

A STUDY OF THE NITROGEN COMPOUNDS OF
ABIETIC ACID

By

WILLIAM J. PROBST

//

Bachelor of Arts

Coe College

Cedar Rapids, Iowa

1950

Submitted to the Faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in Partial Fulfillment of the Requirements
for the Degree of
MASTER OF SCIENCE
May, 1953

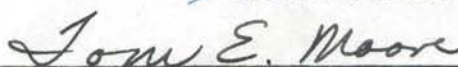
OKLAHOMA
AGRICULTURAL & MECHANICAL COLLEGE
LIBRARY
JUL 6 1953

A STUDY OF THE NITROGEN COMPOUNDS OF
ABIETIC ACID

Thesis Approved:



Thesis Adviser





Dean of the Graduate School

Acknowledgement

The author wishes to express his gratitude for the inspiration and guidance given him during this study by Dr. Henry P. Johnston. He also wishes to express his appreciation for the aid given him by the Department of Chemistry in the form of a teaching fellowship during the time this work was being done.

Table of Contents

	Page
Introduction	1
Historical	2
Experimental	8
Discussion	17
Conclusions	21
Bibliography	22

Introduction

Abietic acid is one of the cheapest and most abundant of the higher organic acids available today. Although many attempts have been made to prepare nitrogen derivatives of abietic acid, and many such compounds have been described in the literature, very little is known of the chemical nature of these compounds. Most of the nitrogen compounds of abietic acid are described empirically, with no mention made of the location of substituent groups, and many conflicting results have been presented. That a clearer elucidation of these products has met with failure is not strange since separation into chemical individuals in most instances is very difficult.

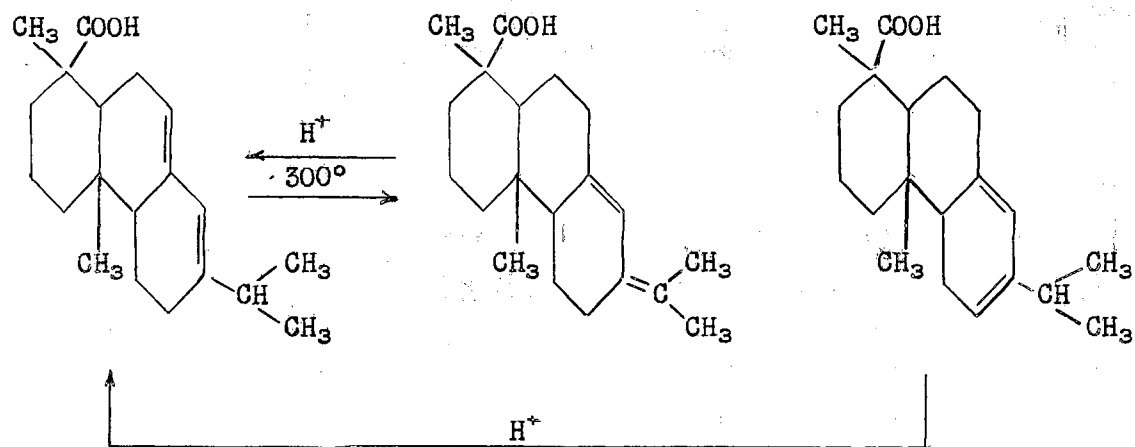
The object of this work was to investigate some of the nitrogen compounds of abietic acid with a view toward studying the properties of such compounds. It was further hoped that the preparation of an amino abietic acid would give a mineral-acid soluble compounds, since such a compound might be expected to have properties similar to the more common amino acids.

Historical

The exudate from incisions cut in living pine trees consists of a viscous solution of about four parts nonvolatile acidic material to one part essential oils. The fresh oleoresin is a nearly colorless, limpid fluid, which rapidly becomes discolored upon exposure to the air. The oils are easily removed by steam distillation leaving a hard resinous mass known as rosin, or colophony as it is often called. The principal constituents of rosin are diterpene acids of the formula $C_{19}H_{29}COOH$, most of which are very sensitive to heat, light, air and acids. Rosin is cheap and abundant and finds wide use in low grade soaps, paper sizes, varnishes and the plastics industry.

Investigations into the chemical nature of the acids found in rosin were first undertaken early in the nineteenth century. The first of these acids to be characterized was abietic acid, isolated by Baup in 1826 from Pinus abies. Although abietic acid is the chief useful product found in rosin, it is probably not a primary acid since it is only a minor constituent of the fresh oleoresin. Abietic acid is formed by isomerization processes from labile resin acids, principally the primary acid levopimaric acid, and can be isolated by careful heating, treatment with mineral acids or distillation. Abietic acid itself is unstable toward heat treatment and can be transformed into neoabietic acid at low temperatures or to a mixture of dehydroabietic acid and di- and tetrahydroabietic acids at higher temperatures.

