



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  
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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.

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