THE PHENOLIC INHIBITOR IN DEHYDROGENATED ROSIN ACIDS

BY

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B.S., Oklahoma Agricultural and Mechanical College, 1942

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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ENTITLED The Phenolic Inhibitor in Dehydrogenated Rosin Acids

BE ACCEPTED* AS FULFILLING THIS PART OF THE REQUIREMENTS FOR

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For the infrared spectrum determinations and interpretations the author is indebted to Dr. F. A. Miller and Mrs J. L. Johnson; he also wishes to acknowledge the assistance of Miss Ruth Johnson and Mr. J. C. Brantley, who were responsible for the ultraviolet spectrum determinations.

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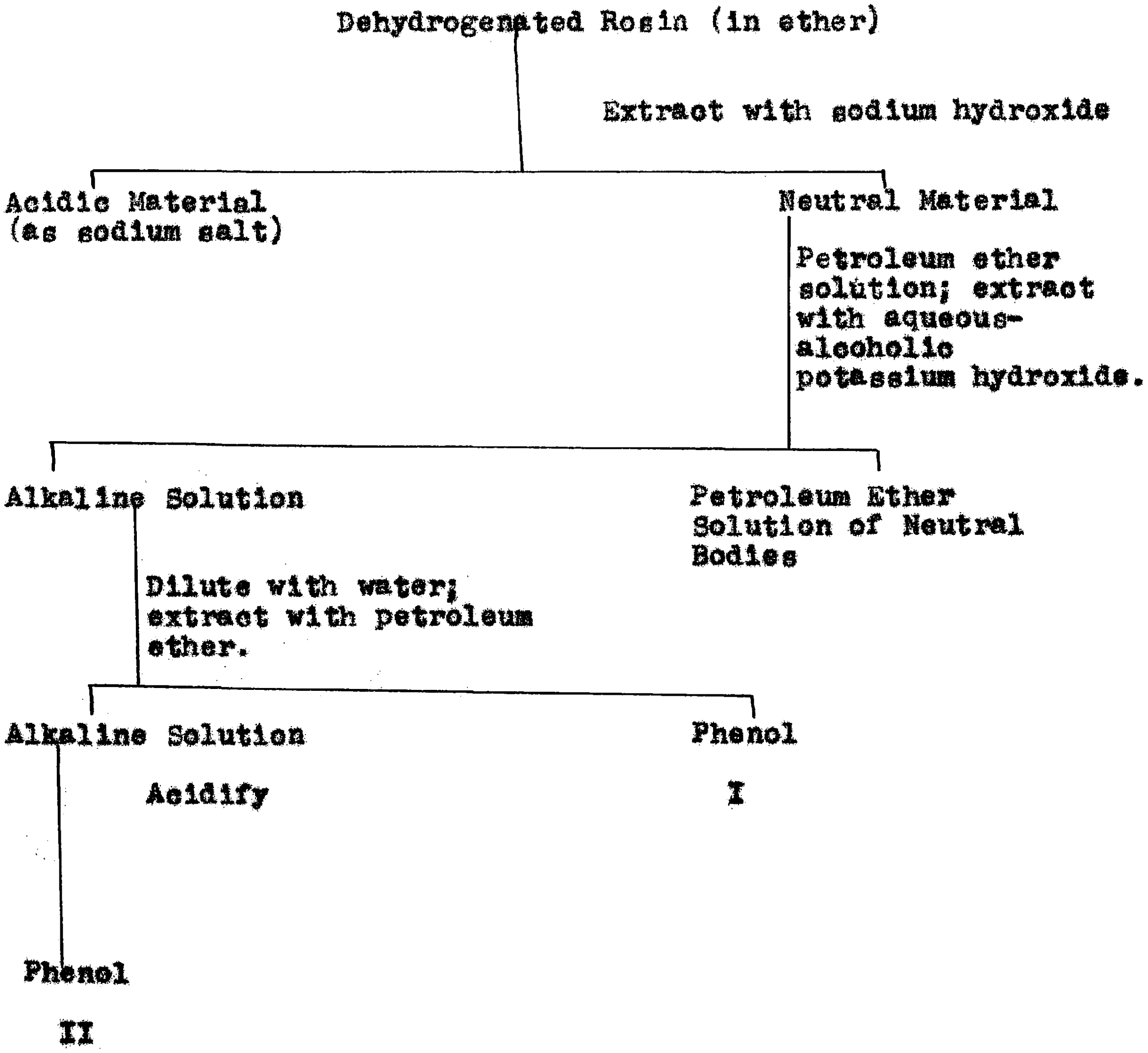
I. INTRODUCTION

The war-prompted search for substitutes for the soap used as an emulsifier in the production of GR-S led to the extensive use of dehydrogenated rosin soap. This material, manufactured under the name of Dresinate 731 by the Hercules Powder Company and consisting largely of sodium dehydroabietate, has proved especially desirable as an emulsifier because it produces a rubber with high tack. As first manufactured it had the disadvantage that it made necessary the use of long polymerization cycles to bring about the desired conversion of rubber. Although this difficulty was later corrected, it was of interest to investigate the substance causing the retarded polymerization, from the standpoint of both determining its structure and of using it or a similar material as an inhibitor in monomer storage.

II. HISTORICAL AND THEORETICAL

The nature of the polymerization retarder in Hercules Resin 731 has been investigated by Hays (1), and by Hays, Drake, and Pratt (2); they employed the following scheme in isolating phenolic concentrates which they found to be powerful retarders:

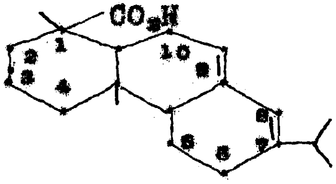


Phenols I and II were dark oils which could not be crystallized, but from ultraviolet spectra it was concluded that I, with maxima at 281 and 287 mμ., resembled p-cresol or menthylphenol, and that II, with maxima at 276 and 282 mμ., resembled resorcinol.

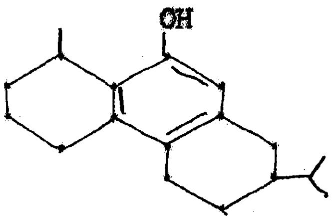
Although no other work has been reported on dehydrogenated rosin, Erdtman (3) working with pine heart-wood isolated 3,5-dihydroxystilbene, and its monomethylether. Cox (4) investigating the neutral fractions of several commercial rosins, isolated 3,5-dimethoxystilbene. Thus it has been established that resorcinols are present in pine wood and in rosin, and it is possible that they would appear in dehydrogenated rosin, although probably in modified form.

Numerous phenols have been reported as products of the destructive distillation of wood, and it is probable that some are present as such in the wood before pyrolysis and hence would be found in rosin. Among those reported are phenol, o-, m-, and p-cresol, 1,3-xylenol-5, pyrocatechol, guaiacol, pyrogallol, and eugenol.

In addition to the phenols which are known to be present in wood or rosin there is the possibility that phenols are present in dehydrogenated rosin as a result of the hydrogenation-dehydrogenation process. l-Abietic acid, V, which is the principal constituent of rosin might be

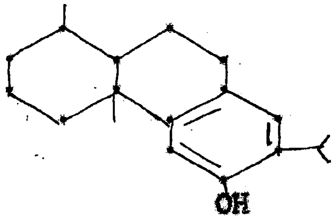


V

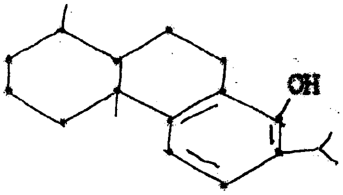


VI

expected to oxidize to a slight extent in the presence of air in a manner similar to that observed with tetralin to yield hydroperoxides. An attack by oxygen at an allylic position 10 would upon subsequent hydrogenation-dehydrogenation yield the phenol VI. By a similar mechanism phenols VII and VIII might also be expected from abietic and dihydroabietic acids, respectively.



VII



VIII

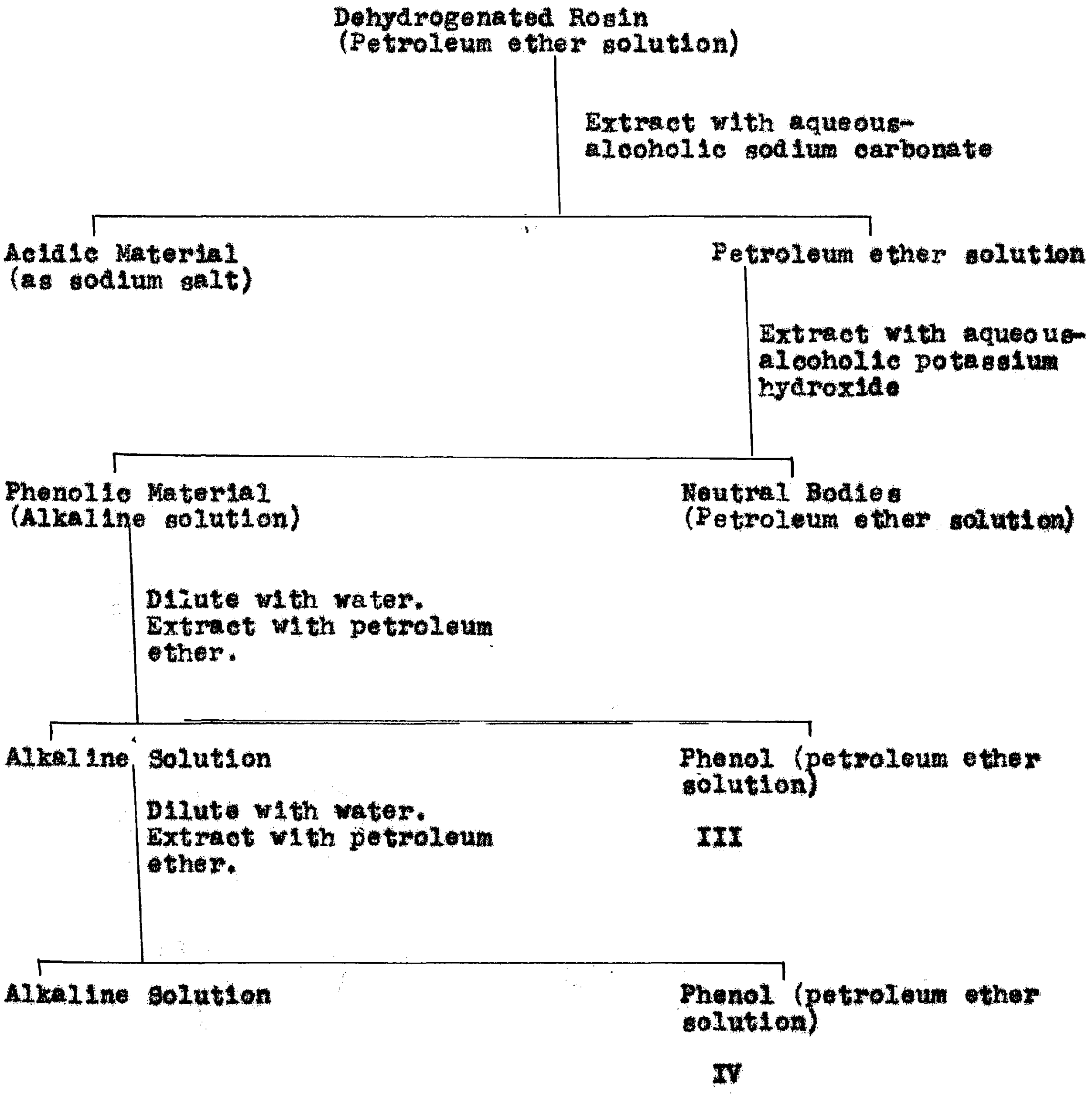
It was the purpose of this work to investigate further the nature of phenolic material from dehydrogenated rosin with a view toward obtaining a pure enough sample of the phenolic concentrate I to allow a further characterization. More specifically it was decided to prepare compounds structurally related to those which might be expected in dehydrogenated rosin in view of the accumulated knowledge of the constituents of rosin and pine wood, and to compare the ultraviolet spectra and other properties of these compounds with those of the phenol present in Hercules Resin 731.

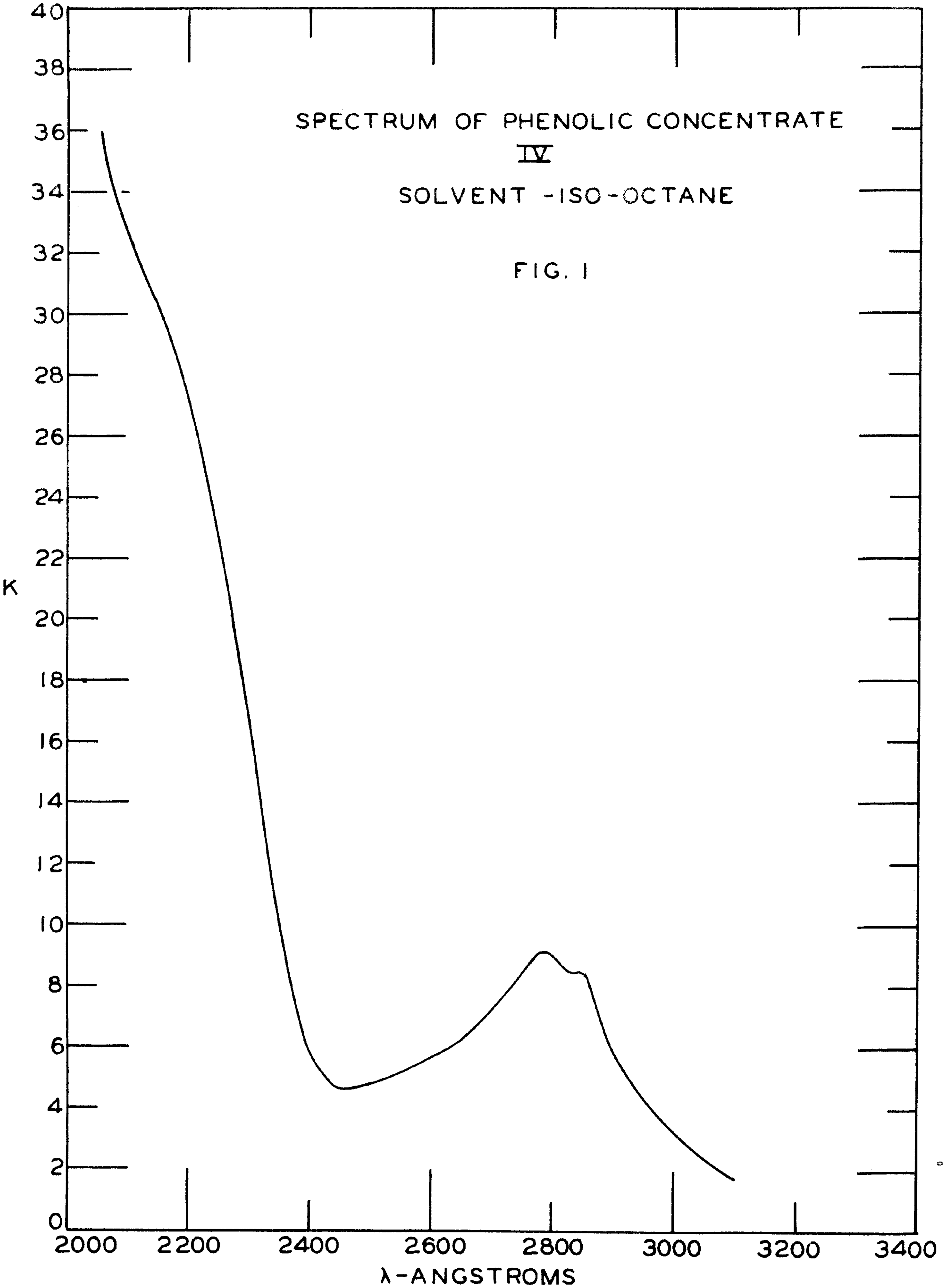
III. DISCUSSION

A. Isolation and Purification of the Phenolic Concentrate.

A logical point of departure in the isolation of the phenolic retarder in Hercules Dresinate 731 was an attempt to duplicate the results of Hays (1), and Hays, Drake, and Pratt (2), who had worked with this problem previously. Since the experimental details of their extraction procedure were not available, it was not expected that their results could be duplicated exactly. The parent acid, Hercules Resin 731, rather than the sodium salt was used as a starting material. The phenolic product isolated was very impure and considerable further purification was necessary. Ten kilograms of resin were treated, and 18.7 g. of a phenolic concentrate was obtained. It was found that the purity of the concentrate could be improved considerably by chromatography on an activated alumina column, but a further purification was necessary before a material comparable to that reported by the previous investigators was obtained. This material was obtained in a yield of only 0.27 g.

