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CHARACTERIZATION OF TAR ACIDS FROM COAL-HYDROGENATION OILS

By E. O. Woolfolk, C. Golumbic, R. A. Friedel, Milton Orchin, and H. H. Storch

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CHARACTERIZATION OF TAR ACIDS FROM COAL HYDROGENATION OILS[1]

By

E. O. Woolfolk,[2] **C. Golumbic**,[3] **R. A. Friedel**,[4] **M. Orchin**,[3] **and H. H. Storch**[5]

Preface

BEFORE the passage of Public Law 290 (78th Cong.) in 1944, with the resulting increase in funds available for synthetic liquid fuel research and development, it was not possible to obtain all the necessary personnel and instruments for detailed characterization and analysis of oils produced by hydrogenation of coal. Although an appreciable amount of work had been done in Bureau of Mines laboratories during the period 1938–44, the effort was limited in scope and served chiefly to emphasize the magnitude of the problem. From the earlier work it was apparent that the oils obtained in the first stage of the hydrogenation of coal are in many ways more complex than crude petroleum. With an augmented staff and modern tools and equipment, it was possible to achieve, in a relatively short time, the results described in this paper. The classical methods of organic chemistry have been supplemented by extensive use of infrared and ultraviolet spectroscopy, by precise distillation, and by countercurrent distribution techniques. Each of these techniques requires a basic understanding of the principles and apparatus involved, and the frequent consultations between the scientists concerned with each technique resulted in a series of approximations that finally led to very precise and accurate information. The work is an excellent illustration of what Dr. Vannever Bush has called the most important single attribute of a scientific staff, namely, the ability to perform as a group this function of estimating and balancing, integrating and interrelating. Extensive application of the basic information contained in this paper is already apparent to chemists engaged in the production of bulk organic chemicals.

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INTRODUCTION AND OBJECT OF PRESENT RESEARCH

For more than a decade, the Bureau of Mines has been investigating the production of synthetic liquid fuels by the hydrogenation of coal. The liquefaction of coal by high-pressure hydrogenation produces an oil in which there is a group of weakly acidic aromatic hydroxy compounds or phenols. This fraction can be removed readily by alkaline extraction of the oil, and the mixture of phenols recovered from the alkaline extract is commonly called the tar-acid fraction. A similar fraction can be obtained by alkaline extraction of the oil produced in the carbonization of coal. Some of the phenolic compounds present in the tar-acid fraction are used extensively in industry, and their presence in the oil produced by the hydrogenation of coal is consequently of considerable economic importance.

It is possible, under favorable hydrogenation conditions, to produce from 100 tons of a high-volatile bituminous coal about 6.4 tons (on a dry, ash-free basis) of marketable tar acids. Because the object of the commercial hydrogenation of coal is the production of gasoline, estimates have been made on tar-acid recovery based on gasoline production from coal. The consumption of gasoline in the United States in 1945 was 672,630,000 barrels. In order to supply 10 percent of this quantity of gasoline, about 17,100,000 tons of a high-volatile bituminous "B" coal (on a dry, ash-free basis) such as that found in Illinois would have to be processed. The hydrogenation of this quantity of coal would result in the production of about 1,100,100 tons of marketable (boiling below 235° C.) tar acids. This amount is more than 16 times the quantity of tar acids used in the entire plastics industry in the United States in 1943.[6] It is obvious from this example that, if the hydrogenation of coal to produce gasoline is undertaken even on a small commercial scale, vast quantities of important chemicals such as the phenols may become available. More exact knowledge of the constitution of the phenolic fraction would serve to indicate those industrial markets in which the particular phenols might be utilized as raw materials.

It has been shown[7] that the conversion of coal to a liquid product can, under certain conditions, be achieved by the consumption of less than 1 percent of hydrogen, and that the critical hydrogenolysis reaction probably occurs at carbon-to-oxygen linkages in the original coal. Unpublished work in this laboratory has demonstrated that nearly all the oxygen in the carbon-containing products from coal hydrogenation is present as hydroxyl oxygen. Perhaps a little less than half of the hydroxyl oxygen is present as oxygen in phenolic compounds, and information concerning the nature of these compounds is thus of obvious importance. The phenolic compounds have also been shown to be of interest in connection with the carbonization of coal[8] and the structure of some constituents of the tar.

To obtain some insight into the nature of oxygenated groups in the coal, it is desirable to produce the phenols under as mild conditions as possible, so that there is the minimum disturbance to their structure during the conversion of coal to a liquid or soluble product. For this reason the coal investigated in the present paper was hydrogenated under mild conditions not selected to give a maximum yield of tar acids of present commercial value; thus, this work cannot be construed as indicating the commercial feasibility of tar-acid recovery from coal-hydrogenation oils.

The purpose of this investigation was to separate and identify as many of the principal phenolic compounds produced by the mild hydrogenation of Pittsburgh-bed (Bruceton) coal as possible and to determine with the greatest possible accuracy the proportions in which they are present.

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[6] Clarke, E. A., Tar Acids. Estimated Production Possible if Coal is Hydrogenated to Produce 10, 20, and 50 Percent of the Country's Gasoline Requirements: Office of Synthetic Liquid Fuels Report, Pittsburgh, Pa., 1947, 7 pp.

[7] Orchin, M., and Storch, H. H., Solvation and Hydrogenation of Coal: Ind. Eng. Chem., vol. 40, 1948, pp. 1385–1389.

[8] Green, S. J., and Muksherji, S. M., The Insoluble Matter of Coal Tar. V. Coal Tar Resins: Jour. Soc. Chem. Ind., vol. 68, 1949, pp. 16–19.

SUMMARY

The tar-acid fraction of the *n*-hexane-soluble portion of the liquid product obtained by the hydrogenation of Pittsburgh-bed (Bruceton) coal was isolated by methanolic alkali extraction of the benzene solution of the oil. The yield of tar acids was 9.4 percent by weight of the *n*-hexane-soluble oil, or 5.2 percent of the total oil produced in the hydrogenation (4.0 percent based on dry, ash-free coal). The tar acids were subjected to distillation, and 136 fractions were collected. The refractive index of each fraction and the densities of the higher-boiling fractions were determined. It was shown that careful interpretation of the data on physical constants makes it possible to select those fractions that are rich in any desired phenol known to occur in the oil. Prior to active work on the fractions, extensive preliminary experiments were conducted on model compounds. A study of the distribution (partition) of various phenols between cyclohexane and a buffered aqueous phase led not only to the development of rules and formulas relating partition coefficient to ionization constant, but also to a more complete understanding of the factors governing the extractibility of phenols. The differences in partition coefficients of isomeric phenols permitted the application of the countercurrent distribution method for their separation and determination of purity. The infrared spectra of many phenols of known constitution were determined, and this information was applied to the qualitative and quantitative estimation of the composition of most of the tar-acid fractions. The ultraviolet absorption spectra of all the phenols known to occur in the oil obtained from the hydrogenation of coal were determined and are given in an appendix. The more classical methods of organic chemistry, such as crystallization, preparation of derivatives, and degradative studies, also were used. Chemical and physical investigation of the various fractions resulted in the identification of 16 individual phenols. Inconclusive evidence for the presence of two others was obtained.

Phenol and *o*-cresol were isolated as pure compounds and *m*- and *p*-cresol as *m*- and *p*-methylphenoxyacetic acids. Four isomeric xylenols were found: 3,5-xylenol and 2,5-xylenol were isolated as pure compounds; 2,4-xylenol was identified through its *N*-(2-fluorenyl)carbamate and *p*-nitrobenzyl ether; and 3,4-xylenol was shown by infrared spectroscopy to be present in small quantities, but it could not be detected by chemical methods. Chemical evidence for the presence of 2,3-xylenol was obtained, but this was inconclusive. *m*-Ethylphenol was identified by chemical methods, and its isomers *o*- and *p*-ethylphenol were shown to be present by infrared spectra measurements. Some chemical evidence was obtained for the presence of mesitol, but it was also inconclusive. Considerable quantities of pure 3-methyl-5-ethylphenol were isolated. The two most simple dicyclic phenols, 4- and 5-indanol, were isolated as a result of countercurrent distribution studies. The presence of *o*- and *p*-phenylphenols was also definitely established.

The phenols whose presence was demonstrated are listed in table 1 together with the proportions in which fourteen of them were found.

TABLE 1.—*Tar acids found in the oil from hydrogenation of Bruceton coal*

Compound	Percent of—		Pounds per ton of total oil	Pounds per ton of coal[1]
	Hexane-soluble oil	Total oil		
Phenol	0.24	0.13	2.6	2.0
o-cresol	.37	.20	4.0	3.1
m-cresol	.55	.30	6.0	4.7
p-cresol	.25	.14	2.8	2.2
2, 4-xylenol	.23	.13	2.6	2.0
2, 5-xylenol	.14	.08	1.6	1.2
3, 5-xylenol	.25	.14	2.8	2.2
3, 4-xylenol	.05	.03	.6	.5
2, 3-xylenol[2]	--------	--------	--------	--------
o-ethylphenol	.03	.02	.4	.3
m-ethylphenol	.42	.23	4.6	3.6
p-ethylphenol	.09	.05	1.0	.8
Mesitol[2]	--------	--------	--------	--------
3-methyl-5-ethylphenol	.27	.15	3.0	2.3
4-indanol	.19	.10	2.0	1.6
5-indanol	.13	.07	1.4	1.1
o-phenylphenol[3]	--------	--------	--------	--------
p-phenylphenol[3]	--------	--------	--------	--------
Total	3.20	1.77	35.40	27.60

[1] Dry, ash-free coal.

[2] Presence indicated by chemical methods, but presence could not be confirmed spectroscopically.

[3] Definitely shown to be present, but quantity not estimated.

ACKNOWLEDGMENTS

The authors wish to thank the many Bureau of Mines workers for help given in this work, in particular, Lois Pierce, Lois Harnack, and Marion Springer, who determined the ultraviolet and infrared absorption spectra; Julian Feldman and Mary Myles for the precise fractional distillation of the crude tar-acid mixture; John J. Vidosh and Edward C. Ralson, who were responsible for most of the drawings; George Goldbach, who assisted in some of the experimental work; Sol Weller for valuable advice on the theoretical aspects of partition measurements; E. L. Clark and Martin A. Elliott, who planned the operation of the Coal Hydrogenation Plant; and Robert Grass and Rose Hartner, who gave valuable aid in the preparation of the manuscript. We also wish to thank Professor M. F. Dull, of the University of Pittsburgh, who acted as cosponsor for the portion of the work that was used as a doctorate thesis for E. O. Woolfolk. We also wish to acknowledge the courtesy of the editors of the Journal of the American Chemical Society, Analytical Chemistry, and Industrial and Engineering Chemistry in permitting us to quote large sections from articles by the present authors, which appeared in the journals of the American Chemical Society.

HISTORY OF PREVIOUS WORK

Although probably several hundred compounds are present in coal tar, only about 180 of them have been isolated and characterized. The product obtained by the hydrogenation of coal is a material much more complex than coal tar; consequently, the complete characterization of this product presents a problem of gigantic proportions. Because the task of examining coal-hydrogenation oils and tars is, at least qualitatively, the same as that involved in the examination of coal tar, it is of some value to comment briefly on the latter.

CHARACTERIZATION OF COAL-CARBONIZATION PRODUCTS

Coal tar, which is a co-product of coal carbonization, has been for many years a major source of a certain small group of organic chemicals. It is rather surprising, then, that comparatively so little work has been done on the composition of coal tar. Until recently, the composition of tar has been chiefly of commercial interest. In 1940, chemicals accounted for only 4.8 percent of the total tar distilled in the United States. Selling the tar after removal of only a few constituents has been so profitable that the few tar distillers have been reluctant to spend much research effort toward its characterization. One of the few early incentives in this direction was the discovery by Graebe and Liebermann [9] that alizarin, a valuable dyestuff, could be prepared from anthracene. Dumas [10] probably was the first to discover the presence of anthracene in coal tar, but after Graebe and Liebermann's discovery there was a flurry of activity, which resulted in improved methods for the isolation and purification of anthracene. Another impetus toward the use of coal tar as a source of chemicals was the discovery by Weissgerber [11] of the alkali-melt technique. This paved the way for the commercial isolation of some important, weakly acidic, coal-tar constituents such as fluorene. During the past 30 years, a steady stream of publications has come from the laboratory of O. Kruber.[12] In a series of more than 30 papers, he has described the isolation and structure of many interesting compounds present in tar. Much of this work has been incorporated in patents assigned to the Gesellschaft für Teerverwertung. It is no secret that the polynuclear compounds sold by this German firm were far superior in quality and number to those now available in this country.

The application of chromatographic absorption to the purification of compounds of coal tar as developed by Winterstein and coworkers [13] led to important discoveries concerning the nature of some of the high-molecular-weight polynuclear constituents. By using this technique, it was possible to obtain compounds of a degree of purity unobtainable by crystallization.

Much of the recent research on coal tar was stimulated by the discovery [14] that crude coal tar, when dissolved in benzene and painted on the ears of rabbits, could cause cancer of the skin. It was then of great scientific interest to learn which particular compound, if any, present in the coal tar was responsible for its carcinogenic activity. A series of brilliant investigations by Kennaway, Cook, Hewett, Hieger, and coworkers at the Royal Cancer Hospital in London,[15] in which fluorescent and ultraviolet spectroscopy played a great part, led to the isolation of a small quantity of 3,4-benzopyrene [16] from 2 tons of tar. This compound was shown to be a very active cancer-producing substance. Whether or not this particular compound was the one responsible for the carcinogenic properties of crude tar is not definitely known, and Berenblum and Schoenthal [17] reopened the question recently. The interest in the relationship of coal-tar

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[9] Graebe, C., and Liebermann, C., [Alizarin and Anthracene]: Ber. Deut. chem. Gesell., vol. 1, 1868, pp. 49–51.

[10] Dumas, J. B. A., Ann. chim., vol. 50, 1832, pp. 182–197.

[11] Weissgerber, R. [Sodium Derivative of Indene]: Ber. Deut. chem. Gesell, vol. 42, 1909, pp. 569–572.

[12] Kruber, O. [The Progress of Coal-Tar Research in the Period 1910–40]: Angew. Chem., vol. 53, 1940, pp. 69–74.

[13] Winterstein, A., and Stein, G. [Fractionation and Purification of Organic Substances by the Principle of Chromatographic Adsorption Analysis. I]: Ztschr. physiol. Chem., vol. 220, 1933, pp. 247–263.

Winterstein, A. [Colored Hydrocarbons of Coal Tar]: Naturwissenschaften, vol. 22, 1934, pp. 237–238.

Winterstein, A., and Schon, K. [Fractionation and Purification of Organic Substances by the Principle of Chromatographic Adsorption Analysis. IV. Polycyclic Aromatic Hydrocarbons]: Ztschr. physiol. Chem., vol. 230, 1934, pp. 146–158.

Winterstein, A., Schon, K., and Vetter, H. [Fractionation and Purification of Organic Substances by the Principle of Chromatographic Adsorption Analysis. V. Anthracene, Chrysene, and Pyrene]: Ztschr. physiol. Chem., vol. 230, 1934, pp. 158–169.

Winterstein, A., and Vetter, H. [Fractionation and Purification of Organic Substances by the Principle of Chromatographic Adsorption Analysis. VI. 1,2-Benzopyrene]: Ztschr. physiol. Chem., vol. 230, 1934, pp. 169–174.

[14] Yamagiwa and Ichikawa, Mitteil. Med. Fakultat.: Univ. Tokyo, vol. 15, 195, p. 295.

[15] British Medical Bulletin, vol. 4, 1947, pp. 309–426, contains an outstanding and complete review of the subject of chemical carcinogenesis.

[16] Cook, J. W., Hewett, C. L., and Hieger, I., Coal-Tar Constituents: Nature, vol. 130, 1932, p. 926.

[17] Berenblum, I., and Schoental, R., Carcinogenic Constituents of Coal Tar: British Journal of Cancer, vol. 1, 1947, pp. 157–165.

constituents to carcinoma resulted in a phenomenal growth in the number of investigations into the synthesis and properties of polynuclear hydrocarbons. In each of the years between about 1932 and 1940 there were probably more publications in this field than in the entire history of organic chemistry prior to that time. The amount of information now available should simplify any systemic investigation of coal tar. New techniques, like molecular distillation and chromatography, and the background of infrared and ultraviolet absorption data now available also would facilitate such an investigation.

The above paragraphs have summarized the work on coal tar in an extremely brief fashion. The subject has been reviewed completely by Rhodes.[18] Individual publications of value to the present investigation will be referred to in the sections in which they are utilized.

Because the present investigation is concerned only with phenolic compounds, it is appropriate to list the 38 phenolic compounds isolated from the products of coal carbonization. These are phenol; *o*-, *m*,- and *p*-cresol; *o*-, *m*-, and *p*-ethylphenol; 2,3-, 2,6-, 2,4-, 2,5-, 3,5- and 3,4-xylenol; *o*-isopropylphenol; 2-methyl-4-ethylphenol; 2-methyl-5-ethylphenol; 3-methyl-5-ethylphenol; 3,5-diethylphenol; 2,4,5-trimethylphenol; 2,4,6-trimethylphenol; 2,3,5-trimethylphenol; catechol; 7-hydroxycoumarone; 4-indanol; 3,4,5-trimethylphenol; durenol; 5-indanol; 4-methylcatechol; resorcinol; 1-naphthol; hydroquinone; 2-naphthol; pyrogallol; *o*- and *p*-phenylphenol; 2-hydroxydiphenylene oxide; 2-hydroxyfluorene; and 2-hydroxyphenanthrene.

PREVIOUS INVESTIGATIONS OF COAL-HYDROGENATION PRODUCTS

Previous characterizations of coal-hydrogenation oils have generally been incidental to the engineering research involved in the process of converting coal to hydrocarbon fuels. The amenability of the various types of coals in the United States to hydrogenation has been studied at the Bureau of Mines experimental plant.[19] The oils produced in these coal-hydrogenation studies were extracted with 10 percent sodium hydroxide solution to separate the tar acids and 10 percent sulfuric acid to separate the nitrogen bases. The remaining neutral oil was then distilled, and the probable components of the distillate were deduced from density, refractive index, and sulfuric acid-solubility data. The yield of tar acids from the alkali-soluble portion increased with decreasing rank (increasing oxygen content) of the coal. The lower-rank coals, including lignite, subbituminous, and high-volatile bituminous, gave 12 to 16 percent of tar acids on the basis of the moisture- and ash-free coal, whereas the higher-rank coals gave 5 to 15 percent of tar acids. About half of the tar acids boiled below 235° C. at atmospheric pressure. Of these low-boiling tar acids, about 50 percent appeared to be xylenols, 30 percent cresols, and 20 percent phenol. Of the tar acids boiling above 235° C., 55 percent boiled in the range between 235° to 270° C., 28 percent between 270° and 300° C., 28 percent between 270° and 300° C., and 17 percent between 300° to 330° C.

Kaplan, Storch, and Orchin[20] investigated an oil, boiling in the gasoline range, which was produced as a minor product in the low-pressure hydrogenation of coal. This coal was separated into acidic, basic, and neutral fractions by extraction with sodium hydroxide and sulfuric acid, respectively. The tar-acid fraction up to and including the xylenols and the tar-base fraction up to and including the toluidines were studied. The probable components of the neutral fraction were deduced from a long series of careful physical measurements and calculations.

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[18] Rhodes, E. O., Chemistry of Coal Utilization; H. H. Lowry (ed): John Wiley & Sons, Inc., New York, vol. 2, 1945, p. 1325.

[19] Hirst, L. L., Boyer, R. L., Eisner, A., Pinkel, I. I., and Storch, H. H., Hydrogenation of High-Volatile Bituminous Coals: Ind. Eng. Chem., vol. 33, 1941, p. 1068.

[20] Kaplan, E. H., Storch, H. H., and Orchin, M., Hydrogenation and Liquefaction of Coal. Part V. Characterization of Light Oil: Bureau of Mines Tech. Paper 690, 1946, 18 pp.

PRELIMINARY INVESTIGATIONS ON EXPERIMENTAL TECHNIQUES

The most distinctive property of phenols is their weakly acidic nature, which is attributable to the combination of a hydroxyl group with an unsaturated nucleus; that is, the presence of an "enolic" group. The acidic character as well as many other chemical and physical properties of phenols are largely determined by the position of substituent groups in the nucleus. To learn more about the relationship between the structure and properties of phenols, an extensive preliminary investigation was undertaken with model compounds. Techniques to be tested for the separation and identification of the phenols in coal-hydrogenation oils were applied first to model compounds. Studies were made of partition coefficients and their relationship to ionization constants, molecular structure, and extractibility of phenols; of countercurrent distribution; of methylation and demethylation; of the use of 2-fluorenylisocyanate as a reagent for the characterization of phenols; of chromatography; and of the infrared and ultraviolet absorption spectra of phenols.

PARTITION STUDIES ON MODEL COMPOUNDS

A compound that has some solubility in each phase of a system composed of two immiscible solvents will distribute itself between the solvents according to a definite equilibrium. If the molecular weight of the compound is the same in both solvents (no association), its distribution between them is constant at constant temperature. The ratio of the concentrations in the two solvents is called the partition coefficient (or distribution coefficient).

As tar acids are weakly acidic compounds, their separation from liquid products of coal hydrogenation may be achieved by partition between an organic phase and an immiscible alkaline phase.

MEASUREMENTS OF PARTITION COEFFICIENTS

The partition coefficients of 20 phenols used as model compounds were determined,[21] with the results shown in the second column of table 2. A solution of 0.5 mg. of the phenol per ml. of spectrographic-grade cyclohexane was shaken for 2 minutes with an equal volume of the aqueous phase, which was either water or 0.5M phosphate ($Na_2HPO_4+Na_3PO_4$). Equilibration and phase separation were carried out in 125-ml. centrifuge separatory funnels. Preliminary mutual saturation of the immiscible layers was unnecessary, because it was found to have no effect upon the partition coefficient. The initial concentration of 0.5 mg. per ml. was convenient for analysis and also was well below the concentration at which association effects might be expected. Doubling this concentration in a few instances changed the partition coefficient only slightly within the error of the method.

TABLE 2.—*Partition coefficients and ionization constants of phenols* [1]

Compound	k (H_2O)	k at pH 6.65	k' at pH 11.08	pK calculated	pK literature
Phenol	0.19	0.22	0.02	10.0	[2]9.97 [3]9.99
o-cresol	1.34	1.96	.24	10.2	[2]10.20
m-cresol	.70	1.01	.09	10.0	[2]10.01
p-cresol	.80	1.14	.11	10.1	[2]10.17
2,6-xylenol	19.0	21.7	3.57	[4]10.5	[2]10.60 [3]10.58
2,5-xylenol	5.85	7.46	1.16	10.3	[2]10.32
2,4-xylenol	5.71	7.06	1.63	10.4	[2]10.47
3,5-xylenol	3.50	4.02	.33	10.0	[3]10.09 [3]10.18
o-ethylphenol	6.75	10.4	1.45	10.2	------
m-ethylphenol	2.65	4.31	.31	9.9	------
p-ethylphenol	2.78	4.43	.40	10.0	------
3-methyl-5-ethylphenol	7.77	14.6	1.49	10.1	------
o-phenylphenol	102	351	[5].39	9.6	------
p-phenylphenol	12.3	30.7	.45	9.1	------
o-cyclohexylphenol	------	------	[5]3.81	------	------
p-cyclohexylphenol	------	------	[5].92	------	------
4-indanol, I	4.5	5.3	.62	10.2	------
5-indanol, II	3.7	5.8	.83	10.2	------
5-hydroxy-1,2,3,4-tetrahydronaphthalene, III	25.3	64.4	7.5	10.1	------
6-hydroxy-1,2,3,4-tetrahydronaphthalene, IV	8.6	30.8	2.1	9.9	------

[1] All measurements were made at room temperature, 28°±2°.

[2] Boyd, D. R., The Hydrolysis of Sodium Phenoxides in Aqueous Solution: Jour. Chem. Soc., vol. 107, 1915, p. 1538.

[3] Wheland, G. W., Brownell, R. M., and Mayo, E. C., The Steric Inhibition of Resonance III. Acid Strengths of Some Nitro- and Cyanophenols: Jour. Am. Chem. Soc., vol. 70, 1948, p. 2492.

[4] Calculated at pH 12.26.

[5] k' at pH 12.54.

Measurements of pH were made with the Beckman model M pH-meter employing a type E glass electrode. All analyses of the phenol concentration in the distribution layers were made by measuring ultraviolet absorption bands with a Beckman quartz spectrophotometer. An absorption curve for each phenol was prepared to determine the wave length most suitable for analysis. To determine the accuracy of this method, experiments were made in which both immiscible phases were

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[21] The *m*-cresol, *p*-cresol, and ethylphenols used in this work were supplied by Dr. J. J. McGovern, Koppers Co. Fellowship, Mellon Institute, Pittsburgh, Pa.

analyzed after distribution. It was found that the sum of the quantities of phenol in each layer agreed within 5 percent or less of the original amount. Thereafter, analyses were usually confined to the cyclohexane phase, except where the partition coefficient was very high or low.

The method described above is not suitable for measuring partition coefficients higher than 20. However, satisfactory measurement of partition ratios up to 400 was made possible by decreasing the ratio of organic to buffer phases and by repeated reextraction of the organic phase with fresh buffer. The partition coefficient can then be calculated by applying the equation

$$A\left(\frac{kr}{kr+1}\right)^n = B, \tag{1}$$

where A is the initial quantity of phenol in the organic phase, B is its amount after n extractions with buffer, and r is the ratio of the volumes of organic and buffer phases.

Despite the fact that no close temperature control was maintained during distribution, duplicate partition coefficients determined at intervals of several days agreed within 5 percent of each other in the intermediate range and within 10 percent in the very high or low range. As a 30-percent change in partition coefficient would affect the calculated pK ($-\log$ ionization constant) value by only a 0.1 unit, it is believed that the calculated values are within about ± 0.1 pK unit of the exact values.

The partition coefficients measured in the systems cyclohexane $-0.5M$ phosphate buffers of pH 11.08 and 6.65 are represented by k' and k, respectively, in table 2.

RELATIONSHIP BETWEEN PARTITION COEFFICIENT AND IONIZATION CONSTANT

In the partition of a weak acid (HA), such as a phenol, between a nonionizing solvent and an aqueous phase, the following equilibria are established when no association occurs in either phase:[22]

$$\begin{tikzcd}
\text{Organic phase} & HA \arrow[d, shift left, "(a)"'] & \\
\text{Aqueous phase} & HA \arrow[u, shift left] \arrow[r, shift left, "(b)"] & H^+ + A^- \arrow[l, shift left]
\end{tikzcd}$$

(a) Partition of unionized acid between the two phases, measured by the partition coefficient, **k**.

$$k = \frac{[HA]_o}{[HA]_w} \tag{2}$$

(b) Ionization of the acid in the aqueous phase, measured by the ionization constant, **K**.

$$K = \frac{[H^+]_w[A^-]_w}{[HA]_w} \tag{3}$$

As part of the acid in the aqueous layer is in ionic form, the observed partition coefficient, k', is given by the expression

$$k' = \frac{[HA]_o}{[HA]_w + [A^-]_w} \tag{4}$$

From equation (3),

$$[A^-]_w = \frac{K[HA]_w}{[H^+]_w}$$

Substitution of this value of $[A^-]_w$ into equation (4) and rearrangement of terms results in the following equation:

$$k' = \frac{1}{1+\frac{K}{[H^+]_w}} \cdot \frac{[HA]_o}{[HA]_w} \tag{5}$$

From equation (2), the last term of equation (5) is k, hence,

$$k' = \frac{k}{1+\frac{K}{[H^+]_w}} \tag{6}$$

When the aqueous phase contains a buffer of sufficient alkalinity so that $[H^+] \ll K$, the unity term in the denominator of equation (6) became negligible in comparison with the other term; hence, equation (6) becomes:

$$k' = \frac{k[H^+]}{K}$$

or, logarithmically,

$$\log k' = \log k + \log [H^+] - \log K$$

$$\log k' = pH + pK + \log k \tag{7}$$

According to equation (7), a plot of $\log k'$ vs. pH would be a straight line with a slope of -1. Experimental results, represented graphically in figure 1, verified this relation. In figure 1, the observed partition coefficients of 14 phenols, distributed in the system cyclohexane-0.5M phosphate buffer, are plotted as a function of pH. A straight line with a slope close to -1 (mean, -0.97 ± 0.10) occurred in all instances. This observation also shows that there was no significant association in the organic phase.

For dibasic acids, the slope of the $\log k' - p$H curve should be 1 to 2 when $pK_1 \ll pH \ll pK_2$, and 2 where $pH \gg pK_2$, provided that no association occurs.

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[22] Craig, L. C. [Identification of Small Amounts of Organic Compounds by Distribution Studies. Application to Atebrin]: Jour. Biol. Chem., vol. 150, 1943, pp. 33–45.

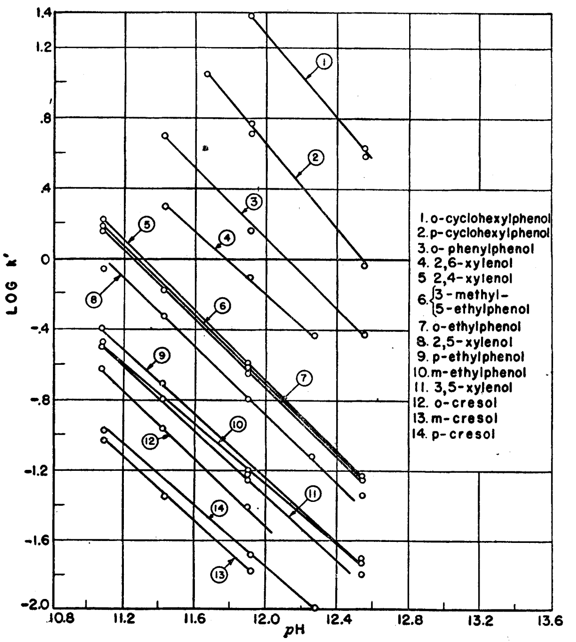


FIGURE 1.—EFFECT OF CHANGE OF *p*H ON PARTITION COEFFICIENT.

DISTRIBUTION OF HA WHEN ASSOCIATION OCCURS IN THE ORGANIC PHASE

If association leads to the formation of dimers according to the reaction $2HA\rightleftharpoons(HA)_2$, the total concentration of unionized acid in the organic phase, which is shown as $[HA]_o$ in equation (2), becomes $[HA]_o+2\ [(HA)_2]_o$, or $[HA]_o\ (1+2K_a^2\ [HA]_o)$ where K_a is the association constant. If Craig's derivation [23] is carried out, a relationship is obtained for the observed partition coefficient, as shown in equation (8):

$$K'=k\frac{1+2K_a^2[HA]_o}{1+\frac{K}{[H^+]}} \qquad (8)$$

If dimerization proceeds nearly to completion, the observed partition coefficient, k', is not independent of initial concentration of HA, as is the case when no association occurs.

