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Pulping and Bleaching of Red Lauan Wood*

By

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レッドラワン材のパルプ化と漂白*

ジャマール・サヌシ**

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1. Introduction

1.1 Background

The present work was carried out to study the pulping and bleaching of red lauan wood. Wood constituents were examined and their behaviors during pulping and bleaching were also studied. The use of red lauan wood in this experiment is agree with the willingness of the author, who came from the tropical zone of Indonesia to study the utilization of tropical hardwoods for pulp and paper making.

Indonesia, which extends from lat. 6°N. to lat. 11°S., and from long. 95°E. to long. 141°E., has a typical equatorial climate. The characteristics of which are constant high temperature throughout the year, high humidity, and high rainfall.

Indonesia has a total area of 191.9 million ha, of which 119.3 million ha or 62.2% is covered by forest. The forests in Indonesia consist of 117.6 million ha of natural forest and 1.7 million ha of plantation forest. A great part of the

natural forest belongs to the tropical rainforest and the remainder belongs to monsoon forest, peat forest, swamp forest, mangrove forest, and littoral forest. The most important characteristic of the tropical rainforest is the enormous number of tree species mixed together.

Approximately 4,000 tree species are found in the natural forest, of which only a few species have been known with regard to their properties and uses, while 120 species are now commonly known as commercial wood, especially species from Dipterocarpaceae family.

Trees of Dipterocarpaceae family, which are of colossal dimensions and characterized by their peculiar veining of the leaves and winged fruits, are dominant in most tropical rainforest. Kalimantan has the largest number of Dipterocarpaceae species in the world, viz, 450 species, especially of the genera *Shorea, Dipterocarpus, Hopea, Vatica, Dryobalanops, Cotylelobium,* and *Upuna.*

In addition to the tropical hardwoods, there are also two groups of long fibers from *Pinus merkusii* and *Agathis* sp., found in natural stands as well as in plantations. *Pinus merkusii* grows in about 182,000 ha in natural stands in Aceh, and in 418,000 ha in plantations in North Sumatra and Java, while *Agathis* scatters in small stands in Central Kalimantan, Central Sulawesi, some islands in Maluku, and Irian Jaya.

Up to 1979, production of hardwoods in Indonesia was 26.427 million m^3 of which 19.61 million or 74.2% were exported, and the remainder was used for plywood, veneer, and sawn timber industries. However, from the third Five-year Development Plan which was started on April 1, 1979 up to now, export of logs was being restricted gradually to stimulate the development of domestic wood industries, such as, plywood, veneer, sawn timber, and pulp.

In the connection with pulp and paper industry, Indonesian government is building a new kraft mill at Cilacap in Central Java, and planning to build a huge pulp plant at Sungai Sesayap in East Kalimantan to overcome the shortage of pulp supplies to the paper mills.

At present, the paper mills in Indonesia are using bamboo, rice straw and imported pulp as their raw materials. The utilization of harwoods as a main raw material for pulping has not been realized, while standing stock of bamboo is decreasing. Therefore, it is important to seek a new fibrous resources to substitute their raw materials.

The new fibrous resources, which would be expected to supply Indonesian paper mills, are tropical hardwoods. However, information about the utilization of tropical hardwoods for pulp and paper in Indonesia is rather limited. In this respect, Indonesia is still left behind in the knowledge with regard to the utilization of tropical hardwoods for pulp and paper compared with other countries like Japan, India, Phillipines, and Australia.

One reason of this is the lack of Indonesian researcher in the field of pulp and paper technology, and the other is no University in Indonesia, conducting research on the field of pulping and paper making.

For the abundance of tropical hardwoods as potential resource and for the lack of Indonesian researcher, the author decided to study the pulping and bleaching of tropical hardwood in this laboratory.

1.2 Problem

As mentioned previously, there are approximately 4,000 tree species found in Indonesian tropical forest, which differ widely in physical, morphological, and chemical properties.

The anatomical structure of hardwoods is more complex than softwoods. The structure of hardwoods consists of fibers which vary from about 0.5 to 3.0 mm in length, vessels which are large and much wider in diameter, and ray cells which have thin-walled and occupy from 5 to 35% of the volume of the orginal wood [1].

Physical Properties: The physical properties, which much influence on pulp and paper production, are wood density and hardness. Dense wood has more wood substances and less void space per unit volume than does less dense wood.

The wood density of tropical hardwoods ranges from about 120 kg/m^3 to 1,200 kg/m^3. Generally, the woods with high density will produce pulp in high yield on the basis of volume, but increase the cost of logging. If the high density of the wood is caused by the high extractives and lignin content, the yield of the resultant pulp will be lower. KAYAMA [2] found that there was a negative correlation between pulp yield and wood density and that this negative correlation depended on high extractives and lignin content of the wood.

Wood with high density tends to produce pulp of low breaking length and burst factor as pointed out by the data published by many researchers [3～5]. The woods with high density are generally known to require long impregnation and cooking period. However, some of the dense woods are easily cooked as indicated by their low screening rejects and low kappa number. The results show that liquor penetration of chips depends not only on the density but also on the anatomical structure and chemical constituent of woods [6].

The problems arised from hardness of the wood are associated with felling, bucking, cutting, and chipping. High density woods with high hardness require high power consumption, and accelerate the bluntness of the knives of the equipment. To obtain good and uniform chip size, frequent changing and sharpening of the chipper knives are necessary.

Morphological Properties: The morphological properties which affect greatly on sheet strength and other sheet properties are fiber length, fiber width, lumen diameter, and cell-wall thickness.

Hardwoods have short fibers and produce pulps with lower tear strength than the pulps obtained from softwoods, therefore, they could not be used for paper where high tearing strength is required. NAVARRO [6] evaluated 79 species of tropical hardwoods from Surinam and showed that fiber width had no correlation with any of the physical and strength properties of plup handsheets, but lumen diameter and cell-wall thicknwss had good correlation with breaking length, burst factor, and sheet bulk.

LANGE noted that the thick-walled rigid libriform fibers of decidous trees retained their tubular shape during beating and did not become flattened, so that, they yielded paper sheets with lower tensile strength [7].

There was a highly significant quantitative relationship between hardwood pulp properties and morphological fiber characteristics [3, 4, 8]. Furthermore, KAYAMA [2, 9] showed that the pulp properties of the tropical hardwoods were related to the morphological and chemical properties of the woods. The chemical properties of the woods were mainly related to the pulping behavior, and the morphological properties of the fibers were mainly related to the paper strength.

With regard to mechanical pulping, MARTON *et al.* [10] studied the morphological limitations to the quality of groundwood from hardwoods. They showed that the length of fibers in the raw material did not influence on the strength and optical properties of resultant groundwood. However, the width and cell-wall thickness were dominant factors, which influenced the way that the particles were separated from the wood logs. On the other hand, hardwoods contained vessels with a large number of morphological discontinuities that contributed advantageously to the opacity of the pulp.

Chemical Properties: Chemically, wood consists of cellulose, hemicellulose, lignin, extractives, and other minor component. Discussion on chemical properties of wood is emphasized on extractives which cause a major problem in pulp and paper industries.

With regard to pitch problem, tropical hardwoods are well known for their extractives content, which varies widely in nature and amount, especially resin, which is responsible for pitch problem when wood chips are cooked and bleached to chemical grade pulps.

In hardwoods, the resin acids are almost completely absent, but a large amount of fatty acids are contained, which may account from 60 to 90% of the weight of the extracts [11]. Hardwood species generally contain more unsaponifiable material than softwoods and alkali can not readily solubilize the unsaponifiable fraction. Hardwoods generally encounter more of pitch problem than softwoods, even though the softwoods have much higher content of ether-extractives than hardwoods [12].

Pitch is a major problem in the pulp and paper industry, because of the tendency of the resin to deposit on the paper processing equipment, to reduce pulp brightness, and to cause spots on the final paper. OHTANI, TACHIBANA, and SUMIMOTO [13] found that rengasin (6, 3′, 4′-trihydroxy-4-methoxy aurone) was the major wood extractive responsible for pitch problem in rengas wood, and it was converted during the cooking stage to the intermediate, which was further transformed to brown pitch specks during the final bleaching stages.

KAYAMA [2], in his work with tropical hardwoods, found that a large number of brown spots appeared on pulp sheets of some species, belong to Dipterocarpaceae, after aging procedure.

Problem caused by accumulation of pitch deposits during production of paper

from unbleached *Pinus radiata* bisulfite pulp was reported by NELSON and HEMINGWAY [14], who found that the fatty acid and unsaponifiable fractions showed the great tendency to accumulate in pitch deposits.

There was a relationship between the initial effective alkali concentration and composition of the residual wood resin in kraft pulps as pointed out by DOUEK and ALLEN [15]. Increasment of the initial effective alkali concentration in the pulping liquor was found to reduce substantially the amount of residual extractive content in the pulps because of saponification of fats and solubilization of neutral and unsaponifiable material by alkali.

1.3 Objectives

From the discussion of the problems in section 1.2., it is clear that pulpings of tropical hardwoods, both mechanical and chemical pulpings, are not free from problem. To minimize those problems, this study has been performed with the following objectives:

1. To study the effect of chemical pretreatments of the wood chips on the strength properties of resultant chemithermomechanical pulps (CTMP). To study whether or not chemical pretreatments prior to fiberization could make the chips more soften and facilitate their fiberizing in mechanical action.
2. To introduce new pulping methods, such as, alkali-methanol and cresol-water pulpings, as well as conventional kraft pulping, with expectation that the presence of solvent in cooking liquor would help to dissolve a large amount of resin during cooking.
3. To study the bleaching of chemical pulps with ozone and hydrogen peroxide. To determine the effect of ozone and hydrogen peroxide belaching on the brightness, brightness reversion, bleached yield, and physical properties in comparison with those of the pulps bleached by the conventional CEDED sequence.
4. To study the constituents of wood which account for the pitch problem and to clarify the behavior of these constituents during pulping and bleaching.

2. Chemithermomechanical Pulping

2.1 Introduction

It is well known that hardwood has short fibers and differs widely in properties, such as, physical, morphological, and chemical properties. Hardwood has abundant vessels and ray cells, and its fibers show higher stifness than softwood fibers, therefore, hardwood produces pulp with inferior strength properties when pulped in mechanical manner.

A number of investigations dealing with chemically pretreated chips prior to fiberization has been done to enhance the strength properties of hardwood mechanical pulp. RICHARDSON and LEMATHIEU [16] have discussed results obtained in a commerical chemimechanical pulp (CMP) system. They impregnated aspen chips for 15 min at 170°F and 160 psi with a liquor composed of sodium hydroxide at

a concentration range of about 0.8 to 1.4 g/ℓ and sodium sulfite at a concentration of about 15 g/ℓ. The resultant pulp had tearing and especially bursting strength better than those of stone groundwood from spruce, but with a slightly lower bulk and definetely lower opacity. The pulp properties and power consumption could be controlled over a wide range by varying the caustic soda consumption.

LEASK [17] showed that an alkaline impregnation of hardwood chips with a mixture of sodium sulfite and sodium hydroxide prior to refining resulted in a significant improvement in physical characteristics of the pulp. The pulp characteristics could be varied by changing the percentage of sodium sulfite and sodium hydroxide absorbed by the chips.

A pilot plant investigation, which was designed to explore the possibilities for the mechanical pulping of hardwood species from trembling aspen, white and yellow birches, red and sugar maples to attain the yields of about 90% and above, was described by ALLAN, SKEET, and FORGACS [18]. They showed that the addition of sodium hydroxide both at the feed of the impressafiner and at the bath resulted in a significant increase in pulp strength for all the species studied, with a significant reduction in brightness. However, the addition of sodium sulfite to the impregnation liquor improved also the brightness for aspen and white brich pulps. They suggested that the severity of the chemical pretreatment necessary to develop mechanical pulp strength was a function of the original strength of green wood.

SINKEY, and CHARTERS [19] reported that preimpregnation of hardwoods with sulfite liquor over a wide pH range and with a green liquor, caustic-carbonate liquor, and cold soda was used to produce ultra high-yield (89～94%) hardwood pulps. They found that the quality of pretreated hardwood pulps was superior to that of untreated hardwood thermomechanical pulps (TMP), but generally inferior to that of softwood TMP pulps.

For the reason that hardwood yields mechanical pulp of very poor strength properties, which are not substantially improved by pressurized refining, MARTON *et al.* [20] examined the effect of chemical pretreatment on six harwood species of varying specific gravity, morphology, and mechanical strength properties. Chemical pretreatment of all hardwoods with 4% sodium hydroxide and 3.1% sodium sulfite at temperature 80°C for 3 min made the woods more flexible and improved greatly the quality of the resultant pulps.

JANSON and MANNSTROM [21] studied the behavior of birch wood towards sodium hydroxide and sulfur dioxide, and found that the reaction of carbohydrates with alkali and the reaction of lignin with sulfite were optimal at the different pH intervals. Based on these results, they treated birch wood with alkali at a concentration range of 0.12～0.18 mol NaOH/ℓ at temperature 75°C for 2 hours in the first stage, and cooked the chips with sodium sulfite (pH 6.5) at a concentration range of 0.7～0.8 mol SO_2/ℓ at temperature 125°C for 30 min in the second stage. Both CMP and CTMP obtained from these chips showed very great improvement in both tensile strength and tear factor.

KOJIMA, KIRYU, and KAYAMA [22] discussed the effect of chemical pretreat-

ment on birch wood. Alkaline sulfite, neutral sulfite, bisulfite, acid sulfite, and cold soda were used as chemicals for treatment prior to fiberization. Their data showed that all chemical pretreatments increased the strength properties of pulp and the effect was strongest in the neutral sulfite pretreatment.

Another chemical pretreatment was employed to produce ultra high yield pulp by SAKAI and KONDO [23], who treated birch wood chips with chlorite, peracetic acid, neutral sulfite, kraft, and alkali prior to fiberization. They showed that the chemical pretreatments of the chips facilitated their fiberizing in the following order: oxidative delignification>neutral sulfite cooking>alkali treatment. This reflects the importance of an optimal delignification by proper treatment.

The strength properties of the peracetic acid pretreated pulp which was fiberized at room temperature could be improved by steaming at 150 and 170°C for 5 min. The strength properties of the pulps were similar to those of the pulps produced by pressurized fiberization at corresponding temperatures [24].

WEGNER [25] evaluated the effects of chemical pretreatment, of process location for the treatment, and of temperature on the strength properties of CTMP from aspen. He concluded that the strength properties of aspen TMP could be substantially improved by the use of a mild chemical pretreatment in conjunction with the thermomechanical treatment. The improved strength of the sheet appeared to be the results of increased fiber-fiber bonding which was caused by improved flexibility and conformability of the fibers. Sodium hydroxide and sodium sulfite/sodium carbonate were more effective than sodium bisulfite.

Production of fine paper from pure hardwood CMP had been tried by GAVELIN *et al.* [26] using eucalypt chips, which were impregnated with alkali and refined in a defibrator pilot plant unit. The resultant pulp was belached with 4% peroxide to a brightness of 75% ISO. The pulp yield was found to be 90% before bleaching and 88% after 90% of the peroxide added was consumed in the bleaching process. A 75 g/m^2 paper was made at 25 m/min on the pilot paper machine. They commented that tensile, tear, and strech were at the levels that offered no serious threat to the runnability on a fine paper machine.

This investigation was undertaken with the following objectives:

1. To determine the yield of pulps produced by cold soda, hot soda, alkaline sulfite, bisulfite, and neutral sulfite pretreated chips.
2. To determine the change of lignin content of the pulps during chemical pretreatments.
3. To determine the effect of chemical pretreatments on the physical properties of the pulps.
4. To determine the optical properties of the pulps produced by the unterated and pretreated chips.

2.2 Material and Experimental Methods

2.2.1 Material

Red lauan wood (*Shorea negrosensis*: belongs to Dipterocarpaceae family) im-

proted from Philippines was used in this experiment. The wood was chipped to the size of 20×15×2.5 mm, and a part of the chips was grounded by a wiley mill to 40~60 mesh screen, for analysis of chemical composition.

The specific gravity and fiber dimensions of red lauan wood had been measured by ARTUZ-SIEGEL *et al.* [8]. The specific gravity was 0.41 based on oven dry weight and oven dry volume. The average fiber length, fiber width, cell-wall thickness and lumen diameter were 1.64, 0.021, 0.0053, and 0.0104 mm, respectively.

Chemical composition of red lauan wood is shown in Table 1. Solubility in ethanol-benzene is higher but solubility in 1% sodium hydroxide is lower than those of birch wood. Klason lignin content is extremely high (38.8%), nearly two times than that of birch wood (19.9%). This indicates that the red lauan wood would not easily turn into pulp, both in mechanical and chemical pulping methods.

Table 1. Chemical Composition of Wood Meal

Chemical composition	Red lauan (%)	White birch* (%)
Ethanol-benzene extracts	3.0	1.9
1% Sodium hydroxide extracts	17.7	19.9
Cold water extracts	1.8	—
Klason lignin before 1% NaOH extraction	38.8	19.9
Klason lignin after 1% NaOH extraction	27.8	—
Holocellulose	66.1	82.4
Total cellulose	53.8	—
Alpha cellulose	37.9	—
Ash	0.12	—

*) KOJIMA *et al.* [22]

The holocellulose content of red lauan wood (66.1%) is lower than that of white birch wood (82.4%). The total cellulose and alpha cellulose are 53.8% and 37.9%, respectively. Solubility in cold water is 1.8% and ash content is 0.12%.

2.2.2 Chemical Pretreatment

In this experiment, various cooking liquors were employed during treatments prior to fiberization to produce CTMP pulps. The conditions of the chemical pretreatment are given in Table 2. In cold soda treatment, chips were soaked in 5% sodium hydroxide for 120 min at 20°C. In hot soda treatment, chips were cooked with 5% sodium hydroxide for 30 min to 120°C and for 30 min at 120°C. In alkaline sulfite, chips were cooked with 5% sodium hydroxide and 5% sodium sulfite for 30 min to 120°C and for 60 min at 120°C. In neutral sulfite treatment, chips were cooked with 5% sodium sulfite and 1% sodium carbonate for 60 min to 160°C and for 120 min at 160°C. In bisulfite treatment, chips were cooked with 5% sodium bisulfit for 60 min to 160°C and for 120 min at 160°C.

After chemical pretreatments, the chips were washed to remove residual chemicals and substances which were dissolved in cooking liquors during the pretreatment.

Table 2. Conditions of Chemical Pretreatment and Yield of CTMP

Treatment	% Chemical concentration	Time (min)	Temp. (°C)	Yield (%)
Untreated	— —	1440	20	98.2
Cold soda	5% NaOH	120	20	95.9
Hot soda	5% NaOH	30–30	120	76.8
Alkaline sulfite	5% NaOH, 5% Na_2SO_3	30–60	120	73.7
Neutral sulfite	5% Na_2SO_3, 1% Na_2CO_3	60–120	160	73.8
Bisulfite	5% $NaHSO_3$	60–120	160	71.1

Unterated chips were soaked in cold water for 24 hr to achieve fiber saturation point.

The chips were prepared to 50～60% moisture content by air drying and the yields of the untreated and pretreated chips were determined after conditioning of the moisture content.

2. 2. 3 Fiberization and Refining

The pressurized fiberization was carried out in a defibrator type D which consists of a horizontal chamber 255 mm in diameter, surrounded by a steam-heated jacket. A diagram of the defibrator type D is shown in Fig. 1 [27]. The rotor equipped inside the chamber is a longitudinal shaft with four blades connected to

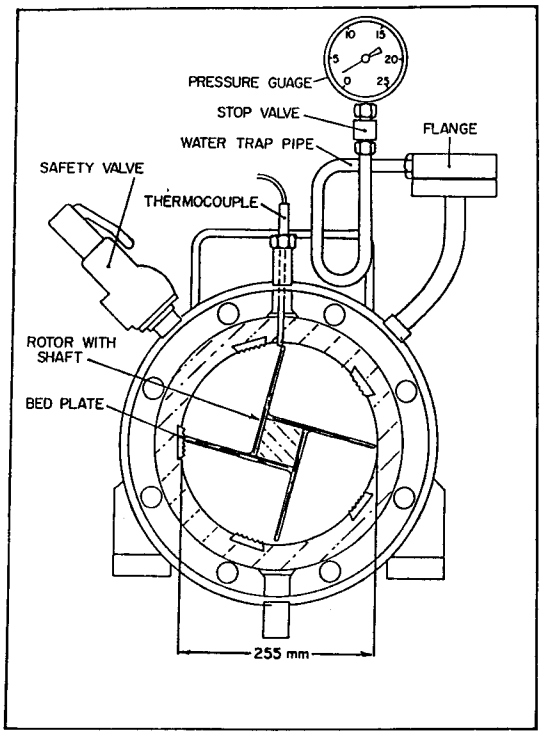


Fig. 1. Laboratory Defibrator Type D.

the sides of the shaft. Five groved bed plates are built into the wall of the chamber. The gap between the blades and the bed plate is 3 mm. The four blades devide the space in the chamber into four compartments where the raw material is placed for presteaming and subsequent fiberization.

Before fiberization, the defibrator type D was preheated with saturated steam of 2.2 kg/cm^2 in the chamber and 1.5 kg/cm^2 in the jacket for 5 min. About 25 g of oven dry wood chips with 50~60% moisture content were placed in each compartment of the chamber so that the chamber contains 100 g of chips. The cover was bolted on and the steam was turned on.

The conditions of pressurized fiberization as a first stage were steaming at 2.2 kg/cm^2 for 4 min and 3 min fiberization. The resultant plup was disintegrated in a disintegrator with hot water for 3000 revolutions and then the disintegrated fibers were screened on a laboratory screen with 0.012 in slot plate.

The resultant pulp samples from the first stage after screening had a freeness of 640 to 750 mℓ CSF, and should be further processed in a second stage to produce appropriate freeness. The seond stage or atmospheric refining was carried out in a PFI mill with 30 g (as oven dry weight) of screened pulp at 20% consistency, using clearance of 0.55 mm. Refining at atmospheric pressure was done until freeness about 285 CSF was achieved. Freeness was determined in according with the JIS standard 8121~76.

2. 2. 4 Determination of Physical, Chemical, and Optical Properties

When the second stage atmospheric refining was performed at a high consistency, the fibers were entangled and rolled together, which known as latency. In order to develop better strength properties of the sheets, latency should be removed after the second stage refining. The removal of latency was carried out in the disintegrator where the pulp at 0.5% consistency was disintegrated for 3000 revolutions at 80 to 90°C prior to forming the sheets.

The forming of handsheets was carried out according to the JIS standard 8209~79 without recirculation of white water. Ten sheets were made for each pulp sample. After pressing, the sheets on stainless plates were placed in drying rings, fanned for 3 hr, and finally the sheets were removed from the plates and were conditioned in a humidity controlled room maintained at 20°C and 65% R. H. for one day.

After conditioning the handsheets, eight sheets were selected to represent each pulp sample. Basis weight, thickness, tensile strength, bursting strength, and tearing strength were determined according to the appropriate JIS standards. All tests were carried out in the same humidity controlled room where the pulp sheets had been conditioned.

After the second stage refining, the each pulp sample was classified into five fractions i. e. fraction retained on 28 mesh, fraction passed through 28 mesh and retained on 48 mesh, fraction passed through 48 mesh and retained on 100 mesh, fraction passed through 100 mesh and retained on 200 mesh screen, and fraction passed through 200 mesh screen. The classification of the pulp was carried out

in a Bauer McNett Classifier according to TAPPI standard T 233 os~75.

