Reaction of 3-Methyl Phenol with Tung Oil

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Synopsis

The aromatic ring substitution reaction of 3-methyl phenol with tung oil under acidic conditions was carried out. The product was analyzed to find out if 3-methyl phenol was subjected to the ring substitution reaction with tung oil at its conjugated double bonds. Up to two molecules of 3-methyl phenol were addition-reacted with the conjugated triene of one eleostearyl group of triglyceride of α-eleostearic acid which is the major component of tung oil. The 4-position of 3-methyl phenol was preferentially subjected to the cresol's ring substitution. Therefore, up to 6 mol of 3-methyl phenol was added to 1 mol of tung oil, most of which was bonded to 3-methyl phenol at its 4-position. When 3-methyl phenol was reacted with a relatively large amount of tung oil, the substitution reaction occurred at the 6- as well as 4-position of 3-methyl phenol to yield a tung oil dimer having 3-methyl phenol units in its molecule. The above results were confirmed by infrared (IR), nuclear magnetic resonance (NMR), and high-speed liquid chromatographic (HLC) analyses.

INTRODUCTION

Phenolic resins[1] used in industry are frequently modified by adding some tung oil so as to have flexibility. Because triglyceride of α-eleostearic acid, which is the major component of tung oil, has three conjugated trienes, under acidic condition phenols react easily with α-eleostearic acid.

A number of papers have reported on the reaction products between tung oil and phenols, but they have reported little on the reaction between tung oil and phenols.[2–16] In this paper, more detailed discussion about the amount of 3-methyl phenol reacted with tung oil, the bond position in 3-methyl phenol and so on are made from the results of IR, NMR, and HLC analyses.

EXPERIMENTAL

Reagents

Tung oil of an industrial grade from China was used. 3-Methyl phenol and 2,5-, 3,5-, 3,4-, and 2,3-xylenols used were of the first reagent grade. *p*-Toluenesulfonic acid used as catalyst was of the first reagent grade. Methyl alcohol used was of the special reagent grade. Tetrahydrofuran (THF) and chloroform used as HLC solvents were of the first reagent grade.

Analytical Method

Infrared Analysis (IR)

For infrared analysis of samples, Hitachi Co., IR Model 285 was used.

Nuclear Magnetic Resonance Analysis (*NMR*)

NMR analysis of the reaction products, some of which were acetylated, were carried out by use of Hitachi Co., NMR Model R-24.   Deutero chloroform and tetramethylsilan were used as solvent and internal standard, respectively.

The procedure of acetylation was as follows: 0.1 g of the sample was dissolved in 0.2 mL of pyridine in a test tube and it was cooled to 0–5°C, and then 0.3 g of cooled acetic anhydride was dropped into it.   The test tube was then allowed to stand for about 24 h.   After that, 0.4 mL of chloroform was dropped into the test tube and the chloroform phase was washed by water several times.

High-Speed Liquid Chromatographic Analysis (*HLC*)

Toyo Soda Co., HLC Model HLC-802, in which one column of TSK G-3000H_6 columns of TSK G-2000H_6 and RI detector were employed, was used.   THF was used as the elution solvent at flow rate of 1.5 mL/min.   Tung oil and 3-methyl phenol were immersed in 1.1 wt % THF solution and the reaction products in 2.2 wt % THF solution.

Figure 1 shows the relationship between the elution volume and the molecular weight, and Figure 2 shows the relationship between the concentration and the peak height of tung oil and 3-methyl phenol.
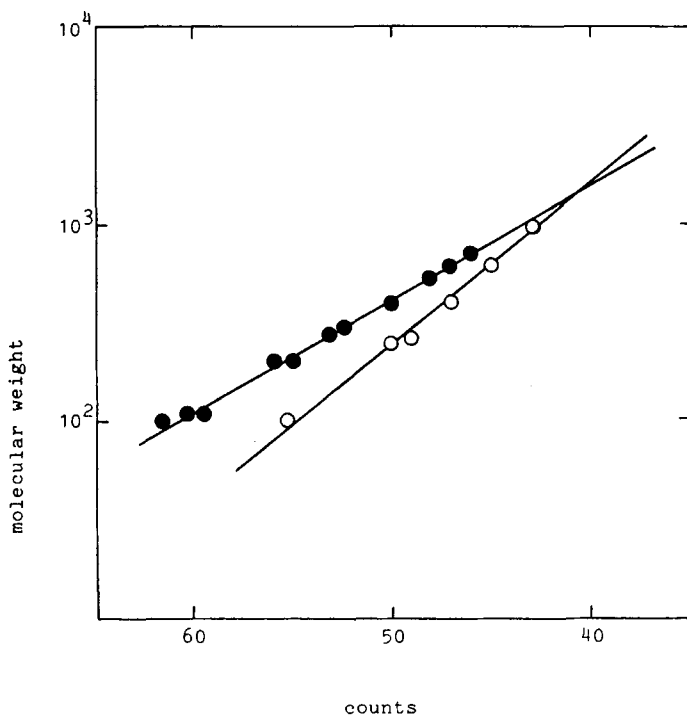