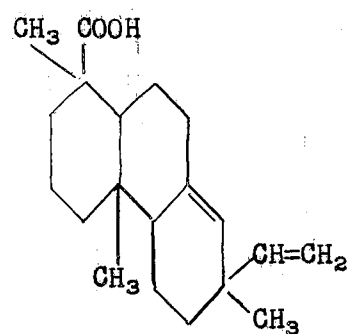
THE ROSIN ACIDS
Chart I(7)



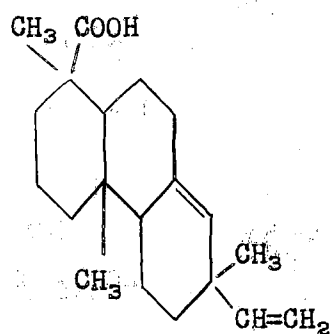
Abietic acid

Neoabietic acid

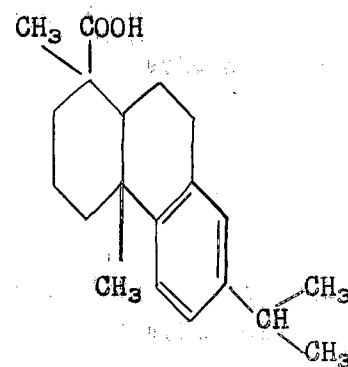
Levopimaric acid



d-Pimaric acid



7-Iso-d-pimaric acid



Dehydroabietic acid

Following the work of Baup, the chemical constitution of rosin received wide attention. Although most of this work centered on abietic acid, numerous other impure acids, usually named for their source or method of isolation, were described. Much difficulty was encountered in the investigation of these acids due to their susceptibility to air oxidation and the ease with which they disproportionate and isomerize. In addition to these difficulties, the chemical constitution of resin varies widely according to the season of the year during which it is collected. It is now known, however, that there are seven true acids of the formula $C_{19}H_{29}COOH$ which can be isolated from Pinus palustris. (Chart I)(7)

The structure of abietic acid was largely proven by Ruzicka and Meyer (18), P. Levy (13), Rydon (19) and R. Haworth (10). The basic structure, a perhydrophenanthrene nucleus, was determined through oxidative degradation and by dehydrogenation to retene, another material found in rosin. Following the establishment of the basic structure of abietic acid, there remained only the problem of locating the two double bonds present in the molecule. These bonds were assigned the positions of 7-8 and 9-14 by Fieser and Campbell (6) and Ruzicka (17) on the basis of evidence furnished by the absorption spectrum of abietic acid and certain reactions characteristic of open chain and cyclic dienes.

The majority of the nitrogen compounds of abietic acid described in the literature are the products obtained on treatment with nitric acid. The first nitro derivative of abietic acid was reported by Easterfield and Bagley (5) in 1904. This nitro compound was obtained by treating a glacial acetic acid solution of abietic acid with nitric acid, but no experimental data were given. In 1909, Kessler (12) obtained a patent for the treatment of rosin with nitric acid, but did not describe the products obtained.

The first crystalline nitro derivative of abietic acid was obtained, by Johansson, (11), by the action of fuming nitric acid on abietic acid. The melting point of this compound was given as 178-184°C. and $[\alpha]_D = 44.25$ degrees (in acetone). Characterized by Johansson as the dinitro derivative of abietic acid and reported as being light sensitive, it was later shown by Virtanen and Aschan (21), in 1921, to be dinitropinabietic acid. Virtanen used a method similar to that of Johansson in preparing the dinitropinabietic acid and concluded from its physical constants, melting point 190-193°C. and $[\alpha]_D = 43.89$ degrees (in acetone) that in reality Johansson had been using pinabietic acid instead of abietic acid. In 1938, Fieser and Campbell (6) found that the physical constants of the methyl ester of Johansson's acid corresponded to those of the methyl ester of dinitrodehydroabietic acid. This similarity led Fieser and Campbell to conclude that Johansson and Aschan and Virtanen had been in error as to the compound they had obtained.

In 1927, Dubourg (3)(4) reported that treatment of a boiling solution of abietic acid in ethanol with concentrated nitric acid gave a crystalline product which he described as decahydrodinitroretene-carboxylic acid. The melting point of this acid was 162-165°C. and $[\alpha]_D = -115.2$ degrees. Dubourg found its molecular formula to be $C_{19}H_{26}O_2(NO_2)_2$ and proposed that it was produced by substitution of a nitro group for one hydrogen and one methyl group in the abietic acid molecule. The same product was obtained by slow addition of nitric acid to a solution of abietic acid in glacial acetic acid, but addition of nitric acid to abietic acid in carbon tetrachloride (or other solvent inert to nitric acid) gave a yellow mass which contained unidentified decomposition products and $C_{20}H_{27}O_2(NO_2)_2$. Further treatment of the dinitro acid gave a trinitro compound whose molecular formula was reported by Dubourg as $C_{16}H_{17}N_3O_8$. The melting point of this acid was

156-158°C. and $[\alpha]_D = -136.2$ degrees. Dubourg also investigated the effect of fuming nitric acid on abietic acid and reported that abietic acid was completely soluble in fuming nitric acid giving a yellow amorphous polynitrate upon dilution of such a solution with water. This polynitrate gave bright red sodium, potassium and ammonium salts which were very soluble in water.

