PREPARATION OF THE HALOGEN DERIVATIVES
OF ABIETIC ACID
AND THE INVESTIGATION OF THEIR PROPERTIES

By

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INTRODUCTION

The halogenation of abietic acid has received little or no attention in publications and the ultimate value of such compounds is therefore not known. Due to the availability and low cost of the acid this is surprising. However, the inability to obtain the acid in a pure and reproducible form is no doubt the chief reason that chemists have not investigated the problem.

The object of this work was to halogenate abietic acid under varying conditions, to separate the products, and to determine as many of the properties as possible.

HISTORICAL

The investigation of rosin acids began in the early Nineteenth Century, but only in the past fifty years has the complexity of the material been clearly understood. During this time much work has been done in separating and elucidating the structures and related reactions of the various components.

The limpid oleoresin that exudes from incisions cut in the bark of living pine trees can be separated by steam distillation into two fractions. The resulting materials are composed of a steam-volatile fraction, gum turpentine (1 part), and a non-volatile residue that will set, when cooled, to a yellow or brown glass, known as rosin or colophony (4 parts). This residual solid matter is melted and strained into barrels becoming the ordinary rosin of commerce. It comes into the market graded according to color. That sold under "Mark A" is nearly black and numerous qualities exist between that and the rosin marked "W.W" which is "water white," rosin of the finest quality.

The rosin production in the United States in the year ending March 31, 1948, was 1,990,831 drums, (520 pounds). About 60% of the production is normally exported (1). Rosin is used in low-grade soaps, in the sizing of paper, as a basis for cheap varnishes and of resinate driers, and as an adulterant of shellac.

Three major difficulties have been encountered in the study of the chemistry of rosin: (a) the complexity of the rosin, or as they are unfortunately often termed "resin" acids in many publications; (b) rosin from different pine trees and at different seasons of the year contain different acids, and (c) methods of treatment or so-called isolation frequently alter the character of the acids. These factors have made it exceedingly difficult to even compare, much less reconcile a good deal of one observer's work with

that of another.

Despite these facts, it is now known that rosin is composed largely of diterpene acids of the formula $C_{19}H_{29}COOH$ in various stages of isomerization (Chart 1).
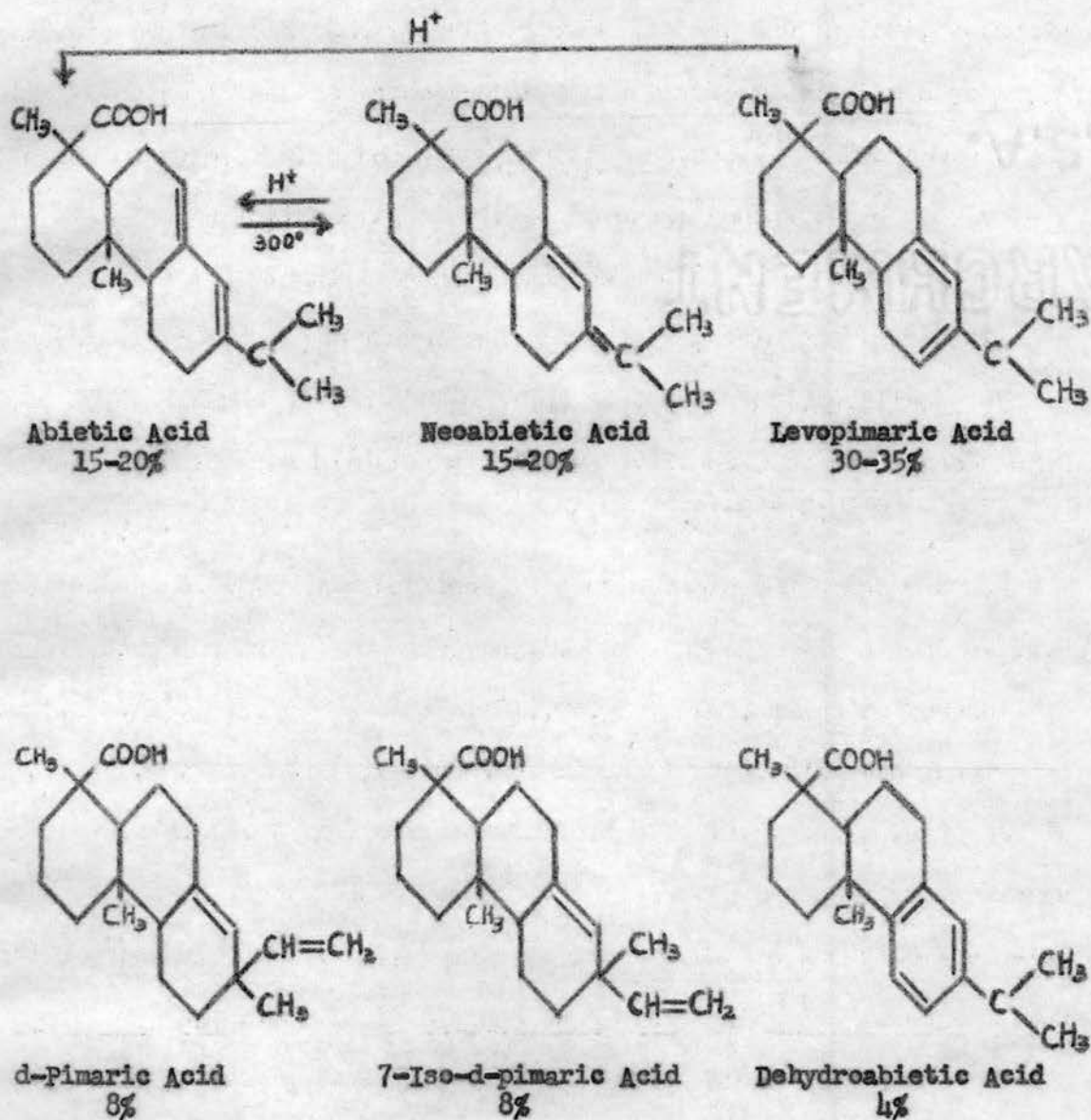
One of the first rosin acid investigators was Baup, who in 1826, succeeded in isolating a crystalline substance from colophony and gave it the name abietic acid because of its source, the Pinus abies tree. Much of the early work dealt with the isolation of acids from different sources, and many substances of doubtful individuality were described and named. Attention was directed particularly to the abundant and relatively stable abietic acid. Crude abietic acid is one of the cheapest and most abundantly available of higher organic acids. Pure abietic acid is now available for seven cents a pound in drum lots.

