

Reaction of 3-Methyl Phenol with Methyl α -Eleostearate

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Synopsis

The aromatic ring substitution reaction of 3-methyl phenol with methyl α -eleostearate 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 methyl α -eleostearate at its conjugated double bonds. Up to two molecules of 3-methyl phenol were addition-reacted with the conjugated triene of the eleostearyl group of methyl α -eleostearate. The 4-position of 3-methyl phenol was preferentially subjected to the cresol's ring substitution. When 3-methyl phenol was reacted with a relatively large amount of methyl α -eleostearate, the substitution reaction occurred at the 6- as well as 4-position of 3-methyl phenol, to yield a methyl α -eleostearate 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, and the results of a previous paper connected with reaction of 3-methyl phenol were supported by the results of this paper.

INTRODUCTION

Phenolic resins¹ used in industry are frequently modified with tung oil so as to have flexibility. Phenols are addition-reacted with tung oil via the conjugated triene structure of α -eleostearic acid, the triglyceride of which is the main component of tung oil, and then reacted with formaldehyde on the phenolic nucleus to yield flexible phenolic resins. A number of papers have reported on the reaction products between tung oil and phenols, but they have reported little on the reactions between tung oil and phenols.²⁻²⁰

We reported about the reaction of 3-methyl phenol with tung oil. But we reported nothing but the average structure of the reaction product of 3-methyl phenol with tung oil in its report. The reason was that the molecular weight of tung oil was high as 878, the reaction activated points of tung oil were many as six in one molecule, and the reaction activated points of 3-methyl phenol were three in one molecule, so that reaction product's molecular weight were very high and we worked hard in reaction analysis. Therefore, we tried to make clear the reaction of 3-methyl phenol with tung oil by examining the reaction products of 3-methyl phenol with methyl α -eleostearate.

EXPERIMENTAL

Reagents

Tung oil of an industrial grade from China was used. 3-Methyl phenol and phenol used were of the first reagent grade. *p*-Toluenesulfonic acid used as catalyst was of the first reagent grade. Methyl alcohol and sodium hydroxide

used as reagent for preparation of methyl α -eleostearate were of the special reagent grade. Tetrahydrofuran (THF) and chloroform used as HLC solvents were of the first reagent grade.

Analytical Method

Infrared Spectroscopic Analysis (IR). For IR analysis of samples, Hitachi Co., IR Model 285, was used.

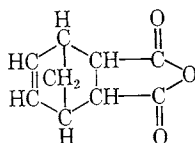
Nuclear Magnetic Resonance Spectroscopic Analysis (NMR). NMR analysis of the reaction products, some of which were acetylated, were carried out by use of Hitachi Co., NMR Model R-24 or JEOL Ltd., NMR Model FX 270. Deutero chloroform and tetramethylsilan were used as solvent and internal standard, respectively. 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, followed by sufficient mixing and the chloroform phase was washed by water several times. The chloroform phase finally obtained was heated under reduced pressure to remove the chloroform and the remaining water.

High-Speed Liquid Chromatographic Analysis (HLC). The HLC Model HLC-802, (Toyo Soda Co.), in which one column of TSK G-3000H₈, three columns of TSK G-2000H₈, and RI detector were employed, was used and THF was used as the elution solvent at flow rate of 1.5 mL/min. Hitachi Co., HLC Model 635, in which one column of TSK G-3000H₈, three columns of TSK G-2000H₈, and RI detector, UV detector were employed, was used, and DMF was used as the elution solvent at flow rate of 1.1 mL/min. Samples were immersed in 1.1–2.2 wt % THF solution or DMF solution.

Fractionation. For fractionation of the reaction products, HLC Model 635 (Hitachi Co.), 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 a Hitachi Perkin-Elmer 115 Molecular Weight Apparatus.