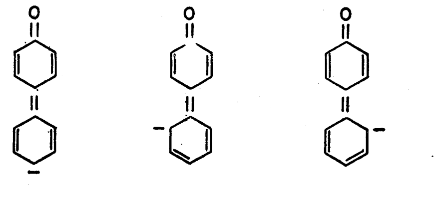
CALCULATION OF IONIZATION CONSTANT FROM PARTITION MEASUREMENTS

Equation (7) was used for making an approximate evaluation of the ionization constant of each phenol studied. The partition coefficients observed in the systems, cyclohexane-0.5M-phosphate buffers of *p*H 11.08 and 6.65 (table 2) were used for k' and k, respectively. At *p*H 6.65, the ionization of a simple phenol is negligible; hence, the observed partition coefficient at this *p*H measures the distribution of the unionized phenol between the organic and aqueous phases. The partition coefficient at *p*H 6.65 is higher than that observed when the aqueous phase is pure water (table 2, columns 2 and 3), showing that concentrated buffers produce an appreciable "salting-out" effect. Comparison of calculated ionization constants with literature values (table 2) shows good agreement and further substantiates the validity of equation (7). This method of estimating approximate ionization constants has the advantages of simplicity of measurements and applicability to difficultly soluble phenols.[24]

RELATIONSHIP BETWEEN IONIZATION CONSTANT AND MOLECULAR STRUCTURE

Introduction of alkyl groups into the nuclear positions of a phenol decreases its acid strength, the effect being most pronounced in ortho and para substitution.[25] This is understandable, as the electron release effect of alkyl groups in the ortho and para positions can be transmitted to the oxygen of the hydroxyl group, whereby proton removal becomes more difficult and acid strength is decreased. This effect cannot be transmitted when substituents are at the meta position, and for this reason the meta-substituted phenols in any isomeric series are the strongest acids. Thus, it was not surprising to observe that in the ethylphenol series, in which no exact ionization constants are available, the calculated *pK* value of the meta compound is the lowest of the isomers (table 2). Substitution at the ortho position decreases acid strength even more than para substitution because of the special so-called "ortho" effect, which is probably electrical in nature.[26] Diortho substitution, of course, magnified this effect; 2,6-xylenol is the weakest acid of the xylenols.

It may be noted that the phenylphenols are stronger acids than phenol. This is to be expected, because the greater number of resonance possibilities among the phenylphenols (as compared to the mononuclear homologues) stabilize the ion. Such resonance forms are as follows:



The corresponding nonionic resonance forms shown below do not make a large contribution

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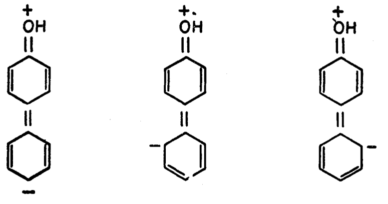
[23] Work cited in footnote 22.

[24] Golumbic, C., Orchin, M., and Weller, S., Partition Studies on Phenols. I. Relations between Partition Coefficient and Ionization Constant: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 2624-2627.

[25] Wheland, G. W., The Theory of Resonance: John Wiley & Sons, Inc., New York, 1944, p. 185.

[26] Watson, W., Modern Theory of Organic Chemistry: Oxford University Press, Oxford, 1941, pp. 241-243.

to resonance stabilization because of their rather large charge separation:



EFFECT OF "TRUE" PARTITION COEFFICIENT (k) AND IONIZATION CONSTANT ON THE OBSERVED PARTITION COEFFICIENT (k')

The above discussion has shown that both the partition coefficient and ionization constant of a phenol are affected by changes in its molecular structure. The observed partition coefficient is a function of both the "true" partition coefficient and the ionization constant. In the alkaline *p*H region in which equation (7) is valid, the ratio of observed partition coefficients for any two phenols (*c* and *d*) is given by the expression:

$$\frac{k'c}{k'd}=\frac{kc\,Kd}{kd\,Kc} \tag{9}$$

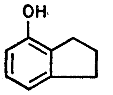
This ratio is greater than the corresponding ratio in neutral or weakly alkaline regions in those instances in which both kc/kd and Kd/Kc are >1. Thus, the data of table 2 show that the ratio of partition coefficients of 2,4- and 3,5-xylenols at *pH* 11.08 is almost three times that at *p*H 6.65. For this reason, it is desirable to employ an alkaline buffer as one of the immiscible phases for separating these isomers by a partition method such as countercurrent distribution.[27] [28] Buffers also allow adjustment of partition coefficients to any desired value, which is a decided advantage when dealing with slightly soluble acids. As will be shown below, these observations find practical application in the separation of isomeric phenols.

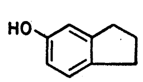
RELATIONSHIP BETWEEN "TRUE" PARTITION COEFFICIENT (k) AND MOLECULAR STRUCTURE

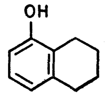
The addition of alkyl groups to a phenol increases the partition coefficient because of the decreasing solubility in the aqueous phase associated with increasing molecular weight. The magnitude of this effect depends on the position of the entering group. An alkyl group introduced into a meta or para position, both relatively remote from the solubilizing hydroxyl group, should have a similar effect upon the partition coefficient. The data of table 2 show that approximately equal partition coefficients are obtained for *m*- and *p*-cresol and also for *m*- and *p*-ethylphenols. However, in each series the ortho isomer has an appreciably higher partition coefficient. An explanation concerning the nature of this type of "ortho" effect can be suggested. Solubility of a phenol in the aqueous phase is probably partly caused by hydrogen bonding between the hydroxyl of the phenol and the water molecules. As the presence of an alkyl substituent in the ortho position would tend to hinder the approach of a solvent molecule to the hydroxyl group, the ortho-substituted phenol would be less hydrogen bonded than its isomers and, therefore, less soluble. The greater the size of the ortho substituent, the more pronounced would be its effect on hydrogen bonding. Coggeshall[29] has shown the decrease in shift of the hydroxyl band in the infrared spectrum of a phenol, as a result of ortho substitution, can be used as a criterion of the extent of hydrogen bonding. Bulky alkyl groups produce no appreciable shift, whereas methyl groups do. It is possible that partition coefficients that show an ortho methyl effect are a more sensitive index of the extent of hydrogen bonding than are the reported spectral data.

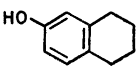
A rather interesting demonstration of the application of partition measurements to structural problems concerns the contention of Arnold and co-workers[30] that the relative steric influence of methylene groups in six-membered rings is greater than that of five-membered rings.

A careful study of the partition coefficients of the dicyclic phenols, I–IV, listed in table 2 supports this hypothesis.


I


II


III


IV

The partition coefficient (*k*) of 5-hydroxy-1,2,3,4-tetrahydronaphthalene, III, is 5.6 times that of 4-indanol, I. It would be expected, of course, that III would have less solubility in water than I solely on the basis of its greater molecular weight; but that III's high partition coefficient is due mainly to steric inhibition of hydrogen bonding is shown by comparison with its isomer, IV, the hydroxyl group of which is unhindered. The ratio of partition coefficient of IV/I is only 1.9, as compared to III/I of 5.6. That the five-membered ring provides little or no steric interference with hydrogen bonding is shown by the nearly equal *k* values of I and II. This picture is given additional support by the

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[27] Work cited in footnote 22.

[28] Golumbic, C., Partition Studies on Phenols. II. Separation of Isomeric Phenol Homologues by Countercurrent Distribution: Jour. Am. Chem. Soc., vol. 71, 1949, p. 2627.

[29] Coggeshall, N. D., Infrared Spectroscopic Investigations of Hydrogen Bonding in Hindered and Unhindered Phenols: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 1620–1624.

[30] Arnold, R. T., and Richter, J., Steric Effect of Methylene Groups IV: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 3505–3507.

Orchin, M., and Golumbic, C., Partition Studies on Phenols. III. Steric Effects: Jour. Am. Chem. Soc., vol. 71, in press.

infrared absorption spectra of these isomers described on page 20.

EXTRACTABILITY OF PHENOLS

The literature records many instances of failure to extract phenols from an organic phase by aqueous alkali. It is common practice to use a methanolic potassium hydroxide solution called Claisen alkali for extracting such phenols, which have been separately classified as "cryptophenols" or phenols with hidden phenolic properties.[31] An examination of equation (7) reveals the probable reason for this phenomenon. Three factors affect the partition of a phenol between the organic and aqueous phases: *p*H of the aqueous phase, ionization constant of the phenol, and partition coefficient of the unionized phenol. When aqueous sodium hydroxide is used for extraction, the *p*H is about 14. The ionization constant (*pK*) of the phenols in most cases varies within small limits, so that differences in extractibility are generally not a result of differences in acid strength. The partition coefficient, *k*, is then mainly responsible for differences in extractibility. The solubility in water of the undissociated form of the phenol is the reason why many phenols cannot be extracted from an organic phase. The presence of alcohol in the water increases the solubility of the undissociated phenol in the aqueous phase and hence results in greater extractibility.

The improvement in extractibility of phenols by using methanolic alkali instead of aqueous alkali is shown by the results in table 3. A typical experiment was conducted as follows: A weighed sample of the selected phenol was dissolved in a definite volume of benzene. The solution was extracted twice with an equal volume of alkali and once with half its volume of alkali. The unextracted phenol in the organic layer was determined by evaporating the solvent and weighing the residue.

TABLE 3.—*Extraction of phenols*

Phenol	Percent extracted—	
	With aqueous alkali	With methanolic alkali
o-phenylphenol	95	97
o-cyclohexylphenol	40	99
2′-hydroxy-1-phenylnaphthalene	10	99

Not only methanol but other water-soluble solvents can be used in the aqueous phase to improve the extractibility of phenols. Such other solvents include the cellosolves (ethers of ethylene glycol), carbitols (ethers of diethylene glycol), polyethylene glycols, the Dowanals (1-methoxy-2-propanol, dipropylene glycol methyl ether, tripropylene glycol methyl ether), and related compounds. The improvement achieved in extractibility of some phenols by using certain of these solvents is shown in table 4.

TABLE 4.—*Extractibility of phenols*

Compound [1]	Extraction solvent (aqueous)	Partition coefficient	Percent extracted
Di-tert-butyl-p-cresol	KOH [2]		0
Do	KOH-methyl cellosolve [3]	0.21	82.5
2′-hydroxy-1-phenyl-naphthalene.	KOH [2]	.81	55.4
Do	KOH-thylene glycol [4]	.042	96.0
Do	KOH-methyl cellosolve [3]	.027	97.4
Do	KOH-carbitol	.083	92.4
o-cyclohexylphenol	KOH [2]	.094	91.4
Do	KOH-ethylene glycol [4]	.022	97.8
Do	KOH-methyl cellosolve [3]	.007	99.3
Do	KOH-carbitol [5]	.068	93.6

[1] Phenol dissolved in cyclohexane (0.5 mg. per ml.).

[2] Aqueous KOH=350 gm. KOH per liter.

[3] Aqueous KOH-methyl cellosolve=350 gm. KOH+250 cc. H_2O diluted to a liter with methyl cellosolve.

[4] Aqueous KOH-ethylene glycol=350 gm. KOH+250 cc. H_2O diluted to a liter with ethylene glycol.

[5] Aqueous KOH-carbitol=100 gm. KOH+250 cc. H_2O diluted to a liter with carbitol.

COUNTERCURRENT DISTRIBUTION STUDIES ON MODEL COMPOUNDS

It was shown above that isomeric phenols have significant relative differences in their partition coefficients when distributed between an organic solvent and alkaline buffer. These differences are great enough to permit application of the countercurrent distribution method [32] in separating individual phenols and testing their purity.[33]

The technique of countercurrent distribution is analogous in principle to fractional crystallization and is shown diagrammatically in figure 2. Equal volumes of two immiscible solvents (previously saturated with each other) are placed in a separatory funnel or tube, indicated by the circle numbered 0 in figure 2, and the compound or mixture to be distributed is added. After shaking, the lower solvent layer is drawn off into tube 1 and fresh lower and upper layers are added to tubes 0 and 1, as indicated. At this point, one complete transfer or plate has been applied. Tubes 0 and 1 are shaken, and the layers are separated, as illustrated. Two equilibrium steps or plates have now been completed. The process can be continued for

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[31] Niederl, J. B., Diisobutylphenol-Synthesis-Structure-Properties-Derivatives: Ind. Eng. Chem., vol. 30, 1938, pp. 1269–1274.

[32] Craig, L. C., Identification of Small Amounts of Organic Compounds by Distribution Studies. II. Separation by Countercurrent Distribution: Jour. Biol. Chem., vol. 155, 1944, pp. 519–534.

[33] Work cited in footnote 28.

any given number of plates. The diagram of figure 2 represents a 6-plate operation.

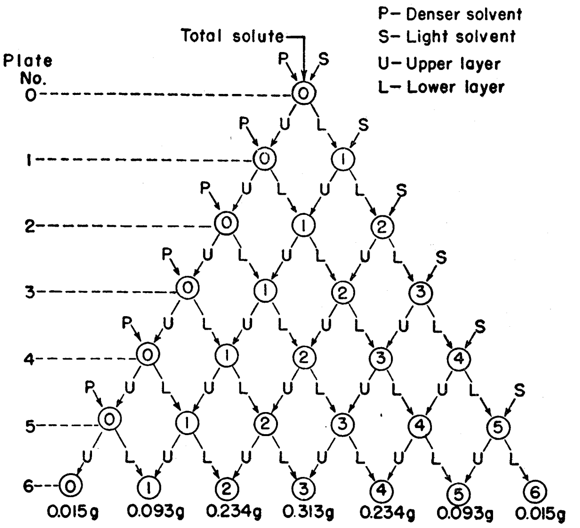

FIGURE 2.—COUNTERCURRENT DISTRIBUTION OF 1.0 GM. OF MATERIAL WITH A PARTITION COEFFICIENT OF UNITY.

In practice, it is cumbersome to carry the procedure beyond eight plates if separatory funnels are used. By using a commercially available apparatus,[34] 50 plates or more can be applied conveniently. With this apparatus, the lighter layer rather than the heavier layer is transferred, a procedure contrary to that employed with separatory funnels.

The fraction of material carried from one plate to the succeeding plate is given by the equation $k/(k+1)$, where k is the partition coefficient. If the process is stopped after many plates have been applied, the original sample is distributed among the various tubes according to a Gaussian distribution; that is, a plot of tube number *vs.* amount in each tube gives a distribution curve. When the partition coefficient is unity, the peak of this curve coincides with the position of the center tube; if the coefficient is greater or less than one, the peak concentration will be to the right or left, respectively, of the center. The exact position, N, of the peak is given by the expression

$$N=(n)\left(\frac{k}{k+1}\right) \tag{10}$$

where n is the total number of plates and k is the partition coefficient. In figure 2, the last horizontal line shows the distribution of 1 gram of a substance with partition coefficient of unity at the end of a six-plate distribution.

When a mixture of compounds having different partition coefficients is to be separated, each compound distributes itself independently of the others, if a small sample is used initially to provide ideal conditions. A series of distribution curves may thus be obtained that can be analyzed mathematically for the number and approximate concentration of components in the mixture.

This mathematical interpretation is possible, because, as shown by Williamson and Craig,[35] countercurrent distribution can be defined in terms of a binomial expansion $(X+Y)^n$, where Y is the fraction transferred in the upper phase $\left(\text{or } \frac{k}{k+1}\right)$, and X is the fraction remaining in the lower layer $\left(\frac{1}{k+1}\right)$. The binomial expression then becomes:

$$\left(\frac{1}{k+1}+\frac{k}{k+1}\right)^n. \tag{11}$$

Expansion of this expression of any given distribution of n plates gives a series of terms from which the fraction of original substance present in each tube can be calculated. The value of any term can be calculated by the expression:

$$Tn,r=\frac{n!}{r!(n-r)!}\left(\frac{1}{k+1}\right)^{n(k^r)} \tag{12}$$

where Tn, r is the fraction of the original substances present in tube r in a distribution of n plates.

An alternate, expression, which can be used when the number of applied plates is large, is the following:

$$y=\left(\frac{1}{\sqrt{2\pi\frac{k}{(k+1)^2}n}}\right)e^{\frac{-X^2}{2\frac{k}{(k+1)^2}n}} \tag{13}$$

where y is the fraction of the original substance present in the tube, which is X tubes removed from the maximum.

By means of formulas (12) or (13), a theoretical distribution curve can be drawn for any given value of k. The partition coefficient can be determined in several ways, most simply by location of the peak of the experimental curve, followed by substitution in equation (10).

If a substance is pure and its partition coefficient does not change appreciably with concentration, the experimental distribution curve should agree very closely with the theoretical calculation. If the experimental curve is regularly skewed, it denotes a nonlinear parti-

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[34] Craig, L. C., and Post, O., Apparatus for Countercurrent Distribution: Anal. Chem., vol. 21, 1949, pp. 500–504.

[35] Williamson, B., and Craig, L. C., Identification of Small Amounts of Organic Compounds by Distribution Studies: Jour. Biol. Chem., vol. 168, 1947, pp. 687–697.

tion isotherm.[36] If it is wider than the calculated curve, the presence of more than one component is indicated, and the spread between the experimental and theoretical curves is a measure of the non-homogeneity present.

To obtain the experimental curve, it is necessary to measure the amount of original material present in each tube after distribution. This can be done by any suitable technique, such as ultraviolet or infrared measurements or by direct weighing of the residue in each tube after removal of solvents.

If a component of a mixture has been separated by the countercurrent distribution process, its percentage in the mixture can be calculated by the equation:

$$\frac{\text{Weight of component in tube } n}{Tn,\ r \text{ (Weight of sample)}} \times 100 = \text{percent} \qquad (14)$$

Tube *n* is a tube containing the desired component in a pure or nearly pure form. The choice of *n* can be made by comparison of theoretical and experimental distribution curves. The value of *Tn, r* is obtained from equation (12). In those instances where the desired component is extracted into the upper phase before analysis,[37] it may be necessary to make a correction for material remaining in the other phase. This is done by re-extraction of the latter phase with fresh solvent followed by application of the formula:

$$\text{Total weight of component} = \left(\frac{W_1}{W_1 - W_2}\right)(W_1),$$

where W_1 and W_2 are the amounts in the first and second extraction, respectively.

When ultraviolet analysis is employed for determination of the concentration of components in distributed samples, it is necessary to know the extinction coefficients of each pure component before the calculations described can be applied. However, if the sample is a mixture of closely related compounds whose ultraviolet absorption maxima occur in the same spectral region, a rough estimation of composition (usually within 20 to 30 percent of the true value for each component) can be made on the assumption that the extinction coefficients of the components are approximately equal. After the individual components have been isolated and their ultraviolet spectral absorption curves determined, the approximate calculations can be made exact.

HOMOGENEITY STUDIES

For this purpose, 53-plate distributions were run in a 54-tube Craig distribution machine [38] employing cyclohexane and 0.5M phosphate buffer as the immiscible phases. Preliminary measurements of the partition coefficient at different *p*H values were made to select a buffer that would provide a partition coefficient close to unity.[39] After distribution, the total amount of phenol in each tube of the distribution machine was determined by ultraviolet measurement at the wave length of maximum absorption.

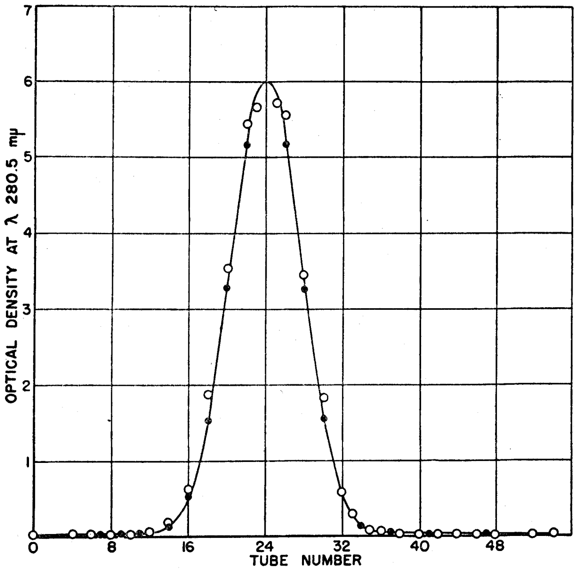

FIGURE 3.—DISTRIBUTION OF 3-METHYL-5-ETHYLPHENOL. ○, EXPERIMENTAL; ●, THEORETICAL.

A typical example of the results is shown in figure 3, which represents the distribution of a 50 mg. sample of 3-methyl-5-ethylphenol in cyclohexane-phosphate buffer of *p*H 11.26. Because this compound was isolated from a tar-acid fraction of a coal-hydrogenation product (see p. —) containing several homologues and isomers, it was considered advisable to obtain this independent check on its homogeneity. From the position of the maximum of the distribution curve, the partition coefficient was calculated. A theoretical distribution curve for a compound with this partition coefficient (0.8) was calculated according to the method of Williamson and Craig;[40] the theoretical and experimental curves agreed very

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[36] Craig, L. C., Golumbic, C., Mighton, H., and Titus, E., Identification of Small Amounts of Organic Compounds by Distribution Studies. III. The Use of Buffers in Countercurrent Distribution: Jour. Biol. Chem., vol. 161, 1945, p. 321.

[37] Barry, G. T., Sato, Y., and Craig, L. C., Distribution Studies. XII. Purity of Crystalline Penicillins: Jour. Biol. Chem., vol. 174, 1948, pp. 221–233.

[38] Work cited in footnote 32.

[39] Work cited in footnote 24.

[40] Work cited in footnote 35.

closely. Such data provide very strong evidence for the purity of a compound.[41]

SEPARATION OF ISOMERS

Mixtures of *m*- and *p*-cresols, xylenols, and ethylphenols were subjected to 53-plate countercurrent distributions. Meta- and para-cresols form a mixture, the components of which cannot be separated into its components by distillation, because they boil within a degree of each other. By countercurrent distribution, a partial separation was effected.

A mixture of 100 mg. each of *m*- and *p*-cresols was distributed in the system, benzene-phosphate buffer of *p*H 11.08. Ultraviolet measurements were made at wave lengths of 280 *mμ* and 286 *mμ*. At both wave lengths, *p*-cresol exhibits a maximum in its ultraviolet curve, whereas *m*-cresol has a strong band only at 280 *mμ*. Therefore, when separation of these isomers occurs during the distribution, the optical density values at 280 *mμ* should be much higher than at 286 *mμ* for those tubes relatively rich in *m*-cresol and about the same in tubes in which the *p*-cresol is concentrated. The experimental results represented graphically in figure 4 show that *m*-cresol predominates in tubes 0 to 26 and that *p*-cresol is the major component in tubes 28 to 54.

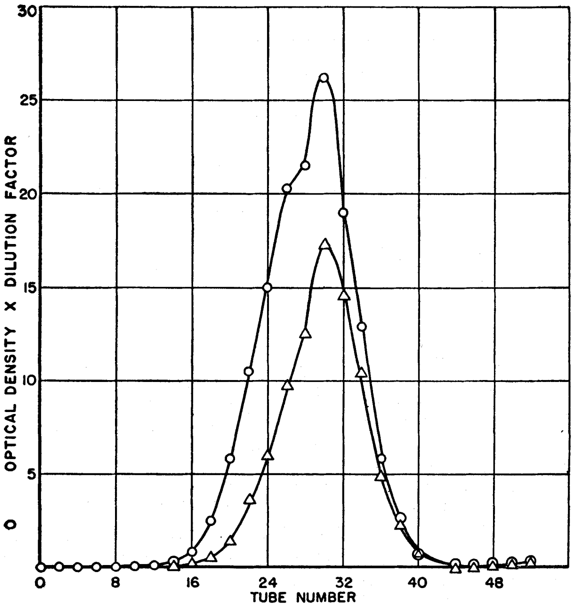

FIGURE 4.—DISTRIBUTION OF CRESOL MIXTURE: 0=280 *mμ*; Δ=286 *mμ*.

The amount of each isomer in each tube of the distribution machine was determined by solution of two simultaneous equations derived in the usual way from ultraviolet measurement at two wave lengths.[42] When plotted, the calculated amounts give curves (1 and 2 of fig. 5) that clearly show the degree of separation attained. Complete separation could be achieved by application of more plates by the technique of "alternate withdrawal" or "single withdrawal".[43] Comparison of the experimental curves with theoretical curves (indicated by dotted lines) shows that the *m*- and *p*-cresol used were not entirely pure. The inhomogeneity present, determined as previously described,[44] amounts to about 5 percent for each isomer.

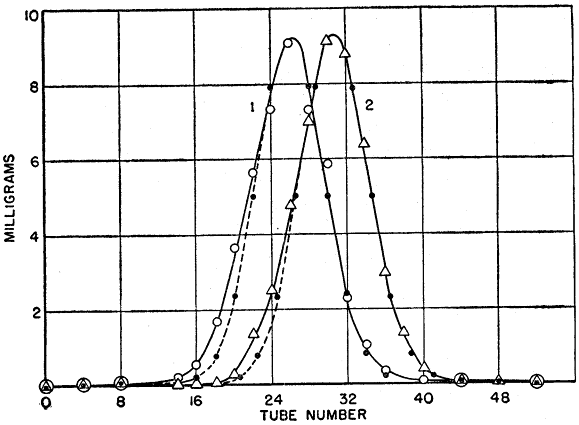

FIGURE 5.—SEPARATION OF CRESOLS BY 53-PLATE DISTRIBUTION: ○, CURVE 1, *m*-CRESOL; Δ, CURVE 2, *p*-CRESOL; ●, THEORETICAL.

A 53-plate distribution was run on a mixture of 10 mg. each of 2,4-, 2,5-, and 3,5-xylenol in the system cyclohexane-phosphate buffer of *p*H 11.08. Optical densities were measured at wave lengths of 275 *mμ*, 281 *mμ*, and 285 *mμ*. From these measurements, three simultaneous equations were derived for determination of the quantity of each isomer in each tube.[45]

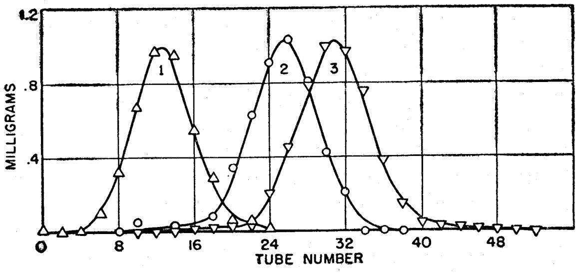

FIGURE 6.—SEPARATION of XYLENOLS by 53-PLATE DISTRIBUTION: Δ, CURVE 1, 3,5-XYLENOL; ○, CURVE 2, 2,5-XYLENOL; ▽, CURVE 3, 2,4-XYLENOL.

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[41] Craig, L. C., Mighton, H., Titus, E., and Golumbic, C., Identification of Small Amounts of Organic Compounds by Distribution Studies. Purity of Synthetic Antlimalorials: Anal. Chem., vol. 20, 1948, pp. 134-139.

[42] These equations are considered to measure total amounts of isomers in each tube with an accuracy of the order of 2 percent for the cresols and 5 percent for the xylenols and ethylphenols.

[43] Work cited in footnote 37.

[44] Work cited in footnote 41.

[45] See footnote 42.

The calculated amounts are plotted in figure 6 (curves 1, 2, and 3), which shows that 3,5-xylenol separates readily from 2,4- and 2,5-xylenol. From the shape and appearance of each curve, it is evident that each compound distributes itself essentially independently of the others in accordance with the distribution law. As the ratios of the partition coefficients of the unionized forms of these isomers are similar,[46] their separation in this distribution is a result, mainly, of their different acid strengths.

An experiment using similar quantities and a similar solvent pair was conducted with a mixture of *o*-, *m*-, and *p*-ethylphenols. For determination of each compound, optical densities were measured at wave lengths of 272 $m\mu$, 279 $m\mu$, and 285 $m\mu$.[47]

The plot of these calculated amounts given in figure 7 shows that the *o*-ethylphenol separates easily from the meta- and para-isomer. This is so because the ortho compound has a higher partition coefficient and a greater pK than the other isomers.[48]

For both xylenols and ethylphenols, the isomers separate in order of decreasing acid strength. When dealing with a material suspected of containing a mixture of isomeric phenols, important clues concerning structure can be obtained from the countercurrent distribution curves by identifying one component and then applying correlations between molecular structure, partition coefficients, and ionization constants.

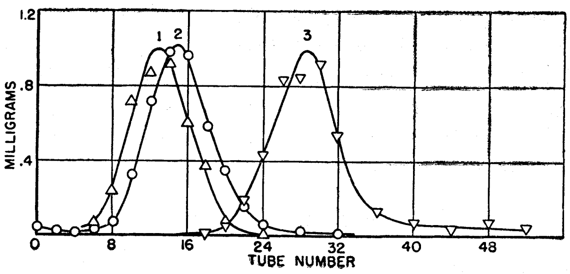
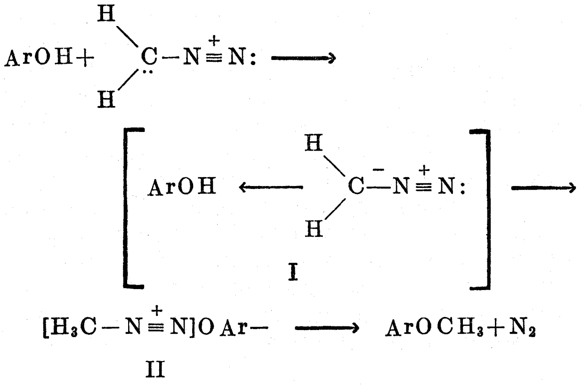


FIGURE 7.—SEPARATION OF ETHYLPHENOLS BY 53-PLATE DISTRIBUTION: Δ, CURVE 1, *m*-EHTYLPHENOL; ○, CURVE 2, *p*-ETHYLPHENOL; ▽, CURVE 3, *o*-EHTYLPHENOL.

METHYLATION OF PHENOLS

It has been suggested that the reaction of a phenol with diazomethane to form a methyl ether proceeds according to the following scheme: [49]



$$ArOH+{}^{H}_{H}\!>\ddot{C}-\overset{+}{N}\equiv N:\longrightarrow$$

$$\underset{I}{\left[ArOH\longleftarrow{}^{H}_{H}\!>\overset{-}{C}-\overset{+}{N}\equiv N:\right]}\longrightarrow$$

$$\underset{II}{[H_3C-\overset{+}{N}\equiv N]OAr^-}\longrightarrow ArOCH_3+N_2$$

A hydrogen bond is formed between the acidic hydrogen atom of the phenol and the negatively charged carbon atom of the diazomethane. The intermediate, I, rearranges to the diazonium salt, II, which loses nitrogen to form the methyl ether, $ArOCH_3$. The above scheme suggests that the reaction between a phenol and diazomethane will be greatly affected by the acidity of the phenol and its capacity to form a hydrogen bond. The structural characteristics of a phenol determine its acidity and also its capacity for hydrogen bonding. Introduction of alkyl groups into the nuclear positions of a phenol decreases its acid strength, the effect being most pronounced with ortho and para substituents.[50] In addition, substitution of large alkyl groups at the ortho position of a phenol decreases its hydrogen bonding capacity.[51] The failure of diazomethane to methylate a sterically hindered phenol is reported in the literature. However, methylation was accomplished by use of dimethyl sulfate.[52]

WITH DIAZOMETHANE

Diazomethane was prepared by the convenient method outlined in Organic Synthesis.[53] Attempts to methylate an ether solution of 2′-hydroxy-1-phenylnaphthalene were unsuccessful. *o*-phenylphenol gave a 30-percent yield of 2-methoxybiphenyl in the same solvent. The yield of 2-methoxybiphenyl was increased, however, to 88 percent, when the methylation was carried out in a solvent consisting of four parts of ether to one part of absolute alcohol.