Chemical analyses were performed according to appropriate standards. Klason lignin, ash content, and solubilities in ethanol-benzene, 1% sodium hydroxide and cold water were determined according to the appropriate JIS standards. Holocellulose content was determined according to the Wise method.

Lignin content of fines fraction (passed through 200 mesh screen) was calculated by the following formula:

$$Lf = \frac{[Lw Aw] - (L28 \times A28) + (L48 \times A48) + (L100 \times A100) + (L200 \times A200)]}{Af}$$

Where,

Lf: Lignin content of fines fraction (%)
Af: Amount of fines fraction (g)
Lw: Lignin content of whole pulp (%)
Aw: Amount of whole pulp (g)
$L28$: Lignin content of fraction (+28 mesh) screen (%)
$A28$: Amount of fraction (+28 mesh) screen (g)
$L48$: Lignin content of fraction (+48 mesh) screen (%)
$A48$: Amount of fraction (+48 mesh) screen (g)
$L100$: Lignin content of fraction (+100 mesh) screen (%)
$A100$: Amount of fraction (+100 mesh) screen (g)
$L200$: Lignin content of fraction (+200 mesh) screen (%)
$A200$: Amount of fraction (+200 mesh) screen (g)

The delignification of the pulps was calculated by the following formula:

$$D = \frac{(W \times Lw) - (Yp \times Lp)}{(W \times Lw)} \times 100\%$$

Where,

D: Delignification (%)
W: Wood, expressed as 100 (%)
Lw: Lignin content of wood (%)
Yp: Yield of pulp (%)
Lp: Lignin content of pulp (%)

Brightness was determined according to the JIS standard P 8123. Opacity was determined according to printing opacity (JIS P 8138) i. e. $R_0/R_\infty \times 100\%$, where R_0 is the reflectance of a sheet of paper backed by black body of reflectance, and R_∞ is the reflectance of a pad of paper of sufficient thickness to opaque.

The specific scattering coefficient of the sheets was calculated by the following formula:

$$S = 1/W \frac{2.303}{1/R_\infty - R_\infty} \log \frac{[(R_{0.902} - 1/R_\infty)(0.902 - R_\infty)]}{[(0.902 - 1/R_\infty)(R_{0.902} - R_\infty)]} \times 10{,}000$$

where,

S=Specific scattering coefficient cm^2
W=Basis weight g/cm^2
R_∞=Reflectance of a pad of paper of sufficient thickness to the opaque
$R_{0.902}$=Reflectance of a sheet of paper backed by white body of 0.902 absolute reflectance

2. 3 Results and Discussion

2. 3. 1 Yield

Table 2 shows the conditions of chemical pretreatment and yields of CTMP. The pulp yields of cold soda, hot soda, alkaline sulfite, bisulfite and neutral sulfite pretreated chips are 2.3, 21.4, 24.5, 24.4 and 27.1% less than that of the untreated chips, respectively.

The lower yields in hot soda, alkaline sulfite, bisulfite, and neutral sulfite pretreated chips are caused by the higher delignification during these pretreatments. Relations between yield and delignification are plotted in Fig. 2, which shows that in the range of 76.8~71.1% yields the delignification increases sharply from the level of 28.7 to 55.9%.

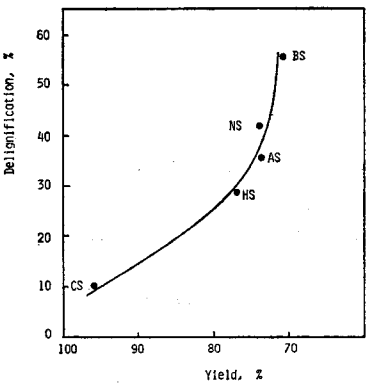


Fig. 2. Relation between Yield and Delignification of Pulps from the Pretreated Chips.
C S = Cold soda
H S = Hot soda
A S = Alkaline sulfite
N S = Neutral sulfite
B S = Bisulfite

The amounts of lignin and other substances removed during the treatments are shown in Table 3. A 1.8% of substance removed in untreated chips derives from cold water soluble extract, because the chips were soaked in cold water for 24 hr prior to refining. In cold soda pretreated chips, 3.9% of lignin and 0.2% of extractives were removed during the treatment. In hot soda, alkaline sulfite, bisulfite and neutral sulfite pretreated chips, a large amount of lignin and hemicellulose is removed. The quantities of removed lignin and hemicellulose are almost equal in alkaline processes, while sulfite processes remove 2 to 3 times higher quantity of lignin than that of hemicellulose.

The hemicellulose removed during cooking with sodium hydroxide, alkaline sulfite, bisulfite, and neutral sulfite are 12.1, 12.5, 7.2, and 9.8%, respectively, as shown in Table 3. The removal of hemicellulose in alkaline processes is greater than that in sulfite processes in spite of the higher cooking temperature of sulfite process (160°C) than that of alkaline process (120°C). The alkaline processes cause swelling of cell wall, but at a high temperature (over 100°C), the alkali degrades and partially dissolves the hemicellulose [23, 28, 29].

The higher removal of lignin in bisulfite and neutral sulfite processes may

Table 3. Yield and Amount of Lignin and Other Substances Removed during Treatment

Treatment	Yield (%)	Lignin (%)	Other substances	Total (%)
Untreated	98.2	—	1.8*	100
Cold soda	95.9	3.9	0.2*	100
Hot soda	76.8	11.1	12.1**	100
Alkaline sulfite	73.7	13.8	12.5**	100
Neutral sulfite	73.8	16.4	9.8**	100
Bisulfite	71.1	21.7	7.2**	100

*) Extractives (%)
**) Hemicellulose (%)

be caused by the higher temperature (160°C), and longer cooking time (3 hr) than those of hot soda and alkaline sulfite processes.

2. 3. 2 Change of Lignin Content of the Pulps during Chemical Pretreatment

Lignin content of unfractionated whole pulps and fractionated pulps from the untreated and pretreated chips are given in Table 4. During chemical pretreatments, a large amount of lignin in wood is removed as can be seen in Table 4, the values in parentheses indicate the degree of delignification.

Table 4. Lignin Content of the Unfractionated Whole Pulp and Fractionated Pulp from the Untreated and Pretreated Chips, in (%)

Fraction	Chemical pretreatment					
	Untreated	Cold soda	Hot soda	Alk. sulfite	Neutral sulfite	Bisulfite
Unfractionated whole pulp	38.0 (0)	34.9 (10)	34.4 (28.7)	32.2 (35.7)	28.8 (42.3)	22.6 (55.9)
+28 mesh	34.1	32.3	31.1	28.9	25.7	21.7
+48 mesh	34.6	32.5	31.4	29.7	25.8	20.5
+100 mesh	35.9	33.3	31.9	29.6	26.3	20.2
+200 mesh	35.2	34.2	33.3	31.0	27.3	22.6
−200 mesh	41.9	38.9	40.5	38.5	36.2	25.8

The value in parentheses indicate the degree of delignification (%).

The amounts of lignin removed during bisulfite, neutral sulfite, and alkaline sulfite pretreated chips are 55.9, 42.3, and 35.7%, respectively. In the case of sodium hydroxide pretreatment, there is a significant difference in the removal of lignin between cold soda and hot soda pretreated chips with the degree of delignification 10 and 28.7%, respectively.

The higher delignification of hot soda pretreated chips is explained by the large amount of alkali soluble fraction in wood lignin as can be seen in Table 1, which shows that the lignin contents of the wood before and after extracted with 1%

sodium hydroxide are 38.8 and 27.8%, respectively. Similar results were reported by OGIYAMA *et al.* [30].

After the second stage refining of the pulps with the freeness of about 285 mℓ CSF, there is an enrichment of lignin in the fines fraction (−200 mesh) compared with those in whole pulp from both the untreated and pretreated chips, as shown in Table 4. The results imply that a large part of fines is derived from the middle lamella and primary wall since lignin is concentrated in these layers.

The coarse fraction (+28 mesh) and middle fraction (48～200 mesh) of the untreated and pretreated chips contain small amount of lignin compared with those of the whole pulp. According to the data published by CHANG *et al.* [31], in the first stage of refiner mechanical pulp (RMP) and TMP, lower lignin content was found in the coarse and middle fraction than that of whole pulp, and further refining in the second stage, the lignin cnotent of these fractions decreased in a small percentage. The lower lignin content in coarse and middle fractions, and the higher lignin content in fines fraction might be mainly influenced by heterogenous distribution of lignin in cell wall.

The mechanism of the rupture of pretreated chips into fibers was shown by KOJIMA [28] and IWAMIDA *et al.* [32]. Their results indicated that the alkaline and alkaline sulfite pretreated chips were ruptured in the fiber wall, while the neutral sulfite and bisulfite pretreated chips ruptured in the midle lamella. In the latter case, midle lamella around fiber wall was removed by peeling from fiber surface during refining.

Change of lignin content of unfractionated whole pulps and fractionated pulps during chemical pretreatment is shown in Fig. 3. Lignin contents of the fines fractions of the untreated chips, cold soda, hot soda, alkaline sulfite and neutral sulfite pretreated chips sharply increase as a result of fragmentation of the middle lamella. In the case of bisulfite pretreated chips, lignin content of the fine fractions shows a small increase, which indicates that a large amount of the middle lamella lignin is dissolved during cooking.

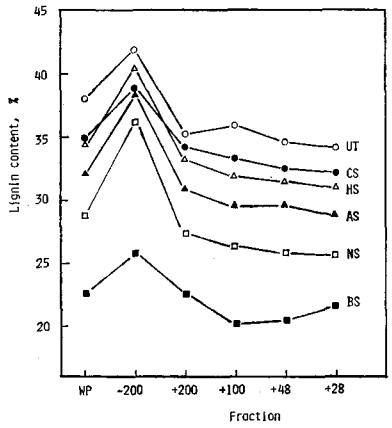


Fig. 3. Changes of Lignin Content of Unfractionated Whole Pulps (WP), and Fractionated Pulps during Chemical Pretreatments.
Designation of symbols: see Fig. 2.

It can be seen in Fig. 3 that there is no substantial change in lignin content of the middle and coarse fractions of the pulps obtained from chemically pretreated chips except that from bisulfite pretreated chips. In the latter pulp, the lignin content of the coarse fraction is a little higher than that of middle fraction.

2. 3. 3 Physical Properties

The strength properties of the pulps obtained

Table 5. Physical Properties of Pulps from the Untreated and Pretreated Chips

	Untr.	Cold soda	Hot soda	Alk. sulf.	Neut. sulf.	Bis.
Basis weight, g/m^2	57.3	60.9	61.6	59.0	60.9	58.7
Density, g/cm^3	0.240	0.291	0.435	0.383	0.412	0.470
Freeness, mℓ CSF	280	295	286	270	270	300
Breaking length, km	0.55	1.73	3.10	2.60	3.92	4.36
Tear factor	23.1	27.9	65.0	74.6	105.9	90.9
Burst factor	0.25	0.72	2.00	2.27	3.10	2.84
Bauer McNett fiber classification						
% Retained on:						
+28 Mesh	11.8	16.6	26.8	31.9	49.4	36.3
+48 "	20.6	22.9	22.0	21.7	11.9	15.0
+100 "	18.8	14.5	10.7	10.0	6.9	12.5
+200 "	5.5	12.8	9.1	5.5	3.5	6.2
−200 "	43.3	33.2	31.4	31.0	28.2	30.0

from the untreated and pretreated chips are given in Table 5. All pulps from the pretreated chips were superior in strength properties to those of the untreated chips, except pulp from cold soda pretreated chips.

KATZ *et al.* [33] found that the increase in strength of the pulp from alkali pretreated chips was related to an increase in the swelling of the fiber walls. However, in this experiment, pulp from cold soda pretreated chips was slightly improved in breaking length, tear factor, and burst factor in comparison with those from the untreated chips. In this case, fiber walls were not swollen as was expected and the fibers were still rigid. These could relate to the higher yield of pulp and the lower content of long fiber fraction. The pulp yield and fiber length distribution are closed to those of the unterated chips as shown in Fig. 4.

Fig. 4 shows that there is no substantial difference in the fines content of the pulps from chemically pretreated chips, but there is an increase in the long fibers content and a decrease in the middle fraction content in the following order: cold soda<hot soda<alkaline sulfite<bisulfite<neutral sulfite pretreated chips. This indicates that the chemical pretreatments make the wood chips more soften and facilitate the fiberizing in the first stage and the refining in the second stage of the softened wood chips according to the order mentioned above.

Handsheets made from the pulps produced by bisulfite and neutral sulfite pretreated chips

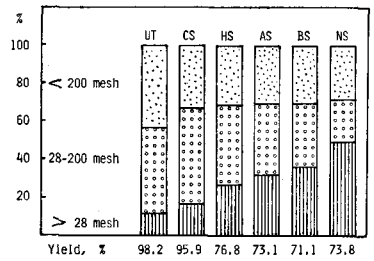


Fig. 4. Bauer McNett Classification of the Pulps from Untreated (UT), and Pretreated Chips (CS, HS, AS, BS, NS).
Designation of symbols: see Fig. 2.

have breaking length more than seven times higher and burst factor more than eleven times higher than those of the pulp from the untreated chips. On the other hand, the alkaline sulfite and hot soda pretreated chips have less value than those from the bisulfite and neutral sulfite pretreated chips in breaking length and burst factor but still higher than those from the untreated and cold soda pretreated chips. The higher breaking length of the pulps from neutral sulfite and bisulfite pretreated chips suggests that the interfiber bonding is superior to that from the other pulps. The better interfiber bonding of those pulps is evidently due to higher delignification which makes the fibers more flexible and conformable (Table 5).

The sheet density of the pulps from bisulfite pretreated chips was higher than that of the other pulps but handsheets made from hot soda, alkaline sulfite and neutral sulfite pulps were much higher in sheet density than those of the pulps from cold soda pretreated and the untreated chips. Sheet density as a function of the strength properties is illustrated in Fig. 5 and 6. The breaking length and the burst factor increase steadily with increasing the sheet density.

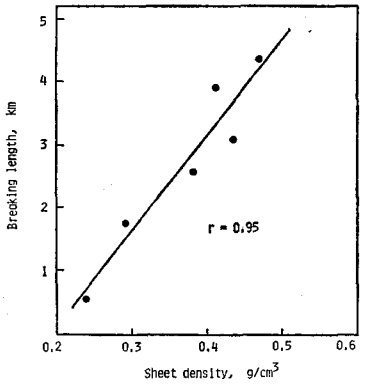


Fig. 5. Sheet Density as a Function of Breaking Length of Pulps from the Untreated and Pretreated Chips.

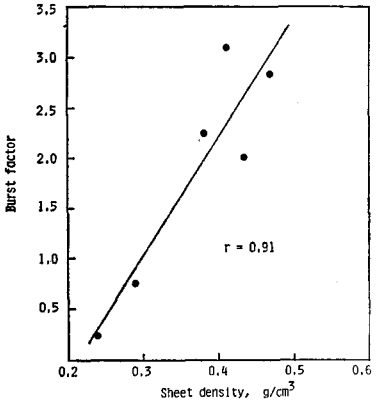


Fig. 6. Sheet Density as a Function of Burst Factor of Pulps from the Untreated and Pretreated Chips.

One of the most important factors affecting the tear strength is fiber length distribution in pulps. The relation between the tear strength and the content of long fibers fraction is shown in Fig. 7. There is a highly significant correlation ($r=0.98$) between tear factor and long fibers content, where tear factor increases greatly with increasing the long fibers fraction as shown in Fig. 7. MOHLIN [34] showed that an increase in the size of the coarse fraction had a large positive influence on tear index, but affected the surface smoothness negatively, especially when the pulp contained stiff fibers.

The effect of long fibers fraction on the burst factor is illustrated in Fig. 8. This figure also shows that the burst factor increases greatly with increasing the long fibers fraction in the pulps with the coefficient correlation $r=0.96$.

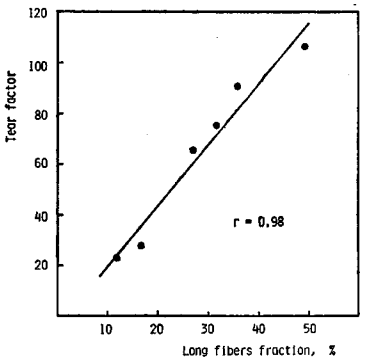


Fig. 7. Relationship between Long Fibers Fraction and Tear Factor of Pulps from the Untreated and Pretreated Chips.

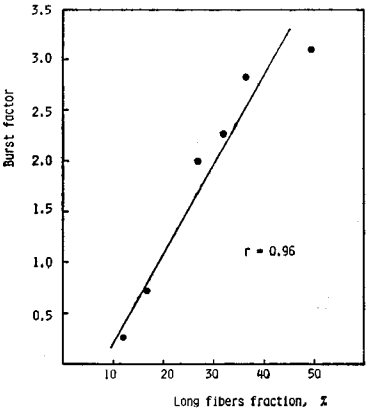


Fig. 8. Relationship between Long Fibers Fraction and Burst Factor of Pulps from the Untreated and Pretreated Chips.

MOHLIN [34] and LINDHOLM [35] showed that apparent density and tensile index increased with increasing the amount of fines fraction in the pulp. However, in this experiment, no relationship could be observed between the amount of fines fraction in the pulps and strength properties.

The effects of chemical pretreatment on the strength properties of the pulps made from the untreated and pretreated chips are illustrated in Fig. 9, 10, and 11. Tear factor and burst factor increase in the order of the untreated chips<cold soda<hot soda<alkaline sulfite<bisulfite<neutral sulfite pretreated chips as shown in Fig. 9 and 10, respectively. Breaking length incrases in the order of the untreated chips<cold soda<alkaline sulfite<hot soda<neutral sulfite<bisulfite pretreated chips as shown in Fig. 11.

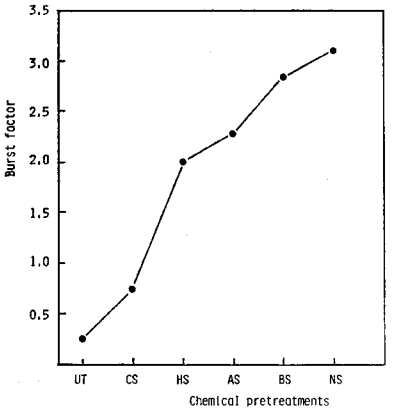


Fig. 9. Effect of Chemical Pretreatments on Tear Factor of Pulps from the Untreated and Pretreated Chips.
Designation of symbols: see Fig. 2.

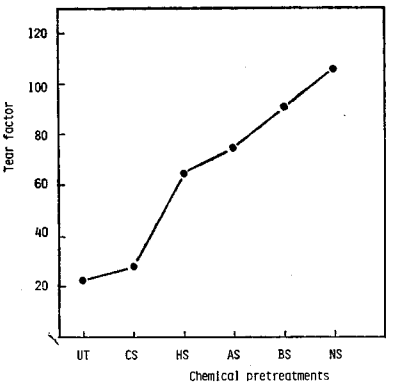


Fig. 10. Effect of Chemical Pretreatmenes on Burst Factor of Pulps from the Untreated and Pretreated Chips.
Designation of symbols: see Fig. 2.

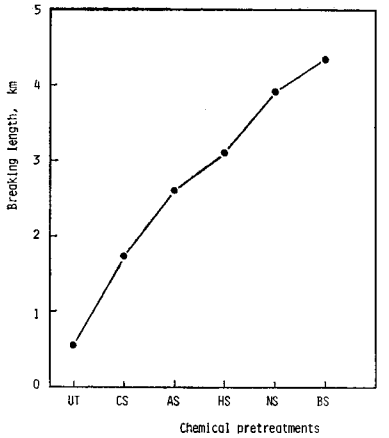


Fig. 11. Effect of Chemical Pretreatments on Breaking Length of Pulps from the Untreated and Pretreated Chips.
Designation of symbols: see Fig. 2.

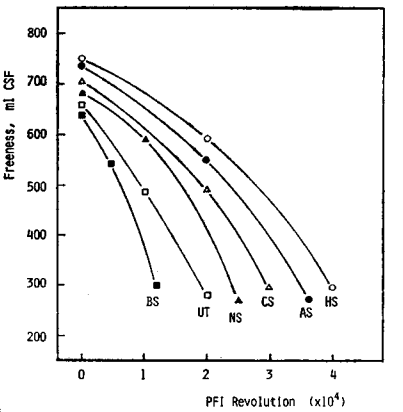


Fig. 12. Changes of Freeness during Second Stage Refining of Pulps from Untreated and Pretreated Chips.
Designation of symbols: see Fig. 2.

When the pulps were refined in the PFI mill to the freeness of 285 mℓ CSF, the pulps from the pretreated chips require considerably higher energy (PFI mill revolution) than the pulp from the untreated chips, except the pulp from bisulfite pretreated chips as shown in Fig. 12.

Pulp produced by the untreated chips was very stiff and brittle, so that during second stage refining the fibers fractured more rapidly and produced a large amount of fines. The numbers of revolution of the PFI mill for the pulps from neutral sulfite, cold soda, alkaline sulfite, and hot soda pretreated chips were 1.25, 1.5, 1.8, and 2.0 times higher than those of the pulp from the untreated chips, respectively.

Generally, the easiness of refining of the pulps from the pretreated chips depends on the degree of softening of the chips. Pulp from bisulfite pretreated chips was more soften than the other pulps, therefore, it was easily refined in the second stage refining. CHO [36] suggested that the good beatability of 80% yield pulp from bisulfite pretreated chips was due to the dissolution of some portion of lignin and hemicellulose and the increased flexibility of fibers by the sulfonation of residual lignin in pulp. It is well known that lignin causes the wood fibers stiff and brittle, so that lignin is undersirable in view of pulping and paper making. The removal of a part of lignin during chemical pretreatments makes the wood more soften. As indicated in Fig. 2, the amount of lignin removed during chemical pretreatments is in the order of bisulfite>neutral sulfite>alkaline sulfite>hot soda>cold soda pretreated chips. This implies that the softening of those pulps increases according to this order. Increasing the softening of the pretreated chips will reduce the energy for beating of the pulps to reach a specified freeness, except pulp from cold soda pretreated chips, which has still rigid structure and easily fracture during refining.

Table 6. Optical Properties of Pulps from the Untreated and Pretreated Chips

Treatment	Brightness (%)	Opacity (%)	SSC (cm^2/g)
Untreated	19.5	99.8	330
Cold soda	22.2	98.8	417
Hot soda	21.5	99.5	340
Alkaline sulfite	15.2	99.4	335
Neutral sulfite	15.9	99.6	310
Bisulfite	14.6	99.5	324

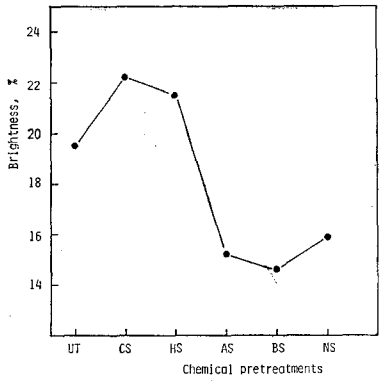


Fig. 13. Effect of Chemical Pretreatments on Brightness of Pulps from the Untreated and Pretreated Chips. Designation of symbols: see Fig. 2.

2. 3. 4 Optical Properties

Brightness of the pulps from the untreated and pretreated chips is in the range of 14.6～22.2% as shown in Table 6. The effect of chemical pretreatments on the brightness is shown in Fig. 13, which shows that the brightness of the pulps from cold soda and hot soda pretreated chips increases in comparison with the pulp from the untreated chips. The brightness of the pulps from alkaline sulfite, bisulfite and neutral sulfite pretreated chips decreases sharply below the brightness of the pulp from the untreated chips. The reduction of the brightness of the pulps from the pretreated chips is in line with the reduction of their yields.