Levy (15), in the course of investigations concerning the oxidative degradation products of abietic acid, found that prolonged treatment of abietic acid with nitric acid gave acids similar to those obtained by oxidation of abietic acid with potassium permanganate. Levy (14) also stated that no nitro abietic acid was produced by treatment of abietic acid with nitric acid alone and concluded that it depended entirely upon experimental conditions whether nitration or oxidation occurred.

A further study of the nitration of abietic acid was made in 1930, by Goldblatt, Lowy and Burnett (8), using a method of preparation similar to that of Dubourg (3)(4). Two main products were reported; a white crystalline dinitro abietic acid and a yellow amorphous nitrogen-containing product decomposing above 100 degrees. The white dinitro compound was obtained in 40-56 percent yields and melted at 170-171°C. Attempts were also made to treat abietic acid or sodium abietate with nitric acid alone, but oxidation occurred in each case and the product proved to be the yellow nitrogen-containing compound. This compound had the same properties as the polynitrate reported by Dubourg (3)(4), in so far as it also gave dark red solution with sodium hydroxide, potassium hydroxide and ammonium hydroxides. Analytical data showed the yellow nitrogen-containing compound to be a hydroxylated acid, but no further identification of this product was made. Both the white dinitroabietic acid and the yellow nitrogen-containing compound were subjected to reduction, but again no identification of reduction

products was given beyond the fact that either ammonia or nitrogen oxides were evolved during reduction.

In addition to the nitration products of abietic acid reported in the literature there are several reported nitro derivatives of dehydroabietic acid. The conventional method of nitration, via a mixture of nitric acid and sulfuric acid, was used by Fieser and Campbell (6) to prepare dinitrodehydroabietic acid. Littmann (16) has reported the preparation of dinitrodehydroabietic acid also, and Hasselstrom and Hopkins (9) prepared the mononitro derivative of sulfodehydroabietic acid by the action of fuming nitric acid. In the case of the dinitrodehydroabietic acid prepared by Fieser and Campbell, later work by Campbell and Morgana (2) showed that substitution had taken place in the 6 and 8 positions.

Experimental

PREPARATION OF ABIETIC ACID. Three hundred and sixty-four grams of abietic acid was dissolved in 400 ml. of hot methanol and the resultant dark red solution cooled in an ice-salt bath with occasional vigorous stirring. The light yellow crystals, which separated from the solution, were removed by suction filtration, washed twice with 5 to 10 milliliter portions of methanol and filtered as dry as possible. The filtrate and washings were combined and evaporated to approximately one half their original volume and cooled to obtain a second crop of crystals. The two crops of crystals were combined and recrystallized from methanol to give 90 g. of white crystalline abietic acid which melted at 148-152°C.

After the second crop of crystals had been obtained, the mother liquor was allowed to stand several days in order to obtain a third crop. The yield of this third crop of crystals, after two recrystallizations from methanol, was seven grams and the melting point of the white crystalline abietic acid 149-154°C.

The total yield of abietic acid recovered was ninety-seven grams or 24.64 percent of the starting material. Further recrystallization of a five gram sample of the purified abietic acid yielded crystals which melted at 160-163°C.

