

METHODS OF SEPARATION OF THE CONSTITUENTS IN THE
257⁰ CENTIGRADE FRACTION OF CEDAR WOOD OIL

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THESIS

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By

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CHAPTER I

INTRODUCTION

A. The Problem Stated

The principal purpose of this investigation is to find methods of separating the various constituents of the 257° centigrade fraction of New Braunfels cedar wood oil.

B. Why the Problem Was Chosen

Exhaustive fractionation of the crude oil has not proved to be successful as a means of separating the components, for experimentation with fractions obtained in this manner indicates that they are mixtures of two or more compounds. Consequently, research students have encountered difficulty after chemical reactions in resolving the complex mixtures and isolating any product in a pure state.

In view of this fact this problem was undertaken to attempt to find a more satisfactory method

by which the various constituents could be separated.

C. History and Related Work

When first settled, the San Marcos region contained a relatively small amount of cedar which was used largely as posts and in foundation material. This vegetation, being of a very prolific nature, however, soon spread over grazing land, decreasing the value of the property.

Nothing was done to clear grazing land of excess cedar, however, until the Federal Government subsidized its removal. Under this program, much land was cleared and all cedar not used for posts was burned. Chemists regarded this as a waste of natural resources and surmised that products of commercial value could be obtained from this vegetation.

In 1937, Mr. Howard Black, under the direction of Dr. Carroll L. Key, began investigation in the chemistry laboratories of Southwest Texas State Teachers College to determine if any valuable products could be obtained from cedar. Mr. Black and, later, other research students have found the original surmise to be correct and a number of

individuals and corporations are now engaged in the production of cedar oil for which there is a steady demand.

D. Source of the Sample

The sample of oil used in this problem was obtained from the combined remnants of crude and unused fractions from previous investigations. This crude mixture was subjected to exhaustive fractionation by the method described by Lemmons¹

¹Charles A. Lemmons, A Partial Separation of Constituents of Heart Wood Cedar Oil, Unpublished Master's Thesis, (1938), pp. 6-8.

with the boiling points being used as a basis for recombination. After the fourth distillation, samples were obtained which were considered to be pure enough for experimentation. The 257° centigrade fraction was chosen and used in this research.

E. Limitations

This investigation is confined to different methods of separating the constituents in the 257° centigrade fraction of New Braunfels cedar wood oil.

CHAPTER II

PROCEDURE AND EXPERIMENTATION

A. Ethyl Alcohol as a Solvent

It was found by experimentation that ninety-five percent ethyl alcohol would dissolve the oil at a ratio of one to twenty at room temperature. The ratio increased to one to three when the temperature was raised. If enough alcohol were used, the fraction completely dissolved. Alcohol of this concentration is, therefore, unsatisfactory as a selective solvent for extraction.

By investigating the solvent action of alcohol in different concentrations, it was found that eighty percent ethyl alcohol dissolves sixty percent of the oil when heated under a pressure of approximately 1.3 atm. A ten ml. sample of the fraction was subjected to continuous extraction under these conditions until no more oil would dissolve.

The extracted product upon removal of the solvent and when dried over anhydrous magnesium sulfate, had the following constants: boiling

point 257° centigrade, refractive index 1.5051.

That part of the sample which failed to dissolve, after being dried in the same manner, had these constants, boiling point 256° centigrade, refractive index 1.5041. The characteristics of both the soluble and insoluble samples varied from those of the original oil.

According to McElvain¹, 2,4- dinitrophenyl-

¹ Samuel N. McElvain, The Characterization of Organic Compounds, pp. 90-91.

hydrazine serves as an excellent reagent with which to test for the presence of aldehydes and ketones. In an effort to ascertain what classes of compounds are soluble in eighty percent alcohol, this reagent was added in three ml. portions to each of three test tubes. Two drops of the original oil was added to the first test tube, two drops of soluble oil to the second, and two drops of the insoluble oil to the third. When the test tubes were later examined, it was observed that crystals had formed in those containing the original oil and the soluble oil, thus giving a positive test for the presence

of aldehydes or ketones in these samples.

Using the method suggested by McElvain²,

²Ibid., p. 133.

another attempt was made to classify the soluble oil. Two ml. of Fehling's solution was added to each of three test tubes containing the original, soluble, and insoluble oils respectively. After being heated at steam-bath temperature for three minutes and allowed to stand, it was observed that the original oil and soluble oil had caused the precipitation of cuprous oxide but no reaction was noticeable between the insoluble oil and the test reagent. This indicated that the aldehydes present in the original sample were soluble in eighty per-cent ethyl alcohol at the conditions given.