The opacity of all pulps made from the untreated and pretreated chips is high, range from 98.8 to 99.8%, as shown in Table 6. The higher opacity is related to the lower brightness of the pulps.

Specific scattering coefficients of the pulps from the untreated and pretreated chips refined at freeness level of 285 mℓ CSF are given in Table 6. The specific scattering coefficient of all the pulps is in the range of 310 to 340, except the pulp obtained from cold soda pretreated chips with the specific scattering coefficient of 417. The higher specific scattering coefficient of the pulp from cold soda pretreated chips is reflected in the higher brightness of paper sheets formed from this pulp.

Specific scattering coefficient as a function of the fines content of the pulps obtained from the pretreated chips is shown in Fig. 14. Specific scattering coefficient decreases with increasing fine content of the pulps [35]. This suggests that hot soda, alkaline sulfite, bisulfite, and neutral sulfite pretreated chips produced pulps with higher bonding ability. ATACK *et al.* [37] showed that the specific scattering coefficients of CMP and CTMP decreased with

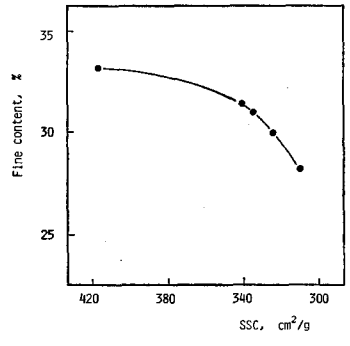


Fig. 14. Specific Scattering Coefficient (SSC) as a Function of Fine Content of Pulps from the Pretreated Chips.

increasing sulfonate content because of increased interfiber bonding and reduced production of fines.

2.4 Conclusions

The effects of various chemical pretreatments on the strength properties of corresponding CTMP pulps from red lauan wood were studied.

Chemical pretreatments of the wood chips at a temperature 120～160°C made the wood more soften and the strength properties of the pulps from the pretreated chips were greatly improved. Sulfite pretreatment prior to fiberization was more effective than alkaline pretreatment in promoting interfiber bonding.

The yield of cold soda pretreated chips was high (95.9%), however, the yields of hot soda, alkaline sulfite, bisulfite, and neutral sulfite pretreated chips were in the range of 71.1 to 76.8%. The lower yields of those pulps were caused by the higher delignification and the removal of a part of their hemicelluloses during cooking.

There was a close relationship between sheet density and strength properties of the pulps, which showed that the breaking length and the burst factor increased greatly with increasing the sheet density. Increase in the long fiber content in the pulps was found to improve tear factor and burst factor with high coefficient correlation $r=0.98$ and 0.96, respectively. Pulp from bisulfite pretreated chips was more soften than the other pulps, therefore, it was easily refined in the second stage refining. Increase in the softening of the pretreated chips will reduce the energy for beating of the pulps to reach a specified freeness, except the pulp from cold soda pretreated chips, which has still rigid structure and is easily fractured during refining.

Brightness of the pulps from the untreated and pretreated chips was in the range of 14.6～22.2%, and opacity was in the range of 98.8～99.8%. The specific scattering coefficients of all pulps were in the range of 310 to 340 cm^2/g, except the pulp obtained from cold soda pretreated chips with the specific scattering coefficient of 417 cm^2/g. The higher specific scattering coefficient of this pulp was reflected in the higher brightness of paper sheets formed from this pulp.

3. Chemical Pulping

3.1 Introduction

In alkaline pulping, soda and kraft processes have been used for the pulping of wood. The kraft process is superior to the soda process with respect to the rate of pulping, pulp yield, and pulp quality, and has been currently predominant in alkaline pulping industry [38].

The kraft process has been found to be the most promising method for the pulping of tropical hardwoods [39], and many experiments have been done to study the pulping of tropical hardwoods with kraft process. Laboratory investigations, which were carried out at the Forest Products Research Institute, College, Laguna, Philippines, showed that tropical hardwoods responded well to the kraft pulping and the pulps with sufficient strength properties were produced from them [8, 40,

41]. However, some problems still arised from the kraft process : offensive odor and pitch problem.

KAYAMA [2] found that a large number of brown spots appeared on bleached kraft pulp sheets from some species, belong to Dipterocarpaceae after aging procedure. Studies on pitch problems caused by pulping and bleaching of tropical hardwood were done by OHTANI *et al.* [13], who found that rengasin (3′, 4′, 6-trihydroxy, 4-methoxy aurone) was the major wood extractive responsible for the brown pitch specks on a sheet of the bleached kraft pulp.

From the view point of these problems, new pulping methods, such as alkali -methanol and cresol-water pulping were studied in this experiment with expectation that the presence of solvent in the cooking liquor could dissolve a large amount of pitch during cooking.

Alkali-methanol pulping is known as one of the pollution free pulping method using methanol in place of sodium sulfide in kraft process. The recovery of methanol is easy because of its low boiling point. Cresol-water pulping is found by SAKAKIBARA *et al.* [42] and being developed as one of the organosolv pulping processes. This process also attracts special interest because the spent liquor is easily separated into two layers, water and organic layers, as the temperature decreases.

In this experiment, red lauan wood was pulped with kraft, alkali-methanol and cresol-water processes, and the effect of anthraquinone (AQ) on the kraft and alkali -methanol pulpings was studied. The use of AQ in kraft and soda pulping attracts many attentions in recent years because of its role as a catalyst in delignification and stabilization of carbohydrates in alkaline process.

The concept of catalyzed alkaline pulping with AQ has been discussed by many researchers [43～46]. All of these investigations showed that the use of small aount of AQ in kraft and soda pulping processes accelerated delignification in both the processes and increased yields without affecting the strength properties of the pulps.

Trials at several Finnish mills designed to clarify the economic aspects of using AQ showed that the economics depended very much on the mill and local conditions. Four trials were done in hardwood/softwood kraft mill, hardwood kraft mill, sawdust kraft mill, and neutral or semialkaline sulfite mill. The results of these trials showed that only hardwood/softwood kraft mill was not economic, while other trials were economic [47].

Recently, organosolv pulping has been gaining attention as an alternative to kraft process, which can solve environmental problems arised from pulping based on sulfur. From the stand point of pitch problem, pulping based on solvent seems to be effective because solvent, like alcohol, dissolve wood resin.

The action of aqueous alcohol upon various woods at temperature 185°C was studied by KLEINERT [48, 49]. Bulk delignification was found to take place according to two dinstinct mechanism of pseudo first order, and the strength properties of the resultant pulps were approximately in the same range as those of bisulfite pulps produced from the same wood [48]. Evidently, bulk delignification was a composite

phenomenon involving breakdown of high molecular lignin as well as solubilization of its breakdown products [49].

Another approach was described by NAKANO *et al.* [50, 51], using 40 g/ℓ sodium hydroxide and 400 g/ℓ methanol. They found that at the same level of lignin content in pulp alkali-methanol cooking resulted in more rapid dissolution of lignin and higher retention of carbohydrate than kraft cooking. There was no difference between the sheet strength of both pulps except tear factor. The rapid delignification during alkali-methanol cooking was due to the prevention of condensation through the methylation of active benzylalcohol groups in lignin molecule [52].

Behavior of carbohydrate during alkali-methanol cooking was studied by DAIMA *et al.* [53], who concluded that the peeling-off reaction was supressed in alkali-methanol cooking. It suggests that isomerization rate of glucose end group to fructose end group might be slower in alkali-methanol cooking than in soda cooking and/or the stopping reaction might be more accelerated in the former than in the latter.

Although alcohol is easily recovered in the evaporation of black liquor, the production cost of alkali-methanol pulp is higher than that of kraft pulp. The increase of production cost is mainly due to the steam cost for methanol recovery, furthermore, additional cost of equipment for prevention of explosion and safety counterplot for operator should be taken into consideration [54].

The problem of economic recovery of alcohol in organosolv pulping makes it not yet promised within the paper industry. However the future possibilities for reducing the power requirement in recovery process can be realized by invention of a new technology.

Another organosolv pulpings, hydrogenolysis and solvolysis pulpings, were reported by SAKAKIBARA *et al.* [42, 55]. The hydrogenolysis pulping was proposed as a new process which is pollution free, energy saving, and if required, the process is possible to separate biomas into starting materials for various fermentation process or chemical conversions. Satisfactory results of this process were obtained with the solvent of cresol-water even under the reaction pressure 18 kg/cm². The screened pulp yields were 50～63%, and the strength properties of pulp sheets were almost equivalent to those of kraft pulp except tear factor [55].

Solvolysis pulping with a mixture of cresol and water at various ratio was more merit process than the hydrogenolysis process [42]. SAKAKIBARA claimed that cresol-water system might be less energy intensive among other organosolv pulping processes, because heat of evaporation of cresol is lowest within them.

This investigation was undertaken with the following objectives:

1. To determine the chemical composition of kraft, alkali-methanol, and cresol -water pulps. To determine the amount of ethanol-benzene extracts in the original wood removed during kraft, alkali-methanol, and cresol-water pulping.
2. To determine the yield of kraft, alkali-methanol, and cresol-water pulps cooked at various cooking temperature.

3. To determine the physical properties of kraft, alkali-methanol, and cresol-water pulps. To determine the effect of AQ on the yeild and the strength properties of kraft and alkali-methanol pulps.

3.2 Experimental

Cooking conditions of kraft, alkali-methanol, and cresol-water pulpings are shown in Table 7. All chips were cooked with liquor ratio of 5 ℓ/kg in an autoclave of 4 liter capacity.

Table 7. Cooking Condition and Yield of Kraft, Alkali-methanol and Cresol-water Pulps

Cooking condition	Cook. no.	Temp. (°C)	Time (min)	Yield (%)
Kraft pulp	23	180	90–90	38.9
Active alkali 20% (as Na_2O)	24	175	90–90	43.9
Sulfidity 25%	25	175*	90–90	44.9
	26	170	90–90	46.5
	27	170*	90–90	47.0
Alkali-methanol pulp	31	175	90–60	45.5
Methanol 40%	32	175*	90–60	45.0
Sodium hydroxide 40 g/ℓ	33	170	90–60	51.5
	34	170*	90–60	50.8
Cresol-water pulp	41	190	90–90	54.5
Crosol : water = 8 : 2	42	190**	90–90	52.6
	43	185	90–90	60.3
	44	185**	90–90	56.3

*) 0.1% Anthraquinone addition.
**) 10% Acetic acid addition.

The kraft pulping conditions used are 20% active alkali (as Na_2O), and 25% sulfidity. The duration of the cook is 180 min : 90 min to the maximum temperature and 90 min at the maximum temperature. The maximum temperatures studied are 170, 175 and 180°C. AQ (0.1% based on oven dry wood) is added in the case of the conditions no. 25 and 27 cooked with maximum temperature of 175 and 170°C, respectively, in order to study the effect of AQ in the kraft pulping.

The alkali-methanol pulping conditions used are 40 g/ℓ sodium hydroxide and 400 g/ℓ methanol. The duration of the cook is 150 min : 90 min to the maximum temperature and 60 min at the maximum temperature. The maximum temperatures studied are 170 and 175°C. The effect of AQ on the alkali-methanol pulping is studied by adding 0.1% AQ to the cooking liquor of conditions no. 32 and 34.

In cresol-water pulping, chips are cooked with a mixture of cresol and water in a ratio of 8 : 2. The duration of the cook is 180 min : 90 min to the maximum temperature and 90 min at the maximum temperature. The maximum temperature

studied are 185 and 190°C. The cooking liquors of conditions no. 42 and 44 contain 10% acetic acid (AA). The resultant pulps were washed with about 1% sodium hydroxide solution at about 50°C until cresol in the pulp completely removed. The pulps were then washed with water and screened on a 0.008" cut flat screen.

The physical and chemical properties of the resultant pulps were determined according to the methods described in section 2.2.4.

The delignification of the pulps were calculated by the formula described in section 2.2.4.

The percentages of removal of ethanol-benzene extracts in the orginal wood during kraft, alkali-methanol, and cresol-water pulpings were calculated by the following formula:

$$R=\frac{[W\times Ew]-[Yp\times Ep]}{[W\times Ep]}\times 100\%$$

where,

W: Wood, express as 100 (%)
R: Removal of extracts (%)
Ew: Extracts content of wood (%)
Yp: Yield of pulp (%)
Ep: Extracts content of pulp (%)

3.3 Results and Discussion

3.3.1 Chemical Composition

The pulps from kraft and alkali-methanol processes and the pulp from creasol -water process were analyzed chemically. The results of the chemical composition are given in Table 8.

These data show that the ethanol-benzene extracts of the resultant pulps are 2.6~3.5% for kraft, 1.3~2.2% for alkali-methanol, and 0.6~1.2% for cresol-water pulps. It is calculated that the percentages of removal of the total ethanol-benzene extracts in the orginal wood during kraft, alkali-methanol, and cresol-water pulpings are 53~61%, 62~80% and 78~90%, respectively.

These results indicate that the presence of solvent in the cooking liquor reduces a large amount of ethanol-benzene extracts during cooking. In the two organosolv pulping methods, the amount of ethanol-benzene extracts removed by the cresol -water process is larger than those by the alkali-methanol process. However, the amount of extracts removed in the alkali-methanol pulps cooked at 175°C (75.7~80.5%) is comparable with those from the cresol-water pulps cooked at 185°C (77.5~81.9%) as shown in Table 8.

Solubility in 1% sodium hydroxide of cresol-water pulps are extremely high i. e. 23~27%, compared to those of 1.4~2.2% of kraft and 2~4% of alkali -methanol pulps. This showed that the 1% sodium hydroxide extracts from cresol -water pulps probably contained a large amount of polyphenols and others [30, 56].

Klason lignin was determined before and after 1% sodium hydroxide extraction

Table 8. Chemical Composition of Kraft, Alkali-methanol, and Cresol-water Pulps

Type of pulp	Cook. no.	EtOH-benz. extr. (%)	Amount of EtOH-ben. extr. removed (%)	1% NaOH extr. (%)	Lignin content (%)*	Lignin content (%)**	Delignification (%)
Kraft	23	3.5	54.6	1.5	1.8	1.6	98.2
	24	3.2	53.3	2.0	3.0	1.1	96.6
	25	2.6	61.1	2.2	3.0	1.3	96.5
	26	2.9	55.1	1.6	5.3	3.5	93.6
	27	2.8	56.1	1.4	4.4	3.1	94.7
Alkali-methanol	31	1.6	75.7	2.4	7.9	6.8	90.7
	32	1.3	80.5	2.0	5.5	4.6	93.6
	33	2.2	62.2	3.9	11.7	8.8	84.5
	34	2.1	64.4	4.0	8.8	5.9	88.5
Cresol-water	41	0.8	85.5	25.2	13.0	4.1	81.7
	42	0.6	89.5	22.6	9.1	2.9	87.7
	43	0.9	81.9	27.1	16.0	4.5	75.1
	44	1.2	77.5	17.7	12.9	4.2	81.3

*) Determined before 1% sodium hydroxide extraction.
**) Determined after 1% sodium hydroxide extraction.

of the pulps. Lignin contents of the pulps before the extraction are very high as shown in Table 8. On the other hand, lignin contents of the pulps after the extraction are 1.1～3.5% for kraft, 4.6～8.8% for alkali-methanol, and 2.9～4.5% for cresol-water pulps. The reduction of Klason lignin contents of the pulps after the extraction seems to be due to the removal of polyphenols and others by 1% sodium hydroxide treatment. It could be assumed that a large amount of polyphenols remained in the cresol-water pulps because of the acidic cooking conditions.

Fig. 15 shows relation between yield and delignification of kraft, alkali-methanol and cresol-water pulps. Delignification increases in line with decreasing the yield of kraft, alkali-methanol and cersol-water pulps. Addition of AQ in kraft and alkali-methanol processes results in increasing the rate of delignification. Similar result is found in cresol-water process

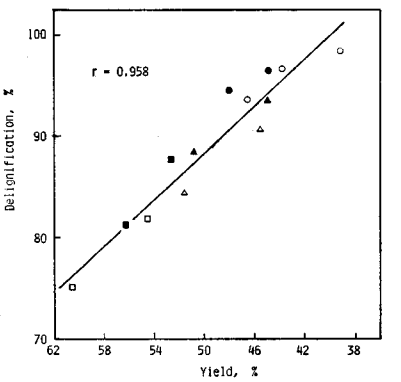


Fig. 15. Relationship between Yield and Delignification of Kraft, Alkali-methanol, and Cresol-water Pulps.

▲ = Alkali-methanol AQ
□ = Cresol-water
■ = Cresol-water AA
○ = Kraft
● = Kraft AQ
△ = Alkali-methanol

by adding 10% AA to the cooking liquor. Delignification of kraft, alkali-methanol and cresol-water pulps is in the range of 93.5~98.2%, 84.5~93,6% and 75.1~87.8%, respectively.

3. 3. 2 Yield

The total yeilds of kraft, alkali-methanol, and cresol-water pulps are in the range of 38.9~47.0%, 45.0~51.5% and 52.2~60.3%, respectively, as shown in Table 7. Increase of 5°C in cooking temperature of each process results in decreasing yields range from 2.1~4.9% for kraft, 5.8~6.0% for alkali-methanol and 3.7~5.8% for cresol-water pulps.

Fig. 16 and 17 show relationship between cooking temperature and yield of kraft, alkali-methanol and cresol-water pulps. When the cooking temperatures were raised from 170°C to 175°C and from 175°C to 180°C for kraft pulping, the yeilds droped 2.7 and 4.9%, respectively. This suggests that the higher yield drop at the cooking temperature of 180°C is caused by degradation of carbohydrate owing to the over cooking. Fig. 16 also shows that the pulp yield slightly increases by the use of AQ in kraft pulping.

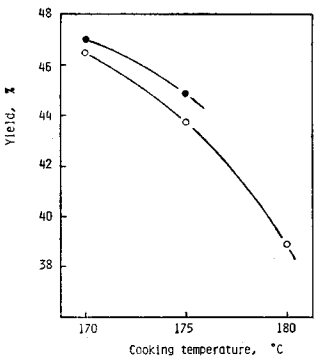


Fig. 16. Relationship between Cooking Temperature and Yield of Kraft Pulp.

○=Kraft
●=Kraft AQ

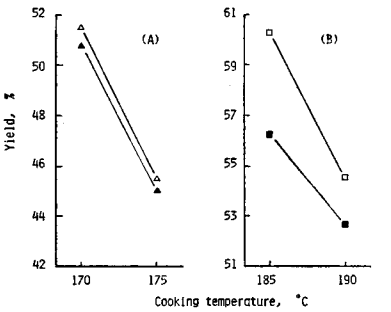


Fig. 17. Relationship between Cooking Temperature and Yield of Alkali-methanol (A) and Cresol-water (B) Pulps.

△=Alkali-methanol □=Cresol-water
▲=Alkali-methanol AQ ■=Cresol-water AA

The yields of alkali-methanol and cresol-water pulps decrease sharply by increasing 5°C of the cooking temperature as shown in Fig. 17. Addition of AQ in alkali-methanol and AA in cresol-water pulpings results in a slight decrease in the yield of alkali-methanol pulp and and a high decrease in the yield of cresol-water pulp. Effects of the cooking additives were different between kraft and organosolv cooking.

3. 3. 3 Physical Properties

The strength properties of kraft, alkali-methanol and cresol-water pulps are shown in Table 9. In kraft pulps cooked at temperatures 170, 175 and 180°C, the tear factor, breaking length, burst factor and folding endurance are in the range

Table 9. Physical Properties of Kraft, Alkali-methanol and Cresol-water Pulps

Type of pulp	Cook. no.	Freeness (mℓ CSF)	Bright. (%)	Tear factor	Break. length (km)	Burst factor	Fold. end.
Kraft	23	370	13.8	143	6.1	4.5	55
	24	395	15.1	134	6.3	4.3	45
	25	380	15.1	133	6.3	4.5	38
	26	355	14.3	130	5.8	4.6	31
	27	355	16.6	139	5.8	4.3	38
Alkali-methanol	31	378	12.4	98	4.8	3.6	20
	32	385	12.4	115	5.2	3.7	20
	33	350	11.7	112	5.6	4.2	30
	34	340	11.2	127	6.2	4.7	43
Cresol-water	41	370	9.9	63	4.0	2.1	11
	42	320	10.0	64	4.7	2.7	22
	43	387	9.8	66	3.8	1.9	8
	44	350	10.7	73	4.1	2.2	10

of 130～143, 5.8～6.3 km, 4.3～4.6 and 31～55, respectively. The tear factor and folding endurance of the pulp cooked at temperature 180°C are higher than those of the pulps cooked at temperatures 175 and 170°C. The breaking length of the pulps cooked at temperature 175°C is higher than that of the pulps cooked at temperatures 180 and 170°C. There is no substantial difference in burst factor among the pulps cooked at temperatures 180, 175 and 170°C.

At the cooking temperature 170°C (cooking nos. 26, 27, 33 and 34), there are no difference between the strength properties of alkali-methanol and kraft pulps except the slight reduction of tear factor in the former pulps. NAKANO *et al.* [57] reported that there was no difference between the sheet strength of alkali-methanol and kraft pulps from beech wood except tear factor at the same level of lignin content in pulp.

In alkali-methanol pulping, reducing the cooking temperature from 175°C to 170°C results in increasing yield 5.8～6%, increasing lignin content 1.3～2% and improving the strength properties of the pulp. Similar results were reported by MARTON and GRANZOW [58], who cooked spruce wood with ethanol-alkali at temperature 170°C and 160°C for 2.5 hr, and they found that the 55.3% yield pulp obtained at 160°C had higher lignin content, burst index and tear index than the 47.4% yield ethanol-alkali pulp obtained at 170°C.

According to SAKAKIBARA *et al.* [42, 55], pulping of birch chips with cresol -water process at 180°C, gave satisfactory results. The screened pulp yield was 50～63%, and the strength properties of pulp sheet were almost equivalent to those of kraft pulp except tear factor. However, in this experiment, the strength properties of pulps from red lauan wood produced by cresol-water process are found

to be too inferior compared with those of kraft pulps. An explanation of this fact is that the cresol-water pulps contains a large amount of polyphenols owing to the acidic cookng. The polyphenols might be responsible for the low strength properties of the cresol-water pulps.

Fig. 18 shows relation between breaking length and tear factor of kraft, alkali-methanol and cresol-water pulps. The breaking length and the tear factor of kraft pulps are high, and those of alkali-methanol pulps are close to those of kraft pulps especially in breaking length by AQ additive cooking. The effect of AQ on the strength properties of kraft pulp is not significant. However, the effect of AQ on the strength properties of alkali-methanol pulp is significant in spite of slight reduction in pulp yield (Fig. 17-A). In the case of cresol-water pulps, the breaking length and the tear factor are very low. The addition of AA into cresol-water pulping results in increasing breaking length. Similar results were found on the pulps from coniferous wood [59].

Changes of freeness during refining of kraft, alkali-methanol and cresol-water pulps are shown in Fig. 19. The numbers of revolutions in a PFI mill required for refining of the pulps from kraft and alkali-methanol processes are 4～5 times higher than that of the pulp from cresol-water process. The cresol-water pulps are produced by acid process, so that it is easier to refine the pulps than the kraft and alkali-methanol pulps produced by alkaline processes.