WITH DIMETHYL SULFATE

Best results were obtained by using the following procedure:[54] The phenol was dissolved in a solution of the theoretical amount of potassium hydroxide in a minimum amount of abso-

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[46] Work cited in footnote 24.

[47] See footnote 42.

[48] Work cited in footnote 24.

[49] Eistert, B., Newer Methods of Preparative Chemistry: Interscience Publishers, Inc., New York, 1948, p. 518.

[50] Work cited in footnote 25.

[51] Work cited in footnote 29.

[52] Cook, J. W., and Preston, R. W. G., Polycyclic Aromatic Hydrocarbons. XXIX. Derivatives of 1,2,5,6-di-benzofluorene: Jour. Chem. Soc., 1944, pp. 553–561.

[53] Blatt, A. H., Organic Synthesis: John Wiley & Sons, Inc., New York, coll. vol. II, 1943, p. 165.

[54] Waliaschko, N., Arch. Pharm., vol. 242, 1904, p. 225.

lute ethanol and the mixture evaporated to dryness. The residue was treated with excess dimethyl sulfate. The reaction proceeded exothermally for a short time and was completed by heating in an oil bath at 100° C. for half an hour. The mixture was then cooled and treated cautiously with Claisen alkali to decompose the excess dimethyl sulfate. The reaction product was extracted with benzene and recovered from the washed and dried benzene extract by evaporating the solvent. The methyl ethers remained as residue in a very pure form. The yields of the ethers are given in table 5.

TABLE 5.—*Methylation of phenols with dimethyl sulfate*

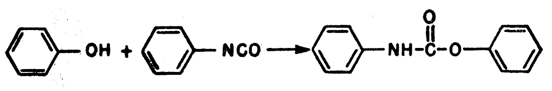
Phenol	Percent yield of ether
o-phenylphenol	94
o-cyclohexylphenol	91
2′-hydroxy-1-phenylnaphthalene	86

DEMETHYLATION OF METHYL ETHERS

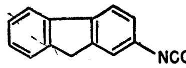
The use of methyl ethers in the separation of tar acids requires subsequent demethylation of the ether fractions to obtain the original components of the tar-acid mixtures. Therefore, the quantitativeness of demethylation of several ethers was tested. It was found that 1-hydroxy-1-(*o*-anisyl)-1,2,3,4-tetrahydronaphthalene,[55] 1-(*o*-anisyl)-3,4-dihydronaphthalene,[56] 1-(*o*-anisyl)-naphthalene,[57] 1-methoxy-2-cyclohexylbenzene, and 2-methoxybiphenyl gave the theoretical methoxyl number to within a maximum error of 1 percent when determined by the semimicro method described by Clark.[58]

2-FLUORENYLISOCYANATE AS A REAGENT FOR PHENOLS

Phenylisocyanate reacts with phenols according to the following reaction:



and the N-phenylcarbamates have been used to characterize phenols from coal tar.[59] [60] [61] However, the use of phenyl- and also α-naphthylisocyanates, for the identification of phenols suffers from several disadvantages. These reagents are unstable, and the carbamates formed by their reaction with phenols are difficult to purify. Morgan and Pettet[62] found *p*-xenylisocyanate well suited to the investigation of phenolic mixtures from coal tar since the carbamates from *p*-xenylisocyanate have considerably higher melting points than the corresponding *N*-phenylcarbamates. As a result, phenolic mixtures, which yield only oily mixtures of the latter, give crystalline derivatives with *p*-xenylisocyanate.



2-fluorenylisocyanate was found, in this investigation, to be a more satisfactory reagent for use on phenolic mixtures. 2-fluorenylisocyanate was readily obtained from 2-aminofluorene and was found to be quite stable. While this work was in progress, Witten and Reid[64] reported the preparation and use of 2-fluorenylisocyanate as a reagent for alcohols.

N-(2-fluorenyl)carbamates have the following advantages over *N*-phenylcarbamates: (1) They are much easier to recrystallize to constant melting point; (2) they show useful alterations of solubility relationships among the various derivatives. This last point was demonstrated in the separation of two different xylenols from one of the xylenol fractions. 2,5-xylenol was identified as the *N*-phenylcarbamate after fractional crystallization. The derivative of 2,4-xylenol could not be isolated because of its greater solubility. 2,4-xylenol was isolated, however, from the same distillate by fractional crystallization of its *N*-(2-fluorenyl)carbamate. The solubility relationships of these two derivatives were reversed for the two isomeric phenols.

PREPARATION OF 2-FLUORENYLISOCYANATE

A solution of 2-aminofluorene (12 gm.) in 250 ml. of warm toluene was saturated with hydrogen chloride gas. The insoluble hydrochloride was precipitated. The mixture was brought to boiling, and phosgene passed in until nearly all of the hydrochloride had dissolved. The mixture was filtered and the solvent removed from the filtrate. The residue of 2-fluorenylisocyanate weighed 9.4 gm. and melted at 68.8° to 70.2° C.

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[55] Orchin, M., Aromatic Cyclodehydrogenation. VI. Synthesis of Ring Oxygen Compounds: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 495–498.

[56] Work cited in footnote 55.

[57] Work cited in footnote 56.

[58] Clark, E. P., A Semi-Micro Zeisel Methoxyl Method: Jour. Am. Chem. Soc., vol. 51, 1929, pp. 1479–1483.

[59] Fromm, E., and Eckard, H. [Lignite Primary Tar]: Ber. Deut. chem. Gesell., vol. 56B, 1923, pp. 948–954.

[60] Steinkopf, W., and Hopner, T. [The Phenolic Constituents of a Producer Tar from a Bohemian Brown Coal]: Jour. prakt. Chem., vol. 113, 1926, pp. 137–158.

[61] Morgan, G. T., and Pettet, A. E. J., Aqueous Liquors from Low-Temperature Carbonization of Coal: Jour. Soc. Chem. Ind., vol. 50, 1931, pp. 72T–74T.

[62] Morgan, G. T., and Pettet, A. E. J., The Use of Arylcarbimides in Identifying Hydroxylic Compounds: Jour. Chem. Soc., 1931, pp. 1124–1126.

[63] Blatt, A. H., Organic Synthesis: John Wiley & Sons, Inc., New York, coll. vol. II, 1943, p. 447.

[64] Witten, B., and Reid, E. E., p-Triphenylmethylphenyl and 2-fluorenylisocyanates as Reagents for Alcohols: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2470–2472.

PREPARATION OF N-(2-FLUORENYL) CARBAMATES

A solution of 1 gm. of 2-fluorenylisocyanate and 1 gm. of the phenol in 50 ml. of toluene was refluxed for 1 hour. The solution was evaporated to dryness under vacuum, and the residue was recrystallized from a mixture of two volumes of skellysolve-B and one volume of benzene. A very small quantity of insoluble material was first filtered and discarded. The carbamates are colorless crystalline solids and were obtained in yields of about 80 percent.

The *N*-(2-fluorenyl)carbamates prepared are listed in table 6.

CHROMATOGRAPHIC ADSORPTION STUDIES

One of the most useful techniques for the separation of organic mixtures is chromatography. In this process, substances are separated according to their relative adsorption affinities for an adsorbent. Although separation by this means is facilitated when the components are colored, its usefulness is not restricted to colored mixtures.

In the chromatography of a mixture of colorless phenols, special devices are required to indicate the positions of the components on a column of adsorbent.

TABLE 6.—*N-(2-fluorenyl)carbamates*

Compound	M. P. (corr.), ° C.	Nitrogen, percent	
		Found	Calculated
2,5-xylenol	169. 6–170. 6	4. 24	4. 25
2,4-xylenol	174. 2–175. 6	4. 24	4. 25
Phenol	186. 4–187. 4	4. 77	4. 65

USE OF FLUORESCENT DERIVATIVES IN CHROMATOGRAPHY

The use of fluorescent derivatives of phenols appeared to be an attractive method for the chromatography of nonfluorescent phenols. It was thought that 2-fluorenylisocyanate might form suitable fluorescent carbamates. The *N*-(2-fluorenyl)carbamates described above, however, did not exhibit fluorescence in ultraviolet light. In addition, they had the undesirable property of decomposing on the absorbents, alumina-celite and silicic acid. No further attempts were made to find a fluorescent derivative for chromatography.

USE OF FLUORESCENT ADSORBENTS IN CHROMATOGRAPHY

Colorless nonfluorescent compounds that absorb ultraviolet light have been chromatographed on fluorescent absorbents.[65] The fluorescence of the adsorbent was found to decrease in those regions of the column where the band of colorless, nonfluorescing adsorbate was located. Suitable fluorescent adsorbents were prepared by mixing a small amount of fluorescent zinc sulfide with silica gel or alumina.

In the present work, the adsorption of phenols on a column packed with silicic acid (Eimer and Amend, E. P., mixed with 2.5 percent by weight of No. 1806 fluorescent zinc sulfide) did not quench the fluorescence of the adsorbent, probably because the wave length of the light source, which was between 390 to 330 $m\mu$, did not coincide with the wave length of the spectral absorption maxima of the phenols. In general, the simple phenols exhibit absorption maxima in the wave length region of 285 to 273 $m\mu$.

INFRARED SPECTRA OF PHENOLS

The infrared spectrum of an organic compound is a unique property of the compound, and in general the compound retains that property on admixture with other compounds. The selective absorption of infrared radiation by an organic molecule arises from the mutual vibration of the atoms constituting the molecule. The vibrational frequencies within a molecule are determined by the masses of the atoms, the strength of the forces that bind them, and the geometrical structure of the molecule. No two compounds, therefore, except a pair of optical isomers, will have a completely identical set of vibrational frequencies. Closely related compounds such as isomeric and homologous phenols have absorption bands at identical wave lengths as well as spectral regions in which characteristic differences are found.

The spectra of various phenols in the rock-salt spectral region have been published by Barnes, Gore, Liddel, and Williams [66] from 5 to 10 μ; by Kletz and Price [67] in liquid and solid states; by Whiffen and Thompson [68] as CS_2 solutions; and by Richards and Thompson [69] in liquid, solid, and solution states.

RELATIONSHIP BETWEEN INFRARED SPECTRUM AND C–H AND O–H BOND STRETCHING

The greatest similarities in the spectra of phenols are found in the spectral bands as a

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[65] Sease, J. W., The Use of a Fluorescent Adsorbent for the Chromatography of Colorless Compounds: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2242–2243.

[66] Barnes, R. B., Gore, R. C., Liddel, U., and Williams, V. Z., Infrared Spectroscopy Industrial Applications and Bibliography: Reinhold Publishing Corp., New York, 1944, 236 pp.

[67] Kletz, T. A., and Price, W. C., Infrared Spectra of Solid and Liquid Alkylphenols: Jour. Chem. Soc., 1947, pp. 644–648.

[68] Whiffen, D. H., and Thompson, H. W., Infrared Absorption Spectra of Cresols and Xylenols and Analysis of Cresylic Acid: Jour. Chem. Soc., 1945, pp. 268–273.

[69] Richards, R. E., and Thompson, H. W., Vibrational Spectra of Phenolic Derivatives and Phenolic Resins: Jour. Chem. Soc., 1947, pp. 1260–1269.

result of vibrations of hydrogen atoms in the C–H and O–H bonds. For example, alkylphenols possess groups of spectral bands at wave lengths of 3.2 to 3.5 μ and at 6.8 to 7.3 μ, which are a result of stretching and bending vibrations, respectively, of the C–H bonds. Positions of these bands are quite independent of the particular alkylphenol. The same is partly true of the stretching vibration of the O–H band; but because intermolecular association through hydrogen bonding may be extensive in phenols, a marked effect on the O–H vibration may result. The O–H vibration for a phenol in very dilute solution, in which it is free of intermolecular association, occurs at about 2.77 μ. When association exists at high concentration or in the solid state, this band may be shifted slightly, or a completely new and broader band may appear between 2.77 and 3.0 μ. Coggeshall [70] showed that phenols in which the O–H bond was sterically hindered by the large butyl or amyl groups in the two ortho positions showed little or no shift in the band between the very dilute solution and the crystalline state, because association could not occur. But with "partly hindered" phenols having one large alkyl group in one ortho position and only a methyl group or no substituent in the other, or with "unhindered" phenols having no groups or only methyl groups in the ortho positions, the O–H band position may shift considerably in the spectrum of the solid. The O–H "dissociation" band may become very weak or disappear

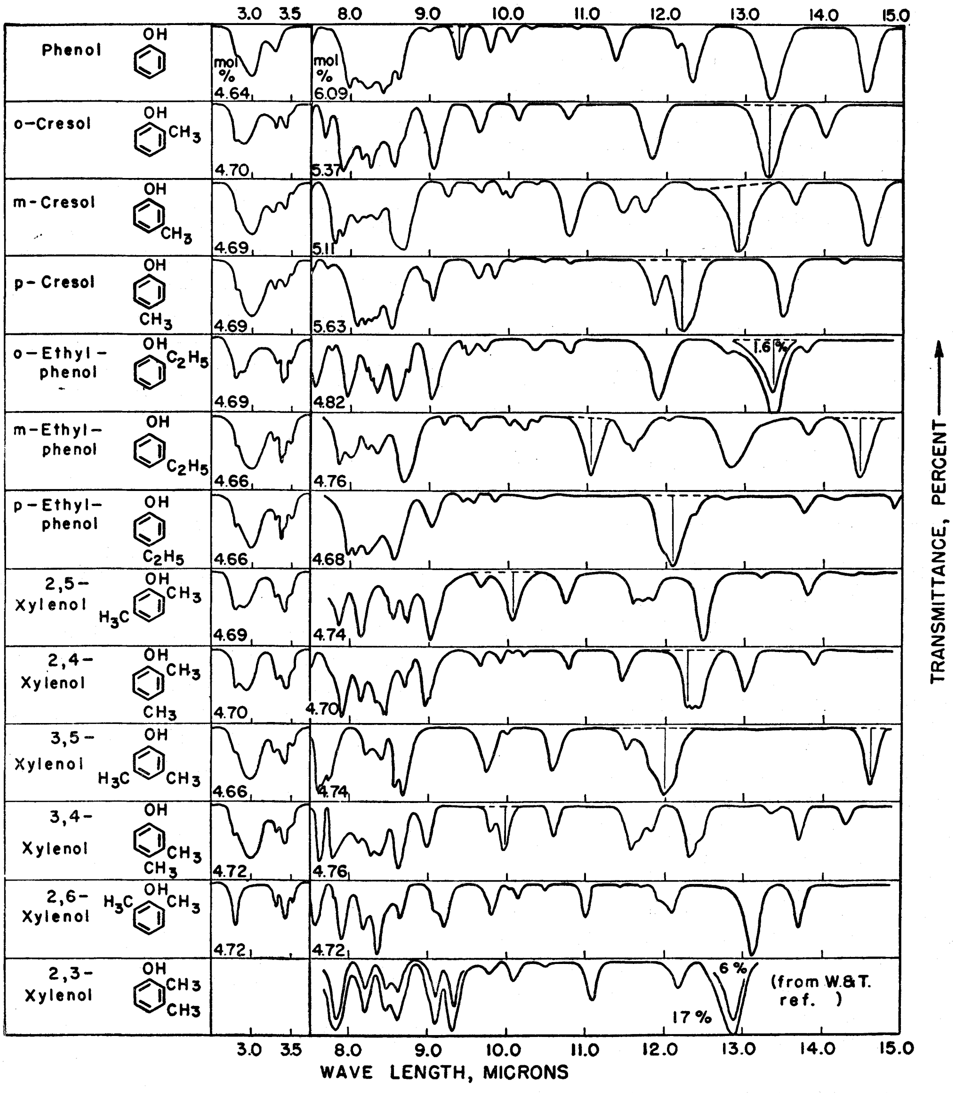

Figure 8.—INFRARED SPECTRA OF PHENOL AND C_7 AND C_8 ALKYLPHENOLS IN CS_2 SOLUTIONS (CONCENTRATIONS IN MOL PERCENT AS INDICATED), ABSORPTION BANDS AND BASE LINES USED IN ANALYSIS ARE INDICATED.

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[70] Work cited in footnote 29.

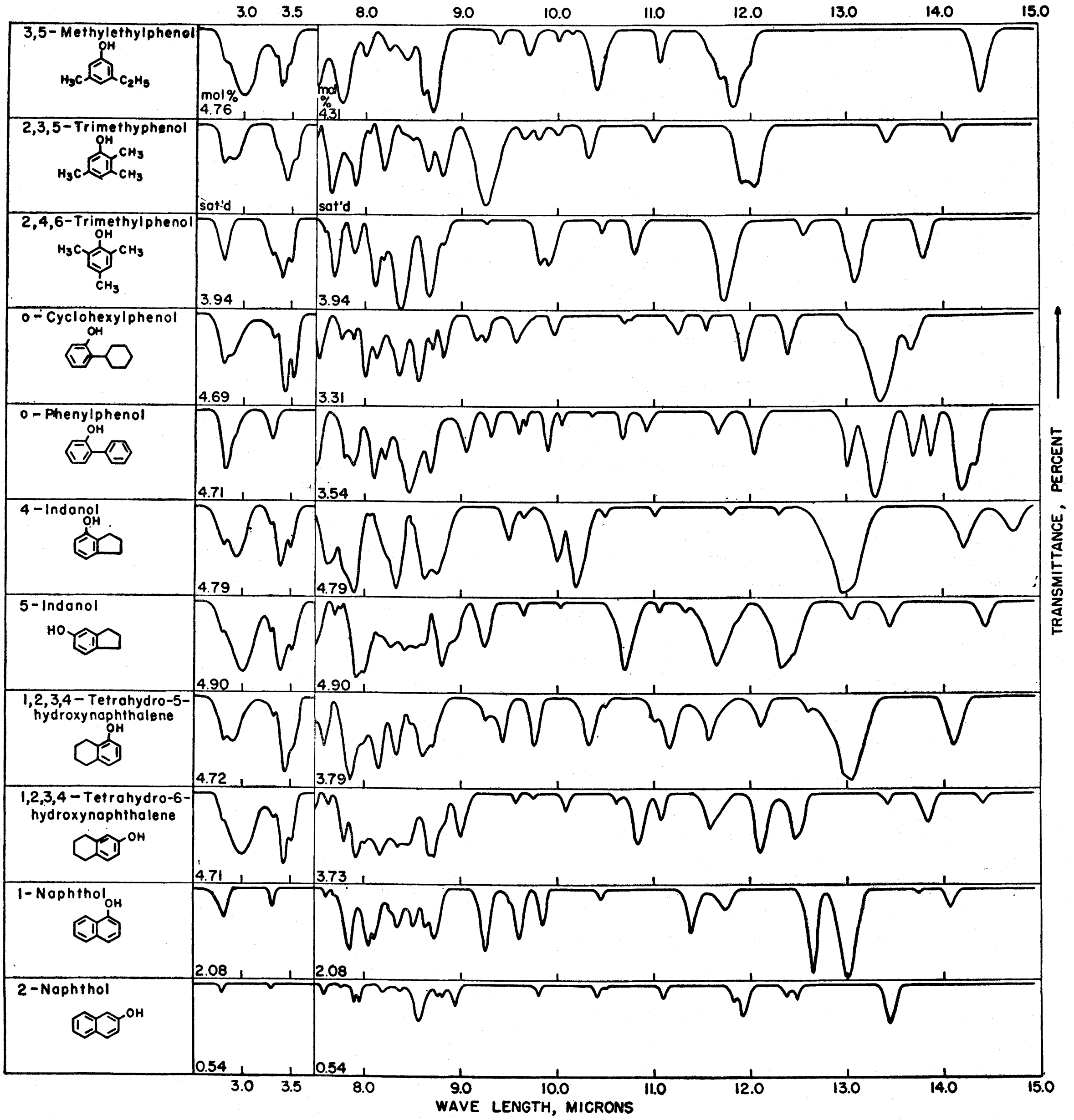

FIGURE 9.—INFRARED SPECTRA OF HIGHER PHENOLS; CS_2 SOLUTIONS (CONCENTRATIONS IN MOL PERCENT AS INDICATED).

with the appearance at longer wave lengths of the "association" band, the position of which depends on the amount of steric hindrance. Richards and Thompson[71] demonstrated the same effect and gave several examples showing the hindering effect of methyl groups in positions ortho to the O–H.

The same sort of correlation has been carried out on the phenols investigated in this laboratory with the additional attempt to show quantitatively the relative extents of associating through hydrogen bonding. The spectra from 2.5 to 3.75 μ and from 7.5 to 15 μ of 22 phenols are given in figures 8 and 9. They were determined in a 0.1-mm. cell in CS_2 solutions. To permit quantitative comparison of O–H bands, the spectra in this region were obtained, when possible, at the same molar concentration, 4.70 mol percent in CS_2.

The spectra in the O–H region illustrate qualitatively the inhibition of intermolecular association by small groups, methyl or ethyl, which are ortho to the O–H group. For the C_7 phenols, *o*-cresol produces a sharp "dissociation" band at 2.8 μ and a broad "association"

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[71] Work cited in footnote 69.

band at 2.90 μ. On the other hand, *m*- and *p*-cresol have only weak bands at the 2.8 μ "dissociation" position but large broad bands at the 3.0-"association" position. The same is true of the three ethylphenols. 2,4- and 2,5-xylenol, with one CH_3 group ortho to the —O–H, resemble *m*- and *p*-cresol, respectively. 2,6-xylenol, with both ortho positions occupied by CH_3 groups, is more strongly hindered than any of the above phenols; at the concentration used, this compound exhibits no "association" band or shoulder. In the C_9 group, 2,4,6-trimethylphenol (mesitol) is similar to 2,6-xylenol; 2,3,5-trimethylphenol is similar to 2,4- and 2,5-xylenol.[72]

These correlations and the correlation of absorption intensity of "association" bands for various classes of phenols are given in table 7. The phenols are classified into four groups according to hindrance or lack of hindrance in the positions ortho to the OH group:

1. *No substituent ortho to the OH.*—The broad "association" band in 10 phenols of this type occurs at 3.00 to 3.01 μ. The average absorption intensity is 73.2 ±2.1 percent.
2. *CH_3 or CH_2 groups ortho to the OH.*—The "association" band occurs at 2.89 to 2.93 μ.
   (a) *CH_2 in five-membered ring.*—The only phenol of this type is 4-indanol, which has an intensity of 67.5 percent.
   (b) *CH_3 or CH_2 in six-membered ring.*—Four phenols of this type show an average intensity of 54.1 ±2.8 percent.
3. *C_2H_5 or larger groups ortho to the OH.*—Three phenols of this type have only weak shoulders at 2.89 to 2.93 μ. Neglecting the anomalous *o*-phenylphenol, the other two have an average intensity of 46.2 ±0.7 percent.
4. *CH_3 groups in both positions ortho to the OH.*—Two phenols of this type have no "association" band or shoulder at concentrations of 4.70 mol percent.

Considerable qualitative and quantitative information concerning the OH bands in a phenol or mixtures of some phenols may be gained by determining the spectrum of the OH region at both the concentration used above and at a higher concentration or in the solid state.

Of the two C_9 dicyclic phenols studied, 5-indanol (formula 2, p. 10) with the —OH group meta to the five-membered ring, is similar to *m*- and *p*-cresols. 4-indanol (formula 1, p. 10) is similar to *o*-cresol, except that more association is apparent in the former, probably because of the greater hindrance of the CH_3 group on the *o*-cresol. In this connection, it is interesting to compare 4-indanol with the corresponding dicyclic C_{10} phenol, 5-hydroxy-1,2,3,4-tetrahydronaphthalene (formula 3, p. 10) with —OH ortho to the six-membered ring. The stronger 3.0 band, which indicates greater association for 4-indanol, may be attributed to the sharper angles of the 5-membered ring, which pulls the interfering CH_2 group farther away from the —OH than does the 6-membered ring of the 5-hydroxy-1,2,3,4-tetrahydronaphthalene.[73] The partition coefficients of these phenols (p. 7) also support the contention of the greater hindrance of the six-membered ring.

TABLE 7.—*OH absorption bands of phenols. Correlation of band intensity with steric hindrance of ortho substituents*

[Concentrations, 4.70 ±0.06 mol percent in CS_2] [1]

	Percent absorption at 2.89-2.93 μ band	Percent absorption at 3.00 μ band
1. *No ortho-substituent:*		
Phenol	---------	69.4
m-cresol	---------	72.6
p-cresol	---------	76.8
m-ethylphenol	---------	71.9
p-ethylphenol	---------	73.7
3,5-xylenol	---------	72.4
3,4-xylenol	---------	72.6
3,5-methylethylphenol	---------	74.8
5-indanol (4.90 percent)	---------	78.0
5,6,7,8-tetrahydro-2-hydroxynaphthalene	---------	69.6
Average	---------	73.2±2.1
2. *CH_3 or CH_2 in ortho position:*		
a. CH_2 in 5-membered ring:		
4-indanol	67.5	---------
b. CH_3, or CH_2 in 6-membered ring:		
5,6,7,8-tetrahydro-1-hydroxynaphthalene	52.0	---------
o-cresol	56.9	---------
2,5-xylenol	50.5	---------
2,4-xylenol	57.0	---------
2,3,5-trimethylphenol	[2]42.0	---------
Average (of first four)	54.1±2.8	
3. *C_2H_5 or larger in ortho position:*		
o-ethylphenol	46.9 (sh)[3]	---------
o-cyclohexylphenol	45.5 (sh)	---------
o-phenylphenol	37.7 (sh)	---------
Average (of first two)	47.2±0.7	---------
4. *CH_3 in both ortho positions:*		
2,6-xylenol	---------	---------
2,4,6-trimethylphenol (3.94 percent) [4]	---------	---------

[1] Data for 1- and 2-naphthol are not included in the table, because their low solubility in CS_2 prevented obtaining their spectra at concentrations comparable to those of the other phenols.
[2] Saturated solution.
[3] sh=shoulder.
[4] 2.80 μ only.

Another interesting correlation may be made between the —OH bands of *o*-cyclohexylphenol and *o*-phenylphenol. Intermolecular association is less for the latter compound, presumably because the strong tendency toward coplanarity of the two aromatic rings increases steric hindrance. In *o*-cyclohexylphenol, rotation about the bond joining the aromatic and naphthenic rings would lessen steric hindrance somewhat and permit more intermolecular association (stronger —OH "association" band shoulder). In this connection, Richards and Thompson [74] state that the anomalous location of the OH "dissociation" band at longer wave lengths for *o*-phenylphenol and the small shift in the solid state are a result of intramolecular

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[72] The 3.0-μ bands for 2,3-xylenol were not included because of insufficient sample.

[73] Work cited in footnote 28.

[74] Work cited in footnote 69.

hydrogen bonding with an ortho carbon atom in the phenyl ring adjacent to the OH.

Another interesting observation on the OH bands is that compounds possessing alkyl substituents para to the —OH produce slightly more intense OH bands than do the corresponding compounds with meta alkyl groups. Thus, the —OH bands of *p*-cresol and *p*-ethylphenol are more intense than those of the meta compounds; 2,4-xylenol produces greater intensity than 2,5-xylenol; 3,4-xylenol shows a slightly more intense band than 3,5-xylenol.

QUANTITATIVE ANALYSIS OF PHENOLS BY INFRARED ABSORPTION

The spectra of all the phenols from 7–15 μ are presented (figs. 8 and 9) to indicate their specificity and, therefore, their usefulness in quantitative analysis. Barnes and co-workers[75] and Whiffen and Thompson[76] have discussed the correlations that can be made between mono-, di-, and tri-substituted benzene rings and their infrared spectra in the region of 7 to 15 μ. This region will be discussed here only in connection with quantitative analysis.

Quantitative infrared analysis is based upon the Lambert-Beer law, which states that the quantity, $\log \frac{1}{\text{transmittance, percent}}$ (optical density or absorbance) is additive with concentration for one component or for mixtures of components in varying concentrations if no chemical reaction is involved. To analyze a four-component mixture, the calibration spectra of the four pure compounds are examined together so that one wave length for each may be chosen where interference from the other three compounds is the least; optical densities are measured at these wave lengths for all four compounds. Then, at these wave-length positions in the spectrum of the mixture, four optical densities are measured. Simultaneous equations, linear according to the Lambert-Beer law, are set up in terms of optical densities and solved for the four unknown concentrations.

The method used to obtain optical densities $\left(\log \frac{1}{\text{transmittance, percent}}\right)$ for quantitative analysis was the base-line technique of Wright[77] and Heigl, Bell, and White.[78] This was chosen because (1) spectral bands of phenols are mainly symmetrical and widely spaced, permitting easy choice of base line, (2) spectra of the pure solvent are not required, as accurate transmittance values are not needed, and (3) qualitative and subsequent quantitative results are obtained from the original spectrum of the unknown without need of further measurements. Absorption bands and base lines principally used for analysis of xylenols and ethylphenols are indicated in figure 8. In the actual analysis, the spectra were not converted to the transmittance plots shown, but, rather, base lines were drawn for analysis on the recorded "sawtooth" curves.

The next step in the quantitative analysis was the preparation of synthetic blends to simulate the unknown phenolic mixtures based on rough quantitative estimates from their original spectra. The analyses of known blends of the phenols used are shown in table 8; maximum error is 1.7 mole percent, and average error of all blends is 0.8 mole percent. Table 9 presents the calibration absorption bands, concentrations, and slit widths used for the analyses. In all analyses, base lines were drawn as nearly as possible in a manner corresponding to the way they were drawn for the pure compounds; that is, between regions of no specific absorption. In some cases the proper position of the base line was not clear without meticulous examination of all the calibration spectra involved. A short-cut answer was obtained by back calculation of the optical density for the mixture from the concentrations as synthesized, followed by calculation of the correct base-line position.

Deviations from the Lambert-Beers law of additivity are the general rule, and empirical corrections are usually necessary; however, optical density vs. concentration curves for six phenol absorption bands used in analysis show virtually perfect linearity (fig. 10). An important contributing factor to this linearity is the high resolving power and, therefore,

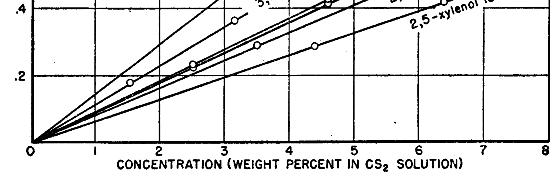

FIGURE 10.—OBEDIENCE OF BEER'S LAW

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[75] Barnes, R. B., Gore, R. C., Stafford, R. W., and Williams, V. Z. Qualitative Organic Analysis and Infrared Spectroscopy: Anal. Chem., vol. 20, 1948, pp. 402–410.

[76] Work cited in footnote 68.

[77] Wright, N., Application of Infrared Spectroscopy to Industrial esearch: Ind. Eng. Chem., anal. ed., vol. 13, 1941, pp. 1–8.

[78] Heigl, J. J., Bell, M. F., and White, J. V., Application of Infrared ectroscopy to Analysis of Liquid Hydrocarbons: Anal. Chem., vol. 19, 47, pp. 293–298.

small spectral slit widths that can be used with this instrument (Perkin-Elmer Model 12B). This is illustrated by resolution of the fine structure of the 15.0μ CO_2 absorption band (fig. 11), in which separations between absorption maxima average 1.6 wave numbers (0.03μ).