Several modifications of the extraction procedure were investigated with a view toward improving the purity of the phenolic concentrate, and a scheme was developed which yielded a product which had a sharp and well-defined ultraviolet spectrum. This procedure is represented schematically as follows:


Dehydrogenated Rosin
(Petroleum ether solution)
Extract with aqueous-alcoholic sodium carbonate
Acidic Material
(as sodium salt)
Petroleum ether solution
Extract with aqueous-alcoholic potassium hydroxide
Phenolic Material
(Alkaline solution)
Neutral Bodies
(Petroleum ether solution)
Dilute with water.
Extract with petroleum ether.
Alkaline Solution
Phenol (petroleum ether solution)
III
Dilute with water.
Extract with petroleum ether.
Alkaline Solution
Phenol (petroleum ether solution)
IV



SPECTRUM OF PHENOLIC CONCENTRATE

IV

SOLVENT -ISO-OCTANE

FIG. 1

The spectrum of fraction IV from the second dilution is shown in Figure 1. This material, although obtained in low yield (0.017 per cent), had a better defined spectrum than that obtained by other methods. Table I shows a comparison of the analytical data obtained on this concentrate with that reported by Hays, Drake and Pratt (2) on the two phenolic fractions (I and II) which they obtained.

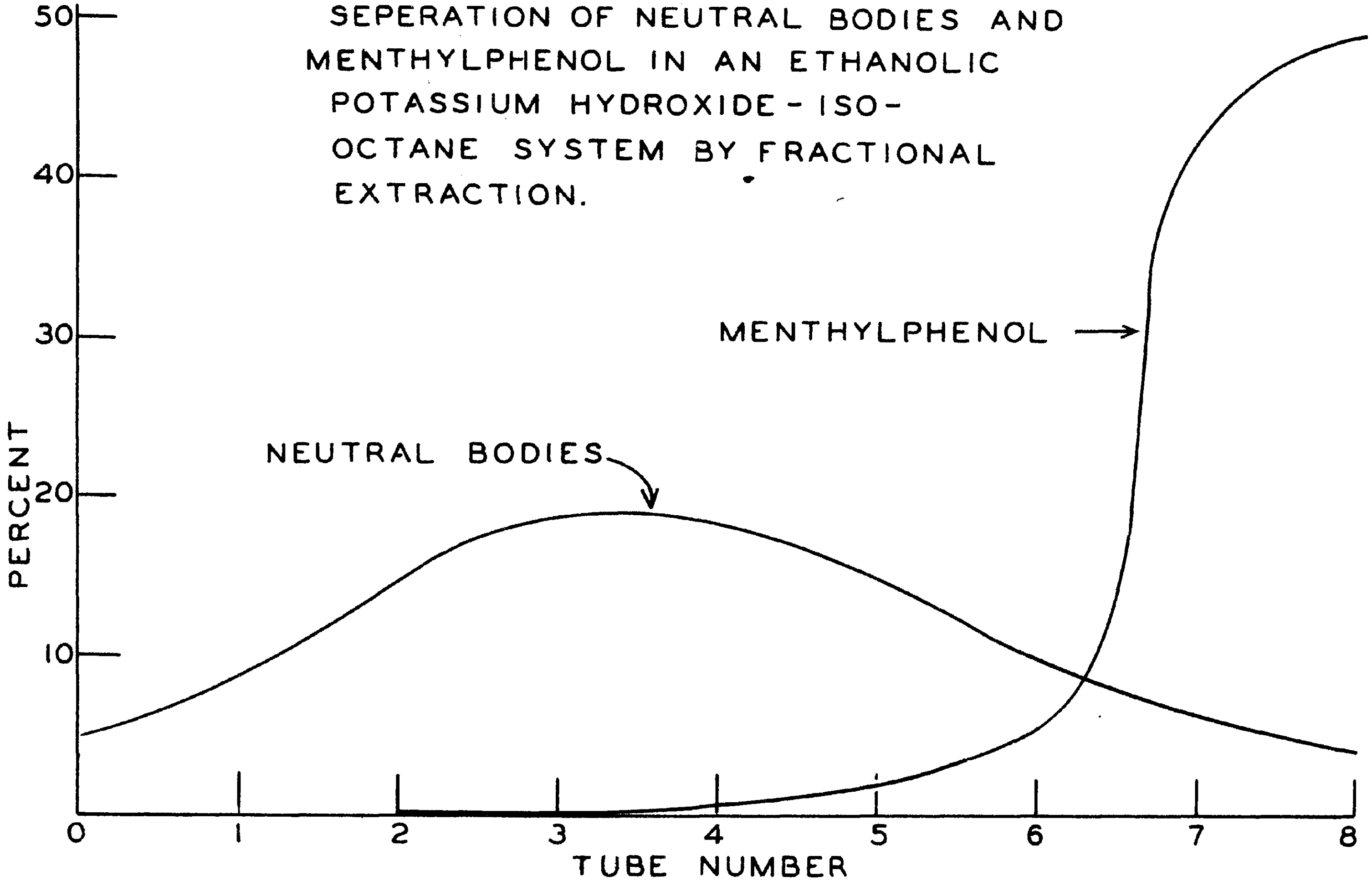
TABLE I

Analytical Data on Phenolic Fractions

	Phenol Fraction I	Phenol Fraction II	Phenol Fraction IV
C	80.1	76.7	77.6
H	10.2	9.6	9.3
OCH_3	5.1	4.8	2.5
M.W. (Rast)	320	282	297
Ultraviolet absorption Maxima	2810 Å	2760 Å	2790 Å
	2870 Å	2820 Å	2850 Å

The analysis of IV corresponds to the empirical formula $C_{19.2}H_{27.3}O_{2.43}$, and it is apparent that this material resembles most closely phenolic fraction II although there is a considerable difference in the per cent methoxyl. It is also apparent from the empirical formula that although phenolic fraction IV has a well-defined ultraviolet spectrum, it is a mixture of two or more materials.

FIG. 2



SEPERATION OF NEUTRAL BODIES AND MENTHYLPHENOL IN AN ETHANOLIC POTASSIUM HYDROXIDE - ISO-OCTANE SYSTEM BY FRACTIONAL EXTRACTION.

The preparation of a crystalline derivative from IV followed by recovery of the phenol offered an attractive route to obtaining a pure specimen of the phenol. However, it was not possible to obtain a crystalline derivative although the preparation of the phenyl-, α-naphthyl- and diphenylurethanes, the benzoate, aryloxyacetic acid, picrate, nitro-, and bromo-derivative was attempted. In every case either a glass or an oil which could not be crystallized resulted.

The process of fractional extraction as utilized by Craig (5) and others has proved very successful in the separation of difficulty separable mixtures; this procedure was investigated in an attempt to further resolve phenolic fraction IV. Since the problem was one of separating the kryptophenol in the resin from neutral and acidic material present, an experiment was first designed in which it was demonstrated that the kryptophenol menthylphenol could be efficiently separated from the neutral material present in the resin. Thus an equal weight mixture of menthylphenol and neutral bodies was separated in an eight-plate extraction set-up with the solvent pair iso-octane* /0.5 per cent ethanolic potassium hydroxide. It was found that this system was very efficient in separating the two materials; the menthylphenol (98 per cent) concentrated in tubes seven and eight of the set-up, while only 10 per cent of the neutral bodies was found in these tubes. These data are represented graphically in Figure 2. The concentrations of the

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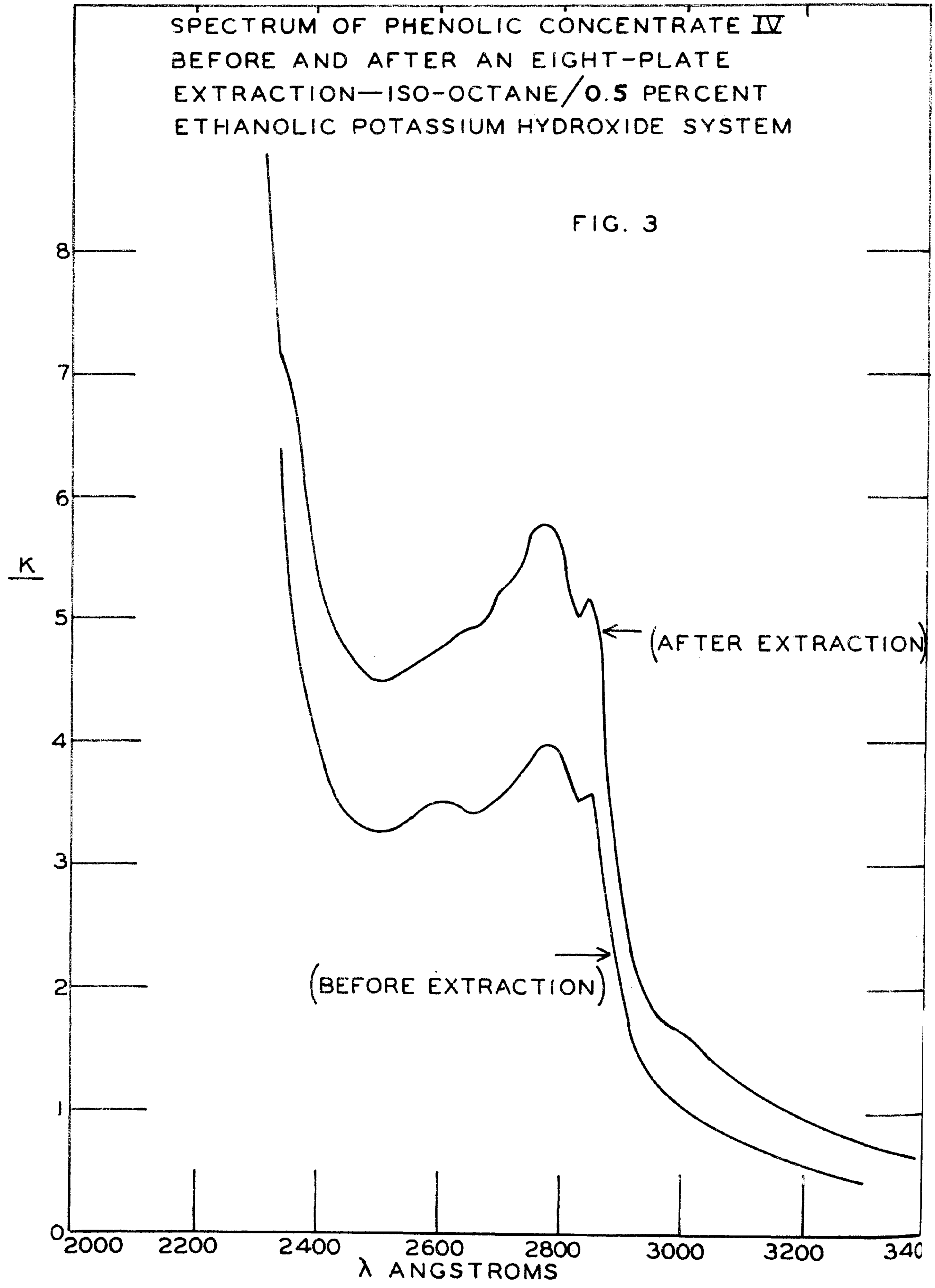
* Iso-octane is Rohm and Haas 2,2,4-trimethylpentane.



SPECTRUM OF PHENOLIC CONCENTRATE IV BEFORE AND AFTER AN EIGHT-PLATE EXTRACTION—ISO-OCTANE/0.5 PERCENT ETHANOLIC POTASSIUM HYDROXIDE SYSTEM

FIG. 3

constituents in each of the tubes was estimated by ultraviolet spectrophotometry.

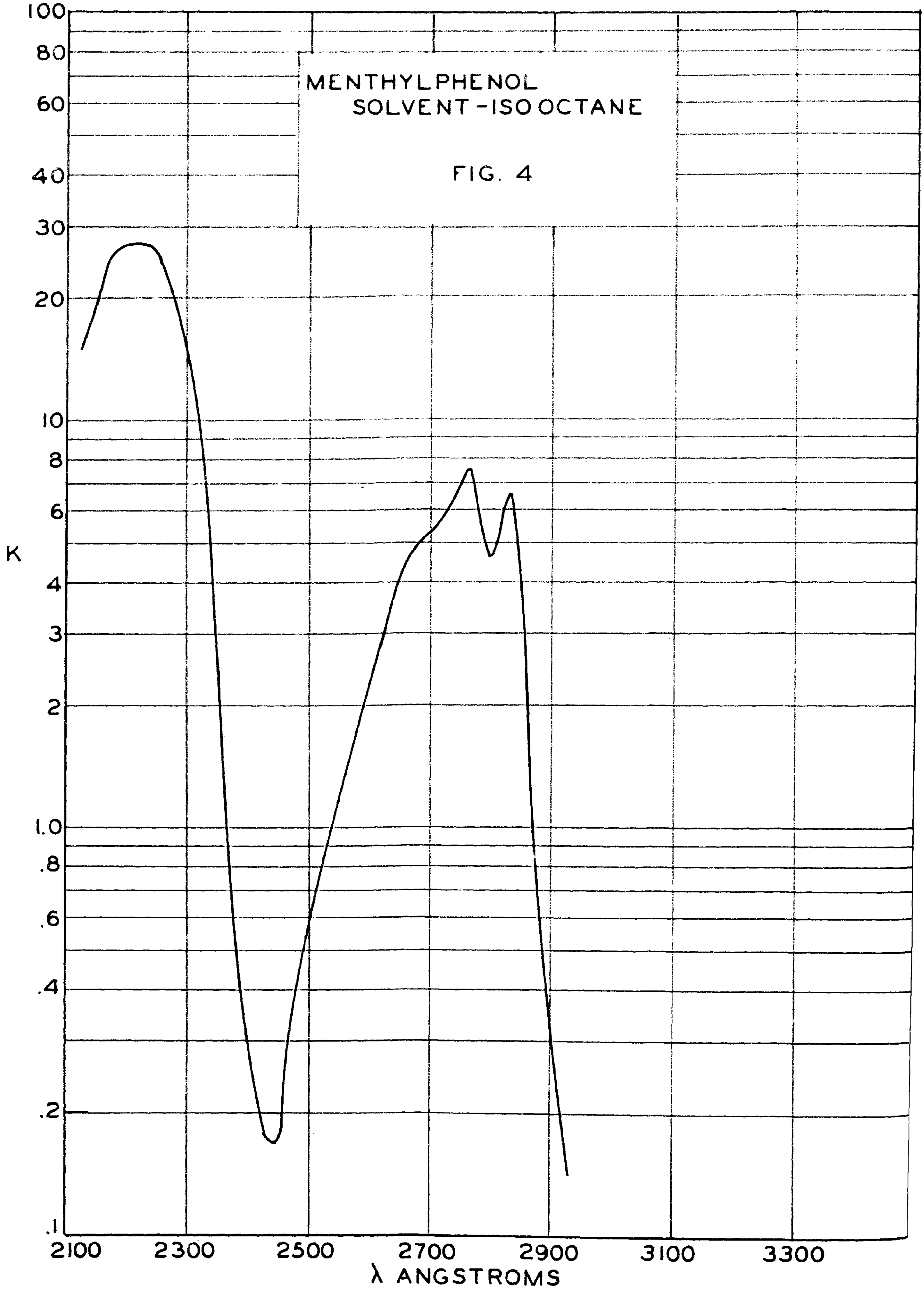
The extraction procedure when applied to phenolic fraction IV effected the removal of retene from the sample; in this instance as with menthylphenol the phenol concentrated in tubes seven and eight. The spectrum of the phenol recovered from tube eight is presented in Figure 3 and shows that the extraction procedure caused the disappearance of the retene peak at 2600 Å.

The fractional extraction procedure while effective as an analytical tool could not be used as a preparative method for obtaining quantities of the purified phenols from the crude concentrate, since to be effective the procedure had to be operated with extremely dilute solutions.