When the pulps from alkaline processess are refined in a PFI mill to the freeness of 350 mℓ CSF, the pulps from alkali-methanol process require more PFI mill revolution numbers than the pulps from kraft processes as shonw in Fig. 19. The differences in energy required for refining between the alkaline-methanol and kraft pulps may be due to the higher lignin content of alkali-methanol pulps than those of kraft pulps.

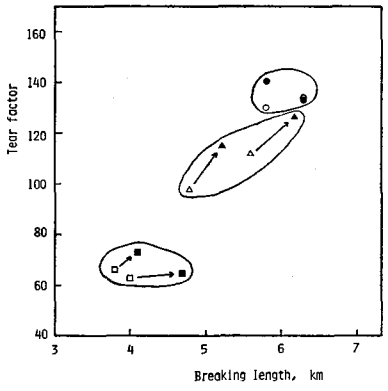


Fig. 18. Relation between Breaking Length and Tear Factor of Kraft, Alkali-methanol, and Cresol-water Pulps.

○ = Kraft
● = Kraft AQ
△ = Alkali-methanol
▲ = Alkali-methanol AQ
□ = Cresol-water
■ = Cresol-water AA

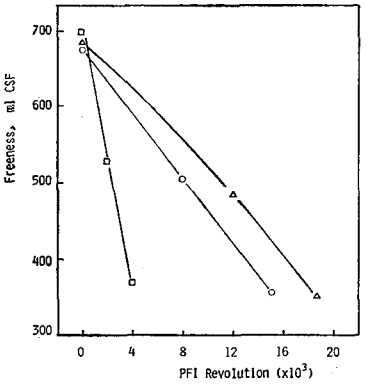


Fig. 19. Changes of Freeness during Refining of Kraft, Alkali-methanol, and Cresol-water Pulps.

○ = Kraft (170°C)
△ = Alkali-methanol (170°C)
□ = Cresol-water (190°C)

3. 4 Conclusions

Red lauan pulps produced by kraft, alkali-methanol and cresol-water processes were studied. At the cooking temperature 170°C, there were no difference between the strength properties of alkali-methanol and kraft pulps except tear factor. In alkali-methanol pulping, reducing the cooking temperature from 175°C to 170°C resulted in increasing yield 5.8～6%, increasing lignin content 1.3～2% and improving the strength properties of the pulps. The effect of AQ on the strength properties of the pulps was significant. The strength properties of the pulps produced by cresol-water process were found to be too inferior compared with those of kraft pulps.

It was suggested that the presence of solvent in the cooking liquor reduced a large amount of ethanol-benzene extracts from the wood chips during cooking. Solubility in 1% sodium hydroxide of cresol-water pulps was extremely high. It could be assumed that these extracts contained a large amount of polyphenols and others as a result of insolubility of the polyphenols in acidic cooking.

4. Bleaching

4. 1 Introduction

Chemical pulps from red lauan wood were bleached with ozone at various ozone charge in the first stage followed by hydrogen peroxide in the second and third stages. Conventional CEDED bleaching sequence was also applied as comparison with the ozone-hydrogen peroxide bleaching.

The use of ozone as an agent for removal of lignin in pulp has been known for many years, but it also attacks cellulose and hemicellulose. The removal of lignin by ozone is mainly caused by the degradation of aromatic structures of lignin [60, 61]. Carbohydrates are also degraded by ozone, which leads to lower yield and degrees of polymerization [62, 63].

In fact, ozone acts as a lignin removal agent more than a bleaching agent. Therefore, ozone is more suitable for use in the primary stage of multistage bleaching for reducing the Kappa number [64].

The amount of ozone consumption required to bleach kraft pulp from 29% brightness (unbleached pulp) to 80% brightness (single stage ozone bleached pulp) was 4.7%, however, by bleaching with three stages ozone and alternated with water-washing, the amount of ozone consumption required was 2.6% at the corresponding brightness achieved by single stage ozone bleaching [65].

The sensitivity of ozone reaction to moisture content of the pulp was shown by SECRIST and SINGTH [66], who bleached hardwood kraft pulps with ozone at a moisture contents of 40～80%, and found that the maximum rate of ozone consumption occurred at 60% moisture contents of the pulps.

In 1974, SOTELAND [64] showed that bleaching of eucalypt kraft pulps with ozone followed by hydrogen peroxide or hypochlorite gave brightness above 85%. More recently, three stages bleaching sequence was studied by SINGH in 1982 [67]

for bleaching hardwood kraft pulp with the sequence ZED (ozone, alkali extraction, and chlorine dioxide) and found that over 85% brightness could be achieved by this sequence.

LIEBERGOTT and LIEROP [68] showed that when ozone delignified spruce and mixed hardwood kraft, kraft-AQ and soda-AQ pulps were further bleached by a DED sequence, less chlorine dioxide was required in the D_1 and D_2 stages than kraft pulps bleached by a CEDED sequence to attain comparable brightness.

According to ROTHENBERG *et al.* [69], oxygen pulps could be bleached with ozone to 80% brightness in one (O_3) or three (O_3EO_3) stages. Ozone was consumed by side reaction with the degraded lignin products more in the one stage bleaching than in the three stage bleaching. Oxygen pulps bleached in two stages with combinations of ozone-hydrogen peroxide (O_3P) and ozone-peracetic acid (O_3A) were somewhat weaker in overall strength properties than those bleached with ozone alone, but the tearing strength of pulps bleached with O_3A was exceptionally high. The pulps bleached with either of the two combinations were more stable to brightness reversion than that of bleached with ozone alone.

LIEBERGOTT [70] investigated the use of ozone for groundwood brightning. At 30% consistency, about 10 point brightness gain could be achieved with a 1% ozone application together with 0.2~0.6% hydrogen peroxide on the pulp. The presence of hydrogen peroxide in the PO_3 sequence was found to be effective in preventing the yellowing of bleached pulp.

Laboratory experiment on ozone bleaching has been done successfully on kraft, sulfite and oxygen pulps, and until recently, however, there is no published paper with regard to the ozonation of alkali-methanol and cresol-water pulps. The present work was carried out to study the ozonation of alkali-methanol and cresol-water pulps as well as kraft pulps from red lauan wood. Problems might be arised from the high lignin contents of the organosolv pulp samples, where the lignin contents of alkali-methanol and cresol-water pulps were 5.5~11.7% and 9.1~16%, respectively, as described in section 3. 3. 1. It could be assumed that the ozonation of those pulps should require longer reaction time and therefore, consume much ozone for removal of their lignin.

This investigation was undertaken with the following objectives:

1. To determine the brightness and the brightness reversion of kraft, alkali -methanol and cresol-water pulps obtained by bleaching with ozone alone, ozone and hydrogen peroxide, and the CEDED sequence.
2. To determine the effect of ethanol-benzene and cyclohexane extracts on the brightness and the brightness reversion.
3. To determine the bleached yield.
4. To compare the changes in the physical properties of kraft, alkali-methanol and cresol-water pulps that occure during belaching with ozone and the CEDED sequence.

4.2 Experimental

4.2.1 Ozone and Hydrogen Peroxide Bleaching

Ozone was produced by passing oxygen through a laboratory Yokogawa ozone generator, type 2132, JIS C 1102, operated at 100 volts. A diagram of this ozone generator is shown in Fig. 20.

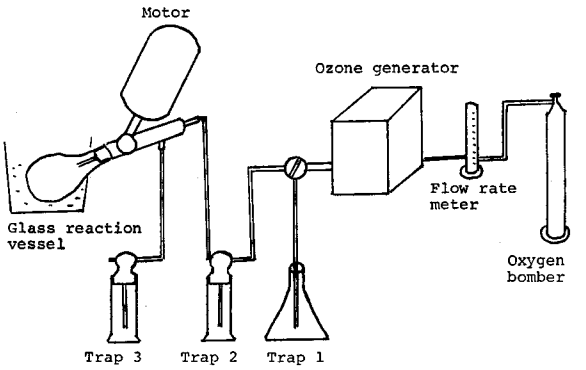


Fig. 20. A Diagram of Ozone Generator.

Prior to ozone treatment, oxygen was passed through the ozone generator at 100 ℓ/hr flow rate and the exit gases were caught in trap 1 containing sodium thiosulfate solution. Every one hour, the rate of ozone production was checked by passing ozonated oxygen into trap 2 containing 150 mℓ of 2% potassium iodide for 1 min and the concentration of ozone in trap 2 was determined. This checking was done several times until the rate of ozone production was constant. Usually 0.07 g/min or 4.2 g/hr of ozone was produced at 100 volts of operation and 100 ℓ/hr of oxygen flow rate.

Prior to ozonation, all pulp samples at approximately 75% moisture content were broken into small agregates (fluffed) to facilitate the contact with ozone and fibers, and then dried by air to 50~55% moisture content.

The fluffed pulp samples of 10 or 20 g (oven dry) were treated with the ozone -oxygen mixture in a glass reaction vessel (Fig. 20), which was rotated by a motor in room temperature for 2~60 min. During ozone treatment, the ozonated oxygen was passed through trap 2, which contained distilled water to a glass reaction vessel.

The exit gas from a glass reaction vessel was caught in trap 3 containing 2% potassium iodide. The concentration of unconsumed ozone in trap 3 was determined at the end of the treatment by titrating with 0.1 N sodium thiosulfate to a starch end point.

The ozone charge and the ozone consumed by the pulps during treatment were calculated by the following formulae:

$$\text{Ozone Charge } (\%) = \frac{\text{Ozone Introduced (g)}}{W} \times 100$$

$$\text{Ozone Consumed } (\%) = \frac{\text{Ozone Intro.(g)} - \text{Ozone in Effl.}}{W} \times 100$$

Where, W is the amount of oven dry pulp in grams.

Ozone bleached pulps were treated with 0.1% sulfurous acid for 1 hr. The treated pulps were then filtered off and washed several times with water.

Peroxide bleaching was carried out by adding the hydrogen peroxide to the pulp samples at 10% consistency for 2 hr at 70°C. Sodium silicate (5% on pulp) and magnesium sulfate (0.05% on pulp) were also added as a stabilizer. The pH of solution was adjusted to 11 by adding sodium hydroxide solution.

The conditions of ozone and peroxide bleaching of kraft, alkali-methanol, and cresol-water pulps are given in Table 10, 11 and 12, respectively. Ozone bleached pulps, which were performed at 15 and 30 min for kraft, 30 and 60 min for alkali -methanol, and 30 and 60 min for cresol-water pulps, were further bleached with hydrogen peroxide. The three stages bleaching with the sequence O_3PP (ozone 30 min, 1% H_2O_2, and 1% H_2O_2) was also applied to bleach kraft, alkali-methanol, and cresol-water pulps.

Table 10. Condition of Ozone and Hydrogen Peroxide Bleaching of Kraft Pulp

Cook. no.	Ozone					Hydrogen peroxide
	Amount of pulp (gram)	Reac. time (min)	Ozone charge (%)	Ozone cons. (%)	Yield (%)	(%)
24	10	2	1.46	1.33	99.2	
	10	5	3.53	2.82	98.2	
	20	15	5.24	3.68	97.4	1
	20	30	10.61	4.77	96.3	1 and 2
25	10	2	1.46	1.32	99.3	
	10	4	2.92	2.45	98.7	
	20	15	5.33	3.55	97.8	1
	20	30	11.01	4.69	96.8	1 and 2
26	20	30	10.46	6.25	—	1 and (1+1)
27	20	30	10.65	6.14	—	1 and (1+1)

Brightness reversion of bleached pulps was measured by the difference in k/s values before and after heat aging, defining the post color number (P. C. no.) as:

$$\text{P. C. no.} = 100\,[(k/s)_{\text{after aging}} - (k/s)_{\text{before aging}}]$$

k/s is the ratio of the coefficient of absorption to the scattering coefficient related to the reflectivity of an "infinite" pile of sheet [71]:

$$\frac{k}{s} = \frac{(1-R_\infty)^2}{2R_\infty}$$

Table 11. Condition of Ozone and Hydrogen Peroxide Bleaching of Alkali-methanol Pulp

Cook. no.	Ozone					Hydrogen peroxide
	Amount of pulp (gram)	Reac. time (min)	Ozone charge (%)	Ozone cons. (%)	Yield (%)	(%)
31	10	5	3.57	3.29	93.6	
	10	10	7.15	6.15	88.3	
	20	30	10.55	9.10	87.7	1 and 2
	20	60	21.52	12.70	86.2	1
32	10	5	3.55	3.18	93.3	
	10	10	7.10	5.86	90.1	
	20	30	10.04	8.00	89.7	1 and 2
	20	60	21.45	10.67	88.7	1
33	20	30	10.58	8.84	—	1 and (1+1)
34	20	30	10.65	8.77	—	1 and (1+1)

Table 12. Condition of Ozone and Hydrogen Peroxide Bleaching of Cresol-water Pulp

Cook. no.	Ozone					Hydrogen peroxide
	Amount of pulp (gram)	Reac. time (min)	Ozone charge (%)	Ozone cons. (%)	Yield (%)	(%)
41	20	30	10.65	9.24	—	1 and (1+1)
42	20	30	10.65	9.37	—	1 and (1+1)
43	10	10	6.81	6.30	88.2	
	10	20	13.63	11.29	83.2	
	20	30	10.44	9.45	84.0	1 and 2
	20	60	21.31	16.16	80.5	1
44	10	10	6.96	5.85	90.2	
	10	25	17.40	12.18	85.8	
	20	30	10.68	9.00	88.1	1 and 2
	20	60	21.17	14.17	85.5	1

where,

K: Coefficient of absorption

s: Coefficient of scattering

R_∞: Reflectivity of an "infinite" pile of sheet, i. e., a number of sheets sufficient so that adding more does not affect the measurement significantly.

Determinations of the brightness and the brightness reversion of bleached pulps were carried out by making two handsheets of about 3.5 g/sheet, and one of

these sheets was heated in an oven at 105°C for 24 hr.

4. 2. 2 Conventional CEDED Bleaching Sequence

In order to know the amount of chlorine used in the first stage, the Roe number of the pulps should be calculated by determining the permanganate number of the pulps. The permanganate number and the Roe number of kraft and alkali-methanol pulps were 20.3 and 5.5, and 36 and 11.6, respectively.

The bleaching conditions of CEDED sequence are shown in Table 13. Chlorination was performed in a 5% consistency at room temperature for 1 hr. The amount of chlorine used in the first stage for kraft and alkali-methanol pulps was 8.25 and 17.4%, respectively, based on pulp (Roe no. ×1.5).

Table 13. Bleaching Condition CEDED Sequence

No. Treatment	Pulp conc. (%)	Temp. (°C)	Reac. time (hr)	Chemicals (% on pulp)
1 Chlorination (C)	5	20	1	Roe No. ×1.5
2 NaOH extraction (E_1)	10	50	1	1.5
3 ClO_2 bleaching (D_1)	10	65	3	1.0
4 NaOH extraction (E_2)	10	50	1	1.2
5 ClO_2 bleaching (D_2)	10	70	4	1.0

Alkali extractions E_1 and E_2 were performed in 10% consistency at 50°C for 1 hr. The amounts of alkali used in E_1 and E_2 were 1.5 and 1.2%, respectively, based on pulp.

Chlorine dioxide treatments D_1 and D_2 were performed in 10% cosistency at 60 and 70°C for 3 and 4 hr, respectively. The amounts of chlorine dioxide used in D_1 and D_2 were 1.2 and 1%, respectively, based on pulp.

Generation of chlorine dioxide in the laboratory was carried out by Calvert's method as follows: A mixture of 40 g of sodium chlorate (powder) and 150 g of oxalic acid was put into a reaction flask and 100 mℓ of mixed solution of sulfuric acid and distilled water in the ratio of 3 : 1 (volume) was added gradually. These mixtures were heated slowly in a water bath up to 55~60°C, then yellow colored chlorine dioxide gas was generated. Chlorine dioxide gas was absorbed in chilled water. The reaction was continued until the stopping of chlorine dioxide gas generation. About 10 g of chlorine dioxide was generated for about 2 hr. The generation method of chlorine dioxide in the laboratory is shown in Fig. 21.

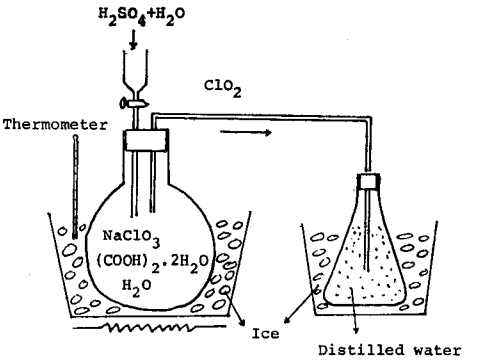


Fig. 21. Generation Method of Chlorine Dioxide in the Laboratory.

However, it is very dangerous to add

sulfuric acid solution to a reaction flask containing a mixture of sodium chlorate and oxalic acid by heating in a water bath. To prevent the danger of explosion in a reaction flask, these procedures were performed with the following modification. The addition of sulfuric acid solution into a mixture of sodium chlorate and oxalic acid was carried out at temperatures below the boiling point of chlorine dioxide (below 11°C).

A mixture of sodium chlorate and oxalic acid in a reaction flask was firstly wet with distilled water and the flask containing agents was cooled in a water bath by ice. During the addition of sulfuric acid solution, the temperature of the water bath was kept at 2~4°C. After all sulfuric acid was added, the temperature of the water bath was increased gradually up to 20°C, then yellow colored chlorine dioxide gas was generated. At the end of the reaction, the temperature could be increased up to 40°C to continue the generation of chlorine dioxide.

4. 3 Results and Discussion

4. 3. 1 Brightness and Brightness Reversion

The brightness of kraft, alkali-methanol and cresol-water pulps bleached with ozone alone, two stages O_3P (ozone and 1% or 2% peroxide) and three stages O_3PP (ozone, 1% peroxide and 1% peroxide) are presented in Table 14.

In kraft pulps, about 67% brightness is achieved by ozone treatment at 15 min reaction time and 81% brightness by bleaching with two stages O_3P (ozone 15 min and 1% H_2O_2) in both kraft and kraft AQ pulps. Increasing ozone treatment to 30 min reaction time does not result in a significant increase of the brightness of the pulps bleached with ozone alone and two stages O_3P.

In alkali-methanol pulp, the brightness achieved by ozone treatment 30 min

Table 14. Brightness of Ozone Bleached Kraft, Alkali-methanol, and Cresol-water Pulps

Bleaching	Kraft		Alk.-metha.			Cresol-water		
	24	25	31	32	41	42	43	44
Unbleaching	15.1	15.3	12.4	12.4	9.9	10.0	9.8	10.7
O_3 (15 min)	66.6	67.8	—	—	—	—	—	—
O_3 (15 min) H_2O_2 (1%)	81.2	81.7	—	—	—	—	—	—
O_2 (30 min)	70.8	70.2	54.4	63.2	33.0	33.9	32.8	45.4
O_3 (30 min) H_2O_2 (1%)	82.8	82.8	70.0	77.9	36.6	37.8	41.0	61.1
O_3 (30 min) H_2O_2 (2%)	83.0	83.4	73.2	81.6	—	—	45.4	63.4
O_3 (30 min) H_2O_2 (1%+1%)	—	—	—	—	51.6	55.3	—	—
O_3 (60 min)	—	—	68.3	72.7	—	—	60.9	70.4
O_3 (60 min) H_2O_2 (1%)	—	—	81.6	83.4	—	—	67.4	79.6

reaction time is only 54.4%, while two stages O_3P sequence, 70% brightness is achieved. At 60 min ozone treatment, the brightness increases significantly both bleached with O_3 and O_3P. In alkali-methanol AQ pulp, about 63% brightness is achieved by ozone treatment 30 min, and in further bleaching with 1% hydrogen peroxide in second stage, the brightness increases to 78%. Increasing reaction time of ozone treatment to 60 min results in increasing the brightness 9.5 point for one stage O_3 and 5.5 point for two stages O_3P.

In cresol-water pulps, ozone bleaching at 30 min reaction time is not effective in increasing the brightness, even if bleached with two stages O_3P. It was pointed out that cresol-water pulps contained a large amount of lignin and polyphenols, therefore, treatment with ozone at 30 min reaction time are not enough to enhance the brightness in the same level of the brightness of kraft pulps. However, by the treatment at 60 min reaction time followed by bleaching with 1% hydrogen peroxide, the brightness increases greatly, particularly in cresol-water AA pulp, which was achieved 80% brightness nearly the same level of the brightness achieved by kraft pulp bleached with ozone 30 min and 1% hydrogen peroxide. This suggests that it is difficult to bleach a chemical pulps to a high brightness before the greater part of the residual lignin has been removed.

Fig. 22 shows the brightness versus ozone consumption for kraft, alkali -methanol, and cresol-water pulps bleached with various ozone charge. In kraft pulps, the brightness increases sharply by increasing ozone consumption up to 3.6% and then there is a levelling off of the brightness even though ozone is consumed continuously. In alkali-methanol and cresol-water pulps, the brightness at first increases slowly up to 3% ozone consumption for alkali-methanol pulps and up to 6% for cresol-water pulps, and then increases rapidly by increasing ozone consumption for both pulps.

The amounts of ozone consumption required to bleach kraft, alkali-methanol, and cresol-water pulps at about 70% brightness are 4.7, 11.7 and 14%, respectively.

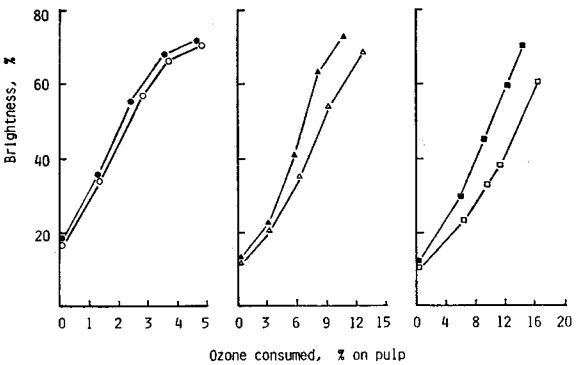


Fig. 22. Relationship between Ozone Consumption and Brightness of Kraft, Alkali-methanol, and Cresol-water Pulps after Ozonation.

○ = Kraft △ = Alkali-methanol □ = Cresol-water
● = Kraft AQ ▲ = Alkali-methanol AQ ■ = Cresol-water AA

Although the ozone consumption of the pulp from cresol-water alone is 2% higher than that of the pulp from cresol-water AA, the brightness of the former pulp is 10 point lower than that of the latter pulp. This phenomenon can be explained by referring to the lignin contents of cresol-water pulps as described in section 3. 3. 1, where the lignin content of the former pulp was 4% higher than that of the latter pulp.

It is interesting that the amounts of ozone consumption required to bleach pulps at 70% brightness are linearly related to the lignin content of each unbleached pulp as shown in Fig. 23. Fig. 23 was illustrated by plotting the lignin content of each unbleached pulp at the ordinate and ozone consumed at the abscissa. The abscissa represents the amounts of ozone consumption required to bleach pulps at 70% brightness, which are derived from Fig. 22.

Plots of ozone consumption versus ozone charge for kraft, alkali-methanol and cresol-water pulps are shown in Fig. 24. Increasing ozone charge by increasing reaction time reduces the ratio of ozone consumption to ozone charge gradually for alkali-methanol and cresol-water pulps and drastically for kraft pulp. The ratio for alkali-methanol pulp is higher than that of kraft pulp, and the ratio for cresol -water pulp is higher than that of alkali-methanol pulp. The differences in these ratios are caused by the differences in the lignin content of each unbleached pulp.