The structure of this acid remained in considerable doubt for a century and not until the past few years have the investigators agreed on the molecular structure (Chart 1). Ruzicka and Meyer (2), P. Levy (3), and more recently Rydon (4), and R. D. Haworth (5), were the principal leaders in the proof of structure of abietic acid. Following their investigations, the only doubt remaining was that of the disposition of the two unsaturated linkages. Fieser and Campbell (6), and Ruzicka (7), have assigned the double bonds to the 9-14 and 7-8 positions, their conclusions based on the isolation and identification of isobutyric acid, an oxidation product.

Many derivatives, such as di- and tetrahydroxyabietic acid, salts and esters of abietic acid, have been reported in the literature but only two references giving pertinent information on the halogenation were found, one being a patent. No physical constants or properties of halogenated abietic acid were located. Borglin (8) claims only the method of halogenation and

ROSIN*

Chart 1 (1)

H⁺

CH₃ COOH

H^+ ⇌ 300°

Abietic Acid
15-20%

CH₃ COOH

Neoabietic Acid
15-20%

CH₃ COOH

Levopimaric Acid
30-35%

CH₃

CH₃

CH₃ COOH

CH=CH₂
CH₃

d-Pimaric Acid
8%

CH₃ COOH

CH₃
CH=CH₂

7-Iso-d-pimaric Acid
8%

CH₃ COOH

CH₃
CH₃

Dehydroabietic Acid
4%

* A dihydroabietic acid also has been isolated as the lactone.

quantitative halogen analysis of the final product. The second article (9) concerns the addition of iodine to the double bonds using Wijs method and it was proved experimentally that the addition was dependant on three variables: (a) temperature of reaction; (b) time of absorption, and (c) amount of excess iodine used. For example: It was shown in this article that using 250% excess iodine and changing the absorption temperature from 21.1 to 32.2° C., the iodine number will change 38 points. Also by increasing the time of reaction from $\frac{1}{2}$ to 2 hours, with 300% excess iodine, the result was an increase in the iodine number of 44 points. The basis of comparison was an iodine number of 145 at 21.1° and 250% excess iodine.

This article points to the fact that one unsaturated linkage is readily available for reaction whereas the second is considerably slower and much less available.

EXPERIMENTAL

General Procedure for the Determination of the Neutralization Equivalent (10).
The neutralization equivalent was obtained for the various halogenated prod-
ucts in this work by dissolving an accurately weighed sample (200-400 mg.)
of the acidic substance in alcohol in a 125-ml. Erlenmeyer flask. Heat was
applied to assist in dissolving the solid. The solution was titrated with
standardized aqueous sodium hydroxide or alcoholic potassium hydroxide, approx-
imately 0.1 normal. Color-change indicators, in most cases phenolphthalein,
were used. Blanks were run on the solvent using the same amount of indicator
as was used in the titration of the sample.

The neutralization equivalent of the compound was calculated as follows:

$$N.E. = \frac{\text{Wt. of sample in grams} \times 1000}{\text{Ml. of base} \times N \text{ of base}}$$

This formula may be written as:

$$N.E. = \frac{\text{Milligrams of sample}}{\text{Milliequivalents of base}}$$

General Procedure for the Determination of the Saponification Equivalent (10).
This saponification equivalent is normally used in regards to esters, the
objective being to hydrolize the ester and determine the amount of alkali
that reacts with the acid produced.

In this work the saponification equivalent should actually be termed the
neutralization equivalent since the compound was not an ester but an acid.
It was necessary to use this procedure due to the difficulty in obtaining a
solution of the product. Thus the material was digested in base and the
excess base titrated.

An accurately weighed sample (200-400 mg.) was dissolved in a known volume of standard base in a 125-ml. Erlenmeyer flask. The resulting solution was then titrated with standard hydrochloric acid using phenolphthalein as the indicator. A blank titration was run on the volume of base used in the original solution with the same indicator. The saponification equivalent was determined using the following formula:

$$\text{Sap. Equiv.} = \frac{\text{Wt. of sample in grams x 1000}}{(\text{ml. of base for blank} - \text{ml. of base for sample}) \times N \text{ of base}}$$

General Procedure for the Quantitative Halogen Determination (11). The electric ignition Parr Sulfur Bomb, Type I, and the flame ignition Parr Micro Bomb, both manufactured by the Parr Instrument Company, Moline, Illinois, were used for quantitative halogen determination in this work.

In using the Parr Sulfur Bomb, an accurately weighed sample (200-300 mg.) of the material was placed in the fusion cup. Five tenths gram of accelerator (benzoic acid or sugar) was added. The bomb head was set in place and the mixture was shaken for 30 seconds. The head was then removed and 1 scoop (15 grams) of high purity sodium peroxide was added. The fusion mixture was shaken for one minute to insure a homogeneous mixture. The cup was then placed in the bell body and the screw cap tightened with a wrench. The bomb was placed in the water jacket with the water flowing, and ignited with the ignition unit.

