



Preliminary investigation of caronic acid esters  
by Tom Ting Charng

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE in Chemical Engineering  
Montana State University  
© Copyright by Tom Ting Charng (1969)

Abstract:

The present potential supply of delta-3-carene, a bicyclic terpene, in the by-product turpentine produced by five western Kraft pulp mills, is more than 1,000 gallons per day.

Two esters of cyclopropane ring-containing dibasic acids (caronic and homocaronic acids) were recovered from the mixture of oxidation products obtained by the potassium permanganate oxidation of delta-3-carene in acetone. The yield of di-butyl caronate and di-butyl homocaronate, based on 41.4 grams of delta-3-carene, was 27.3% and 18.2%, respectively.

The identification of di-butyl caronate and homocaronate was based on gas chromatography and infrared spectroscopy.

Delta-3-carene, 41.4 grams, was oxidized with 260 grams potassium permanganate in 2,000 ml. of acetone at a temperature of 12.5 - 14.5 °C.

The potassium permanganate reacted completely in five hours. Ninety-seven percent of the oxidation products were adsorbed on the surface of the manganese dioxide formed during the reaction. The oxidation products were removed from the manganese dioxide surface with 85% efficiency by washing with hot water.

The aqueous solution of oxidation products was acidified with hydrochloric acid and extracted with ethyl ether. The water phase was extracted again after concentration. The step was repeated three times. Most of the inorganic salts were removed after each concentration.

The water layer, about 80 ml, was mixed with the ether extract.

250 ml. of 1-butanol and 200 ml. of toluene were added. The mixture was subject to total reflux for five hours, after which the crude ester was mixed with 30% ammonium hydroxide and followed with hot water. The water was removed by azeotropic distillation with toluene, an entrainer. The vacuum distillation technique was also applied to prevent the unreacted acid from decomposing at the high temperature.

PRELIMINARY INVESTIGATION OF CARONIC ACID ESTERS

by

TOM TING CHARNG

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemical Engineering

Approved:

*Lloyd Beng*

Head, Major Department

*Lloyd Beng*

Chairman, Examining Committee

*K Goering*

Graduate Dean

MONTANA STATE UNIVERSITY  
Bozeman, Montana

March, 1969

## ACKNOWLEDGMENT

The author wishes to thank the entire staff of the Chemical Engineering Department of Montana State University for their suggestions which led to the completion of this research project. Particular thanks is given to Dr. Lloyd Berg who was the author's research director and major professor. The author thanks Mr. James Tillery and Mr. Silas Huso for their help in equipment fabrication and maintenance. Thanks are also due to Mrs. Joan Hall for typing the final manuscript.

## TABLE OF CONTENTS

	Page
ABSTRACT . . . . .	vii
I. INTRODUCTION . . . . .	1
A. Delta-3-Carene . . . . .	1
B. Oxidation of Delta-3-Carene . . . . .	2
C. Esterification of Oxidation Products of Delta-3-Carene . . . . .	2
D. Potential Utilization of Esters of Cyclopropane Ring- Containing Dicarboxylic Acids from Delta-3-Carene . . . . .	2
E. Incentive for Esterification of Caronic Acids Research . . . . .	3
II. RESEARCH OBJECTIVES . . . . .	4
III. EXPERIMENTAL DATA . . . . .	5
A. Preparing the Caronic Acids for Esterification . . . . .	5
1. Equipment . . . . .	6
2. The Ratio of Raw Materials . . . . .	6
3. Method . . . . .	6
B. Esterification . . . . .	7
1. Equipment . . . . .	8
2. Method . . . . .	9
3. Neutralization . . . . .	9
4. Purification . . . . .	10
C. Gas Chromatography . . . . .	10
1. Analysis of Esterification Products . . . . .	10
2. Analysis Techniques . . . . .	11

TABLE OF CONTENTS (continued)		page
D.	pH Measurement . . . . .	12
E.	Spectroscopy . . . . .	13
F.	Manual Integration Techniques for Calculation of Yield Through Chromatographic Peaks. . . . .	13
IV.	DISCUSSION OF RESULTS . . . . .	15
A.	Identification of Products . . . . .	15
	Di-Butyl Caronate . . . . .	15
	Di-Butyl Homocaronate . . . . .	15
B.	Calculation of Conversion Percentage . . . . .	16
V.	CONCLUSIONS . . . . .	17
VI.	RECOMMENDATIONS . . . . .	18
	APPENDIX . . . . .	19
	LITERATURE CITED . . . . .	34

