Separation of beta-phellandrene from a terpene mixture via extractive crystallization with thiourea
by Edward Leon Handl

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

Abstract:
Turpentine, a complex mixture of organic chemicals called terpenes, is a by-product of the Kraft paper-making process. To best utilize this turpentine, it would be desirable to separate it into the individual terpene compounds. This separation is difficult due to the closeness of physical properties between the terpenes. Indeed, classical separation methods are useless when trying to separate certain terpenes from the mixture, one example being the separation of beta-phellandrene from the "dipentene cut" obtained by distillation of crude turpentine.

To effect the separation of beta-phellandrene, the method of extractive crystallization with thiourea was investigated. A solution of turpentine, thiourea, and a suitable solvent is charged to a crystallizer and cooled. Adduct crystals are formed between thiourea and beta-phellandrene. Removal of the crystals by filtration and subsequent decomposition by steam stripping yields a terpene product enriched in beta-phellandrene. Successive crystallizations of product terpenes can produce beta-phellandrene of purity greater than 99%. In initial investigations it was found that four successive crystallizations were needed to increase the beta-phellandrene purity from 63% to 98%. Optimization techniques were used in hope of increasing recovery. Lower temperatures tended to increase recovery of beta-phellandrene, with 29°C the highest temperature at which recovery was possible. The optimum time for filtration of crystals was when the lowest temperature allowed by the equipment was reached. The optimum beta-phellandrene to thiourea ratio was found to be 0.35 ml/gram. Decreasing the solvent to thiourea ratio increased recovery, but lowered enrichment of product. Methanol proved to be the best individual solvent, and acetone used as an additive increased recovery. Through the optimization techniques employed, a 22-fold increase in recovery was obtained over initial runs.

It was concluded that extractive crystallization with thiourea is an effective method for purifying beta-phellandrene, which was previously unavailable in pure form from turpentine sources.

Statement of Permission to Copy

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature Edward Leon Handl

Date December 13, 1971

SEPARATION OF BETA-PHELLANDRENE FROM A TERPENE MIXTURE VIA EXTRACTIVE CRYSTALLIZATION WITH THIOUREA

by

EDWARD LEON HANDL

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 Berg
Head, Major Department

J. P. McCandless
Chairman, Examining Committee

K Goering
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

March, 1972

ACKNOWLEDGMENT

The author wishes to thank the entire staff of the Chemical Engineering Department of Montana State University for their advice, questions, and criticisms, which were of considerable help during this investigation.

In particular, the author would like to thank Dr. F. P. McCandless for his guidance leading to the completion of the project. Also, special thanks must go to John Sikonia, whose helpful suggestions were much appreciated.

The author was the recipient of a National Science Foundation Traineeship for the interim September 1970 to September 1971. This, and other financial aid provided by Montana State University, was greatly appreciated.

ABSTRACT

Turpentine, a complex mixture of organic chemicals called terpenes, is a by-product of the Kraft paper-making process. To best utilize this turpentine, it would be desirable to separate it into the individual terpene compounds. This separation is difficult due to the closeness of physical properties between the terpenes. Indeed, classical separation methods are useless when trying to separate certain terpenes from the mixture, one example being the separation of beta-phellandrene from the "dipentene cut" obtained by distillation of crude turpentine.

To effect the separation of beta-phellandrene, the method of extractive crystallization with thiourea was investigated. A solution of turpentine, thiourea, and a suitable solvent is charged to a crystallizer and cooled. Adduct crystals are formed between thiourea and beta-phellandrene. Removal of the crystals by filtration and subsequent decomposition by steam stripping yields a terpene product enriched in beta-phellandrene. Successive crystallizations of product terpenes can produce beta-phellandrene of purity greater than 99%.

In initial investigations it was found that four successive crystallizations were needed to increase the beta-phellandrene purity from 63% to 98%. Optimization techniques were used in hope of increasing recovery. Lower temperatures tended to increase recovery of beta-phellandrene, with 29°C the highest temperature at which recovery was possible. The optimum time for filtration of crystals was when the lowest temperature allowed by the equipment was reached. The optimum beta-phellandrene to thiourea ratio was found to be 0.35 ml/gram. Decreasing the solvent to thiourea ratio increased recovery, but lowered enrichment of product. Methanol proved to be the best individual solvent, and acetone used as an additive increased recovery. Through the optimization techniques employed, a 22-fold increase in recovery was obtained over initial runs.

It was concluded that extractive crystallization with thiourea is an effective method for purifying beta-phellandrene, which was previously unavailable in pure form from turpentine sources.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION AND BACKGROUND

Turpentine is a complex mixture of organic chemicals known as terpenes. Produced naturally in wood, turpentine is most generally obtained from the crude gum (oleoresin) of pine trees, from steam distillation of resin-saturated woods, or as a by-product from the Kraft (sulfate) wood-pulping process. Turpentine has long been used as a household paint and varnish thinner, as well as in the industrial manufacture of paint and varnish.

Some of the terpene compounds obtainable from turpentine have found a variety of chemical uses. Products obtained from turpentine-derived compounds include synthetic camphor, pharmaceuticals, perfumes and flavorings, insecticides, petroleum additives, and industrial solvents.(22)

The composition of turpentine can vary greatly, depending on the particular species of wood from which it was obtained. The by-product turpentine from the Kraft wood-pulping process is quite often a result of pulping wood of several different species at one time.

Utilization of by-product turpentine from wood pulping is of interest from the standpoints of reducing waste from the process and of producing by-products to increase the economic return from the process. The turpentine is obtained by condensing relief gases from wood digesters in the pulping step. The condensate can yield

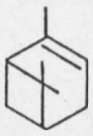
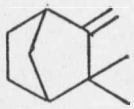
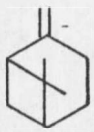
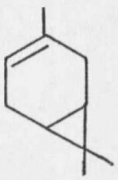
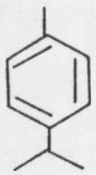
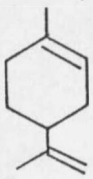
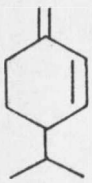
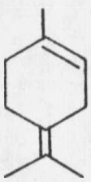
two to ten gallons of oil per ton of pulp produced, the oil being 50 to 60% turpentine.(22)

To be used as chemical intermediates, it would be desirable to separate the individual terpenes in purified form from the turpentine. To effect this separation, the turpentine is usually distilled under vacuum or in the presence of water (steam distillation) to minimize the formation of terpene polymers.(17)

Some of the terpene compounds found in Kraft sulfate turpentine are listed in Table I along with their respective boiling points and relative concentrations. The turpentine shown in Table I was produced while pulping a mixture of lodgepole pine, Ponderosa pine, and western larch. As evidenced by the composition of the turpentine shown in Table I, it is generally found that the most common terpenes in turpentine are alpha-pinene, beta-pinene, dipentene, delta-3-carene, and beta-phellandrene.(3)

Noting the closeness of the boiling points of the various terpenes in Table I, it is evident that separation of the terpenes by distillation is difficult. Using a distillation column with a large number of theoretical plates and a high reflux ratio, however, it is possible to obtain alpha-pinene, beta-pinene, and delta-3-carene in fairly high purity. Note also that dipentene and beta-phellandrene have essentially the same boiling points, and separation of these two terpenes by distillation is impractical.

Table I. Composition of a Typical Sulfate Turpentine Obtained While Pulping Lodgepole Pine, Ponderosa Pine, and Western Larch. (Sample supplied by Northwestern Pulp and Power, Ltd.)

Compound	Structure	Normal Boiling Point, °C	% in Sample
unidentified light hydrocarbons	--	--	1
alpha-pinene		156	14
camphene		160	1
beta-pinene		164	10
myrcene		167	3
delta-3-carene		171	22
para-cymene		176.7	4
dipentene		177.7	7
beta-phellandrene		178	34
terpinolene		185	trace
unidentified heavy compounds	--	--	4

Often a "dipentene cut" is obtained when distilling turpentine. This cut consists of terpenes whose boiling points are close to those of dipentene. Table II shows a typical dipentene cut obtained from distillation of the turpentine listed in Table I.

Table II. A Typical Dipentene Cut. (Obtained From Turpentine Listed in Table I)

Compound	Boiling Point	Percent in Cut
beta-phellandrene	178.0	63.1
dipentene	177.7	25.8
para-cymene	176.7	9.3
unidentified	----	1.8

Clearly, the closeness in boiling points of the compounds listed in Table II shows that further separation of these compounds by normal distillation methods is impractical.

Because of the difficulty of separating terpenes in pure form by distillation, other separational methods have been tried. One method which may be used to separate mixtures of terpenes is through the use of a complexing agent to selectively remove one or more terpenes from a mixture. In one method, clathration was used to selectively remove myrcene from a terpene mixture.(5) Clathration consists of selectively enclosing certain molecules within a three-dimensional complex which is held together by weak intramolecular forces of the Van der Waals or hydrogen bonding type. The selec-

tivity of these complexes for enclosing certain molecules appears to be based on spatial considerations, or size and shape of the enclosed molecules.(2)

A separational technique closely related to clathration is extractive crystallization using urea or thiourea. In this method an adduct is formed between the enclosed molecules of the selected compound and the thiourea molecules. The adduct is quite similar to a clathrate except that in an adduct the enclosed molecules are trapped in a two-dimensional structure which has been likened to a canal or channel.(7,14,24) Adduct formation of this type was first observed between urea and straight-chained hydrocarbons.(14) The discovery of urea adducts was followed in the mid-1940's by the discovery of adducts of thiourea, which tend to be formed with branch-chained or cyclic hydrocarbons.(25) Later research greatly increased the number of known types of compounds which form adducts with urea and thiourea.(8,9) Due to the differences in size and shape of the included molecules between thiourea and urea adducts, it was found that processes of separation using thiourea adduct formation complemented those processes using urea.(20)

Extractive crystallization processes using urea have been used in the dewaxing of petroleum to reduce pour points (6), in the separation of wax mixtures (21), and in the separation of mixtures

of fatty acids.(16). Other separation processes using urea and thiourea and involving a variety of organic chemicals have been described in the literature.(8,9,15) Also, urea and thiourea adducts have been used for "molecular packaging" of compounds (useful for some volatile compounds), and in providing templates for monomers in stereospecific polymerizations.(3,7) Bhatnagar (2) lists an extensive bibliography of urea and thiourea adduct processes.

Although the exact mechanism of adduct formation is not fully understood, it appears that the forces holding the adduct together are similar to those in clathration; that is, Van der Waals forces or hydrogen bonds. It has been observed that the heats of formation of urea adducts are on the order of those for the adsorption of hydrocarbons on solid surfaces, and are in the order of the calculated energy of hydrogen bonding in crystalline ammonia and in water.(27)

The formation of thiourea adducts has been described as the enclosing molecules (thiourea) wrapping around a mandrel of another substance, which is to be enclosed.(14) The enclosed molecules must be of a particular size, preferably 5.8 ± 0.5 A by 6.8 ± 0.3 A in cross-section. If the enclosed molecule is near the size tolerance limits, such an adduct will be unstable, and if not within the limits, the adduct will not form.(20) The stability of a urea or

thiourea adduct is dependent on the included species, and indeed, the dissociation temperatures of such complexes have been used in the identification of enclosed compounds.(13,19)

Some authors (2,24) report that generally terpenes do not form adducts with thiourea. However, Fetterly (8) has reported the formation of an adduct between alpha-pinene and thiourea. This pointed to the possibility that some separation of terpenes--perhaps by their molecular size or geometry--could be accomplished using thiourea.