The brightness and the brightness reversion of kraft and alkali-methanol pulps bleached with ozone alone (ozone 30 min), two stages O_3P (ozone 30 min, 1% peroxide), three stages O_3PP (ozone 30 min, 1% peroxide, 1% peroxide) and conventional CEDED sequence are shown in Table 15. In kraft pulps, about 70% brightness is achieved by ozone treatment 30 min reaction time, 81% by O_3P, and 85% by O_3PP in comparison with 75.4% by the conventional CEDED sequence.

Post color number (P. C. no.) as a measure of the brightness reversion is also presented in Table 15. Aging was conducted in an oven at 105°C for 24 hr. The

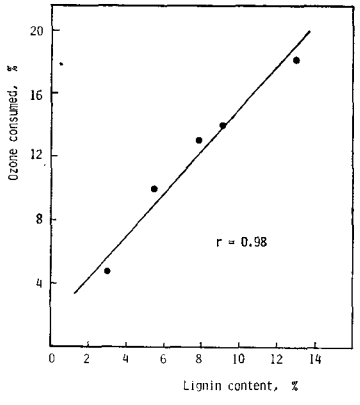


Fig. 23. Relation between Lignin Content of Unbleached Pulp and Ozone Consumed for Bleached Pulp at 70% Brightness.

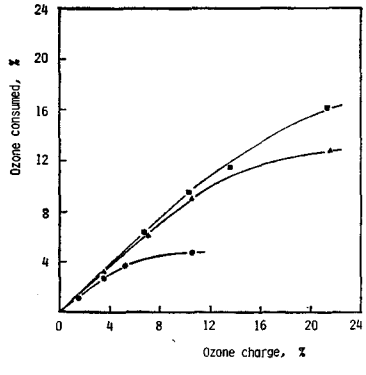


Fig. 24. Plot of Ozone Charge versus Ozone Consumed for Kraft, Alkali-methanol, and Cresol-water Pulps.

● = Kraft ▲ = Alkali-methanol
■ = Cresol-water

Table 15. Brightness and Brightness Reversion of Bleached Kraft and Alkali-methanol Pulps

	Kraft		Alk.-metha.	
	26	27	33	34
O_3				
Original brightness	68.5	70.5	54.0	59.2
Brightness after aging	61.6	62.3	47.7	52.2
P. C. no.	4.73	5.23	9.08	7.83
O_3P				
Original brightness	80.4	82.6	66.1	73.0
Brightness after aging	77.0	77.7	62.7	67.6
P. C. no.	1.04	1.37	2.40	2.27
O_3PP				
Original brightness	85.3	86.3	75.0	82.1
Brightness after aging	81.3	82.1	71.2	76.7
P. C. no.	0.89	0.86	1.66	1.59
CEDED				
Original brightness	75.4	ND	60.7	ND
Brightness after aging	65.0	ND	56.1	ND
P. C. no.	5.4	ND	4.6	ND

ND: Not determined.

P. C. no. of kraft pulp bleached with ozone alone is slightly lower than that of the pulp bleached with CEDED sequence. However, by bleaching with O_3P, the P. C. no. is reduced from 4.7 to 1.0 and further to be 0.9 by O_3PP. RAAKA *et al.* [72] and HARTLER *et al.* [73] reported that peroxide treated pulp was found to be effective in reducing the brightness reversion. ROTHENBERG *et al.* [69] found that oxygen pulp bleached with ozone followed by peroxide resulted in reducing the brightness reversion in comparison with those bleached with ozone alone or three stages O_3EO_3.

In alkali-methanol pulps, the brightness achieved by various bleaching sequences is lower than those of kraft pulps as shown in Table 15. However, in alkali-methanol AQ pulp (AM 34) bleached with O_3PP, the brightness can be achieved 82%. The P. C. nos. of alkali-methanol pulps are higher than those of kraft pulps except that of the pulp bleached with CEDED sequence. Aplication of hydrogen peroxide in O_3P or O_3PP reduces the P. C. nos. from 9.1 to 2.4 and subsequently to 1.7 in O_3PP.

It is found that the application of 2% hydrogen peroxide in O_3P is not appreciable in increasing the brightness of kraft pulps as shown in Fig. 25, however, if 2% (1%+1%) of hydrogen peroxide is applied in O_3PP sequence, about 86% brightness is achieved as shown in Table 15.

The brightness of alkali-methanol pulps bleached with O_3P sequence is illustrated

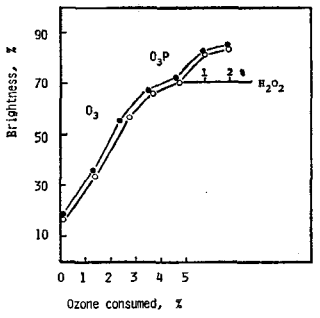


Fig. 25. Brightness of Kraft Pulp Bleached by O_3 and O_3P.
○ = Kraft
● = Kraft AQ

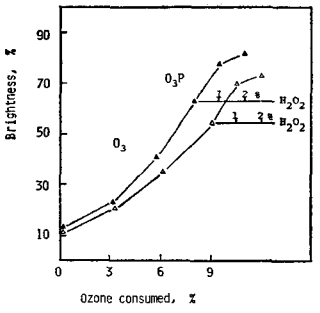


Fig. 26. Brightness of Alkali-methanol Pulp Bleached by O_3 and O_3P.
△ = Alkali-methanol
▲ = Alkali-methanol AQ

in Fig. 26, which shows that the brightness can be increased by bleaching with ozone for 30 min reaction time followed by 1 or 2% hydrogen peroxide in O_3P. It can be seen from Fig. 26 that the application of 2% hydrogen peroxide in O_3P slightly increases the brightness of alkali-methanol pulps. The effect of AQ on the brightness gain is clearly appreciable in this Figure.

4. 3. 2 The Effect of Ethanol-benzene and Cyclohexane Extracts on the Brightness and Post Color Number of Bleached Pulps

It is well known that wood extractives are responsible for pitch problem, for reducing the brightness and for making the bleached pulp unstable in light or aging. The effects of wood extractives on the brightness and the brightness reversion are given in Table 16. In kraft pulps, range of the brightness gain by extracted unbleached pulps prior to bleaching are 3.3～5.2 points and the P. C. nos. of bleached pulps are greatly reduced.

The effect of cyclohexane extracts on the brightness and the brightness reversion is higher than that of ethanol-benzene extracts. The brightness gain by extraction of unbleached pulps with cyclohexane for 24 hr prior to bleaching is 5.2 point and the P. C. no. is lowered from 5.4 to 1.8. JULLANDER and BRUNE [74] found that the brightness reversion of bleached sulfate pulp was lowered 15% by an alchol extraction, which lowered the resin content from 0.73 to 0.008%. In alkali-methanol pulp, extraction of unbleached pulps prior to bleaching results in reducing the brightness, however, the P. C. nos. can be lowered 14% for O_3, 33% for O_3P and 40% for CEDED bleaching sequence.

4. 3. 3 Bleached Yield

Relations between yield and ozone consumption of kraft, alkali-methanol and cresol-water pulps are illustrated in Fig. 27. In kraft pulps, the yields decrease slowly by increasing ozone consumption. In alkali-methanol and cresol-water pulps, the yields rapidly decrease up to 6% ozone consumption for alkali-methanol pulps and up to 9.5% ozone consumption for cresol-water pulps, and then decrease slowly by increasing ozone consumption. This suggests that in the earlier stage of the

Table 16. Effectof Ethanol-benzene and Cyclohexane Extracts on the Brightness and P.C. no. of Bleached Kraft and Alkali-methanol Pulps

	Kraft		Alk.-metha.	
	26	27	33	34
O_3				
Original brightness	68.5	70.5	54.0	59.2
P.C. no.	4.73	5.23	9.08	7.83
Bright. after extraction*	72.4	74.1	54.2	59.6
P.C. no.	3.89	3.85	7.83	5.42
O_3P				
Original brightness	80.4	82.6	66.1	73.0
P.C. no.	1.04	1.37	2.40	2.77
Bright. after extraction*	83.7	86.5	64.0	70.5
P.C. no.	0.80	0.73	1.60	1.59
CEDED				
Original brightness	75.4	ND	60.7	ND
P.C. no.	5.4	ND	4.6	ND
Bright. after extraction**	80.6	ND	58.2	ND
P.C. no.	1.8	ND	2.9	ND

*) Unbleached pulp extracted with ethanol-benzene in a ratio of 2:1 for 6 hr prior to bleaching.
**) Unbleached pulp extracted with cylohexane for 24 hr prior to bleaching.
ND Not determined.

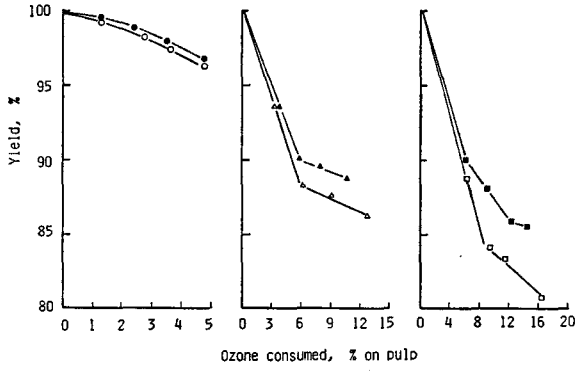


Fig. 27. Relationship between Ozone Consumption and Yield of Kraft, Alkali-methanol, and Cresol-water Pulps after Ozonation.

○=Kraft △=Alkali-methanol □=Cresol-water
●=Kraft AQ ▲=Alkali-methanol AQ ■=Cresol-water AA

reaction, ozone preferentially attacks lignin in the pulp.

It can be seen in Fig. 27 that the yields of alkali-methanol pulps are lower than those of kraft pulps, and the yields of cresol-water pulps are lower than those of alkali-methanol pulps. However, if these yields are calculated on wood, the order of the yield of the cresol-water pulps is reversed as shown in Table 17.

Table 17. Yield of Ozone Bleached Pulps

Type of pulp		Yield % on	
		Pulp	Wood
Kraft	24	96.3	42.2
	25	96.8	43.5
Alkali-methanol	33	87.7	45.2
	34	89.7	45.6
Cresol-water	43	83.2	50.2
	44	85.8	48.3

4. 3. 4 Physical Properties

The physical properties of the pulps bleached with ozone and CEDED sequence are shown in Table 18. The numbers of revolution in the PFI mill required to beat ozonated pulps are lower than that of conventional bleached pulp. Beatability of the ozonated kraft and alkali-methanol pulps is better than that of conventionally bleached pulps. The reduction in energy (PFI revolution) to beat the ozonated pulps were considered to be a result of surface modification, which promoted the increase of fiber swelling and fibrillation [66].

Table 18 shows that the strength properties of all pulps bleached with ozone are improved in comparison with those of unbleached pulps except for tear factor. In kraft pulp, the strength properties of ozonated pulp are higher than those of conventional bleached pulp. However, in alkali-methanol pulp, the strength properties of ozone bleached pulp are lower than those of conventional one.

Table 18. Comparison of Physical Properties of Pulps Bleached with Ozone and CEDED Sequence

Type of pulp	PFI rev. ($\times 10^3$)	Freeness (mℓ CSF)	Tear factor	Break. length (km)	Burst factor	Fold. end.
Kraft						
Unbleached	15	355	129.5	5.6	4.6	31
Ozone (30 min)	10	350	119.4	6.0	4.5	70
CEDED	15	350	119.7	5.5	3.9	52
Alkali-methanol						
Unbleached	16	360	121.0	5.6	4.2	37
Ozone (30 min)	8	340	104.7	5.5	3.9	41
CEDED	11	375	128.8	5.9	4.2	78
Cresol-water						
Unbleached	4	370	63.1	4.0	2.1	11
Ozone (30 min)	4	340	66.6	4.4	2.5	24
Ozone (60 min)	3.5	370	54.7	4.2	2.4	20

In cresol-water pulp, there are no substantial differences between the strength properties of the pulps bleached with ozone for 30 and 60 min reaction time except tear factor. It is interesting that even if ozone charge is doubled by increasing reaction time, the strength properties of ozone bleached pulp are not seriously affected.

4.4 Conclusions

1. Chemical pulps from red lauan wood were difficult to bleach in both ozone and the conventional CEDED sequence. They required a large amount of bleaching agent and the brightness achieved was not sufficient. However, satisfactory brightness could be achieved by bleaching at an optimum ozone consumption followed by 1% hydrogen peroxide in O_3P and additional 1% in O_3PP sequence.

2. Hydrogen peroxide bleaching was found to be effective in reducing the brightness reversion. The absence of ethanol-benzene and cyclohexane extracts in the pulp was found to improve the brightness and the brightness reversion.

3. The yields of ozone bleached alkali-methanol and cresol-water pulps were far lower than the yields of kraft pulps. However, by calculating the yield on wood, the former yields were still higher than the latter yields at the same reaction time of ozone treatment.

4. The strength properties of ozone bleached kraft pulp were higher than those of conventional bleached pulp, and in alkali-methanol pulp the order of this relation was reversed. It was interesting that even if ozone charge was doubled by increasing reaction time, the strength properties of the ozone bleached pulp were not seriously affected.

5. Wood Constituents and Their Behavior During Pulping and Bleaching

5.1 Introduction

It was found in the section 3.3.1 that the amounts of ethanol-benzene extract, which was removed from the red lauan wood chips during kraft, alkali-methanol, and cresol-water pulping, were 53-61%, 62~80%, and 78~90%, respectively.

The effect of ethanol-benzene and cyclohexane extracts on the brightness and brightness reversion has been discussed in the section 4.3.2. It was found that the brightness and the brightness reversion could be improved by extraction of unbleached pulps with ethanol-benzene or cyclohexane prior to bleaching.

In this investigation, the constituents of cyclohexane extract and their behavior during pulping and bleaching were examined. Identification of the compounds was carried out by mass spectroscopy (MS), nuclear magnetic resonance (NMR), gas liquid chromatography (GLC), and gas liquid chromatography-mass spectroscopy (GC-MS).

An investigation of birch wood constituents was reported by SELLEBY [75] who successfully identified 13 acids with even number of carbon atoms between 12 and 24 by GLC analysis. The combined fatty acid fraction, which amounted to

about 70% of the ethyl ether soluble extractives, from the fresh birch wood decreased during the seasoning of the log owing to enzymatic hydrolysis of the fatty acid esters [76].

It is well known that seasoning of the wood before pulping reduces pitch problems considerably. During wood storage the fats and resin acid esters are hydrolyzed and the resultant fatty and resin acids are oxidized [77]. It was noticed during seasoning that the amount of triglycerides decreased, which the free fatty acids increased [78]. ASSARSSON *et al.* [79] showed that chip storage, which is effective in reducing pitch problems, resulted in a loss of 50% of the fatty acids, 65% of the resin acids and about 85% of the fatty acid esters. Similar results were showed by HEMINGWAY *et al.* [80] who treated *Pinus radiata* chips in air at 60 and 85°C for periods up to 7 days and found that levopimaric, palustric, and neoabietic acids were rapidly lost and unsaturated fatty acids and unsaturated fatty acid esters were oxidized.

Phenolic fraction from sepetir paya and rengas in tropical hardwoods has recently been extensively studied by TACHIBANA *et al.* [81] and OHTANI *et al.* [82, 83]. They found that the phenolic fraction was mainly responsible for the yellow color specks appeared on a sheet of bleached pulp, which was a new type of pitch problem.

Six phenolic extractives (I–VI), responsible for the yellow specks appeared on the surface of the bleached pulp, were isolated from the wood of sepetir paya (*Pseudosindora palustris* SYM), and identified as a methyl ferulate (I), methyl *p*-coumarate (II) butein (III), sulphuretin (V), rengasin (VI), and a new compound pseudosindorin (2, 3′, 4, 5-tetrahydroxy chalcone; IV), respectively, as shown in Fig. 28 [81].

The neutral fraction of birch wood was found to act a negative effect on the brightness reversion [84] and to account for the yellowing of bleached pulp [85]. From the neutral fractions of birch wood extractives, β-sitosterol (VII), stigmastanol (VIII) [75], α-sitosterol (IX), and cyclical triterpenes of the cycloartenol (X) were isolated [86]. Furthermore, the neutral fraction contained a methyl ester of betulinic acid acetate (XI) [86] and a small quantity of squalene (XII) [87] (Fig. 29). Investigation of the components of the neutral fraction of lauan resin clarified that saturated higher hydrocarbons, saturated aliphatic alcohols, β-sitosterol (VII), ψ-taraxasterone (XIII), and ψ-taraxasterol (XIV)

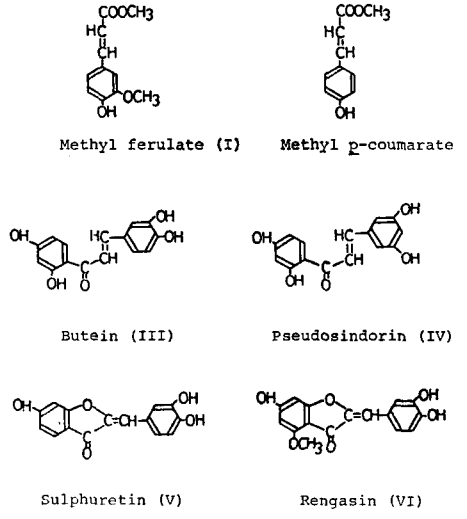


Fig. 28. Phenolic Extractives Responsible for the Yellow Specks from Sepetir Paya Wood, TACHIBANA et al. [81] and OHTANI et al. [82, 83].

were the main constituents responsible for the pitch problems caused by the fractions [88].

According to BERGMAN [85], the yellowing substances in bleached pulp resin did not come from the fatty acids. Instead, as far as it concerned birch, they were likely to consist of chlorination products derived from cyclic triterpenes with a double bond in the cyclic part.

SHIMADA [89] reported that the main constituents of the residual resin of the unbleached pulp from bangkirai wood were fatty acid alcohols and β-sitosterol (VII). In the bleached pulp, fatty alcohols, fatty acids and hydroxy fatty acids were found, but β-sitosterol was not observed.

LINDGREN [90] studied the reactions of cholesterol and its acetate with aqueous chlorine solution as model compounds for the wood sterols. He found that chlorine was mainly added to the double bond in a ring system.

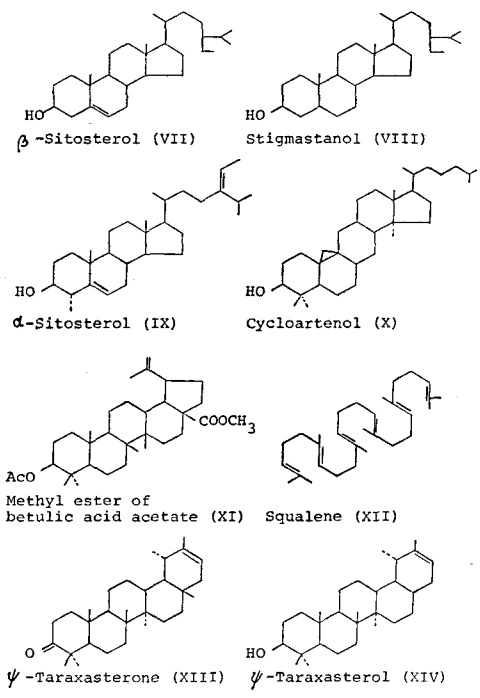


Fig. 29. Neutral Fraction Found in Birch Wood Extractives (VII–XII), SELLEBY [75], BERGMAN et al. [86], BUCHANAN et al. [87], and in Lauan Wood Extractives (VII, XIII, XIV), YAGA et al. [88].

This investigation was undertaken with the following objectives:

1. To determine the composition of the extractives in the original wood, and in the kraft, alkali-methanol, and cresol-water pulps.
2. To determine the composition of neutral fraction obtained from the cyclohexane extracts of the original wood, and kraft, alkali-methanol, and cresol-water pulps.
3. To study the behavior of the wood constituents during pulping and bleaching.
4. To study the reaction of β-sitosterol with aqueous chlorine solution in order to gain further understanding of the behavior of wood sterols during bleaching.

5.2 Experimental

5.2.1 Extraction and Preliminary Fractionation

The wood meal (500 g) was extracted with cyclohexane for 24 hr in a continuous extractor, the extracted wood meal was air dried, and then extracted with acetone for further 24 hr. The cyclohexane extract was concentrated and evaporated to dryness under a reduced pressure. The yield of the extractives was 4.55 g (0.91%).

The cyclohexane extract was fractionated by the procedure shown in Fig. 30. About 1 g of cyclohexane extract was dissolved in 150 mℓ ethyl ether and extracted

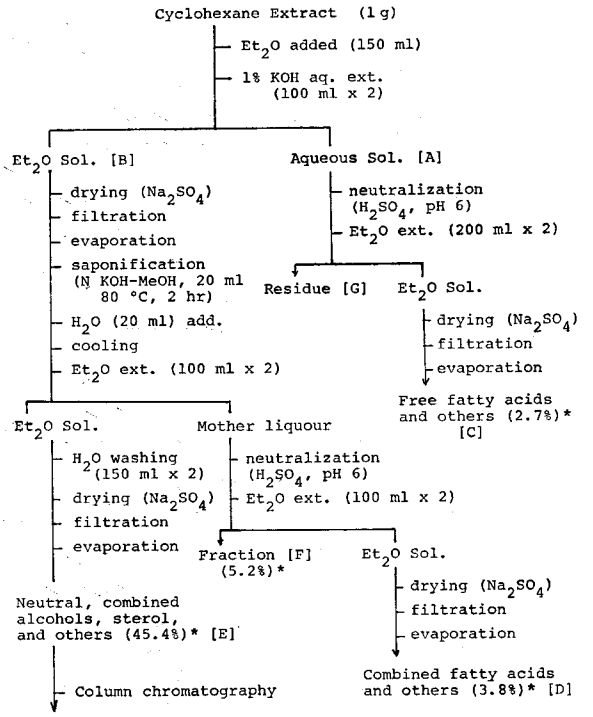


Fig. 30. Fractionation of Cyclohexane Extract from Original Wood.

*) Percentages based on cyclohexane extract.

with 1% aqueous potassium hydroxide (100 mℓ × 2). This procedure yielded three phases, ethyl ether, aqueous phases, and precipitate.

The aqueous phase was neutralized with sulfuric acid to pH 6, and then extracted with ethyl ether (100 mℓ × 2). The ethyl ether solution was dried with anhydrous sodium sulfate for one day, concentrated and evaporated to dryness under a reduced pressure. The dried fraction [C] contains mainly free fatty acids.

The ethyl ether phase after the alkaline extraction was dried with anhydrous sodium sulfate and concentrated. The extract was then saponified as follows: 10 mℓ anhydrous methanol and 20 mℓ alcoholic potassium hydroxide (*N* KOH-MeOH) were added to the extract, and the mixture was refluxed at 80°C for 2 hr. The solution was added with 20 mℓ H_2O, cooled, and extracted with ethyl ether (100 mℓ × 2).

The ethyl ether solution was washed with water (150 mℓ × 2), dried with anhydrous sodium sulfate for one day, concentrated and evaporated to dryness under a reduced pressure to yield the fraction [E]: neutrals, combined alcohols, sterols, and others.

The alkaline solution after saponification was adjusted to pH 6 with sulfuric acid, and then extracted with ethyl ether (100 mℓ × 2) and the ethyl ether solution was dried with anhydrous sodium sulfate for one day and concentrated. The dried

fraction [D] contained mainly combined fatty acids.

5. 2. 2 Chromatography

The neutral fraction [E] obtained after saponification was further fractionated by column chromatography on silica gel, using Wakogel C-200, which was eluted with a mixture of cyclohexane and ethyl acetate in a ratio of 6 : 1. The fractions were collected into a glass collector every 20 mℓ, concentrated and their constituents were monitored by thin layer chromatography (TLC).

