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

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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.

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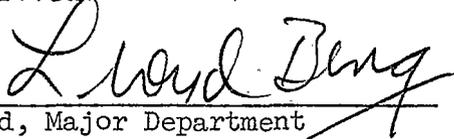fulfillment of the requirements for the degree
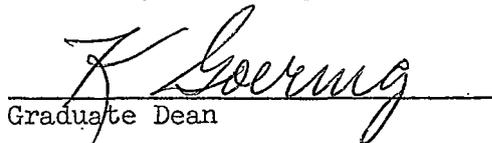
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Chairman, Examining Committee

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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.

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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 tur-
pentine. To effect this separation, the turpentine is usually
distilled under vacuum or in the presence of water (steam distilla-
tion) to minimize the formation of terpene polymers.(17)

Some of the terpene compounds found in Kraft sulfate turpen-
tine 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, di-
pentene, 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 separa-
tion 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
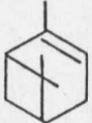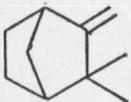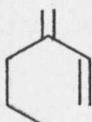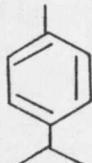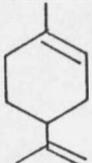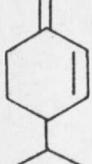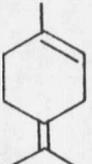
Often a "dipentene cut" is obtained when distilling turpentine. This cut consists of terpenes whose boiling points are close to those of dipentene. Table II shows a typical dipentene cut obtained from distillation of the turpentine listed in Table I.

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 thio-
urea and involving a variety of organic chemicals have been describ-
ed 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 exten-
sive 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 forma-
tion of urea adducts are on the order of those for the adsorption
of hydrocarbons on solid surfaces, and are in the order of the cal-
culated 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 toler-
ance 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-phell-andrene. (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 evalu-
ation 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-phelland-
rene 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 extrac-
tive 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-phelland-rene were more nearly snow-white than the crystals which contained lower purity beta-phellandrene.