## LIST OF FIGURES

	Page
Figure 1. The Structure of Delta-3-Carene . . . . .	20
Figure 2. Cyclopropane Ring-Containing Dicarboxylic Acids Derived From Delta-3-Carene . . . . .	21
Figure 3. Esters Derived From Cyclopropane Ring-Containing Dicarboxylic Acids . . . . .	22
Figure 4. Apparatus for Potassium Permanganate Oxidation of Delta-3-Carene in Acetone . . . . .	23
Figure 5. Conversion % vs. the Amount of Oxidizing Agent . . . . .	24
Figure 6. Vacuum Distillation System . . . . .	25
Figure 7. True-Boiling-Point Curve of 1-Butanol-Caronic Acids- Toluene System . . . . .	26
Figure 8. Sample Collection in Preparative Gas Chromatography . . . . .	27
Figure 9. Gas Chromatogram of the Esterification Product . . . . .	28
Figure 10. Gas Chromatogram of Di-Butyl Caronate . . . . .	29
Figure 11. Infrared Spectrum of the Di-Butyl Caronate from the Mixture of Esterification Product . . . . .	30
Figure 12. Infrared Spectrum of Di-Butyl Caronate . . . . .	31
Figure 13. Infrared Spectrum of Di-Butyl Homocaronate . . . . .	32
Figure 14. Cox Chart for Various Azeotropes . . . . .	33

## ABSTRACT

The present potential supply of delta-3-carene, a bicyclic terpene, in the by-product turpentine produced by five western Kraft pulp mills, is more than 1,000 gallons per day.

Two esters of cyclopropane ring-containing dibasic acids (caronic and homocaronic acids) were recovered from the mixture of oxidation products obtained by the potassium permanganate oxidation of delta-3-carene in acetone. The yield of di-butyl caronate and di-butyl homocarionate, based on 41.4 grams of delta-3-carene, was 27.3% and 18.2%, respectively.

The identification of di-butyl caronate and homocarionate was based on gas chromatography and infrared spectroscopy.

Delta-3-carene, 41.4 grams, was oxidized with 260 grams potassium permanganate in 2,000 ml. of acetone at a temperature of 12.5 - 14.5 °C. The potassium permanganate reacted completely in five hours. Ninety-seven percent of the oxidation products were adsorbed on the surface of the manganese dioxide formed during the reaction. The oxidation products were removed from the manganese dioxide surface with 85% efficiency by washing with hot water.

The aqueous solution of oxidation products was acidified with hydrochloric acid and extracted with ethyl ether. The water phase was extracted again after concentration. The step was repeated three times. Most of the inorganic salts were removed after each concentration.

The water layer, about 80 ml, was mixed with the ether extract. 250 ml. of 1-butanol and 200 ml. of toluene were added. The mixture was subject to total reflux for five hours, after which the crude ester was mixed with 30% ammonium hydroxide and followed with hot water. The water was removed by azeotropic distillation with toluene, an entrainer. The vacuum distillation technique was also applied to prevent the unreacted acid from decomposing at the high temperature.

## I. INTRODUCTION

### A. Delta-3-Carene

The principal starting material in this research was delta-3-carene which was produced in the laboratory at the Department of Chemical Engineering, Montana State University. The structure is given in Figure 1<sup>1</sup>.

Delta-3-carene is in the by-product turpentine produced by five western Kraft pulp mills<sup>2</sup> in the United States and Canada. Only three of them are presently condensing their turpentine<sup>2</sup>. The sources of delta-3-carene are summarized in Table 1.

TABLE I. Availability of Delta-3-Carene in the United States and Canada.

A. Mills producing and condensing delta-3-carene containing turpentine:

Potlatch Forests, Incorporated, Lewiston, Idaho.

Hoerner-Waldorf Paper Products Company, Missoula, Montana.

Southwest Forest Industries, Snowflake, Arizona.

B. Mills producing but not condensing delta-3-carene containing turpentine:

Boise-Cascade Corporation, Wallula, Washington.

Northwestern Pulp and Power, Limited, Hinton, Alberta.

As indicated in Table I, three mills are presently producing and condensing turpentine containing delta-3-carene. The total turpentine volume from these mills is more than 1,000 gallons per day<sup>3</sup>. There is no known commercial use for delta-3-carene up to now that would make its recovery and purification economically attractive.

B. Oxidation of Delta-3-Carene

The oxidation of delta-3-carene and subsequent formation and purification of dicarboxylic acids containing the cyclopropane ring has been reported previously in the literature.<sup>4 5 6 7</sup> The names and structures of these acids are shown in Figure 2. All of the reports, except the last, appeared prior to 1930. None of these reports gave indication of commercial development of the acids.