The author's initial work with terpenes and thiourea was intended to explore if, indeed, broad classes of terpenes, such as monocyclic and bicyclic, could be separated by formation of adducts with thiourea. The completely unexpected result was that a separation of broad classes did not occur, but instead the adducts tended to selectively extract certain individual terpene compounds. It was noted that three terpenes from the sulfate turpentine feed tended to form thiourea adducts. The compounds were later shown to be alpha-pinene (previously reported (8)), beta-pinene, and beta-phellandrene. Of the previously unreported terpene-thiourea adducts, the beta-phellandrene adduct appeared to be the most interesting, as this adduct could be used to further resolve the dipentene cut previously described. The research which is the subject of this thesis resulted from this preliminary work.

Since the terpene beta-phellandrene forms a stable adduct with thiourea, the method of extractive crystallization may be used to separate beta-phellandrene from the dipentene cut previously described. This is a new separation technique as applied to resolving the dipentene cut into its individual components, and effectively presents beta-phellandrene as a new raw material for potential use in the chemical industry.

Occurring naturally in the essential oils of many plants, beta-phellandrene appears to be the fourth or fifth most abundant terpene found in wood pulp turpentines. Probably the largest single potential source for beta-phellandrene in the United States is lodgepole pine turpentine, which consists of over 60% beta-phellandrene.(4,10)

Existing as two optical isomers, beta-phellandrene obtained from turpentine is of the levorotatory type. The dextrorotatory, or d-beta-phellandrene, is found in the essential oils of water fennel and lemon, whereas the levorotatory, or l-beta-phellandrene, is found in sources such as Japanese peppermint oil and turpentine oil.(23)

Beta-phellandrene has the potential of being used for its essential oil qualities; that is, either taste or fragrance. Because it is not readily available, however, it is rarely used in

industries making use of these qualities.(11) Like its enantiomer, l-beta-phellandrene has a pleasant odor. As for taste, no evaluation for l-beta-phellandrene has apparently been made, although the d-enantiomer is reported to have a burning taste.(23) The l-variety, however, could quite possibly have an entirely different effect on the taste sense.

At present there is no industrial demand for beta-phellandrene and hence no commercial separation process is on stream to obtain this terpene in purified form. It should be emphasized, however, that prior to this research, purified beta-phellandrene was not available. Before the development of the thiourea extractive crystallization process for separating beta-phellandrene, no separation process was capable of producing the pure material from the mixtures in which it is found. Now, however, a source of high-purity beta-phellandrene is available with which to explore its potential uses, and hopefully, its industrial demand.

Should a demand for beta-phellandrene develop, the extractive crystallization process, coupled with existing methods and technology, (15,26) could prove an attractive method for obtaining purified beta-phellandrene.

RESEARCH OBJECTIVES

The objectives of this research may be subdivided into three basic areas.

First, it was desired to qualitatively and quantitatively investigate the feasibility of separating the terpene beta-phellandrene from a dipentene cut obtained from crude sulfate turpentine. It was hoped to gain knowledge as to the amount of purification possible by the method of extractive crystallization with thiourea. Also, it was hoped to gain insight into the number of individual purification steps required for this separation, given a feed purity and a desired product purity.

Second, improvement of the methods and materials used in the process was undertaken in hope of obtaining more optimum recovery and separation of beta-phellandrene from feed mixtures. A number of different parameters which could be varied in the process had to be investigated in order to evaluate their effects on the separation scheme. It was hoped to optimize these individual variables in order to maximize the recovery of beta-phellandrene.

Third, through the use of the methods developed in the investigation of this separation process, it was hoped to obtain a quantity of beta-phellandrene in purified form. This would enable potential users of the compound to conduct small-scale tests as to its usefulness and value as a pure chemical.

EXPERIMENTAL PROCEDURE

The basic method for the preparation of thiourea-terpene adducts consists of dissolving solid thiourea in a suitable solvent such as methanol, adding the terpenes to the solution, and cooling the resulting mixture. At a certain point in the cooling process, the adduct begins to form as evidenced by white, needle-like crystals. In cases where agitation is used, the adduct crystals may be very fine, appearing to be a white powder. Filtration is used to remove the adduct crystals from the liquid.

Care must be observed if it is chosen to wash the crystals to remove adhering crystallization liquor, as the crystals are easily decomposed by a variety of solvents.

The crystallization step was carried out in an insulated 250-ml Erlenmeyer flask. Cooling was accomplished by use of a thermo-electric cold plate, Stir-Kool model SK-12 (Thermolectrics Unlimited, Inc.). The cold plate was equipped with a magnetic stirring apparatus, but for runs where crystals of thiourea and adduct were present in large amounts, an external motor-driven propeller-type stirrer was used. Final temperature and rate of cooling could be controlled on the cold plate. Temperatures were measured inside the flask with an iron-constantan thermocouple and a potentiometer (Brown Instrument Co.).

Since the desired terpenes are bound into the adduct crystal lattice as "guest molecules", the adduct crystals must be decomposed in such a manner as to release the terpenes while preferably reclaiming the thiourea. Several methods may be used to decompose the adduct, including heating, distilling, steam distilling, adding a solvent to dissolve the thiourea, or adding a solvent for the guest compounds.

Steam distillation or steam stripping of the crystals was chosen for the decomposition method in this investigation. A steam line, regulated by a needle valve, was fed through a trap to collect any water, and then to a 1000-ml round-bottom 3-neck flask (heated) fitted with a water-cooled condenser. To decompose an adduct, the crystals were placed in the flask and steam was passed through the crystals as the flask was being heated to prevent condensation of the steam. The terpenes were liberated from the crystals, forming an azeotrope with the steam, which then was condensed and collected. On condensation, the azeotrope separated into a water phase and a terpene phase, which was collected with the aid of a separatory funnel. The thiourea, left in the distillation flask as a concentrated water solution, was removed and cooled. On cooling, thiourea crystals were formed which were removed from the solution and reclaimed.

The thiourea used in the quantitative, data-producing runs was reagent grade (Fisher Scientific Co.). The reclaimed thiourea was used in non-quantitative runs which were made to build up a quantity of terpene feedstock enriched in the adducted or "guest" compound.

The methanol used as a crystallization solvent in this investigation was technical grade (LaPine Scientific Co.). Terpene feedstocks were prepared by the Chemical Engineering Department at Montana State University by steam distillation of pulpwood turpentines supplied by Hoerner-Waldorf Corporation, Missoula, Montana, and Northwestern Pulp and Power, Ltd., Hinton, Alberta.

Analysis of feedstock and product terpenes was accomplished by gas-liquid chromatography. A 15-foot column, 0.065-inch ID, packed with beta, beta'-oxydipropionitrile on acid-washed Chromsorb P (15:100 weight ratio) was used in a laboratory chromatograph (Series 700 Hewlett-Packard, F&M Scientific Division). Hydrogen was used as the carrier gas, the flow being 20 cc/min. Column temperature was 80°C and injector temperature was 175°C. The thermal conductivity detector temperature was held at 110°C.

The procedure for a typical run is as follows: To a 250-ml Erlenmeyer flask with a flat ground-glass bottom was added 200 mls of methanol and 20.0 mls of terpenes of the following composition:

78.0% beta-phellandrene, 19.6% dipentene, and 2.4% para-cymene. To this solution was added 20.0 grams of thiourea. The mixture was then warmed slightly to aid in dissolution of the thiourea. When all the thiourea had dissolved, the flask was insulated and placed on the cold-plate apparatus. A few drops of light machine oil were used between the flask and the cold plate to retard frost formation and enhance heat transfer through the glass-metal junction. A thermocouple and a stirrer were placed in the flask and the flask stoppered. After turning on the cooling apparatus, the mixture was allowed to cool to -23.8°C. The flask was then removed from the cold plate and the adduct crystals were collected by filtration in a Buchner funnel. After drying, the adduct crystals were placed in a 3-neck distillation flask and the center neck fitted with a ground-glass stopper. A steam line was fitted to the second neck and a water-cooled condenser fitted to the last neck. As heat was supplied to the flask by an electric heater controlled by a rheostat, steam was passed through the flask. As the adduct crystals decomposed the terpene-water azeotrope was condensed in the condenser and collected in a product flask. The terpenes were then separated from the water in a separatory funnel, measured volumetrically, and analyzed by gas-liquid chromatography.

In the separation of terpenes by the methods used in this investigation, there are two main factors which ideally we would hope to maximize. One of these factors is selectivity, or the preference for one compound of the terpene mixture to be selectively enclosed in the crystal structure of the adduct while leaving the other terpene compounds in the solution. The other factor is the yield, or the relative amount of the preferred crystal-enclosed terpene that can be adducted or enclosed in the crystals for a given amount of that compound in the feed. The ideal step in relation to these two factors would be to exclusively select 100% of one compound out of the terpene mixture by having that compound enclosed in the adduct crystals.

There are a number of variables that could have an effect on some part of the adduct-forming and recovery process, and hence on the yield and selectivity. These variables include: feed purity, temperature of crystallizer, time allowed for a run, relative amounts of solvent, thiourea, and terpenes, and the type of solvent.

It was decided to use a univarient search technique in determining the effects of the variables. In this technique one variable is changed while all other variables are held constant.

Thus, by a series of experiments each of the variables can be tested as to its effect on the property in question. In this case it was desired to know what effects the variables had on yield and selectivity.

RESULTS AND DISCUSSION

Initial Investigations

The first variable that was investigated was the effect of feed terpene purity on the purity of the terpenes enclosed in the adduct crystals. In all cases it was found that the fraction of beta-phellandrene in the product terpenes from the adduct crystals was increased over the fraction of beta-phellandrene in the feed terpene mixture. A number of runs were made, varying the feed purity by using product terpenes from one crystallization run as feed for another run. This tested the range of feed purities over which beta-phellandrene is enriched in the product. The results of this preliminary investigation are shown in Figure 1. Note that this is not an equilibrium relation, as the feed purity indicates an initial condition, while the product purity indicates a condition after the crystallization step.

In the initial runs made, product purity as high as 98.1% beta-phellandrene was obtained. Starting with a feed of 63.1% beta-phellandrene, four successive crystallizations were required to obtain the 98.1% pure product. As adducts with higher purities of beta-phellandrene were produced it was noted that the adduct crystals became smaller in length and diameter, and more uniform. Also, the color of the crystals which contained high purity beta-phellandrene were more nearly snow-white than the crystals which contained lower purity beta-phellandrene.

