

HYDROTROPIC PULPING OF THE BARK FROM
DOUGLAS FIR (PSEUDOTSUGA MENZIESII (MIRB.) FRANCO)
AND THE CHARACTERIZATION OF THE RESULTING
"BARK PHENOLIC ACID"

by

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A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1962

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Date thesis is presented April 28, 1962

Typed by Gloria M. Merideth

Acknowledgment

The research described in this thesis was financed by a grant made by the National Science Foundation to Oregon State University for the support of research entitled "Conifer Bark Lignin Components" under the direction of Dr. Ervin F. Kurth, Department of Chemistry.

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INTRODUCTION

The purpose of this study was to investigate the ability of various hydrotropic solutions to remove "bark phenolic acid" from the bast fiber component of Douglas fir bark and to compare the properties of the hydrotropic bark phenolic acid to those of Douglas fir bark phenolic acid extracted by sodium hydroxide.

Previous studies (29, 32) have found the easily extracted noncarbohydrate portion of bark to more closely resemble a high molecular weight phenolic acid rather than what is generally termed lignin. Therefore, the term "bark phenolic acid" will be used to designate the noncarbohydrate bark material extracted either by hydrotropic or sodium hydroxide solutions. The term "lignin" will be used as a generic term in reference to the total noncarbohydrate bark fraction as usually determined by the Klason lignin analysis.

The structure of Douglas fir bark and the properties of the bast fiber fraction have been described in previous works (29, 32). The properties of the bark fractions used throughout this study are recorded in Table 1. For comparison's sake, the properties of

Douglas fir wood are included in the table.

A hydrotropic solution is one which shows a decidedly greater solubility for slightly soluble inorganic substances than does pure water at the same temperature. This phenomenon is just the reverse of the common "salting out" effect. The hydrotropic effect is shown best by concentrated aqueous solutions of very soluble, neutral alkali or alkaline earth salts of organic sulfonic acids. Diluting the concentrated solutions will cause them to lose their hydrotropic power. The amount a hydrotropic solution must be diluted before it loses its hydrotropic effect is expressed as a dilution factor. A low dilution factor means that a particular hydrotropic solution needs to be diluted only three or four fold, say from 35% concentration to 10% concentration, to cause the solution to lose its hydrotropic power, hence causing the solubilized material to precipitate. A high dilution factor would mean that a solution would have to be diluted many times before it lost its hydrotropic power.

A low dilution factor is desirable, especially in any commercial operation where a major cost of the operation would be involved in the evaporation of excess water in recovering the hydrotropic solution.

Hydrotropic solutions have been used to extract various types of plant lignins but this seems to be their first use on the bark of a tree. Most of the previous studies have dealt with the use of hydro-tropic solutions as pulping agents for wood.

McKee (37, 39) and his students (5, 25, 46) at Columbia University were the first to investigate the pulping qualities of various hydrotropic solutions on wood and bagasse.

They pulped poplar and other hardwoods in 35-40 percent sodium xylenesulfonate solutions at 150°C for 11-12 hours and recovered from the poplar wood a pulp in 52 percent yield with approximately 90 percent alpha cellulose and a copper number of 2 percent. The bagasse was cooked in a similar liquor for 3 hours at 160°C with a 48 percent yield. The alpha cellulose content of bleached bagasse pulp was 85 percent. The hydrotropic liquor could be used for several cooks before it had to be freed of the lignin. Similar cooks carried out on pine, showed that softwoods were not as easily pulped as hardwoods. Although McKee has continuously lauded his hydrotropic pulping process, industry has been reluctant to try it out (38). The process had never been used in a commercial pulping operation.

Later Lau (33) tried hydrotropic pulping of bamboo and more recently Henrick (26) has done additional work on hydrotropic pulping of bagasse. Lau's work consisted of pulping bamboo in a 30-50 percent solution of sodium xylenesulfonate at 180°C-190°C. The most desirable cooking schedule consisted of separate stages of temperature rather than a straight run at constant temperature. A majority of the lignin was soluble at 160°C while only a small proportion required a high temperature for its dissolution. The pulp was obtained in yields of 40-46 percent, with a 3.8-4.5 percent lignin content and containing 93-94 percent alpha cellulose.

Henrick's work on bagasse was an investigation on the effect of several variables as temperature, pH, pressure, time, liquor concentration, and pulping aids. In general, he found 2-4 hours at 160-180°C gave pulps in approximately 40-50 percent yield. A comparison of physical strength properties showed that the hydrotropic bagasse pulp did not have the quality obtainable by using the Kraft or soda process. He also found that the addition of sodium hydroxide to the pulping liquor led to a considerably poorer yield, while addition of acids resulted in slightly improved fiberlation.

The Japanese have also applied hydrotropic pulping to various annual and perennial plants. Migita (41) and co-workers compared the pulping effect of nine kinds of hydrotropic salts. They pulped both hardwoods and softwoods with hydrotropic solutions of 35, 25 and 15 percent concentration at 160°C for four hours. Sodium cymenesulfonate, sodium butylbenzenesulfonate and sodium xylene sulfonate all effectively removed hardwood lignin while only sodium cymenesulfonate showed a considerable hydrotropic effect on softwood lignin.

They concluded that the hydrotropic effect to lignin increases with increasing number and size of the alkyl groups attached to the benzene nucleus and that the delignification effect of alkylarylsulfonates is greater than that of alkylsulfonate.

Shiraishi (48) used sodium xylenesulfonate to pulp the bast fibers of a perennial shrub. These bast fibers are not bark fibers but woody fibers from the phloem similar to those used in making manila rope. He found 35 percent sodium xylenesulfonate at 160°C, and a 4-6 hours digestion, to give a more satisfactory pulp than conventional methods.

Migita and Traynard (40, 51) both have investigated

the mechanism of delignification by hydrotropic solutions, as well as the properties of the lignin extracted by the process.

Traynard worked mainly with sodium benzoate on aspenwood. He compared the lignin and pentosan loss of aspenwood, which had been digested with hydrotropic solutions, buffered hydrotropic solutions, or pure water. Since the prehydrolyzed wood lost more lignin, he concluded that the delignification takes place in two steps. The first seems to be an aqueous hydrolysis followed immediately by the second-dissolution of the lignin in the hydrotropic solution. He also found the properties of the hydrotropic aspenwood lignin to be typical of those of hardwood lignins (52, 53).

Migita also proposed that the dissolution of lignin takes place in two steps. To test this conclusion, he alternately cooked wood samples in pure water and a 35 percent sodium xylenesulfonate solution. He found that the water pre-cook considerably promoted the hydrotropic dissolution of lignin.

At various times, the adjective neutral has been connected with the hydrotropic pulping process. This is a misnomer. Although a pure hydrotropic solution will be pH seven, solutions made from commercially

available hydrotropes are usually around pH eight. During the pulping of wood or bark, the formation of acids lowers the pH of the solution to between three and four. A recycled sodium xylenesulfonate solution used in a wood pulping process will attain a limiting pH of about 3.3 to 3.5 McKee (38), in his hydrotropic process, made his fresh liquor up at pH 3.5. Henrick (26) found that a recycled sodium xylenesulfonate liquor at pH 3.5 pulped bagasse better than fresh liquor, but due to a higher pentosan loss, the quality of this pulp was not quite as good as pulp made with fresh liquor. In pulping with a neutral organic solvent as dioxane, it is necessary to add a small amount of acid before a significant amount of delignification will take place. Experimentation in this study indicates that the formation of acid groups are necessary to have hydrotropic dissolution of "bark phenolic acid". The hydrotropic pulping process cannot be truly referred to as a neutral process.

A number of other works are available on the use of hydrotropic solutions for lignin isolation and for hydrotropic pulping of wood or other fibrous materials. Most of these are covered in Brauns' two volumes of "The Chemistry of Lignin" (6, 7), or are listed in the bibliography of this paper.

A large amount of Douglas fir bark is available to the forest products industry in the Pacific Northwest. Most of this bark is now used as fuel. A higher utilization of this large amount of potential raw material would be most desirable. It is hoped that this investigation will add in a small way to the fund of knowledge that will one day lead to a more complete utilization of this material.

Table 1

PHYSICAL AND CHEMICAL PROPERTIES OF DOUGLAS FIR BARK AND WOOD

Values based on oven dry extractive free material

	<u>Douglas fir bark</u> Fiber ¹	<u>Douglas fir</u> Fines ²	<u>Douglas fir wood</u>
Particle size ³			
% on 65 mesh	1	--	100
% on 200 mesh	52	51	--
% Holocellulose	55.4	29.6	71.9
% Lignin	41.5	59.9	30.9
% Methoxyl on lignin	5.0	5.0	15.25
% Ash	0.7	1.3	0.17
% Methoxyl on wood	4.0	2.1	4.75
pH aqueous slurry	3.7	3.6	--

Values based on oven dry unextracted material⁴

% Solubility in water	6.7	12.6	2.3
% Solubility in alcohol- benzene	7.6	8.3	4.0

1. Silvacon #515
2. Silvacon #472
3. Bark values taken from Weyerhaeuser, Bull. 10-A
4. Successive extractions

EXPERIMENTAL PROCEDURE AND RESULTS
OF HYDROTROPIC COOKS

Hydrotropic pulping procedure

To insure a homogeneous and standardized material throughout the experiment, a commercial bark product* was used. Since this material is readily available, the experimental work herein may be easily repeated. Furthermore, additional results could be compiled by other investigators and added to and compared with existing data.

Extractive free bark fractions were prepared by exhaustively extracting 500 g. batches with an alcohol-benzene mixture in a large, Soxhlet type extractor. Each 500 g. batch was then extracted three times with 4 liter portions of water at 90°C for one hour. Following the water extraction, all the batches were mixed together and air-dried. Extractive values are included in Table 1.

The moisture content of the bark fibers was determined on duplicate samples by oven drying at 110°C

* Silvacon 515 and 472, Weyerhaeuser Company, Tacoma, Washington. The author wishes to acknowledge the generosity of the Weyerhaeuser Company for supplying the Silvacon products used throughout the experiment.

to constant weight.

The hydrotropic pulping was done in an electrically heated hydrogenation apparatus, American Instrument Company Model 406-801DA, equipped with an automatic shaking mechanism. A 750 ml. stainless steel bomb held the pulping mixture.

Cooking time was counted from the time maximum temperature was reached. The length of time needed to heat the bomb to the desired temperature was between 30 minutes required to reach 120°C, the lowest temperature used, and 50 minutes for 180°C, the highest temperature used. The temperature was measured by a thermocouple inserted into a well at the bottom of the bomb. During the run, the temperature would fluctuate no more than one degree from the norm. At the end of each cook, the bomb was removed from the heating mantle and quickly cooled by immersing in a pail of cold water.