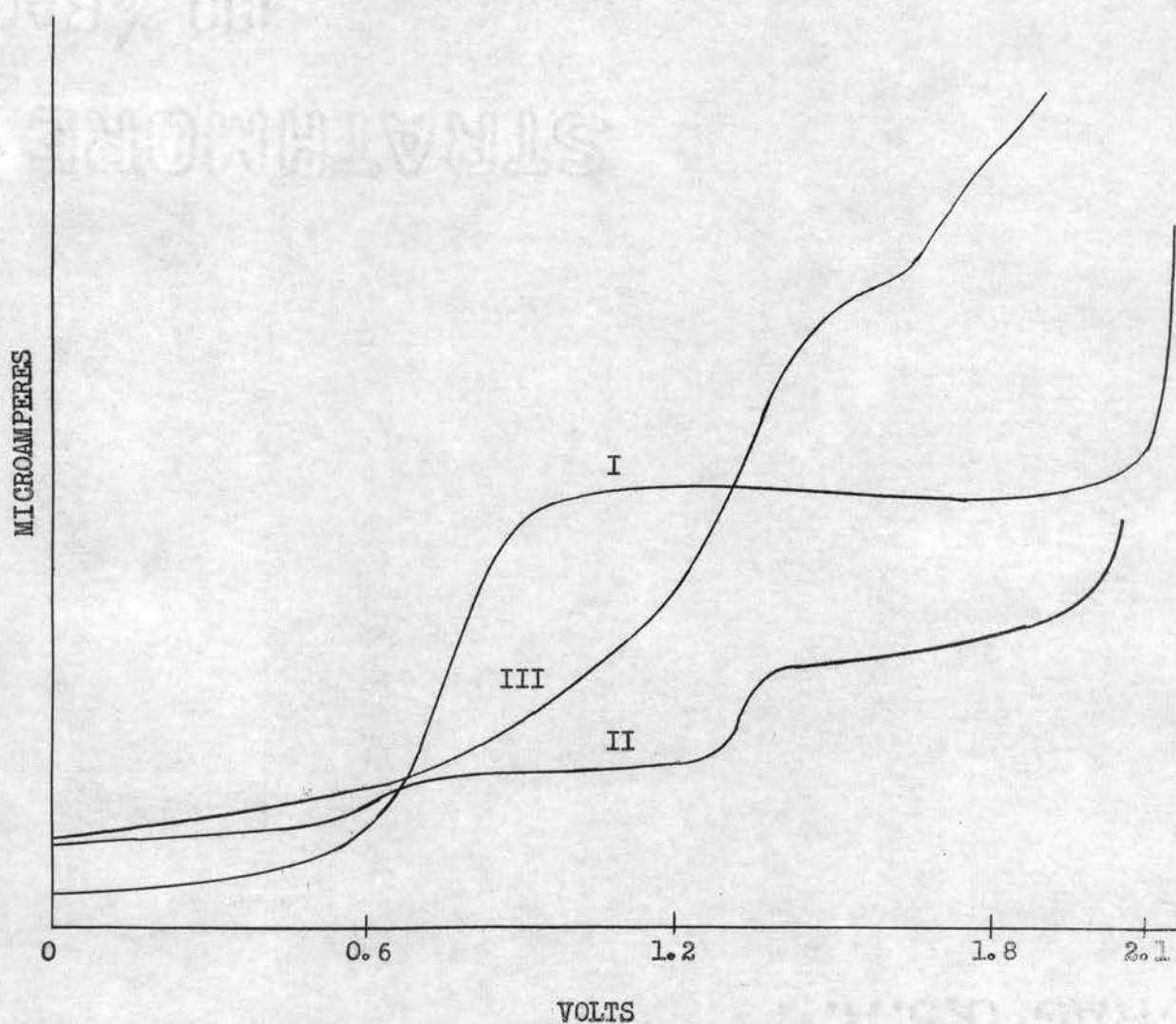
PREPARATION OF YELLOW NITROGEN CONTAINING SOLID. In a three necked, five hundred milliliter flask, fitted with a mechanical stirrer and a reflux condenser, were placed 10 g. (0.033 moles) of abietic acid (melting point

149-154°C.) and sixty ml. of 50% nitric acid. The flask and contents were heated slowly to the reflux temperature of the solution, with vigorous stirring. Violent frothing occurred near the reflux point and considerable nitrogen dioxide was evolved at this temperature. Frothing gradually diminished after refluxing began, and at the end of forty five minutes a viscous orange colored liquid was present on the surface of the nitric acid solution. At the end of one hour, the flask was allowed to cool to room temperature and the contents diluted with sixty ml. of distilled water to yield a light yellow solid. After cooling to 0°C. in an ice bath, the yellow solid was separated by suction filtration, washed several times with 5 to 10 ml. portions of distilled water and air dried. The weight of yellow solid obtained was 12.3 g. and decomposed at its melting point of 100°C. Reported (8): M.P. 100°C. with decomposition.

Similar runs were made using twenty-five percent solutions of nitric acid and concentrated nitric acid ($d = 1.42$). The same amorphous yellow solid was obtained in each case. The reaction with concentrated nitric acid took place spontaneously, without heating, within three to five minutes after mixing the abietic acid and nitric acid. In addition to varying the concentration of the nitric acid, attempts were made to obtain a different product using one to two percent quantities of oleic and linoleic acids as catalysts, but only the amorphous yellow solid was obtained.