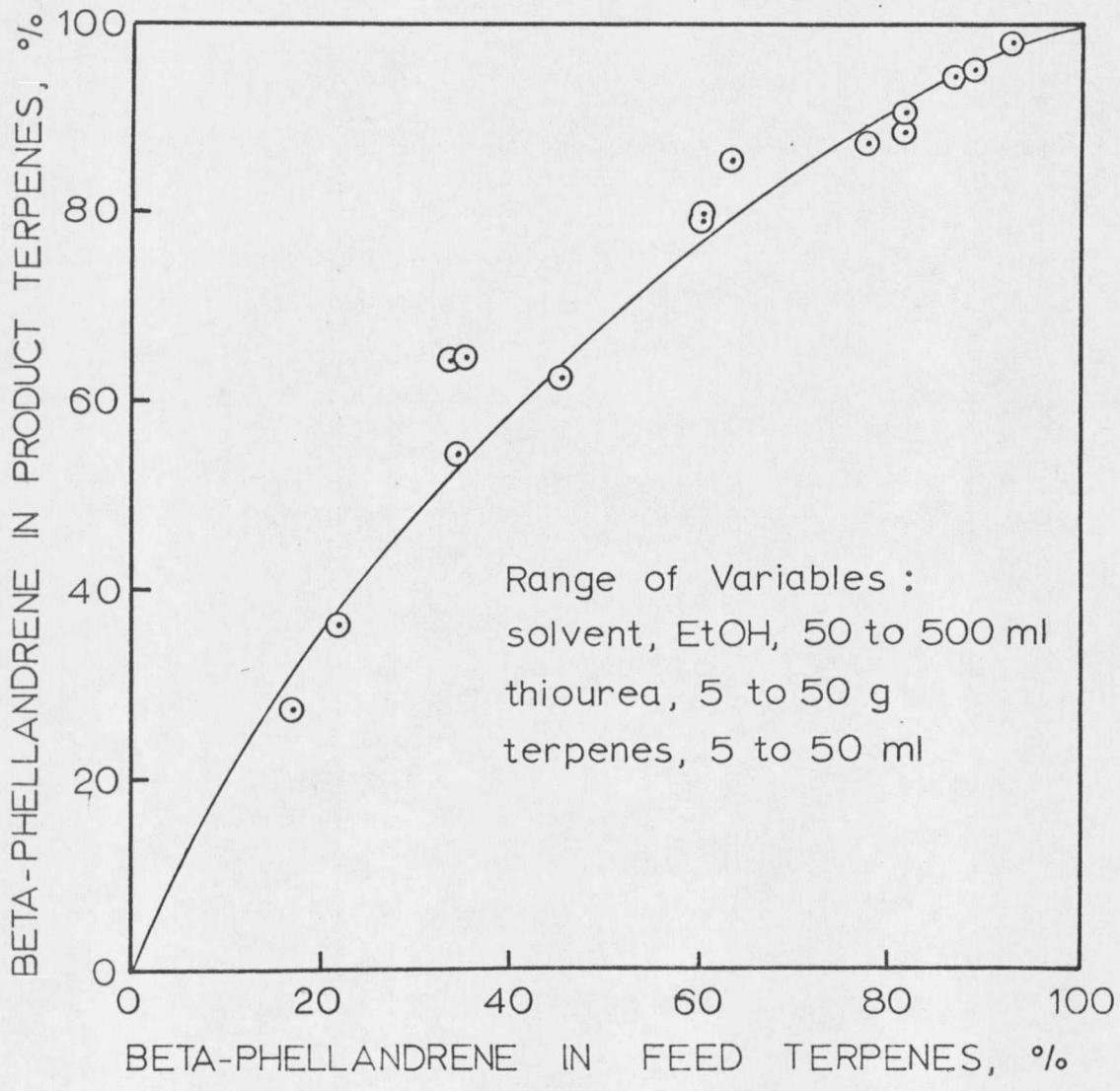


Figure 1. The Effect of Feed Terpene Purity on Product Purity in Initial Investigation.

Of the three main compounds present in the feed terpene mixture, it was found that para-cymene was eliminated most readily in the adduct crystals. After two successive crystallizations essentially no para-cymene remained in the product terpenes. The dipentene, however, was eliminated less readily, being present to the extent of 1.6% even in the 98.1% beta-phellandrene obtained after four successive crystallizations.

The mole ratio of thiourea to terpenes in the adduct crystals was found to vary in the initial runs. In these runs, differing batch sizes, temperatures, times for crystallizations, reagent ratios, and feed purities were used, as noted in Figure 1. Out of 29 of these and later runs, the mole ratio of thiourea to included terpenes varied from 2.71 to 20.80, with an average of 6.42.

Effect of Temperature

The process studied in this investigation is dependent on crystallization; thus one could expect that due to solubility the process would be temperature-dependent. To find the effect of temperature a number of runs were made, differing in the final temperature of the mixture at the time of filtration. Two different terpene feed purities were also used to test the effect of feed purity in relation to temperature dependency.

To quantitatively describe the effects of the different variables in this study, a percent recovery of beta-phellandrene was defined. The percent recovery incorporated both the selectivity for beta-phellandrene and the volumetric yield in its definition.

$$\% \text{ Recovery} = \frac{(\text{product terpene volume})(\text{product purity})}{(\text{feed terpene volume})(\text{feed purity})}$$

The above definition for the recovery of beta-phellandrene was used throughout this investigation.

The effect of temperature on recovery is shown in Figure 2. The graph shows that lower temperatures favor the recovery of beta-phellandrene in the adduct. This is due to the fact that at lower temperatures more adduct is formed because of its decreased solubility in the crystallization liquor. The quantities of reagents charged were such that all components were initially in solution. It can be noted from the graph that the temperature at which the percent recovery is zero is 29°C for this particular ratio of reagents charged. This temperature also corresponds to the temperature at which crystals of adduct were first noticed in the crystallization liquor. Therefore, it appears that the minimum required temperature for adduct formation between thiourea and beta-phellandrene is 29°C.

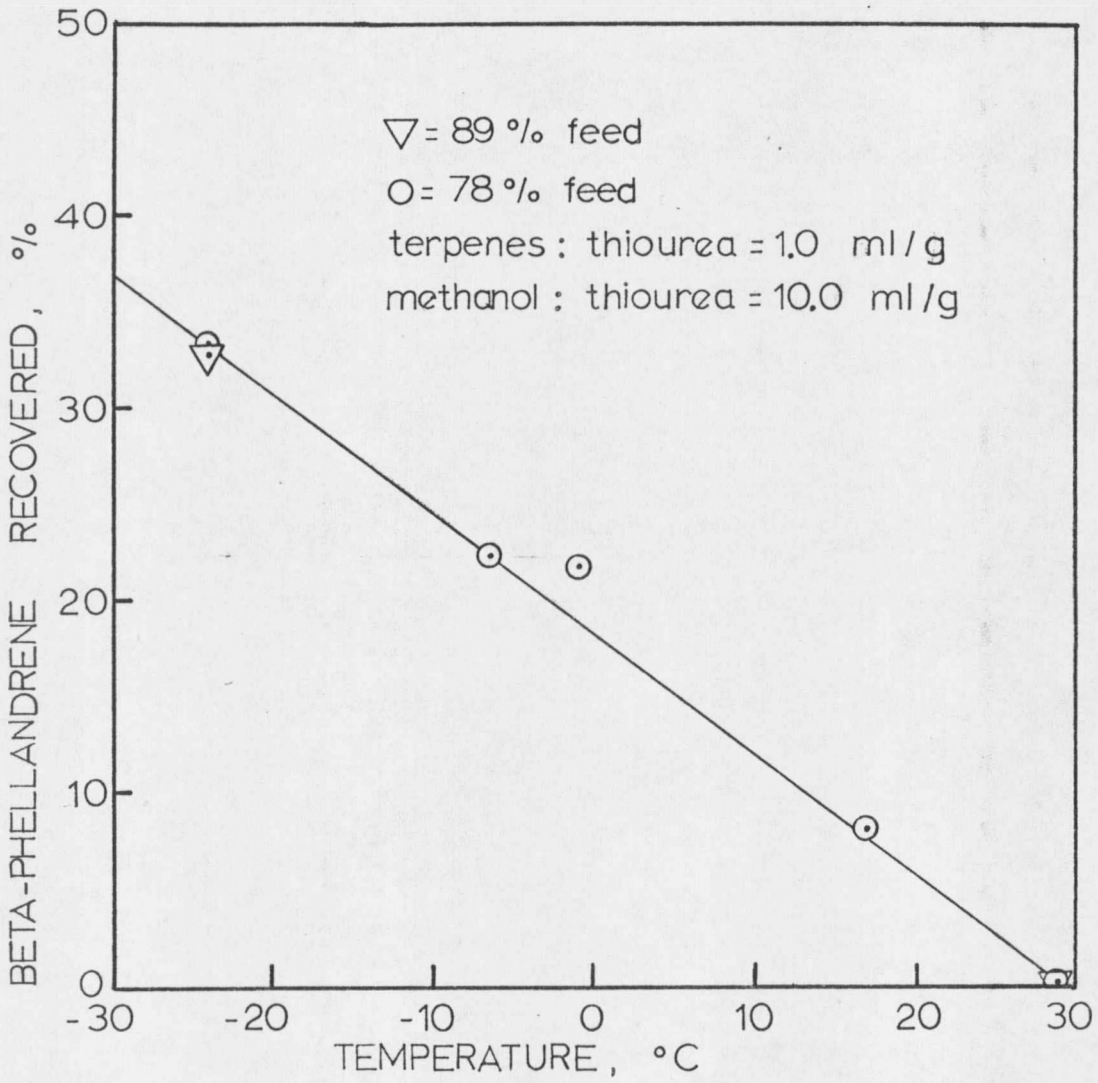


Figure 2. The Effect of Temperature on Recovery of Beta-phellandrene.

Over the range of temperatures studied the recovery of beta-phellandrene appears to increase proportionally with lower temperature. In a large-scale process, however, it would be desirable to use a temperature as close to ambient conditions as possible in order to lower cooling requirements and costs. As will be seen, temperature reduction is only one of several manipulations of variables which can increase the recovery of beta-phellandrene.

It can also be noted from Figure 2 that changes in the feed purity from 78% to 89% did not affect the percent recovery of beta-phellandrene or the temperature required for adduct formation.

Effect of Run Time

The time required to produce a maximum recovery of beta-phellandrene, holding other variables constant, was the next variable studied. Various runs were made using different periods of time between the onset of cooling and the final filtration of crystals. As can be seen from Figure 3, the only increase in recovery of beta-phellandrene is during the time while the solution is being cooled. This fact points out that the optimum time to filter the adduct crystals is as soon as the solution is cooled to the lowest temperature allowed by the equipment. This fact holds for runs where initially all reagents are in solution, as was the case for the data in Figure 3.

