The production of cis- and trans-caronic acids from delta-3-carene
by James Hugh Jarrett

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in CHEMICAL ENGINEERING
Montana State University


Abstract:
The sole known source of delta-3carene, a bicyclic terpene, in the United States and Canada is in the by-product turpentine produced by five western Kraft pulp mills. The present potential supply of delta-3-car-ene is 1000 gallons per day.

Two cyclopropane ring-containing dibasic acids (cis- and trans-caronic acids) were recovered in 99% purity from the mixture of oxidation products obtained by the potassium permanganate oxidation of delta-3-carene in acetone. The yield of cis-caronic acid was 6.5% and the yield of trans-caronic acid was 0.5%.

The identification of cis- and trans-caronic acids was based on commercial analysis for carbon, hydrogen and oxygen, and on infrared and nuclear magnetic resonance spectroscopy. The spectra are included in the thesis.

Delta-3-carene, 4l.4 g, was oxidized with 216.6 g potassium permanganate in 3,600 ml of acetone at a temperature of 16-18°C, The potassium permanganate reacted completely in 18 hours with a delta-3-carene conversion of 85% Ninety-seven percent of the oxidation products were adsorbed on the surface of the manganese dioxide formed during the reaction.

The unreacted delta-3-carene and 3% of the oxidation products remained in the acetone phase. The oxidation products were removed from the manganese dioxide surface with 85% efficiency by washing with hot water.

The relative solubilities of the oxidation products in water varied at different pH values. Thus, they were separated by ether extraction of a water solution with pH control. Cis-caronic acid was recovered by 1) extracting a pH = 3.0 water solution of oxidation products with ether to remove a relatively large amount of oxidation products containing a small amount of cis-caronic acid, 2) extracting the water solution again at a pH of less than one to remove a mixture of oxidation products having a high concentration of cis-caronic acid. Cis-caronic acid crystals precipitated from the pH < 1 extract and were purified by washing with chloroform.

The pH = 3.0 extract was redissolved in water, the pH adjusted to pH = 4.0 and the water solution extracted with ether. The water solution was then acidified (to pH < 1) and extracted again. More cis-caronic acid was recovered from the pH < 1 extract, Trans-caronic acid was concentrated in the pH = 4.0 extract which also contained a mixture of crystals. It was recovered by 1) preparing the ammonium salt of the filtered extract, 2) removing excess water, 3) adding ethanol which dissolved all of the ammonium salts but ammonium trans-caronate, 4) filtering, and 5) converting ammonium trans-caron- ate ¦ to trans-caronic acid.

# THE PRODUCTION OF CIS- AND TRANS-CARONIC ACIDS FROM DELTA-3-CARENE

by

JAMES HUGH JARRETT

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

of

DOCTOR OF PHILOSOPHY

in

CHEMICAL ENGINEERING

Approved;

Lloyd Berg
Head, Major Department

Lloyd Berg
Chairman, Examining Committee

R. J. Goering
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

March, 1968

## 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. Paul E. Simacek for supplying high purity delta-3-carene as a starting material for the research work. Thanks are also due to Mrs. Margaret Parker for typing the final manuscript. The author also wishes to thank Mr. James Tillery and Mr. Silas Huso for their help in equipment fabrication and maintenance.

Special thanks are tendered to Dr. Arthur Howard, Dr. Graeme Baker, and Dr. Richard Geer of the Chemistry Department of Montana State University for their assistance in the operation of analytical equipment and in the spectra analyses leading to the identification of organic products obtained in this research.

The author also wishes to acknowledge the United States Public Health Service for their financial support of the project.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

# LIST OF TABLES

# LIST OF FIGURES

LIST OF FIGURES (continued)



* Oxidation products resulting from the potassium permanganate oxidation of delta-3-carene in acetone.

** The pH = 3.0 extract referred to in Figure 14.

LIST OF FIGURES (continued)



** The pH = 3.0 extract referred to in Figure 14.

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

## ABSTRACT

The sole known source of delta-3-carene, a bicyclic terpene, in the United States and Canada is in the by-product turpentine produced by five western Kraft pulp mills. The present potential supply of delta-3-carene is 1000 gallons per day.

Two cyclopropane ring-containing dibasic acids (cis- and trans-caronic acids) were recovered in 99% purity from the mixture of oxidation products obtained by the potassium permanganate oxidation of delta-3-carene in acetone. The yield of cis-caronic acid was 6.5% and the yield of trans-caronic acid was 0.5%.

The identification of cis- and trans-caronic acids was based on commercial analysis for carbon, hydrogen and oxygen, and on infrared and nuclear magnetic resonance spectroscopy. The spectra are included in the thesis.

Delta-3-carene, 41.4 g, was oxidized with 216.6 g potassium permanganate in 3,600 ml of acetone at a temperature of 16-18°C. The potassium permanganate reacted completely in 18 hours with a delta-3-carene conversion of 85%. Ninety-seven percent of the oxidation products were adsorbed on the surface of the manganese dioxide formed during the reaction. The unreacted delta-3-carene and 3% of the oxidation products remained in the acetone phase. The oxidation products were removed from the manganese dioxide surface with 85% efficiency by washing with hot water.

The relative solubilities of the oxidation products in water varied at different pH values. Thus, they were separated by ether extraction of a water solution with pH control. Cis-caronic acid was recovered by 1) extracting a pH = 3.0 water solution of oxidation products with ether to remove a relatively large amount of oxidation products containing a small amount of cis-caronic acid, 2) extracting the water solution again at a pH of less than one to remove a mixture of oxidation products having a high concentration of cis-caronic acid. Cis-caronic acid crystals precipitated from the pH $< 1$ extract and were purified by washing with chloroform.

The pH = 3.0 extract was redissolved in water, the pH adjusted to pH = 4.0 and the water solution extracted with ether. The water solution was then acidified (to pH $< 1$) and extracted again. More cis-caronic acid was recovered from the pH $< 1$ extract.

Trans-caronic acid was concentrated in the pH = 4.0 extract which also contained a mixture of crystals. It was recovered by 1) preparing the ammonium salt of the filtered extract, 2) removing excess water, 3) adding ethanol which dissolved all of the ammonium salts but ammonium trans-caronate, 4) filtering, and 5) converting ammonium trans-caronate to trans-caronic acid.