Pulping was done at high liquor to bark ratios to insure sufficient mixing and even heating during the cooking period. During initial runs, it was found that reducing the liquor-bark ratio below 8:1 resulted in the fibers packing tightly at the bottom of the bomb. This led to poor pulping and scorching of the fibers. Cooks made at various ratios from 8:1 to 14:1, while holding other conditions constant, showed no

significant differences in pulping action. A 8:1 ratio was initially used, but this resulted in a very viscous spent liquor which was most difficult to filter from the bark fibers. Later on, this pulping ratio was changed to 10:1 which lowered the viscosity of the spent liquor enough to greatly speed up filtering.

Immediately after being cooled, the hydrotropic pulping mixture was removed from the bomb and the fibers separated from the hydrotropic solution by filtering through a tared, medium porosity, sintered glass crucible. The fibers were first washed with 200 ml. of a 10 percent hydrotropic solution. A pure water wash could not be used initially for this would dilute the remaining hydrotropic liquor and cause the "bark phenolic acid" to reprecipitate onto the bast fibers. Following this initial wash, which removed most of the solubilized material, the fibers were washed with approximately 200 ml. of 60-70°C water and 200 ml. of 0.05N HCl solution at room temperature. The fibers were then washed with distilled water until the filtrate was neutral to litmus and solvent dried by washing with acetone and ether. The HCl washing was made to convert any residual sulfonic salt to the acid which then would be washed out by the acetone and ether. Sulfur determination (45) on the residual fibers was

nil, indicating that the above washing schedule satisfactorily removed all the hydrotropic pulping liquor. The fibers were given a final drying in a vacuum oven at 55°C for approximately 3 hours. Following this, the bast fibers were placed in a desiccator, cooled and weighed to determine the yield. A Klason lignin determination was made on each residue according to TAPPI Standard T13m-54.

After filtering off the bast fibers, the hydrotropic filtrate was combined with an equal volume of the initial washings and this solution saved for further analysis. The balance of the washings was discarded. The "bark phenolic acid" was recovered by simply diluting the hydrotropic solution. The amount of diluting depended on the dilution factor of the particular hydrotropic solution. Dilution to 10-15 percent was sufficient to cause the "bark phenolic acid" to precipitate from a 35 percent sodium xylenesulfonate solution, while a sodium p-cymenesulfonate solution had to be diluted to 2-5 percent to insure complete precipitation of the "bark phenolic acid". The precipitate was allowed to settle and then separated from the hydrotropic solution by decanting and centrifuging. The amber color of the solution suggested that a fraction of the "bark phenolic acid" remained in the diluted

liquor. Carbohydrate material and other water solubles remained in the diluted liquor.

The "bark phenolic acid" was repeatedly washed by thoroughly dispersing it in 50-100 ml. portions of distilled water, centrifuging the dispersion, and decanting off the wash water. Sulfur determination on the "bark phenolic acid" indicated that seven washes removed all of the residual sodium xylenesulfonate.

No difficulties were encountered with the "bark phenolic acid" going into colloidal suspension as was reported with sodium hydroxide extracted "bark phenolic acid". It did not filter readily, but when centrifuged separated cleanly from the supernatant liquid. The washed "bark phenolic acid" was first dried in a vacuum desiccator over Drierite followed by drying to constant weight in a vacuum oven at 50-55°C.

A sample of "bark phenolic acid" (methoxyl 4.93 percent) was subjected to a Klason lignin determination as a means of determining if carbohydrate material was present. The yield from the determination was 81.5 percent with a methoxyl content of 4.89 percent. The sulfuric acid filtrate was deionized with ion exchange resin, concentrated, and chromatographed on paper with a water saturated butanol developer using ammoniacal silver nitrate as a spray indicator. No carbohydrate

could be detected in the filtrate. From these analyses it was concluded that the loss in weight of the hydro-tropic bark phenolic acid was due to its solubility in the reagent and that no carbohydrate material was present.

Preliminary cooks with various hydrotropic solutions

Preliminary hydrotropic cooks were run using poplar and Douglas fir woodmeal to check the apparatus and procedure for reliability and to test the pulping ability of the commercial hydrotrope*. Only sodium xylenesulfonate was used in these control cooks, since it was used in the majority of the experimental work. Table 2 shows that poplar wood, as expected, was pulped much more easily than Douglas fir wood. The values for the poplar cook are comparable to those found by other investigations (51, 37) while the values for the Douglas fir cook were similar to the determinations by Migita (41) for spruce, another softwood. The original values of the "bark control cook" were closely reproduced by later bark cooks done under similar conditions. These

* The author wishes to thank Ultra Chemical Works, Paterson, New Jersey, for their generosity in supplying samples of sodium xylenesulfonate, p-cymenesulfonate, and ethyl benzenesulfonate.

data would indicate that both the equipment, procedure and hydrotropic salt are comparable to those used in other works.

A preliminary study was made on the pulping effects of seven hydrotropic salts on Douglas fir bast fibers. All cooks were made with saturated solutions of the hydrotropic chemical at 160°C for six hours, with a liquor to bark ratio of 14 to 1. The pulp yield and phenolic acid recovery from these cooks are recorded in Table 3.

McKee's original work (39) was with the alkyl benzene sulfonates and most subsequent work has been with this group of chemicals. Sodium xylenesulfonate particularly has been preferred, since it exhibits strong hydrotropic action. Migita (41), in his investigation, found sodium cymenesulfonate to show a considerable hydrotropic effect on spruce lignin. This chemical was included in this initial study to see if its hydrotropic effect would carry over to a softwood bark.

Krasnec and Knazko (30) have reported on several new and highly hydrotropic compounds. Two of these, the sodium salts of 2-anthraquinonesulfonic acid and 2-naphthalenesulfonic acid, were available and were used in this initial study.

The 2-naphthalenesulfonic acid sodium salt showed a fair dissolving action on the bast fibers with a high "bark phenolic acid" recovery, but this salt was very difficult to work with due to its very low solubility in aqueous solutions below 90°C. Because of this property, its use was discontinued. The 2-anthraquinonesulfonic acid sodium salt, sodium benzoate, and sodium salicylate, all had very little hydrotropic effect and were not further considered.

Sodium-cymenesulfonate, -ethylbenzenesulfonate and -xylenesulfonate all showed considerable pulping action on the bast fibers with a corresponding high recovery of the "bark phenolic acid". Subsequent experiments were limited to the use of these hydrotropics. Sodium xylenesulfonate was most extensively used due to its availability while only enough sodium ethylbenzene sulfonate and sodium cymenesulfonate were available for one and two additional cooks respectively.

Table 2

COMPARISON OF WOOD AND BARK
HYDROTROPIC PULPING³

<u>Material</u>	<u>Yield¹</u> <u>%</u>	<u>Lignin contents</u> <u>of pulp</u> <u>%</u>	<u>Lignin²</u> <u>Recovery</u> <u>%</u>
Poplar	56	4	75
Douglas fir wood	69	23	41
Douglas fir bark bast fibers	75	38	30

-
1. Based on moisture-free, extractive-free material
 2. Based on Klason lignin content
 3. Cooking conditions: 35% SXS, Liquor Wood ratio 8:1, temperature 160°C, time 5 hours

Table 3

PRELIMINARY COOKS³ OF BARK BASE FIBERS
 COMPARING VARIOUS HYDROTROPIC AGENTS

<u>Cooking liquor</u>	<u>Bark fiber yield¹</u>	<u>Phenolic acid recovery²</u>
Water	95	0
saturated solutions of:		
2-Anthraquinonesulfonic acid sodium salt	92	2
Sodium benzoate	91	3
Sodium p-cyrenesulfonate	76	17
Sodium ethylbenzene sulfonate	76	25
2-Napthalenesulfonic acid sodium salt	85	16
Sodium salicylate	94	0
Sodium xylenesulfonate	75	32

-
1. Based on moisture-free, extracted bark
 2. Based on Klason lignin content (41.5%) of original moisture-free, extracted bast fibers
 3. Conditions: 6 hours - 14:1 liquor-bast fiber ratio - 150°C.

Results of cooks made with selected hydrotropes

Three series of cooks were run each using one of the hydrotropes previously selected by the preliminary study. Due to the availability of sodium xylenesulfonate, the series using this hydrotrope was the most extensive. A total of four cooks were made, each in duplicate, covering the temperature range from 120°C to 180°C. The series using sodium p-cymenesulfonate was comprised of only two cooks at 160°C and 180°C, while sodium ethylbenzene sulfonate was used for only one cook at 160°C. Only limited amounts of these two materials were available. Except for temperature, all conditions were held relatively constant throughout the three series.

The effect of two variables, type of hydrotropic and cooking temperature, was followed by determining three values from each individual cook. The overall hydrotropic effect was followed through the pulp yield, while the hydrotropic effect on the "lignin" fraction of the bast fibers was shown by the Klason lignin value of the pulp. The recoverability of phenolic acid from the various cooks was compared through the "bark phenolic acid yield".

The results of these cooks, plus the sodium hydroxide cook are presented in Table 4. Included in Table 4 are the data from the cook made with "reused liquor". A diluted hydrotropic spent liquor can be evaporated back to its original strength and reused. This procedure would be used in any commercial operation but was not done in this study. Comparison of cooks 3 and 6, of Table 4, indicates that for bast fibers, the hydrotropic effect somewhat decreased with reused liquor. From the "reused liquor" cook 6, Table 4, it can be seen that, although its yield was similar to that of cook 3, its Klason lignin content was much higher. This indicates that the lower pH increased the rate of carbohydrate hydrolysis but did not in turn increase the rate at which the sodium xylenesulfonate could put the phenolic acid into solution. This is contrary to wood pulping where lowering the pH leads to an increase in the rate of hydrolysis of the lignin-carbohydrate bond and thus increased solubility of the lignin.

It should be pointed out here that the Klason lignin determination has not been found entirely satisfactory for bark material. Throughout these cooks it was not possible to equate the original Klason lignin value of the bast fibers to the Klason lignin found in the pump and that recovered from the hydrotropic

liquor. The amount of lignin which could be accounted for after cooking at 120°C or 140°C has been consistently less than the original Klason lignin values, while at 160°C and 180°C the amount of recovered lignin has been greater than the Klason lignin content of the bast fibers. A possible explanation is that at the lower temperatures, part of the bark lignin remains soluble in the diluted hydrotropic liquor, while at the higher temperatures, carbohydrates or other materials which were previously soluble in the Klason lignin determination were condensed or polymerized during the cook so that they are no longer soluble. Even though these discrepancies were present, the Klason lignin determination was used throughout the study, for it still gave reproducible, relative values which were of use in comparing and evaluating the effect of the hydrotropic solutions.

The sodium xylenesulfonate series showed that there is little hydrotropic effect below 160°C. Both cooks 1 and 2 gave high yields of pulp with corresponding small phenolic acid recovery. Above 160°C the hydrotropic effect was much stronger. In cooks 3 and 5, a considerable amount of material went into solution. Neither of these cooks, though, was as efficient in

removing the "bark phenolic acid", as the sodium hydroxide cook number 7. At temperatures below 160°C the sodium xylenesulfonate was slightly preferential in removing the "bark phenolic acid", but above 160°C, the dissolution of carbohydrate material was favored, as indicated by the high Klason lignin content of the pulp from cook 5.