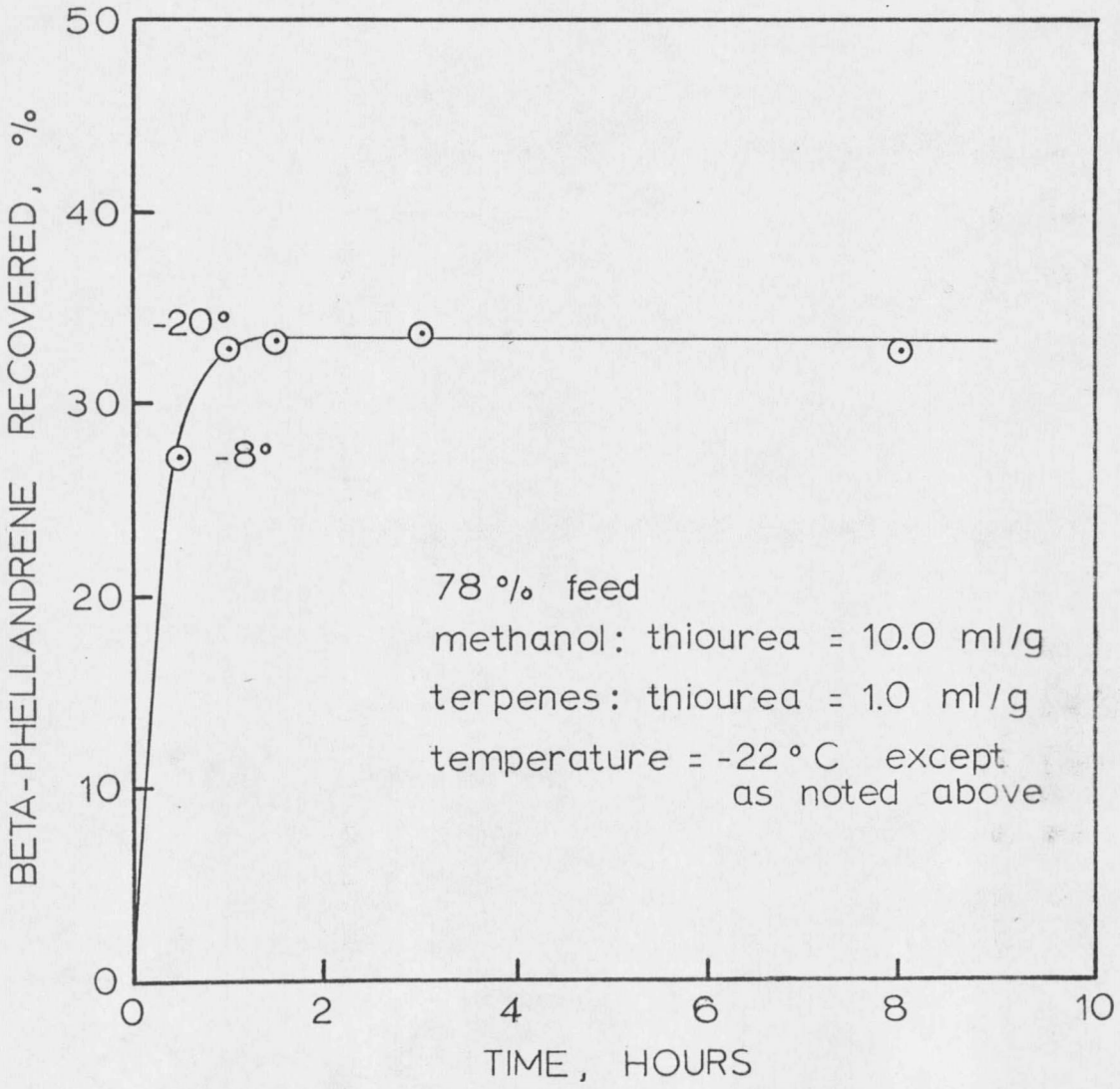


Figure 3. The Effect of Run Time on Recovery of Beta-phellandrene.

Runs could be made with an excess of thiourea so that initially there is solid thiourea present in the mixture. In this case an increase in recovery with time could be expected, as solid thiourea would be dissolved and then incorporated into forming adduct crystals. Later runs made use of this method.

Effect of the Thiourea to Terpene Ratio

It was pointed out that the thiourea-beta-phellandrene adducts have a terpene to thiourea ratio which can vary. Therefore, one important variable in the crystallization step could be the ratio of terpenes to thiourea charged to the crystallizer. The investigation of this variable was performed by making a series of runs varying only the ratio of volume of terpenes to weight of thiourea charged. Another series of runs using a different terpene feed purity was then made, again varying the terpene to thiourea ratio.

The results obtained from varying the terpene to thiourea ratio are shown graphically in Figure 4. It can be noted that separate curves were obtained for both feed purities, and in each case there is an optimum terpene to thiourea ratio which maximizes the percent recovery of beta-phellandrene. Also, the feed of higher purity reaches an optimum recovery at a lower terpene to thiourea ratio than does the lower purity feed. The optimum ratio of terpenes to thiourea charged to the crystallizer appears to be a function of feed purity.

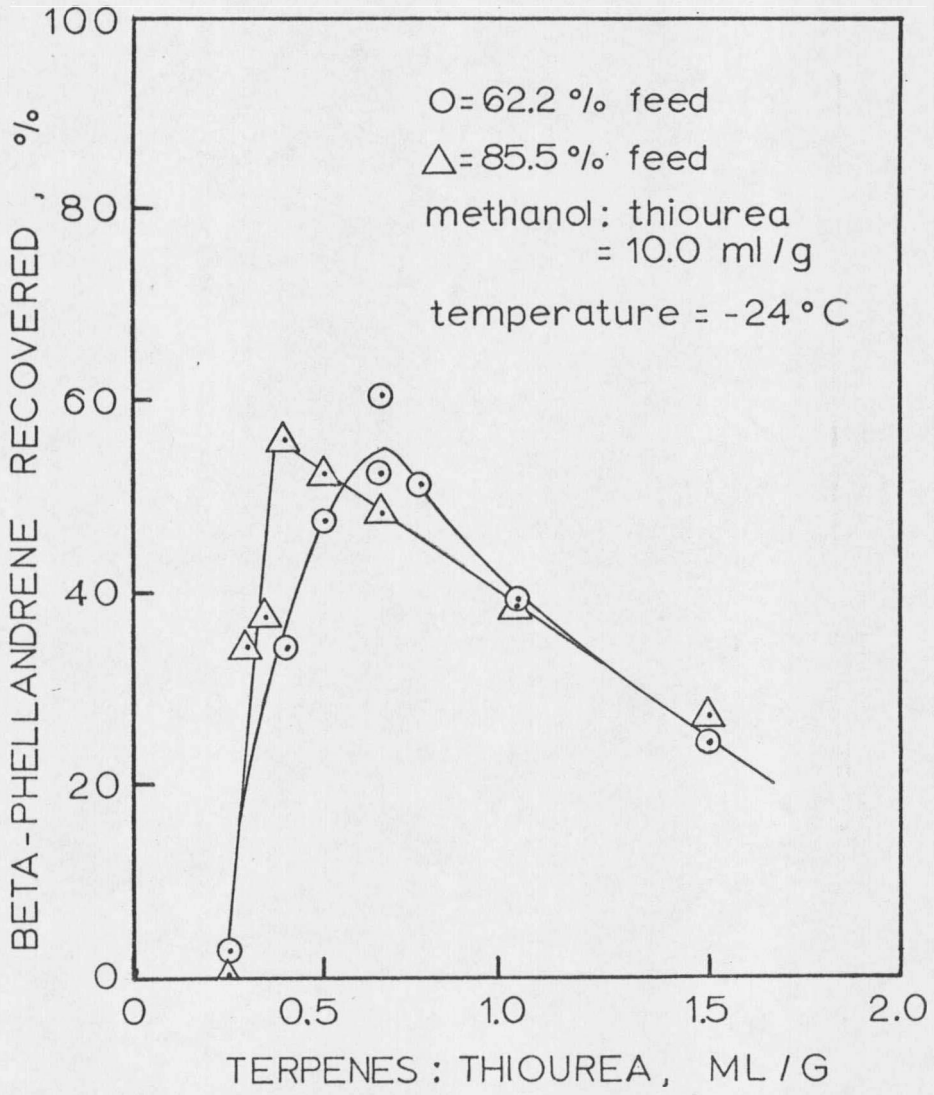


Figure 4. The Effect of The Terpene to Thiourea Ratio on Recovery of Beta-phellandrene.

By using different feed purities, the amount of beta-phellandrene in proportion to the other terpene compounds was different for the two series of runs. By plotting the percent recovery as a function of the beta-phellandrene to thiourea ratio, a single optimum should be found if this ratio was controlling the recovery in the two series of runs. Figure 5, a plot of the percent recovery as a function of the beta-phellandrene to thiourea ratio indeed shows that the optimum ratio is essentially the same for the two series of runs. It can be noted from Figure 5 that the optimum value for the beta-phellandrene to thiourea ratio is 0.35 mls/gram. Also note that there appears to be a minimum value for the ratio below which no recovery is obtained. A value of approximately 0.17 mls/gram is required for adduct formation, and hence recovery, to occur in this case.

In further runs a value of 0.35 mls/gram for the beta-phellandrene to thiourea ratio was used in the hope of obtaining a more nearly optimized recovery.

It should be noted that the use of large excesses of beta-phellandrene in the feed, as evidenced by a high beta-phellandrene to thiourea ratio in Figure 5, tends to decrease the percent recovery.

