_9 unit was calculated using

the formula given below:

$$\text{Carboxylic group}/C_9 = \frac{A \times N \times M}{W \times 1000}$$

Where

A = Volume of NaOH used

N = Normality of NaOH

M = C_9 formula weight of lignin

W = Weight of lignin sample

(g) **Ultraviolet Spectra**.- Although UV spectra studies are in general less informative regarding specific structural features than are those in the IR region, some intensity observations may be made when used as a means of comparing the isolated lignins and provides a valuable tool in identification of unsaturated organic compounds and in the elucidation of the structure. A typical lignin spectrum decreases from a maximum near 260 nm with a pronounced shoulder near 230 nm followed by a maximum near 280 nm. The absorption maxima at 280 nm is due to oxy-substituted benzene ring. The maximum close to 230 nm is due to double bonds in benzene ring. Thus 4-hydroxyl, 3-methoxyl, 1-propyl-benzene constitutes basic lignin spectroscopic Unit (BLSU).

Sample Preparation Technique

For determination of ultraviolet spectra about 20 mg lignin was taken into small tube which was sealed with cotton plug. Then the lignin was dried in vacuum over phosphorous pantaoxide for ten minutes. After vacuum

drying, lignin was heated at 50°C for 18 hours under vacuum. Then dried lignin was dissolved in 25 ml of pure ethanol. Spectra was obtained using Perkin Elmer Model 402 UV and VIS Spectrophotometer, cell length 1 cm (matched quartra). The ultraviolet spectrum of lignins is shown in Fig. 4.6 and 4.7.

*(h) **Infrared Spectra**.-* The range of electromagnetic spectrum extending from 0.8 to 200 micron is referred to as infrared. The region from 0.8 to 50 micron can be explored with most of the commercial instruments. In this region, spectra originates primarily from the vibrational, stretching and bending modes within molecules. Infrared spectrum is one of the most characteristic properties of a compound. It provides a fingerprint for identification and a powerful tool for the study of the molecular structure. Emperical correlation of vibrating group with specific observed absorption bands offer the possibility of chemical identification and coupled with intensity measurements of quantitative estimation.

Like other compounds infrared spectra of lignin macromolecule may show the presence of various functional groups present and idea of their relative amount also.

Both wave length and wave number are used as units to describe the position of absorption bands in infrared spectrum. The wave length is usually measured in microns The wave number is the frequency divided by the speed of light. It indicates the number of wave length for 1 cm

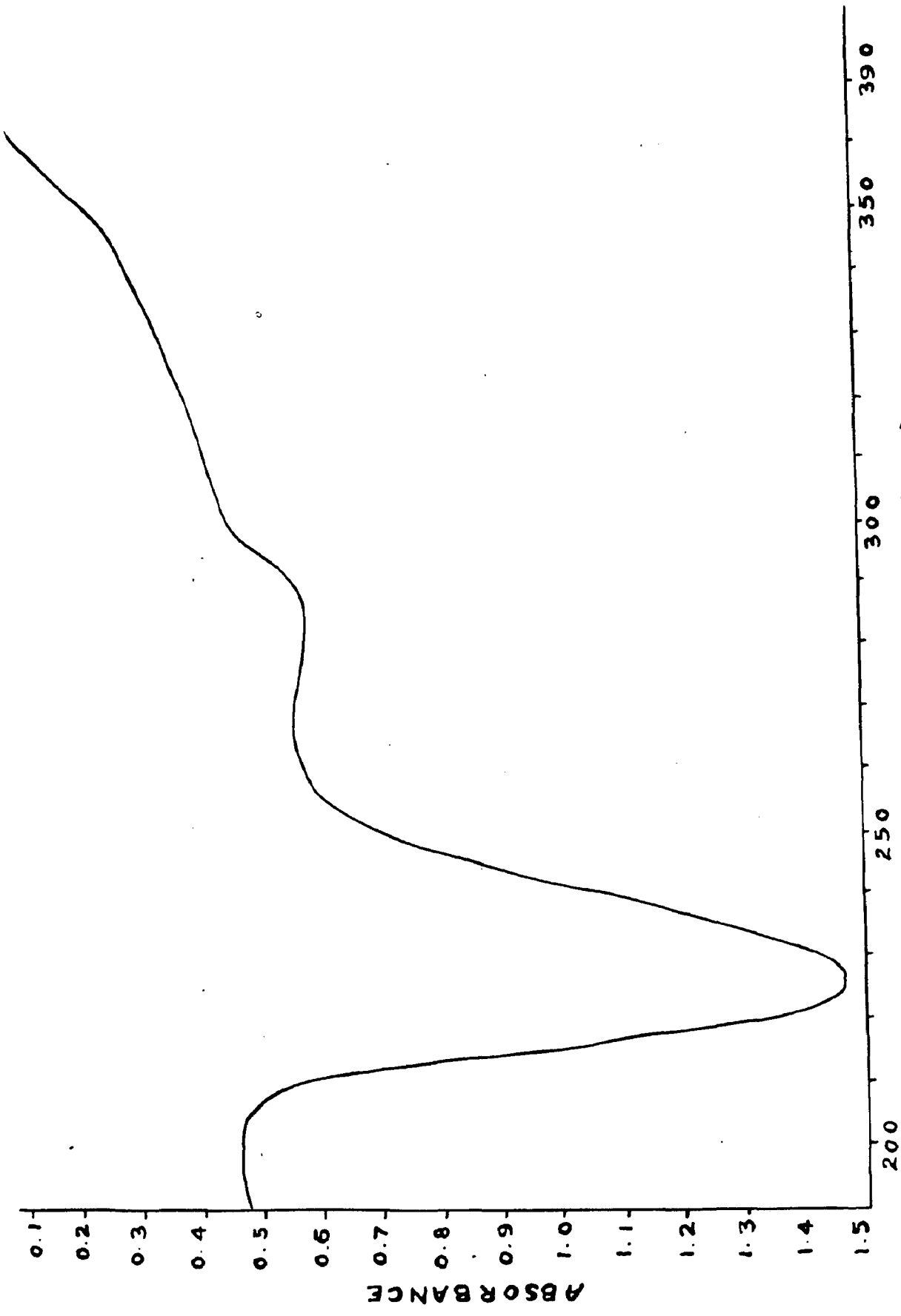


FIG. 4.6. ULTRAVIOLET SPECTRUM OF P. CARIBAEA THIOLIGNIN.

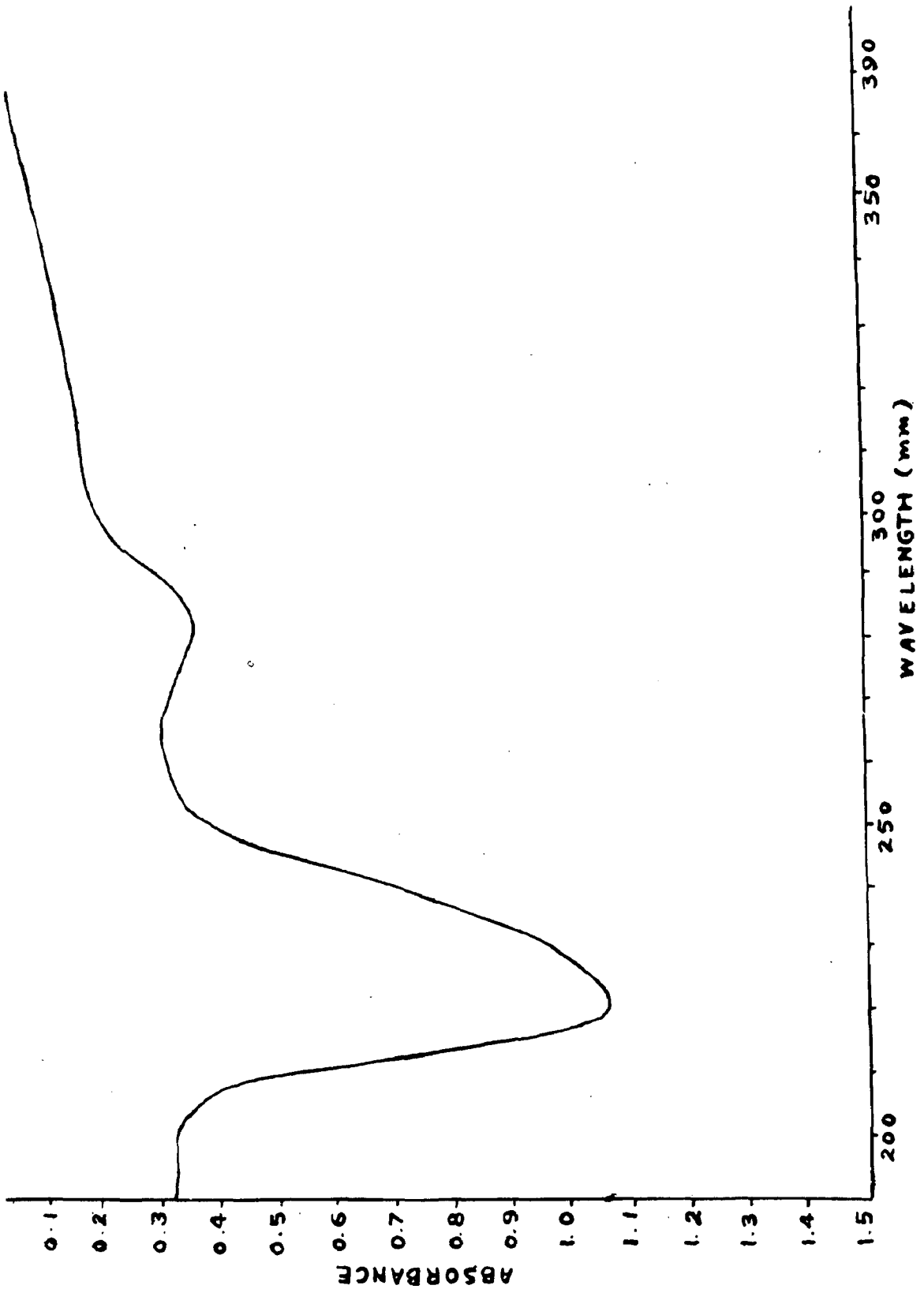


FIG. 4.7. ULTRAVIOLET SPECTRUM OF P. CARIBAEA ETHANOL LIGNIN

distance travelled (cm^{-1}).

A compound may be studied by infrared in the form of solution, thin film, smooth paste (mull), pressed disc, gas or vapour. In the present studies of lignin, pressed disc technique was employed. 4 mg of sample and 100-150 mg of dry potassium bromide was converted to fine powder in a mortar. About 50-70 mg of this mixture was pressed with 10 ton/sq. inch pressure in an evacuated die. Almost a clear transparent disc (pallet) about $\frac{1}{2}$ inch in diameter was prepared which was mounted in the proper frame and placed in the infrared sample beam to record the spectrum The infrared spectrum of lignins are recorded in Fig. 4.8 and 4.9.

