



Some aspects of the oxidation of delta-3-carene, 3, 7, 7-trimethyl bicyclo- (4.1.0) hept-3-ene  
by Ching-E Lai

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF  
PHILOSOPHY in Chemistry  
Montana State University  
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**Abstract:**

Delta-3-carene was isolated from the by-product turpentine produced by a western Kraft pulp mill. Varied oxidation reactions were carried out on this compound leading to the synthesis of keto-acid (V), 1,1-dimethyl-2-(2-oxopropyl)cyclopropyl acetic acid. The keto-acid (V) could be obtained in a pure form through the ozonolysis of delta-3-carene in an aqueous acetic acid solution (25%) followed by oxidative workup of the ozonides formed with hydrogen peroxide solution (3%).

The diacid (VII), 1,1-dimethylcyclopropane-cis-2,3-diacetic acid, could be obtained from keto-acid (V) in a considerably higher yield than previously reported.

The Hofmann elimination reaction of 1,1-dimethyl-cis-2,3-bis-(dimethylaminomethyl)-cyclopropane dimethide, compound (IX), leading to 1,1-dimethyl-2,3-dimethylene-cyclopropane, compound (X), was carried out. A Diels-Alder cycloaddition reaction with 4-phenyl-1,2,4-triazoline-3,5-dione, PTAD, was attempted on compound (X). The normal p4+2p cycloaddition reaction was not observed, however, an adduct product was obtained. A possible structure was proposed in accord with the experimental data.

TO

my parents

116

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by

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Chemistry

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## ABSTRACT

Delta-3-carene was isolated from the by-product turpentine produced by a western Kraft pulp mill. Varied oxidation reactions were carried out on this compound leading to the synthesis of keto-acid (V), 1,1-dimethyl-2-(2-oxopropyl)cyclopropyl acetic acid. The keto-acid (V) could be obtained in a pure form through the ozonolysis of delta-3-carene in an aqueous acetic acid solution (25%) followed by oxidative workup of the ozonides formed with hydrogen peroxide solution (3%).

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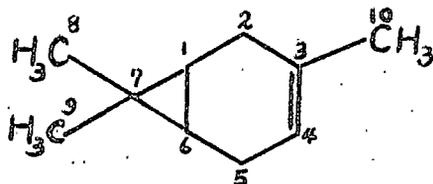
The Hofmann elimination reaction of 1,1-dimethyl-cis-2,3-bis-(dimethylaminomethyl)-cyclopropane dimethide, compound (IX), leading to 1,1-dimethyl-2,3-dimethylene-cyclopropane, compound (X), was carried out. A Diels-Alder cycloaddition reaction with 4-phenyl-1,2,4-triazoline-3,5-dione, PTAD, was attempted on compound (X). The normal " $\pi_4 + \pi_2$ " cycloaddition reaction was not observed, however, an adduct product was obtained. A possible structure was proposed in accord with the experimental data.

## INTRODUCTION

The presence of delta-3-carene in the essential oil derived from the oleo-resin *Pinus longifolia* was first reported by a number of investigators in 1905, but under the incorrect name of sylvestrene. In 1920, the investigations of Simonsen and his collaborators showed that the oil from *P. longifolia* does not contain d-sylvestrene, but a bicyclic hydrocarbon called (+)-delta-3-carene. Both (+)- and (-)- forms of delta-3-carene, a bicyclic monoterpene with a peculiar sweet odor, have since been identified in nature as a constituent of many turpentine oil.<sup>1</sup>