A fixed weight of each sample was accurately weighed in a weighing tube with ground-in 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 endic anhydride was employed as a standard sample. The chemical structure is as follows:



Preparation of Methyl α -Eleostearate. 300 g of methyl alcohol and 6 g of sodium hydroxide were charged in a 1000-mL four-necked flask equipped with

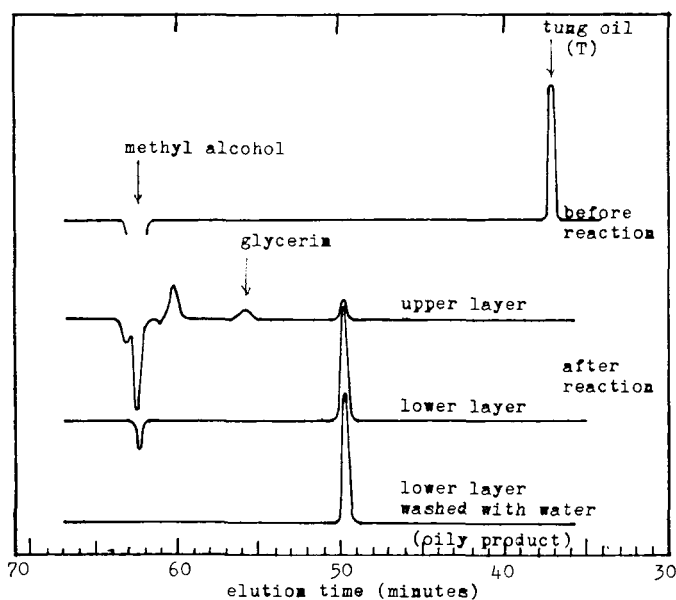


Fig. 1. HLC chromatogram of oily product.

a stirrer, a thermometer, a dropping funnel, and a reflux condenser. Then 300 g of tung oil was added dropwise to the stirred mixture through the dropping funnel at about 20°C. After completion of the dropwise addition of tung oil, the flask was allowed to stand at 20°C for 2 h with stirring. Then the flask was stoppered to stir and left overnight at 20°C.

The reaction mixture separated into two layers on standing. The upper layer was insoluble in THF, and the lower layer was soluble in THF. The lower layer was collected by means of a separating funnel, and it was washed with water. It was subjected to reduced-pressure distillation to remove the remaining water and methyl alcohol. About 300 g of yellow oily precipitate were obtained. In Figure 1, the HLC chromatogram of the oily product obtained are shown. The peak of the oily product appeared at higher counts than that of tung oil, that is, the oily product was lower molecule than that of tung oil. NMR spectra of both tung oil and the oily product are shown in Figure 2. In NMR spectra of the oily product, signals at around 4.1 ppm which correspond to glyceryl's methylene of tung oil disappear and that around 3.5 ppm, which correspond to the methyl group of methyl ester appear as compared with NMR spectra of tung oil. While signals at 5.0–6.4 ppm which correspond to conjugated double bonds, those around 1.4 and 2.0 ppm which correspond to methylene groups, and those around 0.8 ppm, which correspond to methyl groups, are equal to NMR spectra of tung oil. The number of hydrogen atoms of the oily product is determined by NMR and is listed in Table I, compared with that of tung oil. As shown in this table, the proportion of hydrogen of the terminal methyl group, methylene group, and conjugated double bond of the oily product are nearly equal to that of tung oil, and the number of hydrogen atoms of terminal methyl group is equal to that of methyl groups of methyl ester. The average molecular weights of the oily