4. ALKALINE NITROBENZENE OXIDATION OF LIGNIN

Alkaline nitrobenzene oxidation of lignins was carried out according to the method of Stone and Blundel[17].

A sample of about 0.5 g of isolated lignin was weighed accurately and placed in a 10 ml stainless steel bomb. Sodium hydroxide (2N) 7 ml and nitrobenzene 0.5 ml were added. The bomb was sealed and heated with agitation for 2 hours at 160°C. After cooling the reaction bomb, the contents were transferred to a centrifuge tube and centrifuged until the alkaline layer was clear. The alkaline reaction products were extracted continuously with ether to remove excess of nitrobenzene and its reduction products. It was then acidified and further extracted with ether

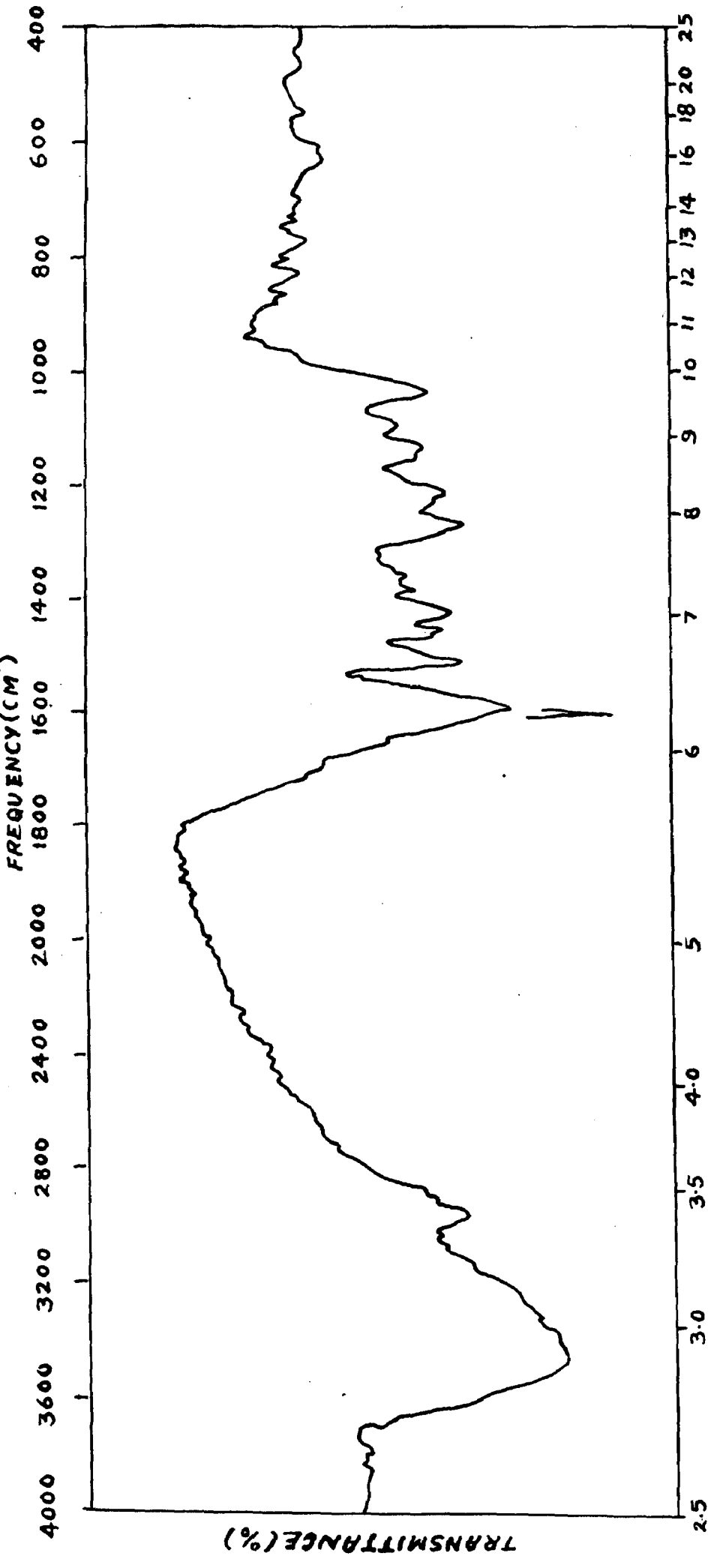


FIG 4.8. INFRARED SPECTRA OF P. CARIBAEA THIOLIGNIN

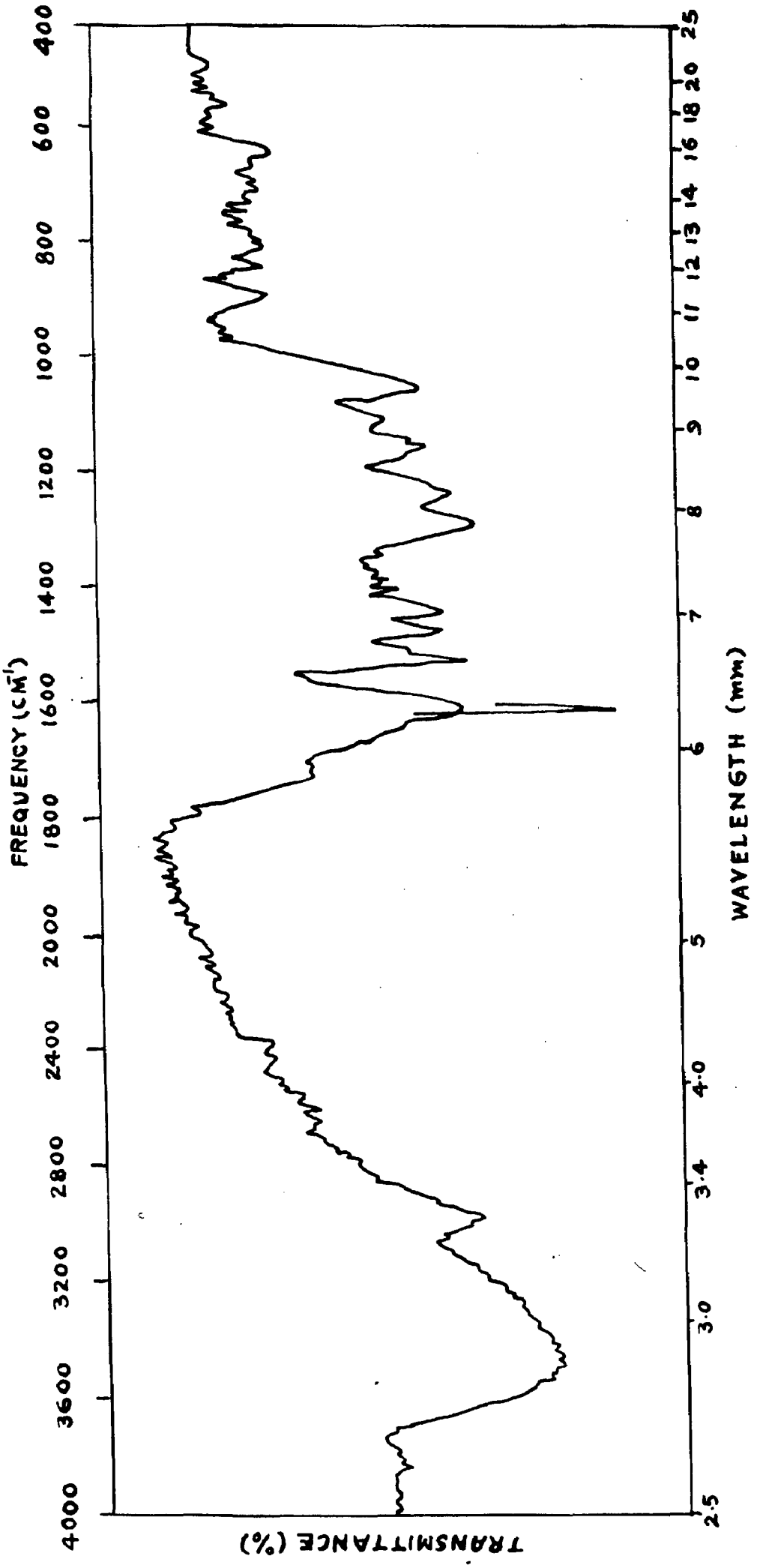


FIG. 4.9. INFRARED SPECTRA OF P. CARIBAEA ETHANOL LIGNIN.

to remove the lignin oxidation products. Solvent exchange with ethanol gave alcoholic solution from which aliquotes were taken for the chromatographic separation. Whatman No. 1 chromatographic paper was impregnated by dipping in 0.05M solution of sodium tetraborate and was allowed to dry in air. This gave better resoution of the compounds.

The aliquot of the alkaline digest containing aldehyde was applied to the base line by means of a graduated micro-pipette, an extra spot of the solution was placed near the edge of the sheet. The aldehydes were then separated by decending method of paper charomatography using solvent in 6 hours. After development 1 inch wide strip was cut off and sprayed with 2-4 dinitrophenylhydrazine solution to locate the aldehydes and enable them to be cut off from unsprayed sheet. The spots were also located and marked by viewing the sheet under an ultraviolet lamp. Vanillin and syringaldehyde gave purple fluorescence spots and p-hydroxybenzaldehyde was visible as brown flourescence spot.

The spots were cut off from the unsprayed sheet using sharp scissors to avoid any fluffing of the edges. The cut pieces were placed in Soxhlate apparatus and extracted with ethanol. The amounts of the individual aldehydes were then determined quantitatively. Results are recorded in Table 4.8.

Presence of three aldehydes viz. p-hydroxybenzaldehyde, syringaldehyde and vanillin was confirmed as follows:

Fraction - I (p-hydroxybenzaldehyde).- This fraction on re-chromatography in solvent benzene - water (1:1) gave a single spot corresponding to p-hydroxybenzaldehyde (Rv=0.16).