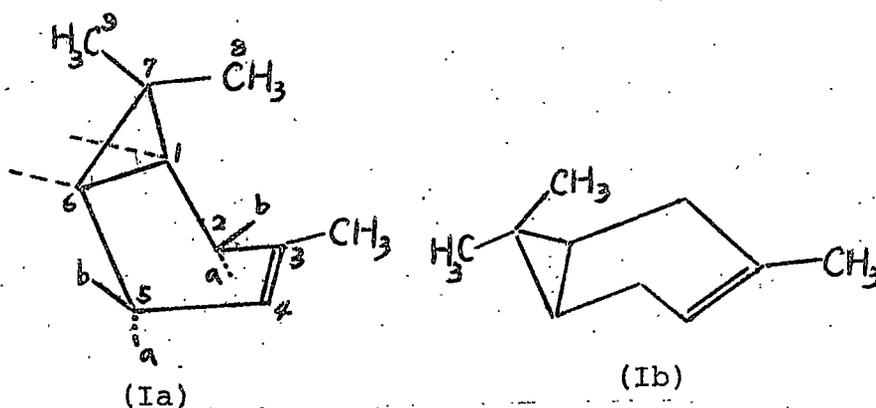
An investigation by Jarrett<sup>2</sup> in 1968, showed that the sole known source of delta-3-carene in the United States and Canada was in the by-product turpentine produced by five western Kraft pulp mills and only three of the five mills condensed their turpentine. These three mills produced and condensed 1000 gallons per day of turpentine containing approximately 25% of delta-3-carene. There appears to be no commercial use for delta-3-carene that makes its recovery and purification economically attractive.

The structure of this bicyclic hydrocarbon (3,7,7-trimethyl bicyclo[4.1.0]hept-3-ene) is shown as follows:



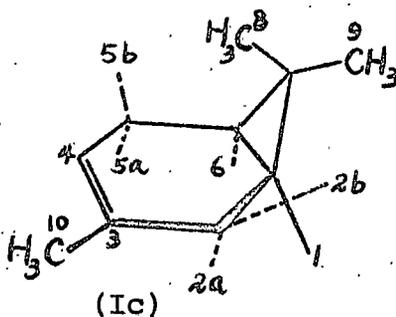
(I)

Hitherto, only two conformations, namely the boat form (Ia) and the inverted boat form (Ib) have been proposed.



(Ia)

(Ib)



(Ic)

A p.m.r. study by Acharya, which interpreted the variable temperature chemical shift data for the 8- and 9-methyl groups, has shown (Ia) as the dominant form, this

being favored over (Ib) by  $1.5\text{Kcal mol}^{-1}$  free energy difference.<sup>3</sup> The electron diffraction pattern of delta-3-carene was interpreted solely in terms of structure (Ia).<sup>4</sup> Mechanistic studies on addition reactions of the olefin have rationalized the observed stereochemistry of the products on the basis of (Ia) predominating.<sup>5,6</sup>

However, in a more recent p.m.r. study of delta-3-carene using a high resolution 220 MHz instrument, Whittaker and co-worker<sup>7</sup> found that, in contrast to the highly buckled structure for the six membered ring previously proposed, the ring is essentially planar (Ic). The evidence for this is the following coupling constant data in Table I. These data require that the dihedral angles between H-1 and H-2a and between H-1 and H-2b to be  $30^\circ$  and  $90^\circ$ , respectively, which is in good agreement with a planar ring structure, while structure (Ia) requires the dihedral angles between H-2a and H-1, H-2b and H-1 to be both  $60^\circ$ . Also, in a planar conformation the eclipsing strains (between H-1 and H-2a, H-6 and H-5a) are relieved to an extent similar to that prevailing in (Ia) while no severe steric interaction (between the 8-methyl and the  $\pi$ -orbital of the double bond) is present.

Table 1. Proton Chemical Shifts (ppm) and Coupling Constant (Hz) in delta-3-carene (CCl<sub>4</sub> Solution)<sup>7</sup>

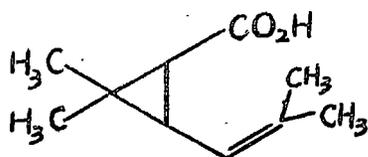
H:	1	2a	2b	4	5a
	0.69*	2.19	1.80	5.30	2.37
H:	5b	6	8-Me	9-Me	10-Me
	1.96	0.59*	0.76	1.04	1.61
<u>Coupling Constant**</u>					
	J(1,2a)	J(1,2b)	J(1,6)	J(2a,2b)	
	7.5	0	8.0	20.0	
	J(5a,5b)	J(5a,6)	J(5b,6)		
	20.0	7.5	0		

\* Assignment of protons 1 and 6 may be reversed.