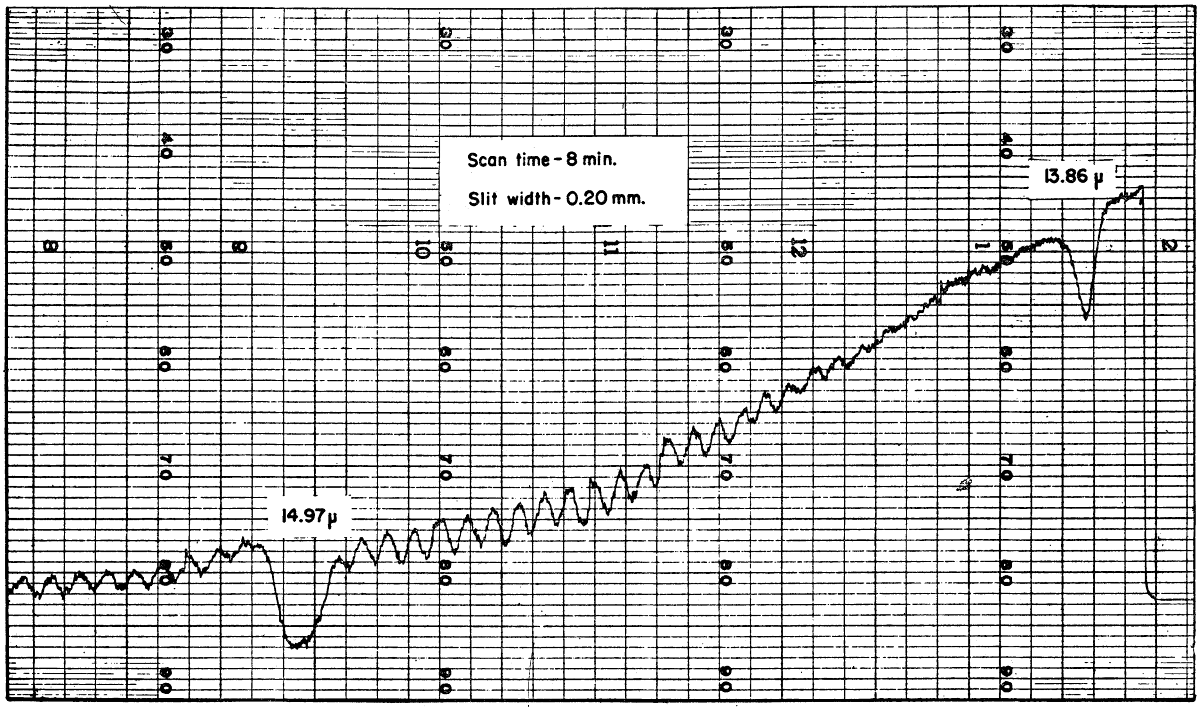

FIGURE 11.—CO_2 FINE STRUCTURE, 15.0μ REGION.

TABLE 8.—*Infrared analyses of synthetic blends of phenols* CS_2 *solutions*

Component	Blend															
	I		II		III		IV		V		VI		VII		VIII	
	Syn.	Anal.	Syn.	Anal.	Syn.	Anal.	Syn.	Anal.	Syn.	Anal.	Syn.	Anal.	Syn.	Anal.	Syn.	Anal.
Phenol	48. 6	48. 4	----	----	----	----	----	----	----	----	----	----	----	----	----	----
o-cresol	51. 4	51. 6	33. 3	33. 8	----	----	----	----	----	----	----	----	----	----	----	----
p-cresol	----	----	34. 4	35. 2	----	----	----	----	----	----	----	----	----	----	----	----
m-cresol	----	----	32. 3	31. 0	----	----	----	----	----	----	----	----	----	----	----	----
1,2,4-xylenol	----	----	----	----	50. 4	50. 4	40. 5	41. 1	10. 5	11. 0	25. 0	26. 2	----	----	----	----
1,2,5-xylenol	----	----	----	----	----	----	41. 0	41. 5	9. 9	9. 2	25. 0	24. 3	----	----	----	----
m-ethylphenol	----	----	----	----	41. 8	40. 5	8. 9	8. 4	40. 1	41. 8	----	----	42. 0	42. 9	----	----
o-ethylphenol	----	----	----	----	7. 9	9. 1	9. 8	9. 0	39. 4	38. 0	----	----	----	----	----	----
p-ethylphenol	----	----	----	----	----	----	----	----	----	----	----	----	----	----	49. 9	49. 5
1,3,5-xylenol	----	----	----	----	----	----	----	----	----	----	25. 0	23. 4	38. 6	38. 3	50. 1	50. 5
1,3,4-xylenol	----	----	----	----	----	----	----	----	----	----	25. 0	26. 1	19. 4	18. 8	----	----

TABLE 9.—*Absorption-band concentration-slit width data used for infrared analyses of phenolic mixtures*

Components	Fractions					
	1–24	25–43	44–51	52–55	56–62	63–71
Phenol	9. 36–7. 43	9. 36–7. 43				
o-cresol	9. 03–2. 42	13. 31–[1] 2. 42				
p-cresol		12. 18–[1] 2. 49				
m-cresol		12. 90–2. 35	14. 55–2. 35	14. 55–2. 35		
1,2,4-xylenol			12. 28–7. 30	12. 28–7. 30		
1,2,5-xylenol			10. 06–7. 39	10. 06–7. 39		
o-ethylphenol			13. 35–1. 60	13. 35–1. 60	13. 35–1. 60	
p-ethylphenol			12. 08–3. 65	12. 08–3. 65	12. 08–3. 65	
m-ethylphenol			14. 46–3. 66	11. 04–7. 43	11. 04–7. 43	11. 04–7. 43
1,3,5-xylenol				11. 98–3. 70	11. 98–3. 70	11. 98–3. 70
1,3,4-xylenol					9. 98–7. 42	9. 98–7. 42

[1] Usable if phenol is low.

Slit widths: 8.0 to 9.2μ=0.105 mm.
9.2 to 11.2μ= .140 mm.
11.2 to 12.8μ= .185 mm.
12.8 to 13.9μ= .240 mm.
13.9 to 15.0μ= .340 mm.

ULTRAVIOLET SPECTRA OF PHENOLS

Ultraviolet absorption spectra arise principally from excitation by incident light of the bonding electrons of molecules; vibrational and rotational excitations also are involved, but these are of considerably lower energy and therefore less important. Ultraviolet spectra of phenol, the cresols,[79] the xylenols,[80] and several higher phenols [81] have been measured in this laboratory with either a Beckman or a Cary spectrophotometer (circled B or C on the spectra). These spectra are shown in the Appendix. Their similiarity made them of little value for analysis of isomers, but interesting correlation studies were possible.

The spectra of all the simple and dicyclic phenols investigated produce one absorption band, with doublet branching, in the near ultraviolet region. It has long been known that a para-substituted benzene ring constituted a resonating system of greater length than the corresponding meta or ortho derivative. The result is a slight bathochromic shift (toward longer wave lengths) of the para-derivative. This is apparent from the spectra of *p*-cresol and *p*-ethylphenol (figs. A–4 and A–7) when compared to the corresponding ortho- and meta-derivatives (figs. A–2, A–5, A–3, and A–6). The same effect is observed for other phenols having some group para to the —OH group: *p*-cyclohexylphenol and *p*-phenylphenol (figs. A–18 and A–19) and the more highly substituted phenols, 2,4- and 3,4-xylenols (figs. A–9 and A–12) 2,4,6-trimethylphenol (fig. A–15) and 5-indanol (fig. A–22). When the group para to the OH is an alkyl group, the position of the longer wave-length branch of the doublet (first band) is near 285 $m\mu$.

A slight difference is observed between meta- and other derivatives in the position of this first band. *o*-cresol and *o*-ethylphenol (figs. A–2 and A–5) show this band at about 278 $m\mu$, whereas the same band in *m*-cresol and *m*-ethylphenol (figs. A–3 and A–6) lies at 279–280 $m\mu$. The same effect is exhibited by the di-ortho- and di-meta-substituted xylenols (2,6- and 3,5-xylenols, figs. A–11 and A–13).

Ortho-, meta-, and para-monosubstituted phenols have bands of characteristic shapes. The para-compounds have sharp doublets with slight, fine structure on the short wave-length branch (similar to phenol itself); the meta-compounds show simple, sharp doublets; and the ortho-compounds have rather rounded doublets, which are probably a result of the production of more vibrational states in the molecule by the slight steric hindrance exerted on the OH group by the nearby CH_3 group. The same band shapes are observed for the symmetrical xylenols, 2,6- and 3,5-isomers; band shapes of the other xylenols can be recognized as combinations of ortho-, meta-, and para-substituents.

The spectra of 4- and 5-indanol (figs. A–21 and A–22) form an interesting pair. As expected from the above discussion of phenols with substituents para to the OH group, the

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[79] International Critical Tables, vol. 5: McGraw-Hill Co., Inc., New York, 1929, pp. 334–379.

[80] Conrad-Billroth, H. [The Absorption of Substituted Benzenes. II. Xylidines and Xylenols]: Ztschr. physik. Chem., vol. B20, 1933, pp. 222–226.

[81] Phenol, 2,4-, 3,4-, 3,5-xylenol, 1-naphthol, 2-naphthol, and o-phenylphenol are present in the American Petroleum Institute Research Project 44 of the National Bureau of Standards. Catalog of Ultraviolet Spectrograms.

bands of 5-indanol lie at longer wave lengths than those of 4-indanol. However, the first band of the former is at appreciably longer wave length (289 $m\mu$) than other para-substituted phenols, and the first band of 4-indanol (277 $m\mu$) is 1 $m\mu$ shorter than in the spectrum of phenol itself; it is contrary to the usual situation that absorption bands of derivatives lie at longer wave lengths than do bands of the parent compound.

SOURCE OF TAR ACIDS INVESTIGATED

PRODUCTION OF OIL BY HYDROGENATION OF BRUCETON COAL

The oil used in this investigation was obtained by hydrogenation of Pittsburgh-bed (Bruceton) coal during 32 hours of operation of the Bureau of Mines experimental hydrogenation plant, following a period of 117 hours of steady operation, during which time the plant was brought to equilibrium. The material hydrogenated was a mixture containing about 40 percent powdered coal, 60 percent heavy recycle oil, and molybdenum trioxide catalyst (equal to 1 percent of the coal used). This mixture was pumped through a preheater and then through two converters in series with hydrogen at 233 atmospheres (3,500 pounds per square inch) at a reaction temperature of 440° C. The heavy recycle oil was a centrifuged product oil from previous runs. The contact time was 1.2 hours. The paste of coal, heavy recycle oil, and catalyst was pumped into the converters at a rate of 4.7 kg. per hour. The heavy-oil product, in which was suspended the ash of the coal, the unreacted coal, insoluble organic materials, and catalyst particles, was discharged from the second converter. The hydrogen absorption was 9.8 percent of the weight of moisture- and ash-free coal used. The average material balance in the plant during the period when the sample was collected was 99 percent. The yield of oil, based upon the moisture- and ash-free coal used, was 77.7 percent. There was also formed 0.49 percent of ammonia, 1.08 percent of hydrogen sulfide, 3.85 percent of water, and 16.8 percent of insoluble matter.

PRELIMINARY FRACTIONATION

This study was confined to the characterization of tar acids present in the *n*-hexane-soluble portion of the total oil. One hundred and twenty-seven kilograms of total oil product was divided into 11 batches. Each batch was poured slowly into eight times its weight of *n*-hexane with efficient stirring and cooling below 10° C. The mixture was allowed to settle overnight. The insoluble material was filtered with suction and washed three times by decantation with successive 4-liter portions of *n*-hexane. The *n*-hexane solution from each batch was distilled on a steam bath to a temperature of 76° C. to remove the *n*-hexane. The yield of oil soluble in *n*-hexane was 69.5 kg. (55 percent of the total oil, or 43 percent, based upon the moisture- and ash-free coal).

EXTRACTION OF TAR ACIDS WITH CLAISEN ALKALI

The phenols contained in 45.8 kg. of oil were isolated by alkaline extraction in 4-liter batches in the following manner: Four liters of *n*-hexane-soluble oil was diluted with 4 liters of benzene in a large separatory funnel equipped with an efficient stirrer. The benzene solution was stirred for 1 hour with 2 liters of 10-percent sulfuric acid sturated with sodium chloride.[82] The mixture was allowed to settle for 1 hour before the aqueous layer was drawn off. The benzene solution was then stirred for 1 hour with 2 liters of Claisen alkali and allowed to stand until good phase separation was obtained. The phenoxide solution was drawn off, and the residual benzene solution in the separatory funnel was again treated in the same manner, first with 2 liters and then with 1 liter of Claisen alkali.

The combined alkaline extracts were steam-distilled to remove neutral oils and volatile amines that had been extracted along with the crude phenols. An insignificant amount of distillate was obtained, which was not investigated. The residue from the steam distillation was extracted with benzene to insure removal of neutral material from the potassium phenoxides.

The crude phenols were recovered by acidifying the alkaline extracts with carbon dioxide to *p*H of 10.0–10.3, separating the precipitated phenols and extracting the aqueous layer with benzene. A preliminary experiment showed that further acidification of the aqueous layer with hydrogen chloride gas liberated only a negligible amount of oil; therefore, only the carbon dioxide acidification was employed. The water was then removed by azeotropic distillation with benzene and the solvent was evaporated. The yield of crude phenols was 4,320 gm., or 9.4 percent of the oil so treated.

FRACTIONAL DISTILLATION OF CRUDE PHENOLS

The crude phenols were distilled at reduced pressure, because, at excessive temperatures, tar acids readily undergo oxidation and polymerization to give large proportions of nondistillable residues. Low pressure reduces the temperature of distillation so that losses as a result of formation of undersirable materials are minimized. A second advantage of distillation in vacuo is that the relative volatility of a given

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[82] Fisher, C. H., and Eisner, A., Determination of Tar Acids and Bases by Extraction Methods: Ind. Eng. Chem., anal. ed., vol. 9, 1937, pp. 213-218.

pair of liquids may be altered by changing the pressure and, hence, the temperature of distillation.[33] The relative volatility, commonly designated as α, is the ratio of volatilities of any two components in a solution. For a binary system that follows Raoult's law, α is equal to the vapor pressure of the lower-boiling component divided by the vapor pressure of the other component. The relative volatility, therefore, is a measure of the ease with which two liquids may be separated by distillation. As the relative volatility, α, is a function of the temperature ($\log \alpha = MT + C$), it is sometimes possible to select some pressure at which the relative volatility becomes large enough to allow an efficient separation by this means. In general, relative volatility increases with decrease in temperature as a consequence of lowered pressure. One disadvantage of distillation in vacuo is that the efficiency of a packed column usually decreases with decrease in the pressure of distillation.

PRELIMINARY DISTILLATION AT REDUCED PRESSURE

The phenolic mixture (4,320 gm.) described in the previous section was rapidly distilled in batches from a 1-liter Claisen flask at a pressure of about 2.5 mm. at the pump, and a total of 2,740 gm. (63.5 percent) of distillate was collected in two fractions. A total of 2,204 gm., boiling up to 130° C., was collected as fraction A, and 536 gm., boiling up to 180° C., as fraction B, at which temperature decomposition was observed. The nondistillable residue (1,575 gm.) was dissolved in benzene and stored. No work on this residue was undertaken in the present study.

PRECISE FRACTIONAL DISTILLATION AT REDUCED PRESSURE

The phenols in the distillate were next redistilled under vacuum through a 91.4-cm. long, 25-mm. I. D. Podbielniak column operating at an efficiency of about 25 theoretical plates. Fraction A first was distilled to 153° C. at 40 mm. Fraction B was then added, and distillation was continued until 82 percent of the total material had distilled. At this point the pressure was reduced to 30 mm., and distillation was continued to completion. Total recovery from the operation was 98 percent. A total of 136 fractions was collected, and the refractive index of each was determined. The distillation curve is shown in figure 12 along with the refractive indexes of the individual fractions and the specific gravities of fractions 68 to 136. Of the 136 fractions collected, those of nearly the same reflux temperature and refractive indexes were combined to give the 70 fractions shown in table 10, which also gives the boiling point and other physical properties of the distillates.

TABLE 10.—*Fractions from distillation of phenols from tar-acid fraction of hydrogenated coal*

Fraction	Volume, ml.	Boiling range, ° C. at 40 mm.	N_D^{20}	d_4^{20}	Percent by volume of total charge
1-3	8.7	67-97	1.5097	----------	0.3
4-7	86.5	97-99	Solid	----------	2.9
9-18 [1]	----------	----------	----------	----------	----------
8, 19, 20	23.5	99-100	1.5462	----------	.8
21	25.5	100-102	1.5450	----------	.9
22-24	74.4	102-104	1.5429	----------	2.5
25-30	94.7	104-113	1.5394	----------	3.2
31-33	75.0	113-114	1.5386	----------	2.5
34-40	177.7	114-115	1.5382	----------	6.0
41-43	71.8	115-116	1.5376	----------	2.4
44-47	102.2	116-120	1.5372	----------	3.4
48-51	100.0	120-125	1.5354	----------	3.4
52-55	100.3	125-128	1.5328	----------	3.4
56-61	128.8	128-129	1.5320	----------	4.3
62	26.0	129-130	1.5328	----------	.9
63-65	79.8	130-131	1.5332	----------	2.7
66	25.0	131-132	1.5328	----------	.8
67	25.0	132-133	1.5330	----------	.8
68-71	103.5	133-138	1.5307	0.992	3.5
72-76	127.5	138-141	1.5265	.999	4.3
77-78	52.0	141-142	1.5270	.991	1.8
79-82	100.0	142-145	1.5275	.991	3.4
83	25.0	145-147	1.5324	1.016	.8
84	25.0	147-148	1.5435	1.041	.8
85	25.0	148-149	1.5485	1.048	.8
86	25.5	149	1.5400	1.038	.9
87	25.0	149-152	1.5354	1.025	.8
88	25.2	152-153	1.5340	1.010	.8
89-92 [2]	28.8	131-150	1.5351	1.010	1.0
93	25.2	150-153	1.5322	.997	.8
94	25.2	153	1.5335	1.003	.8
95	26.0	153-154	1.5370	1.020	.9
96	26.0	154-155	1.5405	1.018	.9
97	25.0	155	1.5415	1.019	.8
98	25.0	155	1.5433	1.032	.8
99	25.5	155	1.5462	1.037	.9
100	25.4	155-156	1.5445	1.028	.8
101	14.6	156-157	1.5410	1.015	.5
102	25.1	157-159	1.5408	1.019	.8
103	25.0	159-160	1.5435	1.023	.8
104	25.0	160-161	1.5455	1.030	.8
105	25.0	161-162	1.5470	1.028	.8
106-107	50.2	162-164	1.5460	1.023	1.7
108	25.2	164-165	1.5425	1.020	.8
109	25.2	165-166	1.5400	1.022	.8
110-112	78.6	166-168	1.5389	1.025	2.7
113	25.2	168-169	1.5432	1.035	.8
114	25.2	169-171	1.5490	1.047	.8
115	13.0	171-173	1.5525	1.045	.4
116 [3]	27.3	165	1.5550	1.045	.9
117-118	56.0	165-168	1.5585	1.047	1.9
119	29.5	168	1.5485	1.033	1.0
120	25.0	168-171	1.5435	1.015	.8
121	25.2	171-172	1.5440	1.018	.8
122	25.0	172-174	1.5457	1.023	.8
123	20.3	174-175	1.5480	1.024	.7
124	27.0	175-178	1.5497	1.023	.9
125	26.0	178-179	1.5532	1.027	.9
126	22.3	179-181	1.5528	1.038	.8
127	25.3	181-183	1.5502	----------	.9
128	20.1	183-185	1.5500	1.037	.7
129	15.4	185-187	1.5492	----------	.5
130	20.0	187-189	1.5492	1.032	.7
131	20.4	189-192	1.5502	1.038	.7
132	26.5	192-194	1.5524	1.031	.9
133	11.7	194-197	1.5545	1.037	.4
134	10.8	197-199	1.5598	1.069	.4
135	13.0	199-201	1.5605	----------	.4
136	20.7	201-207	1.5566	1.014	.7
Residue	77.8	----------	----------	----------	2.6
	2,893.3	----------	----------	----------	96.9

[1] Fractions 9-18 were put back in still pot.
[2] Distillation was interrupted, and fraction B from the first distillation was put in the still pot.
[3] Fractions 116-136 distilled at 30 mm.

From the distillation curve, it will be observed that fractionation of the tar-acid mixture effected only a partial separation of the com-

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[33] Hildebrand, J. H., Solubility of Nonelectrolytes: Reinhold Publishing Co., New York, 2d ed., 1936, p. 29.

ponents. Overlapping was especially prevalent toward the end of the distillation of a phenol of a given molecular weight, at which point appreciable quantities of the next higher homologous phenol, usually the ortho isomer, appeared. The higher volatility of the ortho isomers is a result of the smaller amount of intermolecular hydrogen bonding.[84] Figure 12 shows that the refractive index gradually decreases with increasing boiling point until about 56 percent of the material has been distilled. The decrease in refractive index up to this point is associated with the continuous distillation of mononuclear phenols of increasing length and number of side chains on the aromatic nucleus. As the proportion of the molecular weight due to alkyl chains increases, the index of refraction decreases, because paraffins have low and aromatics have high indexes of refraction.[85] After about 56 percent of the material has been distilled, the index of refraction starts to increase with increase in boiling point. Thereafter, it alternately increased to a maximum and decreased to a minimum in phase with the rise and fall of the density. This behavior signified the appearance of dicyclic phenols, because these are characterized by high refractive indexes and high densities, as compared to mononuclear phenols of equivalent molecular weight.

The indanols are the simplest type of dicyclic phenols. 4-indanol was, in fact, isolated from fraction 85, at which point about 58 percent of the tar acids had distilled. The only other possible indanol, 5-indanol, was isolated from the next fraction of high refractive index and high density (99). It was possible to isolate *o*-phenylphenol and *p*-phenylphenol from other peak fractions (117–118 and 135, respectively). The high-density, high-refractive-index fractions in each case, therefore, represent concentrations of dicyclic phenols. The fractions with low index and low density beyond the 56-percent point contained large amounts of mononuclear polyalkylated phenols. The fact that these fractions all have higher indexes of refraction than the fractions boiling below the 56-percent point is explained by the presence in the latter of a small amount of dicyclic phenols. Such overlapping is to be expected even in very efficient columns.

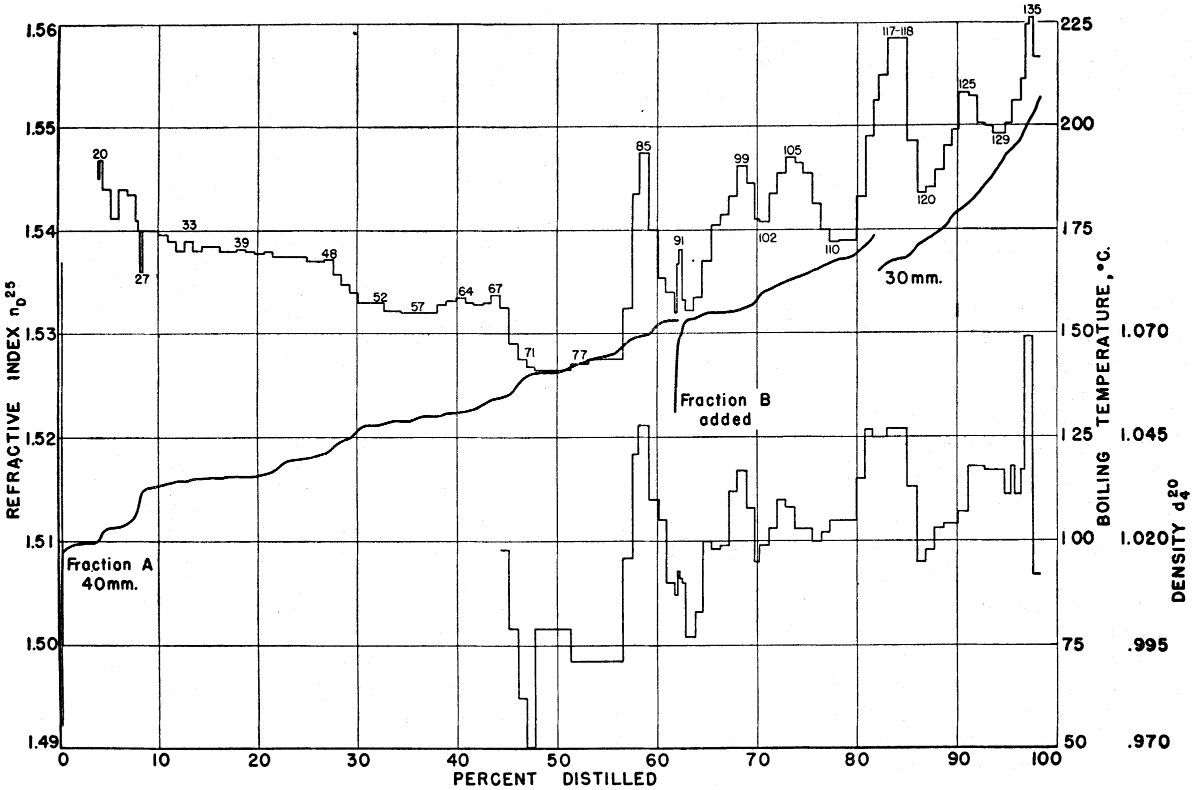

FIGURE 12.—DISTILLATION OF CRUDE PHENOLS FROM TAR-ACID FRACTION OF HYDROGENATED BRUCETON COAL.

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[84] Work cited in footnote 71.

[85] McKinely, J. B., Physical Properties Supporting the Phenolic Nature of a Certain Hindered Phenol; A Synthesis of Tert-butyl p-tolyl Ether: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 1624–1626.

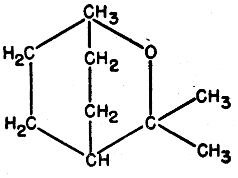
ISOLATION AND IDENTIFICATION OF INDIVIDUAL PHENOLS

PHENOL

Distillation fraction 4–7 (table 10), b.p. 97°–99° C. at 40 mm., solidified at room temperature. Ten and three-tenths grams of this material twice recrystallized from skellysolve-B (b.p. 60°–71° C.) gave 8.5 grams of phenol in colorless needles. Its melting point was 38.8°–39.8° C., which was not depressed when mixed with an authentic sample. As further proof of its identity, the *N*-phenylcarbamate was prepared. Recrystallization of the latter from benzene gave a product melting at 125.0°–126.4° C. A mixed melting point with a standard preparation showed no depression.

ORTHO-CRESOL

The presence of *o*-cresol was established through formation of its molecular compound with cineole (eucalyptole). The quantitative formation of such a compound has been utilized by Potter and Williams [86] for the determination of *o*-cresol in a mixture of isomeric cresols. The compound can be used to identify *o*-cresol, as it is a sharply melting crystalline substance easily separated from adhering oils. In this manner, *o*-cresol was found in fraction 8–19–20 (table 10), b. p. 99°–100° C. at 40 mm., and in fraction 21 (table 10), b.p. 100°–102° C. at 40 mm.



Cineole

A mixture of 1 gm. of the fraction with 1 gm. of cineole was cooled to 0° C. The precipitated molecular compound was filtered and recrystallized, m. p. 56.0°–57.2° C., from petroleum ether (b. p. 30°–68° C.). A mixed melting point with an authentic sample remained unchanged.

Phenol was also detected in these fractions through formation of its tribromide. The filtrate from the molecular compound was extracted with 10 percent sodium hydroxide solution. The alkaline layer was then acidified with dilute hydrochloric acid and extracted with benzene. The benzene solution was dried, and the solvent was removed. One gram of the residue was dissolved in 95 percent alcohol, and the tribromophenol was prepared as described by Shriner and Fuson.[87] The crude tribromophenol gave no depression of melting point on admixture with a reference sample.

Fraction 22–24 (table 10) had a boiling range of 100°–104° C. at 40 mm. This fraction was solid at room temperature. A portion recrystallized from petroleum ether (b. p. 30°–68° C.) gave *o*-cresol in white needles, m. p. 27.0°–29.0° C. The *o*-cresol was identified through its *N*-phenylcarbamate. The melting point of the latter was 143.4°–144.2° C. and was not depressed by mixture with an authentic sample.

META- AND PARA-CRESOL

Although *o*-cresol can be isolated from tar-acid mixtures by precise fractional distillation, the closeness of the boiling points of the meta and para isomers requires other procedures for their separation from each other. It was thought that by bromination of a distillate rich in *m*- and *p*-cresol, bromo derivatives of the two isomers having wide differences in solubility might be obtained. In the case of the para isomer, there is a possibility of forming both di- and tetra-bromo derivatives; whereas, with the meta compound, the tribromo derivative would be the most probable product.

Two and seven-tenths grams of fraction 34–40 (table 10), b. p. 114°–115° C. at 40 mm., was brominated, as described by Shriner and Fuson.[88] A voluminous white precipitate was formed, which, after three recrystallizations from a 2–1 mixture of absolute alcohol and water, melted at 81.2°–82.4° C. A mixture of the product with pure tribromo-*m*-cresol (m. p., 82.4°–83.8° C.) melted at 81.0°–82.4° C., whereas a mixed melting point with pure tribromophenol (m. p., 93.6°–94.2° C.) melted at 54.6°–68.8° C.

Brown and Branting [89] have described the separation and identification, by fractional crystallization of aryloxyacetic acids formed

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[86] Potter, F. M., and Williams, H. B., Determination of *o*-Cresol: Jour. Soc. Chem. Ind., vol. 51, 1932, pp. 59–60T.

[87] Shriner, R. L., and Fuson, R. C., Identification of Organic Compounds: John Wiley & Sons, Inc., New York, 2d ed., 1947, p. 174.

[88] Work cited in footnote 87.

[89] Brown, R. L., and Branting, B. F., Composition of Tar from the Low-Temperature Carbonization of Utah Coal. I: Ind. Eng. Chem., vol. 20, 1928, pp. 392–396.

from them, of the three cresols from tar acids produced in coal carbonization. By a modification of this procedure, the presence of both *m*- and *p*-cresol in the above fraction was established.

To prepare the aryloxyacetic acids, 22 gm. of fraction 34–40 and 24 gm. of sodium hydroxide were dissolved in 250 ml. of water. The water solution was heated to the point of refluxing, and 42 gm. of bromoacetic acid[90] in 50 ml. of hot water was added at such a rate that refluxing was not interrupted. This solution was refluxed for 3 hours, then allowed to cool, and was poured onto an ice-hydrochloric acid mixture. The resulting solid was filtered, taken up in benzene, extracted with 10-percent sodium bicarbonate solution, and acidified. The crude product, when filtered and dried, weighed 9.6 gm.

Extensive fractional crystallization of this mixture of aryloxyacetic acids from benzene gave 4-methylphenoxyacetic acid, m. p. 135.5°–139.0° C., not depressed by an authentic sample. The more soluble fractions, on further fractionation, gave 3-methylphenoxyacetic acid, m. p. 94.4°–96.4° C., not depressed by an authentic sample.