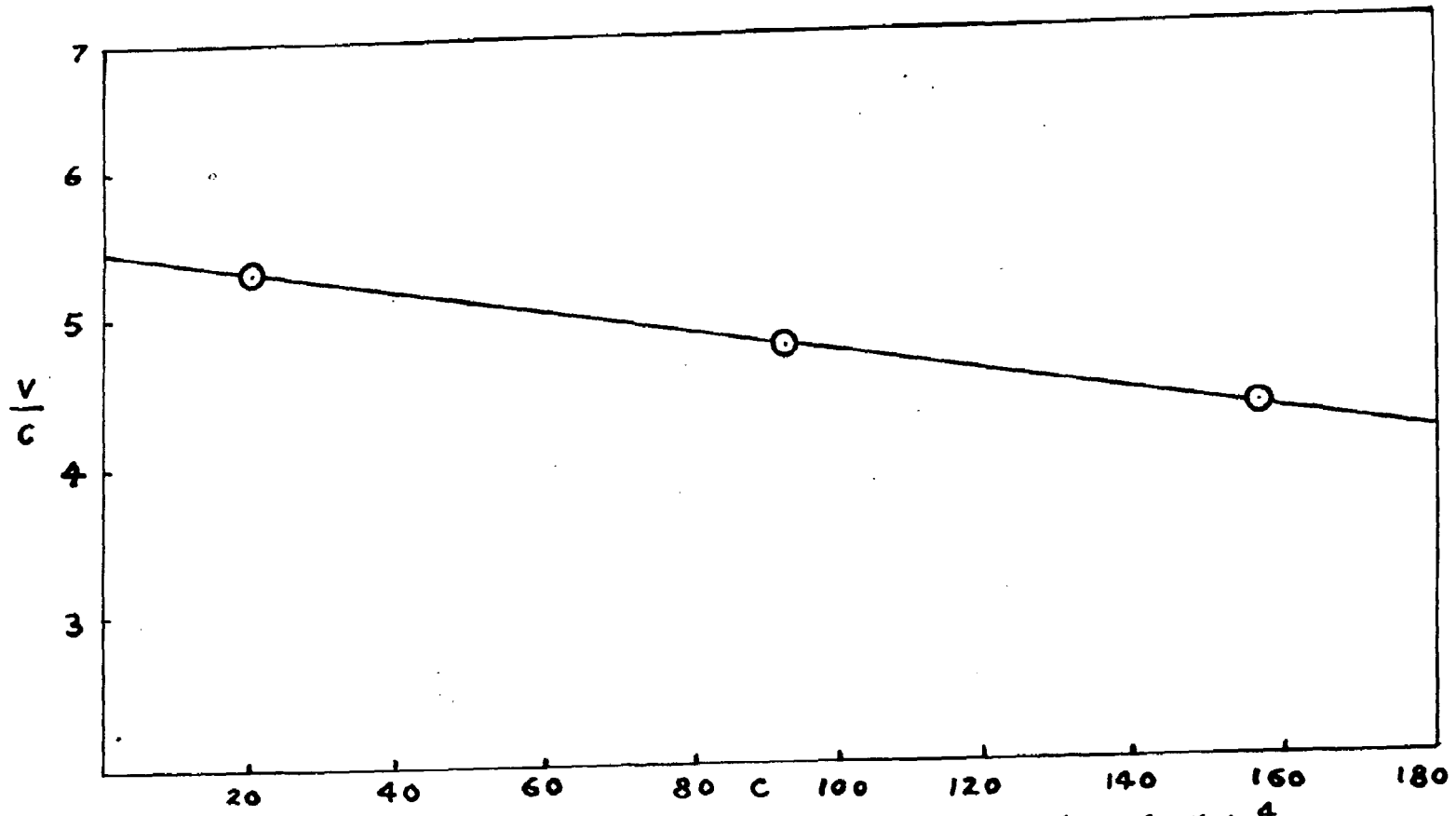
Fraction - II (Syringaldehyde).- This fraction on re-chromatography in solvent benzene - water (1:1) gave a single spot corresponding to syringaldehyde (Rv=0.73) having methoxyl ($-OCH_3$) content 34.2 per cent.

Fraction - III(Vanillin).- This fraxtion gave a single spot on re-chromatography in solvent benzene - water (1:1), corresponding to authentic vanillin (Rv=1.00) having methoxyl ($-OCH_3$) content 20.1 per cent.

5. DETERMINATION OF MOLECULAR WEIGHT

Number average molecular weight (Mu) was determined by vapour pressure Osmometer (302 B) by the method of Marton and Marton[18] (Fig. 4.10).

A drop of solution of lignin in dioxane and a drop of dioxane (solvent) are suspended side by side on two boards in a temperature controlled chamber saturated with dioxane vapour. Since the vapour pressure above the solution is lower than that of the solvent, solvent vapour condenses on the solution sample, and raises its temperature. The temperature rise is proportional to the solute concentration according to the Clausius - Clapeyron equation. The temperatures were measured with



$(V/C)_{C\to 0}$ From graph —— 5.4 —— Calibration Factor K = 1.356×10^4

$$\text{Molecular Weight} = \frac{K}{(V/C)_{C\to 0}} = \frac{1.356 \times 10^4 \times 5.4}{} = 2511$$

FIG. 4.10. MOLECULAR WEIGHT OF P. CARIBAEA ETHANOL LIGNIN

sensitive thermometers, the difference of temperatures in the two boards were read, after a few minutes, through a wheat-stone bridge in resistance units (V). A series of concentrations were used. The V/C values were plotted against concentration C and extrapolated to zero concentration. Mn^- was calculated as follows:

$$Mn^- = \frac{K}{(V/C)\ C \rightarrow O}$$

Calibration constant K was determined for dioxane using cetane ($C_{16}H_{34}$) whose molecular weight is 226.

Calibration factor (K) = $226 \times 60 = 1.356 \times 10^4$

Where the value of V/C for ethanol = 5.4

Molecular weight of

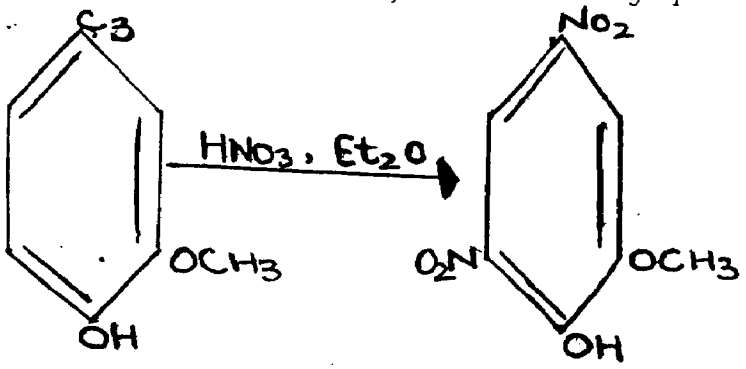
$$\text{Ethanol lignin} = \frac{K}{(V/C)C \rightarrow O} \qquad \frac{1.356 \times 10^4}{5.4} = 2511$$

6. REACTION OF NITROUS ACID WITH DIOXANE LIGNIN

The reaction of nitrous acid with dioxane lignin was carried out by the method adopted by Bolker and co-workers[19]. Sodium nitrate (2g) was dissolved in 150 ml of water and the pH of the solution was adjusted to 2 by adding 28 ml of N hydrochloric acid. 2 g of ethanol lignin was placed in a three necked round bottom flask fitted with mechanical stirrer, a dropping funnel for the addition of the prepared sodium nitrate and inlet for nitroger gas. The solution was added by dropping funnel and the temperature was kept at 70°C for 1 hour in nitrogen atmosphere. A brown insoluble fraction was separated by filtration, washed with distilled water until, neutra

and dried. The yield of nitrated product was 41.5 per cent. The filtrate and washings were combined and extracted with ether (4 times 50 ml each). The ether solution was extracted with aqueous sodium bicarbonate solution (4 times, 50 ml each), the sodium bicarbonate extracts were acidified and back extracted with ether (4 times, 50 ml each). The last ether extracted fraction was dried over anhydrous sodium sulphate and evaporated to a yellow residue. The yield was 2.8 per cent and m.p. was varied from 108-112°C which was identified as 4,6-dinitroguaicol.

The original ether extracted aqueous fraction was re-extracted with chloroform (5 times, 50 ml each), and the combined chloroform extracts after drying with sodium sulphate and evaporated gave a pale yellow compound having a m.p. 240°C and was identified as 2,6-dimethoxy p-benzoquinone.



7. METHYLATION AND OXIDATION OF METHYLATED PRODUCTS

Ethanol lignin was methylated and oxidised by Phillips and Goss method[20].

Dioxane lignin (5 g) in 100 ml of 10 per cent caustic soda solution was placed in 2 litre, three necked flask fitted with a reflux condenser, a dropping funnel and a stirrer. The reaction mixture was heated on a hot plate

at 60°C under reflux condenser. The resulting solution was stirred mechanically while 32 g of dimethyl sulphate was added slowly from a dropping funnel. After all the dimethyl sulphate had been added, the stirring and heating were continued for 1½ hours. The reaction product was removed by filtration and the methylation process was repeated. After the second methylation the reaction product was filtered and washed with distilled water until free from sulphates. The product was dried in vacuum over sulphuric acid. The methylated product has 28.5 per cent content.

A mixture of 2.5 g of methylated lignin and 25 ml of 5N nitric acid was heated on a steam bath for 1½ hours. Whereupon a copious evolution oxides of nitrogen took place. The product was cooled and filtered. An orange amorphous residue (A) was washed till free of sand and dried in vacuum over sulphuric acid. The acid filtrate was repeatedly extracted with ether, the ether solution dried over anhydrous sodium sulphate. The residue on standing deposited crystals (needle like) having a m.p. 182°C was identified as anisic acid (yield 5.2 %).

The acid filtrate, which has been extracted with ether was evaporated to dryness on steam bath. It had a m.p. 275°C and was identified as oxalic acid, (Yield 2.85 %).

