



Delta-3-carene : a raw material for saturated monocyclic monoterpene alcohols  
by Mark Andrew Hannah

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:

Delta-3-carene, a constituent of the by-product turpentine from Kraft pulp mills in the Rocky Mountain region, was used as a raw material for the production of monoterpene alcohols. A four-step process, including hydrogenation, hydrobromination, esterification, and hydrolysis was used.

The final alcohol products were identified as cis- and trans-8-p-menthanol and cis- and trans-8-m-menthanol.

The liquid phase hydrogenation of (+)  $\Delta$ -3-carene was investigated in a continuous fixed-bed catalytic reactor using a reduced nickel catalyst containing 58% nickel on a kieselguhr support (Harshaw Ni-OIO4-T).

The operating conditions were as follows: 25-115°C, 0-1500 psig, LHSV .05-.50, and H<sub>2</sub> rate 38-376 SCF/gal.  $\Delta$ -3. The production of (-) cis-carane was favored by high pressure, lower temperatures, and low space velocity while 1,1,4-trimethylcycloheptane (the major by-product) was favored by low pressures, high temperature, and high space velocity. Carane yields of 90-95% with 100% conversion of  $\Delta$ -3-carene were obtained at 60-70°C, 750-1000 psig, and LHSV .10-.20. The catalyst activity was decreased by a poison suspected to be water. The selectivity was unaffected.

The hydrobromination of carane, was carried out in a semi-batch reactor using gaseous HBr. Organic peroxides were used to try to reverse Markovnikov's rule of addition so that secondary bromides could be obtained. This failed completely with carane, with about equal amounts of the tertiary meta and para derivatives being the only products obtained.

The operating conditions were as follows: 5-100°C and initial carane concentration .30-1.60 g-moles/l. The high temperature favored the meta derivatives slightly while the lower carane concentrations decreased the reaction rate. Conversions of over 95% were obtained in most of the experiments with the reaction proceeding very rapidly generating exothermic heat. The acetate esters were produced from the terpinyl bromides because elimination predominated when direct hydrolysis of bromides was tried. The batch esterification went instantaneously in an acetic acid medium using silver acetate. The operating conditions were as follows: 2-112°C, initial bromide concentration .12-1.30 g-moles/l. and reaction time 2-60 min. Temperature up to about 70°C had no effect on the yield of ester but at 112°C the yield dropped. At higher bromide concentrations the yield was decreased slightly, also. The maximum amount of ester obtained was 60% at 17°C using .25 g-moles bromide/l.

The batch hydrolysis reaction was investigated with menthyl acetate in a Parr bomb using aqueous NaOH. The operating conditions were as follows: 95-245°C, .25-2.92 g-moles NaOH/l. H<sub>2</sub>O, .23-1.08 g-moles ester/l. H<sub>2</sub>O, and reaction time 15 min. to 13 hours. At temperatures over 120°C the reaction went easily with 80-100% conversions and 90-100% alcohol yields. Reaction times over one hour provided nearly complete conversion while reactant concentration had no effect on the reaction. Hydrolysis of crude tertiary esters yielded approximately 50% alcohols at 170°C after 10-12 hours.

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by

MARK ANDREW HANNAH

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fulfillment of the requirements for the degree

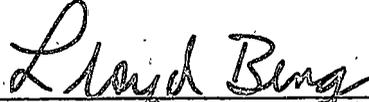
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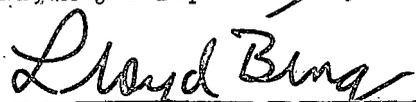
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## ABSTRACT

Delta-3-carene, a constituent of the by-product turpentine from Kraft pulp mills in the Rocky Mountain region, was used as a raw material for the production of monoterpene alcohols. A four-step process, including hydrogenation, hydrobromination, esterification, and hydrolysis was used. The final alcohol products were identified as cis- and trans-8-p-menthanol and cis- and trans-8-m-menthanol.