2,5-XYLENOL

Fraction 44–47 (table 10), b. p. 116°–120° C. at 40 mm., deposited solid material on cooling to −10° C. The crystalline material was separated by centrifuging and was twice recrystallized from petroleum ether (b. p. 60°–68° C.). The recrystallized substance melted at 74.2°–74.8° C. A mixed melting point with a known sample of 2,5-xylenol showed no depression. Further proof of identity was obtained by preparing the *N*-phenylcarbamate, which, once recrystallized from petroleum ether (b. p. 90°–100° C.), melted at 165.2°–168.2° C. The melting point of the latter was not depressed on mixing with an authentic sample.

ATTEMPTED SEPARATION OF XYLENOLS BY FRACTIONAL PRECIPITATION

In an attempt to isolate other isomeric xylenols from fraction 44–47, separation by partial acidification of an alkaline solution of the fraction was investigated.

Three grams of the fraction were dissolved in 10 ml. of 25-percent sodium hydroxide in a 50-ml. separatory funnel. Two mililliters of concentrated hydrochloric acid was added, the separatory funnel was thoroughly shaken, and the precipitated phenols were extracted with benzene. The alkaline solution was then treated three successive times with 2-ml. portions of the same acid. After the addition of each portion of acid, the separatory funnel was thoroughly shaken, and the precipitated phenols were extracted with benzene. Four fractions were obtained by this procedure. Evaporation of the solvent from each fraction left residues that could not be crystallized. An *N*-phenylcarbamate was prepared from each fraction. Recrystallization of the carbamates from the first three fractions, first from petroleum ether (b. p. 90°–100° C.), then from a benzene-petroleum ether (1–2) mixture, and finally from an ethanol-water (2–1) mixture, gave only the 2,5-dimethylphenol *N*-phenylcarbamat in each case. The quantity of *N*-phenylcarbamate formed from the fourth of the above fractions was not sufficient to attempt recrystallization.

2,4-XYLENOL

A solution of 1 gm. of fraction 44–47 and 1 gm. of 2-fluorenyl-isocyanate (p. 17) in 50 ml. of toluene was refluxed for 1 hour. The solution was evaporated to dryness under vacuum, and the mixture of *N*-(2-fluorenyl) carbamates was refluxed with 50 ml. of skellysolve-B. The insoluble material was filtered off, and the soluble portion was fractionally crystallized, but no pure compound was isolated. The insoluble portion was dissolved in benzene and fractionally crystallized, giving the carbamate of 2,4-xylenol, melting at 170.0°–172.0° C. It showed no depression of the melting point when mixed with an authentic sample.

SEPARATION OF PHENOLS IN THE XYLENOL RANGE BY DISTILLATION OF THEIR METHYL ETHERS

The methyl ethers were prepared by the following procedure: 35 grams of fraction 48–51 (table 10), b. p. 121°–125° C. at 40 mm., were dissolved in a solution of 23 gm. of potassium hydroxide in 50 ml. of water. After heating to boiling to effect complete solution, the water was evaporated. Thirty milliliters of dimethyl sulfate were added in portions, with stirring, to the dry residue. The mixture was heated for 1 hour in an oil bath at 110°–120° C. and then refluxed with a large excess of Claisen alkali. After cooling, the reaction mixture was extracted with benzene. The benzene solution was extracted with Claisen alkali, washed well with water, then with saturated sodium chloride solution, and filtered through anhydrous sodium sulfate. Removal of the solvent gave 26 gm. of neutral oil consisting of a mixture of methyl ethers.

This material was fractionally distilled under 1 atm. of nitrogen through a 60.9 cm. long, 8 mm. Podbielniak column operating at an efficiency of about 15 theoretical plates. Ten milliliters of dicyclohexyl was used as a chaser. To prevent foaming, a controlled coil heater

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[90] It has been found that bromoacetic acid gives higher yields of the aryloxyacetic acid than does chloroacetic acid. M. S. Newman and J. Wotiz, personal communication.

was inserted in the still pot near the surface of the sample. Eleven fractions were collected. Total recovery in the distillation was 92 percent. The distillation curve is shown in figure 13, which also shows the fractions collected and their refractive indexes. Several of these fractions were examined, as described in the following paragraphs.

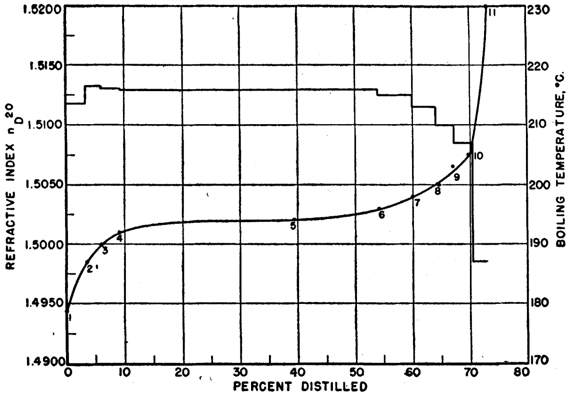


FIGURE 13.—DISTILLATION OF METHYL ETHERS.

Two grams of fraction 4, b. p. 192°–194° C., from the distillation of the methyl ethers (fig. 13) were mixed with 25 ml. of acetic acid and 10 ml. of 48-percent hydrobromic acid. The mixture was refluxed for 17 hours, then cooled and poured into benzene and water. The benzene layer was separated, washed well with water and 10 percent sodium bicarbonate solution, and extracted with 10 percent sodium hydroxide. The alkaline layer was drawn off onto ice and concentrated hydrochloric acid, and the acidic material was extracted with benzene. Upon evaporation of the solvent, 1.5 gm. of phenolic material was obtained.

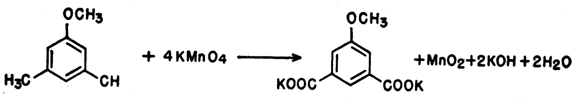
The *p*-nitrobenzyl ether of this material (1.5 gm.) was prepared in the usual manner. Recrystallization from alcohol gave a crystalline substance melting at 104.2°–105.4° C. A small sample (0.157 gm.) of this derivative was chromatographed on alumina-celite (1 : 1 mixture by volume) and the product recrystallized from alcohol. It melted at 104.8°–105.2° C. The melting point, when mixed with an authentic specimen of 2,4-xylenol *p*-nitrobenzyl ether, was unchanged.

2,3-XYLENOL

Fraction 6 (1.7 gm., b. p. 196°–198° C.) from the distillation of the methyl ethers (fig. 13) was hydrolyzed with hydrobromic acid as described above, giving 1.1 gm. of phenolic material which was then converted to the aryloxyacetic acid by treatment with bromoacetic acid. After one recrystallization from water and two from benzene, the melting point of the isolated product was 175°–183° C. Its neutral equivalent was found to be 182. The calculated neutral equivalent for a dimethylphenoxyacetic acid is 180. The aryloxyacetic acid recovered from the neutral equivalent determination showed a melting point of 182°–187° C. This corresponds closely with the value given in the literature for 2,3-dimethylphenoxyacetic acid (m. p. 185°–187° C.).[91] An authentic sample of this acid was not available for determination of a mixed melting point. Despite this evidence of the presence of 2,3-xylenol, its presence was not indicated by a comparison of the infrared spectra of the xylenol fractions with the spectrum reported for 2,3-xylenol.

MESITOL. OXIDATION OF METHYL ETHERS

The combined fractions 7 and 8 (1.9 gm., b. p. 198°–200° C.) from the distillation of the methyl ethers (fig. 13) were suspended in 20 ml. of 10-percent sodium hydroxide, and 152 ml. of 6-percent potassium permanganate was added dropwise and vigorously stirred over a 2-hour period while the mixture was heated on a steam bath. The quantity of permanganate added was sufficient to oxidize the nuclear methyl groups of the methyl ether of a xylenol. Stirring and heating were continued for 4 hours after the addition was completed. The reaction mixture was cooled and left standing overnight. The pink color of the remaining permangate ion was discharged with a few pinches of sodium bisulfite. The solution was separated from the manganese dioxide by centrifugation, and the cold aqueous solution was acidified with concentrated hydrochloric acid. The acid solution was evaporated to dryness, and the residue was extracted with ether, then filtered, and the solvent removed. The resulting crude acids were dissolved in 100 ml. of absolute methanol, and 3 ml. of concentrated sulfuric acid was added. After refluxing for 2 hours, the excess methanol was removed by distillation. The residue was dissolved in ether, and the ether solution was washed with water and 10 percent sodium bicarbonate solution and then dried. Evaporation of the solvent gave 0.31 gm. of residue. After three recrystallizations from petroleum ether (b. p. 60°–68° C.), crystals were obtained that had a sharp melting point of 84.0°–84.6° C. This melting point suggested



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[91] Work cited in footnote 60.

that the acid was methoxytrimesic acid, whose trimethyl ester[92] is reported to melt at 86° C. Its identity could not be definitely established, however, as the attempt described below to obtain an authentic sample was unsuccessful.

ATTEMPTED PREPARATION OF METHOXYTRIMESIC ACID-TRIMETHYL ESTER

An attempt was made to obtain an authentic specimen of methoxytrimesic acid-trimethyl ester for a mixed melting point with the material described above.

An authentic sample of mesitol was prepared from mesidine in the following manner. An aqueous solution of sodium nitrite was slowly added to a hydrochloric acid solution of mesidine, the temperature of which was kept below 10° C. throughout. The acid solution of the diazotized amine was then warmed to about 50° C., after which it was cooled and extracted with benzene. The benzene solution was extracted with Claisen alkali, the alkaline extract was drawn off onto ice and hydrochloric acid, and the precipitated phenol again was extracted with benzene. The solvent was removed, and the residue of mesitol was distilled at 103° C. at 20 mm. After three recrystallizations from petroleum-ether (b. p. 30°–60° C.), it melted at 70°–71° C. (lit. 72.0°–72.5° C.).[93] Its *N*-phenylcarbamate was prepared and melted at 143.2°–144.2° C. (lit. 141°–142° C.).[94] A portion of the mesitol was methylated with dimethylsulfate and the resulting ether oxidized with alkaline permanganate, as described in the preceding section. The acidic product was then esterified in ether solution with diazomethane. From the esterification there was isolated a small amount of product melting at 96.6°–97.4° C. This material was then saponified and the acidic material isolated. Determination of its neutral equivalent gave a value of 170. The alkaline solution from the neutral equivalent determination was acidified with concentrated hydrochloric acid; the precipitated acid was extracted with benzene, and the solvent was then removed. The residue gave a neutral equivalent value of 200. The neutral equivalent calculated for $C_{10}H_8O_7$ (methoxy trimesic acid) is 80. The structure of the material isolated from the oxidation of the methyl ether of mesitol was not established. The methyl groups in mesitol appeared to be resistant to oxidation with alkaline permanganate.

3,5-XYLENOL

The presence of 3,5-xylenol was established in the fraction 63–65 (table 10), b. p. 130°–131° C. at 40 mm. This combined fraction was partly crystalline at −10° C. The crystalline portion was filtered from the oil with suction and recrystallized from petroleum ether (b. p. 60°–68° C.) to a melting point of 62.4°–63.6° C.

META-ETHYLPHENOL

One gram of the combined fraction 56–61 (table 10), b. p. 129°–130° C. at 40 mm., was dissolved in 20 ml. of benzene and shaken with a solution of 0.4 gm. of sodium hydroxide in 10 ml. of water. After separating the two layers, the alkaline layer was shaken with a fresh solution of 1 gm. of the fraction in 20 ml. of benzene. This process of separating the alkaline layer and shaking with fresh portions of the phenols was repeated twice. After the fourth shaking, the alkaline layer was separated, acidified with concentrated hydrochloric acid, and the phenols extracted with benzene. The solvent was evaporated to give an oil, which was designated as fraction I. The four benzene solutions were shaken twice more with sodium hydroxide, in the order described above, to give fractions II and III.

The aryloxyacetic acids of fractions I and II, after three recrystallizations each from petroleum-ether (b. p. 60°–68° C.), gave no depression of melting point on admixture with an authentic specimen of 3-ethylphenoxyacetic acid.

After four recrystallizations of the *N*-phenylcarbamate of fraction III, a melting point of 136.6°–138.6° C. was obtained. A mixed melting point with a known sample of 3-ethylphenyl *N*-phenylcarbamate exhibited no depression.

ORTHO- AND PARA-ETHYLPHENOL

It was not possible to establish the presence of *o*-ethylphenol or *p*-ethylphenol by chemical methods. However, infrared analysis indicated that these phenols were present in small quantities.

3-METHYL-5-ETHYLPHENOL

The combined fraction, 77–82 (table 10), b. p. 141°–145° C. at 40 mm., solidified on cooling to −10° C. The crystalline material was filtered, and after four recrystallizations from petroleum ether (b. p. 30°–60° C.) it was obtained in prisms melting at 50.6°–51.8° C. An authentic specimen of 3-methyl-5-ethylphenol, which is reported to melt at 55° C.,[95] was not available for a mixed melting point.

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[92] Ullman, K., and Brittner, K. [Preparation of 1-Hydroxy-2,6-Dialdehyde-4-Methylbenzene from p-Cresol]: Ber. Deut. chem. Gesell., vol. 42, 1909, p. 2543.

[93] Boyd, D. R., Hydrolysis of Sodium Phenoxides in Aqueous Solution: Jour. Chem. Soc., vol. 107, 1915, pp. 1538–1546.

[94] Work cited in footnote 93.

[95] Kruber, O., and Schmitt, A. [The Phenols of Coal Tar]: Ber. Deut. chem. Gesell., vol. 64B, 1931, pp. 2270–2277.

Analysis, percent:[96]
Calculated for $C_9H_{12}O$: C, 79.37; H, 8.88
Found, C, 79.33, 79.40; H, 8.89, 8.89

The constitution of this substance was established in a manner similar to that previously reported [97] [98] for 3-methyl-5-ethylphenol. This consisted of oxidative degradation of its methyl ether to a methoxydicarboxylic acid, followed by esterification of the acid, giving dimethyl-5-methoxyisophthalate, which, after one recrystallization from petroleum-ether (b. p. 60°–68° C.), melted at 111.2°–111.6° C., compared to a literature value of 109° C.[99]

The benzoate, *N*-phenylcarbamate, and aryloxyacetic acid derivatives were prepared and gave melting points compared to those in the literature [1] as follows:

Benzoate, 36.8°–37.6° C. (lit. 40° C.)
N-phenylcarbamate, 154.2°–155.4° C. (lit. 152° C.)
Aryloxyacetic acid, 90.4°–92.2° C. (lit. 95° C.)

The similarity of the infrared absorption spectrum of the phenol in question to that of an authentic sample of 3,5-xylenol also established it to be a symmetrically disubstituted phenol.

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[96] The macroanalyses were performed by R. Raymond of the Bureau of Mines.

[97] Work cited in footnote 95.

[98] Morgan, G. T., and Pette, A. E. J., Homologs of Phenol: Jour. Chem. Soc., 1934, pp. 418–422.

[99] Work cited in footnote 98.

[1] Work cited in footnote 95.

In previous characterizations of coal-hydrogenation products, the phenols up to and including the xylenol range have been studied rather superficially, but fractions beyond the xylenol range have received scarcely any attention. Furthermore, relatively few of the phenols boiling at higher temperatures have been shown to be present among the products of coal carbonization.

ULTRAVIOLET ABSORPTION SPECTRA STUDIES

In an attempt to obtain some preliminary information on the tar acids boiling above the xylenol range, the ultraviolet absorption spectra of some of the higher-boiling fractions were studied. It was shown in the previous discussion of ultraviolet absorption spectra of phenols that the character of the ultraviolet absorption spectra of simple phenols is determined largely by the position of the alkyl substituents relative to the hydroxyl group. The information gained from the study of the spectra of the phenols was used in an attempt to analyze the ultraviolet absorption spectra of the high-boiling distillates shown in figures 14, 15, and 16. It was observed that for all the curves other than that of fraction 85 (table 10), in which the main band was at 277 *mμ*, the principal band occurred at approximately 280 *mμ*, which suggested the presence of ortho- or meta-substituted phenols. The main band at 277 *mμ* in fraction 85 also indicated that the hydroxyl group was ortho or meta to other substituents. 4-indanol, which is substituted in positions ortho and meta to the hydroxyl group, was later isolated from fraction 85. It was observed that a band at 289 *mμ* began appearing in fraction 96, became stronger in the fractions between 99 and 105, and began to fade in the higher fractions. It had virtually disappeared at fraction 125. It is difficult to be certain of the type of structure that causes the band at 289 *mμ*. The longest wave length band observed in phenols is the band at 285 *mμ* caused by phenols with substituents para to the hydroxyl group. However, in fraction 99 (table 10), where this band exhibited maximum intensity, a para-substituted type of structure, 5-indanol, was isolated.

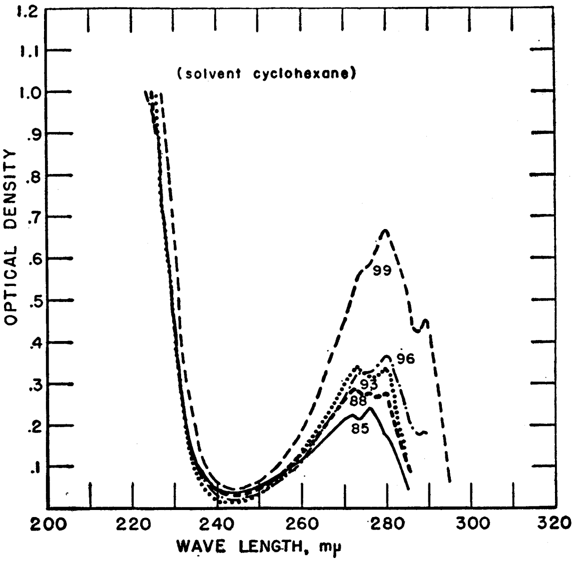

Figure 14.—TAR-ACID DISTILLATION FRACTIONS.

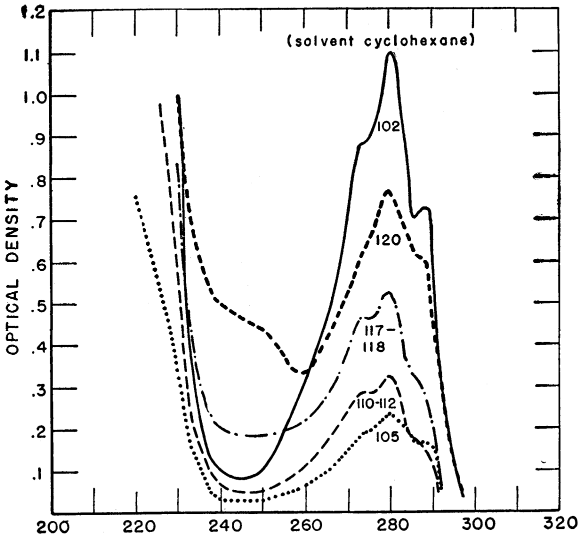

Figure 15.—TAR-ACID DISTILLATION FRACTIONS.

Increased absorption at 250 *mμ* began with fraction 117–118 (table 10) and appeared progressively stronger in fractions 120, 125, 129, and 135. This indicated the presence of diphenyl-type compounds, and, indeed, *o*-phenylphenol and *p*-phenylphenol were subsequently isolated from fractions 117–118 and 135, respectively.

As no bands were observed above 300 *mμ*, these spectra indicated that aromatic fused-ring systems were not present in any appreciable

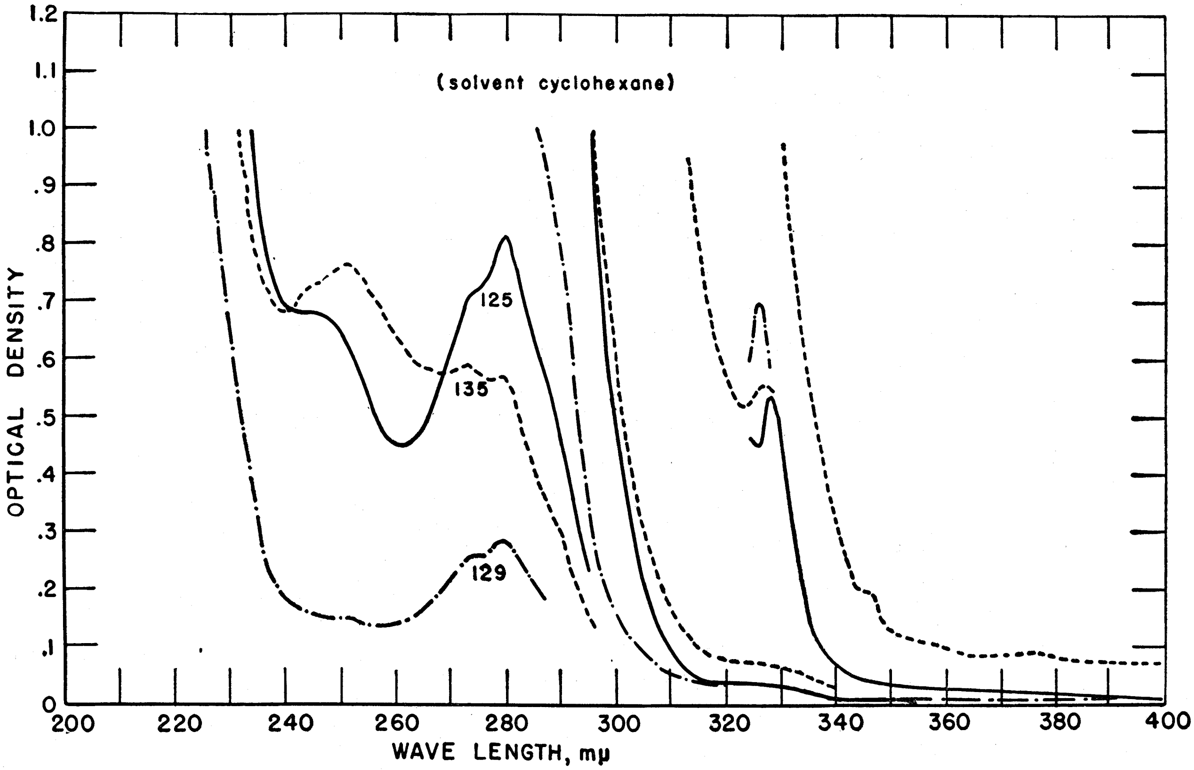

FIGURE 16.—TAR-ACID DISTILLATION FRACTIONS.

quantities and that the higher-boiling tar acids investigated consisted principally of phenol homologues. There was also the possibility that hydroaromatic compounds such as tetrahydronaphthols, cyclohexylphenols, and related hydrogenated ring systems were present. It was thought likely that polynuclear aromatic and hydroaromatic phenols were present in the fractions not distilled (see p. 25) in this work.

DEHYDROGENATION OF TAR-ACID DISTILLATES

Some polynuclear phenols were expected to be present in the tar-acid fractions boiling above the xylenols. However, ultraviolet absorption spectra of these higher-boiling fractions excluded the presence of any phenols with aromatic fused ring structures. Because it is known that large quantities of aromatic and hydrogenated polynuclear hydrocarbon ring systems are formed in the hydrogenation of coal,[2] it is possible that phenols with fused ring structures are present either in a partly or completely hydrogenated form, for such compounds as the tetrahydronaphthols, the 9,10-dihydroanthranols, and partly hydrogenated polynuclear structures with nonconjugated aromatic rings would show, in general, spectra similar to those of the simple phenols. The spectra of 1,2,3,4-tetrahydro-5-hydroxynaphthalene and a 9,10-dihydroanthranol would be similar, for example, to those of phenol and a hydroxydiphenol, respectively.

The dehydrogenation of these hydroaromatic phenols to their parent aromatic structures would eliminate some partly hydrogenated isomers from consideration, whereas the parent aromatic compounds would exhibit characteristic ultraviolet absorption spectra and also could be readily identified by the formation of derivatives. Some of the higher-boiling distillates were examined, therefore, for partly hydrogenated ring systems, using catalytic dehydrogenation experiments. It was realized that catalytic dehydrogenation is complicated by cleavage, formation, or rearrangement of carbon-to-carbon bonds.[3] Also, catalytic liquid-phase dehydrogenations are complicated by disproportionation reactions.[4] It is possible, however, even though disproportionation does occur, that aromatic compounds could be obtained in quantities sufficient for identification.

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[2] Pier, M. [Polycyclic Aromatic Substance as Hydrogenation Products]: Reichsamt Wirtschaftsausbau, Pruf-Nr., vol. 37 (PB L52005), 1940, pp. 67–76; Chem. Abs., vol. 41, 1947, p. 6551.

[3] Plattner, P. A., Newer Methods of Preparative Organic Chemistry: Interscience Publishers, Inc., New York, 1947, pp. 25–54.

[4] Orchin, M., Hydrogenation of Anthracene by Tetralin: Jour. Am. Chem. Soc., vol. 66, 1944, pp. 535–538.

DEHYDROGENATION OF TAR ACIDS BOILING AT 162° C. AT 40 MM.

Three grams of fraction 105 (table 10), b. p. 162° C. at 40 mm., containing 0.3 gm. of 30-percent palladium-on-charcoal were heated at 270°–285° C. for 2 hours and at 295°–300° C. for 30 minutes. The product was then distilled at atmospheric pressure and boiled at 300°–330° C. The ultraviolet absorption spectrum (fig. 17) of this material was identical with that of the original fraction. The gas liberated in this reaction was negligible, whereas tetrahydronaphthol and cyclohexylphenol, as previously shown in model compound studies, liberated hydrogen under the same conditions to give naphthol and phenylphenol, respectively. Failure to liberate hydrogen under dehydrogenating conditions, together with the identity of the ultraviolet absorption spectrum of fraction 105 before and after dehydrogenation, ruled out the presence of hydrogenated phenols in this fraction.

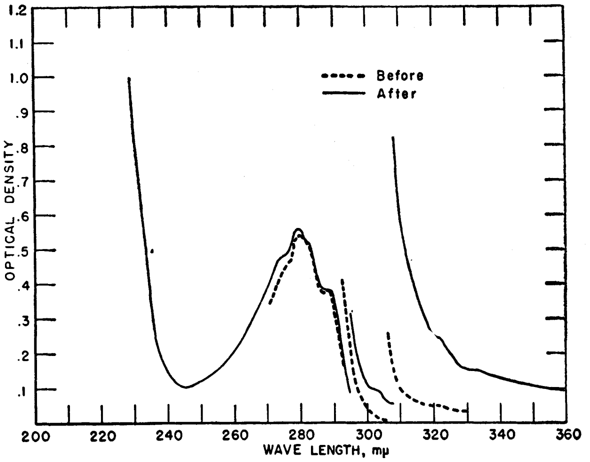

Figure 17.—SPECTRA OF FRACTION 105 BEFORE AND AFTER DEHYDROGENATION.

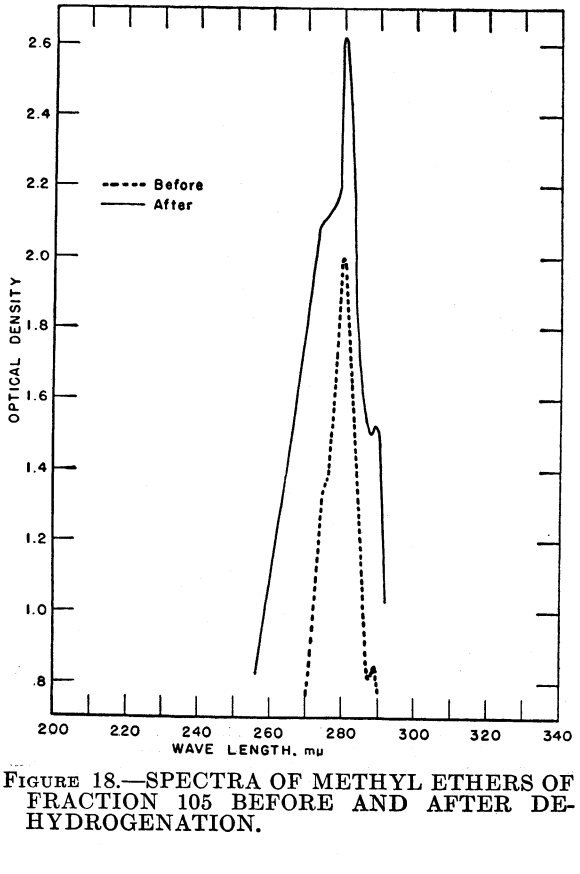

Figure 18.—SPECTRA OF METHYL ETHERS OF FRACTION 105 BEFORE AND AFTER DEHYDROGENATION.

The methyl ethers of fraction 105 were prepared through the dried potassium salts of the phenols by the method previously described. No gas was evolved on treatment of these ethers with palladium-on-charcoal, and no change could be observed in the ultraviolet spectra (fig. 18) of the ethers.

DEHYDROGENATION STUDIES ON TAR ACIDS BOILING AT 179°–183° C. AT 30 MM.

The methyl ethers of fraction 126–127 (table 10) were prepared. A mixture of 2 gm. of the methyl ethers and 0.2 gm. of 30-percent palladium-on-charcoal was heated over a period of 90 minutes as the temperature was gradually raised from 220° C. to 340° C. There was evolved 167 ml. of gas (N. T. P.), which was shown by mass spectrographic analysis to be 99 percent hydrogen. The reaction mixture

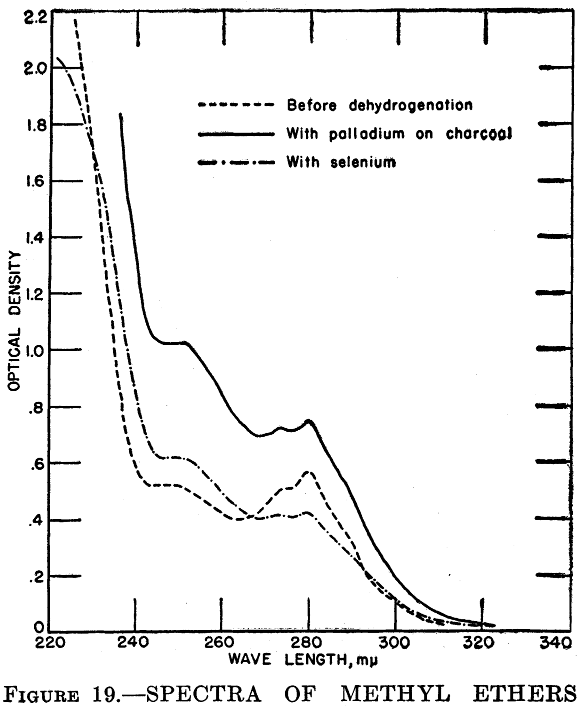

Figure 19.—SPECTRA OF METHYL ETHERS FROM FRACTION 126–127.

was chromatographed on alumina-celite (1:1 by volume). The percolate gave 1.6 gm. of oil having an intense blue fluorescence. As the ultraviolet absorption spectra (fig. 19) of the methyl ethers before and after dehydrogenation were identical, it was concluded that no partly hydrogenated polynuclear aromatic ring systems were present in these tar-acid distillates. The appreciable volume of hydrogen liberated in this experiment could not be explained.