C. Esterification of Oxidation Products of Delta-3-Carene

No references have been made in the literature to either a source of any of these esters or to an experimental work for analytical purpose.

There are five possible combinations of esters of caronic acid and homocaronic acid which are shown in Figure 3. We were not able to locate a sample of instrumental analysis of these esters from any outside source.

D. Potential Utilization of Esters of Cyclopropane Ring-Containing Dicarboxylic Acids from Delta-3-Carene

Since a convenient source of any of these esters has never been available for new product research, it is not surprising that industrial uses have not been reported.

The esters of caronic acids should be, like the esters of most dicarboxylic acids such as adipic acid, effective plasticizers for many polymeric materials, including polyvinyl chloride and its copolymers, natural and synthetic rubbers, polystyrene, and cellulose derivatives.

These plasticizers are easily incorporated into the polymer by the usual methods.<sup>8 9 10</sup> They can also be converted to a higher ester by transesterification as demanded.

These esters can be readily reconverted into acids by simple hydrolysis in the presence of hydroxide ions, or converted into other derivatives. Dicarboxylic acids have been used in the field of synthetic polymers, lubricants, coatings, elastomers and thermosetting compounds.<sup>11</sup>

E. Incentive for Esterification of Caronic Acids Research

The previous work on the oxidation of delta-3-carene proved that it provided possibilities for a new industry located in Montana. We could produce cis-caronic acid in an excellent purity, 99% pure, nevertheless, the yield was not substantial for commercialization.

## II. RESEARCH OBJECTIVES

The overall goals of this research were to produce the esters of cyclopropane ring-containing dicarboxylic acids from delta-3-carene, and to report the yield. The research objectives were as follows:

1. Isolate and confirm the identity of the esters of caronic and homo-caronic acids.
2. Choose a suitable alcohol for a good yield of esterification.
3. Produce esters from delta-3-carene oxidation products.
4. Purify the esterification products.
5. Report yield.

### III. EXPERIMENTAL DATA

#### A. Preparing the Caronic Acids for Esterification

Caronic acids were prepared by potassium permanganate oxidation of delta-3-carene in acetone phase. This oxidation reaction was first reported in 1923 by Simonsen and Rao.<sup>12</sup> The following reaction system was used:

delta-3-carene . . . . .	40.0 grams
potassium permanganate . . . . .	96.0 grams
acetone . . . . .	400.0 ml.
temperature . . . . .	0.0 °C

After all the potassium permanganate had reacted, the  $MnO_2$  was removed by filtration and washed with hot water to remove the oxidation products. This was followed by ether extraction.

An approximate yield of 0.5% of trans-caronic acid was reported and cis-caronic acid was recovered in an unreported yield.

In 1967 Jarrett<sup>7</sup> used essentially the same method to recover cis- and trans-caronic acids. The following system was used:

delta-3-carene . . . . .	41.4 grams
potassium permanganate . . . . .	216.6 grams
acetone . . . . .	3,600 ml.
water bath temperature . . . . .	14.6 °C
temperature range of reaction mixture.	15-18 °C
reaction time . . . . .	18 hours

A yield of 6.5% of cis-caronic acid and 0.5% of trans-caronic

acid was reported.

1. Equipment

The equipment used here for the oxidation reaction was, as given in Figure 4, a 4,000 ml. Erlenmeyer flask which was placed in a cold water bath and stirred with a one-quarter horsepower stirrer.

2. The Ratio of Raw Materials

In the same manner as in previous work, the potassium permanganate oxidation of delta-3-carene was used again. This was improved to give a yield of 9.0% of cis-caronic acid. The relationship between the conversion and the amount of oxidation agent was given in Figure 5. The following system was used:

delta-3-carene . . . . .	41.4 grams
potassium permanganate . . . . .	260.0 grams
acetone . . . . .	2,000 ml.
water bath temperature . . . . .	12,5 °C
reaction time . . . . .	5 hours

The separation procedure was that of Jarrett<sup>7</sup> and 3.74 grams of cis-caronic acid pure white crystals were obtained.