Fig. 1. HLC calibration curve of elution volume–molecular weight: (●) phenol compounds; (○) aliphatic compounds.
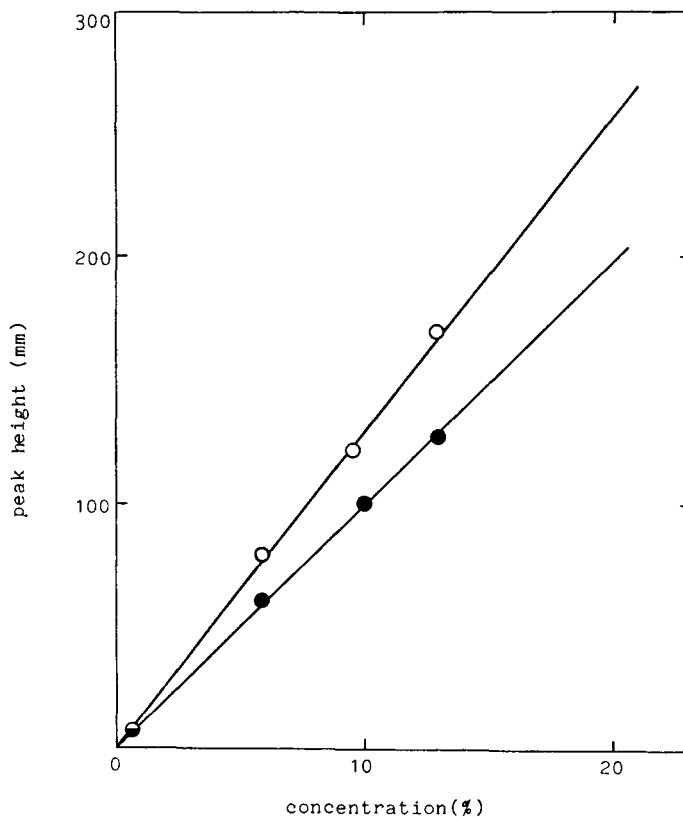
Fig. 2. HLC calibration curve of concentration–peak height: (O) 3-methyl phenol, (●) tung oil.

Fractionation

For fractionation of the reaction products, Hitachi Co., HLC Model 635 equipped with two columns of H202 was employed. Chloroform was used as the elution solvent at flow rate of 1.5 mL/min. Samples were immersed in 11 wt % chloroform solution.

Average Molecular Weight

Average molecular weight of the reaction products were obtained by VPO method with Hitachi Co., Hitachi Perkin-Elmer 115 Molecular Weight Apparatus. Each sample was accurately weighed in a weighing tube with ground stopper and dissolved in a fixed weight of MIBK (bp 114–117°C) to form a sample solution. Each solution was measured at 59°C, and endo methylene-tetrahydro phthalic anhydride was employed as a standard sample.
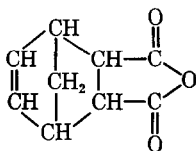
The chemical structure is as follows:

TABLE I
Relationship between the Charging Molar Ratio and the Reaction Molar Ratio of 3-Methyl
Phenol and Tung Oil

| No. | Charging molar ratio | | | Reaction molar ratio of 3-methyl phenol to tung oil |
	3-Methyl phenol (g)	Tung oil (g)	3-Methyl phenol/tung oil molar ratio	
1	3	7	3.5	1.0
2	4	6	5.4	2.0
3	7	3	18.9	4.9
4	9	1	72.8	5.5
5	9.5	0.5	153.8	5.7

Reaction of 3-Methyl Phenol with Tung Oil

The predetermined amounts of tung oil and 3-methyl phenol were charged in a 500-mL four-necked flask equipped with a stirrer, a thermometer, a dropping funnel, and reflux condenser. Then 3 g of 20% aqueous solution of p-toluenesulfonic acid was added dropwise to the stirred mixture through the dropping funnel at about 25°C. After completion of the dropwise addition of p-toluenesulfonic acid, the flask was heated at 80°C for 1 h and then it was cooled. 50 g of methyl alcohol was added into the flask to dissolve the reaction products. Then water was added into the solution to obtain an oily precipitate. It was subjected to reduced-pressure distillation to remove the remaining water and methyl alcohol.