The cooks using sodium p-cymenesulfonate and sodium ethylbenzene sulfonate were similar to their counterparts in the sodium xylenesulfonate series. Cooks 3, 8 and 10 were similar, except each used a different hydrotropic cooking solution. A comparison of these cooks showed the sodium xylenesulfonate to be slightly, but not significantly, better than the others, both in lignin removal and phenolic acid recovery.

Over-all, the hydrotropic solutions do not seem to be especially efficient or selective pulping agents for bast fibers. Under the conditions explored, they do not give a satisfactory delignified fiber, nor can they be easily used to produce a "bark phenolic acid" in greater yield or one that is significantly different than that recovered by sodium hydroxide extraction. A comparison of the properties of the "hydrotropic bast fibers phenolic acid" and sodium hydroxide phenolic acid are made in the following sections.

Table 4

PULPING OF BAST FIBERS WITH SELECTED HYDROTROPIC AGENTS AND SODIUM HYDROXIDE³

Cook No.	Cooking liquor	Temp. C°	Conc. of cooking liquor %	Time at temp. hrs.	Pulp yield %	Klason ¹ lignin of pulp %	Phenolic acid recovery of Klason lignin %	pH		Lignin bark ratio Vol/Wt
								start	end	
1	Sodium ² xylene sulfonate	120	35	4.5	93.3	35.5	9.7	7.8	4.3	8:1
2	"	140	35	4.5	85.4	36.0	9.8	7.8	4.3	10:1
3	"	160	35	4.5	74.5	39.5	31.9	8.0	4.2	8:1
4	"	160	35	8.0	65.3	40.0	35.1	8.0	3.9	10:1
5	"	180	35	5.0	67.7	44.3	58.2	8.0	4.2	10:1
6	Reused liquor	160	35	5.0	72.1	45.1	26.0	4.2	3.8	10:1
7	Sodium hydroxide	160	1	1.0	70.1	26.5	51	—	—	8:1
8	Sodium p-cymene sulfonate	160	35	5.0	77.2	40.5	17.0	6.4	4.2	8:1
9	"	180	35	5.0	71.0	41.8	22.0	6.3	4.3	10:1
10	Sodium ethyl benzene sulfonate	160	30	5.0	76.5	41.9	24.4	9.0	3.9	8:1

1. Original Klason lignin of fibers = 41.5%

2. Ave. of duplicate runs

3. Values based on moisture-free extracted material

PROPERTIES OF HYDROTROPIC BARK PHENOLIC ACID
FRACTIONS AND THEIR COMPARISON TO
SODIUM HYDROXIDE BARK PHENOLIC ACID

Isolation and description of "bark phenolic acids"

Four distinct "bark phenolic acids" were isolated and their properties investigated and compared. Three of these acids came from "hydrotropic" extractions of either bark bast fibers or bark fines. The fourth "bark phenolic acid" was prepared by sodium hydroxide extraction of bast fibers following a method used in previous bark phenolic acid studies (29, 32). The "bark phenolic acid" extracted by sodium hydroxide was prepared to serve as a reference material for the "bark phenolic acid" isolated by "hydrotropic" extraction.

Two of the four "bark phenolic acids" were isolated from the bark bast fibers. One came from the 120°C cook while the other came from the 160°C cook. The "bark phenolic acids" recovered from cooks made at 140°C to 180°C were all similar in color and appearance, while the phenolic acid recovered from the 120°C cook was distinctive in its color and appearance. Since the "bast fiber phenolic acid" from the 120°C cook (bast fiber phenolic acid-I) was unique, it was included in the study as a separate entity. The bark bast fiber

phenolic acid from the 160°C cook (bast fiber phenolic acid-II) was selected as representative of the phenolic acid recovered from the hydrotropic cooks made in the 140°C to 180°C temperature range.

The third "bark phenolic acid" was one isolated from the bark fine fraction by hydrotropic extraction at 160°C (bark fine phenolic acid). It was included as a check of the hydrotropic effect on different bark components. The fourth "bark phenolic acid" was isolated from the bark bast fibers by a 1 percent sodium hydroxide extraction (29). This phenolic acid was the reference material with which the "hydrotropic bark phenolic acids" were compared.

Following the washing and recovery procedure, previously described, the "hydrotropic bark phenolic acids" were purified according to the method of Brauns (6, p. 742-4). A dioxane solution of the "bark phenolic acid" was made with an approximate concentration of 5 mg/ml. The solution was filtered to remove a trace of insoluble fiber and dirt, dried over anhydrous sodium sulphate, filtered, and concentrated in a rotary vacuum evaporator to a thin syrup. The "bark phenolic acid" was reprecipitated by pouring one volume of the concentrated dioxane solution into 30 volumes of rapidly

stirred ether. The precipitated acid was removed from the ether by filtration, air-dried, followed by drying in a vacuum desiccator over Drierite at room temperature, and stored in an air-tight bottle.

The "bast fiber phenolic acid-I" was distinctive in color and appearance. The color was a definite tan color in contrast to the dark, red-brown color exhibited by the "bark phenolic acids" isolated from hydrotropic cooks at higher temperature and by sodium hydroxide extractions. Its appearance was of a light, fine, fluffy powder, whereas the other "bark phenolic acids" were all hard and granular.

A portion of the "bast fiber phenolic acid-II" was purified by the Brauns' method, while another portion received no other treatment than the normal washing of the recovery procedure. The purified and unpurified portions were used throughout the analytical determinations. None of the results indicated any difference between them, hence the results are reported under the single heading of "bast fiber phenolic acid-II".

All of the "bark phenolic acids" exhibited similar solubility properties. The dried acids were easily soluble in dilute alkali, dimethylformamide (DMF),

ethylenediamine (EDA) and slowly dissolved in dioxane, acetone and ethyl acetate. A trace of water in the solvents helped promote solubility. "Bast fiber phenolic acid-I" went into solution much more quickly than any of the other acids. A solution of the "bast fiber phenolic acid-I" was much lighter in color than solutions of the other three acids of equal concentration.

Total and carboxyl acid groups determined in aqueous medium

Two methods were used to determine the carboxyl and phenolic hydroxyl groups in the four "bark phenolic acids". The first was an aqueous method using a barium hydroxide - calcium acetate treatment (14, 31, 44) and the second was a non-aqueous titration method (4, 10, 13). These methods are described in this and the following section.

Total acid

The total amount of acidic groups was determined by Kucharenko's (31, 49) method as modified by Ekman and Enkvist (14). The determination consisted of shaking 50-100 mg samples of the "bark phenolic acid" with 25 ml of 0.1N barium hydroxide in a closed flask

for one-half hour on a water bath at 85°C. After digestion the solution was quickly cooled, centrifuged, and the solution decanted off. A measured excess of hydrochloric acid was then added to an aliquot of the filtrate and back titrated with barium hydroxide. The end point was determined potentiometrically. Blank determinations were made for each set of samples and their consumption deducted from the values found for the main determinations. The average of duplicate determinations is recorded in Table 6.

Carboxyl acid

The determination of the carboxyl group was made by a method used by Ekman and Enkvist (14). In this method 50 to 100 mg of phenolic acid was shaken with 25 ml of 0.4N calcium acetate in a closed flask over a water bath at 85°C for one-half hour.

The solution was cooled and centrifuged. An aliquot of the clear centrifugate was then titrated potentiometrically with 0.1N sodium hydroxide to neutralize the released acetic acid. A blank determination was made for each set of samples and their consumption deducted from the values found for the main determinations. The average of duplicate determinations is recorded in Table 6.

Carboxyl and phenolic hydroxyl groups determined by non-aqueous titrations procedure

It is a well established fact that very weak acids can be titrated in basic solvents which enhance their acidic character (4, 20). A few non-aqueous titrations have been done on wood lignins (10, 15, 24) but not to the author's knowledge on "bark phenolic acid". Non-aqueous titrations as described in the following paragraphs were made on all "four bark phenolic acids".

The non-aqueous titration is specific for acidic functional groups, is free from interference by aliphatic hydroxyl, and can be used to differentiate between carboxyl and phenolic groups. The procedure is also suitable for dihydric phenolics and polyphenols (22). Mercaptans, certain enols, imides, some phenolic esters, lactone of phenols, and certain quinones, if present, will also titrate, and thereby lead to a high acidic content (10). Only phenolic esters, lactone and enols could be expected in the bark phenolic acid preparations. Incomplete titration is exhibited by some chelated or sterically hindered acidic functions (10). Hydrogen bonding also could make some of the acidic groups inaccessible to titration (22). Substituents in the meta position could decrease the acidity of a phenol to such an extent that it would

escape titration (41). In addition, some polyphenols do not titrate completely (22). Incomplete titration for any of these causes would lead to low acid content.

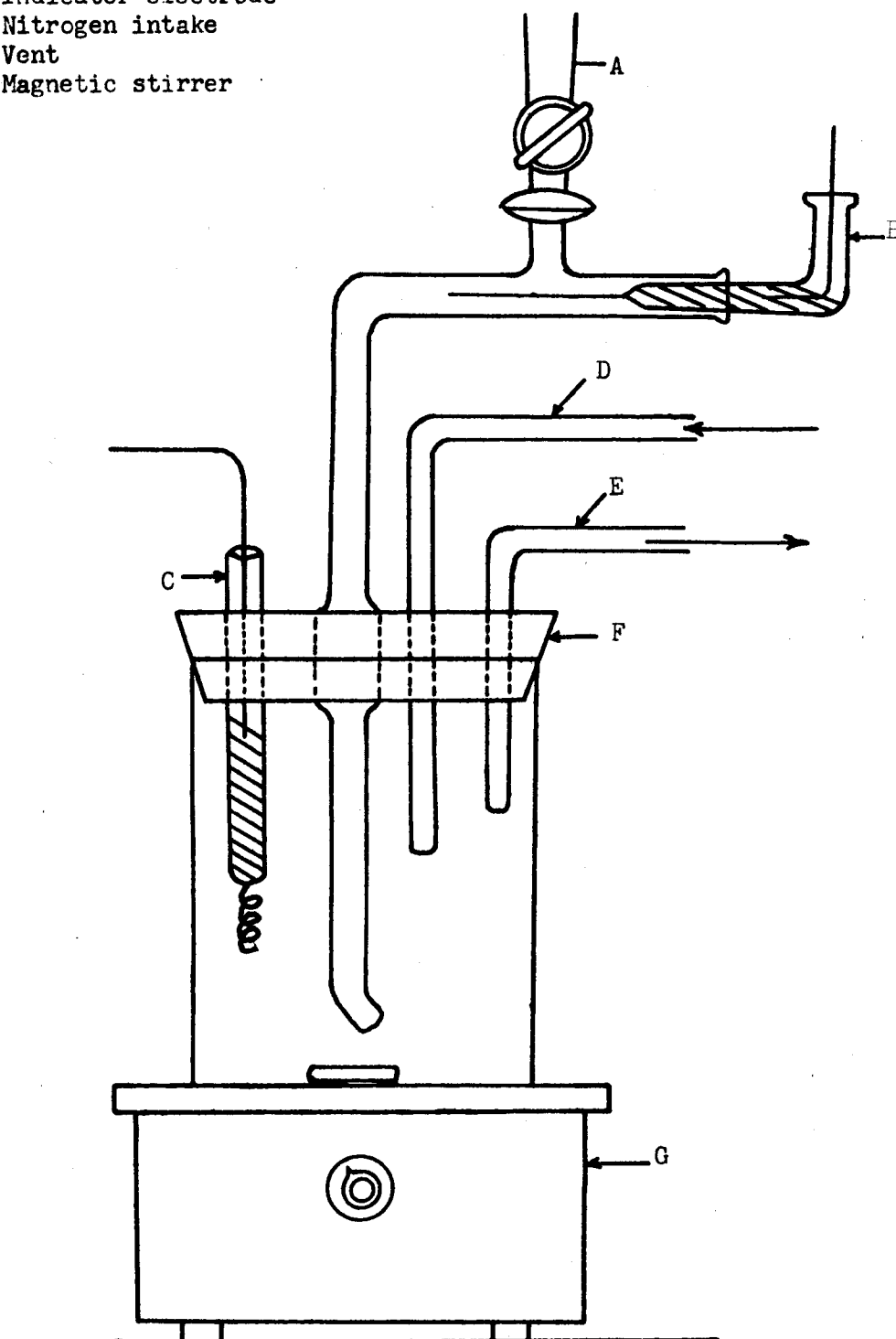
Figure 1 illustrated the titration apparatus. A five milliliter microburet calibrated to read in hundredths of a milliliter was used for all of the titrations. A platinum wire reference electrode was mounted in the buret below the stopcock and contact was made with the platinum wire indicator electrode by immersing the buret's tip into the solution being titrated. This arrangement allowed continual flushing of the reference electrode with fresh titrant.