3. Method

The caronic acid, for the purpose of esterification, was prepared by potassium permanganate oxidation of delta-3-carene with the ratio of starting materials as mentioned above. After the color of the acetone solution appeared water white, i.e., all the potassium permanganate had been consumed, stirring was stopped and separation of the oxidation

products absorbed on the manganese dioxide from the acetone was performed by filtration. The oxidation products were recovered from  $MnO_2$  by two methods. The first method was stirring one part of solid manganese dioxide with two parts of hot water and filtering. This process was repeated until the filtrate had a pH value of 7.5 which was 9.3-10.4 when started. The second method was to make a slurry of one part manganese dioxide with five parts of water and adding the theoretical amount of sodium bisulfite to convert the manganese dioxide to manganous sulfate.

The caronic acid in either of the aqueous solutions was in the form of potassium salt. Reducing the pH value of the aqueous solution to less than 1.0 to form caronic acid is a necessary step. The volume of the solution was then reduced from 4,000 ml. to 250 ml. by evaporating before being acidified.

The mixture was extracted manually with 100 ml. of ethyl ether four times. The water layer after extraction was concentrated to saturation and extracted with ether again. This process was repeated once more. The purpose of this treatment is to remove most of the inorganic by-products formed during the oxidation reaction and the acidification. The ether was recovered by distillation.

#### B. Esterification

No work had been done on the esterification of caronic acids; a few articles reported the esterification of adipic acid.<sup>13 14 15</sup>

Two essential methods of the esterification of adipic acid had been employed to ultimately produce the desired plasticizers.

In one of these methods, known as the high temperature process, acid or acid anhydride was mixed with a substantial excess of alcohol and heated to speed up the reaction and to remove the water of esterification. A second method of esterification involved the use of small excess of alcohol but produced the esterification in the presence of a catalyst. Typical catalysts which may be employed are: hydrochloric acid, sulfuric acid, aromatic sulfonic acid such as benzene sulfonic acid, toluene sulfonic acid, naphthalene sulfonic acid, etc.

Other workers have reported that inorganic salts such as bisulfate salts, and sodium hydroxide in the presence of aluminum oxide pellets (5 mm. diameter), were satisfactory catalysts.

All these methods turned out adipates in a good quality and quantity.

1. Equipment

The equipment used in this investigation consisted of a vacuum distillation system, given in Figure 6, proportional condensing surfaces condenser, and glass laboratory column.

Two different kinds of columns were used in this experiment. One was a one inch by eighteen inch Vigreux column and the other was a one inch by fifty-two inches glass column with outside heating coils and a section forty-two inches long packed with 3/16 inch inside diameter single-turn rings of number 26 B&S gage stainless steel wire.

## 2. Method

Several different straight-chain alcohols (ethanol, 1-butanol, 1-hexanol), were used in the esterification of caronic acids with hydrochloric acid, sulfuric acid, and p-toluene sulfonic acid as catalyst.

As described in Section III-A, 250 ml. of alcohol and 200 ml. of toluene were added to the mixture. The mixtures were then put in a 1,000 ml. flask placed under a one inch by eighteen Vigreux column to take off the water. As soon as the temperature of the distillate rose to 98 °C, the stopcock was closed and the column remained at total reflux for five hours. The water formed had to be withdrawn continuously by azeotropic distillation with toluene during the esterification.

After five hours of total reflux, about 60 ml. of unreacted alcohol were taken off by an entrainer. The reflux ratio in the distillation was twenty to one and was changed to thirty to one as the boiling points changed.

The entrainer, toluene, was recycled in the distillation. The typical true-boiling-point curve was shown in Figure 7.

## 3. Neutralization

The esterification was stopped as the overhead temperature reached 104°C (boiling point of toluene at 630 mm.Hg.), and all the toluene added came out. The stillpot was then taken off the column and the bottoms mixture was neutralized with a few drops of 30% ammonium hydroxide.

Neutralization should have particular attention because either the acidity or causticity of the oil would cause reverse reaction or hydrolysis of the esters. Esters of these reactions would substantially decrease the yield.

#### 4. Purification

The neutralized crude ester mixtures were washed with 100 ml. of hot water four times to take off inorganics and some other impurities.

The oil was subjected to vacuum distillation under a pressure of 20 mm.Hg. A glass column with dimensions of one inch by forty-two inches, stainless steel ring packed, was employed. Water was used as entrainer to take off some low-boiling constituents. The final product, in the bottom, had a brown color.

#### C. Gas Chromatography

Gas chromatography techniques were used both in analyzing the various mixtures of esterification products and in preparing pure samples for spectroscopy.