A comparison as to the degree of unsaturation was made on the three samples of oil by using two percent aqueous potassium permanganate as a test reagent. The permanganate was added drop-wise to the acetone solution of each respective sample. The results of this procedure, judging only from

the speed of the reactions, showed that the major part of the unsaturated compounds was soluble in alcohol.

A five percent solution of bromine in carbon tetrachloride was added to the three samples of oil in an attempt to verify the above results. No difference could be determined in the speeds at which bromine was decolorized by the three samples; however, the soluble sample decolorized more bromine than the other two.

The 257° centigrade fraction was subjected to continuous extraction with eighty percent ethyl alcohol. The pressure in this case was maintained at one atmosphere and the temperature at the boiling point of the solvent. The soluble and insoluble samples obtained in this manner were treated with Fehling's solution. A red precipitate formed in each, proving that all aldehydes were not removed as they had been when the extraction was performed under excess pressure.

B. Sulfuric Acid as a Solvent

According to McElvain³ cold concentrated

³Ibid., pp. 74-76.

sulfuric acid will not dissolve the acyclic, cyclic paraffins, and aromatic hydrocarbons. Since this appears to be a possible means of resolution, concentrated sulfuric acid was added to ten ml. of oil which was at ice-bath temperature. The mixture was thoroughly shaken and allowed to stand until the insoluble portion of the sample had collected as the top layer, then the two layers were separated. The oil in the top layer after being washed with water to remove excess acid and dried with anhydrous magnesium sulfate, had the following constants: boiling point 259° centigrade, refractive index 1.5038.

Tollen's ammoniacal silver oxide reagent was prepared in the following manner which was described by Kamm.⁴ Ammonium hydroxide was added to a ten

⁴Oliver Kamm, Qualitative Organic Analysis, Second Edition, p. 52.

percent solution of silver nitrate until a precipitate formed and redissolved. After the addition of a few drops of sodium hydroxide to increase the sensitivity, this reagent was added to two drops of

the oil obtained as described above and heated to thirty-five degrees centigrade. The reaction mixture was allowed to stand for two hours, but no noticeable change occurred, which indicated that there were no aldehydes present.

Two drops of the oil which was insoluble in sulfuric acid was added to two ml. of 2,4-dinitrophenylhydrazine reagent. This mixture was shaken and then allowed to stand at room temperature over night. No reaction was observed, confirming the fact that the aldehydes and ketones were removed from the fraction by the concentrated sulfuric acid.

Another two-drop portion of the sample was dissolved in two ml. of acetone with two percent aqueous potassium permanganate being subsequently added dropwise. The permanganate color caused by the first two drops persisted, indicating that there were no unsaturated hydrocarbons present.

A five percent solution of bromine in carbon tetrachloride was added to a solution of the oil which had been dissolved in the same solvent. No bromine was decolorized, verifying the fact that the unsaturated hydrocarbons had been removed by the sulfuric acid treatment.

Attempts were made to reclaim the soluble portion of the fraction from the sulfuric acid solution. The acid was neutralized with sodium hydroxide and allowed to stand until the oil layer separated. This layer, when removed by the use of a separatory funnel, was black and very viscous so the boiling point and refractive index could not be taken.

Water was added to another sample of the sulfuric acid solution. Upon standing, an oil layer separated which was then removed. The product obtained by this method exhibited characteristics that were identical to those of the substance mentioned in the preceding paragraph.

C. Acetone as a Solvent

Acetone at room temperature will dissolve cedar oil in the ratio of one to three. If heat is applied to the solution, the ratio is one to one and one-half. By experimenting with the solvent action of different concentrations of acetone and water it was found that eighty percent acetone produced best results as a selective solvent.

Eighty percent acetone was added to ten ml. of

oil from the 257° centigrade fraction and heated until it boiled under a slight pressure. The solution was cooled until the pressure was reduced, then the acetone layer was separated. This process was repeated until all soluble oil had dissolved.

The acetone solution was placed on a steam bath and solvent removed. The oil remaining, after being dried with anhydrous magnesium sulfate, had these constants: boiling point 257° centigrade, refractive index 1.5059. When the oil that was insoluble in acetone was dried in the same manner, it was found to have the following constants: boiling point 257° centigrade, refractive index 1.5049.

The two samples obtained above were then tested for aldehydes and ketones using 2,4-dinitrophenylhydrazine reagent. It was observed that the oil that was soluble in acetone gave a positive test with this reagent while that which was insoluble failed to react, indicating that the aldehydes and ketones were dissolved in this solvent.