When the fusion mixture had ignited, a slight vibration or thumping was noticed. If combustion did not take place, the bomb was removed from the water bath, dried, the cap removed and a new fuse wire inserted. After combustion, the bomb was allowed to cool for 5 minutes, then removed from the bath and opened. Adhering material from the bottom of the cap was washed into an 800-ml. beaker with a stream of water from a wash bottle. The fusion

cup was then placed in the beaker, 50 ml. of distilled water added and the beaker covered with a watch glass. If the reaction did not begin, the beaker was warmed. When the fusion mixture had dissolved, the cap was removed with tongs and washed inside and out with a stream of water from a wash bottle. The washings were caught in the beaker.

The solution was then acidified by the careful addition of concentrated nitric acid with stirring. Any carbon particles present were removed by filtration. The halide was precipitated in subdued light by adding 0.1 normal silver nitrate solution. The precipitate was coagulated by heating the solution and stirring rapidly. The beaker was then placed in the dark for an hour to age the precipitate. The precipitate was collected in a tared porous-bottom filter crucible and dried in an oven at 150-180° C. for an hour.

The procedure followed in using the Parr Micro Bomb was essentially the same as that described above. The samples used weighed 40 to 70 mg. One and one-half grams of sodium peroxide and 30 to 40 mg. of powdered lactose were used as the fusion mixture and were thoroughly mixed by shaking. The mixture was ignited with a small flame, allowed to cool in the air, and finally in water.

The percent halogen was calculated as follows:

$$\% \text{ Halogen} = \frac{\frac{X}{Ag\,X} \text{ x wt. of ppt. x 100}}{\text{Wt. of sample}}$$

General Procedure for the Molecular Weight Determinations (12). The standard Beckmann method of freezing point depression determination using benzene as the solvent was employed for determining molecular weights. A difficulty arose in keeping the benzene dry as the dew point was quite high during the period of time in which this work was being done. This resulted in a clouding

of the solution as the freezing point was approached, and consequently an accurate freezing point of the solvent or the solution was unattainable. Traces of moisture were removed from the solvent by distilling one-fourth of the benzene over and using that which remained in the still pot for the determinations. Thus one freezing point was obtained before the cloudiness returned, however, it was impossible to attain a second like value to ascertain correctness. This method was used on only three samples.

General Procedures for Qualitative Halogen Determination. The Beilstein test for halogens was performed in the following manner: A copper wire was heated to redness until it no longer colored the flame. The wire was then cooled and touched to a small amount of the compound to be tested. When the wire was again heated in the non-luminous flame of a burner, a blue-green flame indicated the presence of a halogen.

Sodium fusion was used to confirm the Beilstein test. A small piece of clean metallic sodium weighing 25-30 mg. was placed in the bottom of a four inch Pyrex test tube and heated until the sodium melted. A 10-15 mg. sample of the substance being tested was added to the fused sodium and the mixture again heated until the sodium vapor rose one-half inch in the test tube. The tube was allowed to cool for a few seconds and another sample of the substance added. This mixture was again heated until the test tube was glowing red. The flame was removed and a 100-ml. beaker containing 20 ml. of distilled water was brought up around the test tube and the tube then broken into the beaker. The resulting mixture was then brought to the boiling point and filtered to remove the particles of glass and carbon. The filtrate was acidified with concentrated nitric acid and one to two ml. of 0.1 normal silver nitrate solution added. A precipitate proved the presence of a halogen.

Preparation of Abietic Acid

Method I: Preparation of Abietic Acid from Rosin. This method consisted essentially of separating the abietic acid from rosin by forming its potassium salt, removing the insoluble material by filtration, and acidifying the filtrate with hydrochloric acid.

Four hundred fifty grams of technical grade rosin were dissolved in 1200 ml. of ether in a 5-liter round-bottom flask. One and eight tenths liters of 0.5 normal potassium hydroxide were added to the solution. The volume of base used was calculated to insure a 50% excess over that amount necessary to form the potassium salt of the abietic acid present in the rosin. The ether layer contained sterols while the lower layer consisted of potassium hydroxide and potassium abietate. A small amount of brown material precipitated and formed a thin layer at the interface of the heterogeneous system. The mixture was stirred once a day. Some solid material representing fatty acids settled out. The mixture was allowed to stand for two weeks. One hundred milliliters of the salt layer were removed from the flask with a siphon. This solution was washed in a separatory funnel with ether and the washings were discarded. The residue was acidified with dilute hydrochloric acid and a dark brown gum separated out. Recrystallization was unsuccessful.

Method II: Preparation of Steele's Abietic Acid (13). Four hundred fifty grams of technical grade rosin and 375 ml. of glacial acetic acid were mixed in a 1-liter round-bottom flask. Solution of the rosin was accomplished by heating the mixture and agitating it. The solution was dark brown in color. The flask was set aside for several days but the abietic acid failed to crystallize.

The solution was refluxed for two hours as suggested by Steele and again set aside. The solution was seeded and stirred to induce crystallization but

to no avail. This method of preparation was discontinued.

Method III: Purification of Commercial Abietic Acid. Three hundred grams of commercial grade abietic acid were purified by recrystallization from methanol. The acid was dissolved in a minimum amount of hot alcohol and the solution cooled in an ice bath to affect crystal formation. The crystals were separated by filtration and dried in a dessicator over sulfuric acid. The crystals lost their original yellow color as successive crystallizations were performed. The melting point increased three to five degrees after two such operations. One more recrystallization failed to raise the melting point, now at 147-150° C., so further recrystallization was unnecessary.