Two solvents were tried, dimethylformamide (DMF) and ethylenediamine (EDA) as titrating medium. Ethylenediamine (36) is an excellent solvent for non-aqueous titrations due to its strong base strength. For the titration of very weak acids, EDA should be anhydrous and free of acid impurities. Ethylenediamine, however, is a disagreeable material to work with. It is corrosive, toxic and an excellent carbon dioxide absorber. In several trial titrations it showed no advantage over DMF, therefore its use was discontinued.

Dimethylformamide is an acceptable solvent for all but the very weakest acids. It is commercially

NON-AQUEOUS TITRATION APPARATUS

- A- 5 ml. buret
- B- Reference electrode
- C- Indicator electrode
- D- Nitrogen intake
- E- Vent
- F- Magnetic stirrer



available at a reasonable price and requires no further purification. It is a carbon dioxide and water absorber but is not as avid as EDA. Dimethylformamide (Eastman Org. Chem. 587C) was used as received from the supplier for all non-aqueous titrations made in this study. It was protected from atmospheric carbon dioxide and water at all times during its storage and used with Ascarite and Drierite absorption tubes. In addition, all titrations were run under nitrogen. Tetrabutyl ammonium hydroxide (11) was used as a titrant throughout the experiment. The titrant was prepared by dissolving tetrabutylammonium iodide in methanol and thoroughly mixing with an excess of silver oxide. The solution was filtered, the filtrate diluted to approximate 0.1N with benzene, and standardized against pure benzoic acid.

Due to the dark color of the "bark phenolic acid" solutions, all of the titrations were done potentiometrically using a Beckman Model H-2 pH meter.

An amount of bark phenolic acid, 20 to 30 mg, corresponding to one to two milliliters of titrant, was weighed into the titration flask. The flask was connected to the titration apparatus and flushed with nitrogen, DMF was added to the 20 ml mark and the magnetic

stirrer started. The titration was started as soon as the "bark phenolic acid" was completely dissolved and the potential had reached a constant value (usually 30-90 seconds). The titrant was added in 0.04 ml increments, except near the end point where 0.01 ml increments were added. The millivolt reading was recorded when it had remained steady for 20 seconds.

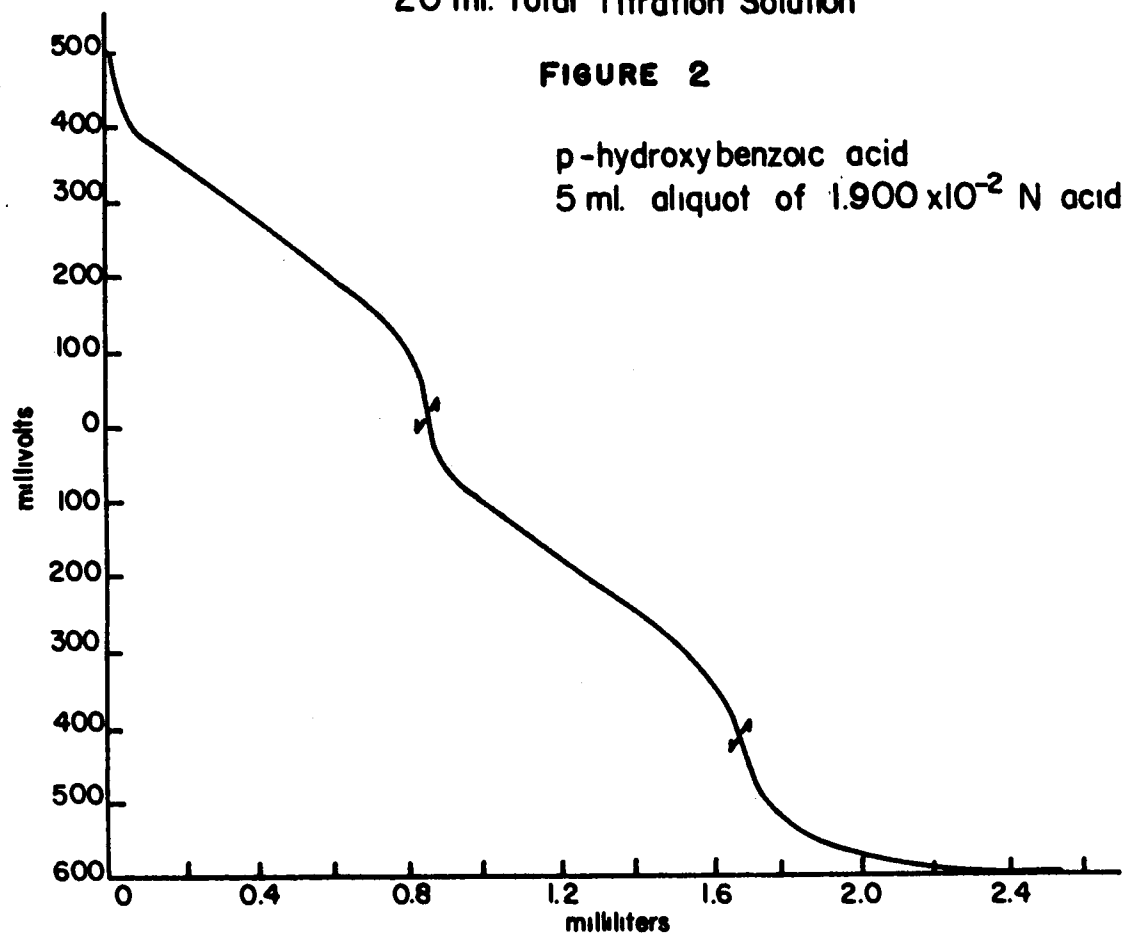
The equivalent points were determined graphically at the points where the slope of the curve was the steepest (see Figure 2 to 6). The amount of standard titrant to the first inflection point was equivalent to the strong acid function, while the difference in titrant between the first and second inflection point was equivalent to the weak acid function. Corrections were made for the acidity of the DMF as measured in a blank determination.

Preliminary titrations were made using three pure compounds, benzoic acid, p-hydroxyl benzoic acid and resorcinol. Solutions of known concentration were made for all the acids using DMF as solvent. Aliquots of these solutions were then used for titration. Table 5 contains the data on the acids, their calculated normality and the normality found by titration. Figure 2 shows the titration curve for p-hydroxyl benzoic acid and benzoic acid. The curve for resorcinol was similar

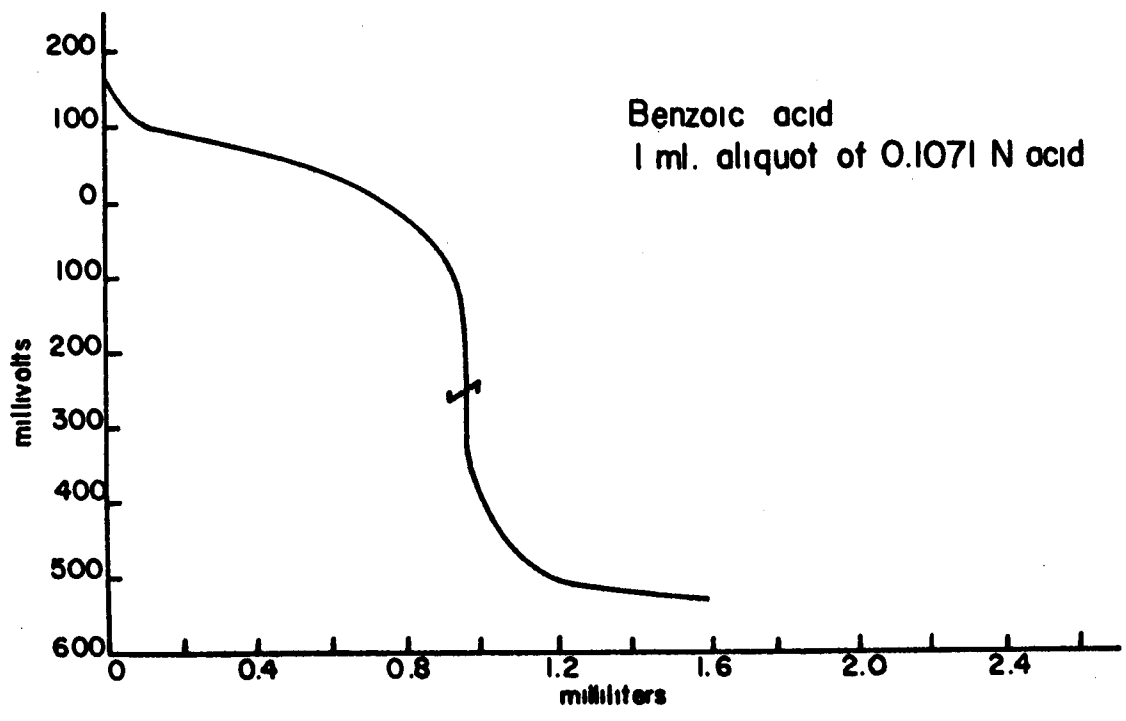
Potentiometric Titration in DMF of Pure Compounds 35
20 ml. Total Titration Solution

FIGURE 2

p-hydroxybenzoic acid
5 ml. aliquot of 1.900×10^{-2} N acid



Benzoic acid
1 ml. aliquot of 0.1071 N acid



to the benzoic acid curve with only one break being present at the equivalent point corresponding to both hydroxyl groups. These results indicated that the non-aqueous titration method was capable of giving accurate and reproducible results.