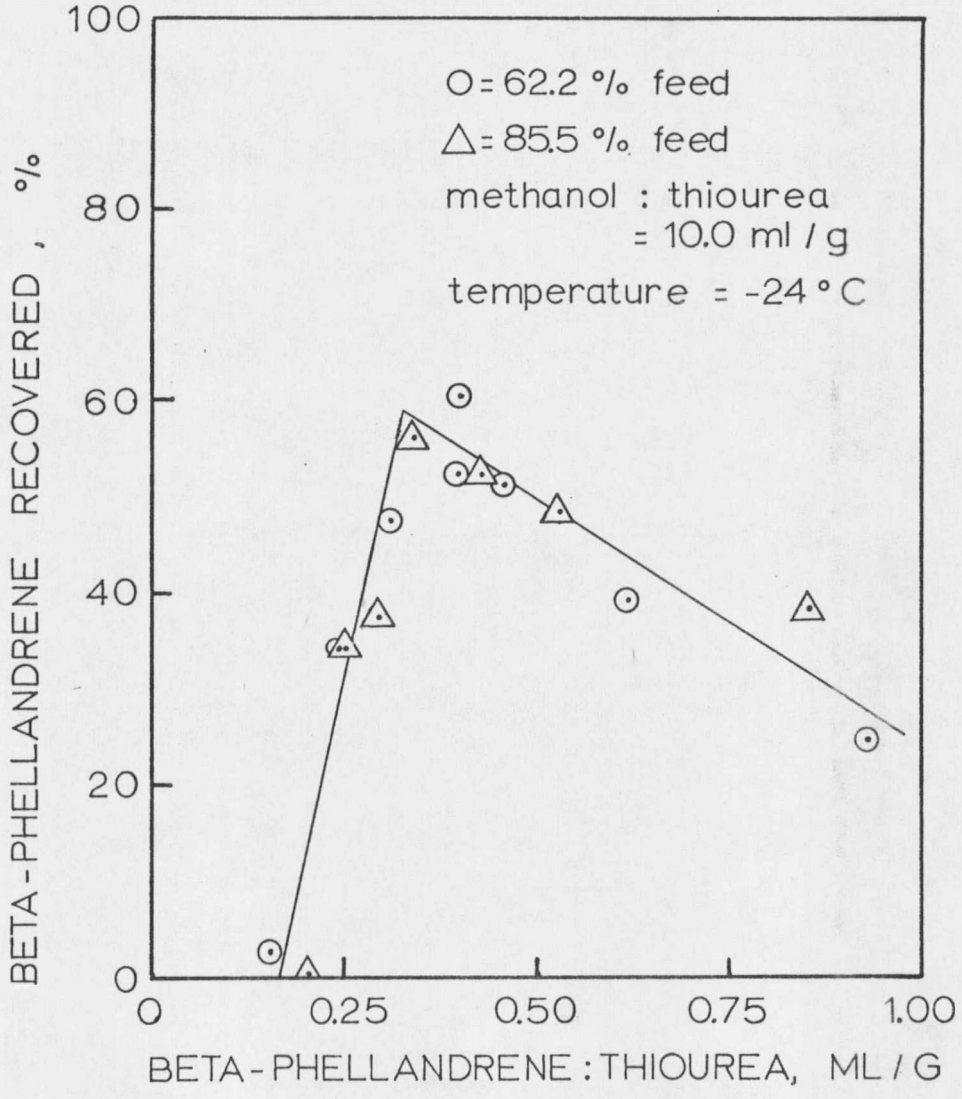


Figure 5. The Effect of the Beta-phellandrene to Thiourea Ratio on Recovery of Beta-phellandrene.

Effect of the Solvent to Thiourea Ratio

In the preparation of the adduct crystals by a finite amount of cooling, a certain amount of thiourea and beta-phellandrene is left in the solvent after filtration of the crystals. It would be desirable to minimize the amount of residual thiourea and beta-phellandrene in order to decrease the amount of residue which must be recycled back through the separation process or discarded. One method which could be used to minimize the residue would be to minimize the amount of solvent used per crystallization.

Several runs were performed to investigate the effect of decreasing the relative amount of solvent (methanol in this case). Table III summarizes the results of those runs.

Table III. The Effect of Decreasing the Solvent to Thiourea Ratio

Run	Methanol to Thiourea, ml/g	% Recovery of Beta-phellandrene	Product Purity, % Beta-phellandrene
36	10.0	56.1	95.0
42	5.0	69.5	91.1
43	3.0	81.0	89.6

temperature = -24°C
beta-phellandrene to thiourea = 0.341 mls/g
feed = 85.2% beta-phellandrene

Table III shows that decreasing the methanol to thiourea ratio or use of less methanol relative to the other reagents increases the

recovery of beta-phellandrene. It was found that decreasing the ratio (methanol:thiourea) below 3.0 ml/gram caused problems in mixing and agitation due to the high content of solids in the mixture. The recovery of beta-phellandrene, however, greatly increases with decreasing methanol:thiourea ratio.

It should also be noted from Table III that as the amount of solvent is decreased, the product purity also decreases. This is an expected result, as decreasing the volume of solvent should increase the concentration of non-adduct-forming terpenes in the solvent for a given amount of terpene feed. Since the solvent then contains more of the impurity terpenes, the adduct crystals will tend to contain a less pure product.

Effect of Solvent

A number of runs were performed to determine the best type of solvent to use in the crystallization liquor. It has been noted that hydrogen bonding is one potential mechanism in the formation of thiourea adducts; hence, hydrogen bonding could be an important phenomenon in choosing a good solvent for the process. Initial qualitative tests showed that the recovery of beta-phellandrene from the primary alcohols as solvents decreased in the order 1) methanol, 2) ethanol, 3) propanol. From these tests it appears that increasing alkane character in the solvent decreases recovery. The next

likely solvent tried was water, being the next compound beyond methanol with decreasing alkane character in the primary alcohol series. No adduct formation was observed to take place with water as the solvent, probably due to the fact that the terpenes are insoluble in water. Also, the freezing point of the water-thiourea-terpene mixture does not permit sufficient cooling to be of use in the process.

A variety of organic compounds were tried as solvents but none of those tried appeared to work as well as methanol in the crystallization. Since methanol indeed appeared to be the best solvent for the process, it was decided to use methanol as the base solvent and treat it with various other compounds to determine if an improved solvent could be obtained through a mixture. It was also hoped to gain some insight on the effect of hydrogen bonding in the solvent, so additives from five classes of hydrogen bonding compounds (1) were tried. The additive compounds were mixed with methanol in a given proportion, then the recovery with the solvent was compared to the recovery expected for the volume-averaged recovery between pure solvent methanol and pure additive. Table IV shows the results of this investigation.

From Table IV it can be noted that the class I and II hydrogen bond formers (1) gave no enhancement of recovery, as they merely

acted as diluents. Methanol is a class II compound, so one could reasonably expect no interaction between compounds of this class. Both class I and II compounds are those which contain hydroxyl (-OH) groups which can actively participate in hydrogen bonding. Two of the three class III additives tried gave increased recovery over pure methanol. The class III compounds are those which contain a donor atom of oxygen, nitrogen, or fluorine. Of the two compounds which improved the recovery, the dimethyl sulfoxide solvent yielded an adduct with essentially the same terpene composition as the terpene feed. A large amount of dimethyl sulfoxide was also observed to be released from the adduct crystals during the decomposition step. These observations point to the probability that the dimethyl sulfoxide formed an adduct with the thiourea, carrying the terpenes into the adduct structure in a non-selective fashion.

It was found that through the use of acetone as an additive to methanol, a higher recovery could be obtained than with either pure methanol or the volume-averaged recovery between pure methanol and pure acetone. Figure 6 shows the relation between the recovery of beta-phellandrene and the amount of acetone as an additive to methanol in the solvent phase. It can be noted that for acetone concentrations of 30 to 60 volume %, the recovery of beta-phellandrene is increased in the order of ten percent over pure methanol.

Table IV. The Effect of Various Additives on the Recovery of Beta-phellandrene.

Compound Added to Methanol (50 vol %)	Hydrogen Bonding Class (1)	Recovery Enhancement
ethylene glycol	I	(0)
ethyl alcohol	II	(0)
isopropyl alcohol	II	(0)
acetone	III	(+)
dimethyl sulfoxide	III	(+)
methyl ethyl ketone	III	(-)
methylene chloride	IV	(-)
n-heptane	V	(-)

Relative Scale:

(0) = no enhancement of recovery.

(+) = recovery increased over volume-averaged value between pure methanol and pure additive.

(-) = recovery decreased over volume-averaged value.

Class I is strongest hydrogen bond former.

Class V forms no hydrogen bonds. (1)

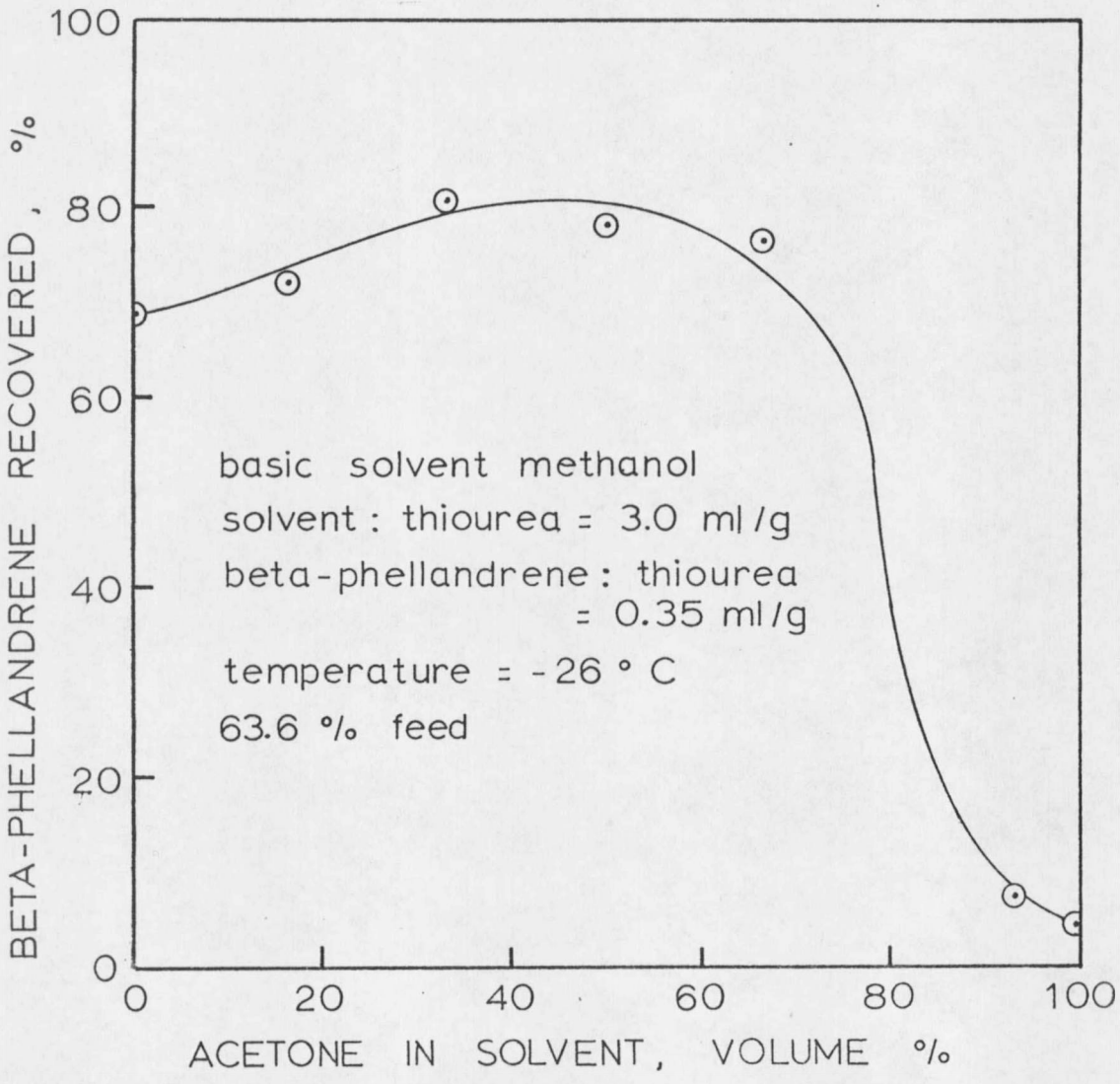


Figure 6. The Effect of Acetone as an Additive to Methanol on Recovery of Beta-phellandrene.

Table V shows that acetone also improves the recovery when ethanol is used as the base solvent.