Because it was possible that a small amount of polynuclear aromatic material was present that could not be detected by ultraviolet absorption measurements, an attempt was made to detect the presence of such substances by molecular complex formation with 2,4,7–trinitrofluorenone.[5] A warm saturated solution of 1 gm. of 2,4,7-trinitrofluorenone in absolute ethanol was added to a warm solution of 1 gm. of the dehydrogenation product in absolute ethanol. A deep-red color was observed on mixing the two solutions. A very few dark-red crystals were formed on standing. These were filtered, and after several recrystallizations from alcohol, benzene, and acetic acid a pure compound was not obtained. The molecular complex was then decomposed on alumina-celite (1:1 by volume), and the ultraviolet absorption spectrum (fig. 20) of the recovered material was determined. This indicated a mixture of polynuclear aromatic compounds. The band at 252 mμ indicated anthracene or phenanthrene. However, the presence of bands from 290 to 330 mμ and the absence of bands beyond 340 mμ excluded anthracene and suggested the presence of phenanthrene in very small amount. The structure exhibited between 260 mμ and 325 mμ, and the very strong band at 232 mμ indicated a naphthalenic structure as the major component of the mixture.

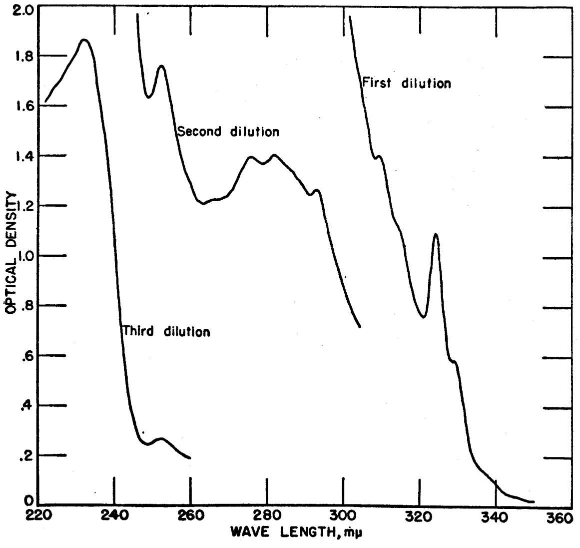

FIGURE 20.—SPECTRUM OF MATERIAL ISOLATED THROUGH T. N. F. COMPLEX FROM FUNCTION 126–127.

It is interesting to note that although hydrogen was evolved in the dehydrogenation of these ethers and ultraviolet absorption measurements gave evidence of the presence of phenanthrene and naphthalene type structures in the dehydrogenated material, methoxyl determinations indicated no demethoxylation. The methoxyl number of the ethers before dehydrogenation was 14.73 percent and after dehydrogenation was 14.64 percent. Experiments made with model compounds showed that dehydrogenation of hydroaromatic ethers is always accompanied by hydrogenolysis of the methoxyl group.

Selenium dehydrogenation of the methyl ethers of fraction 126–127 was attempted. A mixture of equal quantities of the ethers (11.3 gm.) and powdered selenium (11.3 gm.) was heated for 19 hours. Red selenium was still being collected in the bleaching-powder trap[6] when the reaction was stopped. The reaction mixture was dissolved in benzene, filtered, and treated with Norit. A clear solution was obtained on filtering. This was extracted with Claisen alkali. The alkali extract, on acidification, gave 0.35 gm. of oil, which was discarded. Distillation of the neutral material at 3 mm. gave 6.3 gm. of oil. The ultraviolet absorption spectrum (fig. 19) of this material showed no significant differences from the ultraviolet absorption spectrum of the original ethers.

It is apparent, on considering the results of the foregoing experiments, that positive evidence for either the presence or absence of partly hydrogenated polynuclear aromatic ring systems in the higher-boiling tar-acid distillates was not obtained.

COUNTERCURRENT DISTRIBUTION OF HIGHER-BOILING FRACTIONS

Those fractions (85 and above) that represent the pronounced peaks and valleys of the refractive index-boiling point curve (fig. 12) were examined by the countercurrent distribution technique. The countercurrent distributions (53 plates) were carried out in the 54-tube Craig countercurrent instrument[7] in the following manner: A 60-mg. sample was employed in each distribution except for fraction 85, in which a 50-mg. sample was used. The immiscible phases were cyclohexane (spectrographic

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[5] Orchin, M., and Woolfolk, E. O., Molecular Complexes with Trinitrofluorenone: Jour. Am. Chem. Soc., vol. 68, 1946, p. 1727; Orchin, M., Reggel, L., and Woolfolk, E. O.: vol. 69, 1947, p. 1225.

[6] Work cited in footnote 3.

[7] Work cited in footnote 34.

grade) and 0.5M alkaline phosphate. The detailed procedure for operating the Craig countercurrent distribution instrument has been reported.[8] At the end of each run the material of each tube was acidified with HCl and then shaken to permit the phenol in the buffer phase to pass into the cyclohexane layer. Ultraviolet measurements of this layer were made with the Beckman model DU quartz spectrophotometer at the wave lengths at which the original fraction exhibited selective absorption. In those instances in which the entire ultraviolet spectral curves were desired, the Cary recording spectrophotometer was employed.

Infrared measurements were made on a Perkin-Elmer infrared spectrometer. As the minimum sample usually required for infrared spectroscopy is about 100 mg., a micro-technique was devised for infrared examination of samples containing as little as 1–5 mg. of material. By simple evaporation of solvent from a very small piece of rock salt, a film of phenols was obtained which was adequate for spectra determination.

FRACTION 85. ISOLATION OF 4-INDANOL

The countercurrent distribution curve of this fraction is given in figure 21, and the information obtained by detailed interpretation of this curve is summarized in table 11. It is apparent that fraction 85 contains a minimum of five components and that the component exhibiting selective absorption at 277 mμ in the original fraction is concentrated in tubes 0–6.

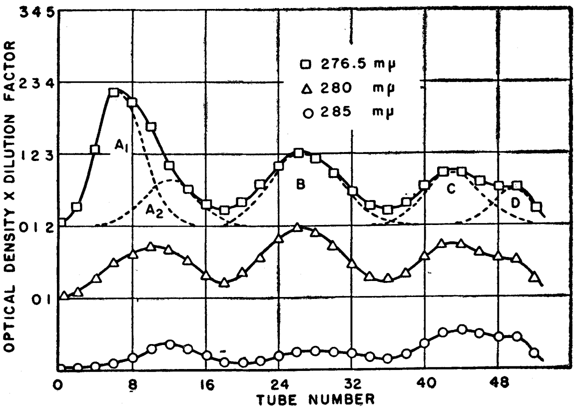

FIGURE 21.—DISTRIBUTION OF FRACTION 85. – – –, THEORETICAL CURVES.

The ultraviolet spectral absorption curve for the components responsible for the major distribution band A is identical to that of 4-indanol. The isolation of this component is described below. Isolation of the other components of this fraction was not attempted, but considerable information on their structural characteristics was obtained. The ultraviolet absorption spectra of distribution bands B and C were similar to those given by alkyl-substituted phenols. Their infrared absorption spectra indicated a meta configuration. The infrared absorption spectra for distribution bands A_2 and D indicated that the former contained 3-methyl-5-ethyl phenol and the latter, a 2,5-dialkyl phenol structure.

On the basis of the value obtained for the partition coefficient of component A, a scheme was devised for extracting it on a large scale from fraction 85. The detailed procedure follows. Five grams of this fraction was dissolved in 1 liter of 0.7M phosphate buffer of *p*H 12.1. This solution was extracted continuously with cyclohexane for 6 hours in a liquid-liquid extractor. The aqueous phase was removed, thoroughly shaken with three 1-liter portions of fresh cyclohexane, and then acidified with concentrated hydrochloric acid. The liberated phenol was extracted with 1 liter

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[8] Work cited in footnote 34.

TABLE 11.—*Countercurrent distribution analysis of fraction 85* [1]

Distribution band	Approximate percent	Partition coefficients [2]		*p*K	Ultraviolet analysis	Infrared analysis	Probable composition
		k'	*k*				
A	[3] 44	0.13	5.3	10.2	4-indanol spectrum	4-indanol spectrum	4-indanol.
A	[3] 11	.29			4-indanol + a meta and/or ortho alkyl-substituted phenol.	4-indanol + 3-methyl-5-ethyl phenol.	3-methyl-5-ethyl phenol.
B	30	1.0			Meta and/or ortho alkyl-substituted phenol.	Meta-substituted phenol.	Alkyl-substituted phenol.
C	15	13.9			do	do	Do.
D	5	0.0			Meta and/or ortho alkyl-phenol and some para-alkyl phenol.	1,2,5-structure	Do.

[1] The countercurrent distribution was run at *p*H 11.90.
[2] Partition coefficients at *p*H of distribution and at acidic *p*H, respectively.
[3] Accurately determined value.

of cyclohexane. The residue obtained upon evaporation of the cyclohexane consisted of 1.9 gm. of crystalline material, which, after recrystallization from petroleum ether (b. p. 30°–60° C.), melted at 47°–48° C.

Analysis, percent:
  Calculated for $C_9H_{10}O$: C, 79.85; H, 7.51.
  Found: C, 79.68; 79.85; H, 7.58, 7.64.
Neutral equivalent of the aryloxyacetic acid:
  Calculated for $C_{11}H_{12}O_3$: 192.
  Found: 192.

As the melting point of this phenol (47°–48° C.) and that of its aryloxyacetic acid (182° C.) are identical with those reported for 4-indanol and 4-indanyloxyacetic acid,[9] respectively, its identity is established.

The quantity of 4-indanol in the fraction was calculated according to the method of Williamson and Craig.[10] A value of 46 percent was obtained, which compares with 53 percent determined from the infrared curve of the original fraction.

FRACTION 93

The countercurrent distribution of this fraction is summarized by the distribution pattern (fig. 22) and the data of table 12. One component (band B) accounts for 70 percent of the fraction. A crystalline substance was isolated from the material in the tubes of band B, but the amount was insufficient for identification. Attempts to carry out large-scale isolation were unsuccessful. From the information recorded in table 12, it is probable that component B is a symmetrical dialkyl phenol, possibly 3,5-diethylphenol.

The material present in band A is a mixture of 4- and 5-indanols. The latter compound, but not the former, has a strong absorption band at 289 mμ, and it is interesting to note that the ultraviolet measurements of tubes 0–10 at this wave length (lowest curve in band A) indicate strongly the presence of 5-indanol.

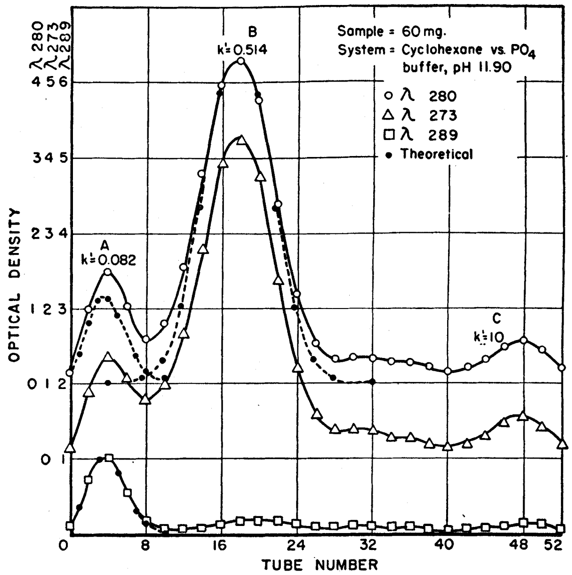

FIGURE 22.—DISTRIBUTION OF TAR-ACID FRACTION 93.

TABLE 12.—*Countercurrent distribution analysis of fraction 93*

Distribution band	Approximate percent	Partition coefficients [1]		*p*K	Qualitative ultraviolet analysis	Qualitative infrared analysis	Probable composition
		k'	*k*				
A	[2] 13 [2] 5	0.028 .082			Bands at 277 mμ and 289 mμ indicative of a mixture of 4- and 5-indanol.	4-indanol present (17 percent).	4-indanol + 5-indanol.
B	70	.514	26.9	10.2	Ortho- or meta-substituted phenol.	Symmetrical configuration.	Symmetrical dialkylphenol; possibly 3, 5-diethyl phenol.
C	10	9.6			Mixture of ortho and/or meta types.		Unknown.

[1] Partition coefficients measured against alkaline ($pH=11.9$) and acidified ($pH=1$) buffer, respectively.
[2] These are accurately determined values.

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[9] Kruber, O., and Schmieden, W. [The Phenols of Coal-Tar Heavy Oil]: Ber. Deut. chem. Gesell., vol. 72B, 1939, pp. 653–656.

[10] Work cited in footnote 35.

FRACTION 99. ISOLATION OF 5-INDANOL

Figure 23 shows the results obtained in a 53-plate distribution of fraction 99. Three distinct bands of varying heights are apparent by ultraviolet analysis, indicating the presence of one major component (A) and two minor components (B and C). Comparison of the experimental measurements with the theoretical calculations (solid dots) shows that component A is freer from overlapping bands than are the other constituents. Its isolation was achieved in the following manner: Ten grams of this fraction was dissolved in 1 liter of 0.75M phosphate buffer of *p*H 11.9. This solution was shaken well with five 1-liter portions of cyclohexane and acidified with concentrated HCl. The liberated phenol was extracted with 1 liter of cyclohexane. Removal of the solvent left 1.9 gm. of crystalline material, which, after two recrystallizations from petroleum ether (b. p. 60°–68° C.), melted at 52.4°–53.8° C. The aryloxyacetic acid of this phenol melted at 157.4°–158.8° C. and had a neutral equivalent of 192. These values are identical with those previously reported [11] for 5-indanol and 5-indanyloxyacetic acid, respectively. After determination of the extinction coefficient of 5-indanol, the amount present in the original fraction was calculated and found to be 44 percent compared to 41 percent by infrared measurement.

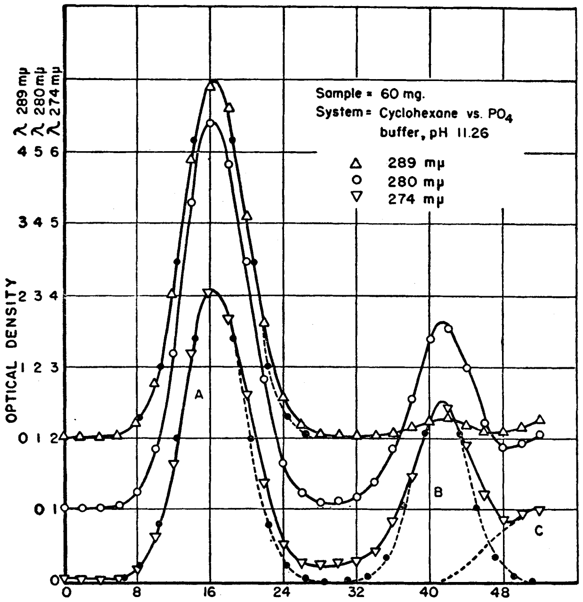

FIGURE 23.—DISTRIBUTION OF FRACTION 99.

Additional information on the relative amount and structure of components of fraction 99, which was obtained by the distribution analysis and by qualitative ultraviolet and infrared examination of peak tubes, is recorded in table 13. Component C showed no characteristic oxygenated functions in the infrared analysis and is probably hydrocarbon in nature. Very likely this hydrocarbon material was entrained in the tar-acid mixture during the original alkaline extraction of the heavy oil despite special precautions to prevent such entrainment.

FRACTION 102

The results of a 53-plate distribution of this fraction are plotted in figure 24. Interpretation of the distribution curve in the usual way (table 14) shows that this fraction is composed of a mixture of 5-indanol, 5-indanol homologues, and meta and/or 3,5-dialkyl-substituted phenols

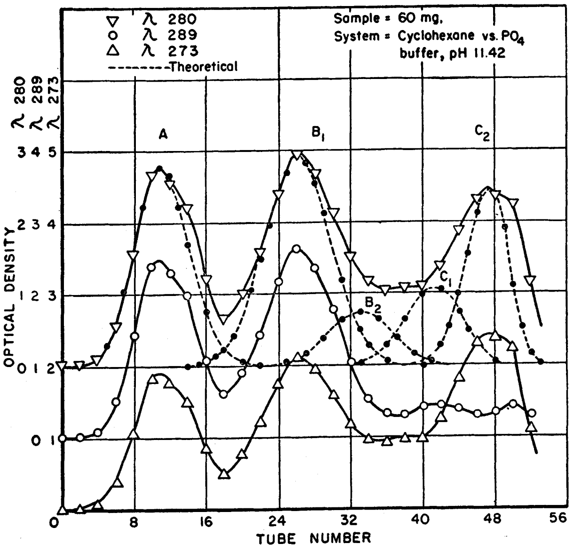

FIGURE 24.—DISTRIBUTION OF FRACTION 102.

No isolation experiments were attempted for this fraction.

FRACTION 105

A 53-plate distribution of this fraction gave the distribution pattern shown in figure 25. It is apparent that this fraction has one major component (A_2) and a number of minor constituents. The concentration and properties of the components, which can be deduced from the distribution curve and from the complete ultraviolet and infrared spectra of peak tubes, are summarized in table 15.

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[11] Kruber, O., and Marx, A. [The Phenols of Coal-Tar Heavy Oil. II.]: Ber. Deut. chem. Gesell., vol. 73B, 1940, pp. 1175–1177.

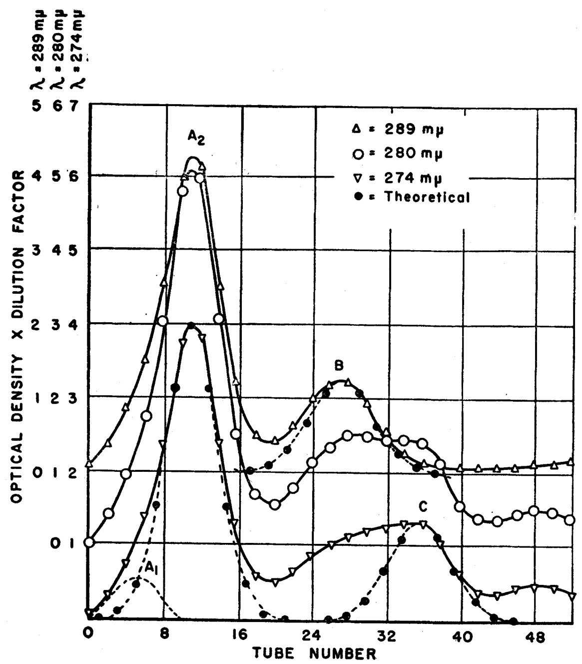

Figure 25.—DISTRIBUTION OF FRACTION 105.

The ultraviolet spectrum and ionization constant (*pK*) of component A_2 are almost identical with those of 5-indanol, but its partition coefficients (k' and k) are twice as great. Component A_2 is very likely a homologue of 5-indanol.

The ultraviolet spectrum of the material in the region of tubes 24 to 28 indicates the presence of phenols with para configuration, whereas, in the vicinity of tube 36, the spectra indicate ortho- and/or meta-substituted phenols.

Aryloxyacetic acid derivative.—The aryloxyacetic acid of fraction 105 (table 10) was prepared. Five recrystallizations from petroleum ether (b. p. 60°–68° C.) did not give a constant melting compound. Determination of the neutral equivalent of the recrystallized acid gave a result that was consistent with the formulation of the compound as an aryloxyacetic acid of either a methylindanol or a C_{10} mononuclear phenol.

N.E., calculated for $C_{12}H_{14}O_3$ (methylindanyloxyacetic acid), 206 for $C_{12}H_{16}O_3$ (C_{10} phenoxyacetic acid), 208. Found: 207.

Table 13.—*Countercurrent distribution analysis of fraction 99*

Distribution band	Amount, approximate percent	Partition coefficients [1]		*p*K	Qualitative ultraviolet analysis	Quantitative infrared analysis	Probable composition
		k'	*k*				
A	[2] 44	0. 44	5. 4	10. 2	5-indanol spectrum	5-indanol spectrum	5-indanol.
B	30	3. 1	2. 1	------	Spectrum of simple *o*- or *m*-alkyl-substituted phenol.	Meta alkyl and/or 3,5-dialkyl phenol; may be same as band B of fraction 93.	Alkyl-substituted phenol.
C	10	2. 6	------	------	No definite structure discernible.	Probably hydrocarbon	Unknown.

[1] Partition coefficients at *p*H of distribution and at acidic *p*H, respectively.
[2] Accurately determined value.

Table 14.—*Countercurrent distribution analysis of fraction 102*

Distribution band	Approximate percent	Partition coefficients [1]		*p*K	Ultraviolet analysis	Infrared analysis	Probable composition
		k'	*k*				
A	[2] 18	0. 27	6. 2	10. 1	5-indanol type spectrum.	Mainly 5-indanol	5-indanol.
B_1	30	. 97	20	10. 1	do	Bands corresponding to 5-indanol, other bands unidentified.	Homologues of 5-indanol.
B_2	10	1. 65	------	------			
C_1	10	3. 4	------	------	Mixture, ortho and/or meta types.	Mixture of meta and 3,5-dialkylphenols. Possibly homologues of phenols in band B, fraction 99.	Mixture of alkyl-substituted phenols.
C_2	20	7. 8	------	------			

[1] Partition coefficients measured against buffer of *p*H 11.42 and *p*H 1, respectively.
[2] Accurately determined value.

TABLE 15.—*Countercurrent distribution analysis of fraction 105*

Distribution band	Approximate percent	Partition coefficients [1]		pK	Ultraviolet analysis	Infrared analysis	Probable composition
		k'	k				
A_1	5	0.10			5-indanol spectrum		5-indanol.
A_2	50	.26	13.2	10.2	do	5-indanol+unknown constituent.	Possibly a homologue of 5-indanol.
B	20	1.0				Phenols with para configuration.	Meta, perhaps also 1,2,5 and 1,3,5-structures.
C	20	2.1			Ortho and/or meta phenols.	Apparently same as band B.	Alkylphenol mixture.

[1] Partition coefficients measured against alkaline ($pH=11.9$) and acidified ($pH=1$) buffer, respectively.

ISOLATION EXPERIMENTS ON FRACTIONS 105–107

Attempts to isolate and identify individual components of fraction 105–107 were unsuccessful. However, the following experimental data support partition and spectroscopic evidence that the principal components in this fraction probably are methyl-5-indanols and C_{10} phenols of symmetrical configuration.

Oxidation of methyl ethers.—The methyl ethers of fraction 106–107 (table 10) were prepared from the dried potassium salts of 42 gm. of the phenolic mixture and dimethyl sulfate.[12] To 34 gm. of the ether mixture suspended in a solution of 90 gm. of sodium hydroxide in 900 ml. of water, a solution of 316 gm. of potassium permanganate in 3,000 ml. of water was added over a period of 3 hours. The solid manganese dioxide was filtered, the water in the filtrate was evaporated, and the dry residue was acidified with concentrated hydrochloric acid. The resulting mixture was filtered. The insoluble portion was extracted with ether, and the ether solution was filtered from a small amount of inorganic material. The acidic substances soluble in ether were converted to their methyl esters by treating their ether solution with an ether solution of diazomethane. Evaporation of the ether gave 13 gm. of crystalline material. This was recrystallized three times from methanol and yielded 4 gm. of product melting at 110°–112° C. A mixed melting point with an authentic sample of dimethyl-5-methoxyisophthalate showed no depression. The isolation of this ester from the oxidation products of the methyl ethers of tar-acid fraction 106–107 suggested that a dimeta-substituted phenol was present.

The water-soluble organic acids produced in the permanganate oxidation were extracted with ether in a continuous liquid-liquid extractor for 2 weeks. The ether extract was concentrated and then treated with an ether solution of diazomethane. Evaporation of the solvent gave 10 gm. of oil that could not be crystallized. The oil was dissolved in benzene and extracted with 10-percent sodium bicarbonate. Evaporation of the benzene gave an oil that still could not be crystallized. It was then distilled at 6 mm., and three fractions were collected, which boiled, respectively, at 150°–190° C., 190°–200° C., and above 200° C., at which temperature decomposition occurred. The 150°–190° C. fraction could not be crystallized, and no further work on it was attempted.

The fraction boiling above 200° C., on recrystallization from methanol, melted at 174°–182° C., but insufficient material for further work remained.

Crystallization of the 190°–200° C. fraction from methanol gave two constant-melting compounds, one melting at 144.2°–145.2° C. and the other at 184.2°–186.4° C. Ultimate analysis of the former coincided most nearly with the theoretical molecular formula, $C_{13}H_{14}O_7$, for a methoxybenzenetricarboxylic acid trimethyl ester.

Analysis, percent:
Calculated for $C_{13}H_{14}O_7$: C, 55.32; H, 4.50; O, 40.18. Found: C, 55.68, 55.88; H, 4.99, 5.19; O, 39.33, 38.93.

Search of the literature failed to reveal an ester consistent with the information given above.

The analytical data for the higher-melting compound could not be interpreted.

Analysis, percent:
Found: C, 62.11, 61.83; H, 4.42, 4.52.

Attempted isolation of the most acidic component.—Five and four-tenths grams of the combined fraction 105–107 (table 10) was dissolved in 1 liter of cyclohexane and extracted with a 1-liter portion of a phosphate buffer of pH 12.1. The organic phase was separated to give fraction 1. The buffer solution containing the most acidic components

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[12] Work cited in footnote 54.

was then extracted three successive times with 1-liter portions of cyclohexane to give fractions 2, 3, and 4. The buffer solution was acidified and again extracted with cyclohexane. Separation of the organic phase gave fraction 5. The cyclohexane was evaporated from the latter fraction, leaving a residue of 1.3 gm. of acidic material.

The separation accomplished in this experiment was followed by ultraviolet absorption measurements on the resulting five cyclohexane fractions. The results are shown in figure 26. It was observed that the shoulder at 275 *mμ* decreased from the first fraction to the fifth, whereas the shoulder at 289 *mμ* increased. The spectrum of the fifth fraction was almost identical with that of 5-indanol, whose spectrum also is shown in figure 26.

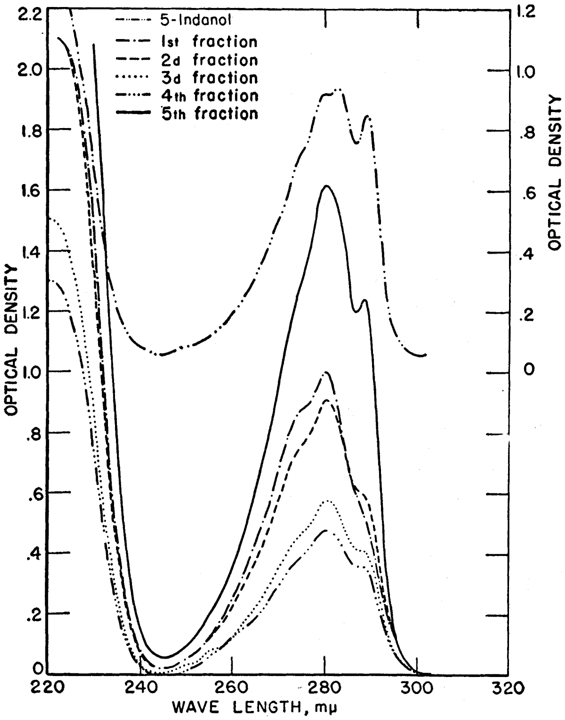

Figure 26.—SPECTRA OF PORTIONS OF FRACTION 105-107

The solvent was removed from fraction 5, and infrared absorption measurements on the residue indicated that it was a mixture containing about 9 percent of symmetrically substituted phenol. The concentration of di-meta-substituted phenol in the original fraction 105–107 was shown by infrared absorption to be approximately 18 percent.

The aryloxyacetic acid of 0.25 gm. of the residue from fraction 5 was prepared. Its neutral equivalent (207) was found to be consistent with either of the formulas considered above. Three recrystallizations of this derivative did not yield a pure, constant-melting compound.

As it was evident that the material obtained in the fifth cyclohexane fraction by the foregoing treatment of fraction 105–107 was a mixture, an attempt was made to purify it further. The most probable impurity was assumed to be 5-indanol itself. Partition studies showed that the partition coefficient for 5-indanol was about half that of the major component, A_2, of these fractions. In order, therefore, to effect further purification, the residue was taken up in 500 ml. of cyclohexane and shaken five times with 500-ml. portions of water. Evaporation of the cyclohexane solution gave 0.6 gm. of material that could not be crystallized. Preparation of the aryloxyacetic acid of this residue and three recrystallizations from petroleum ether (b. p. 60°–68° C.) again failed to give a pure compound.

An attempt was next made to purify the aryloxyacetic acid derivative through its amide. The aryloxyacetic acid (about 0.2 gm.) was dissolved in 5 ml. of ether, 1 ml. of thionyl chloride was added, and the mixture was refluxed for 1 hour. After evaporation of the solvent, 10 ml. of concentrated ammonium hydroxide was added to the residue, and the mixture was refluxed for 1 hour. A precipitate was formed on cooling. This was filtered and taken up in benzene, the benzene solution was extracted with 10-percent sodium bicarbonate solution, then dried, and the solvent removed by evaporation. The residue was recrystallized four times from a mixture of one volume of alcohol and two volumes of water. Crystallization of the amides indicated a mixture the higher-melting component of which melted at 161.2°–162.2° C. At this point the amount of amide remaining was sufficient only for a single carbon- and-hydrogen determination. The analytical data of the amide coincided more nearly with the theoretical molecular formula, $C_{12}H_{15}O_2N$, for an amide of indanyloxyacetic acid than for that of its methyl homolog, $C_{12}H_{15}O_2N$. A mixed melting point, however, of the unknown amide with an authentic sample of the amide of 5-indanyloxyacetic acid (m. p. 144°–145° C.) was depressed. The mixed melting point was 120°–128° C.

Analysis, percent:
  Calculated for $C_{11}H_{13}O_2N$ (amide of indanyloxyacetic acid): C, 69.09, H, 6.85.
  Calculated for $C_{12}H_{45}O_2$ (amide of methyl-indanyloxyacetic acid): C, 70.22, H, 7.37
  Found: C, 68.76, H, 6.61.

FRACTION 110–112

The countercurrent distribution pattern of this fraction and the information on composition obtained by detailed analysis of the distribution curves are given in figure 27 and table 16, respectively. It is evident that this fraction is a mixture of a number of alkylphenols and one or more 5-indanol homologues. Further identification by isolation of components was not attempted.

FRACTION 117–118. ISOLATION OF O-PHENYLPHENOL

A 53-plate distribution was run on fraction 117–118. As shown in figure 28, the distribution splits the fraction into three major portions or bands (A, B, and C). Data obtained by interpretation of this curve are given in table 17.

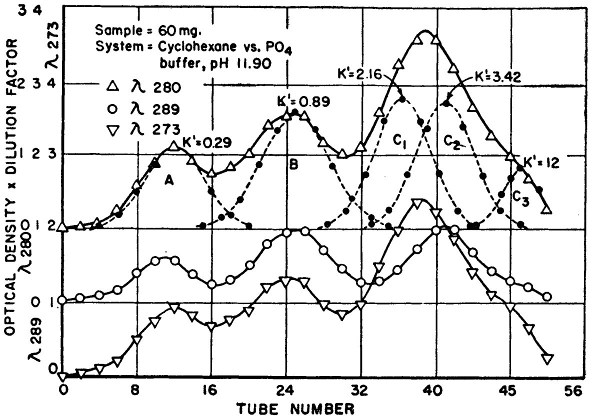

FIGURE 27.—DISTRIBUTION OF TAR-ACID FRACTION 110–112.