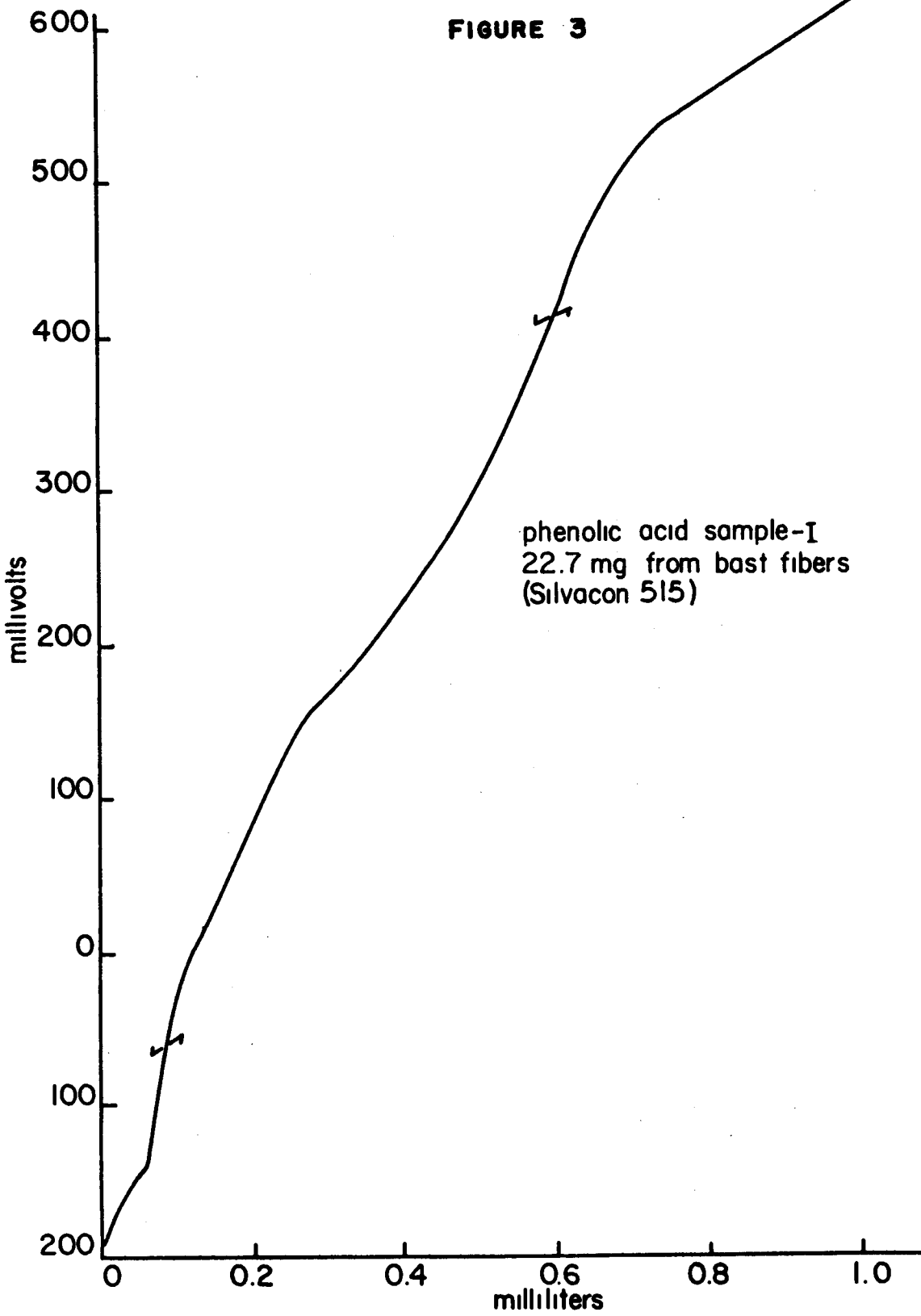
Table 5

COMPARISON BETWEEN CALCULATED VALUES
AND NON-AQUEOUS TITRATION VALUES
FOR SOLUTIONS OF PURE COMPOUNDS

<u>Compound</u>	<u>Calculated value N.</u>	<u>Titration value N.</u>
Resorcinol, Eastman Org. Chem. (222) m.p. 109-10	0.0253	0.0262
p-hydroxyl benzoic acid Eastman Org. Chem. (1520) m.p. 215-17		
OH Group	0.0193	0.0190
COOH Group	0.0194	0.0190
Benzoic acid, Eastman Org. Chem. (37) m.p. 123-25	0.1071	0.1077

Potentiometric Titration in DMF

FIGURE 3



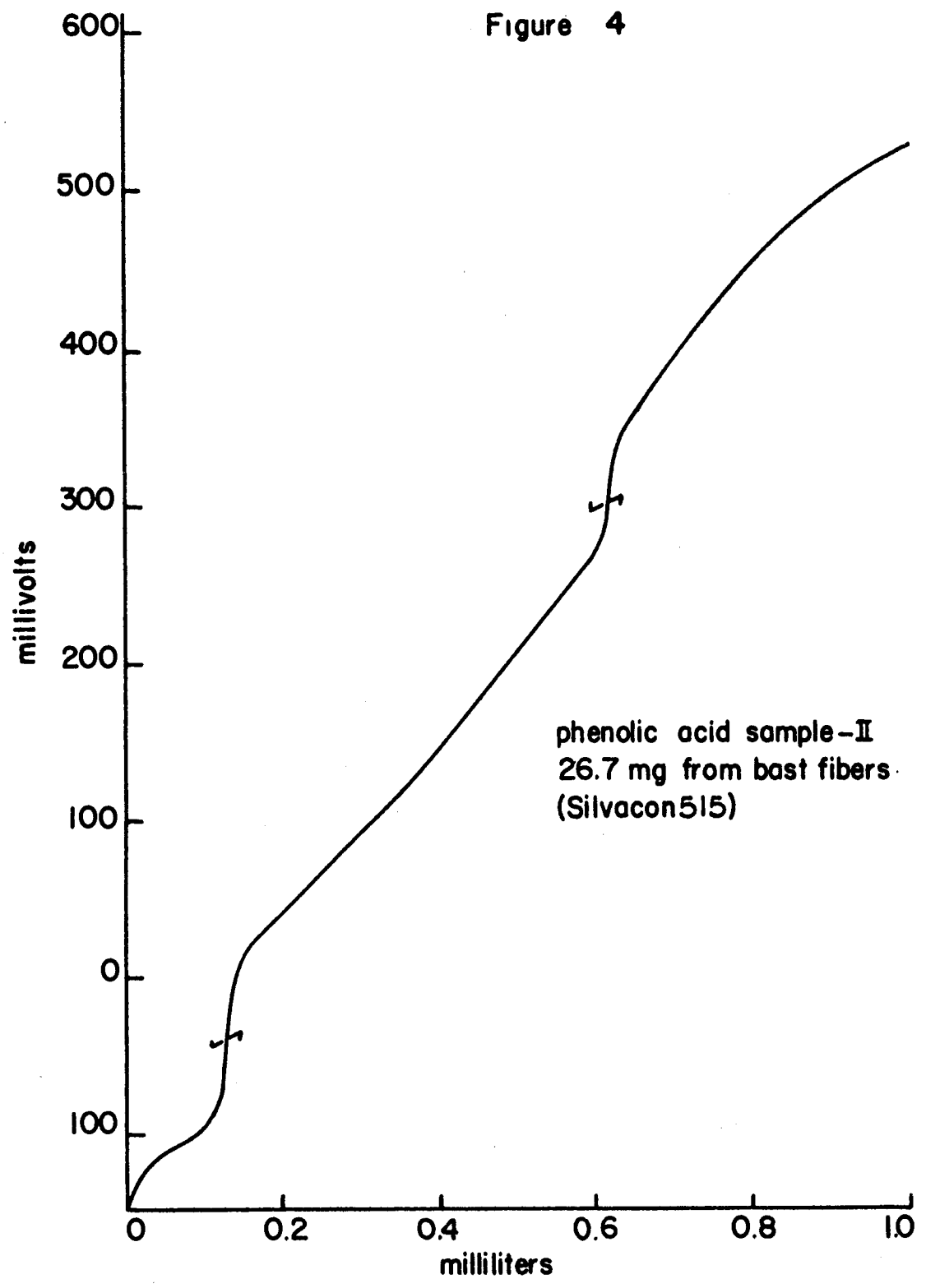
Results of non-aqueous titrations

The results determined by barium hydroxide-calcium acetate treatment and non-aqueous titration for phenolic hydroxyl and carboxyl functional groups of the various bark phenolic acid preparations are given in Tables 6 and 7. Representative titration curves are shown in Figures 3 through 6.