B. Preparation of Terpene Phenols and Comparison with the Resin Phenol.

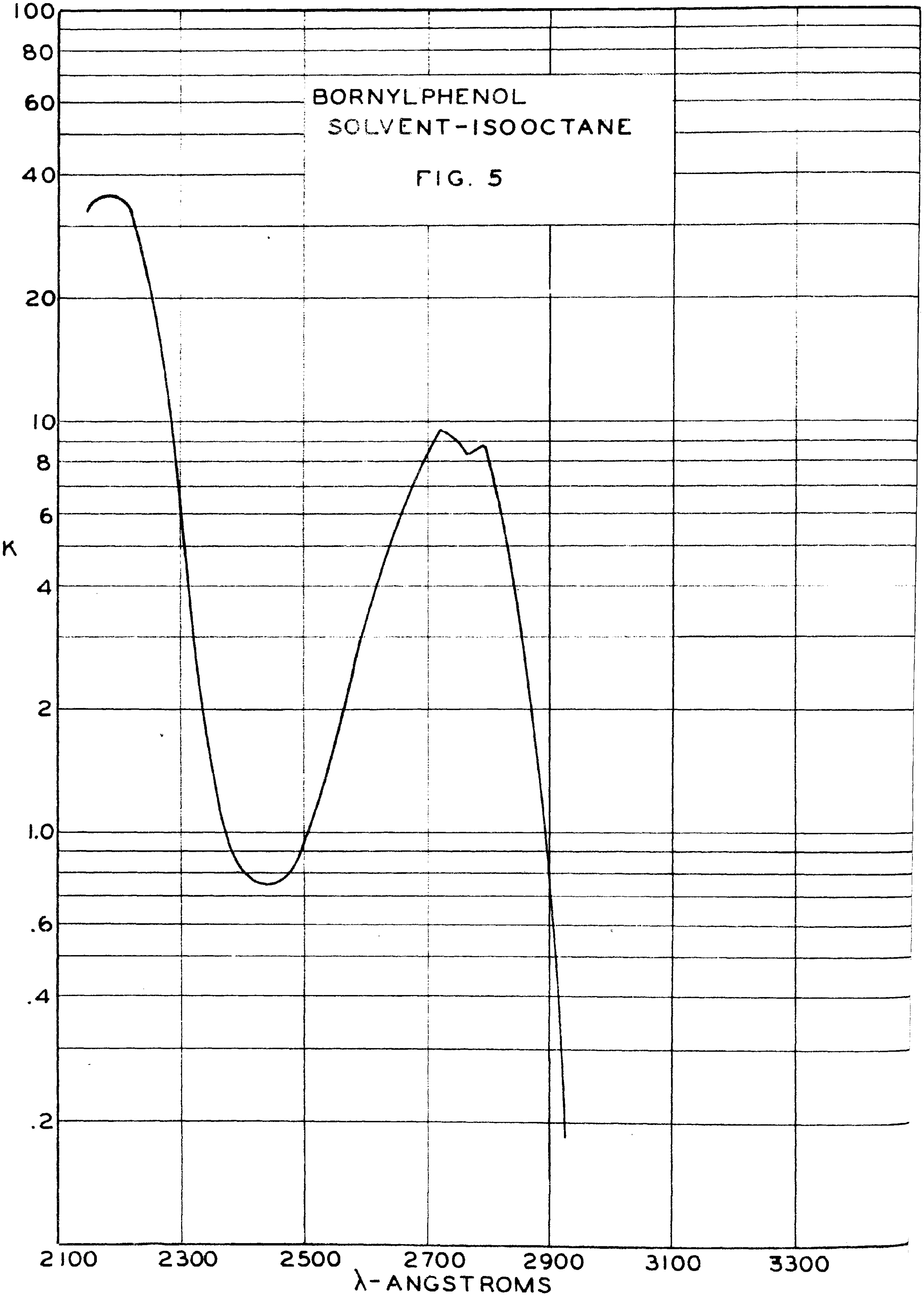
To investigate further the possibility suggested by Hays (1) that the resin phenol might be a terpene phenol such as menthylphenol several terpene phenols were prepared and their ultraviolet spectra examined.

Menthyl-, bornyl-, and fenchylphenols were prepared by reacting the corresponding chlorides with a large excess of phenol at reflux temperature according to the procedure of Kurssanow (6) for menthylphenol. Pinylphenol was prepared by a condensation of pinene and phenol in the presence of *p*-toluenesulfonic acid as described by Rummelsburg (7) for allo-ocimene and phenol. The terpene phenols were readily separable from phenol by virtue of their insolubility in aqueous sodium hydroxide. All the phenols were



MENTHYLPHENOL
SOLVENT - ISO OCTANE

FIG. 4



BORNYLPHENOL
SOLVENT-ISOOCTANE

FIG. 5

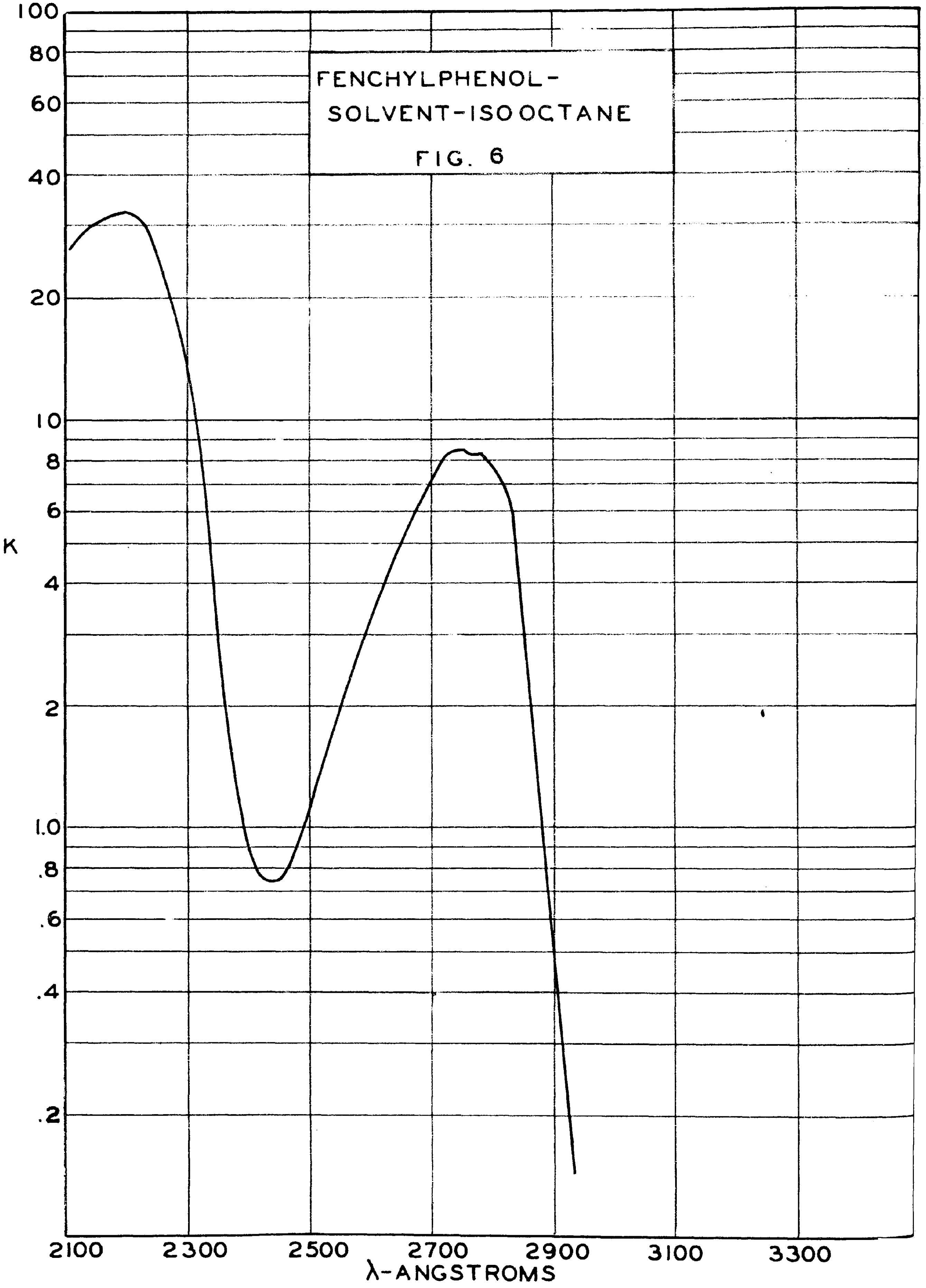
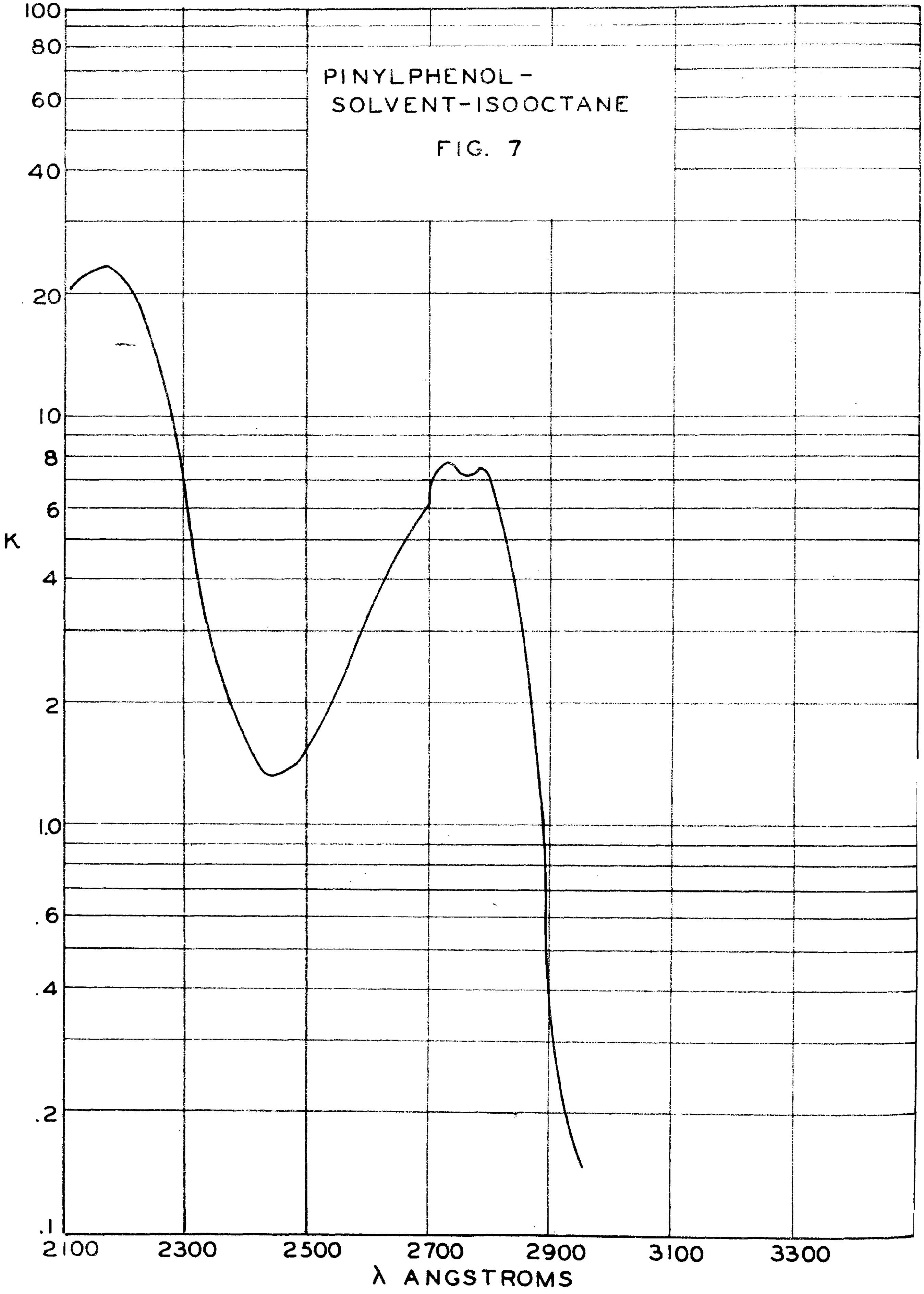

FENCHYLPHENOL-
SOLVENT-ISOOCTANE
100
80
60
40
20
10
8
6
K
4
2
1.0
.8
.6
.4
.2
2100
2300
2500
2700
2900
3100
3300
λ-ANGSTROMS

FIG. 6



PINYLPHENOL -
SOLVENT-ISOOCTANE

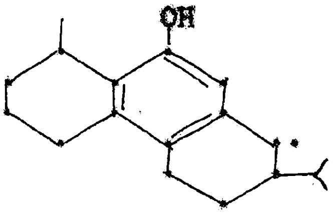
FIG. 7

initially obtained as viscous oils by distillation. Menthylphenol was purified via the phenylurethane and was obtained in crystalline form. Fenchylphenol crystallized after nine months standing. The name menthylphenol is used for convenience; although formed from menthyl chloride, the compound has been shown to be 4-(p-hydroxyphenyl)menthane. Kurssanow (8) showed that the point of attachment of the benzene ring to the menthane portion was in the 4 position, and the infrared measurements, Figures 14 and 15, indicated that attachment to the benzene ring was para to the hydroxyl group.

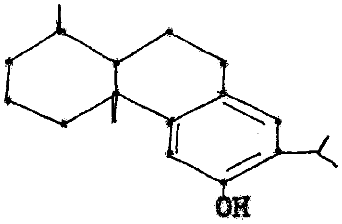
The spectra of the four terpene phenols, Figures 4, 5, 6, and 7 were similar in shape with only slight differences in the location of the absorption maxima. Menthylphenol with maxima at 2765 and 2830 Å most closely resembled the resin phenol; however, the two spectra were sufficiently different in the 2000-2250 Å region to warrant the conclusion that the resin phenol was not entirely menthylphenol. Whereas the terpene phenols had a maximum in the 2000-2250 Å region, the resin phenol had only an inflection. The inflection is characteristic of resorcinol, orcinol, 2-propyl-3,6-dimethylphenol, and 2-propyl-4,5-dimethylphenol but could also have been the result of a mixture of an acid such as dihydroabietic or dextropimaric acid, which has no inflection or maximum, with menthylphenol, which has a definite maximum.

C. Phenols from the Oxidation of Abietic and Dihydroabietic Acids.

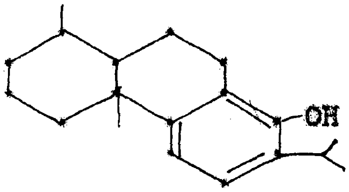
An indirect approach to the problem of obtaining the spectra of the phenols which might result from oxidized rosin acids was considered best. Structurally VI is a 2,3,4,5-tetraalkylphenol; VII is a 2,4,5-trialkylphenol and VIII a 2,3,6-trialkylphenol. Although the absorption coefficients vary depending on the alkyl group, the wave length at which the maximum absorption occurs is relatively independent of the size of the alkyl group; hence the spectrum of any 2,3,4,5-tetraalkylphenol would be expected to resemble that of phenol VI at least insofar as the position of the absorption peaks. With this concept in mind 2,3,4,5-tetramethylphenol (prehnitenol), 2-propyl-4,5-dimethylphenol, and 2-propyl-3,6-dimethylphenol were synthesized as model compounds. Their spectra, Figures 8, 9, and 10, although similar to that of the resin phenol in having an inflection in the 2100 Å range, were quite different in the 2700 Å region.



VI



VII



VIII

2,3,4,5-Tetramethylphenol was synthesized from isodurene. Isodurenesulfonic acid was prepared and subjected to a Jacobsen rearrangement essentially as described by Smith and Cass (8) for durenesulfonic acid. Prehnitenesulfonic acid thus obtained was purified as the sodium salt, which was then fused with alkali to yield after acidification the desired phenol.

