

A SURVEY OF THE CEDAR RESEARCH COMPLETED AT  
THE SOUTHWEST TEXAS STATE TEACHERS COLLEGE

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A SURVEY OF THE CEDAR RESEARCH COMPLETED AT  
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By

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A SURVEY OF THE CEDAR RESEARCH COMPLETED AT  
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CHAPTER I

INTRODUCTION

The Problem Stated

This survey covers the research that has been conducted on the leaf and the wood oils of Juniperus mexicana and Juniperus virginiana under the direction of Dr. Carroll L. Key of the chemistry department of The Southwest Texas State Teachers College, San Marcos, Texas. Included in this survey are the discoveries of new chemical components of the oils and a brief resumé of the reactions used to prove the presence of these components, along with the miscellaneous reactions that have been carried out by the investigators.

Why the Problem Was Chosen

Since 1937 when Howard Black<sup>1</sup> under the direction of Dr. Carroll L.

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<sup>1</sup>Howard Black, An Investigation of Some Chemical Products of Central Texas Cedar.

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Key began to experiment with the cedar oils derived from the varieties of cedar found in Texas, subsequent investigations have amassed a great deal

of information concerning the chemical and physical properties of the oils. This survey was undertaken to consolidate the information obtained in the various works on cedar oils.

Because of the abundance of cedar and its prolific reseeding, the land owners in recent years found it necessary to control its widespread growth; for it was ruining grazing lands. In order to aid in the control of cedar the Federal Government offered a bounty for each acre of pasture land cleared.

Since the methods of clearing were wasteful of this natural resource, several cedar oil mills were established in the area. The mills removed the oil from the wood and the leaves by steam distillation. After the oil was separated from the water in settling tanks, it was partially fractionated without attempt to ascertain the components.

In order to separate the oils more thoroughly and thereby determine new uses for the products, the chemistry department of The Southwest Texas State Teachers College undertook the problem and began research on it in 1937.

#### History and Related Work

Cedar oil, according to Parry,<sup>2</sup> is obtained from the wood of

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<sup>2</sup>Ernest J. Parry, The Chemistry of Essential Oils and Artificial Perfumes, Vol. II, p. 2.

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Juniperus virginiana by steam distillation. It is one of the "essential

oils" which Parry defines as "odoriferous bodies of an oily nature obtained almost exclusively from vegetable sources, generally liquid at ordinary temperatures, and volatile without decomposition."<sup>3</sup> Cedar oils

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<sup>3</sup>Parry, op. cit., p. 1.

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are classified under the field of terpene chemistry. Terpenes are a class of compounds having the general formula  $(C_5H_8)_n$ .

Under laboratory conditions the oil is extracted from the crushed leaves or the wood shavings by means of a steam distillation apparatus described by Lemmons.<sup>4</sup> After the oil has been separated from the water,

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<sup>4</sup>Charles A. Lemmons, A Partial Separation of the Constituents of Heart Cedar Wood Oil, pp. 4-5.

---

it is filtered and dried over anhydrous magnesium sulphate before proceeding with the distillation. This distillation is carried out in an all pyrex glass vacuum still as described by Lemmons.<sup>5</sup>

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<sup>5</sup>Ibid., pp. 6-7.

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Lemmons concluded that the crude cedar wood oil from the Juniperus mexicana was apparently divided into three major portions according to boiling points--7.5% below 250° Centigrade, 60% between 255° and 260° Centigrade, and 32.5% from 288° to 290° Centigrade.<sup>6</sup> Other distillation

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<sup>6</sup>Lemmons, op. cit., p. 36.

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data are available in the work of Daniels,<sup>7</sup> Sadler,<sup>8</sup> Lowman,<sup>9</sup> Ford,<sup>10</sup> and

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<sup>7</sup>Arlie Lee Daniels, The Physical and Some Chemical Properties of Cedar Oil.

<sup>8</sup>Elbert R. Sadler, A Comparison of the Physical Properties of the Oils Obtained from the Varieties of Central Texas Cedar.

<sup>9</sup>Robert G. Lowman, A Physical Separation of Cedar Wood Oil.

<sup>10</sup>Robert E. Ford, The 253.5° Centigrade Fraction from the Fifth Distillation of New Braunfels Cedar Wood Oil.

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others.

The oil was separated and recombined according to the atmospheric boiling points and the refractive indices. A total of five successive distillations was necessary to secure constant boiling fractions. These fractions were used in the investigations.

Experimenting with the light fractions of cedar leaf oil, Coil<sup>11</sup>

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<sup>11</sup>John A. Coil, Pinene in Bastrop Cedar Leaf Oil, pp. 32-37.

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showed that derivatives formed from this oil correspond very closely to those of a-pinene and b-pinene. Other investigation are available on the characteristics of the leaf oils.

Black<sup>12</sup> separated camphor from the leaf oil of Juniperus mexicana

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<sup>12</sup>Black, op. cit., pp. 12-14.

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by chilling the oil obtained by steam distillation of the leaves and removing the precipitated camphor by filtration. He also separated a solid tertiary alcohol from the cedar wood oil of Juniperus mexicana by filtering the last cuts of the first distillation of cedar wood oil and recrystallizing the solid removed.<sup>13</sup> This was assumed to be cedrol as

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<sup>13</sup>Ibid., p. 18.

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its physical properties were similar to those in the literature. Reed<sup>14</sup>

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<sup>14</sup>Thomas E. Reed, The Properties of the Solid Derivatives of Texas Heart Cedar Oil, pp. 11-20.

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employed several solvents in recrystallizing the cedrol obtained from the wood oil of Juniperus mexicana. Wagner<sup>15</sup> also worked with cedrol and

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<sup>15</sup>F. Wagner, Certain Chemical Properties of the Essential Oil of Juniperus Mexicana Boiling Between 250°-300°, pp. 14-16.

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obtained crystals which melted at 85°-86° Centigrade by recrystallization from diacetone alcohol. By acetylating cedrol Wagner<sup>16</sup> obtained an ester

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<sup>16</sup>F. Wagner, Preparation of Cedryl Acetate, pp. 2-3.

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which boiled at 255° Centigrade.

By far the larger quantity of work has been done on the liquid components of cedar wood oil, which will be covered in some detail in this paper.

#### Limitations of This Investigation

This paper is limited to the work done by the graduate students in chemistry at The Southwest Texas State Teachers College and to the published literature where reference to authority is necessary to explain the source of the investigator's conclusion.

Also included in this paper are the results obtained by the writer in his investigation of the 257.7° Centigrade fraction of New Braunfels cedar wood oil.

#### Methods of Collecting Data

The greater portion of the material for this paper was collected by reviewing the work done by the graduate students in chemistry and selecting the data, reactions, and conclusions that were of most importance.

In addition to surveying the work done by other graduate students of this institution, this paper will present the research completed by the writer on a specific cut of cedar wood oil.

## CHAPTER II

### THE INVESTIGATION OF CEDAR LEAF OIL

#### The Liquid Components

##### Pinene in the Lower Boiling Fraction

Physical properties.--The cedar leaf oil that was used in the investigations of the graduate students was obtained chiefly from Juniperus virginiana, or East Texas cedar.

Coil,<sup>1</sup> experimenting with the light boiling fraction, found that its

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<sup>1</sup>John A. Coil, Pinene in Bastrop Cedar Leaf Oil, pp. 32-39.

---

physical properties closely resembled those of pinene. Therefore he attempted to show that the oil did contain pinene as its principal component.