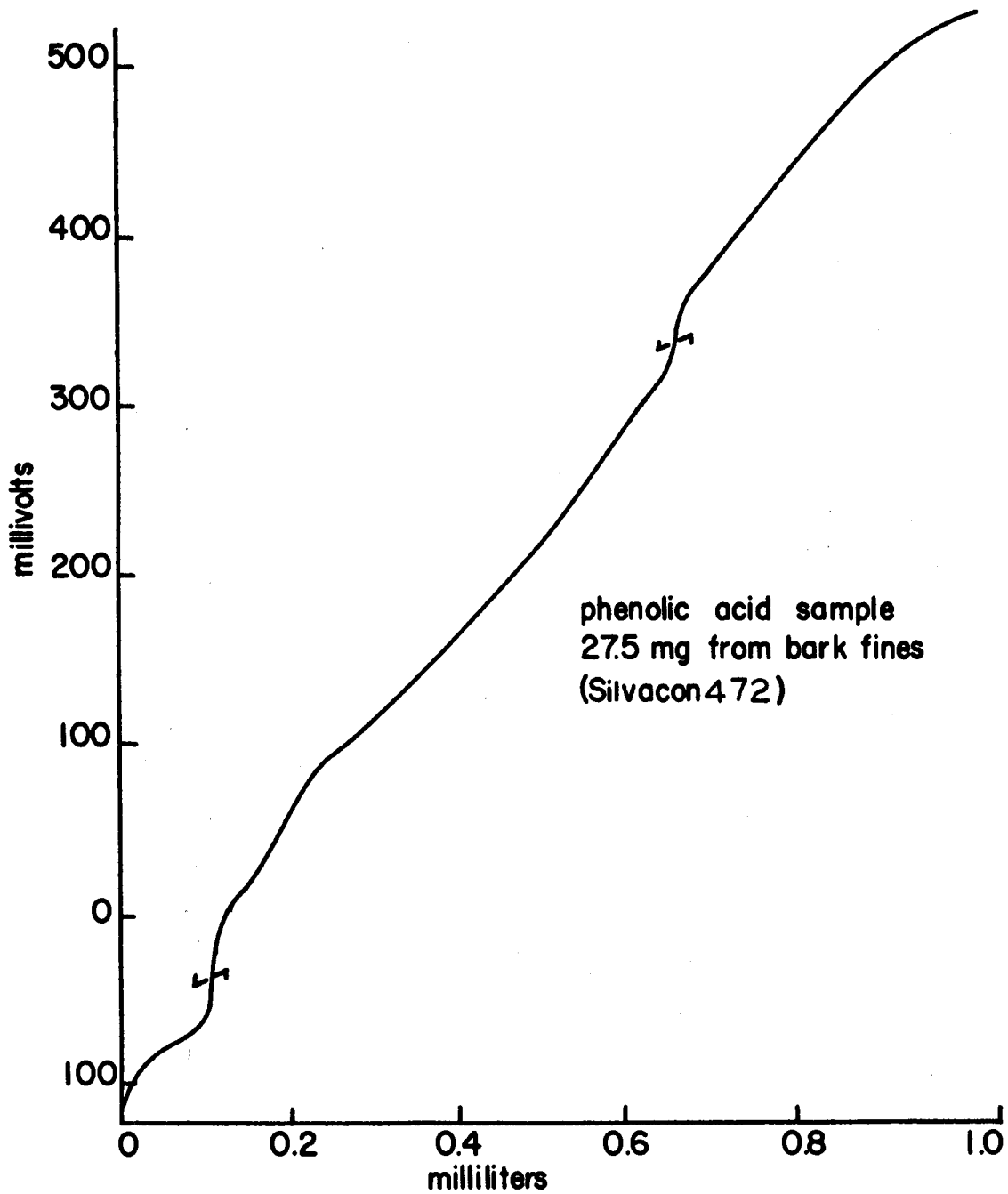
All the non-aqueous titrations curves of the various "bark phenolic acids" were similar, and although steep, showed two definite inflection points. Titration curves for "bast fiber phenolic acid-I" were consistently much smoother but with less pronounced breaks than the curves for "bast fiber phenolic acid-II" and "bark fine phenolic acid". The curves for the latter two acids always exhibited several minor bends and breaks. Duplicate titrations of any of the acids gave similar but not identical curves. The main inflection points came at the expected places, but the minor irregularities of the curves for "bast fiber phenolic acid-II" and "bark fine phenolic acid" were sometimes slightly different. These irregularities might have been due to some instability of the titration system, but smooth curves were consistently obtained from the other two bark phenolic acids and all of the pure compounds. Thus

POTENTIOMETRIC TITRATION IN DMF

Figure 4



POTENTIOMETRIC TITRATION
IN DMF
Figure 5



it seems that these irregularities were due to the nature of the acids, rather than any instability of the titration system.

The bark phenolic acid preparations all gave similar results for both phenolic hydroxyl and carboxyl functions by any one method of determination. The barium hydroxide-calcium acetate method gave consistently higher results than those found by non-aqueous titration. Since the weak acid values in the barium hydroxide-calcium acetate method were found by the difference between total acid and carboxylic value, any error that tends to increase the total acid value will result in a corresponding higher weak acid value. Such an error would occur if the "bark phenolic acid" absorbed any of the barium hydroxide. This method of evaluating acidic determining acidic functions has been questioned by both Braun's (7, p. 251) and Schuerch (47). Its use in this study was meant only as a quick, easy method of obtaining comparable data for a check on the non-aqueous titration values.

A satisfactory enough check was obtained between the two methods to indicate that non-aqueous titration, being a fast, simple, reproducible method, could find advantageous use as another tool for characterizing "bark phenolic acids" and bark lignins.

The acidic determinations also indicated that the use of hydrotropic solutions to isolate "bark phenolic acid" did not lead to a distinctive material. Except for "bark fiber phenolic acid-I", there were similar amounts of each type of acidic functional group in both "hydrotropic and sodium hydroxide bark phenolic acid". Both methods of analyses showed that the "bast fiber phenolic acid-I" had the highest phenolic hydroxyl content and lowest carboxyl content of any of the bark phenolic acids. This could be explained by assuming that condensation of phenolic groups and oxidation to carboxyl groups occurred in the hydrotropic cooks made above 120°C and in the sodium hydroxide extractions, but did not occur under the milder conditions of the hydrotropic cook made at 120°C. The distinctive character of the "bast fiber phenolic acid-I", suggested by its color and solubility properties, is supported by its dissimilar acidic content.

The high phenolic hydroxyl and low carboxyl content gave the "bast fiber phenolic acid-I" a 6:1 ratio for these functional groups. All the other preparations had a ratio around 4:1. The 4:1 ratio was in agreement with that found by methylation studies (29).

The amount of acidic functional groups as

determined by non-aqueous titration was much lower than that found by methylation studies. Kiefer found one carboxyl (5.3%) and 4.14 (8.3%) phenolic hydroxyl functional groups in "sodium hydroxide bark phenolic acid" assuming the acid's molecular weight to be 850. Referral to Table 7 shows that the non-aqueous titration method on "sodium hydroxide bark phenolic acid" gave approximately half these values or one-half carboxyl (2.8%) and 2 (3.7%) phenolic hydroxyl groups. The sodium hydroxide phenolic acid used in this study and that used by Kiefer should be comparable, since they were isolated by identical methods from the same bark component. Similar values were exhibited by the "bark phenolic acids" from the hydrotropic cooks. After being subjected to an additional Brauns' treatment, none of the "bark phenolic acids" exhibited any change in acidic value. This ruled out impurities as being the cause of the lower acidic content. Since the ratio of phenolic hydroxyl to carboxyl came very close to 4:1 in agreement with a ratio found by an independent method of analysis, this would indicate that there was little interference by spurious groupings or due to incomplete titration.

Calculating the molecular weight from the titration data and again assuming that there is one carboxyl and four phenolic hydroxyls per phenolic acid molecule, would indicate a molecular weight in the range of 1500 to 2000 rather than 850.

POTENTIOMETRIC TITRATION
IN DMF

FIGURE 6

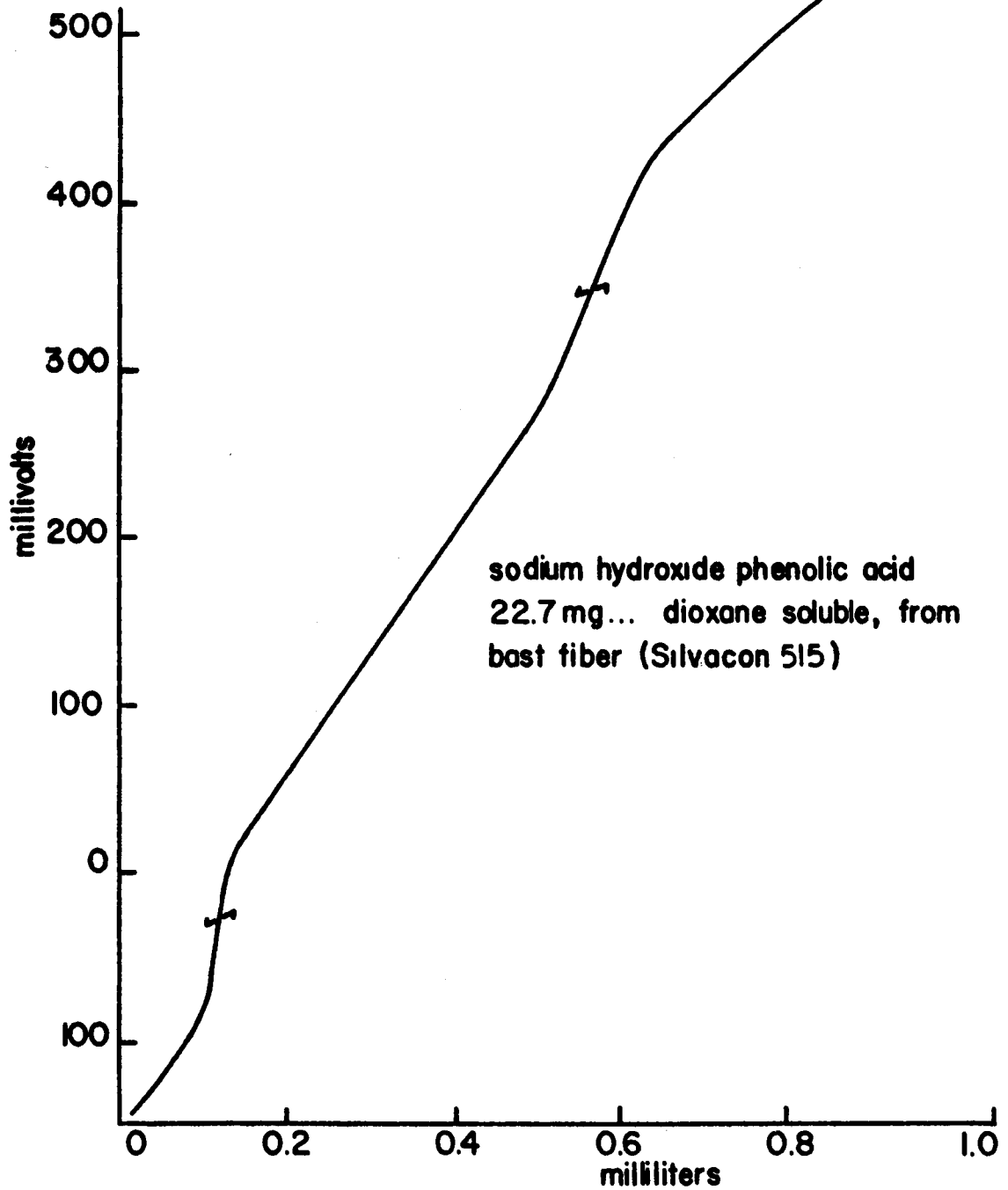


Table 6

ACIDIC FUNCTIONAL GROUPS IN BARK PHENOLIC ACID
DETERMINED BY TREATMENT WITH BARIUM HYDROXIDE
AND CALCIUM ACETATE

Bark phenolic acid	Phenolic hydroxyl (W) (values in Meq. per gram)	Carboxyl (S)	Total acid	Ratio W/S
Bast fiber phenolic acid - II	2.84	0.69	3.53	4.1
Bark fine phenolic acid	2.86	0.82	3.68	3.6
Bast fiber phenolic acid - I	2.95	0.51	3.46	5.9
Sodium hydroxide phenolic acid	2.74	0.74	3.48	3.7

Calculated in percentage values from above

	Phenolic hydroxyl %	Carboxyl %
Bast fiber phenolic acid - II	4.8	3.1
Bark fine phenolic acid	4.8	3.7
Bast fiber phenolic acid - I	5.0	2.3
Sodium hydroxyl phenolic acid	4.7	3.3

Table 7

ACIDIC FUNCTIONAL GROUPS IN BARK PHENOLIC ACID
DETERMINED BY NON-AQUEOUS TITRATION
IN DIMETHYLFORMAMIDE

Bark phenolic acid	Phenolic hydroxyl (W) (values in Meq. per gram)	Carboxyl (S)	Total acid	Ratio W/S
Bast fiber phenolic acid - II	2.09	0.53	2.59	3.9
Bark fine phenolic acid	2.23	0.47	2.70	4.7
Bast fiber phenolic acid - I	2.64	0.44	3.06	6.0
Sodium hydroxide phenolic acid	2.16	0.62	2.78	3.5

Calculated in percentage values from above

	Phenolic hydroxyl %	Carboxyl %
Bast fiber phenolic acid - II	3.5	2.4
Bark fine phenolic acid	3.8	2.1
Bark fiber phenolic acid - I	4.5	2.0
Sodium hydroxide phenolic acid	3.7	2.8

W = weak functional group

S = strong functional group

l = all values based on moisture-free material

Chromatography studies (3, 34)

The four phenolic acid preparations were further compared by descending paper chromatography. Two microliters of a freshly prepared solution of each of the four phenolic acid, 1/mg/ml, in DMF was spotted on strips of No. 1 Whatman filter paper. After air drying, the strips were placed in the chromatography apparatus, equilibrated with the solvent system and developed by the descending method.