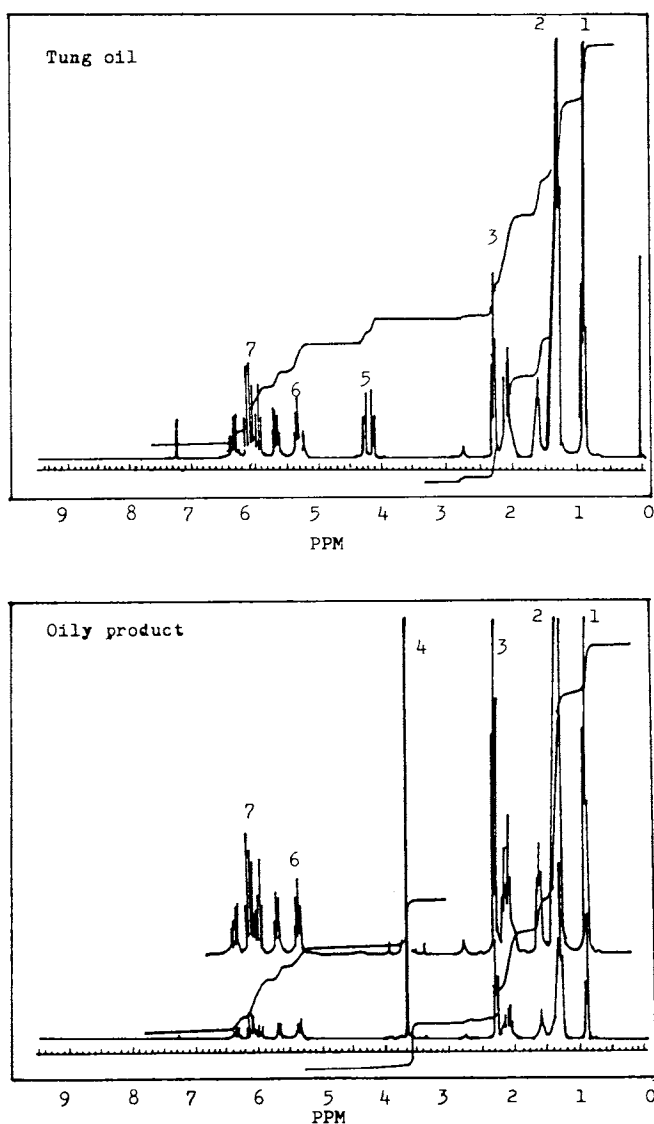


Fig. 2. NMR spectra of tung oil and oily product.

product are listed in Table II. According to these results, it is found that the oily product is methyl α -eleostearate.

Reaction of Phenols with Methyl α -Eleostearate. The predetermined amounts of methyl α -eleostearate (ESA or E) were charged in a 100-mL four-necked flask equipped with a stirrer, a thermometer, a dropping funnel, and a reflux condenser. Then predetermined amounts of 20% aqueous solution of *p*-toluenesulfonic acid was added dropwise to the stirred mixture through the dropping funnel at 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.

TABLE I
 NMR Results of Tung Oil and Methyl α -Eleostearate^a

Peak no.	1	2	3	4	5	6	7
Peak position (ppm)	0.8	1.3	2.1	3.5	4.1	5.3	6.0
Assignment	Terminal			Alcoholic glycerine			
	—CH ₃	—CH ₂ —	—CH ₂ —	—CH ₃	—CH ₂ —	—CH=CH ₃ —	
Tung oil	9.6 (9.0)	49.1 (42.0)	19.2 (18.0)	— (0)	4.2 (4.0)	5.9 (6.0)	12.5 (12.0)
Methyl α -eleostearate	8.3 (9.0)	46.8 (42.0)	18.2 (18.0)	7.9 (9.0)	— (0)	5.2 (6.0)	11.7 (12.0)

^a Numerals show the area ratio of various peaks. Parentheses show the ratio by calculation.

RESULTS AND DISCUSSION

Reaction Products of E and C

Results of HLC_{THF} Analysis. C and E were reacted with the aid of 0.2 wt % PTS at C/E charging weight ratios of 3/7, 7/3, and 9.5/0.5 at 80°C. Figure 3 shows the HLC_{THF} chromatograms of the reaction products.

In order to collect separately compounds each corresponding to the peaks ①–⑤ in Figure 3, the reaction products formed at C/E charging weight ratios of 3/7 and 7/3 were subjected to preparative HLC, the chromatograms of which are shown in Figure 4. Samples of compounds corresponding to the hatched portions of the preparative HLC chromatograms were collected. The HLC_{THF} chromatograms of the samples a, b, c, d, and e are shown in Figure 5, which corresponds to the peaks ①, ②, ③, ④, and ⑤, respectively, in Figure 3.

In Table III are listed the C/E molar ratios of the samples determined by NMR analysis and the average molecular weights of the samples. These results may indicate the following: sample b (peak ①): compound formed from one E molecule and one C molecule; sample c (peak ②): compound formed from one E molecule and two C molecules; sample d (peak ③): compound formed from two E molecules and one to two C molecules; sample e (peak ④): compound formed from two E molecules and three C molecules; sample f (peak ⑤): compound formed from three E molecules and two C molecules.