##### 1. Analysis of Esterification Products

The esters were analyzed with a Wilkens Aerograph "Moduline" Model 202 dual column gas chromatograph having a dual thermal conductivity detector. The chromatograph was used with a Sargent Model SR recorder. A 10-microliter syringe was used for injecting samples. The sample size was from two to eight microliters. The chromatograph column was prepared here at Montana State University with the following

specifications:

stationary phase . . . . . 5% carbowax 20M.  
support . . . . . chromosorb T.  
column . . . . . 20' x 1/4" copper.

operating conditions:

column temperature . . . . . 200°C  
H<sub>2</sub> carrier gas rate . . . . . 60 c.c./min.

2. Analysis Techniques

a. Comparison of Retention Times

The principle of gas chromatography analysis is that a given compound has a constant retention time unless the chromatograph condition changed. Therefore, if an unknown sample has a retention time identical with that of a known sample, it can be said that there is a certain compound in the unknown sample that possibly has the same identity as that of the known compound with the same retention time. However, there is also the other possibility that none of the other compounds in the unknown has the identity of the known compound with that retention time.

b. Peak Enhancement

For further comparison, an unknown compound may be mixed with a known compound. Such a mixture will produce one of two reactions; (1) one peak which will be larger in size or (2) an extra peak. The initial case is the so-called "peak enhancement" which almost always proves the identity of the compound of primary concern.

c. Preparative Gas Chromatography

Preparative chromatography is one of the best ways to collect small amounts of pure compounds for analysis by infrared or nuclear magnetic resonance spectroscopy. Each composition is separated in the chromatograph column and individual compounds are collected at the chromatograph exit.

d. Equipment

The Wilkins Model 202 gas chromatograph with thermal conductivity detector, 5% carbowax 20 M chromatograph column, and a 100-microliter syringe were used.

e. Sample Collection

The sample size injected was 30-60 microliters. The pure compounds were collected at the chromatograph exit in pieces of 4 mm. glass tubing (Figure 8). The loop of the tubing was immersed in a dry ice-acetone bath. Vapor was observed coming out of the glass tube. This atomizing effect was partially minimized by bubbling the vapor into the ether.

D. pH Measurement

A Beckman Model H2 pH meter with a Sargent S-30072-15 combination electrode was used for pH measurements. The meter was standardized with a buffer solution having a pH value close to that of the unknown solution. Commonly used buffer solutions had pH's of 9.0, 7.0, and 3.0. The reproducibility of pH measurements was found to be about  $\pm 0.1$  pH units.

E. Spectroscopy

The infrared spectra were run on a Beckman IR5A spectrophotometer in the Chemistry Department of Montana State University. No solvent was used in this investigation. Typical operating conditions for the Beckman IR5A unit were as follows:

sample . . . . .	Esters
path . . . . .	0.05 mm. (NaCl Plates)
reference . . . . .	Air
ordinate scale . . . . .	Double Beam
gain . . . . .	6.0

F. Manual Integration Techniques for Calculation of Yield Through Chromatographic Peaks

Conversion percentage of the esterification was determined by estimating through the peak area of the gas chromatogram.

The principal manual methods for quantitative evaluation of gas chromatographic peaks are: (1) determination of peak area from height and width measurements, (2) by triangulation, (3) by planimetry, (4) by cutting out the peak and weighing the paper, or (5) by measurements of only the peak height. All of these measurements and operations are carried out on peaks as recorded on the chromatogram. Triangulation has little to recommend it. Cutting and weighing is vulnerable because of variations in paper thickness. Planimetry is less precise than height-width integration for peaks of small area but is comparable or somewhat better in precision for large areas.<sup>16</sup>

Cutting and weighing method was used in this experiment.

Peaks including base lines were printed on heavy paper and cut with small scissors. The paper was weighed on a Mettler analytic balance with 0.1 mg. sensitivity.

#### IV. DISCUSSION OF RESULTS

##### A. Identification of Products

###### Di-Butyl Caronate

The production of di-butyl caronate from the oxidation of delta-3-carene in 27.3% yield was discussed in Section III-B.

The samples collected from the chromatograph exit were compared with di-butyl esters which were made with pure cis-caronic acid; the methods were illustrated in Sections III-C, and III-E. The eighth peak in Figure 9 is identical with the peak in Figure 10. Furthermore, they gave the same infrared spectra, (Figures 11, 12).

The ester was not determined to be whether di-butyl cis-caronate or di-butyl trans-caronate due to the fact that the heat treatment may cause the rotation of the bonds.