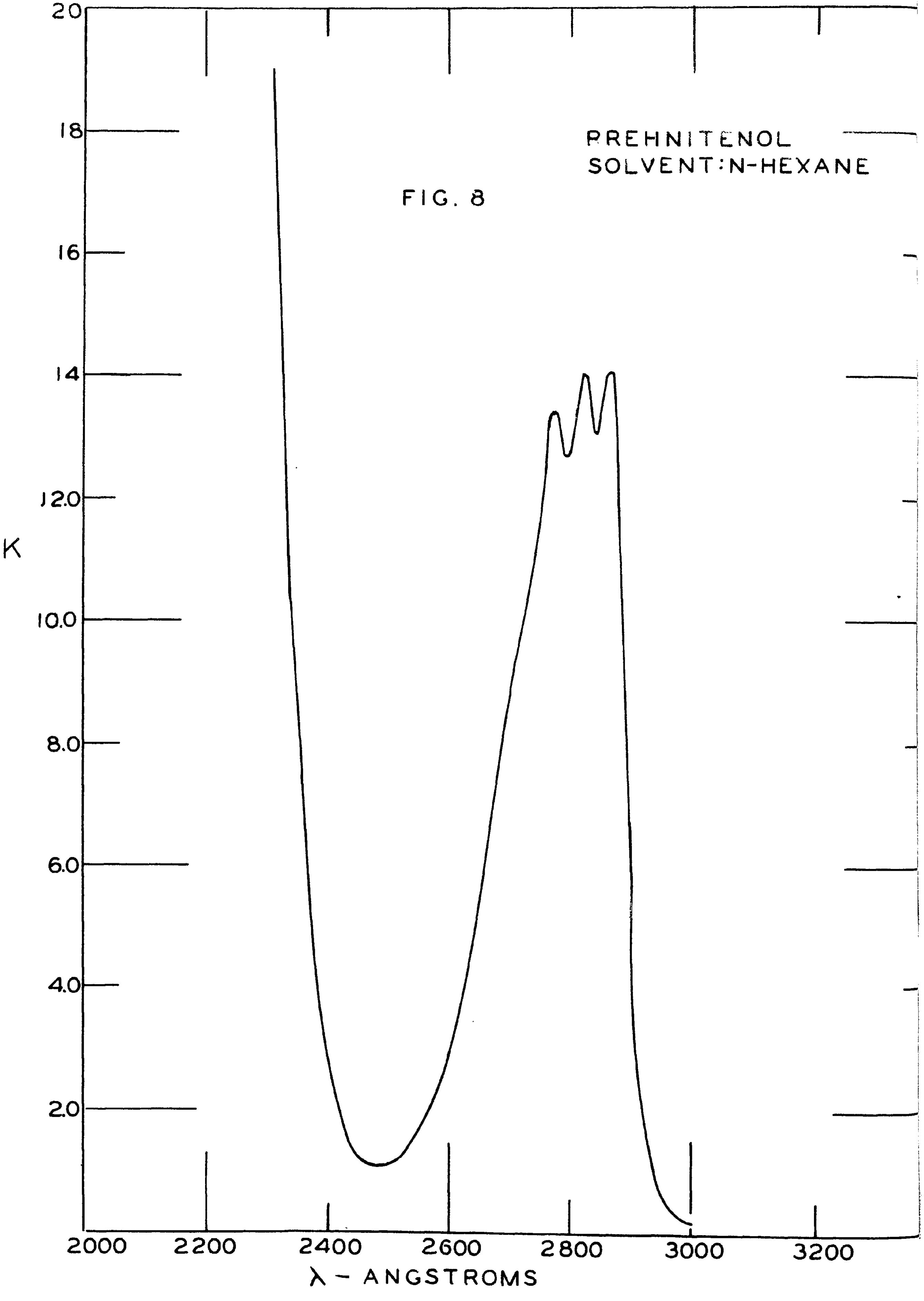
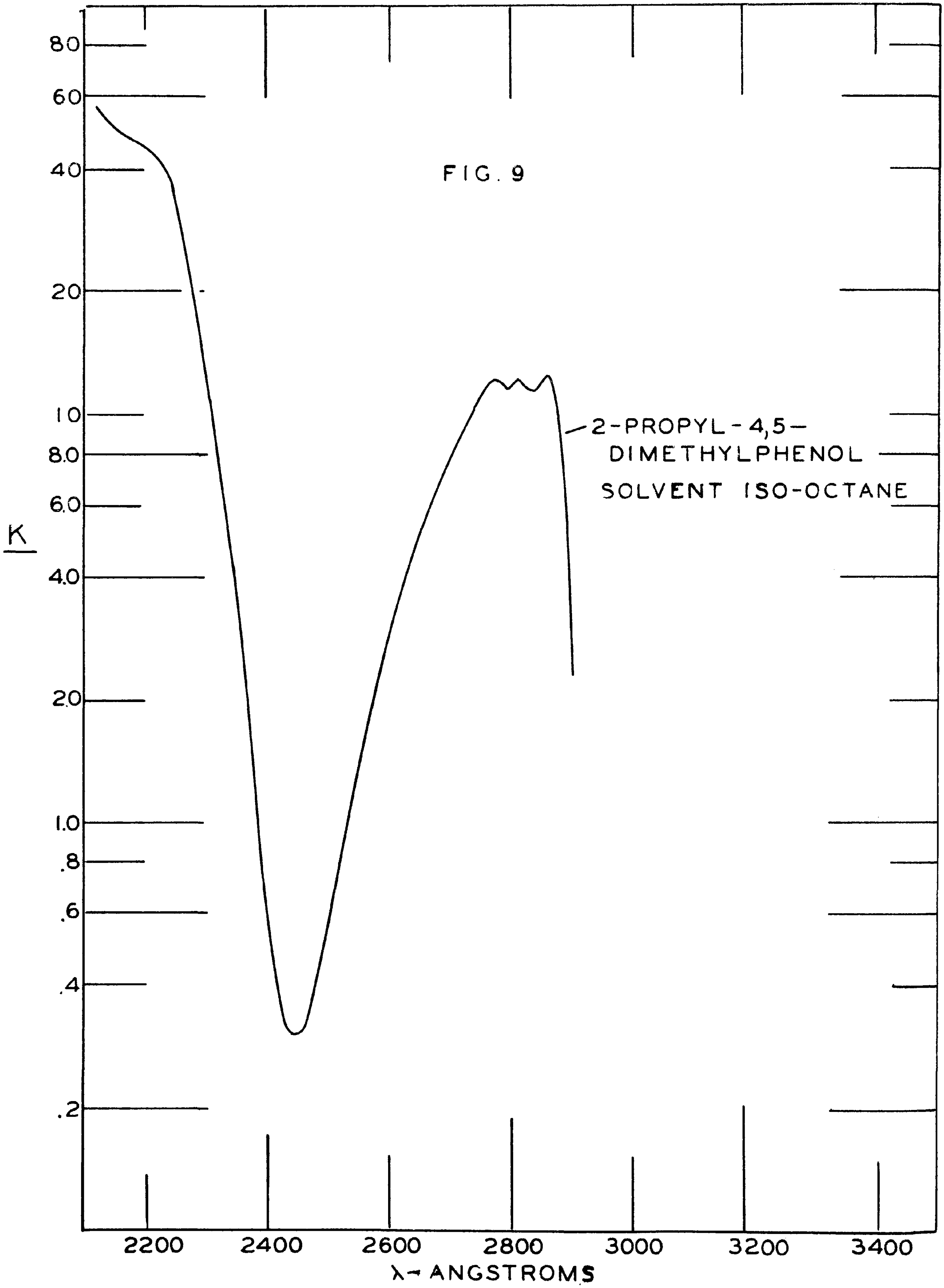

PREHNITENOL
SOLVENT: N-HEXANE
K
20
18
16
14
12.0
10.0
8.0
6.0
4.0
2.0
2000
2200
2400
2600
2800
3000
3200
λ - ANGSTROMS

FIG. 8

FIG. 9


80
60
40
20
10
8.0
6.0
K
4.0
2.0
1.0
.8
.6
.4
.2
2200
2400
2600
2800
3000
3200
3400
λ→ ANGSTROMS
2-PROPYL-4,5-DIMETHYLPHENOL
SOLVENT ISO-OCTANE

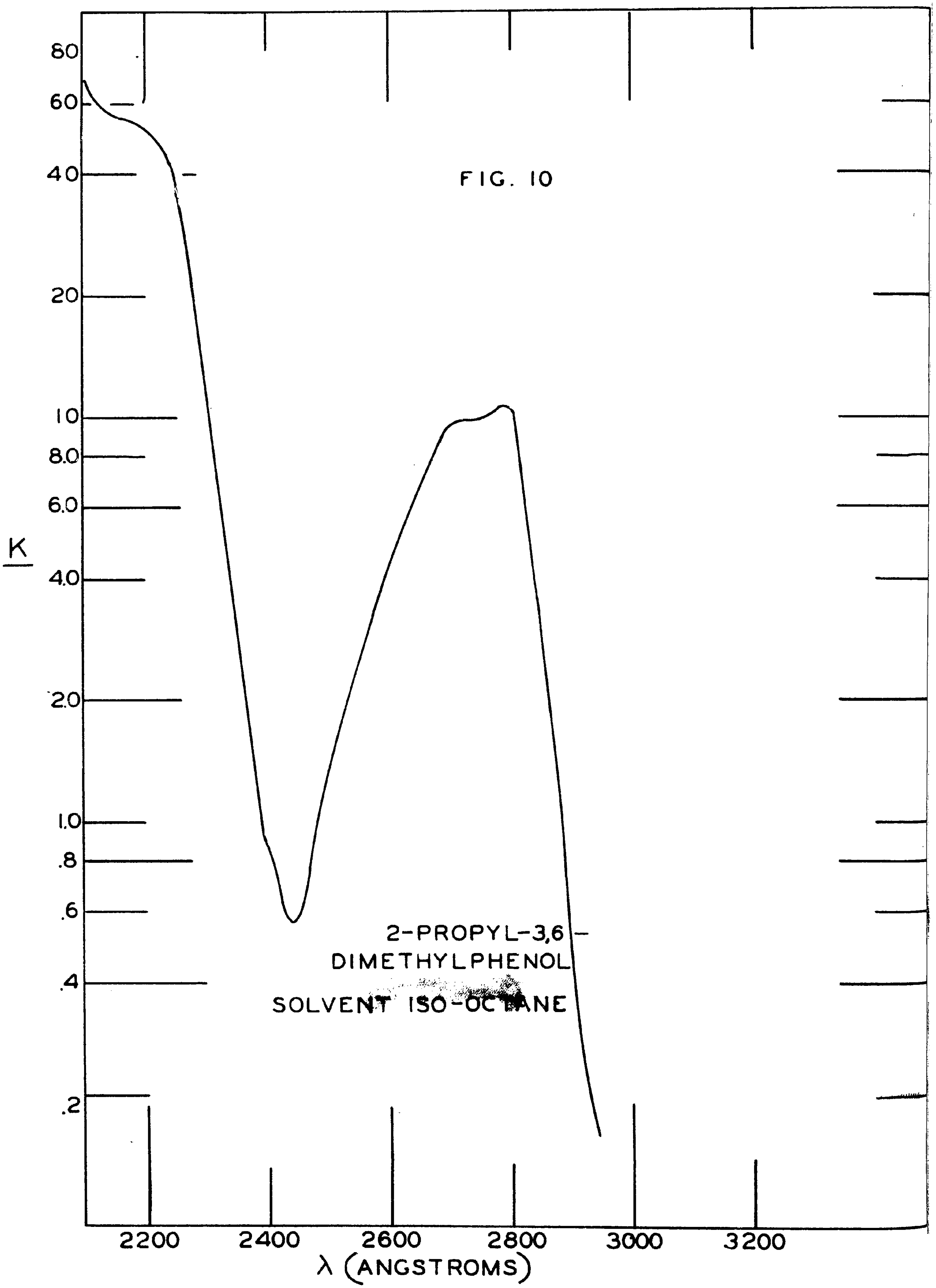
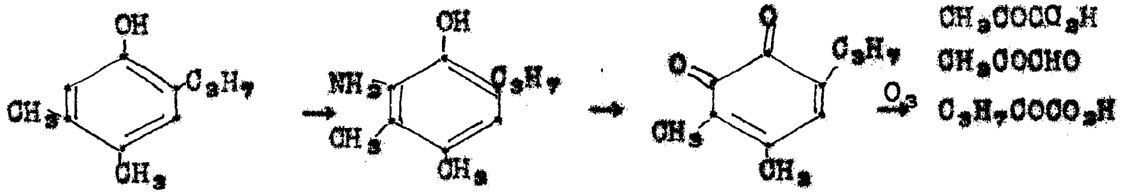


FIG. 10
K
80
60
40
20
10
8.0
6.0
4.0
2.0
1.0
.8
.6
.4
.2
2200
2400
2600
2800
3000
3200
λ (ANGSTROMS)
2-PROPYL-3,6-
DIMETHYLPHENOL
SOLVENT ISO-OCTANE

2-Propyl-3,6-dimethylphenol was prepared from 2-hydroxy-1,4-dimethylbenzene; the allyl ether was first prepared, and this was rearranged to 2-allyl-3,6-dimethylphenol in boiling diethylaniline. This compound was hydrogenated over Raney nickel to give 2-propyl-3,6-dimethylphenol, m.p. 47°, in an overall yield of 35 per cent.

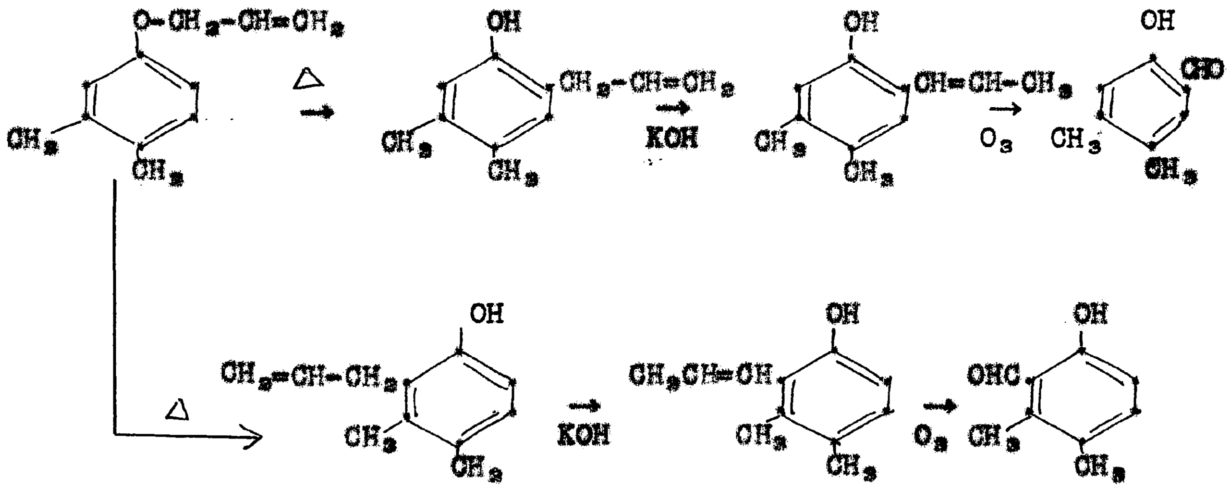
2-Propyl-4,5-dimethylphenol was prepared from 4-hydroxy-1,2-dimethylbenzene by the same procedure. The product, m.p. 59°, was obtained in 21 per cent yield.

Since in this case two *ortho* positions were open to which the allyl group could migrate during the Claisen rearrangement, it was necessary to prove the structure of the product. The first route investigated was unsuccessful:



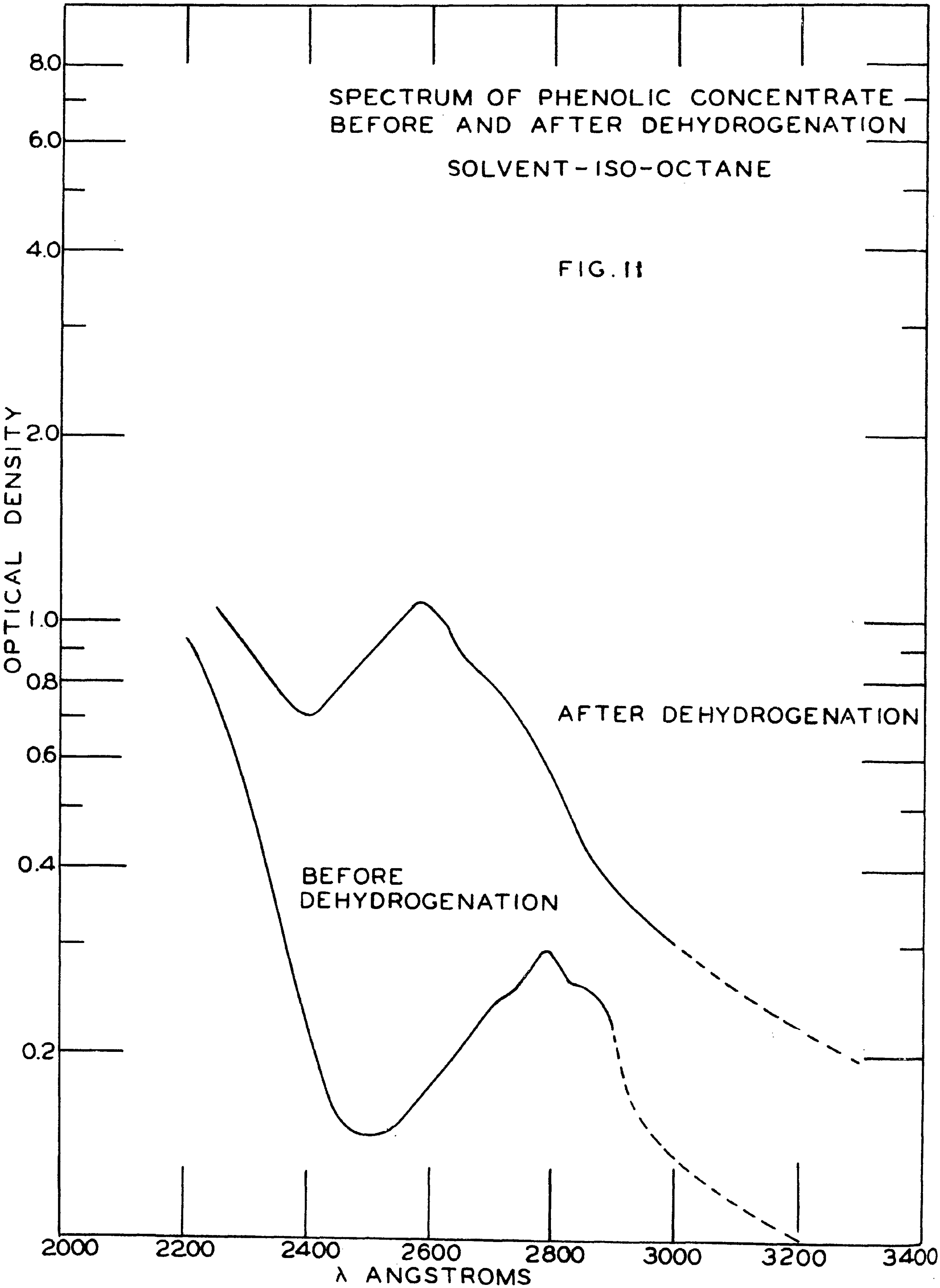
Had it been possible to carry the synthesis through and prove the presence of pyruvaldehyde, the structure of the starting material would have been definitely established, since the isomeric phenol with the propyl group in the *6* position would yield no pyruvaldehyde. However, it was not possible to oxidize the aminophenol to the corresponding quinone in good yield with ferric chloride or potassium dichromate.