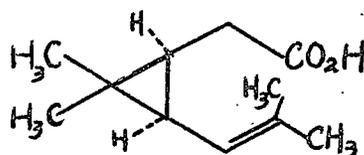
\*\* Other coupling to protons 2a, 2b, 5a, and 5b are  $\leq 2$ Hz and to protons 1 and 6 are  $\leq 1$ Hz.

Since no other conformational study of the bicyclo-[4.1.0]hept-3-ene system seems to have been reported up to the present time, the planarity of the six membered ring in delta-3-carene has yet to be proven.

The insecticidal activity of the naturally occurring esters of chrysanthemic acid (II, "natural pyrethrins")<sup>8</sup> has brought some attention to the chemistry of delta-3-carene. For example, Crombie and coworker<sup>9</sup> established the configurative relationship in absolute terms between



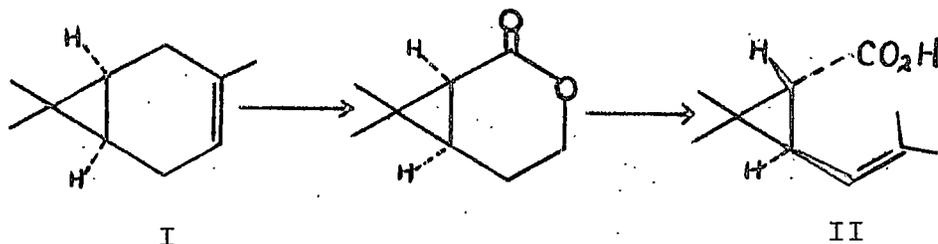
II



III

natural chrysanthemic acids and (+)-delta-3-carene. Matsui et al.<sup>10</sup> described a synthesis of optically pure (+) and (-) trans-chrysanthemic acids and (+)-delta-3-carene. Sasaki and coworkers<sup>11</sup> reported the synthesis of cis-homochrysanthemic acid (III) and its derivatives from delta-3-carene.

A new and more efficient synthesis route for the conversion of (+)-delta-3-carene (I) into (+)-trans-chrysanthemic acid (II) was recently described by S. Dev in 1974.<sup>12</sup>

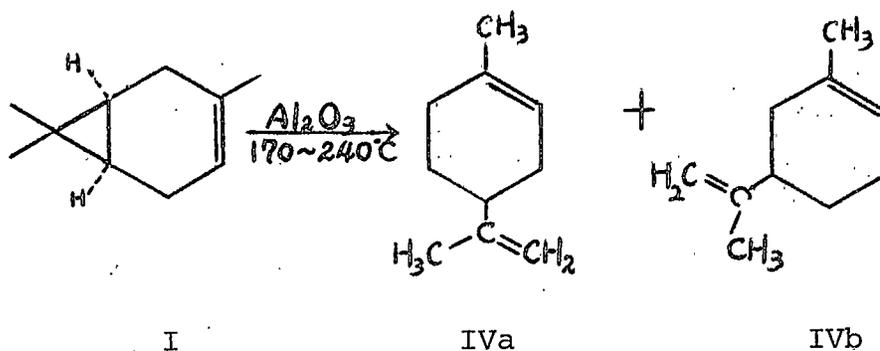


I

II

The first review article of the chemistry of delta-3-carene containing over 200 references was published by J. Verghese in 1965.<sup>13</sup> W. Cocker et al.<sup>14a-e</sup> also investigated various oxidation reactions of (+)-delta-3-carene.