Two drops of each oil was added to equal volumes of Fehling's solution, heated at steam-bath temperature for three minutes, and allowed to stand overnight. It was observed that only the soluble

oil caused the precipitation of cuprous oxide which was a good indication that the aldehydes were soluble in hot acetone.

Two drops of each sample was dissolved in two ml. of acetone with two percent aqueous potassium permanganate being added drop by drop to each solution. The permanganate color persisted approximately twice as long in the insoluble sample as in the soluble, and it took only one-half as much permanganate to give a permanent color in the first sample.

Two ml. of carbon tetrachloride was added to each of the two respective samples of soluble and insoluble oil. A five percent solution of bromine in carbon tetrachloride was added to both solutions until the bromine color persisted for about one minute. Twice as much bromine was decolorized by the soluble as the insoluble oil. These results indicate that the unsaturated hydrocarbons are soluble in acetone.

D. Phosphoric Acid as a Solvent

According to Shriner and Fuson⁵, alcohols,

⁵R. L. Shriner and R. C. Fuson, The Systematic Identification of Organic Compounds, Second Edition, p. 23.

aldehydes, methyl ketones, cyclic ketones and esters dissolve in eighty-five percent phosphoric acid provided that these compounds contain less than nine carbon atoms. When eighty-five percent phosphoric acid was added to a portion of the 257° centigrade fraction and shaken vigorously, it was noted that the acid turned a reddish color. Insoluble oil formed a top layer which was removed and washed with more acid until no more would dissolve, at which time the color disappeared. By measuring the volume of the remaining oil, it was found that four and one-half percent had dissolved in the acid. This sample, after being washed with water to remove excess acid and dried over anhydrous magnesium sulfate, had the following constants: boiling point 256° centigrade, refractive index 1.5062.

Tollen's ammoniacal silver oxide reagent was added to the oil mentioned above. The mixture, upon being agitated and heated to 35° centigrade, failed to react, indicating the absence of aldehydes. This was confirmed when Fehling's solution also gave a negative test.

The 2,4-dinitrophenylhydrazine test was made in an effort to determine if the ketones were also soluble in phosphoric acid. The insoluble oil failed

to react with this reagent; therefore, it was concluded that any ketones present in the original fraction had dissolved.

Eight normal sodium hydroxide was added to neutralize the phosphoric acid extract while at the temperature of an ice-bath. After the solution had stood overnight the oil layer was removed and dried with anhydrous magnesium sulfate. This sample, boiling point 257° centigrade, refractive index 1.5075, failed to give positive tests for aldehydes with either Fehling's solution or 2,4-dinitrophenylhydrazine reagent.

Since the presence of aldehydes in the 257° centigrade fraction has been established, the negative tests for these compounds in both the soluble and insoluble samples indicate that they had reacted with phosphoric acid forming compounds of a different type.

CHAPTER III

CONCLUSIONS

Eighty percent ethyl alcohol and eighty percent acetone, according to the tests that were presented, give almost the same results when used as a selective solvent for cedar oil. When heated with the oil, both dissolve the aldehydes and most of the unsaturated hydrocarbons.

The use of sulfuric acid, as a selective solvent, has one main disadvantage. The acid reacts with the oil that it dissolves, producing a black substance. This solvent has possibilities, however, as a means of separating acyclic, cyclic paraffins, and aromatic hydrocarbons from the original fraction.

With a few exceptions, phosphoric acid will dissolve alcohols, aldehydes, methyl ketones, cyclic ketones and esters. Since phosphoric acid dissolved four and one-half percent of this fraction of cedar oil, it was concluded that one or more of these compounds was present and this solvent offers a method for their separation. Phosphoric acid, as a solvent, is particularly interesting because it dissolves

these compounds without the production of an appreciable amount of heat and color which are frequently encountered when using cold, concentrated sulfuric acid.

Some physical properties of the different oils are shown below.

<u>Sample of Oil</u>	<u>Boiling point</u>	<u>Refractive index</u>
original	257°C.....	1.5043
soluble in alcohol.....	257°C.....	1.5051
insoluble in alcohol.....	256°C.....	1.5041
soluble in acetone.....	257°C.....	1.5059
insoluble in acetone.....	257°C.....	1.5049
insoluble in sulfuric acid....	259°C.....	1.5038
soluble in phosphoric acid....	257°C.....	1.5075
insoluble in phosphoric acid..	256°C.....	1.5062

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