Since pinene has a molecular weight of 136 and a total molecular refraction of 43.54, these constants were used to prove that pinene was in the oil. By substituting in the formula

$$R = \frac{M n^2 - 1}{d n^2 + 2}$$

R = total molecular refraction  
d = density of the liquid at the temperature  
of the experiment = 0.8349  
M = molecular weight = 136  
n = index of refraction of a liquid for light  
of a given wave length = 1.4683

the physical constants of the oil used, we arrive at the value for the molar refraction of 45.3 which is only a 1.76 difference from that of pinene. If the bridge in the formula for pinene acts as a double bond, the molar refraction of pinene would be 45.24.<sup>2</sup>

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<sup>2</sup>Coil, op. cit., pp. 38-39.

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Oxidation.--A fifteen milliliter portion of the oil was stirred slowly with a solution of 25 grams of potassium permanganate and 1 gram of sodium hydroxide in 1400 ml. of water for two hours at 0° Centigrade. After the reaction was complete, the solution was saturated with carbon dioxide and steam distilled to remove any oil that had not reacted. The manganese dioxide formed was removed by filtration, and the reaction mixture was again saturated with carbon dioxide. The water was boiled off until only 250 ml. remained. The acids formed by oxidation were regenerated with dilute sulphuric acid and extracted with benzene. The benzene was distilled under reduced pressure. On standing the residue partially crystallized like the oxidation product of b-pinene while that of a-pinene is liquid.<sup>3</sup>

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<sup>3</sup>Ibid., pp. 32-33.

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Another 15 ml. portion of the oil was oxidized by mixing it with 15 grams of sodium hydroxide in a 1% solution of potassium permanganate. This was stirred, carbonated, steam distilled, and then concentrated to 250 ml.

The heavy, white crystalline precipitate which formed was regenerated with dilute sulphuric acid and extracted with chloroform. After the chloroform was allowed to evaporate, triclinic crystals remained which melted at  $60^{\circ}$ - $61^{\circ}$  Centigrade. This was believed to be l-nopinic acid, nopinone, and b-pinene glycol which are produced when b-pinene is oxidized with potassium permanganate.<sup>4</sup>

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<sup>4</sup>Coil, op. cit., pp. 33-34.

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The dihydrochloride derivative.--A solution of 10 ml. of the oil in 10 ml. of chloroform was cooled to  $-77^{\circ}$  Centigrade with dry ice, and dry hydrogen chloride gas was passed into it for 15 minutes. The reaction mixture became a semi-solid mass and was filtered immediately. When re-crystallized from ethanol and water, the solid melted at  $50^{\circ}$  Centigrade. This corresponds to the melting point of the dihydrochloride of both a-pinene and limonene. Considering the boiling points of a-pinene ( $155^{\circ}$ - $156^{\circ}$  Centigrade), limonene ( $175^{\circ}$ - $176^{\circ}$  Centigrade), and the original oil ( $159^{\circ}$  Centigrade), it is reasonable to assume that a-pinene dihydrochloride was formed.<sup>5</sup>

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<sup>5</sup>Ibid., p. 37.

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#### The $200^{\circ}$ - $230^{\circ}$ Centigrade Fraction

Webb removed the acids by treating a 15 ml. sample of this fraction

with 4 ml. of 0.5N sodium hydroxide and separating the water solution from the oil. When the water layer was acidified with dilute sulphuric acid, a yellow oil, which was distinctly acid to litmus, was obtained. This oil boiled at 213° Centigrade; and its refractive index, 1.4405, was far below that of the original oil. This may suggest a method of purifying the product.

When a drop of an alcoholic solution of ferric chloride was added to a drop of the recovered acid, a reddish-brown coloration appeared. This indicated but did not prove the presence of phenols. The acid was partially soluble in sodium hydroxide and formed a slight precipitate when the solution was saturated with carbon dioxide. This was further evidence of the presence of phenols.<sup>6</sup>

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<sup>6</sup>Morris S. Webb, An Investigation into the Composition of the Portion of Bastrop Cedar Leaf Oil Boiling Between 200° and 230° Centigrade, pp. 47-49.

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Webb treated 0.5 gram of the acid free oil with 1 gram of picric acid in boiling 95% ethanol. This was cooled slowly, and no crystals formed; but after distilling off part of the ethanol and cooling the resulting solution in an ice-bath, yellow needle-like crystals precipitated which melted at 75°-76° Centigrade. No conclusions were drawn as to the identity of this compound.<sup>7</sup>

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<sup>7</sup>Ibid., p. 49.

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A clear blue oil which boiled at 224° Centigrade, 6° higher than the original oil, resulted when heated with flowers of sulphur in an oil-bath at 130°-135° Centigrade for one and one-half hours. When flowers of sulphur and the oil were refluxed at 140° Centigrade for twelve hours, a clear blue oil and a dark viscous liquid were formed. During both of these reactions hydrogen sulphide gas was detected with moist lead acetate paper. These reactions indicated two things. First, when carried out at temperatures below 135° Centigrade and for periods up to one and one-half hours, the result was loss of hydrogen to sulphur. And secondly, if the temperature was raised to 140° Centigrade or higher and the reaction time was more than three hours, there was a polymerization reaction.<sup>8</sup>

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<sup>8</sup>Webb, op. cit., pp. 50-54.

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#### The 267°-295° Centigrade Fraction

Clare titrated this fraction against 0.1N sodium hydroxide and showed that there was a negligible amount of free acid present. After tests with phenylhydrazine, Schiff's reagent, and Tollen's silver oxide reagent proved negative, it was assumed that no carbonyl group was present.<sup>9</sup>

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<sup>9</sup>A. J. Clare, Some Physical and Chemical Properties of the Higher Fraction of Bastrop Cedar Leaf Oil, p. 24.

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Treating the oil with zinc chloride and concentrated hydrochloric

acid resulted in an immediate reaction. This proved the presence of tertiary alcohols.<sup>10</sup>

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<sup>10</sup>Clare, op. cit., p. 24.

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When the oil was dissolved in acetic anhydride and mixed with a drop of concentrated sulphuric acid, a deep blue coloration appeared. Clare concluded that this reaction might indicate the presence of sylvestrene or its isomer.<sup>11</sup>

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<sup>11</sup>Ibid., p. 25.

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Upon treating the oil with flowers of sulphur at 170°-190° Centigrade and distilling the product at about 30 mm. pressure, a deep blue oil was obtained. This may be guaiene or azulene. Clare quoted Simonsen as saying that guaiene is dehydrogenated by sulphur to yield a deep blue oil. The boiling point of the oil thus obtained was 273°-274° Centigrade, and the refractive index was 1.5037.<sup>12</sup>

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<sup>12</sup>Ibid., pp. 26-27.

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#### Miscellaneous Reactions

In an attempt to determine the free acid content of the low boiling fraction of cedar leaf oil, Goodman<sup>13</sup> titrated 5 ml. of the oil against

Using the molecular weight of bornyl acetate (196), the ester content was found to be 0.4%.<sup>15</sup>

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<sup>15</sup>Goodman, op. cit., pp. 31-32.

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No solid alcohol derivative was formed with benzoyl chloride, and no positive results were obtained with phenylhydrazine and sodium bisulphite; and it was assumed that no alcohols or carbonyl groups were present. Then the oil was treated with clean sodium to remove any acids. Finally the hydrocarbons were distilled off, and the following attempts to make the nitrosyl chloride derivative were made.

The gas evolved from dropping a saturated solution of sodium nitrite into concentrated hydrochloric acid was passed through a calcium chloride drying tube into an ethereal solution of 5 ml. of the oil at a temperature below 10° Centigrade. The reaction produced a bright green color, and the characteristic odor of nitrosyl chloride derivatives was present. As the product decomposed below room temperature, no attempt to isolate it was successful. The reaction was repeated, using petroleum ether as the solvent, with the same results.

The oil was dissolved in equal volumes of absolute ethanol and ethyl nitrite and cooled to 0° Centigrade. Then a saturated solution of dry hydrogen chloride gas in ethanol was added to the mixture. There was an apparent reaction, but again the derivative decomposed upon warming to room temperature.