GLC analyses were performed in a Shimadzu GC-4CM equipped with a detector FID-4C, and a glass column 3 mm in diameter, packed with silicon OV-101. The detector was connected with a Shimadzu C-R1A Chromatopac Recorder. The conditions of operation were as follows: injection temperature 330°C, column temperature 210 to 310°C, program rate 5°C/min, and carrier N_2 gas with a flow rate 30 mℓ/min.

The compounds which were isolated by column chromatography were identified by mass and NMR spectra. Other compounds were determined by GC-MS.

5. 2. 3 Chlorination of β-Sitosterol

β-Sitosterol (2 g) was dissolved in 200 mℓ carbon tetrachloride. To the solution, 50 mℓ of aqueous chlorine solution (concentration : 0.69%) was added and the solution was stirred for 20 min at room temperature. At the end of the reaction, water was added to the solution in order to dissolve excess chlorine if any.

The water phase was separated from the carbon tetrachloride solution and was further extracted with chloroform (50 mℓ × 2). The chloroform solution was combined with the carbon tetrachloride solution, dried with calcium chloride, and then evaporated to yield chlorination products.

The chlorination products were fractionated by column chromatography on silica gel using Wakogel C-200 eluted with a mixture of benzene and ethyl acetate in a ratio of 20 : 1.

5. 2. 4 Measurement of Optical Activity

Optical activities of the isolated compounds were measured by an Atago Polax. The appropriate compound was dissolved in 1 mℓ of chloroform and put into the cell (1 dm in length) and measured the optical rotations (α) of the compounds.

Specific rotations of the compounds were calculated with the following formula:

$$[\alpha]_D = \frac{\alpha \times 100}{l \times c}$$

where

α: Measured optical rotation
l: Length of cell (dm)
c: Concentration of the compound in solvent (g/dℓ)

Molecular rotations of the compounds were calculated with the following formula:

$$[M]_D = \frac{[\alpha]_D \times M}{100}$$

where

M: Molecular weight
$[\alpha]_D$: Specific rotation

5.3 Results and Discussion

5.3.1 Cyclohexane and Acetone Extract

Original wood and kraft, alkali-methanol, and cresol-water pulps were extracted with cyclohexane for 24 hr in a continuous extractor, air dried, and further extracted with acetone for 24 hr. The results of these extractions are given in Table 19.

Table 19. Amount of Extractives

Extract	Wood (%)	Kraft pulp % based on		AM pulp % based on		CW pulp % based on	
		Pulp	Wood	Pulp	Wood	Pulp	Wood
	A	B	C	D	E	F	G
Cyclohexane	0.91	3.05	1.42	2.32	1.19	0.54	0.29
Acetone	1.58	0.36	0.17	0.28	0.15	0.45	0.25
Total *1	2.49	3.41	1.59	2.60	1.34	0.99	0.54
Deresination	—	—	36.1*2	—	46.2*3	—	78.3*4

AM: Alkali-methanol; CW: Cresol-water.
*1 Samples extracted with cyclohexane for 24 hr, followed by acetone for 24 hr.
*2 (A−C)/A×100
*3 (A−E)/A×100
*4 (A−G)/A×100

The amounts of cyclohexane extract in kraft and alkali-methanol pulps are higher than that of original wood, however, the amounts of acetone extract in these pulps are 10 times lower than that of original wood. This indicates that the extractives soluble in acentone are easily removed during the pulpings, however, the extractives soluble in cyclohexane are highly resistant for their removal during the pulpings. Furthermore, some components soluble in acetone turn into cyclohexane soluble components during the pulpings. In the case of cresol-water pulping, both the cyclohexane and acetone extracts are lower than those of original wood. By combination of cyclohexane and acetone extracts, it is found that the amounts of the total extracts removed during kraft, alkali-methanol, and cresol-water pulping (deresination) are 36.1, 46.2, and 78.3%, respectively.

Cyclohexane extract of each sample was extracted with ether and then fractionated according to the scheme described in Fig. 30. The main constituent of cyclohexane extracts in red lauan wood is neutral fraction (45.4%). Only a small part of these extractives occurrs as the free and combined acids. The lower percentages of the free acid in original wood, which amounted to 2.7% is due to the considerable longer time for storage of the wood. The wood sample used in this

experiment had been felled several years ago, and chipping of the wood was conducted at least 3 years prior to the use in this experiment. ASSARSSON [91] found that chip seasoning reduces the resin content of the wood. He showed that storing of the wood chips for 3 months in a chip pile resulted in reducing 55% of the free fatty acids.

5. 3. 2 Composition of Neutral Fraction

GLC of the neutral fraction from cyclohexane extracts of the wood is shown in Fig. 31. There are 10 main peaks in this figure, and they are designated as P_1 to P_{10}, respectively.

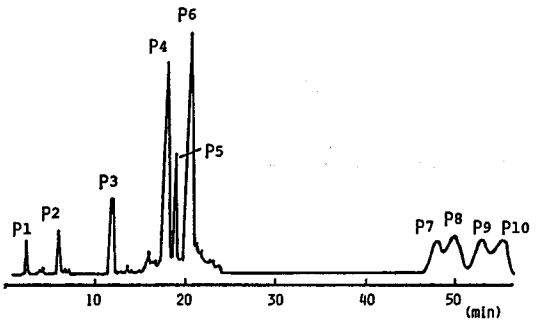


Fig. 31. GLC of the Neutral Fraction of Cyclohexane Extracts from Red Lauan Wood.

P_1: 1-Tetracosanol
P_2: 1-Hexacosanol
P_3: ϕ-Taraxasterone
P_4: β-Sitosterol
P_5: 24-Methylenecycloartanone
P_6: 24-Methylenecycloartanol
P_7: β-Sitosteryl oleate
P_8: 24-Methylenecycloartanyl oleate
P_9 & P_{10}: Esters of 24-methylenecycloartanol

Compounds P_1, P_2 and P_3 were present in a very small amount in the neutral fraction, so that, they could not be separated by column chromatography. GC-MS analysis of these compounds (P_1, P_2 and P_3) gave mass spectra as shown in Fig. 32. From these spectral aspects, the compounds P_1, P_2 and P_3 were identified as 1-tetracosanol (P_1) showing the highest mass ion peak at m/z 336 (M^+-18), 1-hexacosanol (P_2) showing the highest mass ion peak at m/z 364 (M^+-18), and ϕ-taraxasterone (P_3) showing molecular ion (M^+) peak at m/z 424. These three compounds were also detected in lauan resin by YAGA *et al.* [88].

Compounds P_4, P_5, P_6, and P_8 were separated by coloumn chromatography according to the method described in the experimental section.

Compound P_4 (β-sitosterol) obtained from the neutral fraction was recrystalyzed several times to afford crystals in plate from alcohol, which melted at 140°C. The mass spectrum of this compound is shown in Fig. 33. The molecular ion (M^+) peak is observed at m/z 414, and the elemental analysis (C=83.21%, H=12.61%

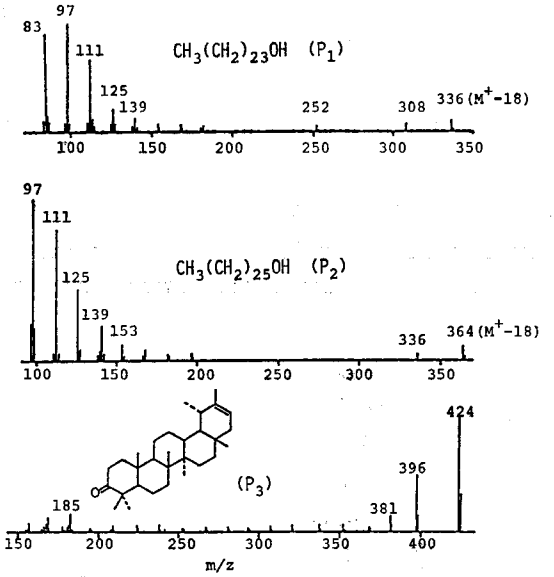


Fig. 32. Mass Spectra of Compounds P_1 (1-Tetracosanol), P_2 (1-Hexacosanol), and P_3 (ψ-Taraxasterone).

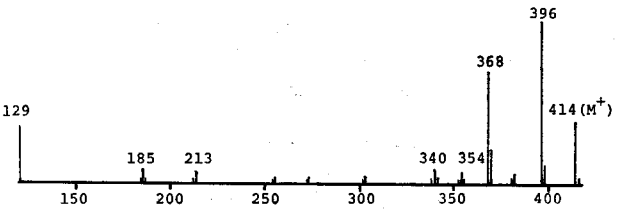


Fig. 33. Mass Spectrum of Compound P_4 (β-Sitosterol).

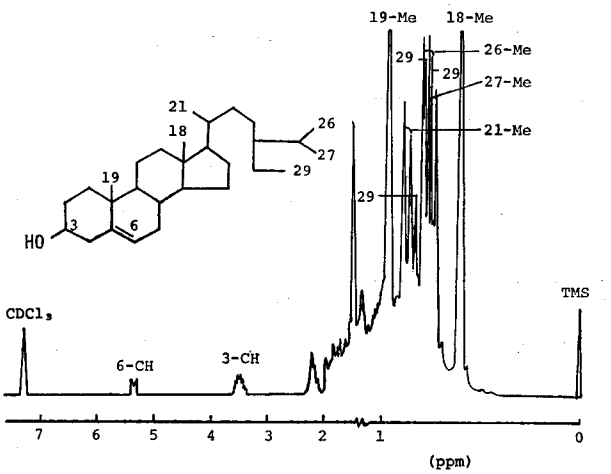


Fig. 34. NMR Spectrum and Chemical Structure of Compound P_4 (β-Sitosterol).

and O=4.18%) indicates the molecular formula $C_{29}H_{50}O_1$. The prominent ion peaks at m/z 396 and m/z 368 are corresponding to the fragments, M^+-18 and M^+-18-28, respectively.

The NMR spectrum and chemical structure of the compound P_4 are shown in Fig. 34. The chemical shifts for the two singlets due to the protons of the C-18 and C-19 methyl groups are 0.68 and 1.008 ppm, respectively. The doublet at 0.921 ppm (J=6.53 Hz) is attributed to the protons of C-21 methyl group. The signals of two methyl groups of C-26 and C-27 appear at 0.834 ppm (J=6.48 Hz) and 0.812 ppm (J=6.83 Hz), respectively. The signal of other methyl group, that is C-29, is observed as a triplet at 0.847 ppm. The signal at 5.336 ppm is assigned to C-6 =CH proton and the signal at 3.602 ppm is due to the signal of 3α-C*H*OH-. Chemical shifts of the protons of the methyl groups of C-18, C-19, C-21, C-26, and C-27 are identical with those of β-sitosterol reported by RUBINSTEIN *et al.* [92]. From these results, the compound P_4 was identified to be β-sitosterol.

Compound P_6 (24-methylenecycloartanol) was isolated from neutral fraction by coloumn chromathography. The NMR spectrum and chemical structure of the compound P_6 are shown in Fig. 35. The signals of two protons of 9 B, 19-cyclopropyl are observed at 0.34 and 0.58 ppm, with individual centers of the pair of doublet with J=4.2 Hz. The signals of two methyl groups of C-29 and C-30 attached to C-4 appear at 0.809 and 0.966 ppm, respectively. Two singlets at 0.966 and 0.898 ppm are attributed to the protons of C-18 and C-31 methyl groups. A doublet at 0.895 ppm indicates the signal of C-21 and a doublet at 1.027 ppm (J=6.38 Hz) is assigned to the protons of C-26 and C-27 dimethyl groups.

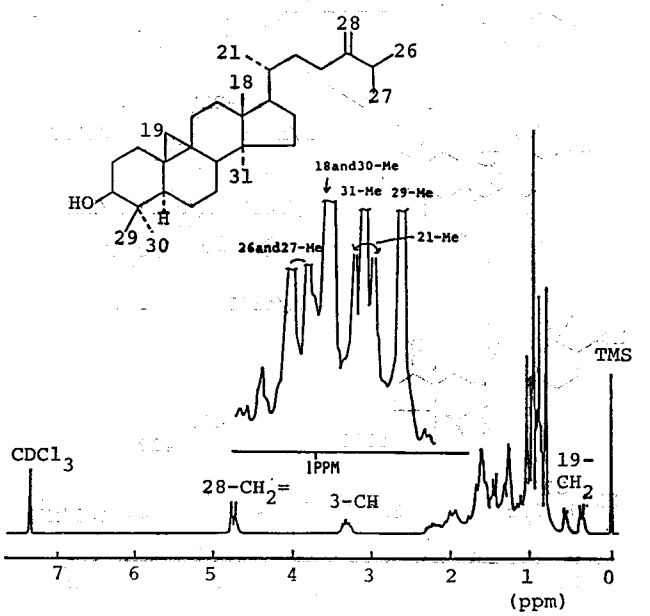


Fig. 35. NMR Spectrum and Chemical Structure of Compound P_6 (24-Methylenecycloartanol).

The multiplet at 3.285 ppm is due to the signal of 3α-C*H*OH. A doublet at 4.7 ppm is attributed to the two protons of vinyl group of C-28. All of these signals of the compound P_6 are identical with those of 24-methylenecycloartanol reported by ITOH *et al.* [93].

The mass spectrum and fragmentation of the compound P_6 are shown in Fig. 36. The mechanism for the formation of these fragments has been depicted by ALPIN and HORNBY [94]. Initial ionisation of the 9-10 bond relieves the strain imposed on ring B and this results in the fission of the activated 5-6 bond followed by transfer of one of the activated C-11 hydrogens *via* a "McLafferty" rearragement leading to form a fragment of *m/z* 300, which corresponds to the fragment derived by loss of ring A plus a hydrogen atom. Fragments at *m/z* 425, *m/z* 422, and *m/z* 407 originate from the loss of methyl radical, water, and methyl plus water from the molecular ion, respectively. The other major fragments involve dehydration (M^+-18) and following partial cleavage of the side change: *m/z* 379 (M^+-18-$C_3H_7\cdot$) and *m/z* 353 (M^+-18-$C_5H_9\cdot$). The remaining ion peaks at *m/z* 315 and *m/z* 297 correspond to the fragments derived by loss of R·($C_9H_{17}\cdot$) and R· plus water from molecular ion, respectively, as shown in Fig. 36. The isolation of 24-methylenecycloartanol (P_6) from red lauan wood is the first case and the compound is very important for pitch problems of the wood.

Compound P_5 (24-methylenecycloartanone), the corresponding ketone of 24

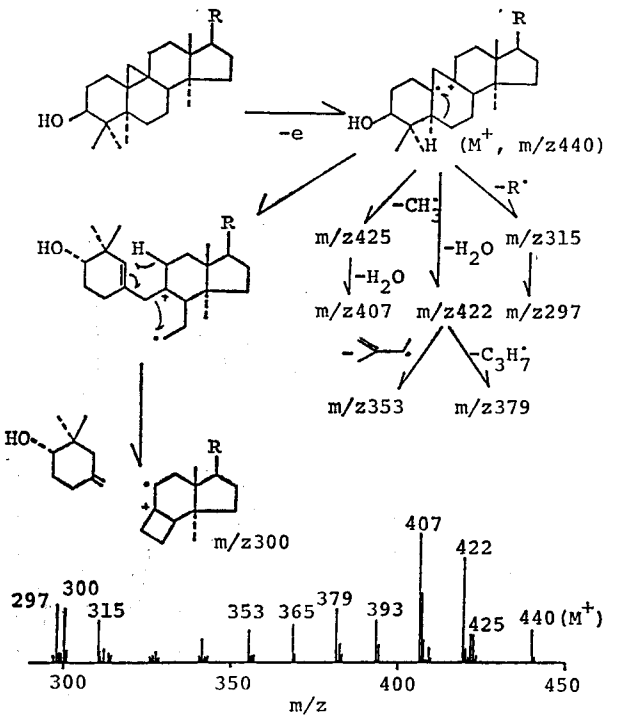


Fig. 36. Mass Spectrum and Fragmentation of Compound P_6 (24-Methylenecycloartanol).

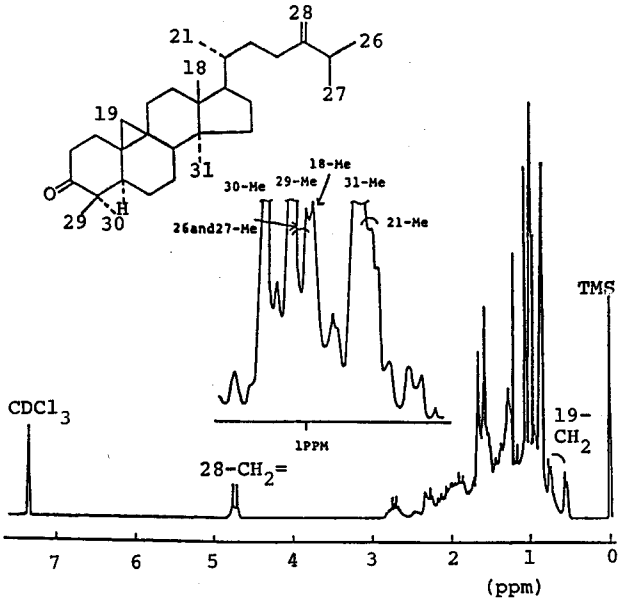


Fig. 37. NMR Spectrum and Chemical Structure of Compound P_5 (24-Methylenecycloartanone).

-methylenecycloartanol (P_6) was isolated from neutral fraction of cyclohexane extract. Its structure was established on the basis of mass and NMR spectra.

The NMR spectrum and chemical structure of the compound P_5 are shown in Fig. 37. Its NMR spectrum shows a pair of doublets at 0.578 ppm (J=4.39 Hz) and 0.791 ppm (J=4.39 Hz), which are characteristic to the protons of the doublets in cyclopropane unit. The chemical shifts for the singlets due to the protons of C-18, C-29, C-30 and C-31 methyl groups are 0.998, 1.047, 1.101, and 0.910 ppm, respectively. The doublet at 1.03 ppm is assigned to the protons of C-26 and C-27 dimethyl groups. The signal of C-21 methyl protons appears as a doublet at 0.884 ppm. A doublet at 4.7 ppm is attributed to the two protons of vinyl group of C-28. The evidence, that the signal of 3α-C*H*OH- observed at 3.285 ppm in the case of 24-methylenecycloartanol (P_6, Fig. 35) was not observed in the compound P_5 and the signals of protons of two methyl groups at C-4 appeared in lower field than those of P_6, indicated the existence of $>$C=O instead of -C*H*OH- group at C-3.

The mass spectrum of the compound P_5 is shown in Fig. 38. The molecular ion (M^+) is observed at m/z 438 which is two mass unit lower than that of P_3. The prominent ion peak at m/z 300 corresponding to $C_{22}H_{36}$• could be assigned to the fragment produced *via* a "McLafferty" rearragement as shown in Fig. 36. An intense ion peak at m/z 313 corre-

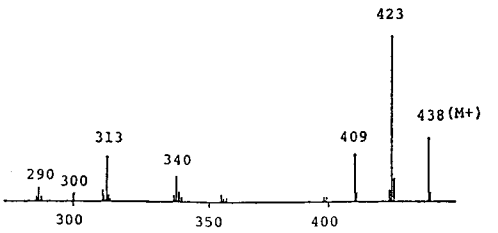


Fig. 38. Mass Spectrum of Compound P_5 (24-Methylenecycloartanone).

sponds to the fragment derived by loss of R·(C_9H_{17}·) from molecular ion. The other ion peaks at m/z 409 and m/z 423 are corresponding to the fragments arised from the molecular ion by the loss of C_2H_5·(M^+-29) and CH_3·(M^+-15), respectively. From these spectral data, the compound P_6 was identified to be 24-methylenecycloartanone. The compound was not reported so far from the woods of red lauan.

Compound P_8 (24-methylenecycloartanyl oleate) was found in a fraction containing the mixture of P_7, P_8, P_9, and P_{10} after chromatography on silica gel. Separation of these compounds was very difficult and their spots were overlapped on TLC. Fortunatelly, the compound P_8 was successfully isolated by repeated chromatography on silica gel eluted with a mixture of cyclohexane and ehyl acetate in a ratio of 20 : 1 from the mixture of compounds P_7–P_{10}. However, other compounds, P_7, P_9, and P_{10} were difficult to separate each other.

Identification of compound P_8 was carried out by mass and NMR spectra as shown in Fig. 39. Its NMR spectrum shows a doublet at 4.69 ppm derived from a vinyl group and four singlets from four C-methyl groups of C-18, C-29, C-30, and C-31 at 0.964, 0.841, 0.964, and 0.893 ppm, respectively. The doublet at 0.86 ppm is attributed for C-21 and the doublets at 1.03 ppm for C-26 and C-27. A pair of doublets at 0.338 and 0.574 ppm indicates the presence of cyclopropane protons. The chemical shifts observed in its NMR spectrum are duplicate with the chemical shifts of 24-methylenecycloartanol in accuracy within ±0.006 ppm except that of 3α-C*H*OR- proton which observed at 4.572 ppm in comparison with that of -C*H*OH- proton which observed at 3.285 ppm in the case of 24-meth-

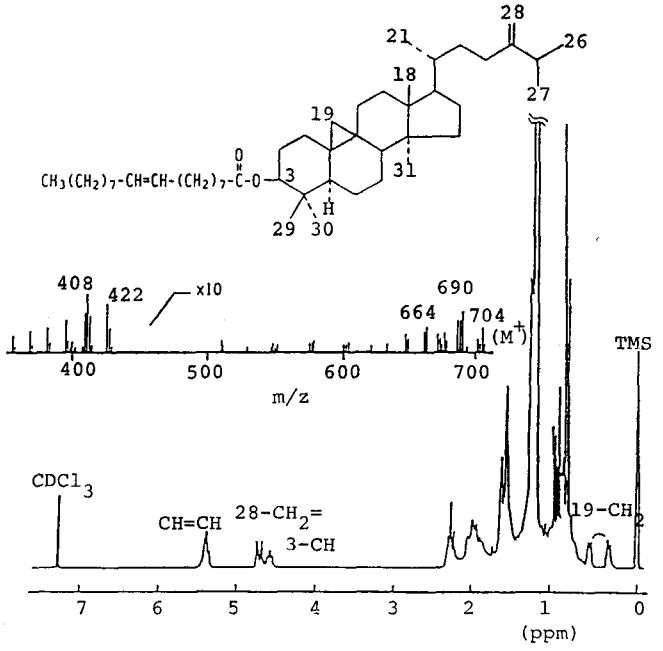


Fig. 39. Mass and NMR Spectra of Compound P_8 (24-Methylenecycloartanyl oleate).

ylenecycloartanol. The down field signal for 3α-C*H*OR- protons of the compound P_8 (24-methylenecycloartanyl oleate) is due to the inductive effect of 3β-oleate residue attached to the carbon atom. The signal at 5.34 ppm could be assigned to CH=CH protons of oleic acid residue.

The molecular ion (M^+) peak of the compound P_8 is observed at m/z 704. A prominent ion peak at m/z 422 corresponding to M^+-282 indicates that the acid bonded with 24-methylenecycloartanol at 3β-position is oleic acid (M=282).

The finding of compound P_8, the ester of 24-methylenecycloartanol and oleic acid from the red lauan wood is the first case and this finding leads to an assumption that the other compounds P_7, P_9, and P_{10} observed in the similar retention time with that of the compound P_8 are also esters. In order to prove this assumption, the fraction containing the compounds P_7–P_{10} obtained from neutral fraction by chromatography on silica gel was saponified with 1 *N* MeOH-KOH by refluxing at 90°C for 5 hr.