Method IV: Purification and Physical Properties of "Tallex." Two thousand two hundred grams of abietic acid (trade name, "Tallex") were obtained from the West Virginia Pulp and Paper Company of Covington, Virginia. The material was light tan in color but became white after three recrystallizations from hot methanol. The melting point was 151-153.5° C.

The observed angle of rotation was determined and the specific rotation calculated as follows (14):

An accurately weighed sample, 3.6370 grams, of Tallex was dissolved in 50 ml. of ethanol and a polarimeter tube 2 decimeters in length was filled with the solution. A second tube of the same dimensions was filled with ethanol and used as a blank in the polarimeter. A sodium lamp was used as the light source. The observed angle of rotation for the blank was zero; for the solution −5.08°.

The specific rotation was calculated using the formula:

$$(\alpha)_D = \frac{100\alpha}{lc}$$

$$= -35°$$

Where:

$\propto$ = observed angle of rotation

l = length of tube in decimeters

c = concentration in grams/hundred ml. of solvent

The neutralization equivalent (N.E.) of Tallex was determined as described previously, using phenolphthalein as an indicator. The neutralization equivalent was calculated to be 293. The theoretical molecular weight of Tallex is 302.

A molecular weight determination of Tallex was attempted using the Beckmann freezing point depression method. Benzene was used as the solvent and the calculated molecular weight was 570. It was later found that abietic acid forms a dimer in benzene (15).

Chlorination of Abietic Acid

Method I: Procedure (8). Fifty grams of recrystallized abietic acid were dissolved in 100 grams of ethylene chloride in a 500-ml. round-bottom flask. The solution had a yellow color, imparted to it by the abietic acid. A water condenser and standard gas dispersion tube were attached to the flask with a two-hole rubber stopper. The dispersion tube used had a porous bottom one inch in diameter and extended one inch below the surface of the liquid. The chlorine bottle was connected to the dispersion tube with rubber tubing and a lead-off from the top of the condenser carried the unreacted chlorine through a water trap into a beaker of sodium hydroxide. The flask was heated with an electric hot plate. The solution was refluxed with the chlorine flowing at the rate of 20 bubbles per minute. The temperature was maintained at about 100° C. After four hours, a suspension of 5 grams of anhydrous aluminum chloride in 200 grams of ethylene chloride was added slowly to the refluxing

mixture. Refluxing was continued for an additional three hours.

The mixture was then cooled and the solution decanted from the small amount of solid in the bottom of the flask. The product was obtained by dilution with water and filtering through a Buchner suction funnel. The filtrate was discarded.

The residue was a golden colored gum. It was dried in an electric oven at 105° C. and crushed in a mortar to a fine powder. The product was very slightly soluble in methanol, ether, and sulfuric acid, and was impossible to wet with sodium carbonate solution. However, it was soluble in hot dilute potassium hydroxide to the extent of about 1 part; 4 parts being insoluble. The base insoluble material was separated by filtration and the filtrate acidified with hydrochloric acid. This acidification resulted in the precipitation of a yellow crystalline substance which was removed by filtration. The filtrate was rejected and the colored residue dried in an oven at 105° C. Analysis. The original product had a melting point of 325-330° C. The melting point of the base soluble material was 125-128° C. Both substances were subjected to sodium fusion. An excessive amount of carbon was obtained and removed from the aqueous solutions by filtration. The filtrates were acidified with nitric acid and both failed to give a precipitate when silver nitrate was added. However, the Beilstein test for halogen was positive for both substances. The materials first burned with smoky yellow flames in the outer cone but after the temperature of the wire was increased by placing it in the hotter inner cone of the Bunsen flame, the characteristic green halogen color was obtained.

The saponification equivalent of the base soluble material was found to be 308. Phenolphthalein was used as the indicator. The neutralization equivalent of the original product, using ethylene chloride as the solvent, was found to be 293.

Quantitative halogen analysis using the Parr Sulfur Bomb and lactose as the accelerator indicated 12.5% for the base soluble material. Excellent combustion was obtained with no carbon resulting. The base insoluble material gave a value of 8.9%. Lactose was used as the accelerator and a small amount of carbon resulted in the combustion. It was removed by filtration before precipitation of the halide with silver nitrate.

Method II: Procedure. This method was essentially the same as Method I. Solvent, reaction time, and catalyst used were identical. To obtain the product, the cooled reaction mixture was washed twice with water. During the second washing, the heterogeneous system was shaken and an emulsion was obtained. The emulsion failed to break after standing overnight so the mixture was subjected to low pressure distillation. After the total volume of the solution had been reduced by half, the emulsion broke and the product separated as a dark brown oil. The remainder of the aqueous layer was removed by decantation and the oil was dried in an oven at 105° C. The resulting brown solid was powdered in a mortar.

It was separated into two portions, a base soluble and a base insoluble material, by adding sodium hydroxide solution, warming, and filtering. The insoluble material was dark brown. The sodium hydroxide solution was acidified with hydrochloric acid and filtered. The base soluble product was light tan. Both the base soluble and insoluble materials were dried in an oven at 105° C.

Analysis. The acidified aqueous solution obtained from sodium fusion of the original product gave a light precipitate when silver nitrate was added. The base soluble material had a saponification equivalent of 345 and melted at 90° C. The Beilstein test was positive after the material had sintered and was subjected to a hotter portion of the flame. Parr bomb analysis indicated 2.0% halogen.

The base insoluble material decomposed above 290° C. The Beilstein test indicated the presence of chlorine. Sodium fusion resulted in a negative test for halogen, however, Parr bomb analysis indicated 3.6% chlorine.

An accurately weighed sample, 0.7359 grams, of the base insoluble material was ignited in a tared porcelain crucible. The material was first burned with a Bunsen burner until it was completely charred. The crucible was then covered and the material ignited for 30 minutes with a Meeker burner. The crucible was cooled in a "Desi-cooler" and weighed. The residue had the appearance of a finely woven ball of snow-white cotton. It weighed 0.0645 grams and represented 8.77% of the sample.