Two solvent systems (32) were used in connection with two indicator sprays. Duplicate chromatograms were made in each solvent; butanol-acetic acid-water (4-1-5) and acetone-methyl isopropyl ketone-water (140-75-40). Each chromatogram was examined under ultra-violet light, the fluorescent region outlined in pencil, and then sprayed with either bis-diazotized benzidine (BDB) or ferric chloride-potassium ferricyanide indicator. The ferric chloride-potassium ferricyanide indicator reacted with the paper to produce a blue color, while the areas containing adsorbed materials remained white. The BDB reacted with the adsorbed material to produce red-yellow or yellow spots which turned to brown upon standing, the paper remaining white.

Graphic illustrations of the chromatograms are presented in Figure 7. Figures 7a and 7c show the spots observed under ultraviolet light. The chromatograms from both solvent systems were similar except for the fluorescence exhibited by the bast fiber phenolic acid-II at Rf 0.6 in the butanol acetic acid-water solvent. This spot was not resolved by the other solvent system and was not indicated by the sprays. No difference was observed in resolution through use of the two sprays. They produced similarly spotted chromatograms. The chromatograms presented in Figure 7b and 7d are representative of the chromatograms sprayed with either of the indicators. The only significant difference was the coloring of the spots. In both solvent systems with ferric chloride potassium ferricyanide spray, the spots were an even white color, but with the EDB reagent the bast fiber phenolic acid-II and sodium hydroxide phenolic acid gave yellow spots with a red area at the bottom of the spot. These colors quickly faded but were most distinct on the freshly sprayed chromatogram.

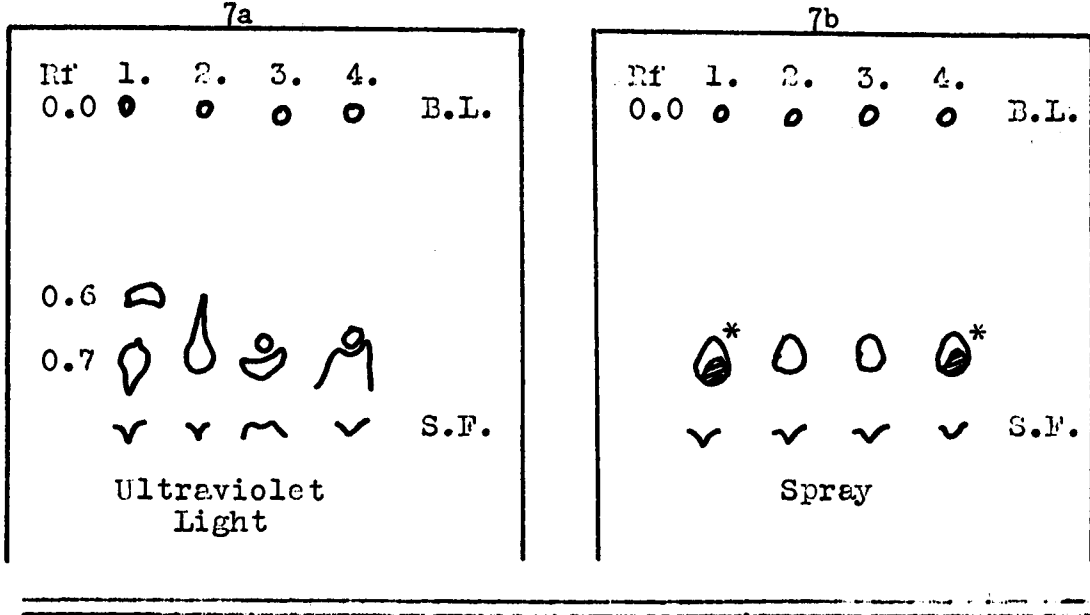
Both of the solvents gave similar resolution. In all cases a certain amount of material remained at the base line. Most of the material was concentrated in a large spot in the region of Rf. 0.7 or 0.8. The

Figure 7

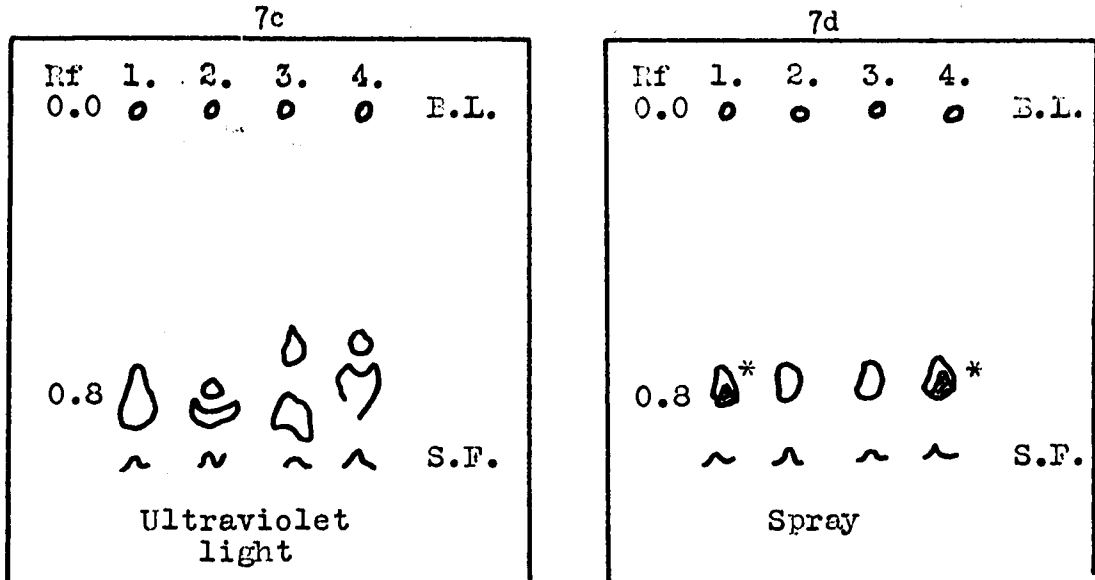
CHROMATOGRAPHIC COMPARISON OF PHENOLIC ACIDS

- 1. - Bast fiber phenolic acid-II
- 2. - Bark phenolic acid
- 3. - Bast fiber phenolic acid-I
- 4. - NaOH phenolic acid

Solvent
Butanol-acetic acid-water (4-1-5)



Solvent
Acetone-Methylisopropyl ketone-water (140-75-40)



* - Red areas only with IBD spray
B.L. = Base line; S.F. = Solvent front.

acetone-methyl isopropyl ketone-water system gave slightly higher Rf values. A small amount of the material was at the solvent front. This would indicate all of the phenolic acids are heterogeneous containing at least three fractions. Bi-colored spots obtained with the BDB spray for NaOH and bast fiber phenolic acid-II may also be due to another constituent. The ultraviolet fluorescent spot found for the bast fiber phenolic acid-II indicates that this phenolic acid has at least four constituents.

Except for the additional fluorescent spot found for the bast fiber phenolic acid-II, the hydrotropic and sodium hydroxide bark phenolic acids gave similar results. Bast fiber phenolic acid-I, which was distinctive in appearance and acidic properties, exhibited no outstanding chromatographic difference from the other bark phenolic acids.

Infrared and ultraviolet absorption of "bark phenolic acids"

Ultraviolet absorption spectra: Ultraviolet absorption spectra were obtained as a further comparison of the four types of phenolic acid. The phenolic acids were dissolved in a 9-1 dioxane-water solution to give an approximate concentration of 3 mg per 100 ml. These solutions were examined in the region between 220 and

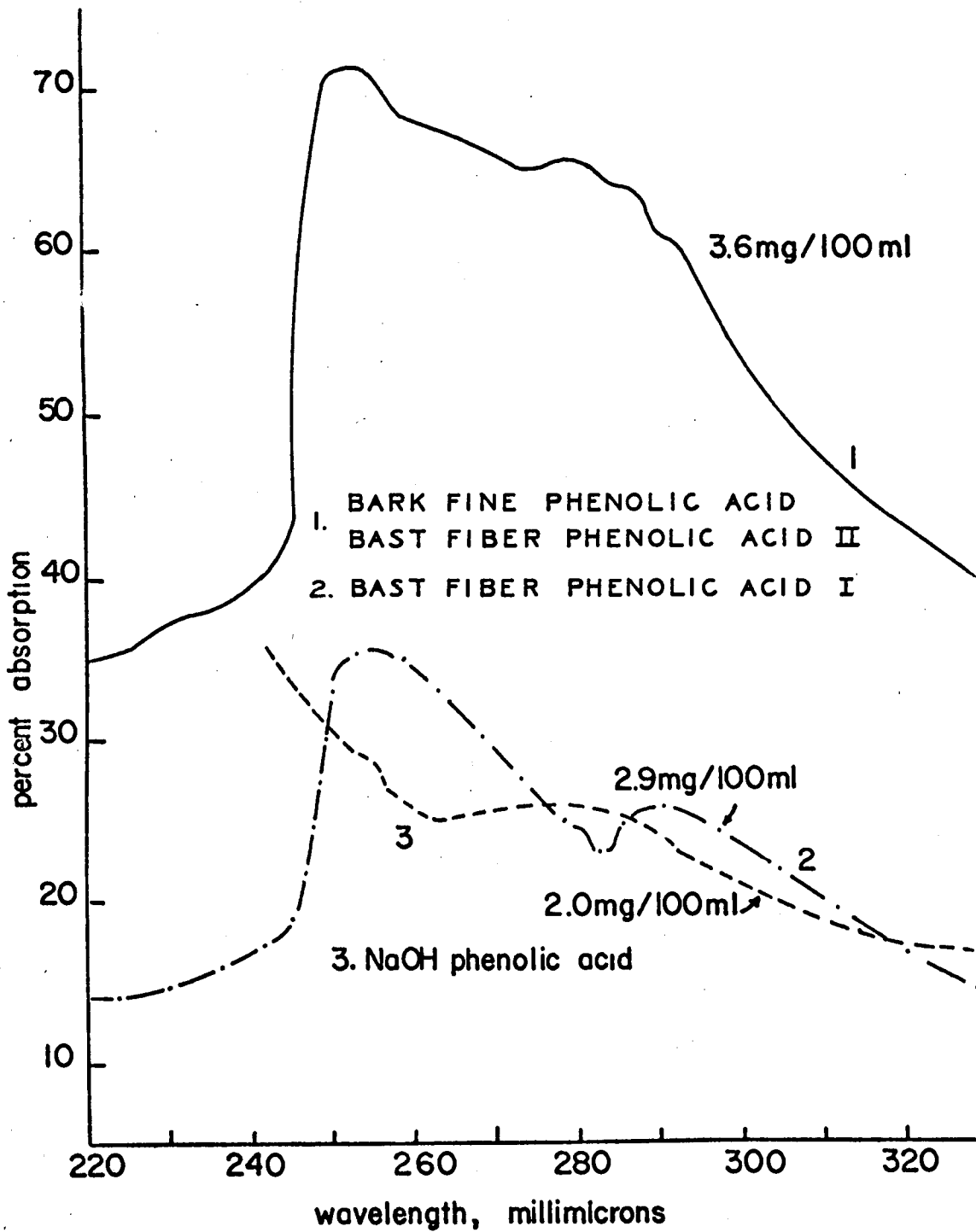
340 millimicrons with a Beckman Model DU quartz spectrophotometer fitted with a photomultiplier.