A petroleum ether solution of the oil was cooled to -30° Centigrade

and treated with the nitrosyl chloride gas as before to form a greenish-white crystalline substance. These crystals could not be filtered in the presence of dry ice and would not crystallize from ethanol.

Several attempts were made to convert the nitrosyl chloride to a more stable amide in order to isolate the amide as an identifiable derivative. Zinc and hydrochloric acid, sodium amalgam and water, and sodium and water were each used to form the necessary nascent hydrogen. However the temperature of the carbon disulphide-dry ice mix was too low for these reactions to take place; and since permitting the reaction temperature to rise to a point where nascent hydrogen could be produced caused the decomposition of the nitrosyl chloride derivative, all of these trials proved futile.

To form the more stable nitrosonitrite or nitrite, a petroleum ether solution of the oil was treated with a saturated sodium nitrite solution and dilute acetic acid at low temperatures. This reaction proceeded as expected, but the product also decomposed upon standing and warming.<sup>16</sup>

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<sup>16</sup>Goodman, op. cit., pp. 33-40.

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Goodman<sup>17</sup> reported that the dihydrobromide of the light fraction

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<sup>17</sup>Ibid., pp. 44-45.

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melted at 60°-61° Centigrade when recrystallized from 95% ethanol. This was similar to the melting point of limonene dihydrobromide (m.p.--64°

Centigrade).

In order to brominate the cedar leaf oil careful controls must be utilized to prevent replacement reactions when addition products are desired. It was illustrated in Wehmeyer's work that addition reactions should be carried out at low temperatures, whereas an excess of bromine should be added to the warmed oil for best replacement results.<sup>18</sup>

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<sup>18</sup>Louis J. Wehmeyer, Some Bromination Products of Bastrop Cedar Leaf Oil, pp. 25-40.

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Reactions of all the fractions with dry hydrogen chloride gas did not provide any conclusive evidence as to the components of the fractions. Although Goodman<sup>19</sup> produced a hydrochloride which had the odor of bornyl

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<sup>19</sup>Goodman, op. cit., pp. 41-43.

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chloride, he was not able to separate it as such from the lower boiling fraction. When the 200°-230° Centigrade fraction was treated with dry hydrogen chloride gas, an odor similar to that of peppermint was obtained.<sup>20</sup>

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<sup>20</sup>Robert L. Bennett, A Study of the Physical and Chemical Properties of Cedar Leaf Oil, p. 24.

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Various methods of iodination were attempted by the investigators without result. Other reactions, particularly oxidation with nitric acid, gave plastic masses which were generally soluble in all organic solvents

but would not respond to crystallization.

These reactions with nitrosyl chloride, the halogens, and nitric acid show that there is need of further investigation of these apparent derivatives. Also it is hoped that the description of these results will aid any future investigator.

### The Solid Component--Camphor

#### Physical Separation and Properties

According to Lemmons,<sup>21</sup> camphor is obtained in good yield from the

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<sup>21</sup>Robert T. Lemmons, A Comparison of the Cedar Leaf Oils Found in Texas, p. 32.

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cedar leaf oil of Juniperus mexicana but not from the leaf oil of Juniperus virginiana. By weight camphor comprises 30% of the leaf oil of Central Texas cedar.

As camphor crystallized in the oil obtained from steam distillation, it was necessary to separate it from the oil before proceeding with the rectification in the vacuum still. To do this Black<sup>22</sup> chilled the oil in

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<sup>22</sup>Howard Black, An Investigation of Some Chemical Products of Central Texas Cedar, pp. 12-14.

---

an ice-salt mix and removed the camphor by filtration. However the camphor contained some oil, and it was necessary to recrystallize it to

obtain the pure compound. After several recrystallizations from a mixture of methanol and water, a sample was obtained that melted at 178° Centigrade.

A molecular weight determination was made by the freezing point lowering method, using naphthalene. The 0.1257 gram sample of camphor was mixed with 0.7845 gram of naphthalene and sealed in a tube. When the mixture was melted to effect an equilibrium, the molecular weight was found to be 156, which was comparable to the molecular weight of camphor from the formula  $C_{10}H_{16}O$ --152.

#### Derivatives

Camphoroxime.--Five grams of the solid filtered from the cedar leaf oil was dissolved in 75 ml. of ethanol. A concentrated water solution of 5 grams of hydroxylamine hydrochloride and 7.5 grams of sodium hydroxide was added to the alcohol solution. The mixture was refluxed on a water-bath for one hour or until a sample remained clear upon addition of water. After diluting with water and filtering, the reaction mixture was made acidic with dilute acetic acid. The camphoroxime separated and was recrystallized from dilute methanol. The melting point was found to be 118.5° Centigrade, and the boiling point 249°-253° Centigrade with decomposition.<sup>23</sup>

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<sup>23</sup>Black, op. cit., p. 15.

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Camphoronic acid.--Five grams of the camphor-like solid was dissolved

in 50 ml. of ethanol and treated with nitric acid at steam-bath temperature until no nitrogen dioxide fumes were given off. Upon recrystallization from dilute methanol the melting point was found to be 164° Centigrade, which was the same as that recorded in the literature.<sup>24</sup>

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<sup>24</sup>Black, op. cit., p. 16.

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Camphor sulphonic acid.---To eight grams of acetic anhydride 4 grams of concentrated sulphuric acid was added, and the mixture was cooled in an ice-bath. When the mixture was thoroughly cooled, 6 grams of the same solid was added gradually. Camphor sulphonic acid appeared in several days. The crystals were filtered and then washed with ether. After recrystallizing the compound from ethyl acetate, colorless prisms were obtained which melted at 190°-191° Centigrade.<sup>25</sup>

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<sup>25</sup>Ibid., pp. 16-17.

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The similarity of the physical properties of the solid found in the cedar leaf oil and commercial camphor is presented above. That the three known derivatives and those herein described are the same is indisputable. These facts clearly prove that the camphor in the leaf oils of Central Texas cedar is the same as that now obtained commercially from the Far East.

## CHAPTER III

### THE INVESTIGATION OF CEDAR WOOD OIL

#### Reactions of the Liquid Components

##### Hydrocarbons

##### Halogenation

Chlorination.--A carbon tetrachloride solution of the oil was saturated with dry chlorine gas at room temperature for two hours. The mixture was washed with a 10% solution of sodium bicarbonate and dried over anhydrous magnesium sulphate; a light yellow oil was obtained which boiled at 255° Centigrade.<sup>1</sup> Similar reactions are to be found in the

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<sup>1</sup>Erwin Graeter, The 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 37-38.

---

work of other investigators. It is hoped that further research may find these exploratory reports useful in completing the identification of the various derivatives that were evidently prepared.

Hydrogen chloride gas.--Dry hydrogen chloride gas was bubbled through an ethereal solution of the oil in an attempt to produce a dihydrochloride. This resulted in a color change to pink and finally to dark brown. When the solution was chilled in an ice-bath, no crystals were obtained nor were any formed after standing for three days. The boiling point of the

recovered oil was found to be higher than that of the original oil.<sup>2</sup> The

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<sup>2</sup>Rubin L. Faseler, Some Chemical and Physical Properties of the 255° Centigrade Fraction of New Braunfels Cedar Wood Oil, p. 8.

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formation of the dihydrochloride derivative should be studied closely in the future.

Bromination.--Fifteen milliliters of the oil was dissolved in 100 ml. of glacial acetic acid, and a solution of 15 ml. of bromine in 60 ml. of glacial acetic acid was added over a period of an hour. When this was poured into 500 ml. of cold water, a precipitate formed immediately. Upon separating the product from the water a brown, waxy-elastic substance was obtained that could be stretched and molded with ease. Using 85% isopropyl alcohol to recrystallize the brominated compound, Graeter<sup>3</sup> obtained

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<sup>3</sup>Erwin Graeter, Some Additional Reactions of the 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 15-16.