When an attempt was made to dissolve the residue in concentrated nitric acid, only a small portion of it went into solution. The clear solution was decanted from the insoluble material and made slightly alkaline. A faint precipitate thus obtained failed to dissolve completely when the solution was made strongly alkaline.

Method III: Procedure. Thirty grams of abietic acid were dissolved in 120 grams of methanol in a 500-ml. round-bottom flask and 4.5 grams of powdered aluminum metal were added. Chlorine gas was passed in at the rate of 20 bubbles per minute and the mixture maintained at reflux temperature for six hours. It was then allowed to cool and the dark brown liquid was decanted from a small amount of black solid in the bottom of the flask.

The product was obtained by diluting the decanted solution with distilled water and removing the tan solid as it formed. The product was redissolved in hot methanol and again precipitated by adding water to the solution. The gum was dried in an oven at 100° C. and the resulting brown solid crushed in a mortar.

Analysis. The saponification equivalent was determined by dissolving the product in alcoholic base and was found to be 510. The material was not completely

soluble in aqueous base.

The neutralization equivalent was determined by titrating an alcoholic solution of the product with alcoholic potassium hydroxide. Phenolphthalein was used as the indicator. The neutralization equivalent was found to be 470. The substance melted between 103-109° C. and burned, after sintering, with a green flame.

The material was subjected to sodium fusion and a white precipitate was obtained when the resulting solution was acidified and silver nitrate was added.

The Parr Sulfur Bomb, using benzoic acid as the accelerator, indicated 21% chlorine while the Parr Micro Bomb using lactose as the accelerator gave values of 19% and 24%. A small amount of carbon was obtained in all three determinations.

Method IV: Procedure. In this chlorination, 30 grams of abietic acid were dissolved in 200 ml. of methanol in a 500-ml. round-bottom flask. Chlorine gas was bubbled through the solution and the mixture maintained at reflux temperature for seven hours, no catalyst being employed. The original light yellow color of the solution became a brown tinged with green. The refluxed solution was cooled and the solvent evaporated over a water bath. The product was a dark brown viscous oil. This was redissolved in a minimum of hot methanol and precipitated as a golden brown gum with water. It was dried in an oven at 70° C.

The product was soluble in aqueous base. The dried material was dissolved in aqueous potassium hydroxide and reprecipitated by adding hydrochloric acid. The precipitate lost its original brown color, becoming a light tan and was firm and crisp. It was dried in a dessicator and pulverized in a mortar.

Analysis. The product gave a positive Beilstein test and sodium fusion

resulted in confirmation of the presence of halogen as a light precipitate was obtained with silver nitrate.

The neutralization equivalent was determined using alcoholic potassium hydroxide as the titrant and methanol as the solvent. It was 490. The saponification equivalent was found to be 440. Phenolphthalein was used as the indicator. The compound melted at 75-78° C. Using the Parr Sulfur Bomb with benzoic acid as the accelerator, the compound analyzed 33.7% chlorine on the first attempt. Combustion took place with only a trace of carbon. A second attempt resulted in only 2.8% chlorine, and still a third in only 2.5%. In the latter two, a heavy brown precipitate was obtained when the fused mix-ture was dissolved in water, however, the precipitate dissolved when the solution was acidified with nitric acid. A considerable amount of carbon was obtained in the latter attempts.

Two more attempts using the Parr Micro Bomb were carried out in the analysis of this compound. Lactose and sodium peroxide were used as the fusion mixture. A considerable amount of carbon was obtained in both in-stances. The calculated halogen content was 1.5% and 2.9%.

A molecular weight determination on the base soluble material was attempted using the Beckmann freezing point depression method. Benzene was used as the solvent and the calculated molecular weight was 497.

Method V: Procedure. This method was an attempt to chlorinate fused abietic acid. Three grams of the acid were placed in a U-tube with a side arm near the top of each vertical portion. The open ends of the tube were stoppered and the chlorine bottle connected directly to one side arm of the U-tube with rubber tubing. The opposite side arm had a lead-off through a trap to a beaker of water where the escaping chlorine was absorbed. The acid in the U-tube was melted with a Bunsen burner and the chlorine allowed to pass through the fused material at the rate of 10 bubbles per minute. The

temperature was maintained above the melting point of abietic acid by a direct gas flame. The reaction period was 40 minutes. The original light brown liquid acid was now nearly black. The fused product was poured from the U-tube into a watch glass and it solidified on cooling. It was pulverized in a mortar and the resulting powder was light tan in color.

Analysis. The neutralization equivalent using alcoholic potassium hydroxide as the titrant and phenolphthalein as the indicator was calculated and found to be 333. The melting point was 77-79° C.

The product imparted a green color to a Bunsen flame when it was placed on a copper wire and held in the outer cone. Sodium fusion resulted in a white precipitate with a minimum amount of carbon obtained in the fusion. Parr Sulfur Bomb analysis indicated 3.5% halogen and combustion resulted in only traces of carbon. Lactose was used as the accelerator.

Method VI: Procedure. This procedure was essentially the same as that used in Method V except the U-tube was heated in an oil bath and the temperature of the bath maintained at 168-174° C. Also the reaction period was extended to five hours. The fused mass was then poured into a watch glass where it solidified immediately. The product was crushed in a mortar and was a light tan color.

Analysis. The neutralization equivalent was found to be 323. The melting point was 78-83° C.

The Parr Sulfur Bomb using lactose as an accelerator resulted in complete combustion with no carbon and the calculated halogen content was 2.3%. The Parr Micro Bomb indicated a halogen content of 2.0%.