Fusion of the yellow solid with sodium gave positive tests for nitrogen as indicated by Goldblatt, *et. al* (8). No qualitative tests for any of the common nitrogen containing functional groups could be obtained however, even though the material gave a positive Tollen's test upon reduction with zinc dust and acetic acid. Attempts were also made to test for nitro groups qualitatively using a polarographic method outlined by Shikata (20). One

FIGURE I
Polarographic Analysis
Current vs. Voltage



Graph I. p-nitrobenzoic acid.
Graph II. Abietic acid.
Graph III. Yellow nitrogen containing solid.

and one half grams of p-nitrobenzoic acid were dissolved in 100 ml. of 0.158N sodium hydroxide. One milliliter of this basic solution was added to 40 ml. of 0.1N potassium chloride and a polarogram (Figure I) taken to serve as a standard. Another polarogram (Figure I) was made under similar conditions using abietic acid instead of p-nitrobenzoic acid. Finally, the yellow nitrogen-containing compound was investigated (Figure I) in the same manner.

Recrystallization of the yellow nitrogen containing solid was attempted from the following solvents: methanol, ethanol, isopropyl alcohol, acetone, carbontetrachloride, petroleum ether, glacial acetic acid, benzene, nitrobenzene, dioxane and n-butyl alcohol. Recrystallization was in general unsuccessful; however, the solid could be reprecipitated from the alcohol solutions by dilution with water. This precipitate was found to be the same yellow colored solid with no change in the melting point.

REDUCTION OF YELLOW NITROGEN CONTAINING SOLID.

A. REDUCTION WITH SODIUM AND ALCOHOL. In a 250 milliliter three-necked flask, fitted with a mechanical stirrer and a reflux condenser, were placed 20 g. of the yellow nitrogen-containing solid dissolved in 100 ml. of absolute alcohol. Ten grams of metallic sodium were added in small portions over a period of three hours. The solution was stirred during the addition of the sodium and the temperature kept below 50°C. by frequent application of an ice bath. The color of the solution changed from light yellow to bright red upon addition of the first sodium. As more sodium was added, the color of the solution changed to dark brown, and a brown precipitate formed in the flask. After all the sodium had been added, the temperature of the reaction mixture was held at 45-50°C. until all the undissolved sodium had reacted. The mixture was then cooled in an ice bath

and filtered by suction in order to remove the brown precipitate. The dark brown solid was extremely soluble in water giving a slightly basic solution. The solid did not melt when held in a bunsen flame and was assumed therefore to be a sodium salt.

The brown solid was dissolved in 100 ml. of distilled water and the water solution acidified with dilute hydrochloric acid. A light brown solid precipitated upon acidification of the water solution, and a small amount of gas evolution occurred. The light brown solid was separated by filtration, washed several times with distilled water and air dried. This solid was reprecipitated from methanol by dilution with distilled water to give 15.0 g. of an amorphous solid which sintered at 165°C . and decomposed above 200°C . The apparently identical brown solid could be obtained by treatment of an alcoholic solution of the yellow nitrogen containing solid with solid sodium hydroxide.

The brown product was found to be soluble in strong base and insoluble in water and acids. Qualitative tests run on the reduction product gave no indications for any of the common nitrogen-containing functional groups, although fusion with sodium gave a positive test for nitrogen. Further reduction of the amorphous brown solid with zinc dust and glacial acetic acid gave a light yellow solid which sintered at $120\text{--}130^{\circ}\text{C}$. and melted at $170\text{--}180^{\circ}\text{C}$.

B. REDUCTION WITH ZINC AND GLACIAL ACETIC ACID. In a 250 ml. three-necked flask, fitted with a mechanical stirrer and a reflux condenser, were placed 10 g. of yellow nitrogen-containing compound dissolved in 50 ml of glacial acetic acid. Ten g. of zinc dust were added to the flask in one-gram portions at a rate which did not produce violent frothing. After addition of the zinc dust was complete, the reaction mixture was refluxed for two hours. At the end of this time, the reduction mixture was filtered,

while still hot, through a glass-wool plug to remove the unreacted zinc. The filtered material was poured, with vigorous stirring, into 200 ml. of distilled water. The zinc dust was washed twice with 5 to 10 ml. portions of glacial acetic acid and the washings were poured into the acetic acid-water solution. The yellow solid, which formed upon dilution with water, was separated by suction filtration and air dried to give 5.5 g. of product. After drying in a vacuum desiccator over anhydrous calcium chloride for two days, the product sintered at 120-130°C. and melted at 170-180°C. Recrystallization from acetic acid by dilution with water gave the same melting point. The melting point of this reduction product was not reported by Goldblatt, Lowy and Burnett (8). The product was found to be insoluble in water, alkali, and mineral acids, but no positive qualitative tests for common nitrogen containing functional groups could be obtained.