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light brown crystals which melted at 64° Centigrade with slight decomposition. The identification of this derivative should lead to the identification of this compound and the preparation of other derivatives.

The bromine number.--Ford<sup>4</sup> and Graeter<sup>5</sup> determined the "bromine

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<sup>4</sup>Robert E. Ford, Some Chemical Reactions of the 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 9-11.

<sup>5</sup>Erwin Graeter, The 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 17-19.

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number" of the 253.5° Centigrade fraction. They defined the "bromine number" as the number of centigrams of bromine consumed per gram sample of oil. Although questioning the usefulness of the following method applied to terpenes, they presented considerable research on this particular reaction.

In this determination the following reagents were used:

0.5N potassium bromide-bromate solution  
0.1N sodium thiosulphate solution  
10% potassium iodide solution  
10% sulphuric acid  
carbon tetrachloride  
starch solution.

The potassium bromide-bromate solution can be made by using 14 grams of potassium bromate and 50 grams of potassium bromide. When these two salts are dissolved together, they form a stable reagent that can be standardized against a standard thiosulphate solution.

Twenty-five milliliters of carbon tetrachloride was mixed with 5 ml. of 10% sulphuric acid in a 250 ml. Erlenmeyer flask fitted with a glass stopper. The solution was cooled to 35°-45° Fahrenheit, and exactly one gram of the neutral cedar wood oil was added. If 2 ml. of the bromide-bromate reagent had produced a permanent dark yellow coloration after shaking for two minutes, the sample would have been rejected. However this was not the case, and the addition of the bromide-bromate solution was carried out in 0.2 ml. portions with thorough shaking until the yellow color persisted. At this point 15 ml. of 10% sulphuric acid and 5 ml. of a saturated solution of potassium iodide were added. The mixture was then titrated against 0.1N sodium thiosulphate using starch as an indicator.

To minimize substitution the reaction flask was kept in an ice-bath throughout the entire procedure.

The "bromine number" may be obtained by substituting in the formula

$$\text{bromine number} = \frac{8(T_1N_1 - T_2N_2)}{\text{weight of sample in grams}}$$

where

- $T_1$  = ml. of bromide-bromate solution  
 $N_1$  = normality of bromide-bromate solution  
 $T_2$  = ml. of the thiosulphate solution  
 $N_2$  = normality of thiosulphate solution.

After performing the indicated calculations, the "bromine number" was found to be 22.

To compute the percentage of unsaturated hydrocarbons by utilizing the "bromine number" the formula

$$U = \frac{MN}{160}$$

must be employed. By substituting the molecular weight of cedrene (204) in the formula, the degree of unsaturation was computed to be 28%.

#### Oxidation

Nitric acid.--When 40 ml. of 1:1 nitric acid was added slowly to a sample of oil at 100° Centigrade, a violent reaction occurred with the evolution of nitrogen dioxide fumes. The brittle reaction product was slightly soluble in glacial acetic acid, ethanol, or ether but could not be crystallized from any of these solvents. After a subsequent treatment with nitric acid for four hours with heating, a solution was formed. This

was neutralized with ammonium hydroxide, heated with bonechar for one hour, and filtered while hot. Acidifying the clear filtrate with hydrochloric acid caused the precipitation of a white solid soluble in either ethanol, ammonium hydroxide, or nitric acid. The dried product melted at 130° Centigrade and formed gelatinous precipitates when its copper, mercury, or lead salts were placed in water. Tests for nitrogen were negative.

Assuming only carbon, hydrogen, and oxygen present, Daniels<sup>6</sup> obtained

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<sup>6</sup>Arlie Lee Daniels, The Physical and Some Chemical Properties of Cedar Oil, pp. 70-73.

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these combustion analysis data: C--51.09%, H--5.2%, and O--43.7%. The empirical formula was therefore  $C_3H_4O_2$ . When molecular weight determinations showed that the molecular weight was 426, the formula was found to be  $C_{18}H_{24}O_{12}$  with a molecular weight of 432.

Phosphoric anhydride.--On the addition of enough phosphoric anhydride to form a thick paste with the oil, a black mass was formed. Seventy per cent of the oil was recovered by suction filtration. After a subsequent treatment with phosphoric anhydride a brown mass was obtained from which 60% of the oil was removed. The oil boiled at 266° Centigrade, and its specific gravity was 0.932.<sup>7</sup> This reaction necessitates further

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<sup>7</sup>Faseler, op. cit., p. 9.

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investigation.

## Miscellaneous reactions

Test for triple bonds.--A test was made for triple bonds using a cuprous chloride solution in ammonium hydroxide. As no evidence of the formation of an acetylide-like compound was found, it was therefore assumed that no triple bonds were present.<sup>8</sup>

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<sup>8</sup>Robert E. Ford, Some Chemical Reactions of the 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, p. 11.

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Color reaction for cadinene.--The addition of a few drops of concentrated sulphuric acid to a chloroform solution of the oil produced a dark red coloration. Since there were no intermediate color changes, the test showed that no cadinene was contained in the oil.<sup>9</sup>

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<sup>9</sup>Faseler, op. cit., pp. 8-9.

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Attempts to form cedrene glycol.--To prepare cedrene glycol from any cedrene present, an emulsion of 80 grams of acetone, 5 grams of oil, and 5 grams of water was formed. Five grams of pulverized potassium permanganate was stirred into the emulsion over a period of three hours while the temperature was kept to 20°-26° Centigrade. After filtering the mixture and adding ethanol to use up any excess permanganate, the filtrate was distilled on a steam-bath to remove the acetone and ethanol. The oil was separated from the water by washing with petroleum ether. Upon allowing the dried petroleum ether extract to stand, it was apparent that no cedrene

glycol was prepared as crystals did not appear.

Metathesis of the glycol by refluxing a bromine derivative of the oil with potassium hydroxide resulted in the formation of needle-like crystals. These were not purified to obtain definite physical and chemical properties.<sup>10</sup>

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<sup>10</sup>Archie O. Parks, The 266°-267° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 10-11.

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### Alcohols

#### Acetylation

Acetic anhydride.--Whenever acetic anhydride was refluxed with the oil or sealed in a tube and heated to 190°-200° Centigrade, it was impossible to form an acetic ester of any alcohols present. Also the use of anhydrous sodium acetate, concentrated sulphuric acid, or 85% phosphoric acid as catalysts caused no reaction under ordinary laboratory conditions.

Acetyl chloride.--A sample of the oil was treated with an equal volume of acetyl chloride and cooled in an ice-bath. By decomposing any excess acetyl chloride present with ice and separating the oil from the water layer, an oil was recovered which boiled at 265° Centigrade and had a specific gravity of 0.9555. When the "ester number" was determined, it was found to be 35.2 as compared to that of the original oil, which was 4.1.<sup>11</sup> This reaction may be used to purify the alcohols that are present.

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<sup>11</sup>Faseler, op. cit., pp. 10-11.

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Acetic acid.--No attempt to form an ester with acetic acid was successful; and whenever any dehydrating agent or catalyst was present, the reaction failed.

#### Phthalic anhydride

Eight milliliters of the oil and 3 grams of phthalic anhydride were heated in a sealed tube at a temperature of 190°-200° Centigrade for one hour. There was no reaction, and it may be assumed that only tertiary alcohols were present.<sup>12</sup>

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<sup>12</sup>Ibid., pp. 9-10.