A molecular weight determination of the product was attempted using the Beckmann freezing point depression method. Benzene was used as the solvent and the calculated molecular weight was 401.

Iodination of Abietic Acid

The procedure consisted essentially of allowing abietic acid dissolved in chloroform to react with Wijs solution. At the end of the reaction time, a large excess of water was added to the solution. Chlorine was converted to the chloride by the addition of excess potassium iodide. Free iodine was removed from the solution with sodium thiosulphate. The product was recovered by decantation and evaporation of the solvent.

Preparation of Wijs Solution (16). Thirty grams of iodine were dissolved in 2160 ml. C.P. glacial acetic acid in a 5-liter round-bottom flask. This weight of iodine represented 14 grams per liter of acetic acid. Five hundred milliliters of the solution were removed and saved in the event an excess of chlorine was allowed to react. Chlorine gas was then allowed to pass through until the solution became translucent. Ten milliliters of the solution were then removed with a pipette and run into a 100-ml. glass stoppered flask. Twenty milliliters of 15% potassium iodide were added and the solution titrated with standard sodium thiosulphate. The addition of chlorine was continued until the original titration of the solution was nearly doubled. The Wijs solution was then preserved in a glass stoppered brown bottle.

Determination of the Iodine Number of Abietic Acid. The reliability of the Wijs solution was determined by running an iodine number on a sample of the abietic acid and comparing the value obtained with those recorded in the literature (9). The abietic acid, 0.2641 grams, was weighed in a glass-stoppered flask containing 20 ml. of chloroform. Twenty eight milliliters of Wijs solution were added. The volume of Wijs solution was calculated to insure a 50-60% excess, that is, from 100-150% of the amount absorbed. The stopper was moistened with 15% potassium iodide solution to prevent loss of iodine or chlorine, but an amount insufficient to run down inside the flask.

The flask stood in the dark for thirty minutes at a temperature of 22° C. During the reaction time another sample was made omitting the abietic acid. The sample contained 20 ml. of chloroform and 28 ml. of Wijs solution. Twenty milliliters of 15% potassium iodide solution and 100 ml. of distilled water were added and the sample titrated with standard sodium thiosulphate solution. The titrant was added slowly with constant shaking, until the yellow color of the solution had almost disappeared. A few drops of starch solution were added and titration continued until the blue color had entirely disappeared. The blank required 90.2 ml. of 0.101 normal sodium thiosulphate solution. At the conclusion of the reaction period, the stopper was removed and titration of the sample was carried out exactly as for the blank. The sample required 59.1 ml. of sodium thiosulphate solution.

The iodine number of abietic acid was calculated using the following formula (10):

$$\text{Iodine number} = \frac{\text{Ml. thiosulphate x normality x .127 x 100}}{\text{Wt. of sample, dry basis}}$$

$$= 150$$

This value indicated the Wijs solution was satisfactory and that two moles of iodine were absorbed per mole of abietic acid.

Method I: Procedure. A sample of abietic acid weighing 2.5 grams were dissolved in 125 ml. of chloroform in a 500-ml. glass stoppered flask and 240 ml. of Wijs solution were added. The resulting solution was allowed to stand in the dark for five days. The solution was then transferred to a 1-liter beaker and 175 ml. of 15% potassium iodide and 500 ml. of distilled water were added. The solution was washed with sodium thiosulphate to remove free iodine and a brown oil separated. The oil was removed by decanting the mixture. Chloroform was evaporated from the oil and the resulting semi-solid

was dried in an oven. The dried product was ground to a fine powder in a mortar.

Analysis. The neutralization equivalent of the product was determined by titrating with standard sodium hydroxide. Bromo-Thymol Blue was used as the indicator. The end point was difficult to determine due to the dark color imparted to the alcoholic solution by the sample. The neutralization equivalent was calculated to be 315.

Method II: Procedure. A sample of abietic acid weighing 2.5 grams was dissolved in 125 ml. of chloroform in a 500-ml. glass stoppered flask and 250 ml. of Wijs solution were added. The resulting solution was allowed to stand in the dark for two days. The solution was then transferred to a 1-liter beaker and 175 ml. of 15% potassium iodide and 500 ml. of distilled water were added. The solution was washed with sodium thiosulphate to remove free iodine and a brown oil separated. The oil was removed by decanting the mixture. Chloroform was evaporated from the oil and the product dried in an oven at 90° C. The product was powdered in a mortar and was light tan in color.

Analysis. The neutralization equivalent of the product was determined by titrating with standard alcoholic potassium hydroxide. Phenolphthalein was used as the indicator. The neutralization equivalent was calculated to be 320. The compound decomposed at 125° C.

The material gave a positive Beilstein test, imparting the characteristic green halogen color to the flame almost immediately. Sodium fusion of the product, acidification of the aqueous solution and the addition of silver nitrate, resulted in a light grey precipitate. Parr bomb analysis for iodide using sodium peroxide and lactose as the fusion mixture resulted in excellent combustion and indicated an iodide content of 20.9%.

Method III: Procedure. Five grams of abietic acid were dissolved in 30 ml. of chloroform in a 500-ml. glass stoppered flask, and 400 ml. of Wijs solution

were added. The resulting solution was allowed to stand in the light for 48 hours and warmed to 60° C. three different times during the reaction period. The solution was transferred to a 2-liter beaker where 300 ml. of 15% potassium iodide and 500 ml. of distilled water were added. The product came down as a red oil and was separated by decantation. It was then washed with 400 ml. of sodium thiosulphate. The oil was diluted with 500 ml. of distilled water. On rapid stirring, the emulsified oil formed a film at the surface of the water and was skimmed off. It was dissolved in methanol and precipitated by the addition of water. The product was dried and crushed in a mortar. It was dark yellow in color.