TABLE - 4.4. COMPOSITION OF PINUS CARIBAEA LIGNINS

S. No.	Type of Lignin	Carbon %	Hydrogen %	Oxygen %	Sulphur %	Methoxyl %
1.	Thiolignin	60.34	6.12	30.99	2.15	13.96
2.	Ethanol lignin	62.52	6.32	31.16	-	14.85

TABLE - 4.5 FUNCTIONAL GROUPS OF PINUS CARIBAEA LIGNIN

S. No.	Type of lignin	Methoxyl %	Total hydroxyl %	Phenolic hydroxyl %	Aliphatic hydroxyl %	Carbonyl per C_9	Carboxylic per C_9
1.	Thiolignin	13.96	9.58	2.12	7.46	0.18	0.07
2.	Ethanol-lignin	14.85	8.12	1.98	6.14	0.21	0.06

TABLE - 4.6 CALCULATED C_9 FORMULAE OF PINUS CARIBAEA LIGNIN

S.No.	Type of Lignin	C_9 Formulae
1.	Thiolignin	$C_9H_{8.29}O_{2.15}(OCH_3)_{0.88}(OH)_{1.1}$
2.	Ethanol lignin	$C_9H_{8.39}O_{1.89}(OCH_3)_{0.91}(OH)_{.90}$

TABLE - 4.7 EMPERICAL FORMULAE OF LIGNIN OF VARIOUS WOOD SPECIES (21)

Sl.No.	Wood Species	Lignin preparation	Emperical Formulae
1.	Spruce	Dioxane lignin	$C_9H_{8.7}O_{2.6}(OCH_3)_{0.98}$
		Milled Wood lignin	$C_9H_{8.8}O_{2.3}(OCH_3)_{0.96}$
		Brauns Native lignin	$C_9H_{8.7}O_{2.6}(OCH_3)_{0.95}$
2.	Beech	Dioxane lignin	$C_9H_{8.5}O_{2.8}(OCH_3)_{0.95}$
		Milled Wood lignin	$C_9H_{7.1}O_{2.4}(OCH_3)_{1.36}$
3.	Birch	Milled Wood lignin	$C_9H_{9.0}O_{2.7}(OCH_3)_{1.58}$
		Brauns Native lignin	$C_9H_{8.0}O_{3.1}(OCH_3)_{0.93}$
4.	Eucalyptus	Dioxane lignin	$C_9H_{11.04}O_{3.06}(OCH_3)_{1.26}$

TABLE- 4.8 NITROBENZENE OXIDATION PRODUCTS OF PINUS CARIBAEA LIGNIN

S. No.	Type of lignin	Vanillin (V) %	Syringaldehyde(s) %	P-hydroxybenzaldehyde %	Total aldehyde %
1.	Thiolignin	13.10	0.86	1.62	15.58
2.	Ethanol lignin	14.25	1.12	2.81	18.18
3.	Pine dioxane lignin	20.6	Trace	1.60	22.20

TABLE 4.9 NITROBENZENE OXIDATION PRODUCTS OF CONIFERS, ACCORDING TO CREIGHTON, GIBBS AND HIBBERT(22)

Species	Klason lignin %	Total aldehydes % of K.L.	Vanillin % of K.L.
Picea glauca(White spruce)	28.6	23.7	23.5
Tsuga canadensis(Hemlock)	31.1	23.2	22.1
Pinus strobus (White pine)	34.9	20.1	18.5
Thuja plicata(Western red cedar)	33.9	24.6	24.0
Sequoia sempervirens (Red wood)	31.8	24.8	23.5
Texus canadensis (Ground hemlock)	32.5	22.0	20.7

TABLE - 4.10 NITROBENZENE OXIDATION PRODUCTS OF LIGNINS OF DIFFERENT FIBROUS RAW MATERIALS(23)

S.No.	Product isolated, percent Lignin	Spruce	Maple	Corn stalks
1.	Vanillin	25.1	10.5	5.3
2.	Syringaldehyde	1.8	34.3	3.2
3.	p-hydroxyl benzaldehyde	0.6	-	1.8

C. RESULTS AND DISCUSSION

The yield of Pinus caribaea thiolignin and ethanol lignin is 5.2 and 8.2 per cent respectively on the basis of wood. The lower yield in thiolignin in comparision to ethanol lignin is due to drastic action during sulphate cooking. The colour of thiolignin is dark brown whereas of ethanol lignin is creamy due to the reason mentioned above.

The results of elementary composition are recorded in Table 4.4. From the results it is evident that carbon content is higher in case of ethanol lignin than thiolignin. But in both cases the carbon content is higher which shows their aromatic nature. The results of chemical composition of Pinus caribaea lignins are comparable to other soft wood lignin as shown in Table 4.1 and 4.2. The results of functional groups like methoxyl and hydroxyl recorded in Table 4.5. show that the values of hydroxyl are in the range of softwood lignin 8.12-9.50 per cent. Value of methoxyl per C_9 is 0.90 of Pinus caribaea which is

comparable to the values of methoxyl per C_9 from spruce lignin (0.96) as shown in Table 4.7. Methoxyl value per C_9 in case of hardwood is generally higher (1.2-1.5) due to syringyl units presents in hardwood. Syringyl units are in traces in soft wood lignin. The value of hydroxyl content is higher in thiolignin in comparason to ethanol lignin to hydroxyl during pulping. The value of hydroxyl content and methoxyl content is almost same in case of ethanol lignin.

The values of carbonyl and carboxylic per C_9 shown in Table 4.5 are comparable with other softwood reported in the literature.

As lignin is built up of phenylpropane monomer units, therefore C_9 formula of thiolignin and ethanol lignin $C_9H_{8.29}O_{2.15}(OCH_3)_{.88}(OH)_{1.1}$ and $C_9H_{8.39}O_{1.89}(OCH_3)_{.91}(OH)_{.90}$ respectively. These C_9 formulae are comparable to other soft wood lignin reported in Table 4.7.

Nitrobenzene oxidation products of Pinus caribaea are recorded in Table 4.8. These are mainly vanillin and with very small amount of syringaldehyde and p-hydroxybenzaldehyde. Higher percentage of vanillin shows that Pinus caribaea lignin is mainly built up of guaiacyl units. Generally soft wood lignins on oxidation gives 20-25 per cent vanillin. The yield of aldehyde in case of Pinus caribaea is 15.38-18.18 per cent which is comparable to pine dioxane lignin (22.2 %) and comparable with the data shown in Table 4.9.

Sarkanen and Ludwig and Browning[24,25] have given in Tabular form assignment of infrared absorption band in lignin. The band at 3315 cm^{-1} represents the presence of hydroxyl group. and the band at 1330 cm^{-1} represents the syringyl ring breathing with carbonyl stretching. The band at 1380 cm^{-1} represents the phenolic hydroxyl groups and the band at 1270cm^{-1} represents the guaiacyl ring breathing with C=O stretching. The chemical analysis data revealing methoxyl, hydroxyl and guaicyl units are confirmed by the spectral analysis. From the above results it can be concluded that Pinus caribaea lignin is composed of mainly guaiacyl units. Ethanol lignin seems to approach protolignin in comparison to thiolignin (Fig. 4.8 and Fig. 4.9).

Ultraviolet spectra of ethanol lignin of Pinus caribea is shown in Fig. 4.6 and 4.7. The characteristic peak at 280 Mu can be taken as a measure of the lignin concentration in solution since the molar abosrbency index (m or E) is fairly constant for most mildly isolated lignin preparations. The absorbency at 210-210 mu is less affected by condensation of lignin. This spectra is quite similar to the spectra of Brauns' native lignin of spruce.

The molecular weight of ethanol lignin is 2511. The reported molecular weight of organosolv lignins are usually believed to be 800 to 7000. Alkali lignins have similarly low molecular weight.

By the action of nitrous acid on ethanol lignin, 4,6-dinitroguaiacol and 2,6-dimethoxy p-benzoquinone were recovered from the oxidation product. The recovery of 4,6-dinitroguaiacol indicates the electrophilic displacement reaction which contributes to the overall degradation. Bolker and co-workers[18] have also identified 4,6-dinitroguaiacol, 4-nitroguaiacol and 2,6-dimethoxy p-benzoquinone by the action of nitrous acid on birch dioxane lignin.

The ethanol lignin was methylated. The methoxyl value of methylated dioxane lignin increased due to the methylation of hydroxyl groups in the lignin. By nitration of methylated dioxane lignin with nitric acid in alcoholic medium, anisic acid and oxalic acid were isolated from the oxidation product. The methoxyl in anisic acid may originally be present in lignin molecule or had been introduced by methylation process. Similar results have been obtained by other investigators.

When methylated ethanol lignin was nitrated, no Dinitro Guaiacel was obtained, showing that phenolic hydroxyl groups para to methoxyl group (guaiacol) must be free for the reaction to occur, as these groups were etherified, no DNG was obtained.

The evidence of elementary analysis with functional groups, the high percentage of aromatic compound obtained by degradation and the spectral results proves without

a doubt that lignin is of predominantly aromatic in structure. Further, the fragments of degradation make it likely that the lignin macromolecule is unit of monomers of phenylpropane type, containing varying amount of methoxyl groups.

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CHAPTER - V

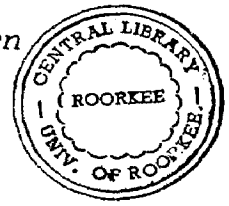
EVALUATION OF PINUSCARIBAEA FOR PAPER MAKING AND DISSOLVING PULP MANUFACTURE

A. INTRODUCTION

Papers are most often classified by function into two broad groups : "cultural" papers which include newsprint, magazine, book and other printing and writing papers and "industrial" papers and paperboards including bag, greaseproof and wrapping papers, corrugated and folding box and wall folding box and wall papers. Tissue, towel and similar crepe papers, moulded pulp products, such as egg, fruit and plants containers, metallized and plastic coated papers and capacitor papers also fall into the class of industrial papers. A newer product of paper machines with many of the properties of cloth fabric the non-woven textile, sometimes called, "disposables" also belong to the industrial paper group.

By variation in raw materials and in process, a great variety of papers can be manufactured, each in response to some market requirement. The first step in the manufacture of paper is the preparation of a dilute suspension in water of separated fibres. Pulp is obtained by the

treatment of fibrous raw material mechanically, chemically or by some combination of both. In order to make strong fibres from wood, chemical treatment is necessary. In addition to fibrous cellulose, wood contains non-fibrous material especially hemicellulose, lignin and resins. The chemical processes have developed in a number of important ways. Chemical recovery process established the economy of sulphate (Kraft) process. It became the basic material for strong brown papers. Its uses were limited, however, by the difficulty of retaining strength during bleaching. Mild nondestructive bleaching process for kraft pulping were developed based on the use of chlorine dioxide. The processes enabled these pulps to make successfully the white paper and also dissolving pulp and other non paper uses. This has changed the process use pattern completely.



Rayon, cellophane, and a wide variety of fibres, films and plastics are made by the chemical conversion of highly purified cellulose, derived principally, but not solely from wood. Wood pulp or any other highly purified form of cellulose manufactured for chemical conversion into derivatives is known as dissolving pulp, or special alpha pulp. The manufacture and availability of dissolving pulps have been an important factor in the development of artificial silks of various kinds, transparent films for packaging and for photography, nitrocellulose for explosives and lacquers, and of cellulosic plastics, The

process of manufacturing of dissolving pulp are generally more complex than those required to make paper pulp. While the process steps sometime appear to be similar, in fact the objectives in terms of pulp properties are quite different and often diametrically opposed to paper pulp properties and acceptability.