The ultraviolet spectrum of the material present in the peak tube of band A is that of a 5-indanol. On this basis, and from the values of the partition coefficients (k' and k), the ionization constant (pK) and the infrared spectrum of this component (table 17), it is concluded that band A represents a methyl homologue of 5-indanol. By combining the contents of tubes 4–14 and removing the solvent, an oil was obtained that crystallized upon cooling. A large-scale selective extraction of fraction 117–118 yielded a low-melting compound that could not be recrystallized to constant melting point.

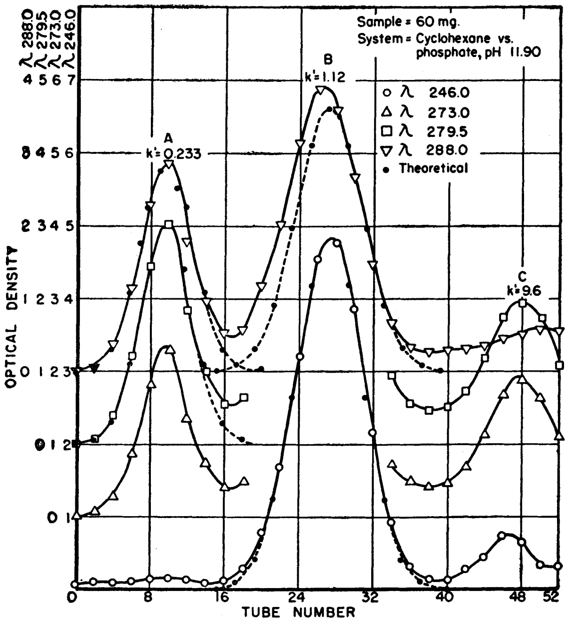

FIGURE 28.—DISTRIBUTION OF TAR-ACID FRACTION 117–118.

TABLE 16.—*Countercurrent distribution analysis of fraction 110–112* [1]

Distribution band	Approximate percent	Partition coefficient, k'	Qualitative ultraviolet analysis	Probable composition
A	15	0.29	5-indanol + alkylphenol spectra	5-indanol homologue + alkyl-substituted phenol.
B	30	.89	do	Do.
C$_1$	25	2.16	Ortho and/or meta substituted phenol	Alkyl-substituted phenol.
C$_2$	25	3.42	Mixture containing phenols with para configuration.	Alkyl-substituted phenols.
C$_3$	5	12.0	Ortho and/or meta substituted phenol	Alkyl-substituted phenol.

[1] This distribution was run at pH 11.90.

TABLE 17.—*Countercurrent distribution analysis of fraction 117–118*

Distribution band	Approximate percent	Partition coefficients [1]		pK	Ultraviolet analysis	Infrared analysis	Probable composition
		k'	k				
A	30	0.23	13.5	10.1	5-indanol type spectrum.		5-indanol homologue.
B	[2] 15	1.12			*o*-phenylphenol + alkyl-substituted phenol.	*o*-phenylphenol spectrum predominates.	*o*-phenylphenol + alkyl-substituted phenol.
C	40	9.6			Mixture, ortho and/or meta type.	Probably ortho types	Alkyl-substituted phenols.

[1] Measured against alkaline (pH=11.90) and acidified (pH=1) buffer, respectively.
[2] This is an accurately determined value.

Band B (table 17) of this fraction contains *o*-phenylphenol mixed with an alkyl-substituted phenol. The *o*-phenylphenol has a strong ultraviolet absorption band at 246 $m\mu$ in contrast to ordinary alkyl-substituted phenols, which have virtually no absorption at this wave length. The ultraviolet measurements of band B at 246 $m\mu$ (lowest curve) clearly pick up the presence of *o*-phenylphenol in tubes 16 to 40. The partition coefficient of *o*-phenylphenol was too close to that of the other component of band B to attempt isolation by selective extraction.

Isolation experiments on fraction 117–118. Selective extraction.—An extraction experiment analogous to that carried out for fraction 99 yielded crystalline material melting, after repeated crystallization from petroleum ether, at 49.4°–55° C. The substance had an ultraviolet spectrum typical of a 5-indanol but was obviously impure. Insufficient material for further purification was at hand.

Isolation of o-phenylphenol.—Forty grams of fraction 117 was converted to potassium salts and methylated with dimethyl sulfate;[13] 37 grams of neutral material was obtained. This was fractionally distilled at 30 mm. pressure in a 60.9-cm. long, 6-mm. micro Piros-Glover spinning-band column operating at approximately 2,000 r. p. m. The 32 fractions that were collected represented a total recovery of 90 percent.

A mixture of 0.67 gm. of fraction 31, 10 ml. of glacial acetic acid, and 5 ml. of 48-percent hydrobromic acid was refluxed for 19 hours. After cooling, the product was poured into a mixture of benzene and water. The benzene layer was separated and extracted successively with 10-percent sodium bicarbonate solution and Claisen's alkali. The alkaline layer was drawn off into a mixture of ice and concentrated HCl, and the precipitated material thus obtained was recrystallized twice from petroleum ether (b. p. 30°–60° C.). The melting point, 53.6°–55.0° C., was not depressed upon admixture with authentic *o*-phenylphenol. The aryloxyacetic acid (m. p. 97°–98° C.) was also identical with that prepared from *o*-phenylphenol.

FRACTION 125

The countercurrent distribution pattern of this fraction is given in figure 29. The information gained from a study of the distributed fraction is summarized in table 18.

It is noteworthy that 5-indanol structures are absent from this fraction. Band B exhibited an *o*-phenylphenol spectrum but had a partition coefficient about twice that of *o*-phenylphenol at the pH of distribution; hence, the constituent responsible for this band is probably a homologue of *o*-phenylphenol. The other constituents of this fraction appeared to be alkylphenols.

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[13] Work cited in footnote 54.

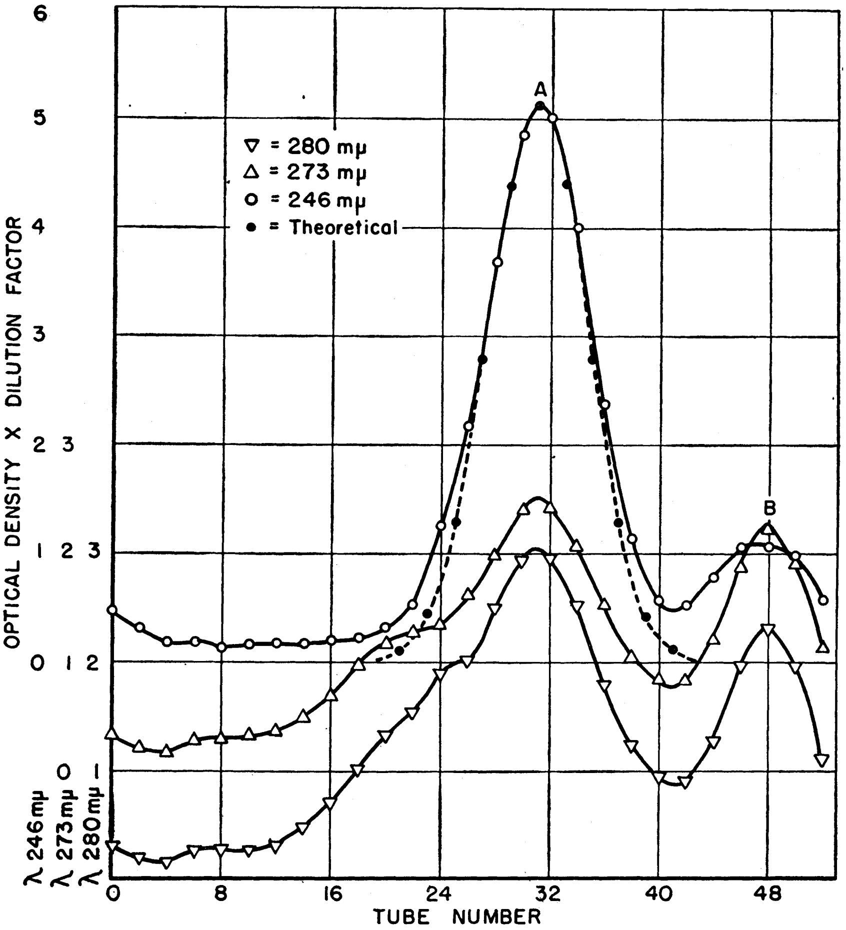

FIGURE 29.—DISTRIBUTION OF TAR-ACID FRACTION 125.

TABLE 18.—*Countercurrent distribution analysis of fraction 125* [1]

Distribution band	Approximate percent	k'	Qualitative ultraviolet analysis	Probable composition
A	[2] 17	1.41	*o*-phenylphenol spectrum	*o*-phenylphenol homologue.
B	50	9.8	Ortho and/or meta alkylphenols	Alkyl-substituted phenols.

[1] This distribution was run at *p*H 11.90.
[2] Accurately determined value.

FRACTION 129

The distribution pattern of this fraction (fig. 30) shows that it is a mixture of many compounds. For this reason, no isolation work was carried out on the fraction. The data summarized in table 19 indicate that 5-indanol homologues, *o*-phenylphenol homologues, alkylphenols, and possibly a little β-naphthol are present in the fraction.

FRACTION 135. ISOLATION OF *p*-PHENYLPHENOL

The distribution of this fraction at *p*H 12.54 disclosed the presence of three major components (fig. 31). Component A differs sharply from the other constituents in exhibiting strong selective absorption at 251 *mμ*. Also, it is a comparatively acidic phenol, because it concentrates at the extreme left of the distribution pattern. Component C is probably a mixture,

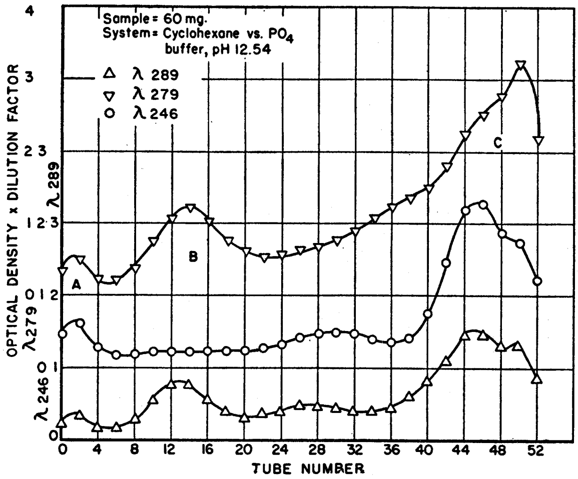

Figure 30.—DISTRIBUTION OF FRACTION 129.

because its experimental curve is wider than a theoretical one. Data on the ultraviolet spectra (table 20) of the components showed that they differ considerably in structure. Component A had the ultraviolet spectrum of *p*-phenylphenol. This compound was isolated and identified. Component B had the spectrum of 5-indanol. However, its partition coefficient is much higher than the parent compound, so that it is probably a homologue. The absorption curve for component C showed the structure in the 270–280 *mμ* region expected of an alkyl-substituted phenol. An unusual feature, however, appeared in the 240-250 *mμ* region. The doublet observed there has never been shown by any of the large number of pure phenols examined. When the absorption spectrum of component C was redetermined at a much higher concentration, the spectrum of phenanthrene emerged. Apparently, a small amount of this hydrocarbon has been carried over from the neutral oil during the original extraction of the tar-acid fraction from the coal-hydrogenation oil.

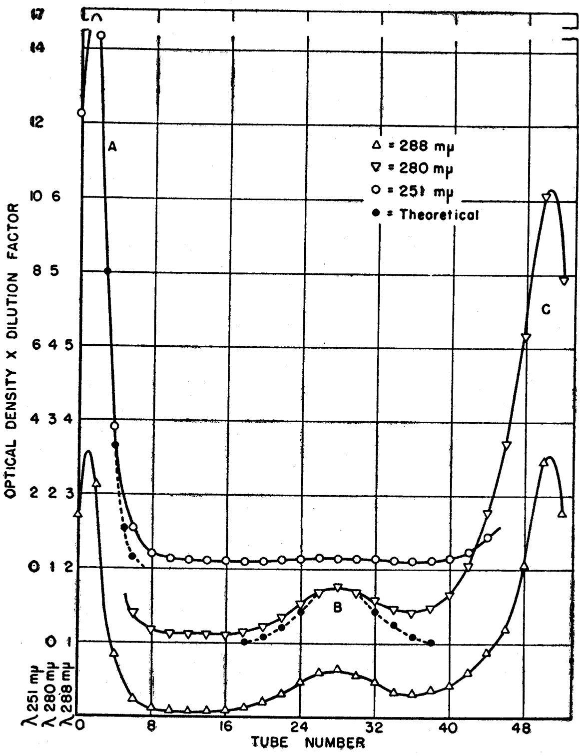

Figure 31.—DISTRIBUTION OF FRACTION 135.

Table 19.—*Countercurrent distribution analysis of fraction 129*

Distribution band	Approximate percent	k'	Qualitative ultraviolet analysis	Probable composition
A	5	0. 02	2-naphthol type spectrum	2-naphthol (?).
B	20	. 33	Mainly 5-indanol type spectrum	5-indanol homologue.
C	60	5. 6 and 12. 0	*o*-phenylphenol + alkylphenol type spectrum.	Mixture of *o*-phenylphenol homologue and alkylphenols.

Table 20.—*Countercurrent distribution analysis of fraction 135* [1]

Distribution band	Approximate percent	Partition coefficient	Qualitative ultraviolet analysis	Probable composition
A	[2] 8	0. 03	p-phenylphenol spectrum	p-phenylphenol.
B	15	1. 0	5-indanol spectrum	5-indanol homologue.
C	70	--------	Ortho and/or meta alkylphenols + phenanthrene.	Mainly alkyl-substituted phenols.

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[1] This distribution was run at *p*H 12.54.

[2] Accurately determined value.

Isolation of p-phenylphenol from fraction 135.—A portion of this fraction was dissolved in petroleum ether (b. p. 30°–60° C.) and cooled at 0° C. The crystalline material that separated was recrystallized from petroleum ether and finally from cyclohexane. The melting point of this substance, 163°–165° C., was not depressed upon admixture with the authentic compound.

INFRARED SPECTROMETRIC ANALYSIS

The theory and method of quantitative infrared analysis of tar-acid mixtures have been discussed in a previous section. The accuracy of the quantitative determinations on the phenol-cresol fractions and the lower-boiling xylenol fractions was ±1 percent, as described above from determined synthetic blends of these components. The higher boiling xylenol (C_8) fractions could not be analyzed completely because of the probable presence of C_9 tar acids, for which calibration spectra were not available. However, quantitative estimates of C_8 tar acids in these fractions were possible. In the C_9 range it was possible to make quantitative estimates of 3-methyl-5-ethylphenol, 4-indanol, and 5-indanol. The calibration spectra of these compounds were determined on authentic samples isolated in the present work. Analytical data for the higher-boiling tar-acid distillates could not be obtained.

The analytical data obtained from infrared analysis of the tar-acid distillates are shown in tables 21 and 22, and the information in these two tables in summarized in tables 23 and 24.

TABLE 21.—*Infrared determination of lower-boiling components* (C_6–C_8) *of tar-acid fractions, percent by weight*

Fraction [1]		Phenol	Cresols			Xylenols				Ethylphenols		
No.	Weight, gm.		Ortho-	Meta-	Para-	2,4-	2,5-	3,5-	3,4-	Ortho-	Meta-	Para-
4–7	86. 7	96. 8	3. 2									
8, 19, 20	23. 5	61. 9	38. 1									
21	25. 5	26. 7	73. 3									
22–24	74. 4	8. 8	91. 2									
25–30	94. 7		55. 0	30. 0	15. 0							
31–33	75. 0		12. 3	60. 5	27. 2							
34–40	177. 7		4. 8	63. 8	31. 4							
41–43	71. 8		2. 3	63. 0	34. 7							
44–47	102. 2			12		56	30			2		
48–51	100. 0			6		36	24			7	20	8
52–55	100. 3			5		10	9	3		3	55	17
56–61	128. 8							19		2	65	14
62	26. 0							63		1	33	3
63–65	[2] [3] 79. 8							47			36	
66	[3] 25. 0							40			12	
67	[3] 25. 0								16		1	
68–71	[3] 103. 5								16			

[1] The weight of the fractions was obtained by multiplying the volume of the fraction by the density.

[2] Infrared analysis was performed on the mother liquors after 32.0 gm. of 3,5-xylenol was separated from the fraction.

[3] Quantitative estimate; C_9's present.

TABLE 22.—*Infrared determination of higher-boiling components identified in tar acids, percent by weight*

Fraction		3-methyl-5-ethylphenol	4-indanol	5-indanol
No.	Weight, gm.			
72–76	127. 5	21	--------	--------
77–78	52. 0	55	--------	--------
79–82	100. 0	50	--------	--------
83	25. 0	20	22	--------
84	25. 0	18	37	--------
85	25. 0	17	53	--------
86	25. 5	16	41	--------
87	25. 0	--------	26	--------
88	25. 2	--------	22	--------
89–92	28. 8	--------	26	--------
93	25. 2	--------	16	--------
94	25. 2	--------	15	--------
95	26. 0	--------	14	15
96	26. 0	--------	13	20
97	25. 0	--------	13	22
98	25. 0	--------	12	29
99	25. 5	--------	10	41
100	25. 4	--------	7	40
101	14. 6	--------	6	30
102	25. 1	--------	5	25
103	25. 0	--------	4	18
104	25. 0	--------	3	10

TABLE 23.—*Distribution of the tar acids in phenol-through-xylenol range*

Compounds	Grams in tar-acid fractions	Percent of total tar acids	Percent of total C_6–C_8 fractions
Phenol	111. 5	2. 6	9. 3
o-cresol	169. 9	3. 9	14. 1
m-cresol	255. 7	5. 9	21. 3
p-cresol	115. 3	2. 7	9. 6
2,4-xylenol	103. 2	2. 4	8. 6
2,5-xylenol	63. 7	1. 5	5. 3
3,5-xylenol	115. 9	2. 7	9. 6
3,4-xylenol	20. 6	0. 5	1. 7
o-ethylphenol	14. 9	. 3	1. 2
m-ethylphenol	188. 0	4. 4	15. 6
p-ethylphenol	43. 8	1. 0	3. 6
Total	1, 202. 5	27. 9	99. 9

TABLE 24.—*Yields of tar acids from the hydrogenation of Bruceton coal*

Compound	Percent of hexane-soluble oil	Percent of total oil	Pounds per ton of total oil	Pounds per ton of coal [1]
Phenol	0. 24	0. 13	2. 6	2. 0
o-cresol	. 37	. 20	4. 0	3. 1
m-cresol	. 55	. 30	6. 0	4. 7
p-cresol	. 25	. 14	2. 8	2. 2
2,4-xylenol	. 23	. 13	2. 6	2. 0
2,5-xylenol	. 14	. 08	1. 6	1. 2
3,5-xylenol	. 25	. 14	2. 8	2. 2
3,4-xylenol	. 05	. 03	. 6	. 5
o-ethylphenol	. 03	. 02	. 4	. 3
m-ethylphenol	. 42	. 23	4. 6	3. 6
p-ethylphenol	. 09	. 05	1. 0	. 8
3-methyl-5-ethylphenol	. 27	. 15	3. 0	2. 3
4-indanol	. 19	. 10	2. 0	1. 6
5-indanol	. 13	. 07	1. 4	1. 1

[1] Dry, ash-free coal.

APPENDIX

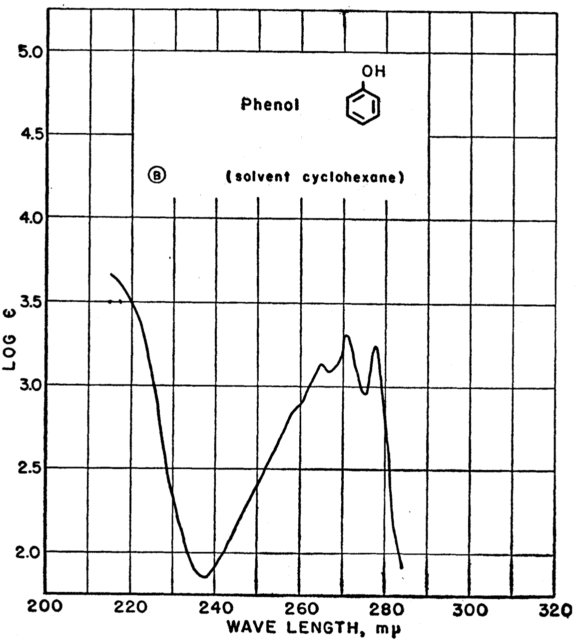

Figure 1a.—Ultraviolet spectrum of phenol.

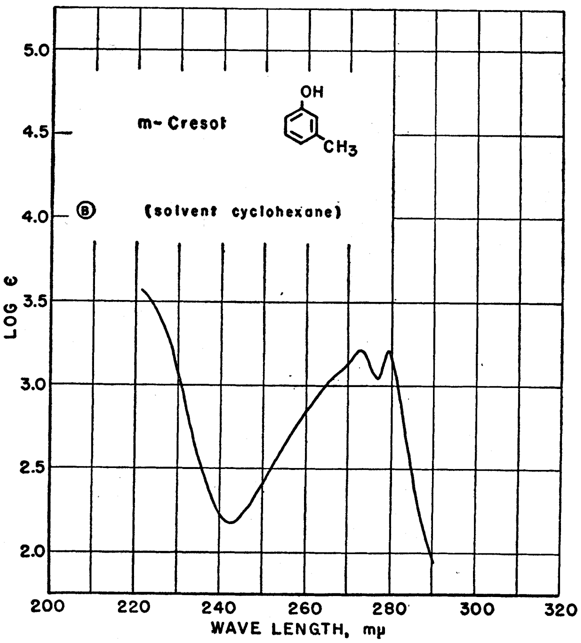

Figure 3a.—Ultraviolet spectrum of *m*-cresol.

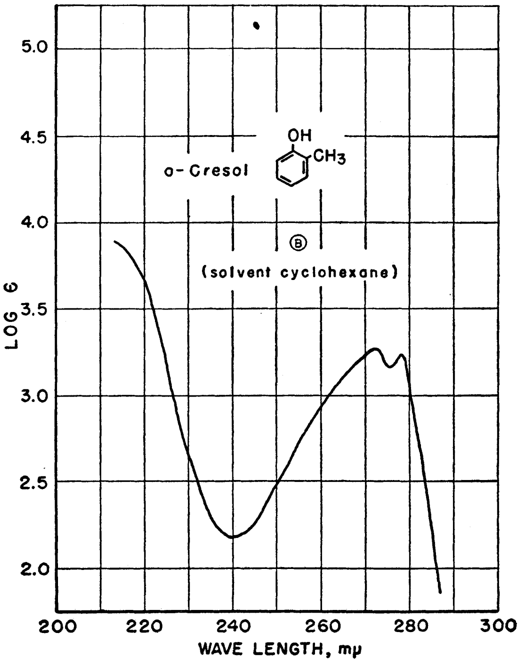

Figure 2a.—Ultraviolet spectrum of *o*-cresol.

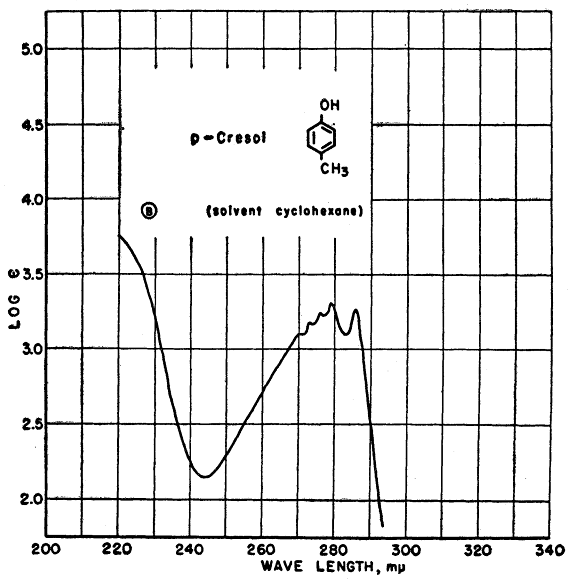

Figure 4a.—Ultraviolet spectrum of *p*-cresol.

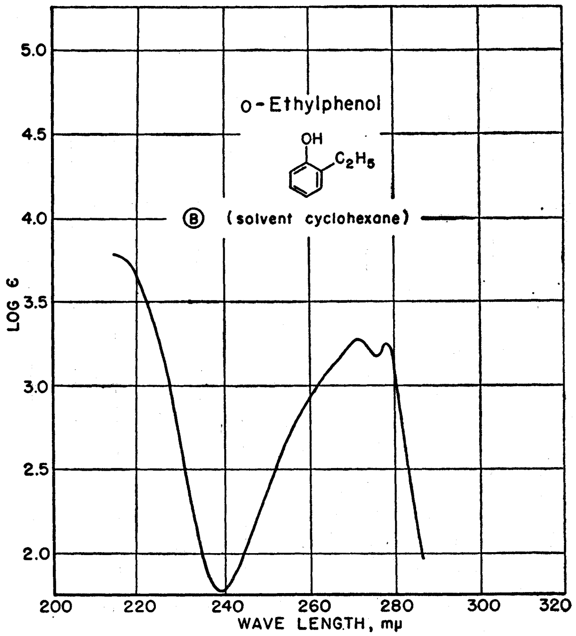

Figure 5a.—Ultraviolet spectrum of *o*-ethylphenol.

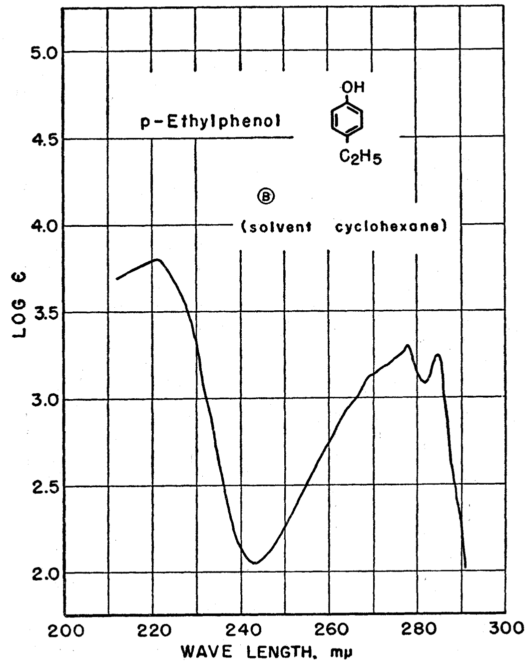

Figure 7a.—Ultraviolet spectrum of *p*-ethylphenol.

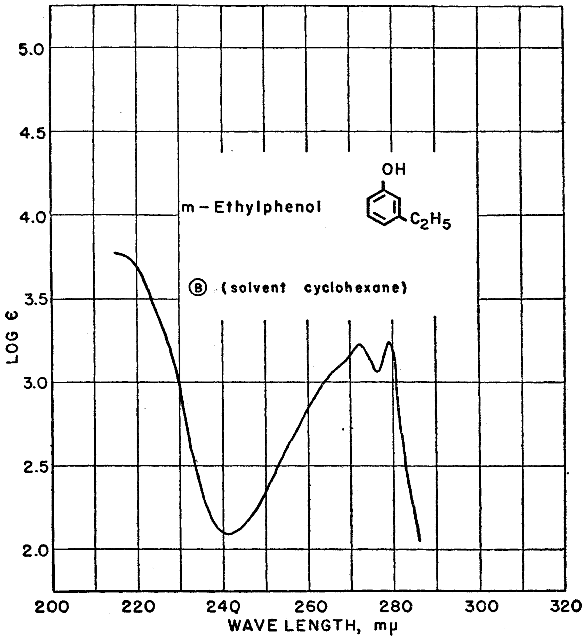

Figure 6a.—Ultraviolet spectrum of *m*-ethylphenol.

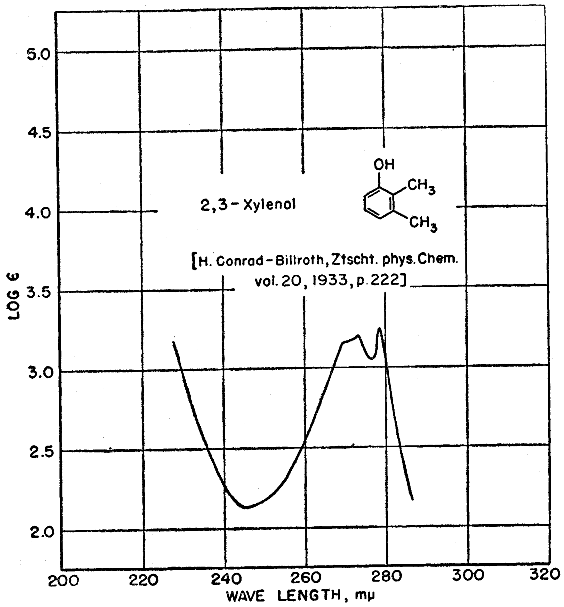

Figure 8a.—Ultraviolet spectrum of 2,3-xylenol.

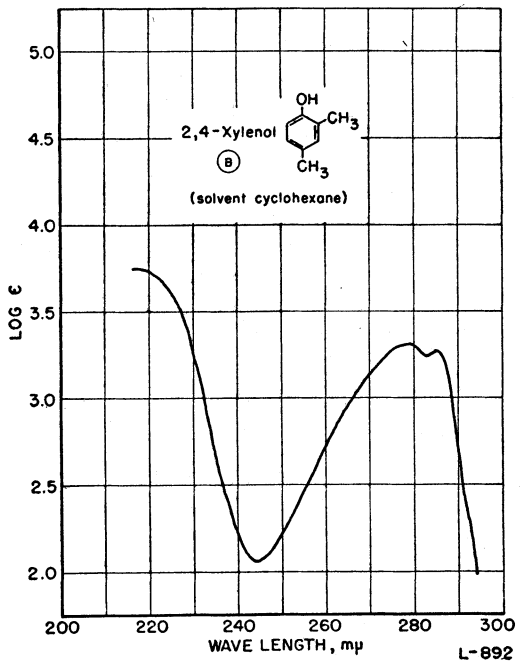

FIGURE 9a.—Ultraviolet spectrum of 2,4-xylenol.

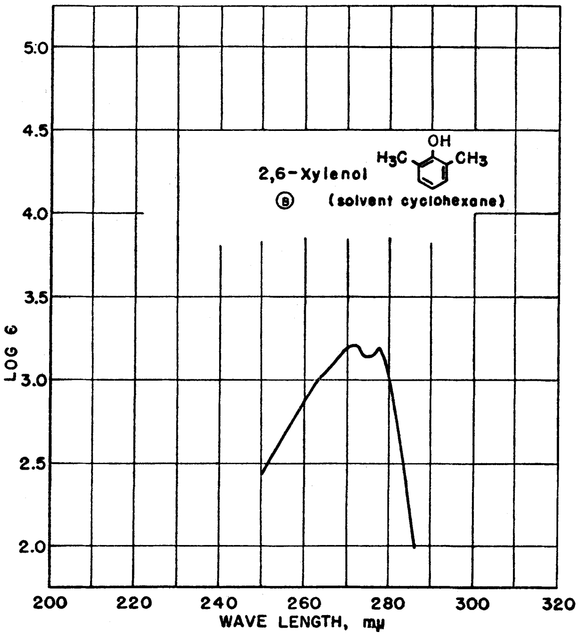

FIGURE 11a.—Ultraviolet spectrum of 2,6-xylenol.