Analysis. The neutralization equivalent of the product was determined by titrating with standard alcoholic potassium hydroxide. Phenolphthalein was used as the indicator. The neutralization equivalent was calculated to be 268. The compound decomposed at 165° C.

The Beilstein test for halogen was positive, the green color becoming apparent immediately on insertion of the substance into the outer cone of the flame. A light grey precipitate was obtained from the sodium fusion procedure when silver nitrate was added to the aqueous sodium fusion solution. A small amount of carbon was obtained from the fusion. Quantitative iodide analysis using a Parr bomb indicated an iodide content of 10%.

Method IV: Procedure. A sample of abietic acid weighing 2.5 grams was dissolved in 125 ml. of chloroform in a 500-ml. glass stoppered flask, and 200 ml. of Wijs solution were added. The reaction period was 40 minutes in the light. The solution was then transferred to a 1-liter beaker where 175 ml. of 15% potassium iodide and 200 ml. of distilled water were added. The solution was washed with sodium thiosulphate and the resulting oil was obtained by decantation. This oil was then dissolved in methanol and extracted with water. A small amount of precipitate was obtained, however, most of the

oil remained as such. The water was decanted and the oil evaporated to dryness in an oven at 100° C. The dark yellow product was crushed in a mortar. Analysis. The neutralization equivalent of the product was determined by titrating with standard alcoholic potassium hydroxide. Phenolphthalein was used as the indicator. The calculated neutralization equivalent was 313. The melting point ranged from 120-127° C. Parr bomb analysis for iodide indicated an iodide content of 5.4%.

Bromination of Abietic Acid

Method I: Procedure (8). Fifty grams of abietic acid were dissolved in 200 grams of ethylene chloride in a 500-ml. round-bottom flask. Twenty grams of bromine were added and the solution refluxed for five hours. A solution comprising 2 grams of aluminum chloride and 20 grams of bromine in 60 grams of ethylene chloride was added slowly to the reaction mixture through the condenser. The resulting solution was then refluxed for an additional three hours, cooled, and diluted with water to precipitate the product. The product was removed by filtration, and dried overnight in an oven at 105° C. The dried substance was black. It was dissolved in alcoholic potassium hydroxide and apparently was completely soluble. The basic solution was acidified with dilute hydrochloric acid and the precipitate removed by filtration. After this recrystallization, the product changed in color from deep black to dark grey. It was dried on a porous plate and powdered in a mortar.
Analysis. The Beilstein test on the product was positive after the substance had sintered and the temperature of the flame was increased. Sodium fusion, acidification of the resulting aqueous solution with nitric acid and the addition of silver nitrate, gave a slowly forming cloudiness. A conductometric titration of an alcoholic solution of the product was deemed unsatisfactory due to a slight amount of insoluble material in the solution. An attempt to

separate the product into base soluble and base insoluble fractions was un-
successful. The insoluble material could not be completely removed by or-
dinary filtration. Quantitative halogen analysis using a Parr bomb with sodium
peroxide and benzoic acid gave evidence of 8.7% bromine.

An accurately weighed sample, 1.0100 grams, of the original product was
ignited in a tared porcelain crucible. The material was first burned with a
Bunsen burner until it was completely charred. The crucible was then covered
and a Meeker burner employed. The material was ignited for thirty minutes
and cooled in a "Desi-cooler." The residue had the appearance of a finely
woven ball of snow-white cotton.

The residue, 0.0126 grams, represented 1.25% of the sample.

Method II: Procedure. Thirty three grams of abietic acid were dissolved in
200 grams of methanol in a 500-ml. round-bottom flask. Four grams of powdered
aluminum metal and 34 grams of bromine were added and the mixture refluxed for
six hours. It was allowed to cool overnight and the product precipitated by
adding water to the decanted dark brown solution. The tan product was sep-
arated by filtration and dried on a porous plate. The filtrate was rejected.

Analysis. The dried material was soluble in methanol, but an attempt to
recrystallize it from this solvent was unsuccessful. The product gave a
positive Beilstein test after it first burned with a smoky orange flame.
Sodium fusion resulted in an excessive amount of carbon and only a slight
precipitate when the aqueous solution was treated with silver nitrate.

The material was partly soluble in aqueous potassium hydroxide and two
fractions were thus obtained; the base soluble by reprecipitation from the
filtrate with hydrochloric acid, and the base insoluble. The base insoluble
was a darker chocolate brown color with a melting point above 330° C. The
Parr Sulfur Bomb using lactose as the accelerator indicated 13.4% bromine.
The base soluble material had almost the same tan color as the original prod-

uct. Its melting point range was 119-143° C. Halogen analysis indicated 3.1%.

Method III: Procedure. A solution consisting of 50 grams of abietic acid, 20 grams of bromine, and 200 grams of ethylene chloride was refluxed for two hours in a 500-ml. round-bottom flask. At the end of the reaction period, the dark brown liquid was transferred to a 500-ml. separatory funnel and washed with distilled water to destroy any excess bromine. The product was drawn off and the solvent partially evaporated over a water bath. The semi-solid material was placed in an oven at 80° C. overnight. The resulting dark brown glass-like substance was crushed to a powder in a mortar.

Analysis. The product was soluble in methanol and aqueous potassium hydroxide. The saponification equivalent, found to be 308, was determined by dissolving the material in alcoholic base. The neutralization equivalent, 320, was determined by dissolving a weighed sample in methanol and titrating with aqueous potassium hydroxide using phenolphthalein as the indicator. The melting point was 96-100° C.

The product gave a positive Beilstein test and sodium fusion resulted in a cloudy solution containing a small amount of precipitate. Parr Bomb analysis resulted in excellent combustion and indicated the presence of 5.3% halogen.