Commercially the production of dissolving pulps is done either by the sulphite process or prehydrolysis alkaline process. Sulphite process is used in United States and Canada for the production of viscose film grade pulps from mixed hardwoods, in Swedon manufacture of acetylation grade pulp from aspen and in Germany, Italy and Australia for viscose grade pulp from birch. In India presently five mills are producing Rayon grade pulps:

1. Gwalior Rayon Silk Mfg (Wvg) Co.Ltd.
   (Wood Pulp Division)
   Birlakootam Kozhikode.

2. Harihar Polyfibres
   Birlagram, Nagda
   Madhya Pradesh.

3. South India Viscose Ltd.
   Tamil Nadu.

4. Andhra Pradesh Rayons Ltd.
   Andhra Pradesh.

5. Century Pulp & Paper
   Nainital.

With their total 1,96,230 tonnes per annual installed capacity and the Central pulp Mills Ltd. Gujarat, is producing Paper grade pulp with 40,000 tonnes/annual Installed capacity.

About 60 per cent of the world production of dissolving pulp is made by the sulphite process, the remainder being pre-hydrolyzed sulphate. The trend in paper pulp manufacture is clearly to the sulphate process, similarly many of the dissolving pulp mills built recently are sulphate mills. The most recent rayon pulp mills in the U.S.S.R. are pre-hydrolyzed sulphate mills. The prehydrolysis step of the sulphate process has the purpose of reducing pentosan content of the wood. Purification of the sulphate dissolving pulp follows sequence similar to those used for bleaching sulphite paper pulp.

The sulphate process is frequently used for the preparation of cellulose for chemical modification, such as xanthation or acetylation, for regenerated fibres and films (rayon, cellulose, acetate) and for etherification for methyl and carboxy methyl cellulose[1]. These pulps require specific properties in the pulp. The specific requirements to be met by dissolving pulps in chemical uses have been shown in Table 5.1. The pulps require a low hemicellulose (high alpha-cellulose) content and a controlled final degree of polymerization of viscosity. Nearly all dissolving pulps are made from wood. The species are generally the same as those used in paper making pulp. The suitability of hardwoods like poplar, birch, maple aspen and softwoods like spruce have been investigated. The only non-wood fibres utilized in dissolving pulp manufacture are cotton linters, bamboo and reeds. The results of some indigenous raw materials

investigated are recorded in Table 5.2.

TABLE - 5.1 SPECIFICATIONS FOR RAYON GRADE PULPS

S.No.		Cellophane	Textile	Tyre cord
1.	Alpha-cellulose %	87-91	89-92	94-96
2.	Beta-cellulose %	5-7	3-5	2-3
3.	Gamma-cellulose %	3-5	3-6	1.5-3.5
4.	Ash %	.05-.13	.04-.13	.04-.08
5.	Ether solubility %	.1-.3	.1-.3	.05-.15
6.	Degree of Polymerization	100-200	250-700	250-700

TABLE - 5.2 ANALYSIS OF RAYON GRADE PULPS FROM DIFFERENT RAW MATERIALS

Species	Alpha cellulose %	Beta cellulose %	Gamma cellulose %	Pentosan %	Ash %
Bamboo	90.1	8.1	1.8	3.5	0.07
Acacia	98.0	3.4	0.8	2.1	0.05
Salai	96.0	4.5	2.0	3.7	0.12
Fir	95.6	2.2	3.2	1.9	0.11
Spruce	92.6	5.7	1.4	2.6	0.08

In India, there are about 250 units producing 20 lakhs tonnes of paper of different varieties per annum and there are 4 Newsprint units with capacity of producing 3 lakh tonnes of newsprint. Four units in the country are using bamboo, eucalyptus as raw material for the production of 2 lakh tonnes of rayon grade pulp by prehydrolysed sulphate proceses.

B. CHEMISTRY OF PULPING AND BLEACHING

1. REACTION OF LIGNIN IN ALKALINE PULPING

The reactions of lignin during alkaline pulping are complex and are not completely understood. It is known that presence of sulphide accelerates lignin dissolution without increasing cellulose degradation and that the attack on lignin molecule involves formation of groups that render lignin soluble in alkali. When the model compound vanillyl alcohol is heated in alkaline solutions containing sulphide, vanillyl monosulphide is the main product as shown in Fig. 5.1. The cleavage of ether linkages on lignin side chains also appears to play an important role in alkaline delignification. According to Geirer[3], hydroxyl ions, acting as nucleophilic agents, bring about cleavage of certain types of ether linkages in alkaline pulping. In sulphate cooking the combination of hydrosulphide and sulphide ions present in less alkaline but more strongly nucleophilic than hydroxyl ions alone. Studies with lignin model compounds have identified three cleavage reactions that probably occur in the alkaline degradation of lignin during sulphate pulping.

(i) Cleavage of alpha-aryl ether bond in phenolic units by way of quinonemethide intermediates[4]. The additional phenolic groups formed in these reactions increase the solubility of the lignin and make it more susceptible to other degradation reactions.

(ii) Cleavage of β-aryl ether bonds in phenolic units by way of episulphide intermediates. This quinone-methide intermediate[5] reacts more rapidly with sulphide ion than with hydroxyl ion. This explains the more rapid and extensive degradation of lignin by Kraft pulping liquors than by soda lignins.

(iii) Cleavage of B-aryl ether bonds in nonphenolic units by way of epoxide intermediates[6]. By this reaction phenoilic and glycolic groups are liberated, resulting in complete separation of neighbouring units in the lignin structure and the formation of more soluble, lower molecular weight fragments.

The delignification reactions in alkaline have been shown in Fig. 5.2.

2. REACTIONS OF CARBOHYDRATES IN ALKALINE PULPING

The reactions of the carbohydrate constituents of wood (Cellulose and hemicellulose) with alkaline cooking liquors have an important affect on the alkali consumption and pulp yield and also affect the physical characteristics of the final pulp. The polysaccharides in wood can respond to the alkaline cooking conditions in several ways. The degradations are quite complex and include both alkaline hydrolysis and end group peeling reactions. Acetyl groups which are mainly linked to hemicellulose portion of the wood are unstable to alkali and are cleaved at a very early stage of the cook. In case of

softwood, some of the hemicelluloses are dissolved during early stage of cook, but only xylan portion remains in polymeric form in cooking liquor while in case of hardwoods, a part of xylan is removed from the wood by alkaline liquor. When cellulose is treated with alkali at high temperature, the degree of polymerization decreases rapidly and this decrease cannot be accounted for by the peeling reactions alone. It has been shown that at temperature of 170°C or higher, alkaline hydrolysis by cleavage within the cellulose chain occurs, producing new reducing end groups that can then participate in the peeling reaction. The mechanism probably involves the formation of a 1,2-expoxide that is readily hydrolysed to a reducing end group, as shown in Fig. 5.2

3. BLEACHING

The principal reason for bleaching is to obtain a brighter pulp. This is achieved in the case of chemical pulps primarily through the removal of lignin. For some grades of papermaking pulps and the pulps to be used in the manufacture of absorbent products, removal of a portion of hemicellulose is beneficial. For dissolving pulp, removal of hemicellulose is beneficial in order to obtain pulp with required properties. The removal of lignin in the bleaching process can be considered as a continuation of cooking process. Usually it is not possible to remove the lignin in the cooking process to the extent

of brightness as satisfactory.

The delignification of pulp is based on phenol oxidation as unbleached pulp contains phenols which are sensitive to oxygen. These include reactions of lignin with aqueous halogen solution at any pH, reaction with chlorinedioxide, hydrogen peroxide etc[7]. Delignification in commercial chemical pulping is interrupted when the lignin content of fibres has dropped to a few residual percent and the carbohydrate portion of the pulp has become more impermiable to continue alkaline treatments. The remaining darky coloured lignin has to be removed from the fibres by delignification methods that are more selective in their attack on lignin than are pulping liquors. One of the most common and most widely used system involves treatment of unbleached pulp fibres with aqueous solutions of chlorine gas. Delignification is achieved by:

1. Aromatic substitution of electrophilic side chain displacement with formation of chlorophenol.
2. Oxidative cleavage of aryl-alkyl linkages (α-o-4, β-O-4 and methoxyl groups) with formation of quinones.
3. Oxidation of aliphatic fragments from displaced and hydrolyzed side chains.
4. Aromatic ring cleavage by conversion of orthoquionones to muconic acid derivatives.
5. Subsequent alkaline hydrolysis of chlorophenols to hydroxyphenols.

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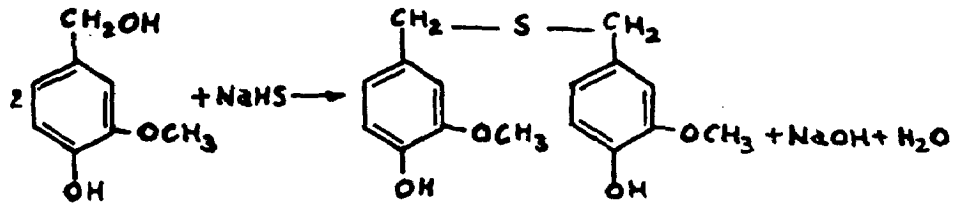

FIG. 5·1. REACTION OF VANILLYL ALCOHOL WITH SULFIDE

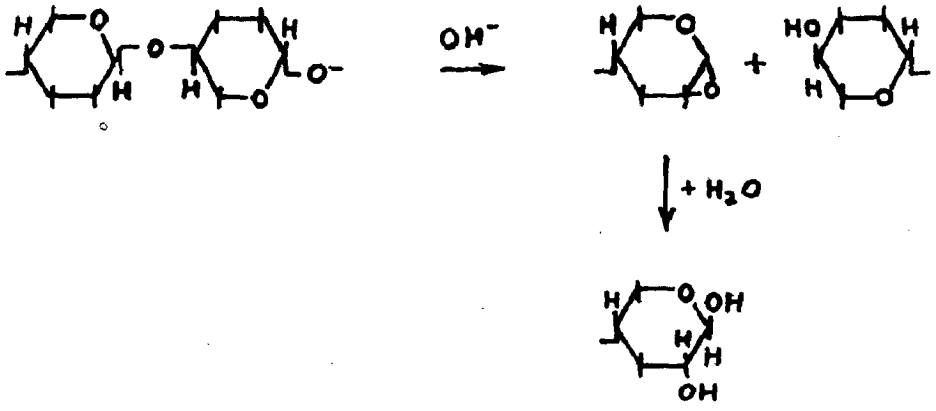

FIG. 5·2. ALKALINE HYDROLYSIS OF CELLULOSE

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3. Oxidation of aliphatic fragments from displaced and hydrolyzed side chains.
4. Aromatic ring cleavage by conversion of orthoquionones to muconic acid derivatives.
5. Subsequent alkaline hydrolysis of chlorophenols to hydroxyphenols.