###### Di-Butyl Homocaronate

In Figure 9, the component producing the peak next to the peak of di-butyl caronate was in a yield of 18.2%. This compound is probably di-butyl homocaronate. This assumption is made on the previous work of the methyl ester of homocaronic acid by Jarrett<sup>7</sup> who noted that:

1. Some homocaronic acid was found in his potassium permanganate oxidation of delta-3-carene,
2. In the gas chromatograms, methyl homocaronate is next to methyl caronate, and,
3. Infrared spectra of methyl caronate and methyl homocaronate, of which we obtained similar spectra.

There is no available outside source for assuring this this assumption is correct. But, by comparing the infrared spectra (Figures 11 and 13), and the gas chromatogram (Figure 9), it has the most possibility that this compound is di-butyl homocarbonate.

B. Calculation of Conversion Percentage

The conversions of caronic acid esters were determined and calculated by the method illustrated in Section III-F. Errors in quantitative evaluation of peaks on a chart are additional to errors occurring earlier in the chromatographic process. Errors associated with peak measurements are primarily indeterminate errors. Indetermined as well as determined errors were introduced in the operations of sample injection and recording.

The 1.25% deviation in cutting and weighing method were caused by nonhomogeneous paper, pickup of moisture, grease from handling, and these errors were minimized by taking an average of several experimental determinations.

## V. CONCLUSIONS

The purpose of this research work was to optimize the oxidation reaction of delta-3-carene with potassium permanganate as an oxidizing agent. Results of this investigation are summarized below:

1. 27.3% of caronic acid and 18.2% of homocaronic acid, in the form of di-butyl esters, were recovered from the potassium permanganate oxidation of delta-3-carene in acetone; the yield reported in former work for cis-caronic acid and trans-caronic acid were 6.5% and 0.5%, respectively.

2. The esters have a color of light-brown. Previous colors were white or yellow. The color is introduced by heat-treatment for a relatively long reaction time.

3. The final product of esterification of the oxidation product is a mixture consisting of two essential compounds, i.e., di-butyl caronate and di-butyl homocaronate.

4. The reaction time and reaction temperature increased as the molecular weight of the alcohol used increased.

5. The higher the molecular weight of the ester, the more difficult the separation.

## VI. RECOMMENDATIONS

Di-butyl caronate and di-butyl homocaronate have been identified as components of the esterification product from the potassium permanganate oxidation of delta-3-carene in acetone. A process of producing 27.3% of di-butyl caronate and 18.2% of di-butyl homocaronate has been developed. The incompleteness of this process is that the esters remain in the form of a mixture. The reasons causing this drawback of the esterification of caronic acid are undetermined.

Recommendations for further work on the research of delta-3-carene are listed below:

1. Investigate the use of an oxidizing agent other than potassium permanganate leading the reaction toward the desired mechanism.
2. Convert caronic acid into chloride before carrying out the esterification.
3. Make higher esters of caronic acid by transesterification.
4. Develop a pilot scale process for the production of caronic acid esters.

APPENDIX

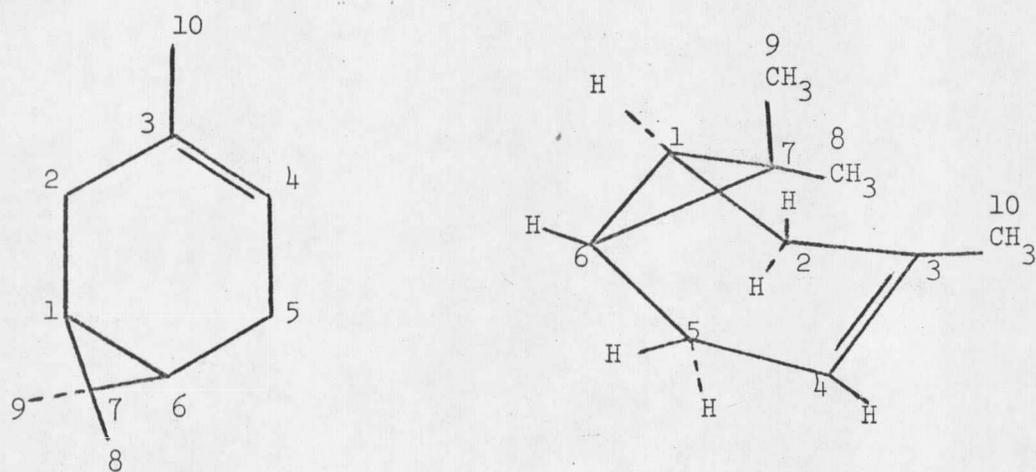


Figure 1. The Structure of Delta-3-Carene





