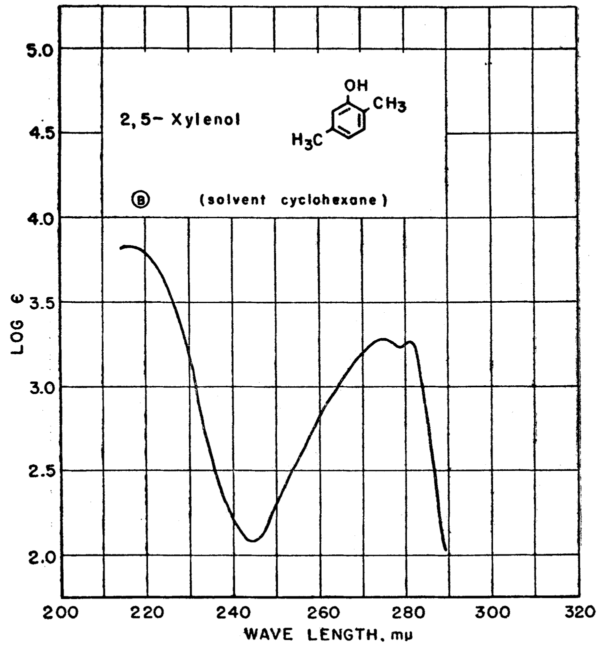

FIGURE 10a.—Ultraviolet spectrum of 2,5-xylenol.

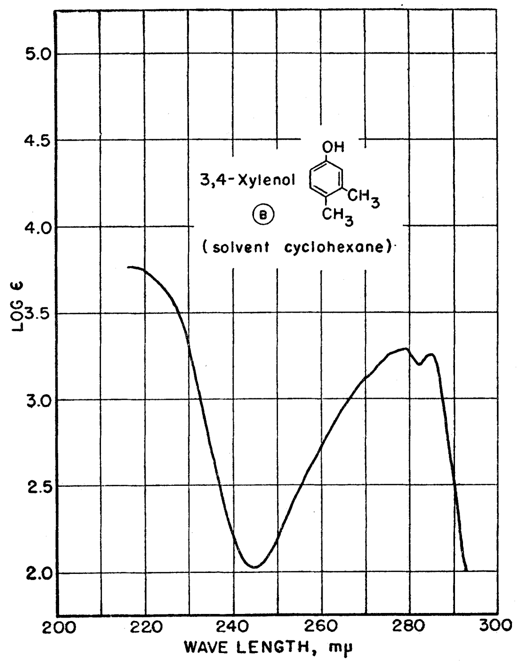

FIGURE 12a.—Ultraviolet spectrum of 3,4-xylenol.

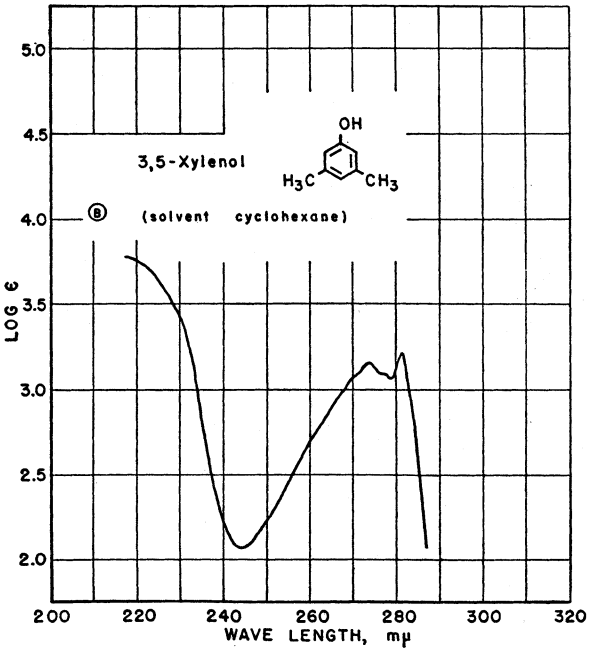

FIGURE 13a.—Ultraviolet spectrum of 3,5-xylenol.

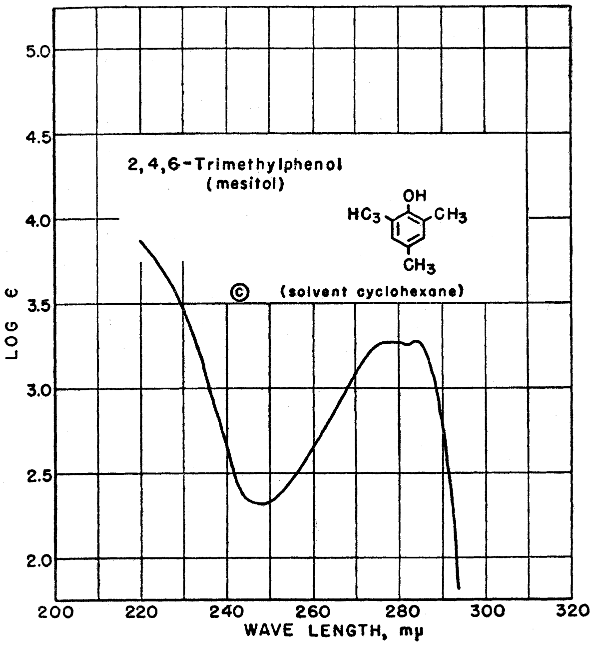

FIGURE 15a.—Ultraviolet spectrum of 2,4,6-trimethylphenol (mesitol).

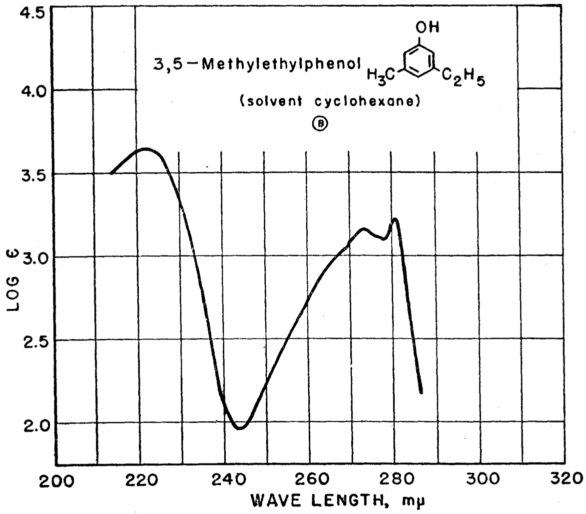

FIGURE 14a.—Ultraviolet spectrum of 3,5-methylethylphenol.

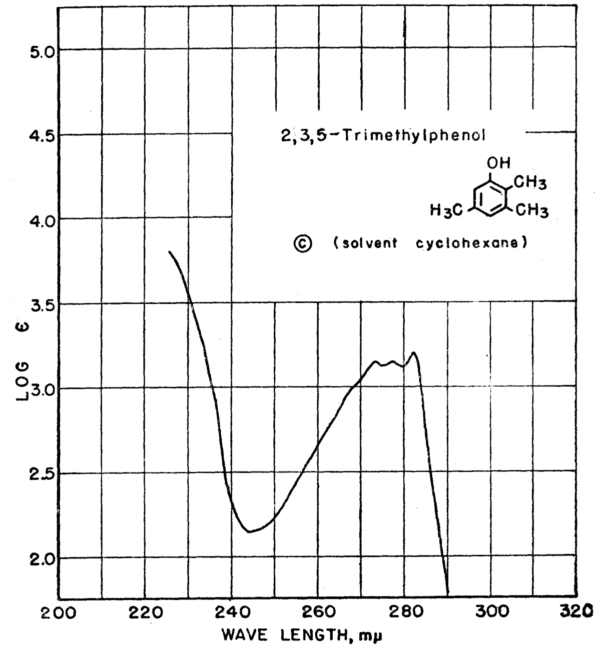

FIGURE 16a.—Ultraviolet spectrum of 2,3,5-trimethylphenol.

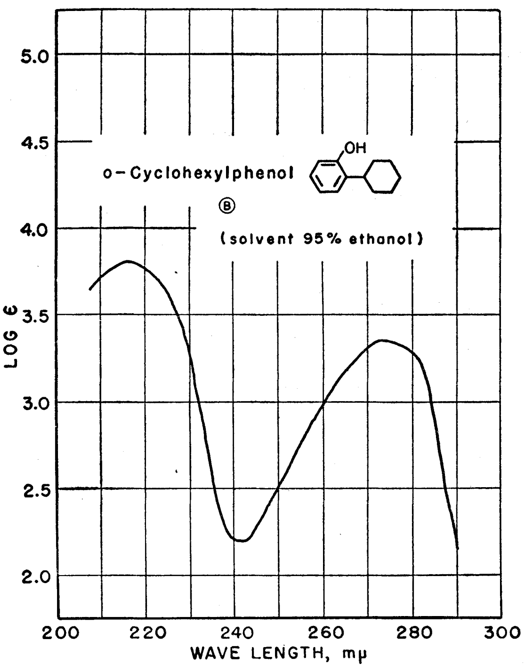

FIGURE 17a.—Ultraviolet spectrum of *o*-cyclohexylphenol.

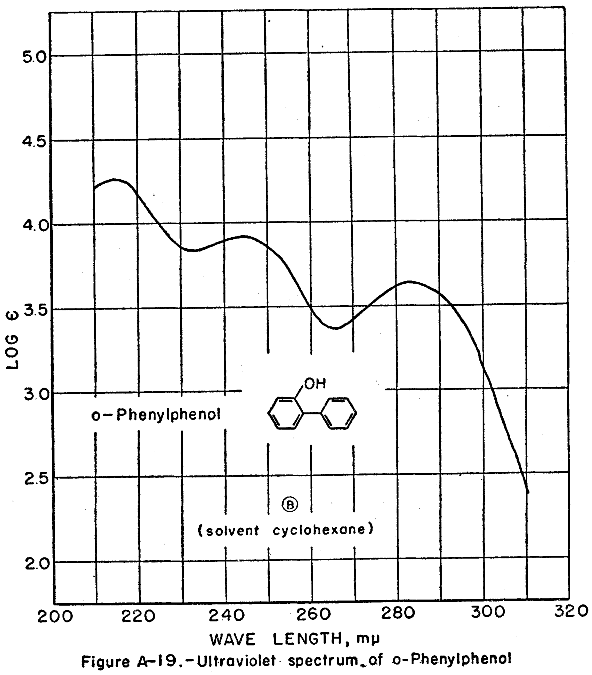

FIGURE 19a.—Ultraviolet spectrum of *o*-phenylphenol.

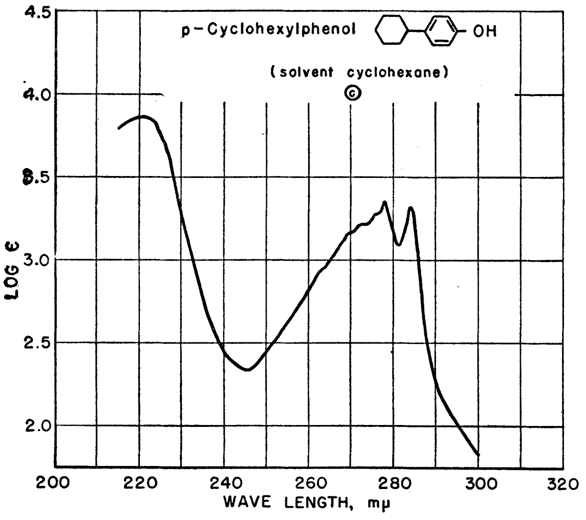

FIGURE 18a.—Ultraviolet spectrum of *p*-cyclohexylphenol.

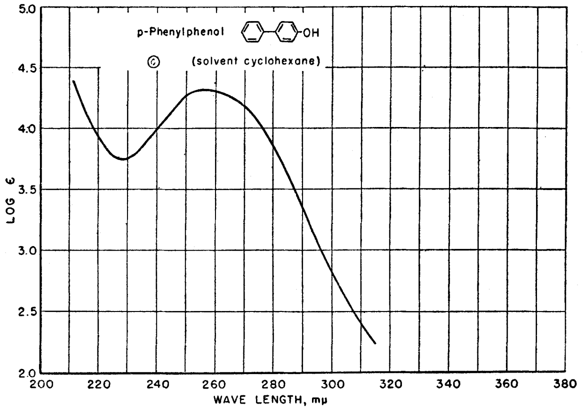

FIGURE 20a.—Ultraviolet spectrum of *p*-phenylphenol.

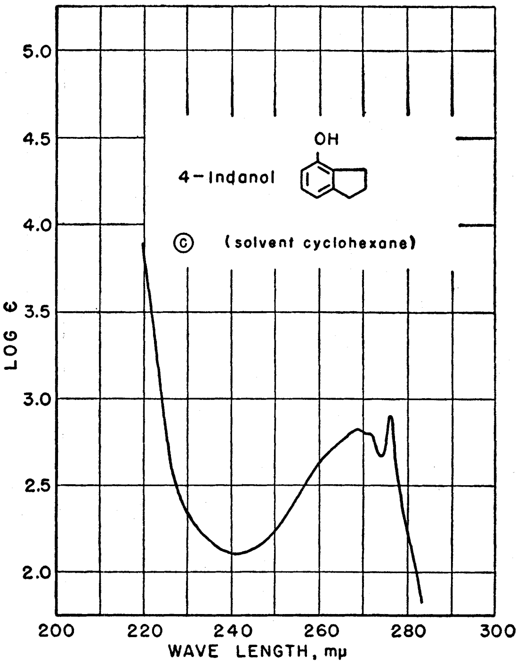

Figure 21a.—Ultraviolet spectrum of 4-indanol.

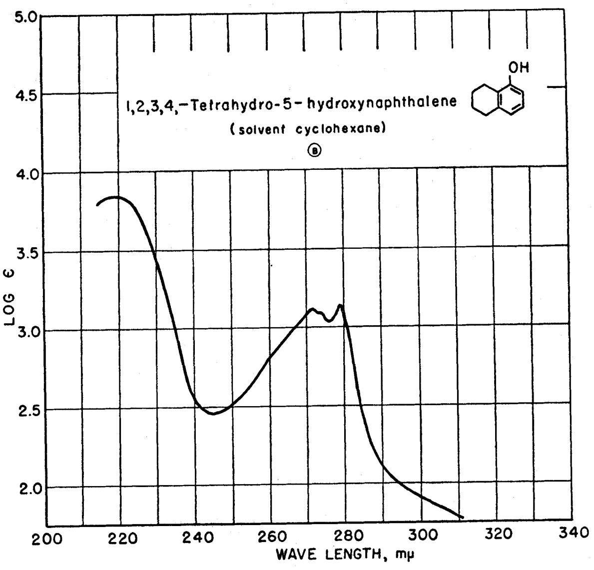

Figure 23a.—Ultraviolet spectrum of 1,2,3,4-tetrahydro-5-hydroxynaphthalene.

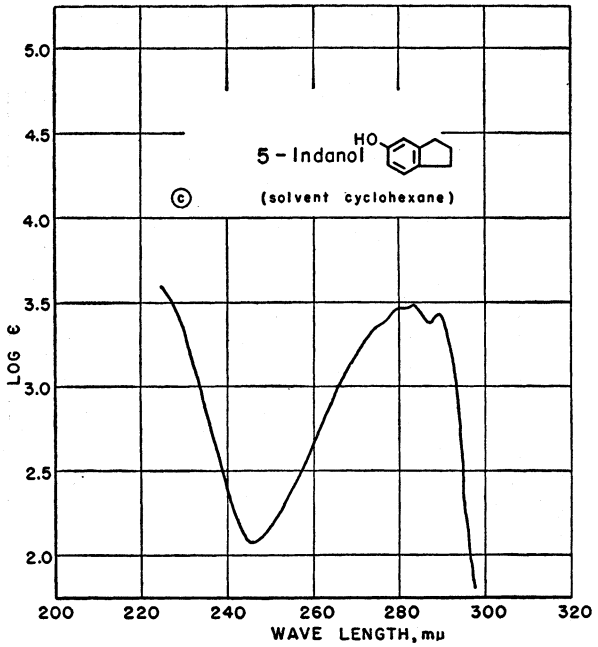

Figure 22a.—Ultraviolet spectrum of 5-indanol.

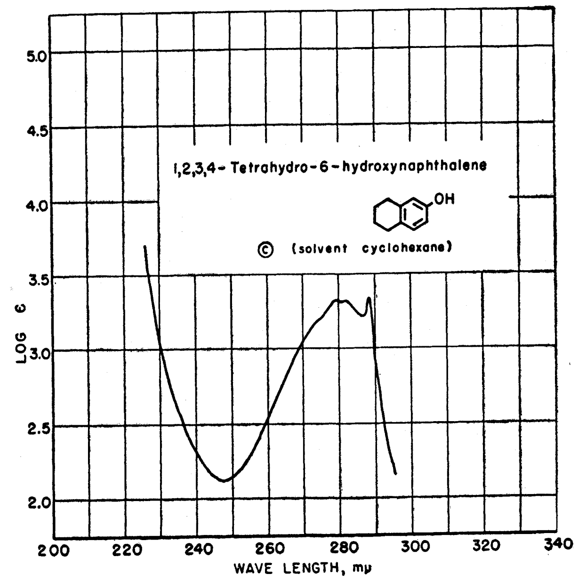

Figure 24a.—Ultraviolet spectrum of 1,2,3,4-tetrahydro-6-hydroxynaphthalene.

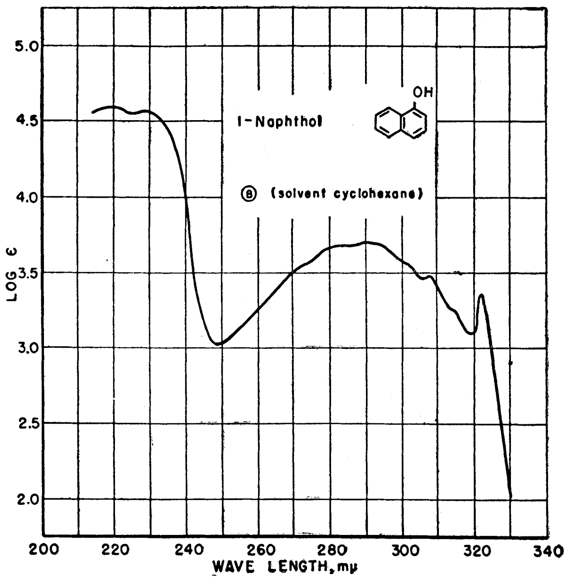

FIGURE 25a.—Ultraviolet spectrum of 1-naphthol.

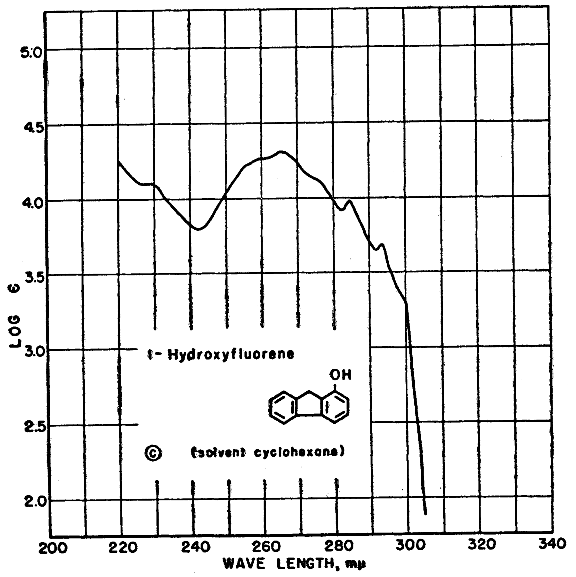

FIGURE 27a.—Ultraviolet spectrum of 1-hydroxyfluorene.

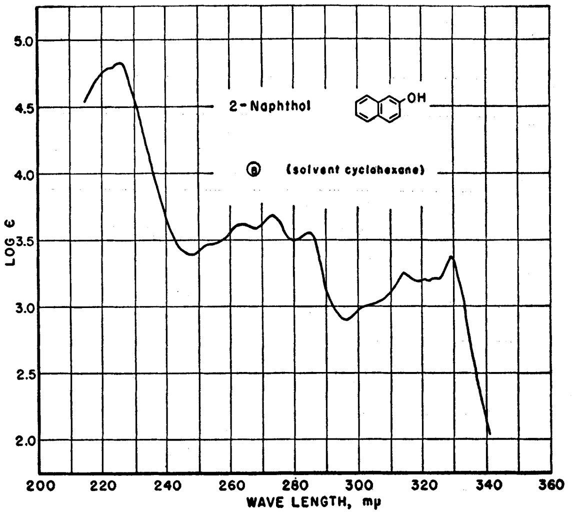

FIGURE 26a.—Ultraviolet spectrum of 2-naphthol.

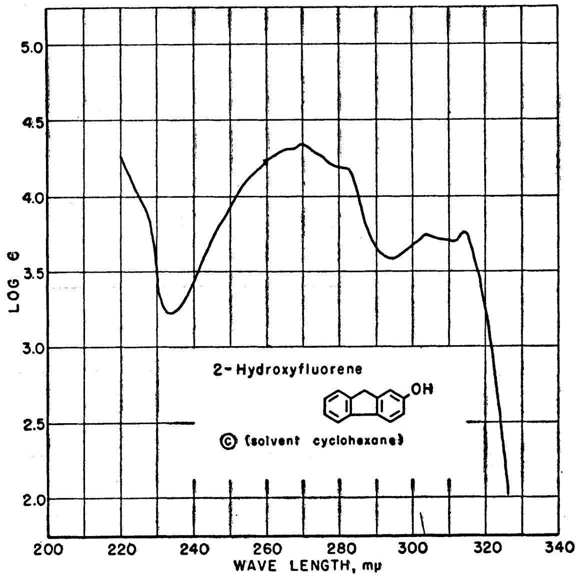

FIGURE 28a.—Ultraviolet spectrum of 2-hydroxyfluorene.

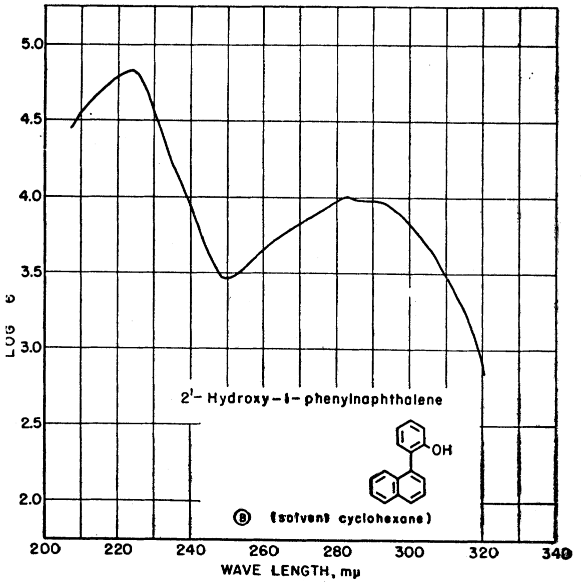

FIGURE 29a.—Ultraviolet spectrum of 2′-hydroxy-1-phenylnaphthalene.

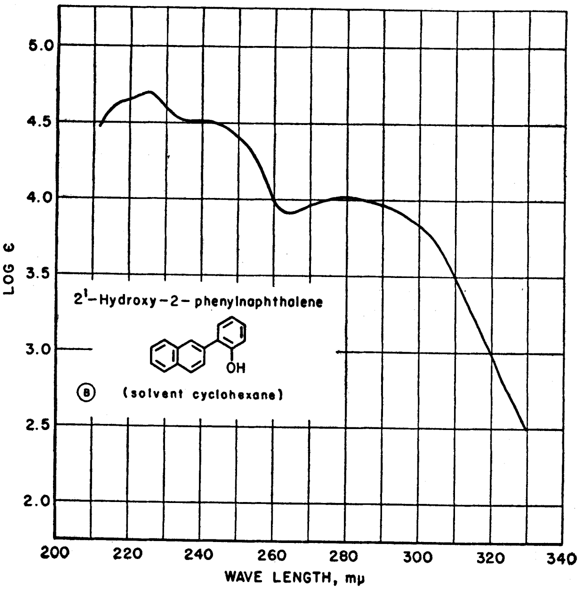

FIGURE 30a.—Ultraviolet spectrum of 2′-hydroxy-2-phenylnaphthalene.

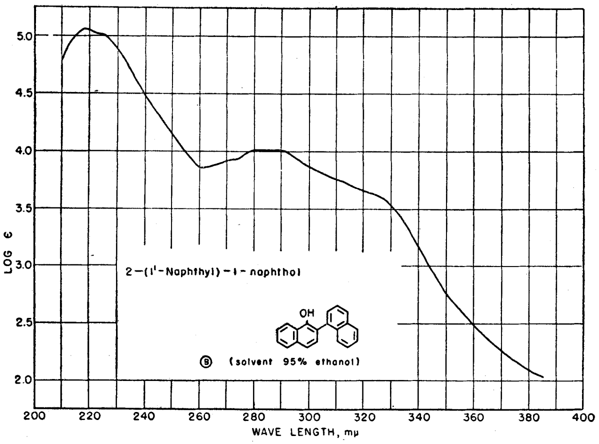

FIGURE 31a.—Ultraviolet spectrum of 2-(1′-naphthyl)-1-naphthol.

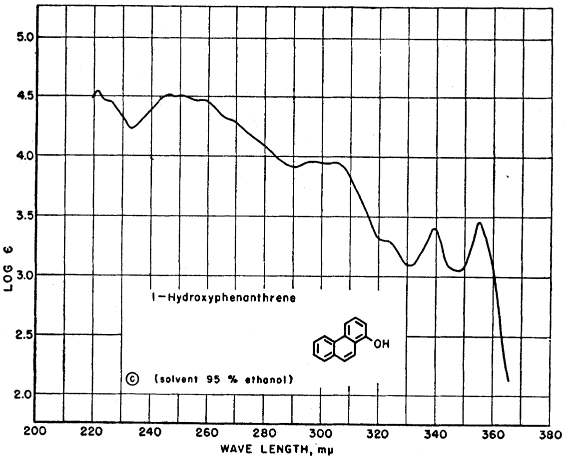

FIGURE 32a.—Ultraviolet spectrum of 1-hydroxyphenanthrene.

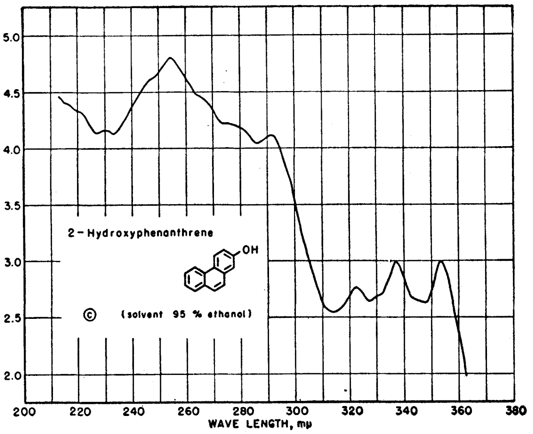

FIGURE 33a.—Ultraviolet spectrum of 2-hydroxyphenanthrene.

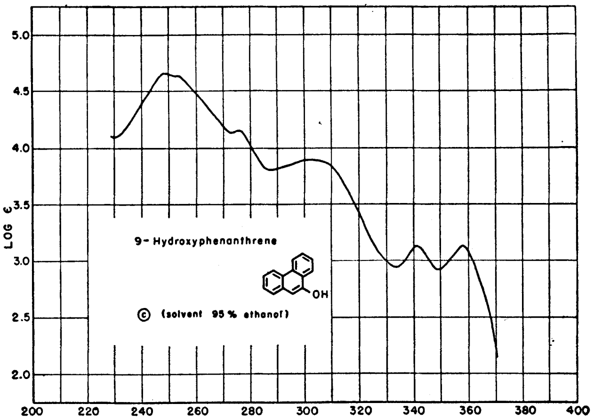

FIGURE 34a.—Ultraviolet spectrum of 9-hydroxyphenanthrene.

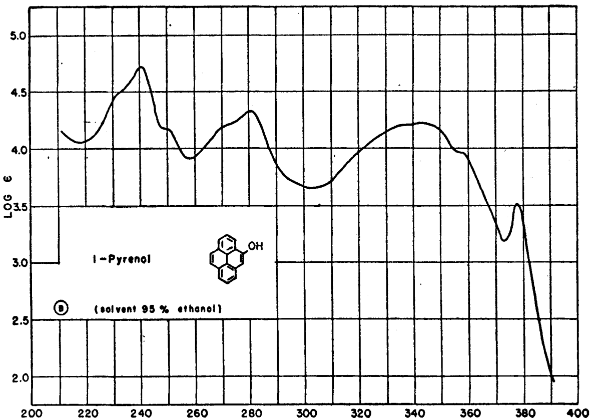

FIGURE 35a.—Ultraviolet spectrum of 1-pyrenol.

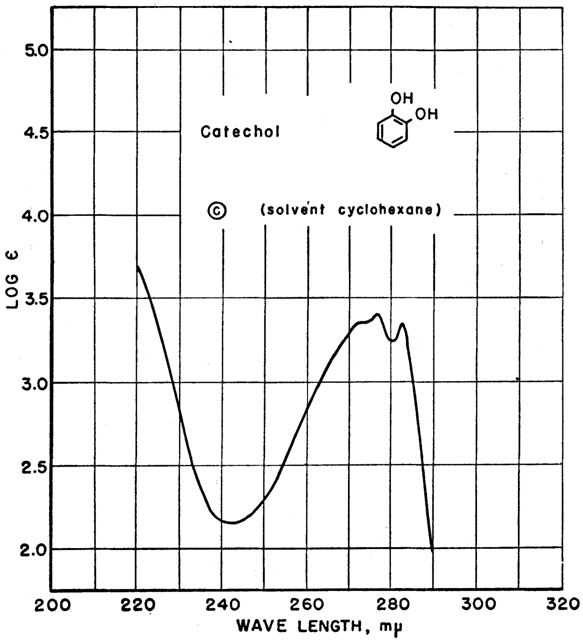

FIGURE 36a.—Ultraviolet spectrum of catechol.

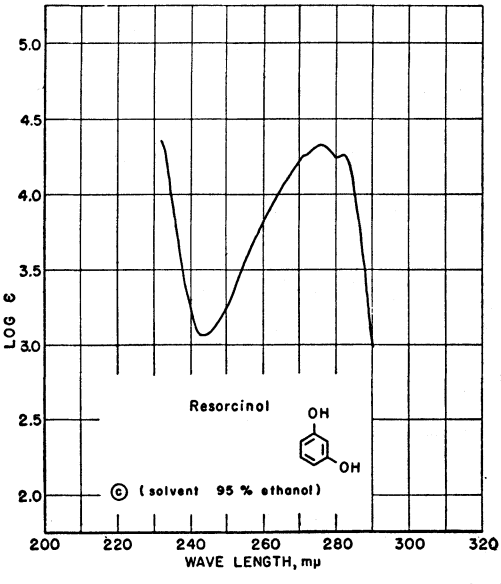

FIGURE 37a.—Ultraviolet spectrum of resorcinol.