The major reactions with lignin prevailing during chlorination and alkaline hydrolysis is illustrated in Fig. 5.3. Delignification is thus achieved by oxidative depolymerization amounting to molecule fragmentation along with chlorination and hydroxylation resulting in increased hydrophilicity. At pH 11 or higher the chlorine molecule exists as hypochlorite ion[8]. Hypochlorite solutions are used in commercial bleaching operation due to their relative selectiveness for lignin oxidation. However, alkaline hypochlorite has been gradually replaced by milder bleaching techniques based on chlorine dioxide, often used in combination with chlorine. Delignification by oxidative lignin degradation with chlorine dioxide is depicted in Fig. 5.4[9].

C. EXPERIMENTAL

1. PHYSICAL CHARACTERISTICS OF PINUS CARIBAEA

(a) Apparent density of wood.- One disc, approximately 20 mm thick was prepared from each log cut at the stated percentage heights of the tree. The green volume was determined by weighing the disc, which had been soaked in water until it was saturated. It was then dried to constant weight at 105 ± 3°C to obtain its oven dry weight. The apparent density in kgm^{-3} was calculated from;

$$\frac{\text{Oven dry weight (g)} \times 1000}{\text{Green (soaked) volume } (cm^3)}$$

(b) Bark content.- The volumetric value was obtained by measuring the overbark (g_o) and underbark (g_u) girths of

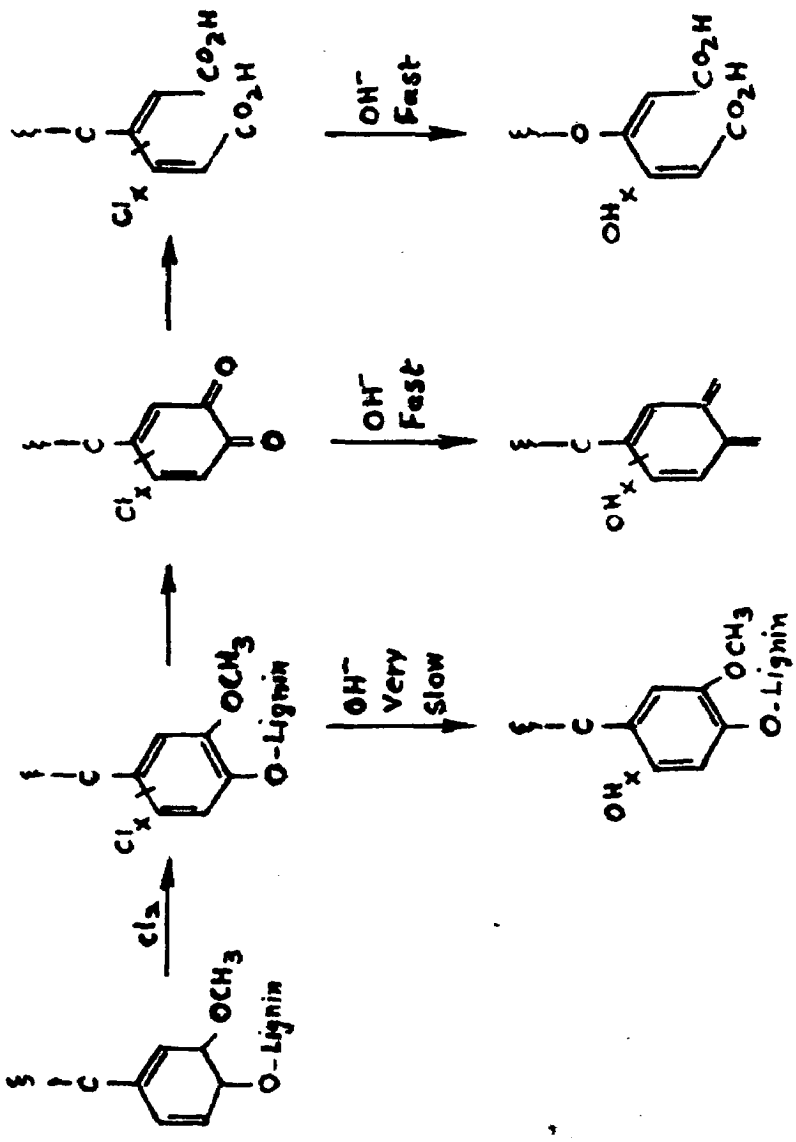

FIG. 5.3. MAJOR DISSOLUTION REACTIONS DURING CHLORINATION AND ALKALINE EXTRACTION.

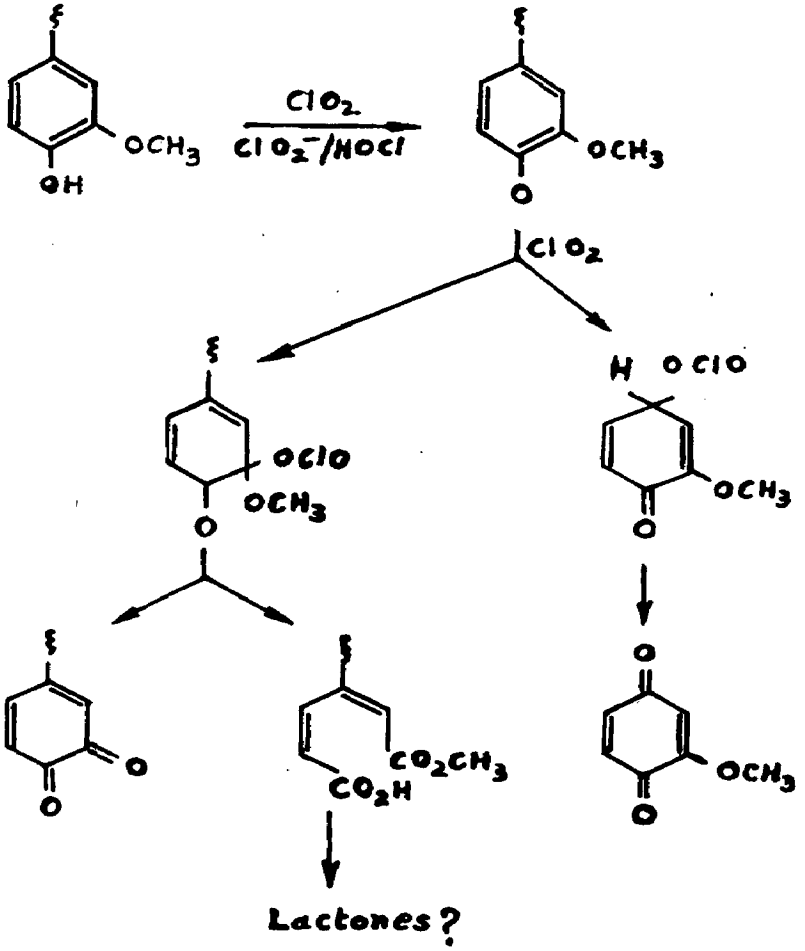

FIG. 5.4. OXIDATIVE DEGRADATION REACTIONS WITH CHLORINE DIOXIDE.

a log as received and calculating the content from:

$$\frac{(g_o^2 - g_u^2) \times 100}{g_o^2}$$

The gravimetric value was determined by drying and weighing the bark from a measured length of log at 105±3°C The dry weight of the wood (log minus bark) was calculated from its volume and apparent density. The percentage bark weight was calculated from:

$$\frac{\text{Weight of bark} \times 100}{\text{Wt. of bark+Wt. of the wood}}$$

(c) **Fibre measurements by microscopy**.- Fibre measurement were made from unbeaten sulphate pulp and they are thus representative of a composite sample. The fibres are mounted in aqueous medium and the length, width and wall thickness of 400 fibres measured. The lengths of all fibre elements, the width of fibres and the wall thickness were determined by measurements of the projected image. For length a magnification of x 45 was used and for width and wall thickness x 800.

These results are recorded in Table 5.3.

TABLE - 5.3 PHYSICAL CHARACTERISTICS OF PINUS CARIBAEA

Bark by volume	%	19.3
Bark by weight	%	12.6
Density	kg/m^3	480
Fibre length	mm(B)	2.225
Fibre diameter	Microns(d)	31.5
Cell wall thickness	microns(w)	6.0
Lumen diameter	micron(t)	29.6

2. **Production of Papermaking Pulp**

(a) **Cooking**.- The chips (200 gm oven dry) were digested in a batch digester using 20-24 per cent chemicals and the ratio of caustic soda to sodium sulphide was kept at 3:1. The chips to liquor ratio was 1:4 and the cooking temperature was 170°C and the cooking period was $4\frac{1}{2}$ hour. After the cooking time was over, the pressure of the digester was released and the pulp along with black liquor was taken out from the digester. The black liquor was separated by squeezing the digested material. The pulp was washed and screened on a screen having 0.35 mm slots. Squeezed and unbleached yield was determined on the basis of original raw material. The Kappa number of the pulps was also determined according to standard procedure. The condition of pulping, yield and Kappa number are recorded in Table 5.4.

(b) **Bleaching**.- The unbleached pulps were bleached by using chlorine, caustic soda, calcium hypochlorite and

chlorine dioxide. The amount of chlorine used depends on the Kappa number of the pulp. The bleaching conditions are recorded in Table 5.5.

(c) **Evaluation of unbleached and bleached pulps**.- 24 g (oven dry basis) of air dried pulp was dispersed in 2 litres of water in a disintegrator. The pulps were then beaten for a range of different number of revolutions of the beater roll in a PFI mill using consistency of 10 per cent. The freeness was measured by Canadian standard Freeness(CSF) tester which was about 500 ml. Standard sheets of 60 g.s.m. were prepared on British sheet-making machine, air dried, the sheets were conditioned at 65 per cent RH and 25°C and tested for physical strength properties.

(d) **Drainability (Canadian Standard Freeness)**.- The beaten pulp was dispersed in 2 litres of water in a disintegrator of 7,500 revolutions. This was then diluted to give a final stock volume of 8 litres. The drainability (Canadian standard freeness) is an emperical measure of the rate at which water will separate from one litre of this 0.3 per cent stock at 20°C through a standard perforated plate, in apparatus calibrated by the Pulp and Paper Research Institute of Canada.

3. **Physical Strength Properties of Paper**

(a) **Grammage (gm^{-2})**.- Determined by weighing a fixed area after standard conditioning and after drying to constant weight at 105 ± 3°C.

(b) Bulking thickness(μm).- Ten sheets were placed on top of the other and their thickness measured at ten points located using template described in Tappi Standard T220 with a dead weight (50 Kpa pressure) motor driven micrometer. The thickness of one sheet in μm was calculated.

(c) Apparent density($g\ cm^{-3}$).- Obtained by dividing the grammage (gm^{-2}) by the bulking thickness (μm) of a single sheet.

(d) Tensile index(Nmg^{-1}), Stretch(%) and Tensile energy absorption index (mJg^{-1}).- Determined using a semi-automatic horizontal instrument with a constant rate of elongation. Ten strips, 15 mm wide were tested with the jaws initially 90 mm apart.