QUALITATIVE MEASUREMENT OF AMMONIA EVOLVED DURING REDUCTION. The acetic acid-water solution remaining after removal of the yellow reduction product was placed in a 500 ml. round-bottom flask, fitted with a reflux condenser, and neutralized with solid sodium hydroxide. The neutralized solution was refluxed for two hours and the gases evolved were bubbled through 50 ml. of 0.1809N hydrochloric acid. At the end of this time the hydrochloric acid was back-titrated with 0.1572N sodium hydroxide to the phenolphthalein endpoint. Twenty ml. of the standard sodium hydroxide were required to neutralize the hydrochloric acid remaining. This corresponded to a loss of 5.90 milliequivalents of acid which had been neutralized with evolved ammonia, or 24.7% of the available nitrogen. Goldblatt, Lowy and Burnett (7) reported the loss of 44.9% of the available nitrogen during reduction of this same compound.

PREPARATION OF DINITROABIETIC ACID (3)(4)(8). In a 500 ml. three-necked flask fitted with a reflux condenser and a dropping funnel, was placed a solution of 10 g. of abietic acid (melting point 158-161°C.) in 20 ml. of 95% ethanol. The flask was placed in a water bath and the alcohol solution heated to boiling. Nine milliliters of concentrated nitric acid ($d = 1.42$) was added to the boiling solution. The first addition amounted to 5 ml. and the remainder of the nitric acid was added in 0.5 ml. portions at half-minute intervals. A violent frothing of the solution began when approximately 7 ml. of the nitric acid had been added, and some nitrogen dioxide was evolved at the same time. At the start of the vigorous reaction, the water bath was removed and the upper portions of the flask cooled in order to prevent the reaction mixture from erupting. The violent frothing ceased within two to three minutes after addition of the last of the nitric acid. The flask was cooled in an ice bath for two hours, but no crystalline products were obtained. The only product obtained upon cooling was the yellow nitrogen-containing solid, which separated as a viscous oil and solidified upon treatment with water containing a small amount of hydrochloric acid. Goldblatt, Lowy and Burnett (8) and Dubourg (3)(4) reported the preparation of a dinitroabietic acid which melted at 170-171°C. by this method.

AMINATION OF CHLOROABIETIC ACID. In a 500 ml. three-necked flask fitted with a mercury sealed stirrer, a dry ice-acetone condenser, and a gas inlet tube, were placed 10 g. of chloroabietic acid. Ammonia gas was admitted through the gas inlet tube and liquified by means of the dry ice-acetone condenser until 150 ml. of liquid ammonia had been collected. Stirring was started and 4 g. of sodium added in 0.5 g. portions over a period of four hours. The mixture was stirred vigorously for one hour after addition of the last sodium. The dry ice-acetone condenser was then removed and the

ammonia allowed to evaporate overnight. The next day 150 ml. of distilled water were added to the solid material remaining in the flask after evaporation of the ammonia. The water solution, which was dark red in color, was filtered to remove the solid material which had failed to dissolve and then acidified with concentrated hydrochloric acid. A light tan solid resulted. The water insoluble material turned to a dark red amorphous gum upon exposure to air and over a period of two to three hours gradually solidified.

Fusion of both the tan solid and the red amorphous solid with sodium gave negative tests for the presence of nitrogen. The tan solid was found to contain chlorine but the red amorphous solid gave negative results here also. The red solid was found to be soluble in methanol-water mixtures and treatment of such solutions with concentrated hydrochloric acid gave the same tan solid described above. The melting point of this tan solid was 95-100°C. with decomposition.

The chloroabietic acid used in the attempted amination had been prepared by Johnston and Bobst (1) and had been shown to be subject to ready dehydrohalogenation.

CHLORINATION OF METHYL ABIETATE. In a 500 ml. three-necked flask, fitted with a gas inlet tube, a sealed stirrer and an outlet tube, was placed a solution of 50 g. of methyl abietate (abalyne) in 100 ml. of technical grade chloroform. One half gram of iodine was added to serve as a catalyst and chloride was added rapidly to the solution with vigorous stirring for seven and one half hours. At the end of this time, the reaction mixture was removed from the flask, placed in a separatory funnel, and washed first with distilled water and then repeatedly with potassium iodide solution to remove the iodine. The solvent was removed under reduced pressure and a thick viscous mass was formed which was taken up in ethanol. When heated to boiling,

filtered, and cooled in an ice-salt bath the ethanol solution produced a yellow solid which softened to a viscous gum at room temperature. The gum was placed in 100 ml. of distilled water and the mixture heated to boiling. Upon cooling the gum solidified to a hard yellow amorphous mass which was separated by filtration, dried and broken up in a mortar. Sixty grams of this product were obtained having a melting point of 75-85°C. Fusion with sodium gave a positive test for chlorine and application of heat caused evolution of hydrogen chloride. The molecular weight, determined by freezing point depression using benzene as a solvent, was found to be 403.