The liquid phase hydrogenation of (+)  $\Delta$ -3-carene was investigated in a continuous fixed-bed catalytic reactor using a reduced nickel catalyst containing 58% nickel on a kieselguhr support (Harshaw Ni-0104T). The operating conditions were as follows: 25-115°C, 0-1500 psig, LHSV .05-.50, and H<sub>2</sub> rate 38-376 SCF/gal.  $\Delta$ -3. The production of (-) cis-carane was favored by high pressure, lower temperatures, and low space velocity while 1,1,4-trimethylcycloheptane (the major by-product) was favored by low pressures, high temperature, and high space velocity. Carane yields of 90-95% with 100% conversion of  $\Delta$ -3-carene were obtained at 60-70°C, 750-1000 psig, and LHSV .10-.20. The catalyst activity was decreased by a poison suspected to be water. The selectivity was unaffected.

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## I. INTRODUCTION

### A. Oil of Turpentine

Oil of turpentine is believed to have been the first essential oil ever isolated, being mentioned by the Greek historian Herodotus<sup>(1)</sup> (484 to 425 B.C.). It has been commercially produced both as a by-product from pulp mills<sup>(2)</sup> and as a direct product from pine tree resins<sup>(3)</sup> for at least 100 years and perhaps even before that.

Turpentine production in the United States had been static at about 30 million gallons annually from 1900 to 1960 but has started to increase and about 40 million gallons is predicted for 1970<sup>(4)</sup>. Its sources, however, have changed from being produced exclusively from pine gum (oleo-resin) in 1900 to about 50% produced now as by-product from Kraft pulp mills, with 25% still coming from pine gum and another 25% coming from steam distilling pine stump resins. The United States leads in world production of turpentine today, with about 40-50% of the total.

### B. Delta-3-Carene

The turpentines from India and Scandinavia were noticed early to be quite different from the American and French turpentines<sup>(3)</sup>. Distillation of these turpentines indicated a much smaller fraction of the Indian and Scandinavian turpentine boiling at 167°C or less (the alpha- and beta-pinene fractions). Simonsen et al<sup>(5)</sup> carefully fractionated the Indian turpentine in 1920 and found it contained alpha-pinene, beta-pinene, a new bicyclic terpene for which the name  $\Delta$ -3-carene was proposed, and a sesquiterpene called longifolene. The properties of the new terpene

hydrocarbon were b.p. 168-169°/705 mm Hg,  $d_{30}^{30}$  .8586,  $n_D^{30}$  1.469, and  $[\alpha]_D^{30} + 7.69^\circ$ . The following structure was eventually assigned.

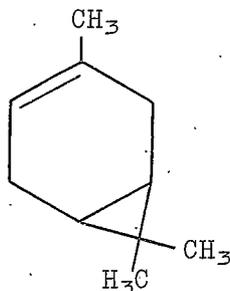


Figure 1. The Chemical Structure of  $\Delta$ -3-Carene.

Delta-3-carene has been found (6,7,8) in the turpentines from many species of coniferous trees of the United States and Canada. It ranges in amounts in different species from only a trace to nearly 100%. Table I gives a summary of the trees containing substantial amount of  $\Delta$ -3-carene and their locations. In addition to North American sources for  $\Delta$ -3-carene, it is also found in other areas of the world, as previously mentioned. The *Pinus longifolia* found in various parts of Asia and Europe is reported (10,11) to have 45-70%  $\Delta$ -3-carene in its turpentine; the *Pinus silvestria* in Poland is reported (12) to have about 35%  $\Delta$ -3-carene; and undesignated pines of Sweden are reported (13) to have 25-33%  $\Delta$ -3-carene. Undoubtedly, it occurs in many other countries which have not been mentioned.

All of the above information indicates the potential availability of  $\Delta$ -3-carene in various parts of the world. In the United States at the present time,  $\Delta$ -3-carene is available only in the by-product turpentine recovered from three western Kraft pulp mills\*, and will be available from two other mills\*\* if and when they start recovering their turpentine. (14) There is no commercial facility in the U.S. now for the sole purpose of separating pure  $\Delta$ -3-carene from turpentine mainly because there is no ready market for it in this country either as a chemical raw material or as an end product in its pure state. However, there has been a considerable amount of research done on the chemistry of  $\Delta$ -3-carene (4,15-27) some of which may open the door for commercial utilization in the near future.

\* Waldorf-Hoerner Paper Products Co., Missoula, Montana.  
Southwest Forest Industries, Snowflake, Arizona.  
Boise-Cascade Corp., Wallula, Washington.

\*\* Potlatch Forests, Inc., Lewiston, Idaho.  
Northwestern Pulp & Power, Ltd., Hinton, Alberta.



























































































































































































































































































































































































































































































































































































