(e) Tear index (mNm^2g^{-1}).- Determined using max-Elemendorf Tearstrips Instruments.

Burst index($kPam^2g^{-1}$).- Eighteen tests were made using a Frank Schopper-Dalen type penumatic burst tester.

(f) Folding endurance.- A test 1 strip, 15 mm wide and under a load of 7.85 N was folded through 112°C until it ruptured using a Kohler-Molin type instrument. The number of double folds for each of eight strips was recorded. The mean of the logarithms (base 10) of the number of double folds for each individual test was calculated to give the folding endurance.

(g) Air resistance(S).- Eight sheets were tested using a closed top Gurley densometer with 577 g inner cylinder.

The time for 100 cm^3 of air to pass through 6.45 cm^2 of sheet was measured by an automatic timing attachment.

(h) ISO - brightness (%) (diffuse blue reflecting factor).- Determined using a Carl Elrepho Reflection Photometer having a filter with an effective maximum transmission wave length of 457 nm. The instrument reading is the ratio of the radiation reflected by a pad of sheets, thick enough to be opaque, to that relfected by a perfect reflecting diffuser under the same conditions. Five readings were made on the rough sides of the sheets.

(i) Opacity (%).- Determined using a Carl Zeiss Elrepho reflection photometer having a CIE tristimulus value Y filter. The reflectance (R_0) from a single sheet over a black back-ground and the reflectance (R_{oo}) from a pad of sheets sufficiently thick enough to be opaque, were measured for ten and five sheets respectively. The opacity was calculated from -

$$\text{Opacity} = \frac{R_o \times 100}{R_{oo}}$$

(j) Kappa Number of Pulp.- The Kappa number of pulp is T. 236 OS-76 the number of cubic centimeters of 0.1n potassium permangnante solution consumed by one gram of moisture free pulp under the conditions specified. With the help of Kappa number relative hardness, bleachability or degree of delignification of an unbleached pulp can be determined. The results of physical strength properties of unbleached and bleached sheets are recorded in Tables 5.6 and 5.7 respectively. For

comparison, the results of Pinus taeda and Pinus patula are recorded in Table 5.8.

TABLE - 5.4 SULPHATE DIGESTION CONDITIONS, PULP YIELD AND KAPPA NUMBER OF PINUS CARIBAEA

	Cook Number		
	A	B	C
Digestion conditions			
Active alkali on oven dry wood %	20	22	24
Sulphidity, %	25	25	25
Liquor to oven dry wood ratio	4:1	4:1	4:1
Maximum temperature, °C	170	170	170
Time to reach maximum temperature, h	$1\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$
Time at maximum temperature h	-3	-3	-3
Yield of Pulp			
yield of oven dry screened pulp on oven dry wood, %	43.1	42.8	41.8
Kappa Number of unbleached pulp	33.4	33.2	25.8

TABLE - 5.5. BLEACHING CONDITIONS OF PINUS CARIBAEA

	COOK NUMBER		
	A	B	C
Bleaching Conditions			
1. Chlorination for 1 hour at 20°C; Pulp consistency 3 %, chlorine applied as Cl_2 on oven dry unbleached pulp, %	12	10	10
2. Alkali extraction for 1 hr at 70°C; pulp consistency 6 % NaOH on oven dry unbleached pulp, %	2	2	2
3. Hypochlorite for 2 hr at 35°C, pulp consistency 5 %, CaOCl as available Cl_2 on oven dry unbleached pulp, % available Cl_2 on oven dry unbleached pulp, %	3.0	2.0	2.0
4. Chlorine dioxide for 3 hr at 70°C; pulp consistency 8 % Cl ClO_2 applied as Cl_2 equivalent on oven dry unbleached pulp, %	3.0	2.5	2.0
Total chlorine applied as Cl_2 on oven dry unbleached pulp, %	18.0	14.5	14.0
Yield of Pulp			
Oven dry bleached pulp on oven-dry unbleached pulp, %	91.6	93.2	95.5
°ISO brightness, unbeaten pulp, %	72.5	73.5	78.0

TABLE - 5.6 EVALUATION OF PINUS CARIBAEA UNBLEACHED PULP

	Cook Number		
	A	B	C
Apparent density, g cm^{-3}	0.52	0.54	0.54
Tensile index Nmg^{-1}	72.3	75.6	76.7
Tear index, mNm^2 g^{-1}	15.1	17.3	16.9
Burst index K Pam^2 g^{-1}	4.81	4.97	5.02
Folding endurance	2.92	2.76	2.32
Air resistance, s	25	32	48

TABLE - 5.7 EVALUATION OF PINUS CARIBAEA BLEACHED PULP

	Cook Number		
	A	B	C
Apparent density, g cm^{-3}	0.57	0.58	0.62
Tensile index, N mg^{-1}	64.2	66.1	69.7
Tear index, mNm^2g^{-1}	13.1	14.1	13.8
Folding endurance	1.91	1.82	2.10
Air resistance, s	32	38	64
Opacity %	57.2	58.8	56.7

TABLE - 5.8 CONDITIONS OF PULPING AND EVALUATION OF UNBLEACHED SULPHATE PULPS OF PINE SPECIES

Cook number	Drainability CSF	Pinus taeda	Pinus patula
Active alkali as Na_2O on oven dry wood, %		20.0	20.0
Sulphidity, %		25.0	25.0
Yield of oven dry digested pulp on oven dry wood, %		42.5	44.7
Pulp Evaluation			
Kappa Number		24.7	27.8
Beating, rev.	300	8,290	7,720
Apparent density, g cm^{-3}	300	0.71	0.68
Tensile index, Nmg^{-1}	300	100	103
Tear index, mNm^2g^{-1}	300	11.0	11.7
Burst index, $kPam^2g^{-1}$	300	6.55	6.85
Folding endurance	300	3.03	3.06
Air resistance, s	300	250	210

4. *PRODUCTION OF RAYON GRADE PULP*

The chips (500 g oven dry) were prehydrolysed with water, keeping the material liquor ratio 1:3.5 at temperature 162°C for a period of 1 hour. The pH of the water after the pre-hydrolysis was determined, which was 3.8. The prehydrolysed chips were digested in a series digester having sulphate process using 20 per cent chemicals as Na_2O and the ratio of NaOH to Na_2S was kept at 3:1. The conditions of pulping are recorded below in Table 5.9.

TABLE 5.9 CONDITIONS OF SULPHATE DIGESTION OF PINUS CARIBAEA

1.	Chemical *	%	22
2.	Material:Liquor		1:3.5
3.	Temperature	°C	162°C
4.	Time	hrs**	5 hours

* Expressed on oven-dry weight of original material.

** This includes 1.5 hours to raise the temperature from room temperature to maximum.

After the cooking time was over, the pressure of the digester was released and the pulp alongwith black liquor was taken out from the digester. The black liquor was separated by squeezing the digested material.

The pulp was washed and screened on screen, squeezed and the unbleached yield was determined which was 35.6 per cent on basis of oven dry weight of the original material. The Kappa no. was determined by Tappi standard procedure and was found to be 20.5.

5. BLEACHING OF PULP

A portion of the pulp was bleached by multistage bleaching process using elemental chlorine, caustic extraction, sodium hypochlorite and chlorine dioxide and finally washed with sulphur dioxide solution. The pulps were washed with water after every stage of treatment. The conditions of bleaching, yield of bleached pulp are

recorded in Table 5.10. The bleached pulp was analysed for alpha, beta and gamma-cellulose, pentosans, ash contents, and ether solubility and brightness etc. according to Tappi standard method. The results of chemical analysis of the bleached pulps are recorded in Table 5.11.

TABLE 5.10 CONDITIONS OF BLEACHING, YIELD & BRIGHTNESS OF PULPS

1. First Stage	a. Chemicals *,	%	6
	b. Consistency,	%	3
	c. Temperature,	°C	35
	d. Time,	hrs	1
2. Second stage	a. Chemicals**,	%	2
	b. Consistency,	%	5
	c. Temperature,	°C	75
	d. Time	hrs	1
3. Third stage	a. Chemicals***	%	3
	b. Consistency,	%	5
	c. Temperature,	°C	35
	d. Time,	hrs	3
4. Fourth stage	a. Chemicals,	%	2
	b. Consistency,	½	5
	c. Temperature,	°C	80
	d. Time,	hrs	2
5. Bleached Yield		%	31.8
6. Brightness	(MgO = 100)		86

* Chlorine water % expressed as available chlorine on oven-dry basis of the pulp.

** Caustic soda % expressed on oven dry basis of the pulp.

6. ANALYSIS OF RAYON GRADE PULP

Rayon grade pulp prepared was analysed for Alpha, Beta and Gamma cellulose content, Pentosan content, Ash content, Cuperaethylenediamine viacosity, degree of poly-

merization according to the method described against each analysis.

(a) **Alpha, Beta and Gamma Cellulose.**- Alpha, beta and gamma cellulose percentage in the bleached pulps were determined according to Tappi Standard 1203-OS-74 with some modifications.

(i) **Alpha Cellulose.**- 3g (O.D.) pulp was placed in a 250 ml Erlenmeyer flask in a water bath at 20 ± 0.2°C. The pulp was macerated with 15 ml of 17.5 per cent sodium hydroxide for 1 minute, 10 ml more for 45 seconds and 10 ml more for 15 seconds. The mixture was stirred and allowed to stand for another 3 minutes. Additional sodium hydroxide solution (10 ml) was added and mixed for 10 minutes more, with addition of 30 ml portions at intervals of 2.5, 5 and 7.5 min. (total volume of sodium hydroxide solution 75 ml). The flask was covered with a watch glass and left in the water bath for 30 minutes more (total time 45 minutes). Distilled water (100 ml) at 20°C was added and mixed and the beaker was left in the water bath for an additional 30 minutes (total time 75 minutes). The contents of the beaker were filtered with suction on G-2 crucible which had been previously dried and weighed. The beaker and residue were rinsed with 8.3 per cent sodium hydroxide solution (25 ml) at 20°C. The alpha cellulose was washed with distilled water at 20°C (5x50 ml) and the filtrate was set aside for the beta and gamma cellulose determinations. The alpha cellulose was washed with water until

free of acid. The crucible and alpha-cellulose were dried at 105°C to constant weight.