The structure was successfully proved by the following scheme:



Allyl 4,5-dimethylphenyl ether was subjected to a Claisen rearrangement and the product isomerized by potassium hydroxide treatment. Ozonolysis and subsequent treatment with water yielded mainly 4,5-dimethylsalicylaldehyde, a known compound. In addition a quantity of 5,6-dimethylsalicylaldehyde was also isolated; the combined yield of aldehydes was 84 per cent. The relative amounts of these two isomers obtained indicated that in the rearrangement of allyl 4,5-dimethylphenyl ether the allyl group migrated about 70 per cent to the unhindered _2_ position and about 30 per cent to the _6_ position.

In the actual preparation of 2-propyl-4,5-dimethylphenol the Claisen rearrangement mixture was hydrogenated and allowed to crystallize. Only one isomer crystallized, but this amounted to about 80 per cent of the material and hence must have been the 2-propyl isomer.



SPECTRUM OF PHENOLIC CONCENTRATE BEFORE AND AFTER DEHYDROGENATION

SOLVENT-ISO-OCTANE

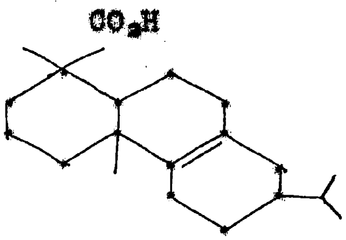
FIG. 11

As a further proof of the identity of the aldehydes obtained they were separately oxidized to the corresponding acids.

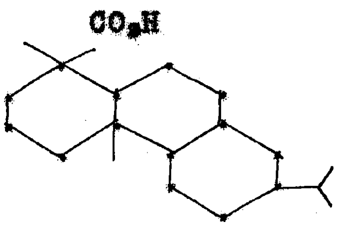
D. Chemical and Infrared Studies on the Resin Phenol.

Chemical and infrared studies have given the most information about the actual nature of the resin phenol IV.

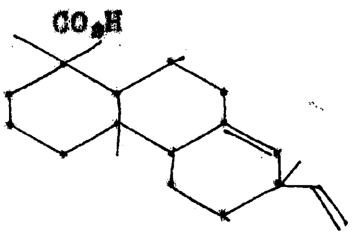
Catalytic dehydrogenation over palladium showed that there was present a considerable quantity of material having a hydrophenanthrene skeleton. This was evidenced by the appearance in the spectrum (Figure 11) of the dehydrogenated material of a strong maximum near 2600 Å and by a general resemblence to the spectra of phenanthrene derivatives. This evidence coupled with the fact that the infrared spectrum of IV showed a strong carboxyl absorption, indicated that a resin acid was still present in IV despite the fact that the extraction procedure was designed to eliminate acids. It has been found that there are at least three of the resin acids which are extremely insoluble in all concentrations of aqueous alkali at 25°, dihydroabietic (IX), tetrahydroabietic (X), and d-pimaric acid (XI). Thus any of these would be expected to concentrate with the phenol.



IX



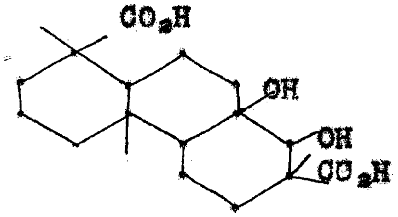
X



XI

The high over-all absorption in the 1000-1500 cm.$^{-1}$ region of the infrared spectrum indicates that in fact there is a mixture of such acids present.

An attempt to prove the presence of d-pimaric acid (XI) by ozonolysis and detection of formaldehyde was unsuccessful because it was found that any phenols present would also give formaldehyde. However, it is significant that a vigorous alkaline permanganate oxidation of IV gave a viscous acidic oil having a neutralization equivalent of 172±3. Vigorous permanganate oxidation of d-pimaric acid would yield the acid XII, neutralization equivalent 177.



XII

Further evidence for the presence of d-pimaric acid in IV is the relatively high absorption of light in the 2400-2500 Å region; having two double bonds (not conjugated) d-pimaric acid would be expected to absorb in this region to an observable extent.

The possibility that the resin phenol was a resorcinol derivative such as the 3,5-dihydroxystilbene isolated from rosin by Erdtman was investigated by a series of tests which have been described by Butenandt and Stodola (9). The resin phenol gave none of the color reactions characteristic of 1,2-,1,3-, or 1,4-dihydroxybenzenes. Further, there was no resemblence between the spectrum of the resin phenol and the spectrum of any of the substituted resorcinols available for comparison (See Table V).

E. Evaluation of the Resin Phenol as a Polymerization Retarder.

It was essential to ascertain whether the phenolic concentrate isolated was actually capable of retarding polymerization when added to the GR-S-10 recipe. This was determined by the conventional bottle polymerization technique, using the twelve-hour conversion as an indication of retarding action. Table II shows that the addition of 0.72 per cent (based on emulsifier) of phenolic fraction IV produced a significant decrease in conversion. At the same concentration the terpene phenols had about the same effect, while 2-propyl-4,5-dimethyl-, 2-propyl-3,6-dimethyl-, and 2,3,4,5-tetramethylphenol exhibited very strong inhibitory action.

TABLE II

Effect of Varous Phenols on Conversion in the GR-S-10 Recipe

Phenol	Per Cent	12-hour Conversion Lowering
Resin phenol IV	0.72	1.8%
2-Propyl-4,5-dimethyl-	"	22.8
2-Propyl-3,6-dimethyl-	"	20.4
2,3,4,5-tetramethyl-	"	40.4
Bornyl-	"	2.4
Menthyl-	"	2.4
Pinyl-	"	3.2
Fenchyl-	"	2.3

The retardation observed in the case of the resin phenol IV cannot be attributed to the presence of resin acids (IX, X, or XI) in the concentrate, since it has been shown by Hays, Drake, and Pratt (2) that these acids are excellent emulsifiers in the GR-S-10 recipe, promoting twelve-hour conversions of nearly 80 per cent.

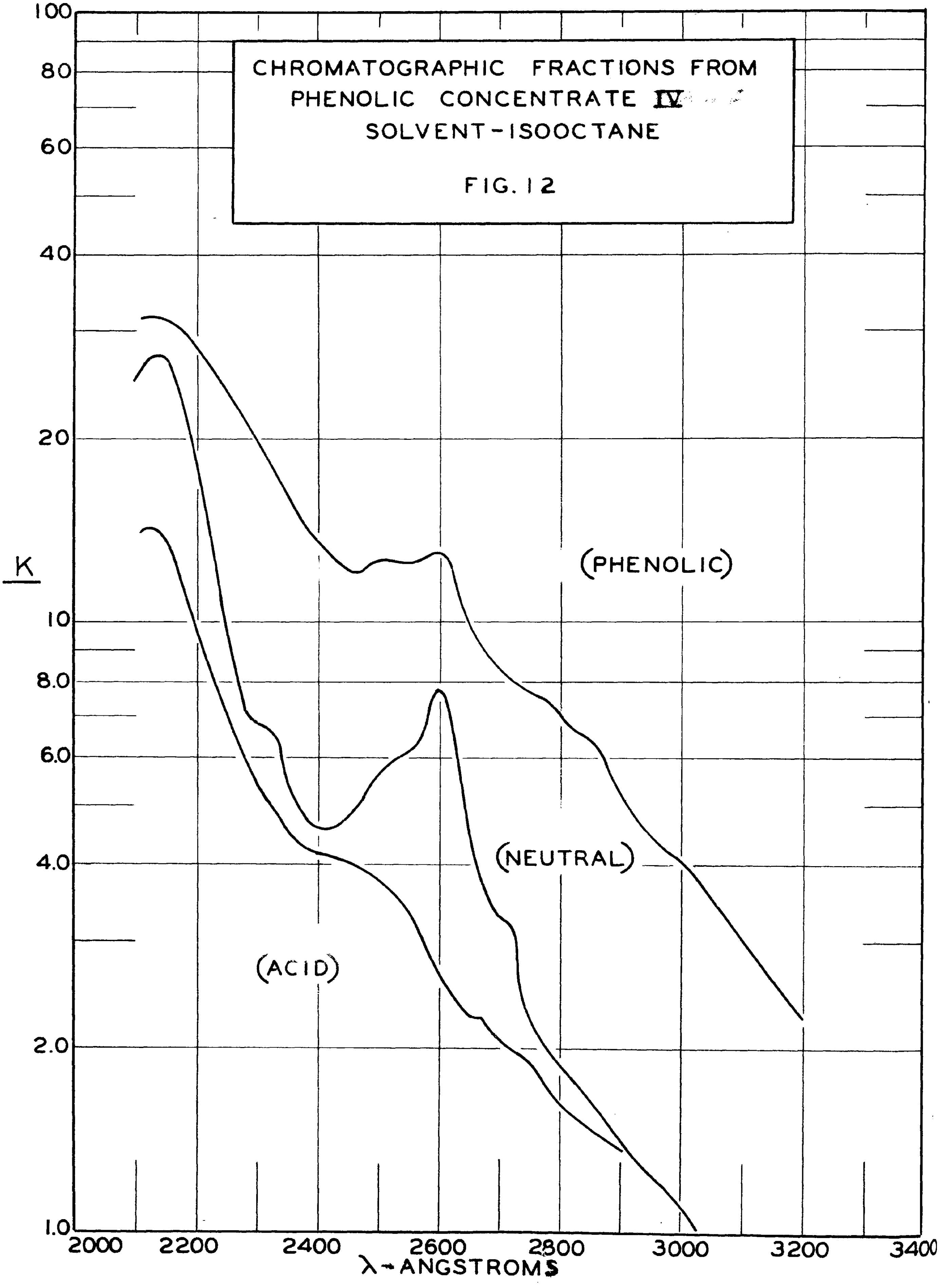
IV. EXPERIMENTAL

<u>Isolation of Phenolic Concentrate from Hercules Resin 731</u>.- Five hundred grams (1.48 moles) of Hercules Resin 731 (sample 45-772) was dissolved in 2 l. of refluxing petroleum ether (b.p. 35-45°), filtered, and extracted with four 1-l. and four 500-ml. portions of 10 per cent sodium carbonate saturated with ethanol. This extraction consumed a total of 429 g. (5.35 times the theoretical quantity) of sodium carbonate. The petroleum ether solution was then extracted with three 100-ml. and eight 50-ml. portions of 11 per cent potassium hydroxide in 50 per cent ethanol. The extract (700 ml) was washed with five 200-ml. portions of petroleum ether (b.p. 35-45°), diluted with 350 ml. of water, and extracted with three 100-ml. portions of petroleum ether. This extract was dried with anhydrous sodium sulfate and evaporated to dryness to yield 0.0934 g. of phenolic material, III. The aqueous alcoholic layer was diluted again an equal amount and more phenolic material, IV, 0.0855 g. isolated as before. Both of these fractions were light yellow viscous oils which did not crystallize. The spectrum of IV is shown in Figure 1.

<u>Anal.</u>* (IV) Found: C, 77.63; H, 9.30; OCH_3, 2.45, 2.34; Mol. Wt. (Rast) 297, $[\alpha]^{25}_{D}$ +0.3° in ethanol.

<u>Separation of Menthylphenol from Resin Neutral Bodies by Fractional Extraction</u>.-The principle and operation of the fractional extraction procedure may be better understood by reference to the

* Microanalyses were run by H. S. Clark, and by the Clark Analytical Laboratory.



CHROMATOGRAPHIC FRACTIONS FROM
PHENOLIC CONCENTRATE IV
SOLVENT-ISOOCTANE

FIG. 12

work of Craig (5), who has applied this method to the resolution of complex mixtures.

It was necessary before attempting a separation of menthylphenol from the resin neutral bodies to establish a method by which the amount of each constituent in the individual tubes could be determined after the fractionation was complete. The most attractive method was ultraviolet spectrophotometry, since this did not involve actual isolation of the minute amounts of material which were present. For complete accuracy it is necessary to make measurements on one component of the mixture at a point in the spectrum at which the other component does not absorb; this was not possible with this particular pair of materials, but it was possible to make measurements on each substance at a point where the absorption of the other was relatively quite low. Thus in the determination of menthylphenol measurements were made on the alcohol phases of all tubes at 2950 Å (a maximum in the spectrum when alcoholic potassium hydroxide is the solvent) where the neutral bodies, Figure 12, do not absorb strongly. The neutral bodies were estimated from the optical densities of the iso-octane phases of all the tubes at 2440 Å, where the absorption of menthylphenol is very low.

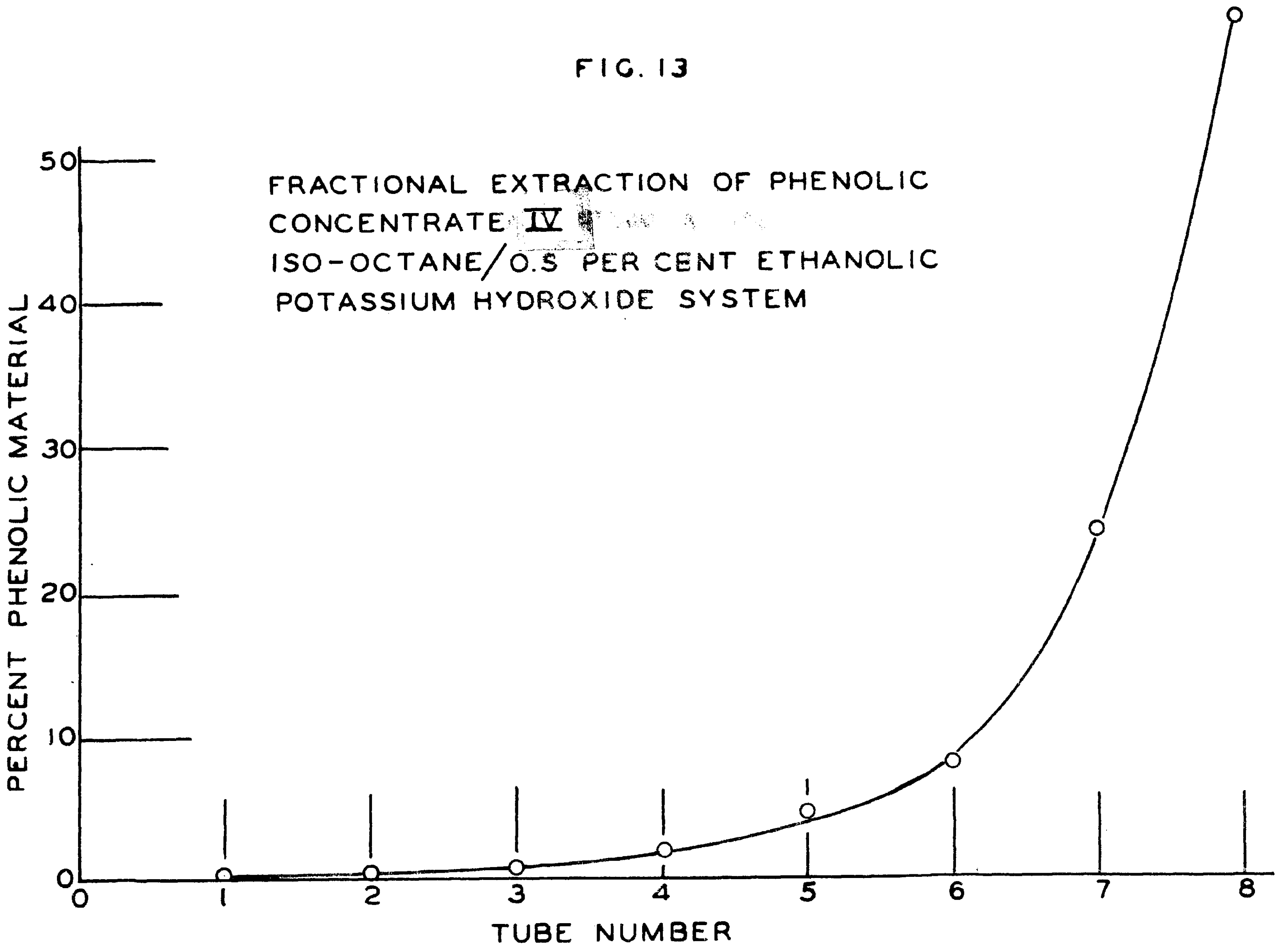
The actual fractional extraction was carried out with nine separatory funnels (an eight-plate fractionation); the funnels, all of 60-ml. capacity, were arranged in a row and numbered from zero to eight. The two solvents employed, 0.5 per cent potassium hydroxide in 95 per cent ethanol and iso-octane, were first mutually saturated one in the other, and 10 ml. of iso-octane phase added to each funnel. To funnel zero was added 10 ml. of alcohol phase containing

25 mg. each of menthylphenol and neutral bodies. The funnel was shaken, allowed to stand until the layers had separated, and the lower (ethanol) layer drained cleanly into funnel one. Next 10 ml. of ethanol phase was added to funnel zero, both funnel zero and one shaken, and both allowed to stand until the layers separated. Then the lower layer of funnel one was added to two, and the lower of zero added to one. Another aliquot of ethanol phase was added to zero and the process continued until eventually the ethanol layer initially in funnel zero reached funnel eight.