AMINATION OF METHYL CHLOROABIETATE. In a 500 ml. three-necked flask, fitted with a mercury sealed stirrer, a dry ice-acetone condenser, and a gas inlet tube, were placed 15 g. of methyl chloroabietate. Ammonia gas was admitted through the gas inlet tube and liquified with the dry ice-acetone condenser until 150 ml. of liquid ammonia had been collected. One gram of metallic sodium was then added to serve as a catalyst for the reaction. When the blue color imparted by the sodium disappeared, the solid present in the flask had changed color from yellow to light brown. The mixture was stirred vigorously at the boiling point of liquid ammonia for four hours, the dry ice-acetone condenser removed at the end of this time and the ammonia allowed to evaporate overnight. The next day 150 ml. of distilled water were added dropwise to the solid residue left in the flask after evaporation of the ammonia. The bulk of the solid material in the flask was found to be insoluble in water and was removed by suction filtration. Fusion of this material with sodium gave only a very faint test for the presence of nitrogen and fusion of the product with soda lime gave no evolution of ammonia.

Discussion

An investigation of the products obtained from the treatment of abietic acid with nitric acid was undertaken to see if a crystalline nitroabietic acid could be obtained by this means. Such a compound has been reported by Goldblatt, Lowy and Burnett (8) and Dubourg (3)(4), but only in an empirical manner with no analytical data given to support their views.

Attempts to prepare a nitro derivative of abietic acid by direct treatment with nitric acid gave only the amorphous yellow nitrogen-containing solid reported by Goldblatt, Lowy and Burnett (8). Violent frothing and a strong evolution of nitrogen dioxide accompanied the reaction of abietic acid with all concentrations of nitric acid indicating that oxidation rather than nitration was the principal reaction. The yellow solid gave positive tests for nitrogen upon fusion with sodium, but no qualitative evidence of any common nitrogen functional group could be obtained. Polarographic analysis, according to the method outlined by Shikata (20) for the qualitative determination of nitro groups, gave evidence for the presence of nitro groups, but such evidence was partially obscured by the presence of other reducible groups. The results of this analysis indicate that some reducible group other than the reducible double bond of abietic acid is present in the yellow nitrogen-containing solid. Apparently either the reaction occurred at the reducible double bond of abietic acid or the nitrogen-containing group gives a wave which overlaps that of the reducible double bond. A comparison of the yellow solid with p-nitrobenzoic acid

seems to indicate that the additional reducible material is not a nitro group.

The white crystalline dinitroabietic acid first claimed by Dubourg (3) (4) and later reported by Goldblatt, Lowy and Burnett (8) in 45-56% yields could not be prepared, although repeated attempts to prepare this compound were made. The only product which could be obtained by slow addition of concentrated nitric acid to an alcoholic solution of abietic acid was an amorphous yellow solid. This yellow solid had the same properties as that obtained by direct treatment with nitric acid. Goldblatt, et. al. presented no evidence in support of the dinitroabietic acid beyond the statement that neutralization equivalents indicated the compound was a nitro and not a nitrate. This lack of evidence coupled with the fact that the dinitroabietic acid could not be prepared in the prescribed manner led to the conclusion that previous workers had not sufficiently characterized the products obtained.

Reduction of the yellow nitrogen containing solid with zinc gave an amorphous brown powder. Deamination occurred during reduction as shown by the evolution of considerable ammonia. The insolubility of the reduction product in strong alkali indicated that decarboxylation may have occurred as well. Exact measurements of the amount of nitrogen evolved as ammonia were not made but the results were such as to indicate 37% of amine. Fusion of the reduction product with sodium gave a positive test for nitrogen, but no indication of an amino group, which would be the expected reduction product, could be obtained.

The failure of the yellow nitrogen-containing solid to give an amine upon reduction led to an investigation of the preparation of such a compound through ammonolysis of a halide with liquid ammonia. The first

attempts were made using a sample of chloroabietic acid prepared by Bobst (1) in 1951. The products obtained by this method contained no nitrogen and indications were that dehydrohalogenation or immediate deamination had been the principal reactions. Bobst had found the chloroabietic acid to be very susceptible to dehydrohalogenation at temperatures above 20°C.

Since the chloroabietic acid was known to be subject to dehydrohalogenation and considerable time had elapsed since its preparation, it was decided to repeat the ammonolysis with freshly chlorinated material. Methyl abietate rather than abietic acid was used for chlorination purposes and found to give an amorphous yellow product in chloroform. Chlorination in aqueous suspension was found to be impractical because of difficulties encountered in keeping the partially chlorinated product in suspension. Molecular weight determinations gave an average value of 403, indicating that addition of slightly more than two chlorine atoms per molecule had taken place. The molecular weight further indicates that chlorination was incomplete, since the addition of a total of four atoms of chlorine per molecule has been shown to occur in abietic acid. The methyl chloroabietate was found to be stable with respect to dehydrohalogenation at room temperature in contrast to the chloroabietic acid prepared by Bobst. Apparently esterification exerts some stabilizing influence on abietic acid with respect to chlorination.