GLC of the neutral fraction obtained after the saponification of the fraction containing compounds P_7–P_{10} is shown in Fig. 40. The main peaks obtained are P_6 (24-methylenecycloartanol, 58%), P_5 (24-methylenecycloartanone, 18%), and P_4 (β-sitosterol, 8%). Other minor peaks are unknown. The compound P_5 must be the oxidation product of the compound P_6 because the compound P_5, which has no hydroxyl group in the molecule, could not be existed as esters. Therefore, 24-methylenecycloartanol becomes 76% (58+18%) of the neutral component of the esters fraction. This suggests that compounds P_7–P_{10} are esters of 24-methylenecycloartanol and fatty acids except an ester of β-sitosterol.

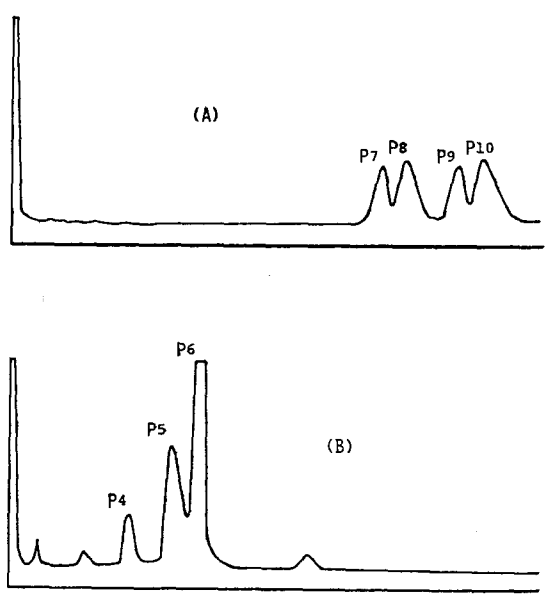


Fig. 40. The GLC of Compounds P_7–P_{10} (A) and Their Hydrolyzates (B): Compounds P_4 (β-Sitosterol), P_5 (24-Methylenecycloartanone), and P_6 (24-Methylenecycloartanol).

GC-MS analysis of peak P_7 gives the molecular ion (M^+) peak at m/z 678 corresponding to that of dehydration products derived from β-sitosterol and oleic acid (414+282-18). Therefore, the occurrence of compound β-sitosterol, peak P_4 in Fig. 40 is believed to be arised from peak P_7 after saponification.

5. 3. 3 Behavior of Wood Constituents during Pulping and Bleaching

The composition of cyclohexane extract from the orginal wood and kraft, alkali-methanol, and cresol-water pulps are shown in Table 20. There is an increase of free acids [C] and neutral fraction [E] during kraft and alkali-methanol pulping in comparison with that of original wood.

Table 20. Composition of Cyclohexane Extract

Fraction*1	% Based on Cyclohexane Extract				% Based on Wood			
	Wood	KP	AMP	CWP	Wood	KP	AMP	CWP
Cyclohex. Ext.*2	0.91	3.05	2.32	0.54	0.91	1.42	1.19	0.29
Cyclohex. Ext.	100	100	100	100	100	156	131	32
Neutrals [E]	45.4	42.6	63.7	45.5	45.5	66.5	83.4	14.6
Combined acids]D]	3.8	0.8	1.7	5.0	3.8	1.2	2.2	1.6
Fraction [F]	5.2	23.7	10.5	10.3	5.2	37.0	13.8	3.3
Free acids [C]	2.7	21.7	19.3	3.6	2.7	33.9	25.3	1.2
Others	42.9	11.2	4.8	35.6	42.9	17.5	6.3	11.4

*1 The designation of the fraction [C]−[F]: see Fig. 30.
*2 See Table 19.
KP: Kraft pulp; AMP: Alkali-methanol pulp; CWP: Cresol-water pulp.

As mentioned previously, the amounts of cyclohexane extracts from the kraft and alkali-methanol pulps are larger than that of original wood. The increases of cyclohexane extracts are considered to be attributed to the chemical changes of the acetone soluble components during the kraft and alkali-methanol pulpings. This means that the increase in neutrals [E] and free acids [C] in both the pulps comes from the acetone soluble components in the original wood. However, it is difficult to estimate the actual structures of the acetone soluble components in this experiment.

Changes of the constituents of the neutral fraction during kraft, alkali-methanol, and cresol-water pulping are shown in Fig. 41. From the neutral fraction of the original wood, small peaks are observed for β-sitosterol (P_4), 24-methylenecycloartanone (P_5), and 24-methylenecycloartanol (P_6), and relatively large peaks for the esters (P_7–P_{10}). In kraft pulping, the major change is the increase of peaks P_4 (β-sitosterol), P_5 (24-methylenecycloartanone), and P_6 (24-methylenecycloartanol), and the decrease of peaks P_7–P_{10}. The increase of peaks P_4 and P_6 is due to the hydrolysis of the compounds corresponding to the peaks P_7–P_{10} during pulping. The increase of peak P_5 is derived from the oxidation of compound P_6 (24-methylenecycloaratnol). In alkali-methanol pulping, the esters (peaks P_7–P_{10}) are completely absent and

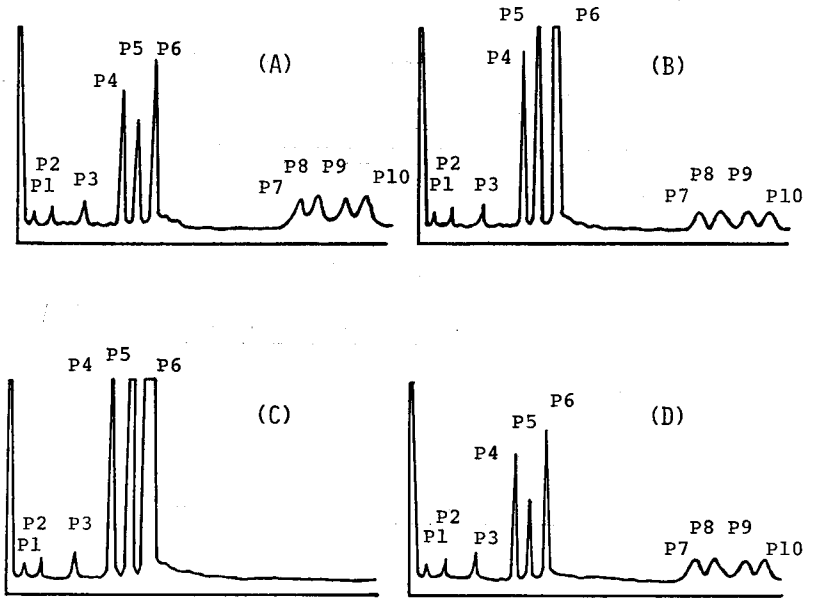


Fig. 41. Changes of Neutral Fraction during Kraft, Alkali-methanol, and Cresol-water Pulping. The designations of simbols: see Fig. 31.

(A): Original woods, (B): Kraft pulp, (C): Alkali-methanol pulp, (D): Cresol-water pulp.

large peaks observed are for β-sitosterol (P_4), 24-methylenecycloartanone (P_5), and 24-methylenecycloartanol (P_6). This suggests that the esters were completely hydrolyzed to β-sitosterol and 24-methylenecycloartanol during alkali-methanol pulping. A reason of this is that the cooking liquor of alkali-methanol pulping, which consists of methanol, sodium hydroxide and water, acts as a more effective saponification reagent than kraft cooking liquor.

The phenomenon was confirmed by an experiment using isolated fraction containing esters. When the fraction was saponified with 1*N* MeOH-KOH at 90°C for 5 hr, the esters were completely hydrolyzed and β-sitosterol, 24-methylenecycloartanol, and 24-methylenecycloartanone were formed in the hydrolyzates. 24-Methylenecycloartanone is derived from 24-methylenecycloartanol by oxidation.

Unbleached kraft pulp was bleached with CE and CEDED sequences, then the bleached pulps were extracted with cyclohexame for 24 hr. The resultant extracts were chromatographed on GLC in order to elucidate the behavior of the neutral fraction during bleaching.

Changes of the kraft pulp constituents during bleaching are shown in Fig. 42. Compound P_1 (1-tetracosanol) and compound P_2 (1-hexacosanol) are found in the extracts of CE and CEDED bleached kraft pulp, indicating that the compounds P_1 (1-tetracosanol) and P_2 (1-hexacosanol) are not changed during bleaching. However, ψ-taraxasterone, β-sitosterol, 24-methylenecycloartanol, and their related compounds are not observed. Instead of disappearance of these compounds, thirteen

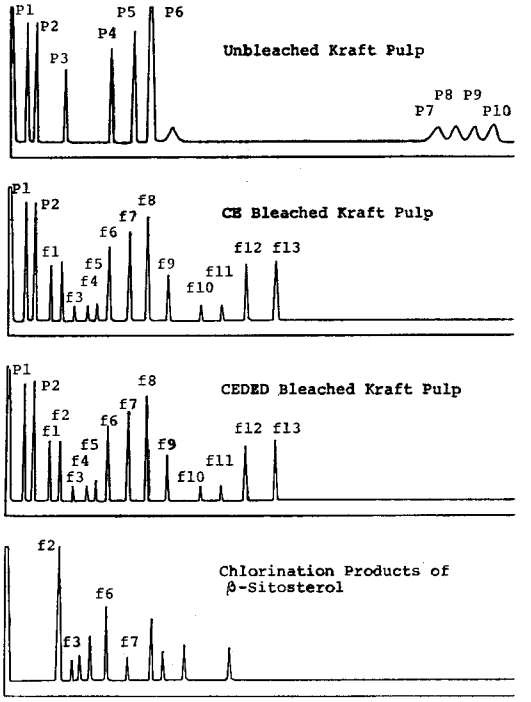


Fig. 42. Changes of the Neutral Fraction from Kraft Pulp during Bleaching and Chlorination Products of β-Sitosterol.
Designations of P_1–P_{10} as in Fig. 31, and f_1–f_{13} are newly formed.

new peaks occur. They are designated as f1 to f13, respectively, as shown in Fig. 42. By comparison the retention times of the new peaks occurred in CE and CEDED bleaching sequences with those of peaks observed in the chlorination products of β-sitosterol, it is found that f2, f3, f6, and f7 originate from β-sitosterol. Other peaks probably derive from ψ-taraxasterone, 24-methylenecycloartanol and its related compounds. There is no difference on GLC in the reaction products of kraft pulp constituents between two stages CE and five stages CEDED bleaching sequences. This implies the significant difficulty of removal of the neutral compounds in the pulps by both the CE and CEDED bleaching procedures, even though chlorination is sufficient enough in the first stage C in both sequences.

The cyclohexane extracts of unbleached, two stages CE bleached, and five stages CEDED bleached kraft pulps from red lauan wood are shown in Table 21. There is no significant difference between the amounts of cyclohexane extracts removed during two stages CE and five stages CEDED sequences. Only a small amounts of

Table 21. Cyclohexane Extract of Unbleached, Two Stages CE Bleached, and Five Stages CEDED Bleached Kraft Pulp

	Cyclohexane extract content (%)*
Unbleached	3.05
CE Bleached	2.70
CEDED Bleached	2.52

* Unbleached pulp basis.

cyclohexane extracts is removed during bleaching (Table 21). Similar results were reported by KAYAMA *et al.* [95].

The structures of the new peaks (f1–f13) in Fig. 42 are not yet known. However, it could be assumed that the ring double bonds in ψ-taraxasterone and β-sitosterol, and the double bonds in vinyl group of the 24-methylenecycloartanol and its related compounds are the main attacking point of chlorine.

The reaction between cholesterol and chlorine has been examined by LINDGREN [90] and BARTON *et al.* [96], and they found that chlorine was mainly added to the double bond in a ring system of the steroid. The main chlorination products obtained were a *trans*-diaxial dichloro compound, two *trans*-diaxial chlorohydrins (5α-chloro-6β-hydroxy- and 6β-chloro-5α-hydroxycholestans), and 5α-chloro-6-on-cholestan [90].

5.3.4 Reaction of β-Sitosterol with Aqueous Chlorine Solution

The resin in plup influences pitch problems, such as, resin specks, brightness reduction, and yellowing of the bleached pulp during storing or heating. It was found in the section 5.3.3 that ψ-taraxasterone, and β-sitosterol, 24-methylenecycloartanol and their related compounds underwent reaction with chlorine during bleaching. In order to elucidate the behavior of these compounds during belaching, it is important to study the reaction of isolated ψ-taraxasterone, and β-sitosterol, 24-methylenecycloartanol and their related compounds with aqueous chlorine solution. However, it is very difficult to isolate and purify ψ-taraxasterone, and 24-methylenecycloartanol and its related compounds in a large amount sufficient for the chlorination study. On the other hand, β-sitosterol is able to obtain commercially. For this reason, β-sitosterol was used as a model compound containing a double bond in its structure in this experiment.

TLC of β-sitosterol, stigmastanol, and chlorination products of β-sitosterol are shown in Fig. 43. Seven chlorination products were isolated from the chlorination products of β-sitosterol, which are designated as S_1 to S_7, respectively. Stigmastanol was also isolated from the mixture of chlorination products of β-sitosterol.

Compound S_1 was obtained by recrystallization from acetone, yielding a crystalline substance with mp 70°C. Its R_f value on TLC (developed with a mixture of benzene and ethyl acetate in a ratio of 5 : 1) is 0.84. Mass spectrum of compound S_1 showed the molecular ion (M^+) peak at m/z 794. However, its structure was not identified. The fragmentation in its mass spectrum indicated that it contained neither hydroxyl nor chlorine groups. Compound S_2 was obtained by recrystallization from ethyl acetate, yielding a

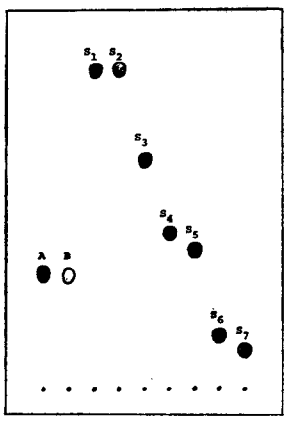


Fig. 43. TLC of β-Sitosterol (A), Stigmastanol (B), and Chlorination Products of β-Sitosterol (S_1 to S_7).
Eluent; benzene : ethyl acetate =5 : 1 (v/v).

crystalline substance with mp 236°C. Its R_f value was the same (0.84) with that of compound S_1. Mass spectrum of compound S_2 showed the molecular ion (M^+) peak at m/z 484. The fragmentation in its mass spectrum indicated that it probably contained one hydroxyl and two chlorine groups. However, its structure was not identified. Compound S_3 (3β-hydroxy-5β, 6α-dichlorositostan) was obtained by repeated coloumn chromatography on silica gel followed by recrystallization from ethanol, yielding a crystalline substance, melted at 113°C. Compound S_4 (3β-hydroxy-5α, 6β-dichlorositostan) was the main compound obtained by recrystallization from eheanol, yielding a crystalline substance with mp 148°C. Compound S_5 (3β, 5β-dihydroxy-6α-chlorositostan) was obtained by repeated chromatography on preparative TLC followed by recrystallization from ethanol, yielding a crystalline substance with mp 136°C. Compounds S_6 and S_7 were obtained by repeated coloumn chromatography on silica gel eluted with a mixture of chloroform and methanol in a ratio of 50 : 1 followed by recrystallization from methanol. The compound S_6 and S_7 melted at 150° and 160°C, respectively. The mass spectrum of compound S_6 showed the molecular ion (M^+) at m/z 430, however, its structure was not identified. The compound S_7 was identified to be 3β, 6α-dihydroxy-5β-chlorositostan.

The molecular ion (M^+) peak, melting point, R_f value, and yield of the compounds obtained by chlorination of β-sitosterol are listed in Table 22. The yields were determined from the weights of the impure fractions separated by coloumn chromatography.

The mass fragmentations of the compounds S_3 and S_4 are the same except the difference in the relative intensities of the fragment ions (Fig. 44 and 45). The highest mass ions at m/z 484 in both the spectra are corresponding to the molecular ions [M^+] of the dichloro derivatives of β-sitosterol. The intense ion peaks at m/z 412, m/z 394, and m/z 267 correspond to the fragment ions formed by successive loss of 2HCl, H_2O, and C_9H_{19}· from the molecular ion in both the cases. Owing to the position of the double bond in β-sitosterol, the dichloro derivatives

Table 22. The Compounds Obtained by Chlorination of β-Sitosterol

	Molecular ion (M^+) peak	Melting point (°C)	R_f* value	Yield** (%)
Stigmastanol	m/z 416	139	0.27	10.0
Unidentified (S_1)	m/z 794	70	0.84	1.2
Unidentified (S_2)	m/z 484	236	0.84	9.5
3-Hydroxy-5β, 6α-dichlorositostan (S_3)	m/z 484	113	0.60	14.7
3β-Hydroxy-5α, 6β-dichlorositostan (S_4)	m/z 484	148	0.40	27.0
3β, 5β-Dihydroxy-6α-chlorositostan (S_5)	m/z 466	136	0.37	9.6
Unidentified (S_6)	m/z 430	150	0.13	6.8
3β, 6α-Dihydroxy-5β-chlorositostan (S_7)	m/z 466	160	0.10	15.2

* On TLC [benzene : ethyl acetate = 5 : 1 (v/v)].

** Yield of the crude fractions separated by column chromatography.

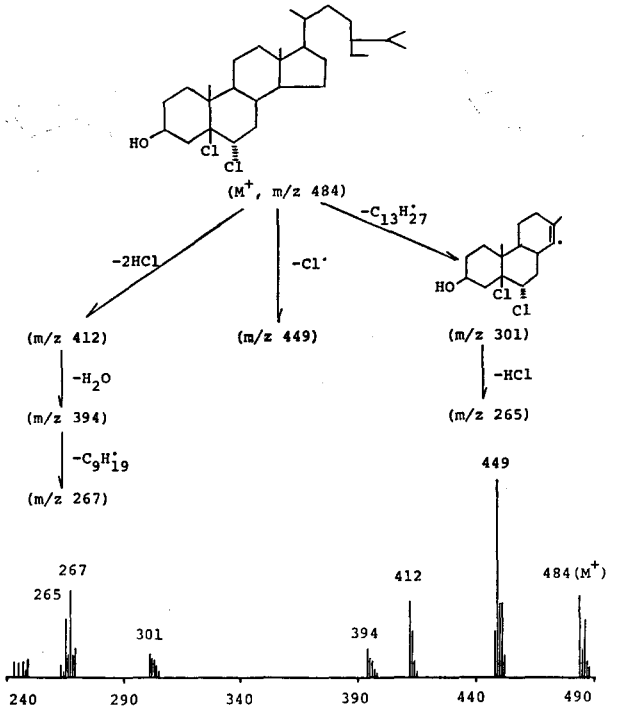


Fig. 44. Mass Spectrum, Chemical Structure, and Fragmentation of Compound S_3 (3β-Hydroxy-5β, 6α-dichlorositostan).

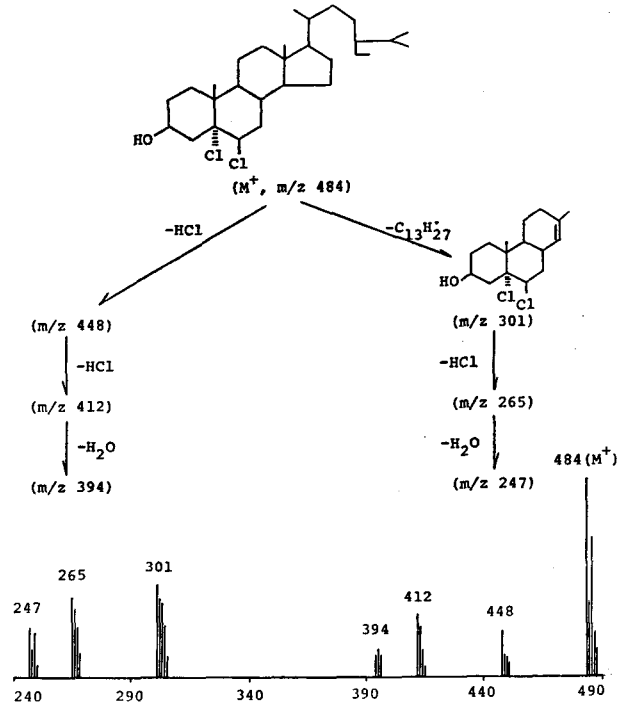
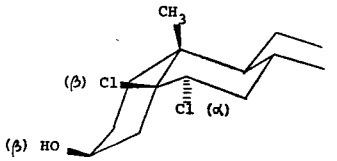
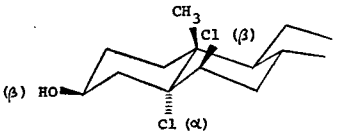


Fig. 45. Mass Spectrum, Chemical Structure, and Fragmentation of Compound S_4 (3β-Hydroxy-5α, 6β-dichlorositostan).



trans-Diequatorial partial structure of 3β-hydroxy-5β, 6α-dichlorositostan (S_3).



trans-Diaxial partial structure of 3β-hydroxy-5α, 6β-dichlorositostan (S_4).

Fig. 46. Configurations of the Compounds S_3 and S_4.

might be the stereoisomers of 5α, 6β-dichloro (*trans*-diaxial)- and 5β, 6α-dichloro (*trans*-diequatorial)-β-sitosterols (Fig. 46).

The chemical shifts of the methyl groups of the compounds S_3 and S_4 are listed in Table 23. The downfild shifts of the signals of protons at C-19 methyl groups of both the compounds must be the reflection of the stereochemical conformations of both compounds, but it is difficult to explain the difference from NMR

Table 23. ^{1}H-NMR Chemical Shifts of Methyl Groups of Stigmastanol, and β-Sitosterol and its Chlorination Products in $CDCl_3$ (δ ppm)

Compound	C-18 s	C-19 s	C-21 d	C-26 d	C-27 d	C-29 t
Stigmastanol	0.645	0.800	0.900	0.825	0.812	0.838
β-Sitosterol	0.680	1.008	0.921	0.834	0.812	0.847
S_3	0.653	1.147	0.900	0.829	0.810	0.847
S_4	0.699	1.360	0.914	0.834	0.812	0.847
S_5	0.650	0.981	0.904	0.829	0.810	0.847
S_7	0.677	1.277	0.911	0.831	0.812	0.847

s : singlet.
d : doublet.
t : triplet.
S_3 : 3β-Hydroxy-5β, 6α-dichlorositostan.
S_4 : 3β-Hydroxy-5α, 6β-dichlorositostan.
S_5 : 3β, 5β-Dihydroxy-6α-chlorositostan.
S_7 : 3β, 6α-Dihydroxy-5β-chlorositostan.

Table 24. ^{1}H-NMR Chemical Shifts of Protons Attached to C-3 and C-6 of β-Sitosterol and of its Chlorination Products in $CDCl_3$ (δ ppm)

Compound	C-3	C-6
β-Sitosterol	3.602	—
3β-Hydroxy-5β, 6α-dichlorositostan (S_3)	4.497	4.154
3β-Hydroxy-5α, 6β-dichlorositostan (S_4)	4.305	4.349
3β, 5β-Dihydroxy-6α-chlorositostan (S_5)	4.306	4.176
3β, 6α-Dihydroxy-5β-chlorositostan (S_7)	4.326	3.954

spectra. The chemical shift of 3 C*H* proton of the compound S_3 is slightly larger than the other compounds (S_4, S_5, and S_7) as shown in Table 24. The difference must be come from the difference in the stereochemistry of both the compounds. From MS and NMR data, it is difficult to determine the stereochemical relationship of the compounds S_3 and S_4.