Thus it was confirmed that the compounds containing three or less E monomer units can be almost completely separated from the E–C reaction mixture by

 TABLE II
 Average Molecular Weight

Sample	Molecular wt by calculation	Average molecular wt by VPO
Tung oil (T)	878	824.0
Methyl α -eleostearate (E)	294	300.6

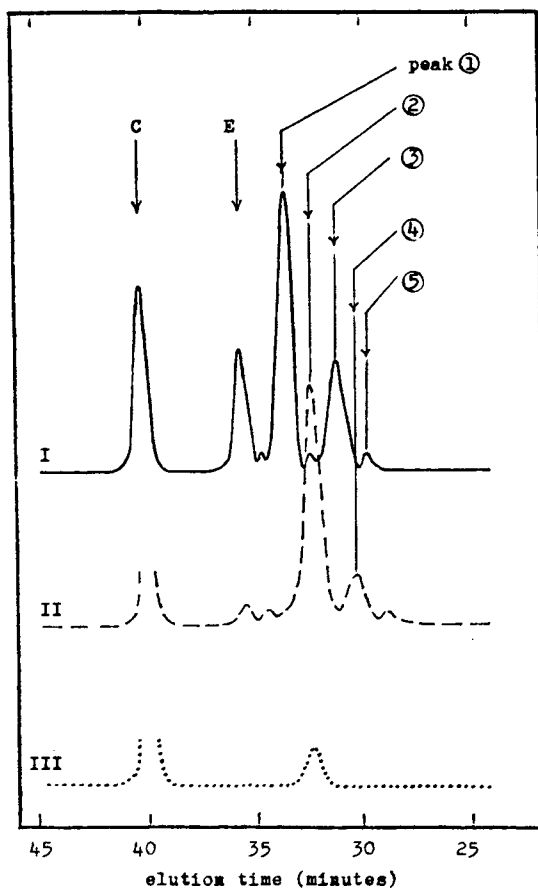


Fig. 3. HLC_{THF} chromatograms of E-C reaction products at varied C/E molar ratios: (I) 3/7; (II) 7/3; (III) 9.5/0.5.

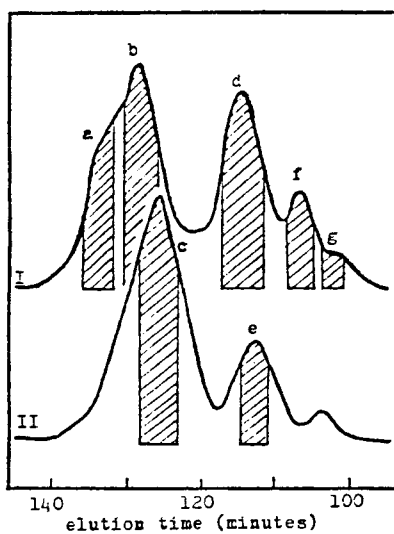


Fig. 4. HLC chromatogram measured by HLC for separation of E-C reaction products at varied C/E molar ratios: (I) 3/7; (II) 7/3.

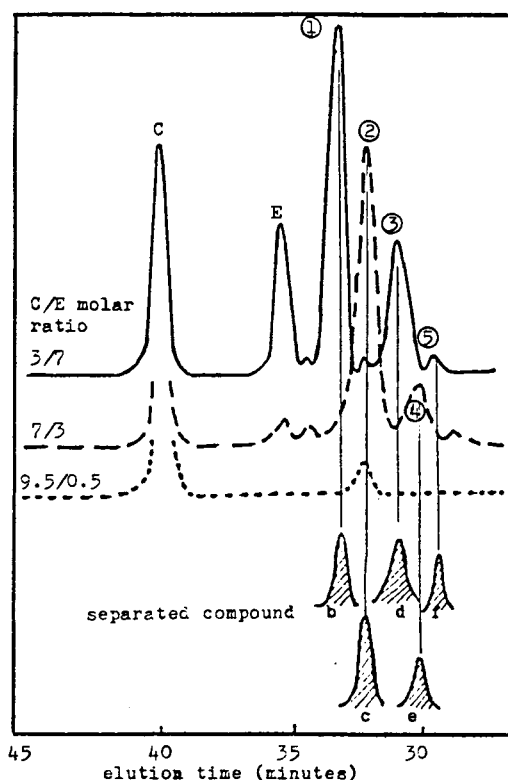


Fig. 5. HLC_{THF} chromatograms of E-C reaction products and separated compound.