Ammonolysis of the methyl chloroabietate failed to give any nitrogen-containing compounds, even though the water added to the solid material after evaporation of the ammonia gave positive tests for the presence of chloride ions. Preliminary investigations into the amination at higher temperatures by means of sodium amide gave results similar to those above.

Future work might include the investigation of other methods of nitration with respect to abietic acid. The study of the stabilizing influence of esterification might prove interesting in future work since the instability of the abietic acid molecule is the greatest block encountered in its study. Further study of the chlorination of methyl abietate might also prove profitable due to the greater stability of this product. Still another route to more stable abietic acid derivatives would be through tetrahydroabietic acid or its esters.

Conclusions

The results of this investigation indicate that the preparation of stable nitrogen products of abietic acid is hampered by ready dehydrohalogenation. This is borne out by the dehydrohalogenation which occurs in the case of chloroabietic acid at temperatures above 20°C., and the even more rapid deamination which occurs almost instantaneously. In general the loss of hydrogen is accompanied by the loss of some hydrogen accepting group from the molecule.

The products obtained in nitration attempts indicate that the loss of hydrogen is an important factor in the preparation of nitro derivatives of abietic acid. The final product in such cases is a mixture of oxidation products, nitro or nitrate products and unreacted material. The nitro or nitrate formed in the reactions with nitric acid is more stable toward the loss of hydrogen at higher temperatures than the halogen and amino compounds, but decomposes by the same route.

The blocking of the carboxyl group of the abietic acid molecule by esterification apparently stabilizes the molecule to some extent. This is shown by the increased stability of the chlorination products with respect to dehydrohalogenation, except at higher temperatures. However, the amino derivative in such cases is still much more unstable than the corresponding halogen product. Apparently the carboxyl group present in the abietic acid molecule is in part responsible for the extreme instability of the molecule.

Bibliography

1. Bobst, Master's Thesis, Oklahoma A. and M. College (1951)
2. Campbell and Morganna, J. Amer. Chem. Soc., 63, 1838 - 43 (1941)
3. Dubourg, Bull. Inst. Pin., 1927, No. 41, 241 - 6
4. Dubourg, Bull. Inst. Pin., 1929, 138 - 47
5. Easterfield and Bagley, J. Chem. Soc., 85, 1238 - 49 (1904)
6. Fieser and Campbell, J. Amer. Chem. Soc., 60, 159 - 70 (1938)
7. Fieser and Fieser. Natural Products Related to Phenanthrene, 3rd ed., New York: Reinhold Publishing Corporation, 1949, p. 41.
8. Goldblatt, Lowy and Burnett, J. Amer. Chem. Soc., 52, 2132 - 6 (1930)
9. Hasselstrom and Hopkins, J. Amer. Chem. Soc., 63, 421 - 2 (1941)
10. Haworth, J. Chem. Soc., 2717 (1932)
11. Johansson, Arkiv. Kemi. Min. Geol., 6, No. 19, 20pp. (1917)
12. Kessler, U. S. Patent 922, 596 (May 5, 1909)
13. Levy, P., Ber., 40, 3658 (1907)
14. Levy, P., Ber., 42, 4305 - 8 (1909)
15. Levy, P., Ber., 62B, 2497 - 2504 (1929)
16. Littmann, U. S. Patent 2,240,936 (May 6, 1941)
17. Ruzicka, Helv. Chim. Acta, 16, 169 (1933)
18. Ruzicka and Meyer, Helv. Chim. Acta, 5, 315 (1922)
19. Rydon, J. Chem. Soc., 257 (1937)
20. Shikata, Trans. Faraday Soc., 21, 42 (1925)
21. Virtanen and Aschan, Ann., 424, 117 - 33 (1921)

VITA

William J. Probst
candidate for the degree of
Master of Science

Thesis: A STUDY OF THE NITROGEN COMPOUNDS OF ABLETTIC ACID

Major: Chemistry

Biographical and Other Items:

Born: August 17, 1923 at Cedar Rapids, Iowa

Undergraduate Study: Coe College, Cedar Rapids, 1946-1950

Graduate Study: O.A.M.C., 1950-1952

Experiences: Army, 1943-1946.

Member of Phi Beta Kappa and Phi Kappa Phi.

Date of Final Examination: July 30, 1952.

THESIS TITLE: A Study of the Nitrogen Compounds of
Abietic Acid

AUTHOR: William J. Probst

THESIS ADVISER: Dr. Henry P. Johnston

The content and form have been checked and approved by the author and thesis adviser. Changes or corrections in the thesis are not made by the Graduate School office or by any committee. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

TYPIST: Mrs. J. O. Richardson