Table V. The Effect of Acetone as an Additive to Ethanol and Methanol. (Feed purity = 63.6%)

Base Solvent	Base Solvent, 100%		50 Volume % Acetone	
	Recovery, %	Product Purity, %	Recovery, %	Product Purity, %
methanol	68.7	81.2	78.4	79.6
ethanol	53.2	83.1	72.6	81.0

It is evident that acetone effectively increases the recovery in the crystallization step. No attempt was made to investigate the mechanism of this recovery enhancement. One potential mechanism is that the acetone reduces the number of active hydrogen atoms engaged in hydrogen bonding, assuming that there is some optimum level of hydrogen bonding for the formation of adduct crystals. This could be accomplished by the coordination of the donor atom of oxygen on the acetone molecule to the active hydrogen atom on the methanol molecule.

Further work in the investigation of various solvent systems could lead to even better solvents for increasing recovery.

Adduct-Residue Equilibrium

Using the optimum conditions found for the variables, an equilibrium curve was constructed to show the relationship between the percentage of beta-phellandrene in the adduct-included terpenes and the residual terpenes. The equilibrium curve is shown in Figure 7. Note that significant increases in the percentage of beta-phellandrene in the adduct crystals can be obtained over the percentage in the residue phase.

The variation in the curvature of the plot can be explained on the basis of feed composition. The points on the graph with residue compositions below 30% beta-phellandrene were obtained by using a feed enriched with a dipentene sample. This sample contained impurities not found in the other runs. Most of these impurities were excluded in the adduct crystals, but some of the terpene impurities, thought to be the alpha- and beta-pinenes, were enriched in the adduct. The points on the graph between 30 and 85 percent beta-phellandrene in the residue were obtained through stepwise use of terpene products from lower purity runs. In this residue composition range, various amounts of para-cymene were present in the feed and hence in the residue (and adducts to a lesser degree). The para-cymene was rapidly excluded from the adducts as progressively purer crystallization feeds were obtained. At feed composi-

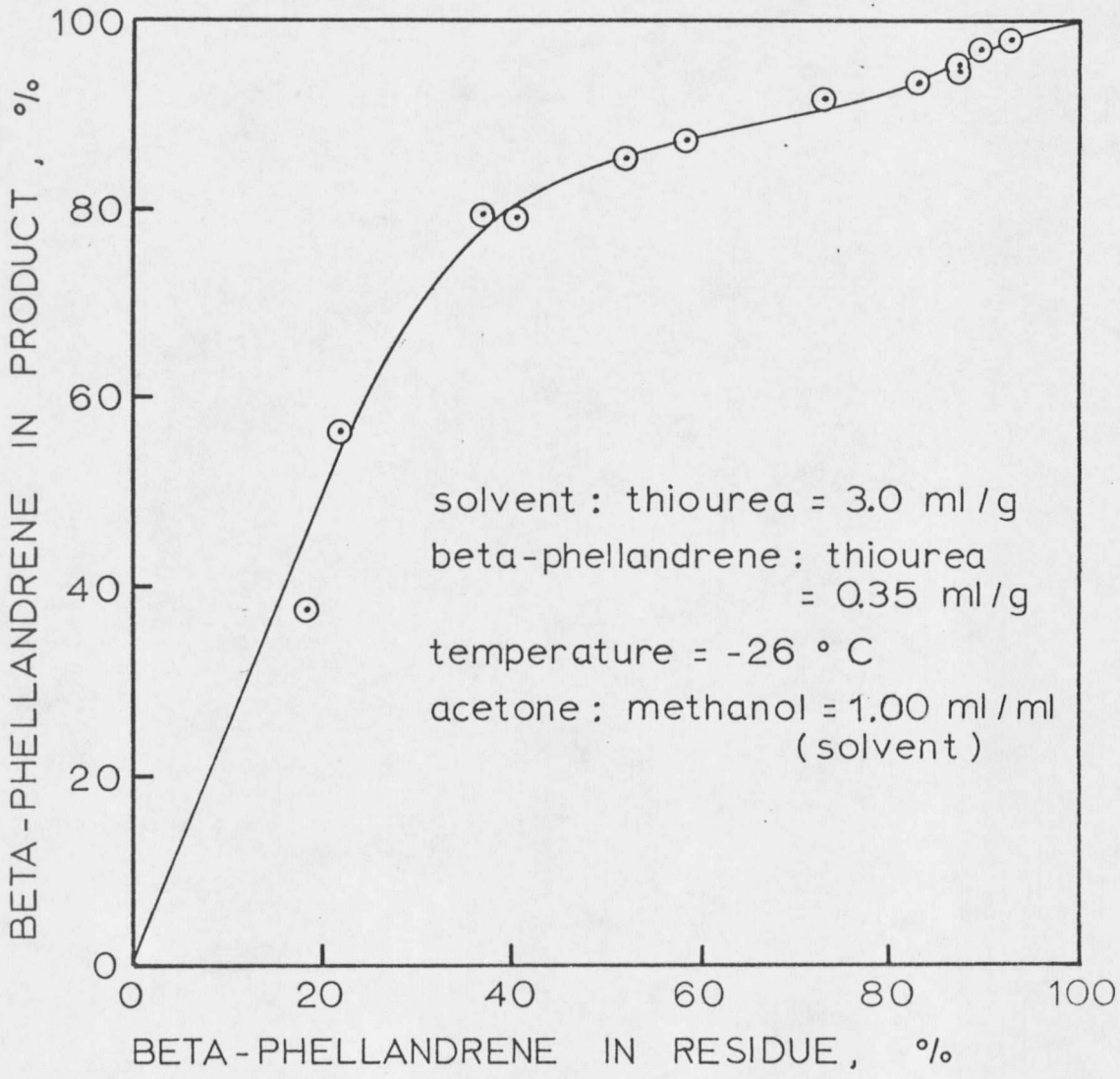


Figure 7. The Equilibrium of Beta-phellandrene Between Adduct and Residue.

tions above 85% beta-phellandrene, no para-cymene was present. The portion of the curve above the residue composition of 30% represents the actual enriching effect obtained when starting with the original three-component wood-pulp turpentine cut previously described.

Results of Optimization

During the first runs performed in this investigation, it was found that recoveries of beta-phellandrene were on the order of 30%. Four successive crystallizations were required to raise the beta-phellandrene purity from 63.1% to 98.1%. Thus, the overall recovery in this process would be $(.30)^4$, or 0.8%. This value assumes no recycle of residue from the crystallization steps.

Through the use of the optimal values found for operating the process, it was found that recoveries of beta-phellandrene could consistently be raised to 75%, and indeed higher. At these conditions, six crystallizations were required to raise the beta-phellandrene purity from 63.6% to 98.2%. The overall recovery in this case would be $(.75)^6$, or 17.8%, assuming no recycle of filtrate. This is a better than 22-fold increase in overall recycle-free recovery from the initial tests.

In a large-scale process, of course, recycle of residues would be performed. This would increase the overall recovery even more. The process, whether continuous or stepwise-batch, would best be operated using the highest recovery possible and the least number of crystallization stages possible for a given product purity. Since it was found that increasing the recovery per crystallization was at the expense of selectivity (hence, product purity), it can be generalized that increasing recovery would necessitate the addition of more ideal crystallization stages to the process.

In a batch-wise process, addition of more crystallization stages would be costly in terms of equipment and processing time. Therefore, the desirability of a continuous process is clearly evident. No attempt, however, was made in this investigation to devise such a continuous process.

Summary

The process of extractive crystallization using thiourea has been shown to be an effective method of obtaining high-purity beta-phellandrene from a dipentene cut of crude sulfate turpentine. The method utilizes a solvent, thiourea, and a terpene feedstock in a crystallizer capable of cooling the mixture lower than 29°C. Recovery of beta-phellandrene from the terpene feedstock is dependent

on temperature, the thiourea to terpene ratio, the solvent to thiourea ratio, and the type of solvent used. By using proper values for these variables, recovery of beta-phellandrene from a single crystallization can consistently be held at 75% without recycle of residual solutions.

Beta-phellandrene, previously unavailable in purified form from turpentine sources, can now be purified using this method. Previous separation methods utilizing distillation were incapable of effecting a highly pure separation of beta-phellandrene due to the presence of other close-boiling compounds. The extractive crystallization process, however, effectively presents purified beta-phellandrene as a new chemical raw material to industry. Should a demand develop for this purified terpene after its evaluation by potential users, the extractive crystallization method using thiourea could prove to be a valuable industrial separation technique for beta-phellandrene.

CONCLUSIONS

Based on the experimental results, a number of conclusions regarding the separation of beta-phellandrene via extractive crystallization with thiourea may be drawn.

1) The use of thiourea as an agent for the extractive crystallization of beta-phellandrene is a feasible method for purifying beta-phellandrene to concentrations greater than 98%.

2) When a 3-component dipentene cut consisting of beta-phellandrene, dipentene, and para-cymene is used as a feed, para-cymene is excluded from the adduct most rapidly, followed by dipentene, while beta-phellandrene is enriched.

3) Adduct crystals of beta-phellandrene and thiourea will form at temperatures below 29°C.

4) Lower temperatures during the extractive crystallization step favor the recovery of beta-phellandrene.

5) In the batch crystallization of the adduct from a saturated solution where no solid thiourea is present, the best time for filtration of the crystals is when the lowest temperature allowed by the equipment is reached (tested to temperatures of -24°C).

6) There exists an optimum thiourea to terpene ratio for maximizing the recovery of beta-phellandrene in a given crystallization.

This optimum ratio is a function of beta-phellandrene feed purity, which demonstrates that there is also an optimum beta-phellandrene to thiourea ratio for maximizing recovery.

7) Decreasing the amount of solvent used in the crystallization step tends to increase the recovery of beta-phellandrene.

8) The type of solvent used in the crystallization step greatly affects the recovery of beta-phellandrene. Generally, the primary alcohols are the best pure solvents, with methanol the best of the group.

9) When acetone is added to methanol as a solvent, recoveries from the resulting mixed solvent are significantly increased over those resulting from methanol alone. This increase in recovery is also noted for ethanol-acetone mixtures.

10) Generally, from the batch crystallizations, increases in recovery of beta-phellandrene significantly decrease the purity of beta-phellandrene in the adduct crystals. Greatest enrichment of beta-phellandrene per crystallization occurs at lowest recovery.

11) Using the best values found for the variables in the crystallization step, recoveries of beta-phellandrene as high as 75% can consistently be obtained from a single crystallization step.

RECOMMENDATIONS FOR FURTHER WORK

This investigation has opened the door to a new separation process as applied to the utilization of the dipentene cut obtained from crude sulfate turpentine. The separation of beta-phellandrene from the dipentene cut may now be performed by a non-distillation method, making this compound available in pure form. Since the process of extractive crystallization with thiourea has been shown to be a feasible method for purifying beta-phellandrene, further work is warranted to develop both the separation process and uses for the product. The following are areas of interest for future work.

1) Samples of purified beta-phellandrene should be supplied to various firms which could have potential uses for the compound. Companies engaged in work involving flavors and fragrances would probably be the most likely potential users. As only small samples are needed for this type of evaluation, a large volume of purified beta-phellandrene is not required for this phase of investigation.

2) The application of a continuous process for performing the separation should be investigated. Continuous processes using urea and thiourea adducts for separations are now in operation in industry. Possibly, such a method utilizing thiourea could be suited for the separation of beta-phellandrene from turpentine.