HLC_{THF} . Therefore, it must be possible to investigate the basics of reaction of 3-methyl phenol (C) with tung oil by tracing the reaction of C with E as a reference with the aid of HLC_{THF} technique.

Comparison between Reaction of Tung Oil (T) with 3-Methyl Phenol (C) and Reaction of E with C. In Table IV, comparison in charging molar ratio (C/T or C/E) and reaction molar ratio (C/T or C/E) is made between the T-C reaction and the E-C reaction. The amount of C reacted in each T-C reaction was substantially the same on the basis of α -eleostearate units as that of C reacted in the corresponding E-C reaction. Therefore, it is apparent that no substantial difference in reactivity with C is present between T and E. The increased charging molar ratio of C to E led to an increase in the amount of C reacted. Up

TABLE III
C/E Reaction Molar Ratio and Average Molecular Weight of Separated Compound

Sample	NMR		
	(C's- CH_3 /E's- CH_3 ratio)	C/E reaction molar ratio	Average molecular weight
b	1.25	1.25	404.4
c	1.91	1.91	492.4
d	0.74	0.74	769.4
e	1.35	1.35	900.6
f	—	—	1053.0

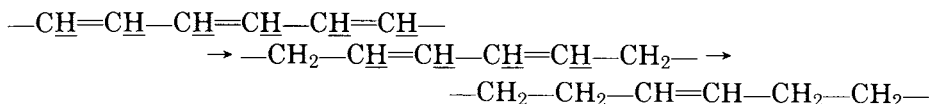
TABLE IV
Relationship between the Charging Molar Ratio and the Reaction Molar Ratio of C and T or E

Sample	Charging molar ratio		Reaction molar ratio	
	C/(T or E) weight ratio	C/(T or E) molar ratio	C/(T or E) molar ratio	(C/ α -eleostearyl group) molar ratio
Tung oil (T)	9.5/0.5	154.5	6.50	2.17
	7/3	19.0	4.24	1.41
	3/7	3.5	2.60	0.87
Methyl α -eleostearate (E)	9.5/0.5	51.7	2.31	2.31
	7/3	6.4	1.64	1.64
	3/7	1.2	1.09	1.09

to about 2 mol of C could be reacted with 1-mol of E. With the increase in the amount of C reacted, the formation of E polymer was suppressed. It was found that, when a maximum of about 2 mol of C was addition-reacted with E, the polymerization of E did not occur.

Other Analyses of E-C Reaction Products (Samples Collected). The results of NMR analysis of the E-C reaction products (samples collected) are shown in Table V.

E has six— $\text{CH}=\text{CH}$ — protons in the molecule, the number of which decreases to two when the conjugated double bonds are completely involved in a reaction as shown below:



The samples d ($\text{E}_2\text{C}_{1\sim 2}$) and f (E_3C_2) have three to four — $\text{CH}=\text{CH}$ — protons per α -eleostearate unit, and may have some conjugated double bonds not always consumed in the reaction. Thus the presence of the samples d and f in the reaction products indicates that some conjugated double bonds may remain unreacted in some cases.

The presence of around three but less than four ring H protons plus — OH proton per C unit in the reaction products indicates that the E-C reaction is a nucleophilic substitution reaction. Detailed analysis revealed that the samples b and c (monosubstituted compounds of C) have around three ring H protons plus — OH proton per C unit, and that the samples d and f (including the di-substituted compounds of C) have two to three ring H protons plus — OH proton per C unit. These values substantially coincide with those calculated. The number of protons (H) attached to double bond carbon atoms is 3.55 for the sample b (1:1 adduct of E with C), around 2 for the samples c and e (adduct with one E molecule) connected with two C molecules, and 3.23 for the sample d (adduct with one or two E molecules) connected with one C molecule. These values also substantially coincide with those calculated.