The charged amount of 3-methyl phenol and tung oil are listed in Table I. The reacted amount of them which calculated from the peak height of HLC chromatogram are also shown in Table I. In Figure 3, HLC chromatograms of the
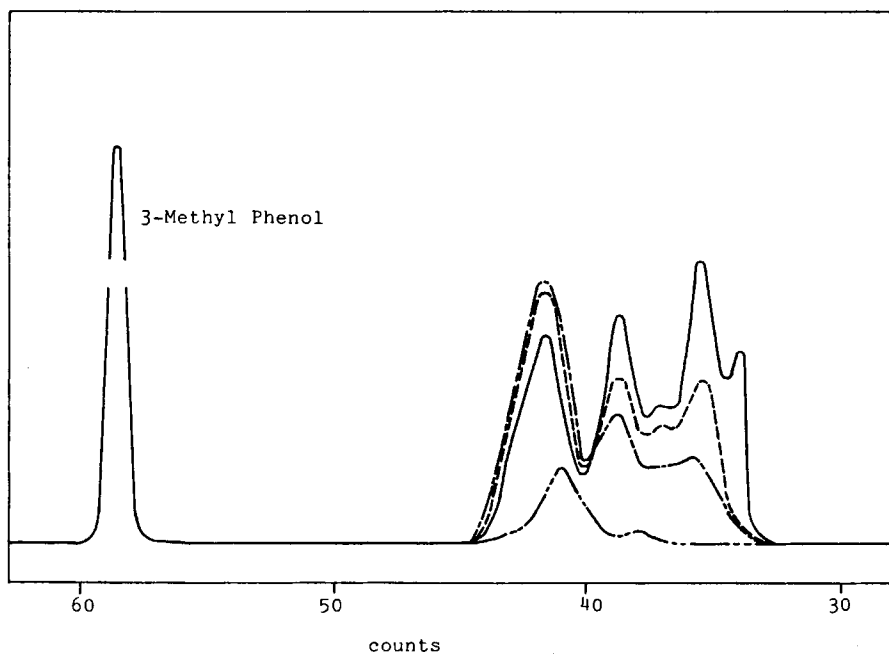

Fig. 3. HLC chromatograms of tung oil 3-methyl phenol reaction products prepared at varied 3-methyl phenol/tung oil molar ratios: (——) 3/7; (- - -) 4/6; (-·-) 7/3; (– - – -) 9/1.

reaction products prepared under several molar ratios of 3-methyl phenol to tung oil are shown.   Two peaks appeared at 59.3 and 43.6 counts are assigned to 3-methyl phenol and tung oil, respectively.   As regards the products obtained by the reactions, the peak due to tung oil completely disappeared and the peak due to 3-methyl phenol diminished in height while the peak due to the tung oil 3-methyl phenol reaction product appeared on the high molecular weight side or on the low count side.

The HLC chromatogram of the reaction product which prepared under the condition that the molar ratio of 3-methyl phenol to tung oil equal to 4/6 is shown in Figure 4.   Four fractions which correspond to shaded parts of the chromatogram (I, II, III, and IV) in this figure were collected.   From HLC chromatograms of each fraction, using THF as solvent shown in Figure 5, it is obvious that fractions I, II, III, and IV correspond to peaks of HLC chromatograms appeared at 36.5, 38.0, 41.3 and 42.5 count in Figure 3, respectively.

The proportion of 3-methyl phenol and tung oil of each fraction were determined from NMR analysis and the results as shown in Table II were obtained. The average molecular weights of them are also listed in Table III.

According to these results, it is found that the molecules of fractions I, II, III, and IV consist of three, two, one, and one molecule(s) of tung oil, respectively, to which some molecules of 3-methyl phenol are bonding.