(ii) Beta and Gamma Cellulose.- The filtrate from the alpha-cellulose determination was transferred quantitatively to a 500 ml volumetric flask and diluted to volume. The contents of the flask were mixed and alliquot was pipetted into a 500 ml Erlenmeyer flask. Potassium dichromate solution (0.4N)(10 ml) was added followed by concentrated sulphuric acid (40 ml) which was poured care fully down the side while the flask was swirled. The solution was heated to 127 ± 20°C for 10 minutes, cooked and transferred quantitatively to a 1000 ml flask with distilled water (500 ml). Potassium iodide (2g) was added and dissolved; after 5 mts the solution was titrated with 0.1N thiosulphate solution, with the addition of starch indicator sulphate solution, with the addition of starch indicator near the end point. A blank test was carried out with 0.5n sodium hydroxide solution (50 Ml) instead of the filtrate.

(iii) Gamma Cellulose.- The original alkaline filtrate (exactly 190 ml) was transferred to a 250 ml glass stoppered graduated cylinder. A 50 ml portion of the sulphuric acid (6N) was added and more acid was added if necessary to make the solution acid to methyl organge. The solution was cooled, diluted to 250 ml, mixed and allowed to stand till beta cellulose had settled. The solution was decanted through a filter paper, the first 50 ml of filtrate was

discarded, and an aliquot of the clear filtrate (50 ml) was oxidized with dichromate and sulphuric acid solution as described above.

The calculations are:

$$\% \text{ of Beta + Gamma Cellulose} = \frac{(V_2 - V_1) \times N \times 6.35}{W}$$

$$\% \text{ of Gamma Cellulose} = \frac{(V_2 - V_1) \times N \times 6.85 \times 1.316}{W}$$

The results of alpha, beta and gamma cellulose are recorded in Table 5.11.

Where

V_1 = Millitres of thiosulphate for titration of filtrate.

V_2 = Militres of thiosulphate for titration of blank.

N = Normality of thiosulphate

W = Weight of moisture free pulp

6.85 = Equivalent weight of cellulose

& 1.316= The aliquot factor for alpha-cellulose.

Value of beta cellulose was found by difference.

(b) <u>Ether solubility (T5m-59)</u>.- The ether soluble of pulp is a measure of such substances as waxes, fats, resins, phytosteroles and non-volatile hydro-carbons. 2 ± 0.1 g of moisture free pulp was placed in Soxhlet extractive flask containing 200 ml of ethyl-ether for 6 to 8 hours. The ether was kept boiling briskly. After the extraction ether was evaporated and contents were kept in oven for 1 hour at 105 ± 3°C and cooled in desiccator. The loss in the original weight is the solubility in ether.

*(c) **Viscosity and Degree of Polymerization:-** SCAN-C15-62 method was used for the determination of viscosity. It is one of the most important methods of pulp analysis for both research and control work. The viscosity test measures the average D.P. of the Pulp Sample mainly that of cellulose. The viscosity test makes it possible to check the extent of degradation caused by the cooking and bleaching processes which greatly influences the quality of both paper and rayon pulp.*

***Procedure:** The viscosity is determined as relative viscosity (ηrel). in a capillarly type viscometer and the result is converted into intrinsic viscosity. Sample of the pulp was weighed in an amount so that the product of pulp concentration and intrinsic viscosity nc. is 3.0 ± 0.5, and put it into the dissolving vessel. 25 ml of distilled water and some copper wire pieces were added to it. In the same time 25 ml of CED solution was added. Finally, closed thevassel with a stopper and shook the bottle until all the sample was disintegrated.*

It was shaken again until the sample was completely dissolved. The temperature of the solution was adjusted to 25°C. A portion of the solution was drawn out by suction and the reflux time was determined at 25°C $\pm$ 0.1°C with an accuracy of $\pm$ 0.25 seconds.

***Calculation:** The relative viscosity was calculated from the equation:*

$$\eta^{rel} = hn. \quad tn.$$

Where

ηrel = Relative viscosity (viscosity of sample solution relative to that of the solvent).

ηhn = Viscometer constant, obtained by calibration, S^{-1}

tn = reflux time for the sample, S.

From the value of relative viscosity, obtained with the aid of Table, the corresponding value for the product $(\eta)C$, Table was constructed using Martin's formula - calculated C from the sample weight and the moisture content (The total volume of the solution is 50 cm^3). Divided the value for $(\eta)C$ obtained from Table C and reported the intrinsic viscosity, (η) as $cm^3/g.$, to the nearest whole number:

$$\eta C = \frac{\frac{X \times 50}{Wt}}{50}$$

D.P. can be calculated from intrinsic viscosity (nC). The formula used for:

D.P. 0.905 = 0.75 (η)

The results are recorded in Table 5.11.

TABLE - 5.11 ANALYSIS OF BLEACHED PULPS

a.	Alpha-cellulose	%	92.6
b.	Beta-cellulose	%	2.8
c.	Gamma-cellulose	%	4.6
d.	Pentosans	%	1.65
e.	Ash	%	0.08
f.	Ether solubility	%	0.29
g.	Degree of Polymerization		372

D. RESULTS AND DISCUSSION

1. PAPERMAKING GRADE PULP

The results of physical chracteristics of Pinus caribaea recorded in Table 5.3 indicate that the amount of bark of each log was determined as the proportion of the whole log (including bark) both by volume and by weight. The average bark content of Pinus caribaea was found to be 12.6 per cent by weight and 19.3 per cent by volume. The proportion of bark is important because the bark is not used for pulping as it consumes more chemicals. The value of bark content was little high than are usually found in temperate pine species used for pulp but similar to those found in other tropical pine, (9 % by weght and 17 % by volume). The density of the wood was determined as oven dry weight/green(soaked) volume. The density of Pinuus caribaea was 480 kg per cubic metre and the woods of density 310-560 kg per cubic metre are commonly used for pulping. The average fibre length of Pinus caribaea is

2.225 mm and diameter is 0.0315 mm, the value of l/d is more than 70. The Runkle ratio 2w/t is 0.4 where w is the cell wall thickness and t is the lumen diameter. This value is less than 1 which indicates that fibre is flexible and will be suitable for strong paper.

The conditions of pulping of Pinus caribaea and pulp evaluation are recorded in Table 5.4. From the Table 5.4, it is evident that by increasing the concentration of chemicals the yield and Kappa number of pulp decreases. The pulp qualities ranging from strong packaging grades to bleachable grades for writing papers were obtained. Less severe digestion conditions yielded pulp with Kappa number 25.8 and yield around 41.8 per cent.

The bleaching conditions of the pulps are recorded in Table 5.5 and strength properties of bleached pulps are recorded in Table 5.6. The pulps were bleached by chlorination, alkali-extraction, sodium hypochlorite and chlorine dioxide (CEHD). The amount of chlorination stage depends on the Kappa number of the pulp. The total amount of chlorine added varied from 14-18 per cent for the pulp with Kappa number of 25.8 to 38.4. In each case approximately 90 per cent of the chlorine added was consumed. The loss of pulp on bleaching was approximately 5-9 per cent giving bleached pulp yield 91.6 - 95.5 per cent (based on original oven-dry pulp). The unbleached yield lies in the range of 41.8 -43.1 and the bleached yield around 40.0 per cent on the bases of raw material. By increasing

the chemical concentration, the strength properties improve by 5-7 per cent and apparent density, opacity also increases. However, there is a loss of about 10 per cent strength properties on bleaching. The characteristics of fibre morphology and physical properties has significant effect on the papermaking properties. The pulps had an ISO brightness of 72.5 - 78 per cent. The bleached pulps had on average 90 per cent strength in comparison of unbleached pulps. However, this value depends on the pulp and method of bleaching.

In order to assess the potential of pinus caribaea as pulp wood, the pulps were compared with pulps of other species of pines used commercially in other countries. The results of evaluation of Pinus taeda and Pinus patula are recorded in Table 5.8.

These exotic species are being planted in our country for different purposes like paper, plywood etc. It can be concluded that the Pinus caribaea can be a potential raw material for Indian Paper Industry in future.

2. **Rayon Grade Pulp**

The prehydrolysis step of the sulphate process has the purpose to reduce pentosan content. The unbleached pulp was bleached with two chlorine dioxide stages because with chlorine dioxide very good brightness is achieved. Hypochlorite stage was also included in the bleaching sequence to assist in the control of degree of polymerization of

cellulose. Ash content was controlled by treatment after bleaching with sulphur dioxide solution.

From the above results, recorded in Table 5.11, it is evident that the pulp of high chemical purity and brightness can be prepared from Pinus caribaea by water prehydrolysis sulphate process followed by multistage bleaching. The standard specifications of rayon grade pulps are shown in Table 5.1. The results recorded in Table 5.11 regarding the analysis of Pinus caribaea for rayon grade pulp, are comparable with the standard specification of rayon grade pulp and thus can be considered in the mill in the manufacture of cellulose derivatives like cellophane, textile and tyre cord.

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CHAPTER - VI

CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

The following conclusions can be derived from the present investigation:

1. The Pinus caribaea is of high extractive content and average Holocellulose (66.8 %) and lignin content.
2. The Pinus caribaea hemicellulose is mainly composed of glucose (65 %) and uronic acid (15.3 %) with relatively smaller amounts of arabinose (3.5 %) xylose (13 %) mannose and galactose (12.5 and 6.0 %) respectively.
3. The Pinus caribaea Lignin is aromatic in nature and its functional groups are methoxyl, hydroxyl, carboxylic, ketonic etc. The oxidation products is mainly vanillin and syringaldehyde is in traces.
4. The Pinus caribaea wood is suitable for writing and printing and wrapping papers by using sulphate process.
5. The Pinus caribaea wood is also suitable for Rayon grade pulp using prehydrolysis, sulphate pulping process.

The Chemistry and Chemical technology of Pulping and bleaching of Pinus caribaea has been studied extensively in this work.

6.2. RECOMMENDATIONS

Based on the present investigation the following recommendations are made for further studies:

1. Organosolv and other oxygen pulping methods for better yields and less pollution should be studied using Pinus caribaea.
2. The effect of age, place of cultivation, growth rate, per hectare yield, Bark and under bark volumes should be studied thoroughly. This shall have effect on the overall economy of pulping operations and yields, as it has been observed that all these parameters have predominent effect on the physical properties of the wood.
3. Pore structure and pore volume distribution studies should be carried out to know the morphology better which can have effect on mass transfer rates during pulping operations.
4. Different type of pulping process should be studied including pollution free pulping processes to know the complete techno-economical analysis for determining the most optimum pulping process and conditions. The studies on chemical constituents carried out in this work shall help in obtaining the optimum process and its conditions.
5. Different bleaching reactions may be studied to determine the most optimum bleaching condition. The studies on lignin and its derivatives carried out in this work shall help in obtaining the optimum bleaching processes and their operating conditions.
6. Studies can also be carried out by mixing the Pinus caribaea pulp with straw pulp to obtain better strength

characteristics of the mix. The optimum pulp combination can be found by using different types of agriculture residues and non-wood fibres based on their detailed techno-economic analysis.