Reaction Products of E and P

The reaction of P with T gave a higher molecular weight reaction product, compared with the reaction of C with T. As a reason for this, the poorer com-

TABLE V
NMR Results of E-C Reaction Product

Sample	Ring H	$-\overline{\text{CH}}=\overline{\text{CH}}-$	Alcoholic $-\overline{\text{CH}}_3$	Terminal $-\overline{\text{CH}}_3$ of RCOOH	Cresol's $-\overline{\text{OH}}$	Ring H/ $-\overline{\text{OH}}$
b (E-C)	3.39	3.55	3.0	2.84	1.25	2.72
c (C-E-C)	6.07	2.09	3.0	2.86	1.91	3.18
d (E ₂ C ₁₋₂)	1.89	3.23	3.0	2.91	0.74	2.56
e (E ₂ C ₃)	4.38	2.19	3.0	3.35	1.35	3.25
f (E ₃ C ₂)	2.26	4.20	3.0	2.93	3.11	1.75
E	—	6.0	3.0	3.0	—	—
C	4.0	—	—	—	1.0	4.0

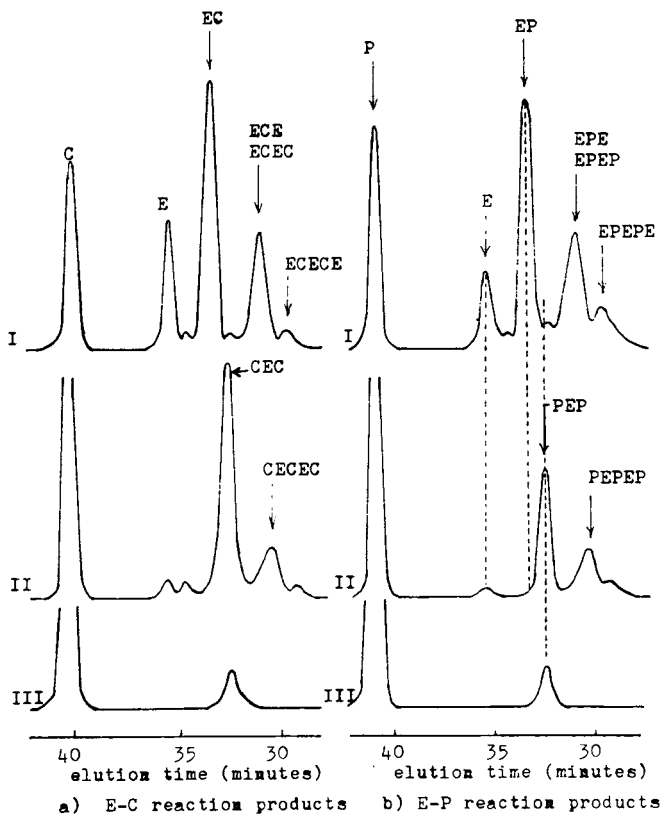


Fig. 6. HLC_{THF} chromatograms of E-C reaction products and E-P reaction products prepared at varied E/C molar ratios and E/P molar ratios: (I) 3/7; (II) 7/3; (III) 9.5/0.5.

patibility of P with T was pointed out. But that has not been supported by any experimental fact. In view of this, investigation was made on the reaction of P with E, which might be easily analyzed.

The HLC_{THF} chromatograms of P-E reaction products are shown in Figure 6. The amounts of P reacted with E are listed in Table VI, calculated from the HLC_{THF} chromatograms.