The proportion of 3-methyl phenol in the reaction products increase as shown in Table I and the molecular weights of them decrease as shown in Figure 3 with increment of the initial molar ratio of 3-methyl phenol to tung oil.   To prepare the adduct of tung oil with 3-methyl phenol, 10 g of tung oil (0.114 mol) is allowed to react with 290 g of 3-methyl phenol (2.685 mol) under the same conditions as described above.

HLC chromatogram of crude product obtained after completion of reaction is shown in Figure 6.

The reaction product was dissolved in 50 g of methyl alcohol and then water was added dropwise until the solution became turbid.

The oily precipitate obtained was collected and was subjected to reduced pressure distillation.   The amount of the final product was 10.5 g.
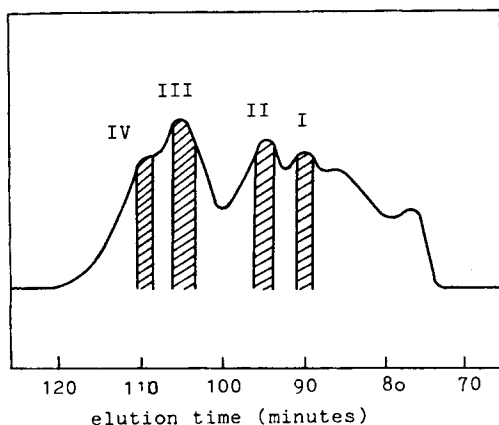

Fig. 4. HLC chromatogram measured by HLC for separation of tung oil–3-methyl phenol reaction product.
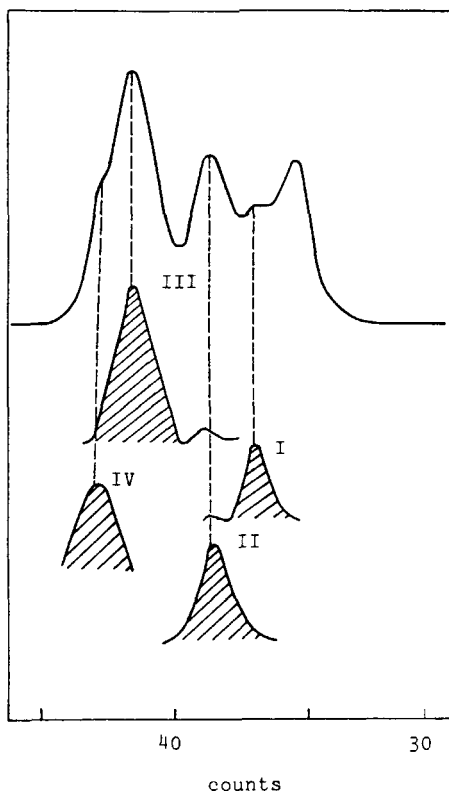
Fig. 5. HLC using tetrahydrofuran of the materials separated by HLC for separation.

RESULTS AND DISCUSSION

Reacting Position of Tung Oil

IR spectra and NMR spectra of both tung oil and the reaction product are shown in Figures 7 and 8, respectively.

Absorption due to the conjugated bonds is recognized easily at 995 cm^{-1} in IR spectra of tung oil, while in IR spectra of the reaction product it disappears, as shown in Figure 7.   In NMR spectra of the reaction products, signals at around 6 ppm, which correspond to the conjugated double bonds of tung oil disappear

TABLE II

Molar Ratio of 3-Methyl Phenol Part to Tung Oil Part in Each Material Separated[a]

Sample	CH$_3$ group of 3-methyl phenol ring (A)	CH$_3$ group of tung oil (B)	(3-Methyl phenol/tung oil) molar ratio
I	0.086	1	0.26
II	1.401	1	4.20
III	0.730	1	2.20
IV	1.530	1	4.60

[a] 3-Methyl phenol/tung oil molar ratio = $A/B \times 3$.

TABLE III
Average Molecular Weight of Material Separated by HLC for Separation

Sample	Average molecular weight
I	4541
II	2707
III	1876
IV	1282

and that around 1.4 and 2.0 ppm, which correspond to methylene groups, and that around 3.3 ppm, which correspond to methine groups, become larger as compare with NMR spectra of tung oil.