DISCUSSION

This work tends to explain the lack of information on the subject in the literature. The halogenation of abietic acid and the analysis of the resulting products seem to prove that the problem is not as simple as its outward appearance. The halogenated product is a mixture of at least two individual compounds; one soluble in aqueous base indicating the carboxyl still present and the other slightly soluble or completely insoluble indicating the carboxyl had been lost or hindered during the course of the reaction.

That material chlorinated in the presence of aluminum chloride gave a residue on ignition, however, the residue was only partly soluble in concentrated nitric acid. Neutralization of the solution with base resulted in some precipitate which in turn was only slightly soluble when the solution was made strongly basic. This indicated that the aluminum salt was not formed to any great extent in the chlorination as was first suspected. The material brominated in the presence of aluminum chloride also gave a residue on ignition. A sample of aluminum abietate was prepared and was found to be completely soluble in base. It was ignited and the percent aluminum calculated was in excellent agreement with the theoretical molecular formula. These two factors, the solubility of aluminum abietate and the percentage residue after ignition, seemed to confirm the conclusion above in regards to the possible formation of the aluminum salt.

The determination of the iodine number of abietic acid indicated two moles of iodine had added per mole of acid, presumably at the two double bonds. However, when the product was separated and the neutralization equivalent obtained, the molecular weight had not increased appreciably. This indicated the neutralization equivalent was not giving a true molecular weight. The physical appearance and the change of melting points of the iodinated compounds

certainly seemed to prove that iodine added to a greater extent than the neutralization equivalent indicated.

The base insoluble chlorinated and brominated compounds had high melting points, above 300° C. This might account for the inability to burn them completely in the Parr bomb and the resulting failure to obtain constant values in repeated determinations. In an attempt to obtain better combustion, the composition and relative amounts of the fusion mixtures were varied. The standard procedure using 15 grams of sodium peroxide and 1 gram of benzoic acid resulted in excessive carbon in most runs. The use of lactose as the accelerator seemed to give better combustion. An attempt at "layering" the sample in 25 grams of peroxide and 2 grams of lactose resulted in a much more violent reaction with very little carbon but no increase in the percentage of chlorine. This mixture fused the lead gasket of the bomb resulting in a loss of gaseous products. Potassium perchlorate and sodium peroxide were tried and apparently resulted in good combustion. Calculations of the results indicated that all of the perchlorate failed to decompose so this method was impractical. The neutralization and saponification equivalents all pointed to a much higher chlorine content than the Parr bomb analysis indicated.

Further work might include the investigation of a whole range of catalysts in connection with mucher longer exposure to halogenation. Certainly the investigation of halogen analysis of known halogenated compounds of a similar nature should be undertaken at the outset.

SUMMARY

This work consisted essentially of the study of various methods of halogenation of abietic acid, the preparation of such halogenated derivatives, their analysis and several physical constants of these compounds.

The methods of chlorination include: (a) chlorination in ethylene chloride with aluminum chloride as the catalyst; (b) chlorination in methanol with metallic aluminum as the catalyst; (c) chlorination in methanol without a catalyst, and (d) chlorination of fused abietic acid.

The methods of bromination include: (a) bromination in ethylene chloride with aluminum chloride as the catalyst; (b) bromination in methanol with metallic aluminum as the catalyst, and (c) bromination in ethylene chloride without a catalyst.

Wijs solution was used in the iodination of the acid. The length of the reaction period and the external catalyst (degree of sunlight) were varied.

Saponification and neutralization equivalents, melting points, and halogen content of the products were determined and in some instances molecular weights were determined using the Beckmann method.

The Parr Sulfur and Parr Micro Bombs were utilized in the quantitative halogen determinations. Various fusion mixtures were used in attempting to obtain better combustion of the halogenated products.

	Solvent	Initial Reaction Time	Catalyst Added	Total Reaction Time	Sap. Equiv.	N.E.	M.P.	% Halogen	
								Sulfur Bomb	Micro Bomb
CHLORINATION:									
Method I	$C_2H_4Cl_2$	4 hrs.	$AlCl_3$	7 hrs.		293	325-30		
(A) Sol. in base					308		108-14	12.5	
(B) Insol. in base							above 300	8.9	
Method II	$C_2H_4Cl_2$	4 hrs.	$AlCl_3$	7 hrs.					
(A) Sol. in base					345		90	2.0	
(B) Insol. in base							dec. 290	3.6	
Method III	MeOH	6 hrs.	Al	6 hrs.	510	470	103-09	21.0	19, 24
Method IV	MeOH	7 hrs.	none	7 hrs.	440	490	75-78	33.7,2.8,2.5	1.5, 3
Method V	none	40 min.	none	40 min.		333	77-79	3.5	
Method VI	none	5 hrs.	none	5 hrs.		323	78-83	2.3	2.0
BROMINATION:									
Method I	$C_2H_4Cl_2$	5 hrs.	$AlCl_3$	8 hrs.			105-20	8.7	
Method II	MeOH	6 hrs.	Al	6 hrs.					
(A) Sol. in base							119-43	13.4	
(B) Insol. in base							above 300	3.1	
Method III	$C_2H_4Cl_2$	2 hrs.	none	2 hrs.	308	320	96-100	5.3	
IODINATION:									
Method I	HAc-CHCl$_3$	5 days	dark	5 days		315			
Method II	same	2 days	dark	2 days		320	dec. 125	20.9	
Method III	same	2 days	heat-light	2 days		268	dec. 165	10.0	
Method IV	same	40 min.	light	40 min.		313	120-27	5.4	

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BIOGRAPHY

Wallace Dean Leslie was born in Dacoma, Oklahoma on November 9, 1922.
He attended Dacoma public grade school and was graduated from the Dacoma High
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