TABLE VI
Relationship between the Charging Molar Ratio and the Reaction Molar Ratio of C or P and E

Sample	Charging molar ratio		(P or C)/E reaction molar ratio
	P/E weight ratio	P or C/E molar ratio	
<i>m</i> -Cresol (C)	9.5/0.5	51.7	2.31
	7/3	6.4	1.64
	3/7	1.2	1.09
Phenol (P)	9.5/0.5	59.4	2.54
	7/3	7.3	1.60
	3/7	1.3	0.57

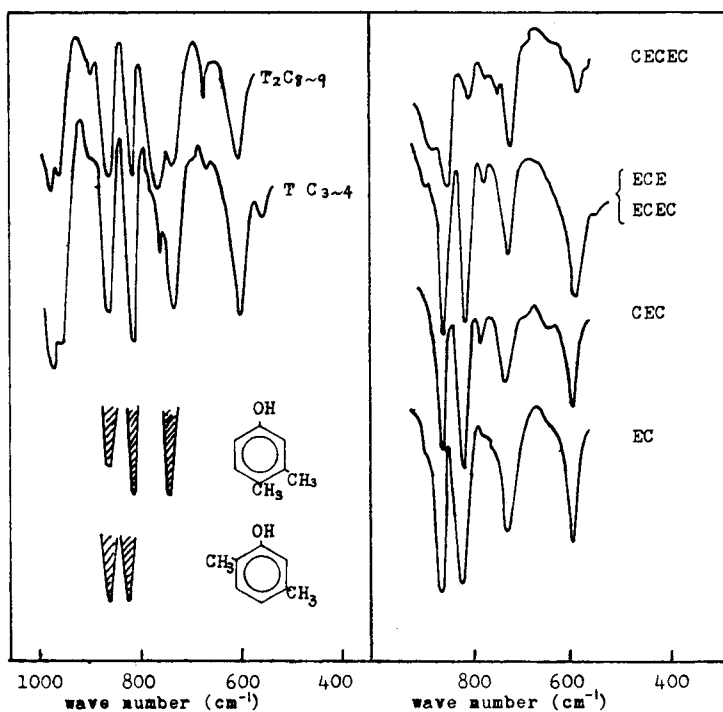


Fig. 7. IR spectra of T-C reaction product and E-C reaction product.

In the reactions with T, a large difference in molecular weight of reaction product was found between P and C as a counterpart reactant. By contrast, in the reactions with E, almost no such difference was found between P and C. It was found that almost no high molecular weight compounds were formed in reaction of P with E.

The results mentioned above will lead to the following conclusion. The polymerization of the C-T reaction system may be due to the advance of the T-P-T reaction. In the reaction, T-rich environments may be formed into which P cannot easily intrude. This may facilitate explanation on the advance of polymerization of the C-T reaction system. In the case of the T-C-T reaction, C may be able to approach T more easily than P in the T-P-T reaction (C-rich environments may be formed which may suppress the polymerization of T).

On the other hand, the use, instead of T, of E having about $\frac{1}{3}$ as high molecular weight at T, brought about little formation of polymer and gave substantially the same type of product in a reaction of it with either C or P. This can be explained without contradiction when attention is directed to the facts that the SP value of E is higher and closer to those of C and P than that of T and that the molecular weight of E is so low as to disperse well in solutions with little colloidal behavior.

Confirmation of Preferential Reaction at Para Position

It is presumed in the previous report that T reacts with phenols preferentially at the para position. In this report, this was confirmed using E in place of T.