Signals at about 5.4 ppm in NMR spectra of the reaction product is assigned as unreacted double bonds of tung oil and its area is about one third of that for whole double bond of tung oil. Therefore, it becomes apparent that the most of the conjugated trienes of tung oil and converted into internal double bonds by the reaction with 3-methyl phenol. In the other words, 3-methyl phenol react with tung oil at the conjugated trienes.
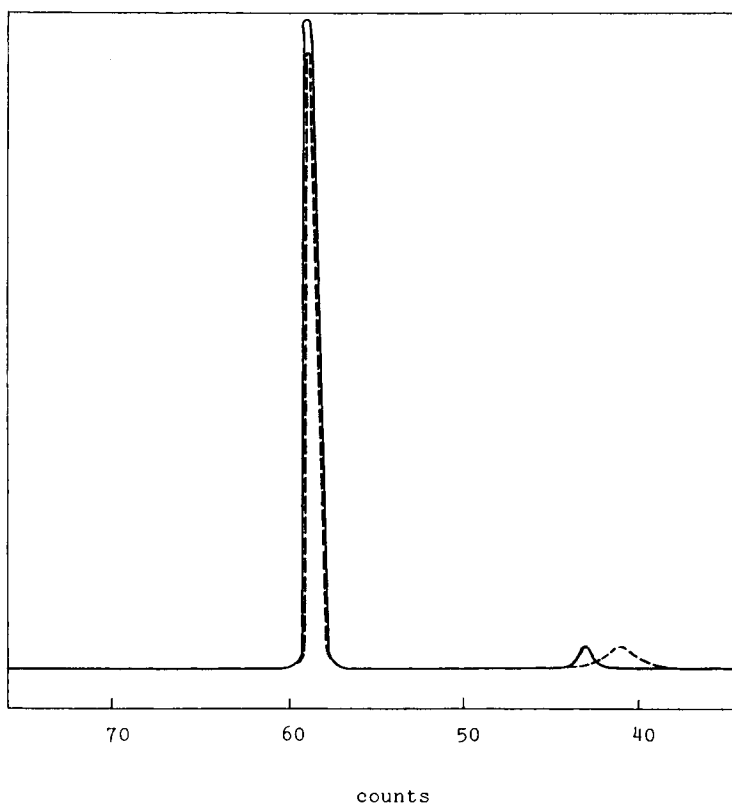

counts

Fig. 6. HLC chromatograms of tung oil–3-methyl phenol systems before (——) and after (- - -) reaction.
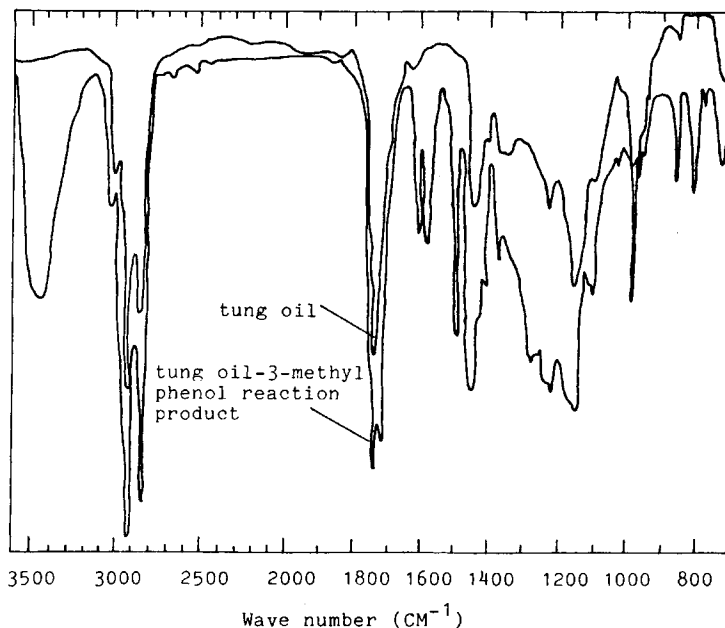
Fig. 7. IR spectra of tung oil and tung oil–3-methyl phenol reaction product.