The layers of all funnels were separated and the optical densities measured at a fivefold dilution, using a Beckman Ultraviolet Spectrophotometer. The sum of the optical densities for the iso-octane layers was considered to represent all of the neutral bodies (25 mg.), and the fraction present in each tube was obtained by dividing the optical density found for that particular tube by the total optical density. The results are presented in Figure 2.

<u>Separation of the Resin Phenol from Neutral Bodies by Fractional Extraction</u>.- With the same solvents employed for separation of menthylphenol and neutral bodies and the same conditions, 25 mg. of phenolic fraction IV was subjected to a fractional extraction. In this case the evaluation of the fractionation was necessarily limited to a determination of the amount of resin phenol present in each tube; the resin phenol content of each tube was determined from the optical densities of the alcohol layers diluted five-fold at 2950 Å (the spectrum of the resin phenol in 0.5 per cent potassium hydroxide in ethanol is different from that in isooctane, the maximum occurring at 2950 Å).

FIG. 13



FRACTIONAL EXTRACTION OF PHENOLIC
CONCENTRATE IV
ISO-OCTANE/0.5 PER CENT ETHANOLIC
POTASSIUM HYDROXIDE SYSTEM

Neutral bodies could not be determined because there was no wave length at which they absorbed strongly and the resin phenol did not. The results of this extraction are shown in Figure 13, and the spectrum of the material in tube eight is shown in Figure 3.

Preparation of 2-Propyl-3,6-dimethylphenol.-The method of Bartz, Miller, and Adams (10) for the preparation of 2-isobutyl-3,6-dimethylphenol was followed.

Allyl 3,6-Dimethylphenyl Ether.-To 175 ml. of absolute ethanol in a 500-ml., three-necked flask, fitted with stirrer, dropping funnel, and condenser, were added 11.5 g. (0.5 mole) of sodium chips. When solution was effected, 61.0 g. (0.5 mole) of 2-hydroxy-1,4-dimethylbenzene was added and the flask heated in an oil bath to 85-90°. The mixture was stirred, and 41.8 g. (0.55 mole) of distilled allyl chloride was added slowly. The reaction mixture was heated for fifteen hours, stirring being discontinued after seven hours. The cooled reaction mixture was poured into 1 l. of water in a separatory funnel and the layers separated. The aqueous layer was extracted with two 100-ml. portions of petroleum ether (b.p. 35-45°), the extract being combined with the previous organic layer. This solution was washed with 10 per cent sodium hydroxide solution to remove unreacted starting material, dried over anhydrous magnesium sulfate, and distilled in a modified Claisen flask. The allyl 3,6-dimethylphenyl ether, boiled at 63-64° (<1 mm.), $n^{20}D$ 1.5177, d_4^{20} 0.9536. The yield was 42.9 g. (53 per cent).

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.45; H, 8.70; MR, 49.87. Found: C, 81.68; H, 8.68; MR, 51.52.

2-Allyl-3,6-dimethylphenol.-The allyl ether, 42.9 g. (0.26 mole) was rearranged by heating with one-half its weight of freshly distilled diethylaniline in a 245° bath for one-half hour. The boiling point of the mixture rose gradually during this time from 215° to 228°. The cooled mixture was dissolved in petroleum ether (b.p. 35-45°) and the diethylaniline removed by several washes with dilute sulfuric acid. The product was then removed as the potassium salt by extraction with aqueous-alcoholic potassium hydroxide (35 g. of potassium hydroxide, 25 g. of water, 90 g. of methanol) in four equal portions. The alkaline solution was washed with petroleum ether, acidified, and extracted exhaustively with petroleum ether. The petroleum ether solution was dried over anhydrous magnesium sulfate and distilled in a modified Claisen flask to yield 32.1 g. (75 per cent) of 2-allyl-3,6-dimethylphenol, b.p. 75-77° ($<$ 1 mm.,) n^{20}D 1.5383, d_4^{20} 0.9836, m.p. 15°.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.45 H, 8.70; MR, 49.76. Found C, 79.94; H, 8.70; MR, 51.62.

2-Propyl-3,6-dimethylphenol.-2-Allyl-3,6-dimethylphenol, 32.1 g., was hydrogenated in ethanol at 25° over Raney nickel, the theoretical quantity of hydrogen for saturation of the allylic double bond being absorbed in fifteen minutes. The catalyst was removed by filtration and the mixture distilled in a modified Claisen flask to yield 28.7 g. (89 per cent) of 2-propyl-3,6-dimethylphenol, m.p. 47°.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.45; H, 9.75. Found: C, 80.53; H, 9.91.

The ultraviolet spectrum of 2-propyl-3,6-dimethylphenol showed a specific absorption coefficient, k, of 10.7 at 2790 Å.

Preparation of 2-Propyl-4,5-dimethylphenol.-The preparation of this compound was carried out in a manner identical with that of 2-propyl-3,6-dimethylphenol.

Allyl 4,5-Dimethylphenyl Ether.-To 175 ml. of absolute alcohol in a 500-ml., three-necked flask, fitted with stirrer, dropping funnel, and condenser were added 11.5 g. (0.5 mole) of sodium chips. When solution was effected, 61.0 g. (0.5 mole) of 4-hydroxy-1,2-dimethylbenzene was added and the flask heated in an oil bath to 85-90°. The mixture was stirred, and 41.8 g. (0.55 mole) of distilled allyl chloride was added slowly. The reaction mixture was heated for fifteen hours, stirring being discontinued after seven hours. The cooled reaction mixture was poured into 1 l. of water in a separatory funnel and the layers separated. The aqueous layer was extracted with two 100-ml. portions of petroleum ether (b.p. 35-45°), the extract being combined with the previous organic layer. This solution was washed with 10 per cent sodium hydroxide solution to remove unreacted starting material, dried over anhydrous magnesium sulfate and distilled in a modified Claisen flask. The allyl 4,5-dimethylphenyl ether, 66.1 g., b.p. 75-79° (3 mm.), $n^{20}D$ 1.5200, d_4^{20} 0.9543, was obtained in 82 per cent yield.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.45; H, 8.70; MR, 49.87. Found: C, 81.40; H, 8.70; MR, 51.28.

Mixed 2- and 6-Allyl-4,5-dimethylphenols.-Allyl 4,5-dimethylphenyl ether, 66.1 g. (0.41 mole), was rearranged by heating with one-half its weight of freshly distilled diethylaniline in a

245° bath for one-half hour. The boiling point of the mixture rose gradually during this time from 218° to 231°. The cooled mixture was dissolved in petroleum ether (b.p. 35-45°) and the diethylaniline removed by several washes with dilute sulfuric acid. The product was then removed as the potassium salt by extraction with aqueous-alcoholic potassium hydroxide (35 g. of potassium hydroxide, 25 g. of water, 90 g. of methanol) in four equal portions. The alkaline solution was washed with petroleum ether, acidified, and extracted exhaustively with petroleum ether. The petroleum ether solution was dried over anhydrous magnesium sulfate and distilled in a modified Claisen flask. The mixed 2- and 6-allyl-4,5-dimethylphenols distilled at 82-85° (1 mm.), n^{20}_{D} 1.5434, d^{20}_{4} 0.9671. The yield was 46.8 g. or 71 per cent of the theoretical amount.

Mixed 2- and 6-Propyl-4,5-dimethylphenols.-Hydrogenation of 46.8 g. of the mixed 2- and 6-allyl-4,5-dimethylphenols in ethanol solution at 25° with a Raney nickel catalyst proceeded smoothly, the theoretical amount of hydrogen being absorbed in twenty minutes. The catalyst was removed by filtration and the mixture distilled in a modified Claisen flask to yield 30.6 g. (65 per cent) of mixed 2- and 6-propyl-4,5-dimethylphenols, b.p. 77-77.5° (< 1 mm.).

2-Propyl-4,5-dimethylphenol.-The mixture of 2- and 6-propyl-4,5-dimethylphenols was a very viscous oil. When this material had stood for two weeks, crystals began to form; crystal growth proceeded, but the whole of the material did not crystallize. The crystals were removed by filtration through a sintered glass filter; thus about half (16 g.) of the material was obtained as a white crystalline solid. This was recrystallized four times from petroleum ether (b.p. 35-45°) to a constant melting point of 59°.

Anal. Calcd. for $C_{11}H_{16}O$: C. 80.45; H, 9.75. Found: C, 80.49; H, 9.83.

The following specific absorption coefficients at maxima were found: k (2770 Å) 12.1; k (2810 Å) 12.2; k (2860 Å) 12.3.

Coupling of 2-Propyl-4,5-dimethylphenol with Diazotized Sulfanilic Acid.-To a solution of 1.06 g. (0.01 mole) of sodium carbonate in 20 ml. of water 3.84 g. (0.02 mole) of sulfanilic acid monohydrate was slowly added. The solution was cooled and to it was added a cold solution of 1.48 g. (0.022 mole) of sodium nitrite in 4.0 ml. of water. The mixture was swirled and quickly poured into 24 g. of ice containing 4.3 ml. of concentrated hydrochloric acid (0.05 mole). After fifteen minutes this slurry was quickly poured into a solution of 3.3 g. (0.02 mole) of 2-propyl-4,5-dimethylphenol dissolved in a solution of 4.4 g. (0.11 mole) of sodium hydroxide in 24 ml. of water cooled to 5° by the addition of 20 g. of ice. A dark red suspension of azo coupling product resulted.

2-Propyl-4,5-dimethyl-6-aminophenol Hydrochloride.-The red reaction mixture was allowed to stand for one hour in an ice-bath, 26 ml. of 10 per cent sodium hydroxide added, the mixture heated to 60°, and 9.2 g. (0.044 mole) of sodium hydrosulfite dihydrate added in small portions. Heating was continued for fifteen minutes during which the mixture slowly cleared and became straw-yellow in color. Another addition of hydrosulfite (0.8 g.) was made and the solution cooled to 25°. This was poured into a solution of 8.0 g. of hydrosulfite dissolved in 200 ml. of water, filtered, a small lump of solid carbon dioxide added, and the reaction mixture placed in the refrigerator overnight. The crystals of aminophenol which formed were removed by suction filtration, immediately transferred to a solution of 0.08 g. of stannous chloride dihydrate and 2.1 ml. of concentrated hydrochloric acid in 40 ml. of water at 55°. The solution was decolorized with 0.05 g. of Norite, filtered, 8.0 ml. of concentrated hydrochloric acid added, and the solution allowed to cool slowly. The crystals which formed were removed by filtration and dried in a vacuum desiccator. The 2-propyl-4,5-dimethyl-6-aminophenol hydrochloride thus obtained weighed 2.8 g. (65 per cent).

Anal. Calcd. for $C_{11}H_{18}ONCl$: C, 61.25; H, 8.42; Cl, 16.46. Found: C, 61.19; H, 8.45; Cl, 16.43.

Attempted Oxidation of 2-Propyl-4,5-dimethyl-6-aminophenol Hydrochloride to the Quinone.

Ferric Chloride Method.-One gram (0.0047 mole) of 2-propyl-4,5-dimethyl-6-aminophenol hydrochloride was dissolved in 30 ml. of water containing a drop of concentrated hydrochloric acid. To the filtered solution was added a cold solution of 2.3 g. (0.014 mole) of ferric chloride and 0.9 ml. of concentrated hydrochloric acid in 5.0 ml. of water. The reaction mixture darkened immediately and a dark oil separated; the mixture was heated with agitation a few minutes on a steam cone. This material was not the desired quinone; when the cooled, solidified oil was removed by filtration it was found to be completely insoluble in petroleum ether, (b.p.

35-45°).

The same result was obtained when the procedure of adding ferric chloride solution to a solution of the amine hydrochloride was reversed.

Potassium Dichromate Method.-A solution of 0.2 g. (0.001 mole) of 2-propyl-4,5-dimethyl-6-aminophenol hydrochloride in 10 ml. of water was covered with 20 ml. of ether, and to this was added dropwise and with vigorous shaking between additions 12 ml. of 10 per cent sulfuric acid containing 2.0 g. (0.0068 mole) of potassium dichromate. When the addition was complete, the ether layer was separated and the aqueous layer extracted with two 10-ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and the solvent removed by distillation to yield 0.11 g. of a dark red gum. This material was soluble in alcohols, benzene, chloroform, and ether but could not be crystallized from any of these solvents.

The material was sublimed under high vacuum at a bath temperature of 195°, the sublimate was a red tar also and could not be crystallized.

Anal. Calcd, for $C_{11}H_{14}O_2$: C, 74.20; H, 7.92. Found: C, 68.57; H, 7.42.

It is apparent that this material was not the desired quinone.

Mixed 2- and 6-Propenyl-4,5-dimethylphenols.-To a 500-ml. round-bottomed flask containing 152 g. of n-amyl alcohol was added 105 g. of potassium hydroxide flakes. The mixture was refluxed for a short time, the clear supernatant liquid decanted, and to it was added 40 g. (0.247 mole) of the rearrangement product from allyl 4,5-dimethylphenyl ether (2- and 6-allyl-4,5-dimethylphenols). The solution was heated at the boiling point for twenty-four hours, the amyl alcohol removed by steam distillation, and the remaining solution acidified with phosphoric acid. The acidified solution was extracted with four 100-ml. portions of ether and the ether solution dried over anhydrous magnesium sulfate and distilled without fractionation. A yield of 24.6 g. (61.6 per cent) of 2- and 6-propenyl-4,5-dimethylphenols was obtained.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.45; H, 8.70. Found: C, 81.90; H, 8.69.

4,5- and 5,6-Dimethylsalicylaldehydes.-A solution of 8.4 g. (0.052 mole) of mixed 2- and 6-propenyl-4,5-dimethylphenols in 400 ml. of chloroform was ozonized for six hours at 0° with approximately 4 per cent ozone. The chloroform solution of the ozonide was treated with 120 ml. of water, and the chloroform was distilled from the mixture under reduced pressure. After the chloroform had been completely removed, the flask was heated vigorously and the contents distilled. A yield of 4.95 g. (63.8 per cent) of aldehyde was obtained from the steam-distillate by ether extraction, while 1.4 g. of material remained in the pot.

The aldehyde thus obtained was converted to the bisulfite addition product by shaking vigorously with nearly saturated sodium bisulfite solution at about 40°. The white crystalline addition product was removed by suction filtration, washed repeatedly with ether, and finally decomposed with 150 ml. of warm 3 per cent hydrochloric acid. The purified aldehyde was recovered by ether extraction drying of the extract, and removal of the solvent by distillation. The solid, light-yellow aldehyde thus obtained was recrystallized from petroleum ether (b.p. 35-45°), the solution being allowed to cool very slowly so that large crystals formed. Two types of crystals were formed, long spike-like needles of 5,6-dimethylsalicylaldehyde and lustrous plates of the 4,5 isomer; a quantity the material was separated into its component crystals mechanically. Thus it was determined that 70 ± 5 per cent of the material crystallized as plates and 30 ± 5 per cent as needles. The two crops of crystals were separately recrystallized first from dilute alcohol and then from petroleum ether (b.p. 35-45°). The plates of 4,5-dimethylsalicylaldehyde melted at 69° and the needles of 5,6-dimethylsalicylaldehyde at 70°.

Anal. Calcd. for $C_9H_{10}O_2$: C, 72.00; H, 6.72. Found: Plates - C, 72.04; H, 6.65. Needles - C, 72.10; H, 6.60.

Clayton (11) who prepared a similar mixture of aldehydes from a Reimer-Tieman reaction on 4,5-dimethylphenol found that 4,5-dimethylsalicylaldehyde crystallized in plates, m.p. 71°, and the 5,6 isomer in needles, m.p. 72°.

6-Hydroxy-3,4-dimethylbenzoic Acid.-About 0.1 g. of 4,5-dimethylsalicylaldehyde was sprinkled into 0.6 g. of fused sodium-potassium hydroxide (50-50 containing a little water) at 210° in a nickel crucible. As soon as gas evolution had ceased the mixture was cooled, dissolved in water, filtered, and acidified. The 6-

hydroxy-3,4-dimethylbenzoic acid which precipitated was collected on a filter, dried, and recrystallized from aqueous methanol. The purified product melted at 197.6°. The literature (11) reports a melting point of 198-9°.