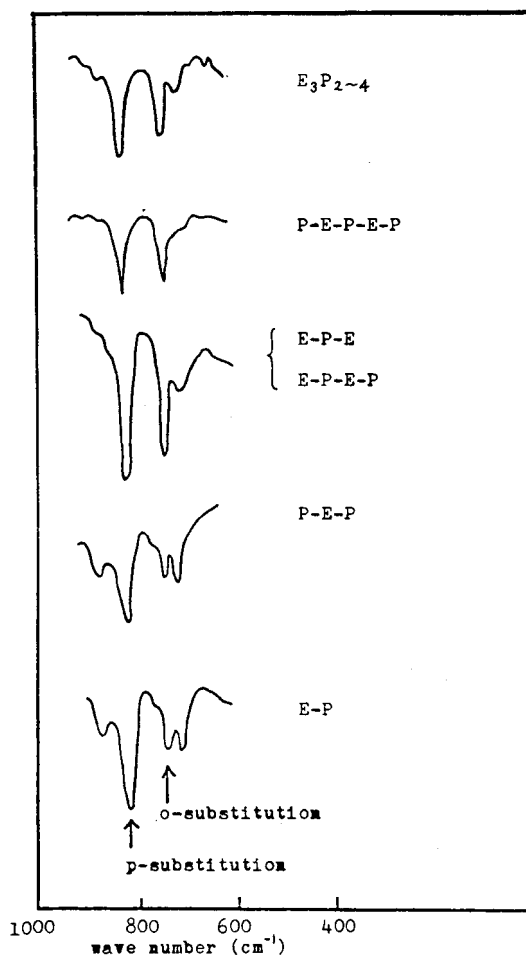


Fig. 8. IR spectra of E-P reaction product.

The IR spectra of the T-C and E-C reaction products are shown in Figure 7. As reported in the previous report, comparison of those reaction products with 2,4- and 2,6-xylenols in IR spectrum indicates preferential reaction at the para position in both T-C and E-C reactions, but does not enable the preferential reaction to be numerically estimated. The ratio of para substitution was determined using the E-P reaction product. In Figure 8 are shown the IR spectra

TABLE VII
p-Substitution Ratio of E-P Reaction Product

Sample	p-Substitution ratio (%)
E-P	73.5
P-E-P	73.5
E-P-E } E-P-E-P }	65.7
P-E-P-E-P	66.7
E-P	63.1

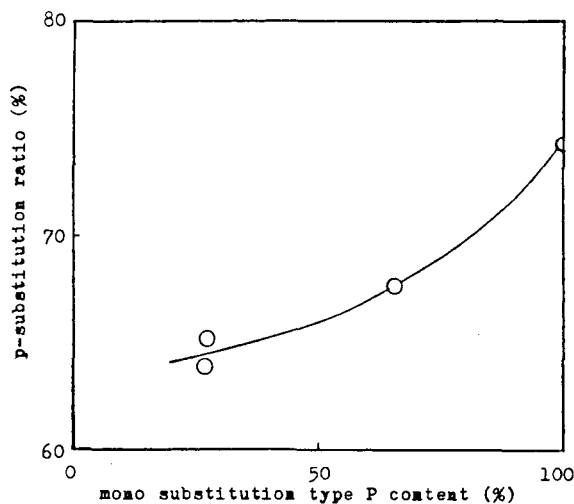


Fig. 9. Relationship between substitution number on benzene ring and *p*-substitution ratio.

of separated samples of the E-P reaction product, from which the ratios of para substitution in the samples were determined, as shown in Table VII. As a result, it was found that the monosubstituted compounds of P such as EP and PEP were more para-substituted than the distributed compounds of P such as PEPEP, EPEP, and EPE, and that an increase in disubstitution of P in reaction product lead to a decrease in para substitution of P, as shown in Figure 9. Thus the preferential para substitution of phenols was confirmed.

The ratio of para substitution was calculated as follows.

$$p\text{-substitution ratio} = \frac{1.44 \times D_{820}}{D_{760} + 1.44 \times D_{820}} \times 100 (\%)$$

(D_{760} = absorbance at 760 cm^{-1} ; D_{820} = absorbance at 820 cm^{-1})

CONCLUSION

Investigation was made on the reactions of phenols with methyl α -eleostearate (E), and led to the following conclusions:

1. It was confirmed that the E-C reaction products can be separated by HLC_{THF} into individual compounds, the amounts of which can also be determined. It also was found that tracing the reactions of phenols with E facilitated accurate analyses of reactions of phenols with tung oil (T).

2. The analysis of E-C reaction revealed:

- (i) that the E-C reaction is a nucleophilic substitution reaction via the conjugated double bonds of E,
- (ii) that, as the C charging molar ratio is increased, the amount of C reacted with E is increased up to a maximum of 2 mol/mol E, and
- (iii) that an increased amount of C reacted with E suppresses polymerization of E, which does not substantially occur when 2 mol of C is reacted with 1 mol of E. In this respect, the E-C reaction was found to substantially coincide with the T-C reaction.

3. The analysis of E-P reaction indicates that formation of a polymeric T-P reaction product is attributed to the solubility of P with T.

4. It was confirmed that the reactions of P occur preferentially at the para position.

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