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#### Sodium reactions

One hundred milliliters of the oil was treated with metallic sodium and refluxed on a steam-bath for 100 hours. At the end of this time 25 ml. of absolute methanol was added, and a suspension was formed. The colloid could not be separated by ordinary filtration, but it was successfully filtered through a mat of asbestos fiber. The oil removed from the filtrate boiled at 258° Centigrade. The residue in the filter was a white which would react with acetyl chloride. This was presented as a possible method of purifying the alcohol.

A portion of the original suspension was mixed with acetyl chloride and refluxed on a steam-bath for fifteen minutes. When the acetyl chloride was decomposed with water, the solution was washed with dilute sodium hydroxide and finally with water. The oil, when dried over

anhydrous magnesium sulphate, seemed to crack at 265° Centigrade and yielded another substance which boiled at 245° Centigrade at 746 mm. After saponifying the ester an oil was obtained which boiled at 265° Centigrade.<sup>13</sup>

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<sup>13</sup>Parks, op. cit., pp. 7-9.

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Proof of the presence of pseudocedrol

Upon adding phthalic anhydride in toluene solution to the oil drained from the cedrol crystals, cedrenol was removed as a hydrogen phthalate; and pseudocedrol remained as an oily residue. The oil separated from this mixture possessed the following physical constants:

Boiling Point	282°-285°
Density	0.9918
Optical Rotation	+18°.

When the above oil was treated with phosphoric anhydride, a liquid with these physical constants was obtained:

Boiling Point	260°-264°
Density	0.9381
Optical Rotation in CHCl <sub>3</sub>	Laevorotary.

This was assumed to be cedrene.

By treating the oil with potassium hydroxide and carbon disulphide, the xanthate was prepared. After the xanthate was hydrolyzed, crystals were obtained which melted at 86° Centigrade. This was assumed to be cedrol.<sup>14</sup>

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<sup>14</sup>F. Wagner, Certain Chemical Properties of the Essential Oil of Juniperus Mexicana Boiling Between 250°-300°, pp. 17-18.

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Proof of the presence of cedrenol

The cedrenyl hydrogen phthalate formed above was hydrolyzed with a 20% solution of potassium hydroxide, and the oil recovered was separated and fractionated. Refluxing this with acetyl chloride produced an ester which boiled at 288° Centigrade; and when this ester was compared to commercial cedrenyl acetate, no difference was found. This proved that cedrenol was found in the higher fractions of the cedar wood oil.<sup>15</sup>

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<sup>15</sup>F. Wagner, Certain Chemical Properties of the Essential Oil of Juniperus Mexicana Boiling Between 250°-300°, pp. 17-18.

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#### Acid and Basic Constituents

Ford<sup>16</sup> attempted to remove the free acid and free basic constituents;

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<sup>16</sup>Robert E. Ford, Some Chemical Reactions of the 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 6-7.

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but whenever the necessary reactions were carried out, he found that these components were present in negligible amounts.

#### Esters

Graeter observed that by treating 35 ml. of the oil with 280 ml. of a 25% solution of sodium hydroxide the boiling point of the 253.5° Centigrade fraction was raised to 258° Centigrade while the specific gravity was not affected.<sup>17</sup>

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<sup>17</sup>Erwin Graeter, Some Additional Reactions of the 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 9-10.

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The "ester number," as determined by the Parry method, of the various cuts was found to be as follows:

Boiling point of fraction (°C)	Ester number
253.5	0.264
255	4.1
266-267	1.8

which indicates that the esters are found chiefly in the oil boiling around 255° Centigrade.

#### Aldehydes and Ketones

##### Sodium bisulphite

The aldehydes and methyl ketones were removed by adding 63 ml. of the oil to 210 ml. of sodium bisulphite reagent and agitating thoroughly using a mechanical stirrer. Upon standing for 24 hours the mixture yielded crystals which proved the presence of a carbonyl group. The oil was subsequently shaken with more bisulphite until no further reaction occurred. Four grams of the dry crystalline product was obtained. When the solid was treated with dilute hydrochloric acid, the oil was removed by washing with ether. About 0.5 ml. of a viscous brown oil was recovered which boiled at 104° Centigrade. Attempts to recrystallize any solid contained in the product from methanol and ethanol proved to be of no avail.<sup>18</sup>

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<sup>18</sup>Robert E. Ford, Some Chemical Reactions of the 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 4-6.

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Acid and dichromate

To test for the presence of an aldehyde a sample of the oil was shaken with an equal volume of potassium dichromate solution. Two layers were formed upon the addition of a few drops of concentrated hydrochloric acid and heat. As the top layer was light green and the bottom light brown and they did not change after twenty-four hours, the presence of an aldehyde was assured.<sup>19</sup>

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<sup>19</sup>Erwin Graeter, The 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 40-41.

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Although other reactions with reagents for the carbonyl group were positive, no results were obtained which would aid in the identification of the components.

#### The Solid Component--Cedrol

##### Comparison of the Cedar Wood Oils Found in Texas

When the cedar wood oil of Juniperus virginiana, or East Texas cedar, is distilled, it is found to contain one-sixteenth cedrol by volume. This is small as compared to the yield of Juniperus mexicana, or Central Texas cedar, from which can be obtained approximately seven-sixteenths cedrol by

volume. This is equivalent to 30-40% by weight.<sup>20</sup>

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<sup>20</sup>Elbert R. Sadler, A Comparison of the Physical Properties of the Oil Obtained from the Varieties of Central Texas Cedar, pp. 5-20.

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#### Purification and Combustion Analysis

The cedrol was removed from the oil by filtration, then dissolved in methanol, chilled, and filtered by suction. The solid was then allowed to dry by aeration for a week. After the drying was complete, the crystals melted sharply at 86° Centigrade. Using diacetone alcohol for the fine recrystallization and allowing it to evaporate slowly, Wagner<sup>21</sup>

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<sup>21</sup>F. Wagner, Certain Chemical Reactions of the Essential Oil of Juniperus Mexicana Boiling Between 250°-300°, pp. 14-16.

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obtained a pure sample of cedrol which melted at 86° Centigrade and boiled at 293° Centigrade. Both of these constants agree with those found in the literature.

Black<sup>22</sup> ran a combustion analysis on the purified solid from the

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<sup>22</sup>Howard Black, An Investigation of Some Chemical Products of Central Texas Cedar, p. 18.

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wood oil. He found it to have the following compositions: C--80.18%, H--11.74%, and O--8.21%. When these results were compared to the calculated composition from the formula  $C_{15}H_{26}O$  found in the literature, there was

little difference to be noted. Upon computing the molecular weight by the freezing point lowering method using naphthalene, he found it to be 223 as compared to 222 from the formula.

#### Proof of the Presence of Cedrol

##### The phenylurethane

One gram of cedrol and an appropriate quantity of phenylisocyanate were allowed to react in the cold. When the excess reagent was removed by distillation, crystals appeared which were recrystallized from ether. The phenylurethane melted at  $106^{\circ}$  Centigrade.<sup>23</sup>

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<sup>23</sup>F. Wagner, Certain Chemical Reactions of the Essential Oil of Juniperus Mexicana Boiling Between  $250^{\circ}$ - $300^{\circ}$ , p. 16.

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##### Chromic oxide oxidation

Upon adding a solution of 1 gram of red chromic oxide in petroleum ether to a cooled cedrol solution, brown crystals formed which melted at  $115^{\circ}$  Centigrade when recrystallized from acetone.<sup>24</sup>

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<sup>24</sup>Ibid., p. 16.

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##### Formic acid dehydration

When 15 grams of cedrol was mixed with 45 grams of 90% formic acid and warmed, the solution thus formed produced a viscous, amber oil. The

oil was extracted with ether, and the ethereal extract was dried over anhydrous magnesium sulphate. When the ether was removed, the oil obtained by distillation at reduced pressure was amber in color. The boiling point was found to be 258° Centigrade, and the specific gravity was 0.9348 at 20° Centigrade. It was assumed to be cedrene.<sup>25</sup>

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<sup>25</sup>F. Wagner, Certain Chemical Reactions of the Essential Oil of Juniperus Mexicana Boiling Between 250°-300°, pp. 16-17.