6-Hydroxy-2,3-dimethylbenzoic Acid.-This material was prepared from 5,6-dimethylsalicylaldehyde exactly as described above for 6-hydroxy-3,4-dimethylbenzoic acid. The 6-hydroxy-2,3-dimethylbenzoic acid melted at 140°. Clayton (11) describes this acid as melting at 142-3°.

Prehnitenesulfonic Acid.-To 100 g. (0.745 mole) of isodurene and 67 ml. of concentrated sulfuric acid in a 1-l. Erlenmeyer flask cooled in an ice bath was added, slowly and with shaking, 33 ml. of 60 per cent fuming sulfuric acid. The flask was removed from the ice bath, allowed to warm to 25°, and shaken vigorously for five minutes. The mixture was then heated at 80°, loosely stoppered, for nine hours. The black, nearly solid mass was partly broken up, and poured over 500 g. of crushed ice. The solid was further broken up, and after fifteen minutes the mixture was filtered. The filtrate was cooled to 10°, and the sulfonic acid was precipitated at that temperature by the slow addition of 250 ml. of concentrated sulfuric acid. The crude prehnitenesulfonic acid, m.p. 98-100°, weighed 115.5 g. The yield was 72 per cent of the theoretical amount.

Sodium Prehnitenesulfonate.-The crude prehnitenesulfonic acid, 115.5 g. (0.54 mole), was dissolved in 340 ml. of water, 22 g. (0.26 mole) of sodium bicarbonate was added, and the mixture was heated to boiling. The solution was saturated with sodium chloride, boiled five minutes, and cooled in ice. The precipitate of sodium prehnitenesulfonate was collected by suction filtration and recrystallized from salt water (25 per cent). The yield of recrystallized product was 73.2 g. (57.5 per cent).

Prehnitenol.-To 87 g. (1.07 moles) of potassium hydroxide in an iron crucible fitted with an iron stirrer and a copper-jacketed thermometer was added 4 ml. of water. The temperature was brought to 250° and 36.6 g. (0.15 mole) of sodium prehnitenesulfonate added as rapidly as feasible. The mixture frothed badly, and it was necessary to push the material down repeatedly. Stirring was started and the temperature brought to 300° in ten minutes; heating and stirring were continued for five minutes. After being allowed to cool slightly the melt was poured into 250 g. of ice. The mixture was acidified with hydrochloric acid, and exhaustively extracted with petroleum ether (b.p. 35-45°). The petroleum ether solution was dried over anhydrous sodium sulfate and the solvent distilled. A yield of 7.3 g. (32 per cent) of crude prehnitenol was obtained. This was recrystallized first from petroleum ether (b.p. 35-45°), then from benzene, and once again from petroleum ether to a constant melting point of 83.5°.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.39. Found: C, 80.20; H, 9.36.

The following specific absorption coefficients at maxima were found: k (2775 Å) 13.4; k (2825 Å) 14.0; k (2865 Å) 14.1.

6-Bromoprehnitenol.-This material was prepared from prehnitenol by the bromination procedure described by Shriner and Fuson (12). After recrystallization from aqueous ethanol the derivative melted at 103.5°.

Anal. Calcd. for $C_{10}H_{13}OBr$: Br, 34.80; Found: Br, 34.67.

Prehnitenol has been prepared previously by Tohl (13) and by Limpach (14). Tohl reported a melting point of 87° and for the bromo derivative 151°, but he gave no supporting analyses. Limpach reported the melting point of the phenol as 81° and offered a supporting analysis. The melting point of isodurenol (2,3,4,6-tetramethylphenol) is reported as 80-81°, but its bromo-derivative melts at 135°. It appears, therefore, that the compound synthesized is the 2,3,4,5-isomer, even through the melting point of its bromo-derivative does not agree with that reported in the literature.

Menthyl Chloride.-To 130 g. (0.623 mole) of phosphorus pentachloride covered with petroleum ether (b.p. 35-45°) in a three-necked flask equipped with condenser and dropping funnel was added 95.0 g. (0.607 mole) of dl-menthol dissolved in 95 g. of the same solvent. The addition was regulated so as to maintain a constant and rapid evolution of hydrogen chloride. When the addition was complete and evolution of hydrogen chloride had ceased, the reaction mixture was poured onto ice, the water layer separated, and the hydrocarbon layer washed with 200 ml. of 10 per cent sodium carbonate and three 200-ml. portions of water. The organic solution was then dried over calcium chloride and distilled from a modified Claisen flask. The menthyl chloride, 73.0 g. distilled at 88-94° (14 mm.), $n^{20}D$ 1.4625, and was obtained in 69 per cent yield.

Menthylphenol.-To a 2-l., round-bottomed flask, equipped with a reflux air-condenser, were added 73.0 g. (0.418 mole) of menthyl chloride and 438 g. (4.65 moles) of phenol. The mixture was heated under reflux for sixteen hours. Hydrogen chloride was evolved rapidly at first, then more slowly, until after sixteen hours the evolution had ceased. The reaction mixture was cooled and poured into a solution of 321 g. of potassium hydroxide in 2 l. of water. This was extracted with three 500-ml. portions of ether, the ether solution dried over anhydrous magnesium sulfate, and the mixture distilled. The crude menthylphenol was a viscous light-yellow oil boiling at 195-198° (13 mm.).

Phenylurethane of Menthylphenol.-The product was purified via the phenylurethane. Twenty grams (0.086 mole) of crude menthylphenol and 15.0 g. (0.126 mole) of phenyl isocyanate were mixed and heated in the absence of moisture at 100° for twenty-four hours. The solid obtained when the reaction mixture was cooled was recrystallized twice from Skellysolve B; a yield of 18.0 g. (62 per cent) of the phenylurethane of menthylphenol, m.p. 138°, was obtained. Kurssanow (6) reported a melting point of 141° for this compound.

Pure Menthylphenol.-To 8.3 g. of the phenylurethane in 100 ml. of ethanol was added 20.0 g. of potassium hydroxide. The mixture was refluxed overnight, cooled in ice, and acidified with 50 per cent sulfuric acid, keeping the temperature below 10°. The acidified mixture was extracted with three 100-ml. portions of ether, the ether solution washed with water, dried over anhydrous magnesium sulfate, and flash distilled. The product, 4.7 g. of a colorless, viscous oil, distilling at 130° (< 0.5 mm.), crystallized on standing overnight. A crystal of this material was used to seed the crude product, which then crystallized. The combined crystalline material was recrystallized from Skellysolve B. The yield was 18.4 g. (19 per cent), m.p. 89°. Kurssanow (6) reported a melting point of 89° for menthylphenol. The ultraviolet spectrum of menthylphenol, is shown in Figure 4; specific absorption coefficients at maxima, k (2210 Å) 28.0; k (2765 Å) 7.46; k (2830 Å) 6.65.

Anal. Calcd. for $C_{16}H_{24}O$: C, 82.60; H, 10.40. Found: C, 82.54; H, 10.46.

Fenchyl Chloride.-To 138 g. (0.665 mole) of phosphorus pentachloride covered with petroleum ether (b.p. 35-45°) in a one-liter, three-necked flask equipped with dropping funnel and reflux condenser was added over a period of three hours 100 g. (0.65 mole) of fenchyl alcohol dissolved in 200 ml. of petroleum ether (b.p. 35-45°). The reaction mixture was allowed to stand two hours, refluxed two hours, and poured onto ice. The hydrocarbon layer was washed with 10 per cent sodium carbonate until free from acid and then with water. The solution was dried over anhydrous calcium chloride and distilled, the fraction boiling at 80-87° (16 mm.) was collected as fenchyl chloride. The yield was 61.0 g. (54 per cent).

Fenchylphenol.-To 61.0 g. (0.35 mole) of fenchyl chloride was added 330 g. (3.5 moles) of phenol. The dark mixture was heated at 190° for sixteen hours and finally boiled for two hours to complete the removal of hydrogen chloride. The cooled solution was poured into a solution of 268 g. of potassium hydroxide dissolved in 2 l. of water, extracted with three 500-ml. portions of ether and the extract decolorized with Norite, dried over anhydrous magnesium sulfate, and distilled from a modified Claisen flask. The crude fenchylphenol boiled at 120-145° (<1 mm.); the yield was 60.0 g. (74 per cent based on the chloride).

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.11; H, 9.60. Found: C, 82.92; H, 9.63.

Fenchylphenol was a light-yellow, extremely viscous oil; after standing for nine months some crystals formed, but the mother liquor was too viscous to permit separation by filtration.

The ultraviolet spectrum showed the following specific absorption coefficients at the maxima: k (2200 Å) 32.5; k (2750 Å) 8.42; k (2780 Å) 8.30.

Fenchylphenol Benzoate.-To 1.0 g. of fenchylphenol dissolved in 6.0 ml. of anhydrous pyridine was added 0.5 ml. of benzoyl chloride. The solution was heated fifteen minutes on a steam cone, poured into 10 ml. of water, and the supernatant liquid decanted. The residual oil was washed well with 5 per cent sodium hydroxide, dissolved in 2 ml. of ethanol, and cooled overnight in the refrigerator. The crude benzoate which crystallized was removed by filtration and recrystallized from ethanol. The purified material melted at 123.5°.

Anal. Calcd. for $C_{23}H_{26}O_2$: C, 82.60; H, 7.84. Found: C, 82.75; H, 7.68.

Fenchylphenol did not yield a crystalline phenyl- or α-naphthylurethane.

Bornylphenol.-A mixture of 61.4 g. (0.356 mole) of freshly distilled bornyl chloride and 374 g. (3.98 moles) of phenol was refluxed for twenty hours. The mixture was cooled and poured into a solution of 266 g. of potassium hydroxide dissolved in 2 l. of water. This was extracted with four 500-ml. portions of ether; the ether solution was washed with two 500-ml. portions of 2 per cent sodium hydroxide and 500 ml. of water. The ether was removed by distillation, and the residue was dissolved in a solution of 40 g. potassium hydroxide in 320 ml. of 50 per cent methanol. This solution was extracted with n-hexane to remove any neutral material present. The alkaline solution was acidified in the cold and the bornylphenol extracted with n-hexane.

The solution was dried with anhydrous magnesium sulfate and the 63 g. (80 per cent) of crude bornylphenol purified by distillation. A heart-cut of 20 g. boiling at 119-121° (0.6 mm.) was taken as bornylphenol and submitted for analysis.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.11; H, 9.50. Found: C, 83.19; H, 9.58.

The purified bornylphenol did not form a crystalline phenyl- or α-naphthylurethane, picrate, or aryloxyacetic acid. The molecular weight as determined by Zerewitinov active hydrogen was 183 (theory 231) indicating that phenol was probably present as an impurity.

The ultraviolet spectrum showed the following specific absorption coefficients at maxima: k (2190 Å) 35.5; k (2730 Å) 9.45; k (2790 Å) 8.72.

Pinylphenol.-To 136 g. (1.0 mole) of pinene and 450 g. (4.8 moles) of phenol in a flask equipped with a reflux condenser was added 1.4 g. (0.007 mole) of p-toluenesulfonic acid monohydrate. The mixture was heated on a steam cone for one hour; the mixture, colorless during the first thirty minutes, darkened appreciably before the heating was stopped. The cooled solution was poured into a cold solution of 300 g. of sodium hydroxide in 3 l. of water and extracted with four 500-ml. portions of ether. The ether solution was washed with two 500-ml. portions of 2 per cent sodium hydroxide and 500 ml. of water, the ether removed by distillation, and the residue dissolved in 200 ml. of Skellysolve B. This solution was extracted with two 100- and two 200-ml. portions of 10 per cent potassium hydroxide in 50 per cent ethanol. After an extraction with 100 ml. of Skellysolve B the solution was acidified in the cold with 50 per cent sulfuric acid and extracted with three 100-ml. portions of ether. The ether solution was dried over anhydrous sodium sulfate and distilled from a modified Claisen flask. After a small forerun of phenol, 21.9 g. (a 9.5 per cent yield based on pinene) of pinylphenol, a viscous oil, was obtained, b.p. 156-162° ($<$1 mm.).

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.11; H, 9.60. Found: C, 81.67; H, 9.61.

The ultraviolet spectrum showed the following specific absorption coefficients at the maxima: k (2170 Å) 24.0; k (2730 Å) 7.83; k (2785 Å) 7.55.

This material formed glassy phenyl- and α-naphthylurethanes which could not be crystallized, decolorized bromine water rapidly but did not yield a crystalline dibromo-derivative, formed an insoluble, amorphous sodium phenolate when treated with 20 per cent sodium hydroxide, and gave an intense red color when coupled with diazotized sulfanilic acid. The material was thought to be a mixture of isomers.

Polymerization Evaluation of the Resin Phenol and Other Phenols as Retarders in the GR-S-10 Recipe.--The retarding action of the resin phenol and other phenols was evaluated with the 72-28 GR-S-10 recipe. The polymerizations were run in clean, dry, 4-oz., screw-cap bottles equipped with punched caps fitted with Buna-N molded gaskets. In preparing the polymerizations, 35 ml. of sodium resinate solution was placed in each bottle, followed by 2 ml. of 3 per cent aqueous potassium persulfate. The sodium resinate solution was prepared by prolonged shaking of Hercules Resin 731 (46-771) with the theoretical quantity of 1 *N* sodium hydroxide. The solution was then diluted with water to such an extent that 35 ml. of solution would contain exactly 1.0 g. of sodium soap. To each bottle was then added 6.40 ml. of a solution of dodecyl mercaptan in redistilled Dow N-100 styrene, containing 0.100 g. of dodecyl mercaptan and 0.0072 g. of the phenol in 6.4 ml. of solution. Phillips Special Purity butadiene was then added in about 0.5 g. excess of the desired 14.4 g. required, the cap was lightly placed on the bottle, and the excess butadiene was allowed to evaporate. The bottle was then capped and allowed to stand until the addition of butadiene to the remaining bottles in the series was complete. All of the bottles were then shaken uniformly to emulsify the contents and were rotated end-over-end in a polymerization bath at 50° ± 1°.

After twelve hours the bottles were removed from the bath and 1 ml. of benzene containing 0.01 g. of β-naphthol injected.

A hypodermic needle carrying a closed stopcock was inserted into the bottle and the total assembly weighed to the nearest 10 mg. The bottle was shaken vigorously, and the latex was allowed to flow through the opened stopcock into a short-stop antioxidant solution in a tared pan. The short-stop antioxidant solution consisted of 5 ml. of a solution of 1.2 g. of phenyl-β-naphthylamine and 0.8 g. of β-naphthol made up to 1 l. of solution with ether. After 5-8 g. of latex was removed, the stopcock was closed, the assembly was reweighed, and the weight of latex determined by difference. After most of the water had evaporated from the pan the residue was dried in a circulating-air oven at 75° for a minimum of twelve hours. The pan and contents were then weighed, and the weight of solid residue was obtained by difference to 1 mg. Hydrocarbon conversions were calculated from the following formula:

$$\% \text{ HCC} = 5(Wd/l - w)$$

where:

W = Weight of total latex, calculated from the recipe.

w = Weight of non-hydrocarbon material in the total latex.

d = Observed weight of dry solids minus weight of short-stop and antioxidant.

l = Weight of the latex aliquot.

In the evaluation of the phenols two polymerization runs were made at different times; a control which contained no phenols was included with each run. The conversions in Tables III and IV represent the average value obtained from two polymerization bottles.

TABLE III

Run No.	Phenol Present	Per Cent HCC
NH-97-9, 10	Resin Phenol IV	65.6 ± 0.9
NH-97-7, 8	None	67.4 ± 0.6

TABLE IV

Run No.	Phenol Present	Per Cent HCC
NH-II-71-1,2	2-Propyl-4,5-dimethyl-	41.5 ± 3.2
NH-II-71-11,12	2-Propyl-3,6-dimethyl-	43.9 ± 1.1
NH-II-71-3,4	2,3,4,5-Tetramethyl-	23.9 ± 0.6
NH-II-71-5,6	Bornyl-	61.9 ± 1.1
NH-II-71-7,8	Menthyl-	61.9 ± 0.6
NH-II-71-9,10	Pinyl-	61.1 ± 0.0
NH-II-71-13,14	Fenchyl-	62.0 ± 0.5
NH-II-71-15,16	None	64.3 ± 0.7

Dehydrogenation Phenolic Fraction IV.-Phenolic fraction IV, 0.4091 g., was mixed with 0.05 g. of 10 per cent palladium on charcoal in the dehydrogenation apparatus described by Fieser (15) and heating started at 220°. The temperature was raised rapidly until there was some evidence of gas evolution (360°). This temperature was maintained for two hours, during which time only 10 ml. of alkali-insoluble, inflammable gas was collected. The reaction was not accelerated by raising the temperature to 400°, so heating was discontinued. The cooled material was dissolved in ether, filtered to remove catalyst, and the ether removed by distillation to leave a residue of dehydrogenated product.