Reacting Position of 3-Methyl Phenol

Absorptions of IR spectrum of the reaction product at 1500 and 1600 cm^{-1} are assigned aromatic ring, as shown in Figure 7, and a signal of NMR spectrum of the reaction product at 7 ppm is assigned protons in aromatic ring as shown in Figure 8. Thus, it is confirmed that 3-methyl phenol reacts with tung oil. The absorptions of IR spectrum at around 1235 and 3430 cm^{-1} correspond to phenolic hydroxide. In NMR spectrum of the acetylated reaction products, a signal at
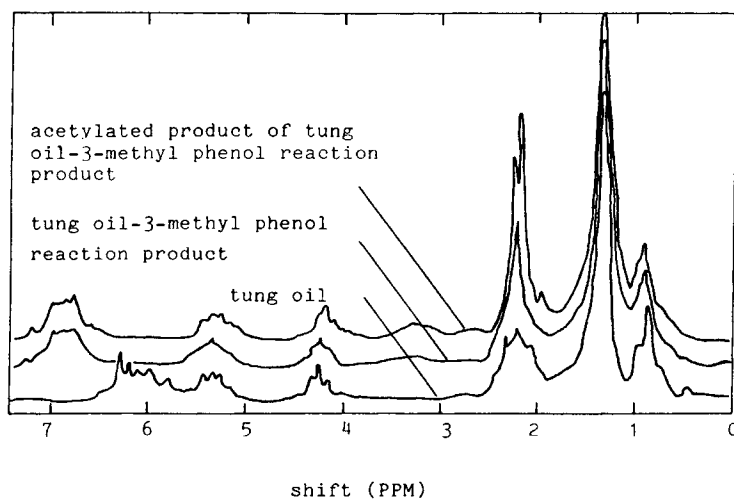

shift (PPM)

Fig. 8. NMR spectra of tung oil and nonacetylated and acetylated tung oil–3-methyl phenol reaction products.

TABLE IV
NMR Results of Tung Oil–3-Methyl Phenol Reaction Product

Sample	NMR peak area		
	—OH	3-Methyl phenol —CH$_3$	3-Methyl phenol ring —H
3-Methyl phenol (calcd)	1.00	3.00	4.00
Tung oil–3-methyl phenol reaction product	1.06	3.00	2.30

2.2 ppm is assigned as methyl protons of acetyl group.   Thus, the reaction product surely have phenolic hydroxy groups.

The number of hydrogens of the reaction products determined by NMR are listed in Table IV, compared with that of 3-methyl phenol calculated.   As shown in this table, the proportion of hydrogen on aromatic ring decreases in the course of reaction.   Therefore, it becomes apparent that 3-methyl phenol surely reacts with tung oil on aromatic ring.

In order to discuss the reacting position of 3-methyl phenol, 2,5-, 3,5-, 3,4-, and 2,3-xylenol were used as standard.   IR spectra of the reaction product and the standards are shown in Figure 9.   The remarkable absorption at 840 cm^{-1}
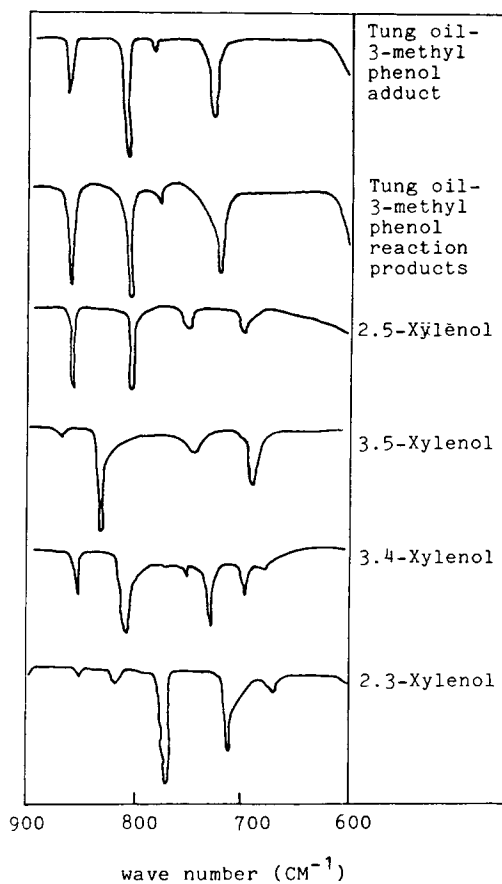

Fig. 9. IR spectra of tung oil–3-methyl phenol adduct and reaction product, and xylenol isomers.