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#### Cedryl Phenylisothiourethane

One gram of cedrol was dissolved in an appropriate quantity of phenylisothiocyanate and refluxed for one hour. The excess reagent was distilled off until crystals formed. When recrystallized from ether, the phenylisothiourethane melted at 118° Centigrade.<sup>26</sup>

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<sup>26</sup>Ibid., p. 20.

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#### Nitration of Cedrol

Fuming nitric acid and cedrol were mixed and produced a viscous liquid. On standing for a few days crystals settled out and were analyzed by the Kjehdahl-Gunning-Arnold method. The results showed that the product contained 6.06% nitrogen. When cedrol was refluxed with concentrated nitric acid, a similar result was obtained. It was observed that if the acid were neutralized with a base or an alkali carbonate no nitrogen could be detected in the derivative.<sup>27</sup> This reaction should prove

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<sup>27</sup>F. Wagner, Certain Chemical Reactions of the Essential Oil of Juniperus Mexicana Boiling Between 250°-300°, pp. 18-19.

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useful to future investigators.

#### Sulphonation of Cedrol

A black mixture formed upon adding concentrated sulphuric acid to cedrol. An oil was recovered which contained sulphur and exploded at 92° Centigrade.<sup>28</sup>

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<sup>28</sup>Ibid., p. 19.

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#### Iodination of Cedrol

An unstable purple oil was obtained when a benzene solution of phosphorus and cedrol was refluxed with iodine, and this oil was assumed to be cedryl iodide. Thus the metathesis of the alkyl halide and the metallic salt to synthesize the ester was not possible as the cedryl iodide would decompose before a reaction could be obtained.<sup>29</sup>

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<sup>29</sup>Archie O. Parks, Acetylation of Some Constituents of Cedar Oil, pp. 13-14.

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#### Acetylation of Cedrol

Acetic anhydride

Parks obtained an amber oil, which boiled at 265° Centigrade at 745 mm., when 10 grams of cedrol, 1 gram of fused sodium acetate, and 15 ml. of acetic anhydride were refluxed at 160° Centigrade for two hours. The percentage of esters was found to be 15.79%. As the boiling point is just 2° above the boiling point of cedrene, it was believed that the major portion of the oil was cedrene.<sup>30</sup>

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<sup>30</sup> Archie O. Parks, Acetylation of Some Constituents of Cedar Oil, pp. 11-12.

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#### Acetic acid

After the reaction between sodium metal and a benzene solution of cedrol was complete, glacial acetic acid was added to the mixture and shaken vigorously. The solution was dried over anhydrous sodium acetate, and the benzene was removed. The apparent ester boiled at 255° Centigrade.

On heating 0.5 grams of cedrol and 0.2 grams of glacial acetic acid in a sealed tube for six hours at a temperature of 200° Centigrade, an oil was obtained which was insoluble in the acetic acid; whereas cedrol was very soluble in the same solvent.<sup>31</sup>

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<sup>31</sup> F. Wagner, Preparation of Cedryl Acetate, p. 3.

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Repeated attempts to esterify cedrol with glacial acetic acid were reported by Parks.<sup>32</sup> He used glacial acetic acid in the presence of

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<sup>32</sup> Archie O. Parks, Acetylation of Some Constituents of Cedar Oil, pp. 10-11.

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fused sodium acetate and either concentrated sulphuric acid or 85% phosphoric acid and refluxed the mixtures at 160° Centigrade. When cedrol, fused sodium acetate, and acetic acid were sealed in a tube with either concentrated sulphuric acid or phosphoric anhydride and heated to 200° Centigrade, no cedryl acetate was obtained.

#### Acetyl chloride

Ten grams of cedrol in ethyl acetate solution was treated with 20 ml. of acetyl chloride for one hour. After decomposing the excess reagent with water, the reaction mixture was washed twice with water and dried over anhydrous magnesium sulphate. The oil recovered was fractionated at reduced pressure; and it boiled at 298° Centigrade, and the specific gravity was 1.011.<sup>33</sup>

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<sup>33</sup> F. Wagner, Certain Chemical Properties of the Essential Oil of Juniperus Mexicana Boiling Between 250°-300°, p. 19.

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A mixture of 40 grams of cedrol and 20 grams of acetyl chloride was stirred at 25° Centigrade for thirty minutes. When the oil was recovered, it boiled at 255° Centigrade; and the density was 0.9326. Upon analysis for esters by the Parry method the ester content was computed to be 9-10%.

Wagner obtained a solid by stirring 20 grams of cedrol and 10 grams

of acetyl chloride at 5° Centigrade. The mixture was brought to room temperature slowly, and the residual solid was recrystallized from ether. The crystals were dextrorotary and melted at 42°-45° Centigrade.<sup>34</sup>

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<sup>34</sup>F. Wagner, Preparation of Cedryl Acetate, p. 2.

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### Plastics from Cedar Wood

#### Urea Treatment

Coarsely ground, oil-free cedar sawdust was mixed with a saturated solution of urea and alternately heated to 80° Centigrade during the day and cooled overnight for a period of one week. After filtering the solution the wood was warmed until almost dry. While still hot, it was placed in a heated mold on a piece of cedar board about three-sixteenths of an inch thick and pressed for three hours. A hard plastic which crumbled on the edges was formed on the wood. As it dried, it adhered to the wood more tenaciously and retained the cedar color and odor.<sup>35</sup>

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<sup>35</sup>Robert L. Dement, Plastics from Central Texas Cedar, pp. 26-27.

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#### Aniline Hydrolysis

By treating 200 grams of 50 mesh wood with 40 grams of aniline and 200 grams of water, aniline-treated wood was obtained. One hundred parts of this wood, 8 parts of furfural, 2 parts of water, and 0.5 parts of zinc stearate were mixed and heated to 100° Centigrade. Dement placed the

mixture in a heated mold and applied pressure to it overnight. This yielded a brown plastic which adhered to the block and hardened as it dried.<sup>36</sup>

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<sup>36</sup>Dement, op. cit., pp. 28-29.

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#### Sulphuric Acid Hydrolysis

One hundred grams of oil-free, 50 mesh cedar sawdust was warmed with 3% sulphuric acid to 90° Centigrade for thirty-six hours; and the acid was removed by filtration. The treated wood was added to 8 grams of aniline, 8 grams of furfural, and 0.5 grams of zinc stearate, and heated to 100° Centigrade and then placed under pressure in a hot mold for four and one-half days. A hard, dark plastic of fine texture was obtained.<sup>37</sup>

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<sup>37</sup>Ibid., p. 33.

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#### Cellulose Acetate Treatment

Fifty grams of coarse cedar sawdust was refluxed with a saturated solution of cellulose acetate in chloroform for several hours. The chloroform was allowed to evaporate until the mixture was almost dry. After pressing in a heated mold and drying for several days, the product retained the cedar odor and color and seemed to be very cohesive. When a completely dry sample was treated similarly, the plastic had an odor like cedar and could be sawed easily.<sup>38</sup>

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<sup>38</sup>Ibid., pp. 35-36.

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CHAPTER IV  
REACTIONS OF THE 257.7° CENTIGRADE FRACTION  
OF NEW BRAUNFELS CEDAR WOOD OIL

Physical Separation and Properties

To obtain this fraction the writer, with the aid of other graduate students in chemistry, ran the fifth distillation of various fractions of the fourth distillation of New Braunfels cedar wood oil that was run by Ford<sup>1</sup> and Graeter.<sup>2</sup> The corrected boiling point of the cut was 257.7°

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<sup>1</sup>Robert E. Ford, The 253.5° Centigrade Fraction from the Fifth Distillation of New Braunfels Cedar Wood Oil, pp. 27-29.