The behavior of the compounds S_3 and S_4 on TLC and the molecular rotations of them, therefore, become very important to determine the conformations of the two stereoisomers. When the results reported by LINDGREN [90] that 5β-substituted derivative of the cholesterol was eluted earlier than 5α-substituted derivative was applied to the behavior of the compounds S_3 and S_4 on TLC, the compound S_3 with a higher R_f (0.60) might be a 5β-substituted compound and S_4 with a lower R_f (0.40) a 5α-substituted compound. This assumption is supported by the result of optical rotation measurements of the compounds S_3 and S_4. The molecular rotations $[M]_D$ of the compounds S_3 and S_4 are +578° and −185°, respectively, as shown in Table 25. The compound S_4 with the lower R_f on TLC shows levo

Table 25. Specific and Molecular Ratations of Chlorination Products of β-Sitosterol (A) and Cholesterol (B)

	$[\alpha]_D$		$[M]_D$	
	A*1	B	A	B
Dichloro derivatives*2				
5β-Chloro-6α-chloro-	+119 (c=0.2)	—	+578	—
5α-Chloro-6β-chloro-	−38 (c=4.8)	−26.9	−185	−123*3
	—	−34.6*4	—	−173
	—	−32.8*4	—	−164
	—	−46.9	—	−215*4
Chlorohydrin derivatives*5				
5β-Hydroxy-6α-chloro-	+39 (c=2.0)	+39.0*4	+182	+188
5α-Hydroxy-6β-chloro-	—	−35.5*4	—	−171
5β-Chloro-6α-hydroxy-	+88 (c=0.6)	—	+428	—
5α-Chloro-6β-hydroxy-	—	−25.0*6	—	−110
	—	−24.0*7	—	−116

*1 Measured in chloroform.
*2 β-Sitosterol dichloro derivative, M=486; Cholesterol dichloro derivative, M=458; Cholesterol dichloro monoacetyl derivative, M=500.
*3 Free, BARTON *et al.* [96].
*4 Acetate, LINDGREN [90].
*5 β-Sitosterol chlorohydrin derivative, M=467.5; Cholesterol chlorohydrin derivative, M=439.5; Cholesterol chlorohydrin monoacetyl derivative, M=481.5.
*6 Free, LINDGREN [90].
*7 Free, ALT *et al.* [97].

rotatory and the value of $-185°$ is very similar to that of 5α-chloro-6β-chloro derivative of cholesterol ($[M]_D$-123°). On the other hand, the compound S_3 with the higher R_f on TLC shows dextrorotatory ($[M]_D$+578°). The results indicated that the compound S_3 is 3β-hydroxy-5β, 6α-dichlorositostan and the compound S_4 is 3β-hydroxy-5α, 6β-dichlorositostan as shown in Fig. 46.

The mass fragmentations of the compounds S_5 and S_7 are the same except the difference in the relative intensities of the fragment ions as shown in Fig. 47 and 48. The highest mass ion peaks at *m/z* 466 in both the spectra are corresponding to the molecular ions (M^+) of the chlorohydrin derivatives of β-sitosterol. The intense ion peaks at *m/z* 448, *m/z* 430, and *m/z* 394 correspond to the fragments formed by successive loss of H_2O, H_2O, and HCl from molecular ion. Owing to the position of the double bond in β-sitosterol, the chlorohydrin derivatives might be the positional isomers of *trans*-diequatorial or *trans*-diaxial configurations (Fig. 49).

The chemical shifts of the methyl groups of the compounds S_5 and S_7 are listed in Table 23, and of the protons at C-3 and at C-6 in Table 24. The NMR data show clearly the positions of hydroxy and chlorine in both the compounds S_5 and S_7, and their stereochemical relationship. Namely, the downfield shift of 6-C*H* proton in the compound S_5 (4.176) than that of S_7 (3.954) is due to the stronger electron negativity of chlorine at 6-C in the compound S_5 than that of oxygen in the compound S_7. In addition, the downfield shift of the protons of C-19 methyl groups of the compounds S_7 (1.277) compared to that of the compound S_5 (0.981) which is similar to that of β-sitosterol implies that the chlorine at C-5 in the compound S_7 is β-configuration. The similar downfield shift is observed in the case of the compound S_3 which has chlorine at C-5 in the β-configuration. These data indicate that the compound S_5 is 3β, 5β-dihydroxy-6α-chlorositostan as shown in Fig. 49.

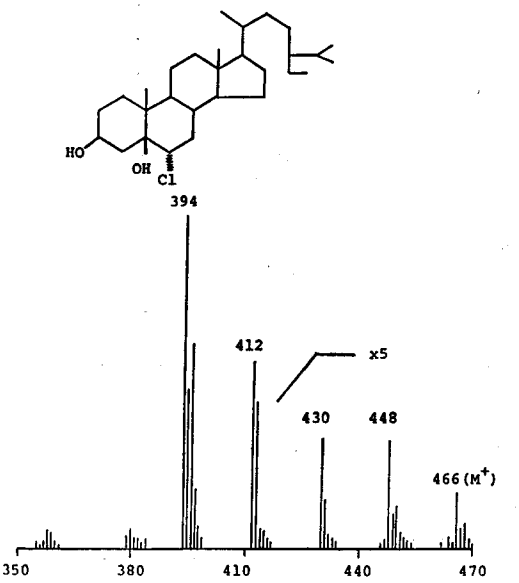


Fig. 47. Mass Spectrum and Chemical Structure of Compound S_5 (3β, 5β-Dihydroxy-6α-chlorositostan).

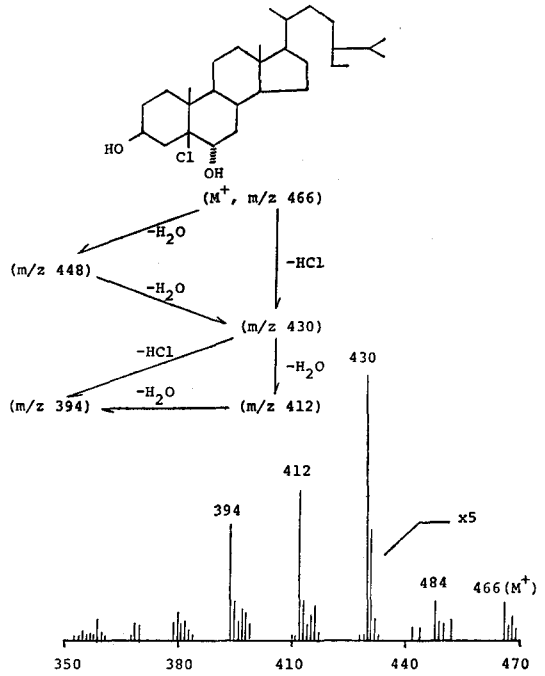
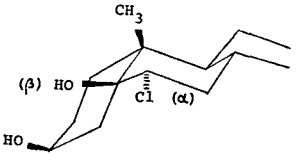
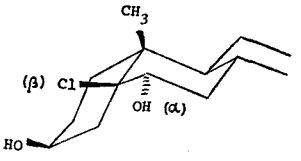


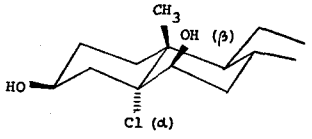
Fig. 48. Mass Spectrum, Chemical Structure, and Fragmentation of Compound S_7 (3β, 6α-Dihydroxy-5β-chlorositostan).



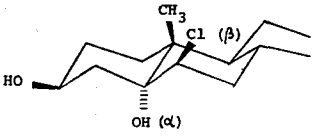
trans-Diequatorial partial structure of 3β, 5β-dihydroxy-6α-chlorositostan (S_5).



trans-Diequatorial partial structure of 3β, 6α-dihydroxy-5β-chlorositostan (S_7).



trans-Diaxial partial structure of 3β, 6β-dihydroxy-5α-chlorositostan.



trans-Diaxial partial structure of 3β, 5α-dihydroxy-6β-chlorositostan.

Fig. 49. Configurations of the Compounds S_5 and S_7 (*trans*-Diequatorial) and Their Stereoisomers (*trans*-Diaxial).

The results of optical rotation measurements of the compounds S_5 and S_7 support the conclusion described above. The molecular rotations $[M]_D$ of the compounds S_5 and S_7 are +182° and +428°, respectively, (Table 25). The dextrorotatory of the compound S_5 is the same as that of 5β-hydroxy-6α-chloro derivative of cholesterol acetate and the value +182° of the former is very similar to that of the latter. (Acetylation does not effect on the optical rotatory, see the other

cases in Table 25). The result indicates clearly that the compound S_5 is 3β, 5β-dihydroxy-6α-chlorositostan. The compound S_7 has dextrorotatory (+428°) and this indicates that the compound S_7 is also a 5β-substituted derivative, the positional isomer of the compound S_7, 3β, 6α-dihydroxy-5β-chlorositostan (Fig. 49).

Unexpectedly, stigmastanol which often occurs along with β-sitosterol in nature was also isolated from the mixture of chlorination products of β-sitosterol. This indicates that stigmastanol which have no double bond in its structure did not react with chlorine during chlorination. It was obtained by recrystallization from ethanol yielding crystals with mp 139°C and amounted to 10% of the total sample used in this experiment. The purity of β-sitosterol sample used in this experiment was determined as 85% by GLC analysis.

The mass spectrum, chemical structure, and fragmentation of stigmastanol are shown in Fig. 50. The molecular ion (M^+) peak is observed at m/z 416. The intense ion peaks at m/z 401 and m/z 383 derive from the successive loss of CH_3• and H_2O from the molecular ion peak. The intense ion peaks at m/z 398 and m/z 215 correspond to the fragments formed by successive loss of H_2O and $C_{13}H_{27}$• from the molecular ion peak. The intense ion peak at m/z 233 corresponds to the fragment derived by the loss of $C_{13}H_{27}$• from the molecular ion peak.

The chemical shifts of the methyl group of stigmastanol is shown in Table 23. The chemical shift for two singlets of the methyl protons attached to C-18 and C-19 are observed at 0.645 and 0.800 ppm, respectively. The signal for C-21 methyl group appears as a doublet at 0.900 ppm (J=6.8 Hz). Two doublets at

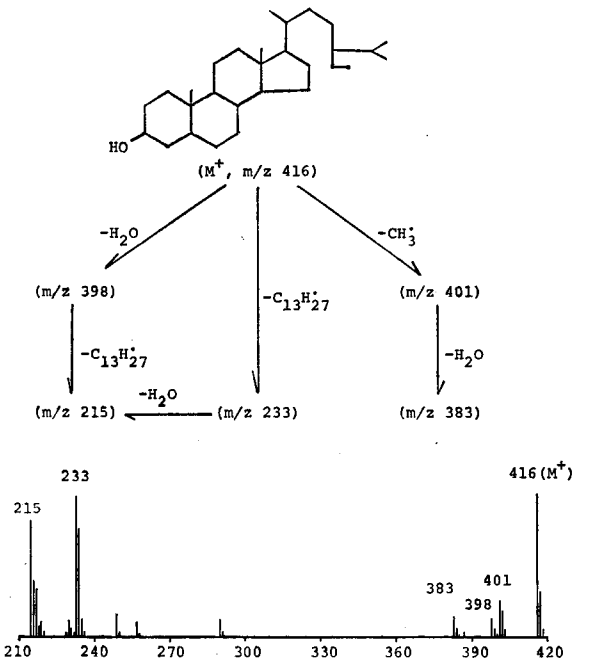


Fig. 50. Mass Spectrum, Chemical Structure, and Fragmentation of Stigmastanol.

0.825 and 0.812 ppm are attributed to C-26 and C-27 methyl groups, respectively. The triplet at 0.838 ppm is assigned to the signal of protons of C-29 methyl group. The chemical shift of the protons attached to C-18, C-19, C-21, C-26, C-27, and C-29 methyl groups are identical with those of stigmastanol reported by RUBINSTEIN *et al.* [92].

5.4 Conclusion

The composition of cyclohexane extract in red lauan wood was studied in order to elucidate the behavior of wood constituents during pulping and bleaching. Cyclohexane extract consists of neutral fraction (45.4%), free acids (2.7%), combined acids (3.8%), and others (42.9%).

Compounds 1-tetracosanol, 1-hexacosanol, ψ-taraxasterone, and β-sitosteryl oleate from neutral fraction were identified by GC-MS. Four compounds responsible for the pitch problems were isolated from neutral fraction, and identified as β-sitosterol, 24-methylenecycloartanol, 24-methylenecycloartanone, and 24-methylenecycloartanyl oleate.

During kraft and alkali-methanol pulping, the esters were hydrolyzed, resulted in the increase of the amounts of β-sitosterol, 24-methylenecycloartanol and 24-methylenecycloartanone.

In the CEDED bleached pulp, 1-tetracosanol, 1-hexacosanol were found, however, ψ-taraxasterone, β-sitosterol, 24-methylenecycloartanol, 24-methylenecycloartanone and their related compounds were not found because of the reaction of these compounds with chlorine during bleaching. Several new peaks were found in GLC.

The reaction of β-sitosterol with aqueous chlorine solution has been examined to clarify the behavior of wood sterols during bleaching. The reaction products were separated by silica gel chromatography. Seven chlorination products were isolated from the chlorinated β-sitosterol. Among the isolated chlorination products, four were identified as compounds 3β-hydroxy-5β, 6α-dichlorositostan, 3β-hydroxy-5α, 6β-dichlorositostan, 3β, 5β-dihydroxy-6β-chlorositostan, and 3β, 6α-dihydroxy-5β-chlorositostan. Compounds S_1, S_2, and S_6 were not identified. Stigmastanol which often occurs along with β-sitosterol in nature was also isolated from the mixture of chlorination products of β-sitosterol.

6. General Conclusions

1. The effects of various chemical pretreatments on the strength properties of corresponding CTMP pulps from red lauan wood were studied. Chemical pretreatments of the wood chips at temperature 120~160°C made the wood chips more soften and the strength properties of the pulps from the pretreated chips were greatly improved.
2. Red lauan pulps produced by kraft, alkali-methanol, and cresol-water processes were studied. At the cooking temperature 170°C, there were no differences between the strength properties of alkali-methanol and kraft pulps except tear factor. In alkali-methanol pulping, reducing the cooking temperature from

175°C to 170°C resulted in increasing yield 5.8～6%, increasing lignin content 1.3～2%, and improving the strength properties of the pulps. The effect of anthraquinone (AQ) on the strength properties of the pulp was significant. The strength properties of the pulps produced by cresol-water process was found to be too inferior compared with those of kraft pulps.

3. Chemical pulps from red lauan wood were difficult to be bleached in both ozone and conventional CEDED sequence. They required a large amount of bleaching agent and the brightness achieved was not sufficient. However, satisfactory brightness could be achieved by bleaching at an optimum ozone consumption followed by 1% hydrogen peroxide treatment in O_3P and additional 1% hydrogen peroxide treatment in O_3PP sequence. Hydrogen peroxide bleaching was found to be effective in reducing the brightness reversion. Ethanol-benzene and cyclohexane extracts had a negative effect on the brightness and brightness reversion.
4. The behavior of wood constituents during pulping and bleaching was studied. Four compounds responsible for pitch problems were isolated from neutral fraction of cyclohexane extracts. They were identified as β-sitosterol, 24-methylenecycloartanol, 24-methylenecycloartanone, and 24-methylenecycloartanyl oleate. Beside the last ester compound, several ester compounds were detected. During kraft and alkali-methanol pulping, the esters were hydrolyzed and this increased the amount of β-sitosterol, 24-methylenecycloartanol, and 24-methylenecycloartanone in the neutral fraction of those pulps. In the bleached pulps, the saturated compounds, such as, 1-tetracosanol and 1-hexacosanol were remained, however, the compound with unsaturated bond, such as, ψ-taraxasterone, β-sitosterol, 24-methylenecycloartanol, and their related compounds were connected to chlorinated compounds owing to the reaction with chlorine during bleaching.
5. The reaction of β-sitosterol with aqueous chlorine solution has been examined in order to clarify the behavior of wood sterols during bleaching. The reaction products were separated by silica gel chromatography. Seven chlorination products were isolated and four of them were identified as 3β-hydroxy-5β, 6α-dichlorositostan, 3β-hydroxy-5α, 6β-dichlorositostan, 3β, 5β-dihydrody-6α-chlorositostan, and 3β, 6α-dihydroxy-5β-chlorositostan. Stigmastanol which often occurs along with β-sitosterol in nature was also isolated from the mixture of chlorination products of β-sitosterol.

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要　　約

目的：本研究は，インドネシアに多く産するレッドラワン材を原料とし，この原料に適したパルプ化法を開拓すること，生成パルプの適切な漂白法を確立することを目的とした。

インドネシアでは，主としてムギワラやタケなどの非木質材料を原料としてパルプが製造されており，他は輸入に頼っているのが現状である。これから急増が予想される紙・パルプの需要に答えるには，非木質材料からのみならず，木質材料からのパルプ製造が必須である。そのためには，インドネシア国産材を利用したパルプ作りが今後の重要課題となるであろう。

しかしながら，南洋材を通常のパルプ化法で蒸解する際には，抽出成分が多いことに由来する種々のピッチトラブルが生じることがこれまでの研究でも指摘されて来ている。

本研究においては，レッドラワン材から種々の方法でパルプを製造し，その物理化学的性質を検討し，パルプ化法を比較評価するとともに，化学パルプについては種々の漂白法で漂白し，漂白パルプの色もどりや物理化学的性質を検討し，漂白法を比較評価した。

硫酸塩法 (KP 法) で製造したパルプを塩素系多段漂白することで生じる色もどりの原因物質を究明し，その色もどり機構を解明するとともに色もどり防止の対策について検討した。

実験方法： 用いたパルプ化法は，資源の有効利用を考慮した高収率パルプ化法と，通常用紙向けの化学パルプ化法である。すなわち前者として，化学前処理をいろいろ変えた化学熱機械パルプ化法 (Chemithermomechanical pulping 法，CTMP 法) を，後者として最も広く行われている KP 法および，アルカリ・メタノール法 (AM 法)，クレゾール・水法 (CW 法) などの新しい加溶媒蒸解法を採用した。

生成パルプの漂白法は，従来行われている塩素系多段漂白法 (塩素処理・アルカリ抽出・二酸化塩素処理・アルカリ抽出・二酸化塩素処理：CEDED 法) に加えて，新しい漂白法として注目されつつあるオゾン法 (O_3 法)，オゾン・過酸化水素多段漂白法 (O_3P，O_3PP 法) などを採用し，比較検討した。

パルプの物理化学的性質については，蒸解後のパルプ，漂白後のパルプの収率や，引っ張り，破裂，引き裂き強度，白色度，PC 価などの物理的性質を調べ，残存リグニン，溶媒可溶性成分，1% 苛性ソーダ可溶性成分等の化学成分を分析した。

パルプ中の色もどり原因物質の分析のため KP パルプをシクロヘキサンで抽出し，可溶性成分をシリカゲルカラムクロマトグラフィーで分離し，単離化合物を器機分析により構造を解明した。原因物質の 1 つと判明した β-sitosterol については，塩素水との反応を検討し，反応生成物を単離し構造を明らかにした。

結果： 1. 高収率パルプ化法 (CTMP 法) について：120～160°C でソーダ，バイサルファイトなど種々の化学前処理を行うことにより，収率 71～77% で物理的強度の高いパルプを得た。なかでも，5% $NaHSO_3$ を用い，160°C で 60 分加熱処理するバイサルファイト法 (BS 法) で得られた CTMP パルプは，引き裂き，破裂，引っ張り強度が最も高かった。一方，白色度の高い CTMP パルプは，アルカリで処理 (冷アルカリ，熱アルカリ処理) することで得られるが，物理的強度は BS 法のものに次ぐ。BS 法処理後のチップは，他の前処理のものに比べて格段に軟らかく，続く解繊に要するエネルギーが少なくて済む利点をも有している。ただし，白色度は他に劣っているのが難点である。しかしながら，この点は漂白による改質が可能である。

2. 化学パルプについて： KP 法で得られたパルプを塩素系多段漂白すると色もどりが生じ問題となる。この原因物質は蒸解後もパルプに残存する抽出成分に由来する。したがって，蒸解中に抽出成分を溶解除去しうる加溶媒蒸解はピッチトラブルの防止に適当と考えられた。すなわち CW 法では 78～90% の抽出成分が，一方，76～80% の抽出成分が AM 法で除去され，両方法は，KP 法の 53～61% の除去率をしのいで良好であることが判明した。ただし，パルプ

の強度や漂白処理後のパルプの強度はKP法でのパルプが最も勝れており，AM法，CW法でのパルプがこれに次ぐ結果となった。AM法ではアンスラキノン (AQ) の添加効果があり，収率，強度の点でも改良された。CW法は抽出成分除去能力に勝れているが，パルプの物理的強度，漂白適性の点で劣り，現状ではレツドラワンへの適用はむつかしい。今後，さらに検討が必要である。

3. 漂白法について： レツドラワン材から製造したKPパルプをCEDED法で漂白しても充分な白色度の向上が得られず，かつ色もどりが生じる。この点を改善すべく，リグニン分解能の高いオゾン (O_3) の利用を検討したところ，O_3のみでは効果が認められないが，過酸化水素 (H_2O_2, P) を並用することで著しい色もどり防止効果を発揮することが判明した。すなわち，KP法で得たパルプをO_3で処理 (30分) 後，H_2O_2 (P) で1～2回処理することで白色度を87%まで向上させることが出来，色もどりもないパルプへと改質された。また，本法による漂白パルプの強度は，CEDED法のものよりも勝れていた。一方，KPパルプをシクロヘキサンであらかじめ抽出しておくことでCEDED法で漂白しても色もどりのない漂白パルプを得ることが出来た。

4. CEDED法漂白後のパルプの色もどりの原因究明： KPパルプをシクロヘキサンで抽出し，可溶性成分をカラムクロマトで分離した。GS/MSにより 1-tetracasanol (**1**), 1-hexacosanol (**2**), ψ-taraxasterone (**3**), β-sitosteryl oleate (**4**) の存在が判明し，β-sitosterol (**5**), 24-methylenecycloartanol (**6**), 24-methylenecycloartanone (**7**), 24-methylenecycloartanyl oleate (**8**) を単離し構造を明らかにした。KP法やAM法で蒸解すると**8**を含むエステル類が加水分解され，**5**, **6**, **7**の量が増加することがGLCにより判明した。エステル形成能のないケトン化合物**7**が増加するのは，相当するアルコール化合物**6**が二次的に酸化するためと推定される。分子内に二重結合を有する化合物**4**, **5**, **6**, **7**, **8**は，塩素処理によって消失し，新しい未知化合物へと変わることがGLCで認められた。そこでβ-sitosterol (**5**) をモデルとして，塩素水との反応を検討した。7つの新化合物を単離し，そのうち4つを，3β-hydroxy-5β, 6α-dichlorositostan (**9**), 3β-hydroxy-5α, 6β-dichlorositostan (**10**), 3β, 5β-dihydroxy-6α-chlorositostan (**11**), 3β, 5α-dihydroxy-5β-chlorositostan (**12**) と同定した。**9**, **11**, **12**は5β型の *trans*-diequatrial 部分構造を有する化合物であり，これはLindgrenらの choresterol の塩素処理によって得た結果，すなわち，5α型の *trans*-diaxial の部分構造を有する化合物を主として得た結果とは対照的であった。これら塩素付加体，クロロヒドリン化合物が続くDED処理においてもKPパルプ中に残存し，色もどりの原因となる。