Besides the synthesis of the chrysanthemic acids, delta-3-carene has also been utilized in the synthesis of dipentene (IVa) and carvestrene (IVb) which, in turn, are used in the manufacture of terpene resins for perfumes, chewing gums, and pressure sensitive adhesive.<sup>15</sup>



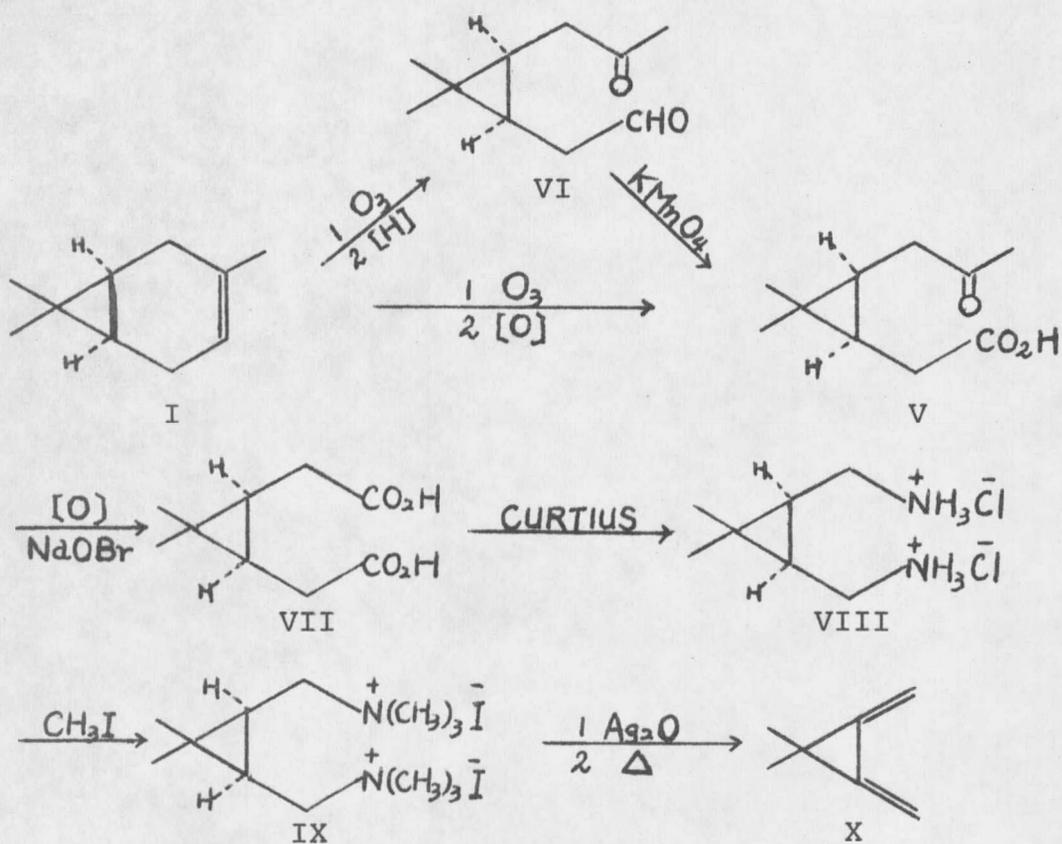
Other uses that may make delta-3-carene commercially attractive are: "liquid gold" preparation used to coat thin layer of gold on glasses, glazed china and ceramics,<sup>16</sup> and pinene-free flotation agents.<sup>17</sup>

In the biological area, delta-3-carene is active in inhibiting the growth of various microbes in vitro,<sup>18</sup> an insect attractants in young pine stand,<sup>19</sup> toxic to

*Paramecium caudatum* and effective as an antimicrobial effects on microorganisms isolated from the human body and pig-skin.<sup>20</sup>

## RESEARCH OBJECTIVES

In 1971, S. Miller<sup>21</sup> reported the synthesis of 1,1-dimethyl-2,3-dimethylene cyclopropane from delta-3-carene (I), which is summarized as follows:



This synthesis path offered several interesting intermediates which initiated the thoughts of this research project.

a) The recent observations that simpler derivatives of (+)-trans- or (+)-cis-chrysanthemic acid (II) showed











































































































































