<sup>2</sup>Erwin Graeter, The 253.5° Centigrade Fraction of New Braunfels Cedar Wood Oil, pp. 29-31.

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Centigrade, and the specific gravity at 32° Centigrade was 0.933.

Chemical Classification

Tests for Aldehydes and Ketones

Sodium bisulphite addition.--A sodium bisulphite reagent was prepared as suggested by Shriner and Fuson,<sup>3</sup> and 10 ml. was added to 5 ml. of the

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<sup>3</sup>R. L. Shriner and R. C. Fuson, The Systematic Identification of Organic Compounds, p. 58.

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oil. The mixture was shaken thoroughly and set aside for a week. There was no precipitate which indicated that no aldehydes or methyl ketones were present.

Phenylhydrazine.--One-half gram of the oil was dissolved in 2 ml. of ethanol, and water was dropped in until the precipitated oil just redissolved. To the solution one-half gram of phenylhydrazine was added. As the solution remained clear for several minutes, a drop of glacial acetic acid was used as a catalyst. Kamm<sup>4</sup> suggested this as a test for water

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<sup>4</sup>Oliver Kamm, Qualitative Organic Analysis, p. 155.

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insoluble aldehydes. There was no reaction, and it was assumed that no aldehydes or ketones were present.

Tollen's ammoniacal silver oxide.--Tollen's ammoniacal silver oxide reagent was prepared according to Shriner and Fuson.<sup>5</sup> Two milliliters of

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<sup>5</sup>Shriner and Fuson, op. cit., p. 62.

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the oil was treated with 3 ml. of the reagent. When only a very slight brown precipitate was formed, it was assumed that a negligible amount of aldehyde was present.

Fehling's solution.--Fehling's solution was prepared as given in the handbook.<sup>6</sup> Two milliliters of the oil was permitted to react with 2 ml.

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<sup>6</sup>Handbook of Chemistry and Physics, p. 1275.

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of the reagent and heated with a luminous flame. There was no precipitate of red cuprous oxide.

#### Saponification and Ester Value

To saponify the esters and neutralize any acids present, 25 ml. of the oil was refluxed with 50 ml. of 25% sodium hydroxide for two hours as suggested by Kamm.<sup>7</sup> The reaction mixture was suction-filtered while hot

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<sup>7</sup>Kamm, op. cit., p. 157.

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to remove any impurities. The filtrate was allowed to cool; and the unreacted oil was removed by washing the mixture with three 20 ml. portions of ether, and the ether extract was dried over anhydrous magnesium sulphate. The water layer would contain the sodium salts of acids from three types of reactions, which are: first, the salt of any neutralized acid; second, the salt of any acid from a saponified ester; and third, the salts of any acids formed by the Cannizzaro reaction.

To recover any acids from the sodium salts formed, the water layer was neutralized with concentrated hydrochloric acid. During the neutralization the reaction mixture was kept in an ice-bath, and methyl orange paper was used as an indicator. When the solution became neutral to methyl orange, a white crystalline precipitate was formed. This was removed by filtering with light suction. All attempts to recrystallize the solid from the common organic solvents were futile. The crude product did not melt when heated in an oil-bath to 305° Centigrade.

After the filtrate from the reaction above was made acid to methyl orange, a strong fruity odor was prevalent. Ether was used to extract the oil from the water solution, and the ether extract was dried over anhydrous magnesium sulphate. A light brown oil was obtained which boiled at 49° Centigrade.

The oil recovered from saponification boiled at 253.5° Centigrade. The boiling point was 4.2° lower than that of the original oil. As a matter of interest, the free acid value of the oil recovered above was obtained. It was found that 0.16 milligrams of potassium hydroxide was used to neutralize 1 gram of the oil.

To determine the "ester number" of the original oil, an alcoholic solution of caustic potash was prepared according to Parry.<sup>8</sup> If a sample

<sup>8</sup>Ernest J. Parry, The Chemistry of Essential Oils and Artificial Perfumes, Vol. II, pp. 288-289.

of oil is refluxed with an alcoholic solution of caustic potash, all the esters should be saponified. After titrating the cooled reaction mixture and a blank prepared by using water instead of the oil with a standard solution of hydrochloric acid, the amount of potassium hydroxide consumed in the saponification was computed. The "ester number," the number of milligrams of potassium hydroxide necessary to saponify one gram of oil, was found to be 10.26.

By substituting the "ester number" of the oil in the formula

$$\frac{(M)(A)}{560} = \text{percentage of ester}$$

where

M = molecular weight  
A = ester number

the approximate percentage of ester can be obtained. Assuming the molecular weight to be 200, the ester content was estimated to be 3.66%.

#### Fusion Tests for Nitrogen, Sulphur, and the Halogens

Fused sodium metal.--The sodium fusion was done according to McElvain.<sup>9</sup> When the reaction mixture was treated with the necessary

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<sup>9</sup>Samuel M. McElvain, The Characterization of Organic Compounds, pp. 40-42.

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reagents, none of the elements mentioned above was found to be present.

The potassium carbonate-magnesium mixture.--When a 0.1 ml. sample of the oil was decomposed over a fused mass of potassium carbonate and magnesium metal in a soft glass test tube, the tube was heated to a dull redness and dropped into a 15 mm. test tube containing 20 ml. of water. The resulting solution was filtered, and samples of the filtrate were tested with the appropriate reagents.<sup>10</sup> No nitrogen, sulphur, or halogen

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<sup>10</sup>Ibid., pp. 42-43.

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compounds were detected.

Acidic and Phenolic Compounds

Acid value.--The free acid value, the number of milligrams of a base necessary to neutralize one gram of the unknown compound, was determined by titrating a solution of the oil in ethanol with a 0.1022N solution of potassium hydroxide. The 4.665 gram sample of the original oil was dissolved in 50 grams of 95% ethanol and heated to boiling in a hot water bath. When the solution was warmed thoroughly, two drops of phenolphthalein was added as an indicator; and the solution was titrated with the standard potassium hydroxide. Only one milliliter of the base was necessary to obtain a neutral mixture. After computing the acid value, it was found to be 1.23.

Test for phenols.--No color change resulted from treating an alcoholic solution of the oil with alcoholic ferric chloride. McElvain<sup>11</sup> gave this

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<sup>11</sup>McElvain, op. cit., p. 141.

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as a test for phenolic and enolic compounds. Therefore it was assumed that the oil contained no components of this type.

#### Tests for Alcohols

Benzoylation.--When 20 ml. of the oil, 10 ml. of benzoyl chloride, and 35 ml. of 10% sodium hydroxide were shaken vigorously until the odor of benzoyl chloride was not noticeable, a white semi-solid mass was formed. A solid was removed by suction filtration which proved to be benzoic acid. Since this was the only solid formed, it was desirable to ascertain the "ester number" of the oil in the filtrate. To do this the oil was

separated from the water by washing with ether. After the ethereal extract was washed with a saturated solution of sodium bicarbonate and water, it was dried over anhydrous magnesium sulphate. The ether was removed by fractional distillation on a steam-bath. When a sample of the recovered oil was saponified by refluxing it with alcoholic potash, the "ester number" was determined to be 17.8. The percentage of ester, using a molecular weight of 200, was estimated to be 6.3%. Apparently a liquid ester was formed but was not isolated because it would require careful fractional distillation at reduced pressure. This also indicated that the alcohol content may be considered negligible.

One milliliter of the oil, 2.5 ml. of benzoyl chloride, and 5 ml. of pyridine were refluxed for one hour. The reaction mixture was cooled in an ice-bath and then washed with a 5% solution of sodium bicarbonate. No solid derivative was precipitated by further chilling. McElvain<sup>12</sup> stated

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<sup>12</sup>McElvain, op. cit., p. 136.