3) Other solvents should be tried for the crystallization of the adducts. With the wide variety of solvents available, a solvent better than the acetone-methanol mixture could possibly be found. Of interest in this area would be quantitative evaluation of hydrogen bonding in the solvent as to its effect on adduct formation.

4) Further optimization of operating variables could increase the recovery even more. In particular, inter-variable effects were not extensively investigated, and work in this area could prove fruitful.

APPENDICES

OTHER THIOUREA-TERPENE ADDUCTS

As was noted in the Introduction and Background section, three compounds present in the original sulfate turpentine were found to form thiourea adducts. This thesis describes the utilization of the adduct with beta-phellandrene. Alpha-pinene and beta-pinene also form adducts with thiourea, the beta-pinene being previously unreported.

The following are summaries of tests for alpha- and beta-pinene adducts:

Alpha-pinene Adduct:

200 ml methanol, 20.0 g thiourea, and 30.0 ml alpha-pinene were mixed in a flask. The resulting solution was placed in a freezer at -15°C for approximately 12 hours. White needle-like adduct crystals formed, which were removed by filtration. Decomposition of the crystals by steam stripping yielded 6.3 mls of alpha-pinene.

Beta-pinene Adduct:

200 ml methanol, 20.0 g thiourea, and 30.0 ml beta-pinene were mixed in a flask. The resulting solution was placed in a freezer at -15°C for approximately 12 hours. White needle-like crystals were formed. (The crystals were larger and thicker than

those noted for the alpha-pinene adduct.) Removal of the crystals by filtration, and subsequent decomposition of the crystals by steam stripping yielded 7.6 mls of beta-pinene.

DATA ON THE PROPERTIES OF BETA-PHELLANDRENE

A sample of beta-phellandrene of 99.3% purity (determined by gas-liquid chromatography) was used in obtaining the following data:

Appearance:

A water-clear liquid, comparable in viscosity to a very light oil. The smell is pleasant, described by the author as somewhere between citrus and licorice.

Infrared Spectra:

The infrared spectra, shown in Figure 8, agrees with the spectra obtained for beta-phellandrene by Mitzner, et al., (see Applied Spectroscopy 19, No. 6, 169, (1965).) The sample obtained by Mitzner was through a synthetic route.

Specific Rotation:

The specific rotation of the undiluted sample was: $[\alpha]_D^{20} = -17.5°$. As previously reported, beta-phellandrene obtained from turpentine is indeed levoratatory.

Refractive Index:

The refractive index, obtained at 20°C with a white light source, was $n^{20} = 1.4865$.

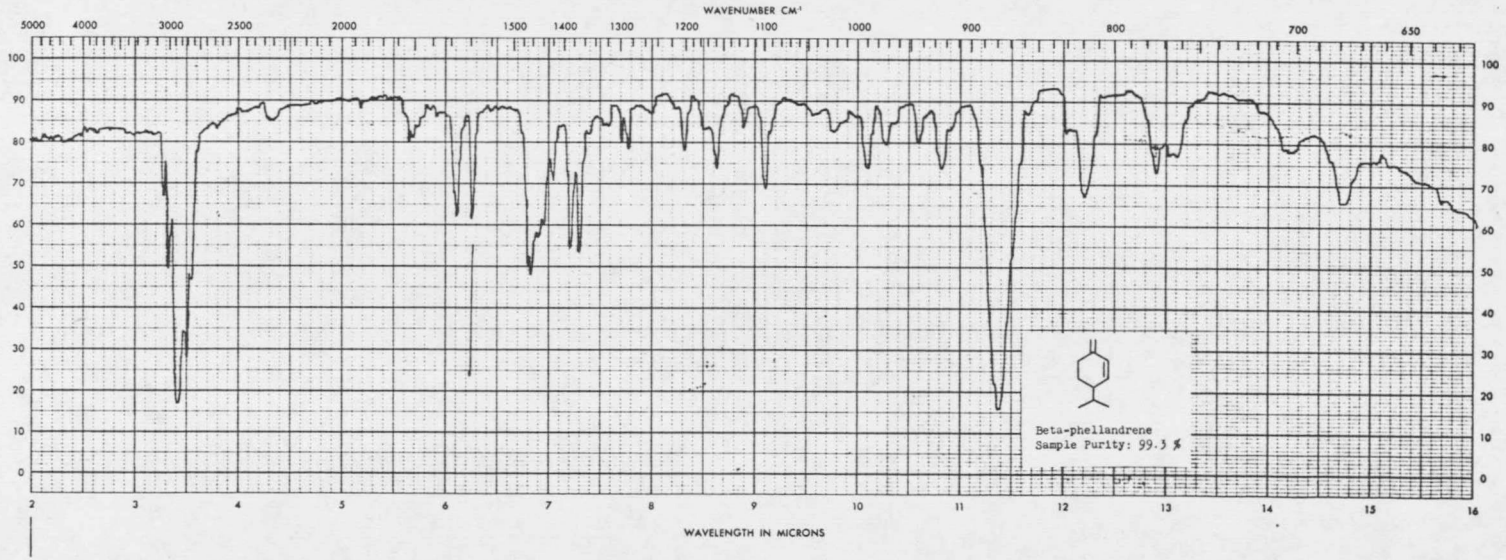


Figure 8. The Infrared Spectrum of Beta-phellandrene.

Freezing Point:

The freezing point, determined by cooling the sample with liquid nitrogen and monitoring the temperature with an iron-constantan thermocouple, was -116°C.

Density:

Measured at 20°C, the density of the sample was 0.8430 g/ml.

Table VI. A Summary of the Experimental Data. (B = Beta-phellandrene, D = Dipentene, and P = Para-Cymene.)

run	time hr	temp °C	FEED CHARGE solvent ml, type	thio-urea g	ter-pene ml	B %	D %	P %	ADDUCT wt. g	ter-pene ml	B %	D %	P %
B1	—	-15	200 EtOH	11.0	16	35.5	51.3	13.1	7.28	1.6	64.9	35.1	0
B2	—	-15	200 EtOH	11.0	25	33.8	51.3	13.0	9.40	2.8	64.4	34.0	1.6
2B2	—	—	— EtOH	—	—	60.1	37.9	2.0	—	—	79.7	20.3	0
BII	—	—	50 EtOH	5.0	5	60.1	37.9	2.0	2.73	1.3	79.5	20.5	0
BIII	—	—	300 EtOH	30.0	50	63.1	25.8	9.3	30.7	9.7	85.7	13.5	0.8
BIV	—	—	100 EtOH	10.0	10	81.6	17.0	0.8	9.8	2.8	90.6	8.7	0
R80	—	—	200 EtOH	20.0	20	77.8	18.1	2.5	19.8	5.9	87.7	11.2	0
R81	—	—	500 EtOH	50.0	30	81.4	17.8	0	—	—	88.3	10.9	0
L1	—	—	100 EtOH	10.0	10	45.8	46.9	6.2	—	—	62.5	31.1	0
R90	—	—	300 EtOH	30.0	20	88.8	10.3	0	—	—	95.6	4.0	0
L2	—	—	100 EtOH	10.0	10	34.7	60.4	4.9	—	—	54.7	45.3	0
R95	—	—	300 EtOH	30.0	20	92.3	7.2	0	—	7.7	98.1	1.6	0
Z1	—	—	100 EtOH	10.0	15	22.0	44.0	17.5	—	—	36.4	33.0	8.3
Z2	—	—	100 EtOH	10.0	15	17.3	45.8	18.8	—	—	27.6	37.5	6.9

Table VI. (Continued)

run	time hr	temp °C	FEED CHARGE solvent ml, type	thio-urea g	ter-pene ml	B %	D %	P %	ADDUCT wt. g	ter-pene ml	B %	D %	P %
1	5	-6	1000 MeOH	100	100	63.1	25.8	9.3	—	7.5	86.1	13.4	tr.
2	1.5	12	1000 MeOH	100	100	63.1	25.8	9.3	28.1	4.6	84.1	15.9	tr.
3	5.5	12	1000 MeOH	125	100	63.1	25.8	9.3	63.8	10.2	85.9	13.2	0
4	3	8	1000 EtOH	125	100	63.1	25.8	9.3	89.9	8.5	83.2	13.2	1.7
5	12	-1	1000 MeOH	125	100	63.1	25.8	9.3	86.9	25.6	83.0	14.8	0
6	18.2	10	1000 MeOH	125	100	63.1	25.8	9.3	60.0	10.0	—	—	—
7	5	0	1000 MeOH	125	100.0	63.1	25.8	9.3	51.7	—	—	—	—
8	8.5	-6.4	200 MeOH	20	20	78.0	19.6	2.4	13.5	3.8	91.0	8.2	0
9	8.2	-23.8	200 MeOH	20	20	78.0	19.6	2.4	18.2	5.7	91.1	8.1	tr.
10	8	-0.8	200 MeOH	20	20	78.0	19.6	2.4	12.6	3.8	90.0	9.0	tr.
11	8	16.8	200 MeOH	20	20	78.0	19.6	2.4	5.34	1.4	90.5	8.7	tr.
12	—	29	200 MeOH	20	20	78.0	19.6	2.4	0	0	—	—	—
13	42	-22	200 MeOH	20	7	94.2	6.0	0	11.6	1.0	96.7	2.4	0
14	8	-23.5	200 MeOH	20	20	89.0	10.2	0	19.0	6.1	95.5	3.5	0

Table VI. (Continued)

run	time hr	temp °C	FEED CHARGE solvent ml, type	thio-urea g	ter-pene ml	B %	D %	P %	ADDUCT wt. g	ter-pene ml	B %	D %	P %
15	—	27	200 MeOH	20.0	20	61.9	27.1	9.6	0	0	—	—	—
16	—	26	200 MeOH	20.0	20	18.2	51.5	16.2	0	0	—	—	—
17	1.5	-22	200 MeOH	20.0	20	78.0	19.6	2.4	18.15	5.7	91.0	—	—
18	3.0	-22	200 MeOH	20.0	20	78.0	19.6	2.4	21.32	5.9	89.0	10.1	0
19	1.0	-19.6	200 MeOH	20.0	20	78.0	19.6	2.4	19.83	5.8	88.4	11.24	0
20	0.5	-7.2	200 MeOH	20.0	20	78.0	19.6	2.4	8.64	0	—	—	—
21	0.5	-8.0	200 MeOH	20.0	20	78.0	19.6	2.4	—	4.8	83.1	14.3	1.3
22	2	-24	200 MeOH	20.0	20	62.2	27.9	9.1	18.55	5.8	84.2	14.4	0.3
24	2.25	-24.5	200 MeOH	20.0	10	62.2	27.9	9.1	18.56	3.6	82.5	14.8	1.5
25	2	-21	200 MeOH	20.0	30	62.2	27.9	9.1	16.35	3.2	88.0	11.2	0.8
26	2.25	-24	200 MeOH	20.0	5	62.2	27.9	9.1	11.09	0.1	85.0	—	—
27	3.0	-23.4	200 MeOH	20.0	30	62.2	27.9	9.1	18.93	5.2	86.9	11.8	0.5
28	3.2	-24.5	200 MeOH	20.0	15	62.2	27.9	9.1	21.93	5.8	82.7	14.9	1.4
29	1.2	-24.3	200 MeOH	20.0	18	62.2	27.9	9.1	13.54	2.0	85.0	12.7	0.4