Chemical Tests on Phenolic Fraction IV.-Butenandt and Stodola (9) have prepared various substituted resorcinols and have reported their spectra and the results of several chemical tests on the compounds. The spectrum of each resorcinol prepared shows a single maximum in the 2770-2860 Å range (the spectrum below about 2300 Å was not reported). The chemical tests which they employed with these resorcinols along with the results obtained in this laboratory on the resin phenol are shown in Table V.

The tests used in this work were conducted as follows:

Phosphomolybdic acid.-The phenol (5 mg.) was dissolved in 1 ml. of ethanol, a crystal of phosphomolybdic acid added, and the color of the solution observed. Then a few drops of ammonium hydroxide were added and the color observed. Under these conditions 1,2-dihydroxybenzene compounds give a green color changing to blue on addition of ammonium hydroxide, 1,3-dihydroxy compounds colorless changing to blue, and 1,4-dihydroxy compounds blue remaining blue. Most monohydroxybenzenes give a colorless solution changing to blue.

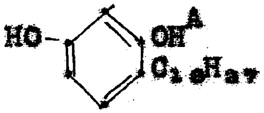
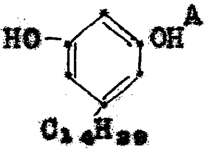
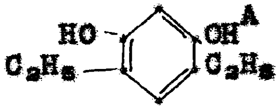
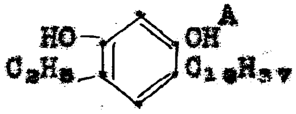
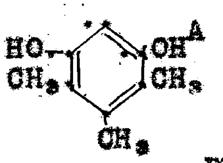
Ferric Chloride.-This test is well known and requires no discussion.

Fluorescein.-The phenol (2 mg.) was heated for five minutes over a microflame with a mixture of 4 mg. of phthalic anhydride and three drops of concentrated sulfuric acid. A small drop of the resulting solution was added to alcoholic potassium hydroxide. Resorcinols having an unsubstituted position meta to the hydroxyls ordinarily give a green fluorescence in this test.

Liebermann.-To 1 mg. of the phenol dissolved in two drops of acetic acid were added 1 ml. of concentrated sulfuric acid and a crystal of sodium nitrite. Most phenols having an unhindered ortho or para position open give blue colors in this test.

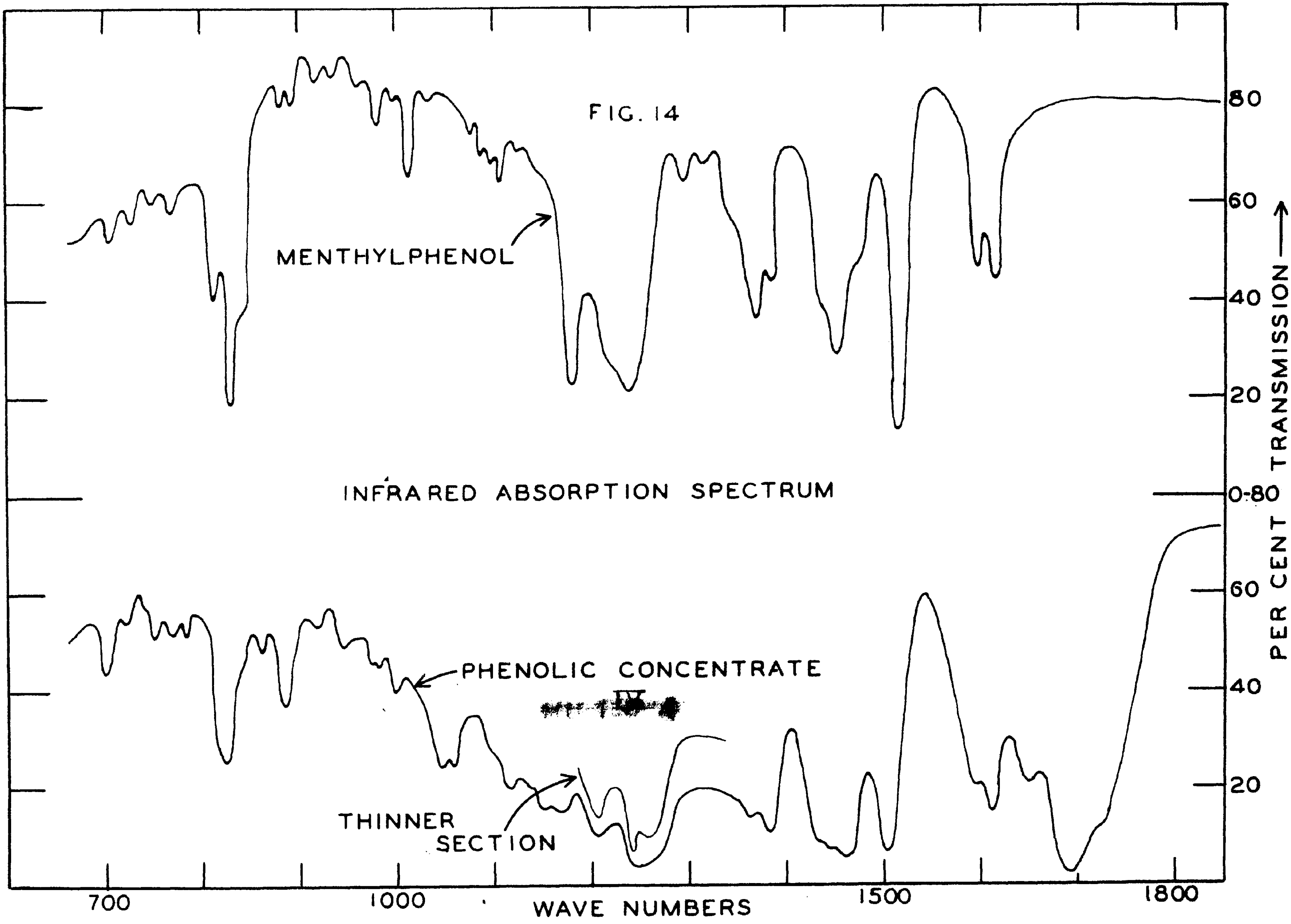
TABLE V

Chemical Tests on Resorcinols and the Resin Phenol

TEST						RESIN PHENOL IV
Phosphomolybdic acid	Colorless blue	Colorless blue	Colorless blue	Colorless blue	Colorless blue	Colorless faint blue
Ferric chloride	green-brown	negative	blue-green	green ppt.	green ppt.	rose
Fluorescein	blue-green fluoresc.	negative	green fluoresc.	green fluoresc.	negative	negative
Liebermann	deep blue	negative	negative	negative	negative	negative
Vanillin	red	red	red	red	red	colorless
Guareschi	red	red	negative	negative	negative	negative
Mercuric Nitrate	white ppt.	white ppt.	white ppt.	white ppt.	white ppt.	negative
Ultraviolet Spectrum Maximum	283 mμ.	277 mμ.	286 mμ.	285 mμ.	285 mμ.	279 and 285 mμ.

A - These are the data of Butenandt and Stodola (9).

FIG. 14


MENTHYLPHENOL
INFRARED ABSORPTION SPECTRUM
PHENOLIC CONCENTRATE
THINNER
SECTION
700
1000
1500
1800
WAVE NUMBERS
80
60
40
20
0-80
60
40
20
PER CENT TRANSMISSION →

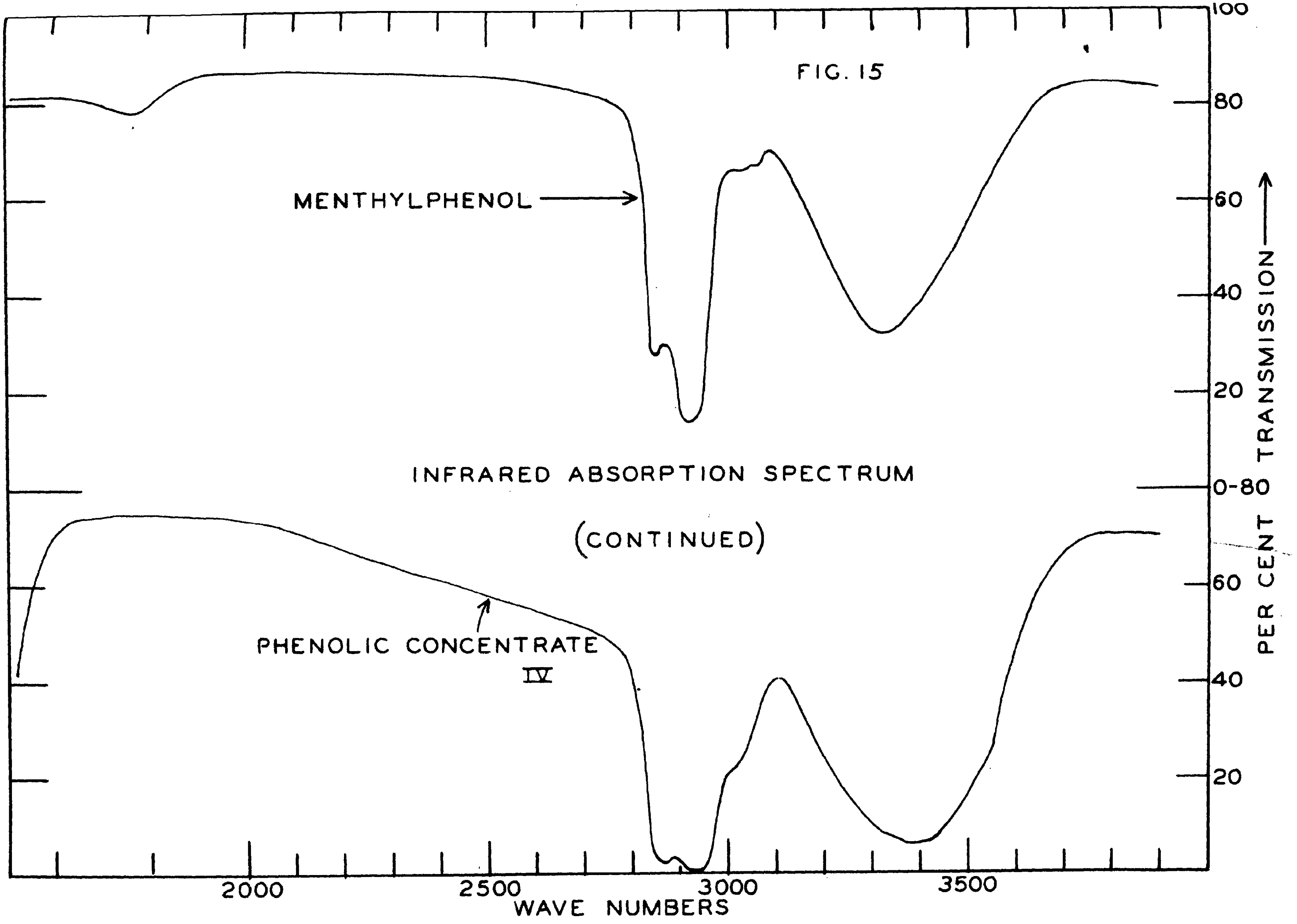


FIG. 15

INFRARED ABSORPTION SPECTRUM

(CONTINUED)

Guareschi.-Several milligrams of the phenol were dissolved in 0.5 ml. of chloroform and a small crystal of sodium or potassium hydroxide added. A positive test is indicated by the development of a red color when the reaction mixture is heated.

Vanillin.-One milligram of the phenol dissolved in 0.5 ml. of acetic acid was treated with several drops of a solution of vanillin in acetic acid and two drops of sulfuric acid. The development of a red color is characteristic of resorcinols, but thymol also gives a positive test.

Mercuric Nitrate.-A solution of 0.5 mg. of the phenol in 75 per cent ethanol was treated with several drops of mercuric nitrate in the same solvent. The formation of a white precipitate in this reaction is unique to resorcinols.

The results of these tests as applied to the resin phenol strongly indicate that it is not a substituted resorcinol of any type.

Infrared Absorption Spectrum of Phenolic Fraction IV.-Figures 14 and 15 present the infrared spectra of phenolic fraction IV and menthylphenol. The measurements were made on thin smears of the pure materials (no solvent) with a Perkin-Elmer recording spectrophotometer.

Figures 14 and 15 show that the phenolic concentrate IV exhibits the following:

1) Strong bonded OH absorption at ca. 3400 cm.$^{-1}$
2) Normal C-H stretching frequencies at ca. 2900 cm.$^{-1}$
3) A C=CH stretching frequency above 3000 cm.$^{-1}$, probably a phenyl-hydrogen.

4) Several $-CH_2-$ bending frequencies at ca. 1450 cm.$^{-1}$

5) Two $-CH_3$ bending frequencies at 1383 cm.$^{-1}$ and 1363 cm.$^{-1}$

6) Phenyl ring absorption at 1614, 1595, 1504 cm.$^{-1}$, and in the long wave-length region at about 823 cm.$^{-1}$. The last bond is in the region assigned to a *para*-substituted phenyl group, and it is between the regions assigned to 1,2,4- and 1,3,5-substituted rings.

7) Strong C=O absorption at 1693 cm.$^{-1}$ and a weaker absorption at 1720 cm.$^{-1}$. These bands could be due to an acid, ketone, or aldehyde.

8) Strong absorption in the $-\overset{\|}{C}-O$ region (about 1250 cm.$^{-1}$) of acids, esters, phenols, and other compounds containing an unsaturated carbon atom. There are also two medium strength bands in the saturated $-\overset{|}{\underset{|}{C}}-O$ region at 1049 and 1058 cm.$^{-1}$

The infrared absorption spectrum of menthylphenol in carbon disulfide was found to be the same as that of the pure solid material.

The infrared absorption spectra of dehydro-, dihydro-, and tetrahydroabietic acids were also obtained but are not reported. In all cases the C=O occurred at 1693 cm.$^{-1}$, and so might account for the similar absorption in phenolic fraction IV; other strong absorption bands such as the =C-O band at about 1280 cm.$^{-1}$ were obscured in the spectrum of the phenolic concentrate. The high over-all absorption in the 1000-1500 cm.$^{-1}$ region indicated that actually a mixture of resin acids was present.

A comparison of the spectra of phenolic fraction IV and menthylphenol shows that there are similarities in the OH (3350 cm.$^{-1}$), phenyl (1510, 1595, 1615, 860 cm.$^{-1}$), = C-O (1237 cm.$^{-1}$) CH_3 (1370 cm.$^{-1}$), and $-CH_2-$ (1350, 2850, 2950 cm.$^{-1}$) regions. However, the strong substituted phenyl absorption of the menthylphenol occurs at a higher wave number than the 823 cm.$^{-1}$ absorption of the phenolic concentrate, as does its phenyl absorption at 1515 cm.$^{-1}$. Other differences in the $-\overset{//}{C}-O$ region (1175-1250 cm.$^{-1}$) and elsewhere indicate that the phenol present in the concentrate probably is not menthylphenol, but is probably quite similar.

Oxidation of Phenolic Fraction IV with Poassium Permanganate.- To 45 ml. of water containing 3 ml. of 5 per cent sodium hydroxide was added 0.1810 g. of IV. The mixture was heated on a steam bath and 3 per cent potassium permanganate added dropwise with vigorous shaking. A total of 17 ml. was added over a twenty-hour period. The cooled reaction mixture was carefully acidified with sulfuric acid and heated for thirty minutes with 5 ml. more potassium permanganate solution. The mixture was then clarified by treatment with sulfur dioxide and extracted with two 25-ml. portions of ether. The ether solution was extracted with four 5-ml. portions of 5 per cent sodium carbonate; this extract was in turn washed with 5-ml. of ether and acidified. The combined ether solutions were dried and the solvent removed by distillation to yield 0.1202 g. of neutral material. The acidified aqueous solution was then extracted with five 10-ml. portions of ether. The ether solution was dried over anhydrous sodium sulfate and the ether removed by distillation to yield 0.070 g. of a clear very viscous oil, neutralization equivalent 172 ± 3, which could not be crystallized.

V. SUMMARY

A procedure for isolation of the phenolic polymerization retarder in Hercules Resin 731 (dehydrogenated rosin) which yielded a concentrate richer in phenolic material than that reported by previous investigators has been developed.

This phenolic concentrate has been shown to retard the copolymerization of butadiene and styrene in the GR-S-10 recipe.

From a study of the ultraviolet spectra, infrared spectra, and from the general physical and chemical properties it has been concluded that the phenolic constituent resembles menthylphenol. It has also been shown that the retarding effects of menthylphenol and the resin phenol are of the same magnitude.

It has been shown that in addition to the phenol there is present in the phenolic concentrate a mixture of resin acids, probably predominantly d-pimaric acid.

Incidental to the investigation it has been shown that in the Claisen rearrangement of allyl 4,5-dimethylphenyl ether the allyl group migrates approximately 70 per cent to the unhindered 2 position and 30 per cent to the 6 position.

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VITA

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