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that this reaction could be used to indicate the presence of any alcohol because all of this type compound will form solid benzoates except the lower aliphatic alcohols.

Sodium metal.--Two milliliters of the oil was treated with several small pieces of clean sodium metal. As there was no immediate reaction, the mixture was allowed to stand for a week. At the end of this time no change had taken place except that the oil was light brown in color. No sodium derivative was separated, and it was assumed that there were no

alcohols present.

### Hydrocarbons

Permanganate oxidation.—To oxidize the oil a fifteen milliliters saponified sample was refluxed with approximately 100 ml. of 2.5% potassium permanganate and 5 grams of sodium hydroxide until the purple color was completely removed. The reaction mixture was neutralized with dilute sulphuric acid using methyl orange paper as an indicator. Then solid sodium bisulphite was added to destroy the manganese dioxide formed by the reaction. Upon washing the mix with ether to recover the oil, the ethereal solution was dried over anhydrous magnesium sulphate; and the ether was distilled off on a steam-bath. The boiling point of the oil recovered was 253.5° Centigrade which was the same as the oil before oxidation. The oil obtained from the above reaction was tested with benzoyl chloride to form a solid derivative with any alcohols present. When one milliliter of the oil was refluxed with 2.5 ml. of benzoyl chloride, and 5 ml. of pyridine for one-half hour, all alcohols except those of the lower aliphatic series should form solids and precipitate after the solution is added to 20 ml. of 5% sodium bicarbonate and cooled. As there were no crystals on the filter after the mixture was suction-filtered, it was assumed that no alcohols or glycols were formed by the oxidation.<sup>13</sup>

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<sup>13</sup>McElvain, op. cit., p. 136.

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After adding 5 drops of the recovered oil to 5 ml. of a prepared

reagent containing 2,4-dinitrophenylhydrazine, the mixture was boiled gently. Adding 2 drops of concentrated hydrochloric acid caused no color change. When this solution was boiled for two minutes, water was added dropwise until a cloudy mass was formed; and this suspension was set aside for several hours. Upon filtering the solution no solid was obtained. From these results it may be assumed that no carbonyl group was present in the oxidized oil.

There was no color change when an alcoholic solution of the oil was treated with alcoholic ferric chloride which indicated that no phenolic compound was formed by the reaction.

About three milliliters of the oil was washed twice with five milliliters of 20% sodium bicarbonate. The solution was shaken with 2 ml. of ether to remove any suspended oil. When the bicarbonate was neutralized with dilute hydrochloric acid, no solid acid precipitated; nor was there any oil separated. This might prove that no acids were synthesized.

To estimate the acid content the free acid value was determined by refluxing a sample of the oil with alcoholic potash. This was computed to be 4.4. When this value was compared to that of the oil from saponification, it was found to be approximately 30 times more acid than before. This was evidence of oxidation, and it may be assumed that an acid was formed. However there was not enough acid in the oil to be separated as an identifiable derivative.

Tests for unsaturation.--Two-tenths milliliter of the oil was dissolved in 2 ml. of chloroform. After the solution was allowed to stand for a few seconds, a 5% solution of bromine in carbon tetrachloride was

added dropwise. The oil used approximately fifteen times its volume of the bromine solution which might indicate the presence of unsaturated compounds in the oil.

If a 0.2 ml. sample of the oil in acetone was treated with a 2% solution of potassium permanganate in water, only one-tenth milliliter of the reagent was decolorized by the oil. This test, the Baeyer test, was more accurate than the bromine addition; and it indicated that the unsaturates constituted only a small portion of the oil.<sup>14</sup>

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<sup>14</sup>McElvain, op. cit., pp. 130-131.

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Tests for triple bonds.--To a hot solution of 3.5 grams of hydrated cupric sulphate and 1 gram of sodium chloride in 12 ml. of water, a solution of 1 gram of sodium bisulphite in 10 ml. of 5% sodium hydroxide was added with thorough shaking. The mixture was cooled, and the precipitated cuprous chloride was washed by decantation and dissolved in approximately 10 ml. of a mixture of concentrated ammonium hydroxide and water. One milliliter of the oil was mixed with 10 ml. of the cuprous chloride reagent. After reaction and filtration, there was no solid acetylide-like product obtained. A subsequent treatment with ammoniacal silver nitrate also proved negative. As these reactions were supposed to form solid addition products between the silver or the cuprous ions and any triple bonded carbon atoms present in an organic compound, it was assumed that none of the components of the oil contained triple bonds.<sup>15</sup>

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<sup>15</sup>Roger Adams and John R. Johnson, Elementary Laboratory Experiments in Organic Chemistry, pp. 123-125.

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Reaction with amyl nitrite.--To 14 grams of the oil 20 ml. of amyl nitrite and 34 ml. of glacial acetic acid were added. The solution was well cooled, and half its volume of a mixture of equal volumes of glacial acetic acid and fuming hydrochloric acid was added in small portions with constant stirring allowing the blue coloration to disappear before adding more acid.<sup>16</sup> The blue color was obtained as described above. After

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<sup>16</sup>Allen's Commercial Organic Analysis, Vol. IV, p. 429.

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complete addition of the reagent the reaction mixture became green and finally dark brown. When this mix was washed with a concentrated solution of sodium bicarbonate and separated with ether, the ethereal extract was dried over anhydrous magnesium sulphate and distilled on a steam-bath. The residue was a black, plastic mass which was not recrystallized from common organic solvents.

Friedel-Crafts reaction.--When 50 ml. of oil, 35 ml. of benzoyl chloride, 35 grams of anhydrous aluminum chloride, and 100 ml. of carbon disulphide were refluxed on a water-bath for an hour, a dark mass resulted. The carbon disulphide was removed, and the reaction mixture was steam distilled to separate any volatile substances remaining. The residue was taken up in ether, and this solution was dried over anhydrous calcium

chloride. When the ether was distilled off, a chocolate brown, plastic product was obtained which could not be recrystallized from common organic solvents. No further investigation was made.<sup>17</sup>

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<sup>17</sup>Ludwig Gattermann, Laboratory Methods of Organic Chemistry, p. 334.

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The 257.7° Centigrade fraction of New Braunfels cedar wood oil was found to contain no carbonyl, phenolic, or alcoholic components. It was assumed that this oil was chiefly composed of hydrocarbons and that the very small percentages of acids and esters contained in the cut would have to be separated by extensive fractional distillation at reduced pressure.

## CHAPTER V

### CONCLUSION

From the investigation of the cedar leaf oil it was evident that the oils obtained from Juniperus mexicana and Juniperus virginiana were different. This difference was more pronounced in the camphor content than in any other respect. As camphor can be obtained from Juniperus mexicana only, it was this camphor that was shown to be the same as that procured from the Far East. Pinene was also isolated from the cedar leaf oil, and several derivatives were synthesized from it.

The presence of pseudocedrol, cedrenol, and cedrol was established; and various derivatives were produced from these three homologous alcohols. Though these were the only concrete results obtained in the study of the cedar wood oil, many exploratory reactions and classifications have been made. It is hoped that these may aid the future investigators in their work.

In regard to the 257.7° Centigrade fraction of New Braunfels cedar wood oil, this writer has set forth a system of classification reactions and individual tests which he hopes may suggest a possible approach to the problem in any subsequent systematic analysis of a fraction of the oil. Also he has shown that the oil contains hydrocarbons as the principal components and small amounts of esters and acids. No carbonyl groups, phenols, or alcohols have been found in the fraction.

It is hoped that this paper as a whole may give the reader an idea of the research conducted on the cedar oils and may present many ideas for further study.

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