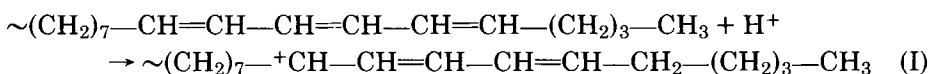| | NMR peak area | | |
Sample	—OH	3-Methyl phenol —CH$_3$	3-Methyl phenol ring —H
3-Methyl phenol (calcd)	1.00	3.00	4.00
Tung oil–3-methyl phenol adduct	1.02	3.00	2.91

seen in IR spectrum of 3,5-xylenol cannot be found in that of the reaction product. The absorption at 850–860 cm^{-1} in IR spectrum of the reaction product is as same as that of 3,4- and 2,5-xylenol. These data suggest that 3-methyl phenol reacts with tung oil not better at 5-position, but easily at 4- and 6-position. In analogy with 3,4-xylenol, IR spectrum of the reaction product has a strong absorption at 710–720 cm^{-1}.

At 780 cm^{-1}, 2,3-xylenol shows a remarkable absorption, but in IR spectrum of the reaction product it is very weak. It follows from the above results that 3-methyl phenol reacts with tung oil at 2-, 4-, and 6-position and the reactivity of these position is as follows: 4- > 6- > 2-position. However, the order of reaction among 2-, 4-, and 6-positions cannot be determined from only these above-mentioned observation. It is known from Table IV that 1.7 hydrogens on aromatic ring of 3-methyl phenol on the average react with tung oil. This indicates that some molecules of 3-methyl phenol react with two or three tri-α-eleostearoids.

The number of hydrogens of tung oil–3-methyl phenol adduct are determined by NMR and the results shown in Table V. From the fact that 1.09 ring hydrogens are consumed during reaction, it is apparent that 3-methyl phenol reacts with tung oil only at one position of the ring. IR spectrum of the adduct shown in Figure 9 is similar to that of 3,4-xylenol. It indicates that 3-methyl phenol is bonded to tung oil at 4-position in the adduct.

The mechanisms of the reaction between 3-methyl phenol and tung oil are proposed as follows:

A hydrogen cation dissociated from p-toluene sulfonic acid attacks tung oil to form cation (I) in accordance with Markownikoff's rule:

$$\sim(CH_2)_7—CH=CH—CH=CH—CH=CH—(CH_2)_3—CH_3 + H^+$$
$$\rightarrow \sim(CH_2)_7—{}^+CH—CH=CH—CH=CH—CH_2—(CH_2)_3—CH_3 \quad (I)$$

Then the electrophilic substitution of I with 3-methyl phenol occurs to form compound II:

$$\sim(CH_2)_7—\overset{H}{\underset{|}{C}}—CH=CH—CH=CH—CH_2—(CH_2)_3—CH_3 \qquad (II)$$
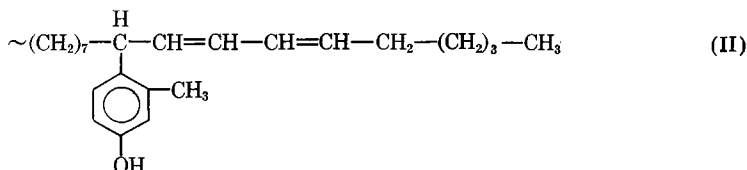
In a similar manner as above, when another molecule of 3-methyl phenol adds to II, compound III is formed:

$$\sim(CH_2)_7—CH—CH_2—CH=CH—CH—(CH_2)_4—CH_3 \qquad (III)$$
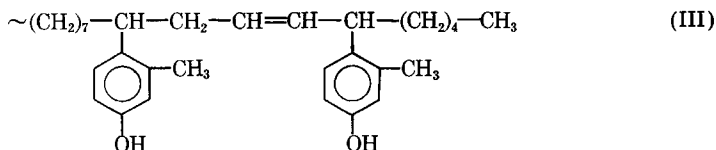
Thus, two molecules of 3-methyl phenol can be added to one eleo-stearoyl group of tung oil.   Therefore, it is assumed that the principal structure of the molecule of the reaction product is represented by the following formula:

$$H_2COCO(CH_2)_7-\overset{H}{\underset{|}{C}}-CH_2-CH=CH-\overset{H}{\underset{|}{C}}-(CH_2)_4-CH_3$$

$$HCOCO(CH_2)_7-\overset{H}{\underset{|}{C}}-CH_2-CH=CH-\overset{H}{\underset{|}{C}}-(CH_2)_4-CH_3 \qquad (IV)$$