The ultraviolet spectra are shown in Figure 8. Bast fiber phenolic acid-II and bark fine phenolic acid both exhibited similar curves. Curve one is a representative curve for these two preparations. Both of these phenolic acids exhibited maxima in the range of 280 millimicrons, which has been reported in earlier works on Douglas fir bark components (29, 32). A maximum at this wave length has also been reported for various wood lignins (6, p. 218-219). The curve for "bast fiber phenolic acid-I" was similar to curve one, but had a much more pronounced maximum at 290 millimicrons. In general, the sodium hydroxide phenolic acid gave a rather smooth, non-specific curve with a broad, weak maximum at 280 millimicrons and a strong absorption after 250 millimicrons. It was quite different from the curves obtained from the hydrotropic bark phenolic acids.

Infrared absorption spectra: Infrared absorption spectra were run for each of the "bark phenolic acids" on an automatic recording, double-beam Perkin-Elmer Model 21 spectrophotometer. Curves were obtained between 600 and 3900 wave numbers with the sample contained

ULTRAVIOLET ABSORPTION SPECTRA
OF DOUGLAS FIR BARK PHENOLIC ACIDS

Figure 8



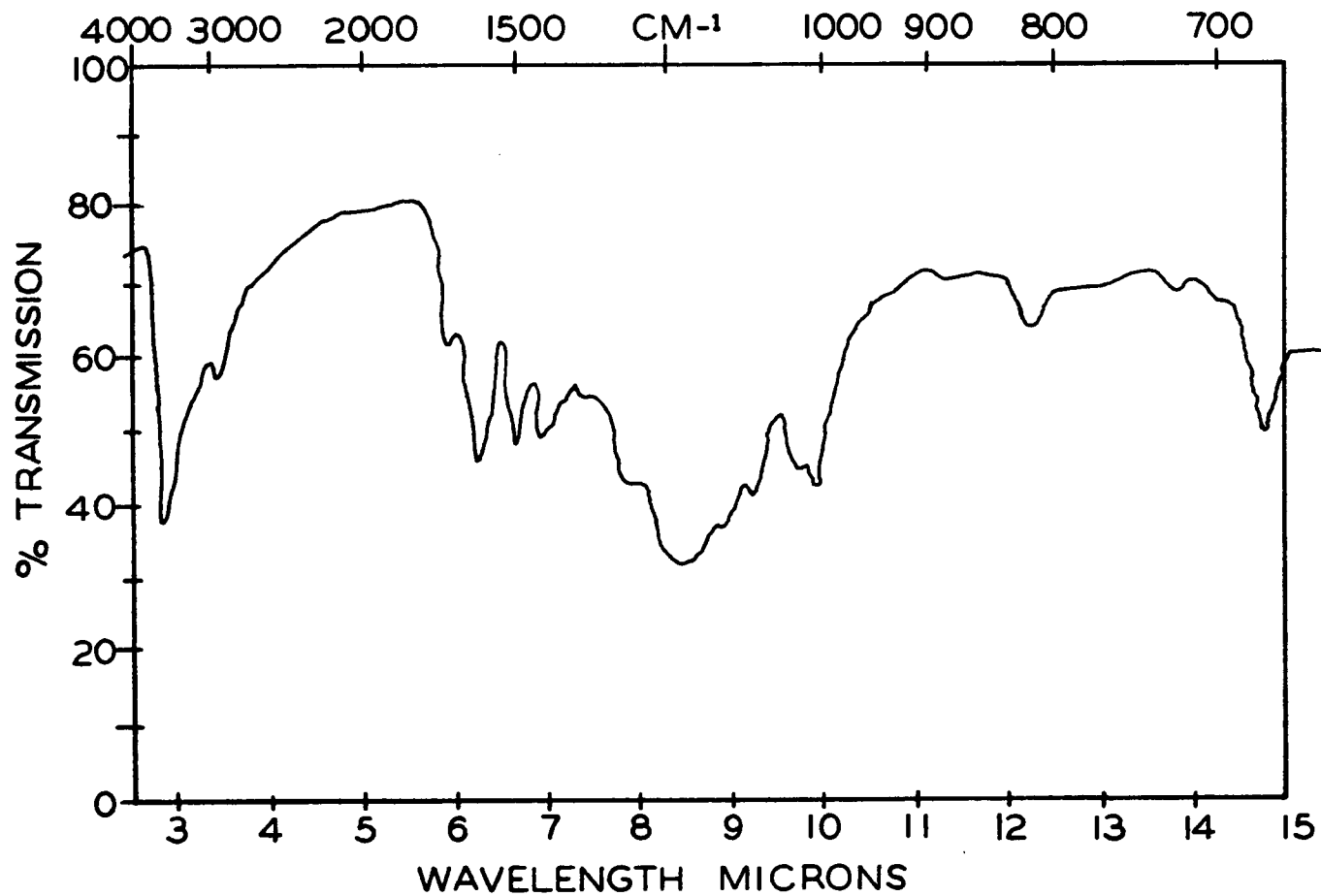
in a potassium bromide disc. All of the "bark phenolic acids" exhibited almost identical infrared spectra. Figure 9 shows a representative example of the infrared spectra. The presence of the carbonyl group is indicated by the small peak at approximately 1700 wave numbers. No further attempt will be made to interpret the spectra, since they were included only as another means of comparing the various "bark phenolic acids".

Methoxyl content

The methoxyl content of each of the four "bark phenolic acid preparations" was determined according to TAPPI standard T 13m-54. The results are listed in Table 8.

The "sodium hydroxide bark phenolic acid" had a methoxyl content of 4.3 which was identical to that found by Kiefer (29). All of the "hydrotropic bark phenolic acids" exhibited slightly higher methoxyl contents. Assuming a molecular weight of 850 and using 4.9 as an average methoxyl value would give the "hydrotropic bark phenolic acids" 1.6 methoxyl groups per unit molecule, while only 1.2 methoxyl groups were found in the "sodium hydroxide bark phenolic acid". This would be in accordance with the

TYPICAL INFRARED SPECTRA OF BARK PHENOLIC ACIDS
FIGURE 9



ultraviolet spectra data which also points to a slight difference between the "hydrotropic" and "sodium hydroxide bark phenolic acid".

Table 8

METHOXYL CONTENT OF THE BARK PHENOLIC ACIDS	
<u>Preparation</u>	<u>Methoxyl¹</u> <u>%</u>
Bast fiber phenolic acid-I	4.95
Bast fiber phenolic acid-II	5.01
Bark fine phenolic acid	4.97
Sodium hydroxide phenolic acid	4.30

1. Values based on moisture-free material

SUMMARY OF RESULTS

Hydrotropic solutions have been used to pulp wood and other fibrous material as bagasse and bamboo. This suggested their use as a delignifying agent for Douglas fir bark components such as bast fibers. It was thought their unique pulping action might be more successful in delignifying the Douglas fir bark than previous used reagents. Also, it was hoped that the extracted hydrotropic bark phenolic acid would have distinct properties, making it more amiable to utilization.

Preliminary cooks were made on Douglas fir bark bast fibers to compare the pulping ability of several different hydrotropic solutions. From those tested sodiumcyeme, sodium ethylbenzene, and sodium xylene-sulfonate were selected for showing the best hydrotropic effect on the bast fibers.

Additional cooks were made using the three selected hydrotropes to study the effect of liquor-to-bark ratio, concentration of hydrotropic solution, type of hydrotrope, time, and temperature of cook. Table 4 contains the results of these cooks. Of the five variables within the ranges studied, only temperature and type of hydrotrope were significant. Cooking at

higher temperatures promoted a greater hydrotropic effect, i.e. greater solubility of the bast fibers, but did not aid in selectively removing the bark lignin. Type of hydrotrope is significant as shown in the preliminary study but there was little difference between the three hydrotropes selected for additional study.

Cooking between a liquor-to-fiber ratio of 8:1 to 14:1, between a liquor concentration of 25 to 35 percent, or with a different type hydrotrope, had little effect on the yield of pulp or its lignin content. Only a small hydrotropic effect was apparent when cooks were made for less than three hours, with less than a 25 percent hydrotropic solution or at a temperature below 140°C. Increasing the reaction time only solubilized more material without any beneficial effect.

Under the conditions studied, the hydrotropic solutions were not good pulping agents for bark components. They solubilized too large an amount of carbohydrate material and were not selective in their removal of "bark lignin".

A non-aqueous titration method using DMF was applied for the first time to determine the acidic

functional groups in "bark phenolic acid". It proved to be a simple, easy procedure which gave accurate, reproducible values.

Comparison of the hydrotropic and sodium hydroxide "bark phenolic acid" indicated they were very similar but not identical in nature. The two methods used to determine acidic functional groups found both types of phenolic acids to contain on an average 5.0 percent phenolic hydroxyl and 3.0 percent carboxyl. This was approximately half as many as found by methylation studies. Molecular weight of both types of "bark phenolic acid" calculated from the titration values was in the range of 1500-2000. This was twice as large as the previous assumed molecular weight of 850.

The ratio of phenolic hydroxyl to carboxyl in both types of "bark phenolic acid" was found to be 4:1. This was in agreement with values found by methylation studies.

There were only slight differences in the paper chromatograms and methoxyl content of the "hydrotropic and sodium hydroxide bark phenolic acid" and no difference in their infrared spectra. Only their ultraviolet spectra showed considerable difference.

The experimental work showed that hydrotropic solutions were not good pulping agents for Douglas fir bark components and that the hydrotropic "bark phenolic acid" when compared to sodium hydroxide "bark phenolic acid" showed no distinctive properties.

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