Table VI. (Continued)

run	time hr	temp °C	FEED CHARGE solvent ml, type	thio-urea g	ter-pene ml	B %	D %	P %	ADDUCT wt. g	ter-pene ml	B %	D %	P %
30	1.8	-28	200 MeOH	20.0	13	62.2	27.9	9.1	—	5.7	81.5	16.1	1.3
31	1.5	-22	200 MeOH	20.0	13	62.2	27.9	9.1	15.07	3.8	85.0	—	—
32	3.0	-26	200 MeOH	20.0	13	62.2	27.9	9.1	—	6.1	80.3	16.4	2.3
33	1.5	-24.5	200 MeOH	20.0	13	62.2	27.9	9.1	17.92	5.1	82.9	15.3	1.1
34	2.5	-24	200 MeOH	20.0	13	85.2	13.4	0.6	—	5.8	91.8	6.8	0
35	3.5	-24	200 MeOH	20.0	10	85.2	13.4	0.6	18.33	4.8	93.0	5.9	0
36	2.0	-24.4	200 MeOH	20.0	8	85.2	13.4	0.6	—	3.9	95.0	3.9	0
37	2.0	-24.4	200 MeOH	20.0	5	85.2	13.4	0.6	—	0	—	—	—
38	2.3	-24	200 MeOH	20.0	20	85.2	13.4	0.6	—	7.0	92.7	6.2	0
39	1.2	-24.4	200 MeOH	20.0	6	85.2	13.4	0.6	—	1.9	92.3	6.4	0
40	2.3	-25.2	200 MeOH	20.0	30	85.2	13.4	0.6	—	7.9	92.5	6.4	0
41	3.0	-24.0	200 MeOH	20.0	7	85.2	13.4	0.6	13.54	2.4	93.5	5.2	0
42	2.0	-24.2	150 MeOH	30.0	12	85.2	13.4	0.6	—	7.8	91.1	7.3	0
43	1.5	-24.0	150 MeOH	50.0	20	85.2	13.4	0.6	—	15.4	89.6	10.4	0

Table VI. (Continued)

run	time hr	temp °C	FEED CHARGE solvent ml, type	thio-urea g	ter-pene ml	B %	D %	P %	ADDUCT wt. g	ter-pene ml	B %	D %	P %
44	–	–	150 MeOH	75.0	30	85.2	13.4	0.6	–	20.2	88.2	11.0	0
46	–	-22.0	150 EtOH	50.0	27.5	63.6	27.2	7.8	–	10.2	82.4	17.0	0.4
47	9.5	-17.1	150 MeOH	50.0	27.5	63.6	27.2	7.8	–	13.4	84.4	10.1	5.0
48	–	-19.0	75 MeOH 75 H_2O	50.0	27.5	63.6	27.2	7.8	–	–	68.1	25.6	6.3
49	–	0	100 MeOH 50 H_2O	50.0	27.5	63.6	27.2	7.8	–	3.3	78.9	18.8	1.5
50	–	-7	125 MeOH 25 H_2O	50.0	27.5	63.6	27.2	7.8	–	17.6	73.6	21.4	4.3
51	4.5	-24.5	50 MeOH 100 Acetone	50.0	27.5	63.6	27.2	7.8	–	16.6	80.5	16.2	2.5
52	4.7	-26	150 Acetone	50.0	27.5	63.6	27.2	7.8	–	1.0	76.0	19.8	3.8
53	5	-26	140 Acetone 10 MeOH	50.0	27.5	63.6	27.2	7.8	–	1.5	87.5	11.7	tr.
54	4	-26	100 MeOH 50 Acetone	50.0	27.5	63.6	27.2	7.8	–	17.2	82.2	16.1	0.9
55	2.5	-28	150 MeOH	50.0	27.5	63.6	27.2	7.8	–	14.8	81.2	16.7	2.2
56	2.2	-27	25 Acetone 125 MeOH	50.0	27.5	63.6	27.2	7.8	–	15.4	81.8	15.5	2.1
57	2.6	-26.5	75 MeOH 75 Acetone	50.0	27.5	63.6	27.2	7.8	–	17.2	79.6	16.3	3.3
58	3.0	–	75 Et Glycol 75 MeOH	50.0	27.5	63.6	27.2	7.8	–	8.0	85.1	12.7	1.8

Table VI. (Continued)

run	time hr	temp °C	FEED CHARGE solvent ml, type	thio-urea g	ter-pene ml	B %	D %	P %	ADDUCT wt. g	ter-pene ml	B %	D %	P %
59	—	-26	75 MeOH 75 CH_2Cl_2	50.0	27.5	63.6	27.2	7.8	—	1.4	91.3	8.3	tr.
60	1.8	-27	75 MeOH 75 n-heptane	50.0	27.5	63.6	27.2	7.8	—	1.8	91.2	8.8	tr.
61	3.5	-27	75 MeOH 75 EtOH	50.0	27.5	63.6	27.2	7.8	—	13.2	84.3	15.7	0
62	4.8	-26	75 MeOH 75 MEK	50.0	27.5	63.6	27.2	7.8	—	3.5	72.3	17.3	10.4
63	7	-26	75 MeOH 75 DMSO	50.0	27.5	63.6	27.2	7.8	—	13.1	64.9	25.9	9.2
64	4.0	-26	75 MeOH 75 1-PrOH	50.0	27.5	63.6	27.2	7.8	—	6.7	86.8	13.2	tr
65	5.7	-26	75 EtOH 75 Acetone	50.0	27.5	63.6	27.2	7.8	—	15.7	81.0	16.5	2.5
66	4.7	-26	150 EtOH	50.0	27.5	63.6	27.2	7.8	—	11.2	83.1	15.5	1.4
67	39	-27	75 MeOH 75 Acetone	50.0	27.5	90.3	9.7	tr.	—	13.5	93.5	6.5	0
68	9.6	-26	75 MeOH 75 Acetone	50.0	22.4	78.1	18.6	2.1	—	15.2	87.5	12.5	0
69	4.5	-26	75 MeOH 75 Acetone	50.0	18.9	92.5	6.2	0	—	11.5	95.7	3.4	0
70	17.2	-23	75 MeOH 75 Acetone	50.0	48.4	36.2	39.4	13.4	—	19.7	56.7	25.6	3.4
71	24	-27.5	75 MeOH 75 Acetone	50.0	18.9	92.5	6.2	0	—	12.8	94.8	4.1	0
72	96	-26	75 MeOH 75 Acetone	50.0	23.4	74.9	21.0	3.2	—	16.0	85.5	13.9	0

Table VI. (Continued)

run	time hr	temp °C	FEED CHARGE solvent ml, type	thio-urea g	ter-pene ml	B %	D %	P %	ADDUCT wt. g	ter-pene ml	B %	D %	P %
73	24.8	-27	75 MeOH 75 Acetone	50.0	69.7	25.1	46.8	14.7	—	23.9	37.8	38.1	7.0
74	18	-28	75 MeOH 75 Acetone	50.0	20.3	86.1	12.1	0.5	—	14.0	91.9	7.5	0
75	23	-26	75 MeOH 75 Acetone	50.0	27.5	63.6	27.2	7.8	—	16.4	79.3	19.0	1.2
76	63	-22	75 MeOH 75 Acetone	50.0	18.4	95.5	3.9	0	—	14.2	97.2	2.4	0
77	21	-29	75 MeOH 75 Acetone	50.0	18.0	97.2	2.0	0	—	14.6	98.2	0.9	0

LITERATURE CITED

1. Berg, Lloyd. "Azeotropic Distillation." Montana State College Bulletin, 3, No. 2, July, 1948.

2. Bhatnagar, V. M. Clathrate Compounds. Chemical Publishing Co., New York, 1970.

3. Brown, J. F., and White, D. M. J. Amer. Chem. Soc., 82, 5671, (1960).

4. Drew, John, and Pylant, G. D. "Turpentine from the Pulpwoods of the U. S. and Canada." The Glidden Co., Jacksonville, Florida, presented at 51st annual TAPPI Mtg., New York, Feb., 1966.

5. Dubal, G. P. "A Preliminary Investigation of Clathration for the Selection of Monoterpenes." Masters thesis in Chemical Engineering, Montana State University, 1969.

6. Fetterly, L. C. Petroleum Refiner, 36, No. 7, 145, (1957).

7. Fetterly, L. C. "Organic Adducts." Ch. 8, Non-Stoichiometric Compounds, L. Mandelcorn, ed., Academic Press, New York, 1964.

8. Fetterly, L. C. U. S. Patents 2,499,820; 2,520,715; 2,520,716; 1950.

9. Fetterly, L. C. U. S. Patents 2,569,984; 2,569,986; 1951.

10. Guenther, Ernest. The Essential Oils, Vol. II, Van Nostrand Co., New York, 1952.

11. Ibid., Vol. VI.

12. Klouwen, M. H., and Ter Heide, R. Gas Chromatography Inter. Symp., 3, 485-505, (1961).

13. Knight, H. P., L. P. Witnauer, J. E. Coleman, W. R. Noble, and Daniel Swern. Analytical Chemistry, 24, No. 8, (1952).

14. Marschner, R. F. Chemical and Engineering News, 33, 494, (1955).

15. McKay, D. L. U. S. Patent 2,813,851; Nov. 19, 1957. Chem. Abstract 52, 6399, (1958).

16. Newey, H. A., E. C. Shokal, A. C. Mueller, T. F. Bradley, and L. C. Fetterly. Ind. & Engrg. Chem., 42, 2538, (1950).

17. Pinder, A. R. The Chemistry of the Terpenes. Wiley, New York, 1960.

18. Randolf, A. D. Chemical Engineering, 80-96, May 4, 1970.

19. Redlich, O., C. M. Gable, L. R. Beason, and R. W. Millar. J. Amer. Chem. Soc., 72, 4161, (1950).

20. Schiessler, R. W., and D. Flitter. J. Amer. Chem. Soc., 74, 1720, (1952).

21. Schlenk, W. Analyst, 77, 867, (1952).

22. Shreve, R. N. Chemical Process Industries. McGraw-Hill, New York, 1967.

23. Simonsen, J. L. The Terpenes, Vol. I, Cambridge University Press, 1953.

24. Swern, D. "Inclusion Compounds." Encylopedia of Chemical Technology, 1st Suppl. Vol. R. E. Kirk and D. F. Othmer, eds. Wiley, New York, 1957.

25. Swern, D. Ind. and Engrg. Chem., 47, No. 2, 216, (1955).

26. Treybal, R. E. Mass Transfer Operations, 2nd Ed., McGraw-Hill, New York, 1968.

27. Zimmerschied, W. J., R. A. Dinerstein, A. W. Weitkamp, and R. F. Marschner. Ind. and Engrg. Chem., 42, 1300, (1950).