$$H_2COCO(CH_2)_7-\overset{H}{\underset{|}{C}}-CH_2-CH=CH-\overset{H}{\underset{|}{C}}-(CH_2)_4-CH_3$$
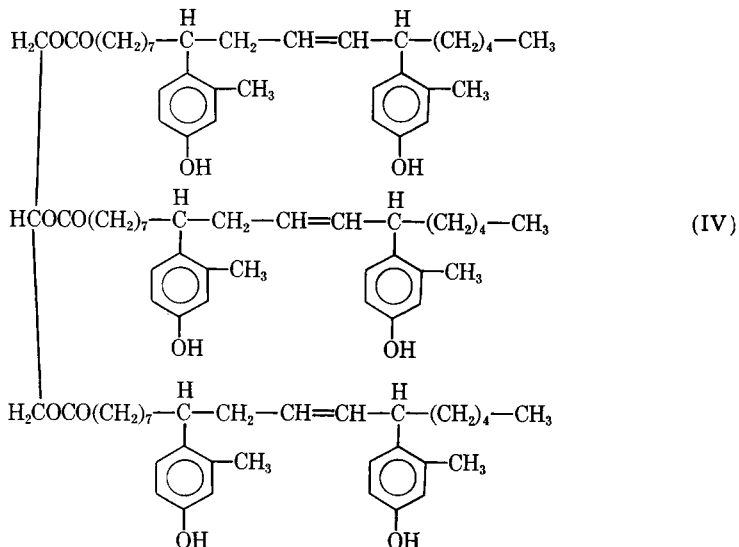
The limiting structure of alkyl phenol are represented by the following formula:

o-isomer

m-isomer

p-isomer
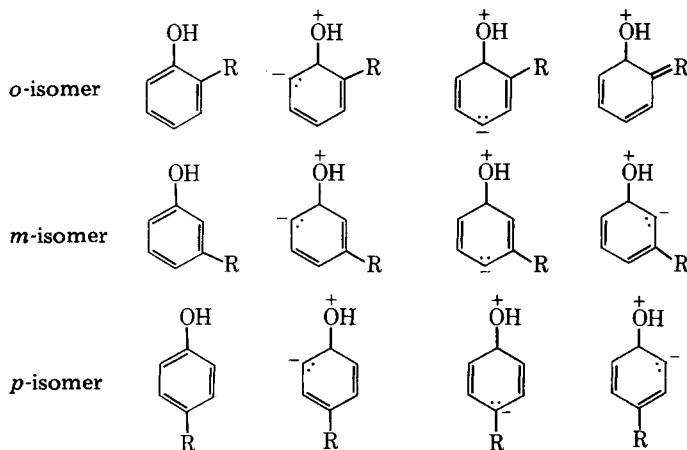
It is well known that the orientation of alkyl group in a benzene derivative is less than that of hydroxyl group.

Therefore, tung oil reacts with 3-methyl phenol at 4- and 6-positions.

However, it cannot be explained by electronic theory that the 4-position is selected rather than 6-position.   It is assumed that the long chain molecule such as tung oil cannot approach the 6-position due to the effect of steric hindrance. This assumption is supported by the fact that the small molecules such as isoprene and styrene can bond at the 6-position of 3-methyl phenol.[16,17]

CONCLUSIONS

The ring substitution reactions of 3-methyl phenol with tung oil under acidic conditions were carried out, and the resulting products were analyzed.   As a result, the following facts were observed:

(1) The ring substitution reaction of 3-methyl phenol with tung oil occurs via the conjugated double bonds present in tung oil molecule.

(2) The increased amount of 3-methyl phenol to 6 mol led to an increased amount of 3-methyl phenol reacted with 1 mol of tung oil.

(3) The increased amount of 3-methyl phenol that reacted with 1 mol of tung oil led to a decrease in the average molecular weight of the resulting product. The decreased average molecular weight was a result of the corresponding suppression of tung oil polymer formation that was eliminated when a maximum of 6 mol of 3-methyl phenol was added.

(4) An increase in the amount of 3-methyl phenol addition-reacted with 1 mol of tung oil led to the decrease in number of substituted ring protons of 3-methyl phenol.

(5) The number of substituted ring protons of 3-methyl phenol is 1.0 to one molecule of 3-methyl phenol and an ortho/para substitution ratio is minimum, when a maximum of 6 mol of 3-methyl phenol is addition-reacted with 1 mol of tung oil.

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