

T H E S I S

on

Optically Active Pinenes from Oregon Woods

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This investigation was undertaken for the purpose of studying pinenes obtained from Port Orford cedar oil and Douglas Fir Balsam.

While both of these products are available in Oregon in immense quantities, very little commercial use is made of them at the present time. It is believed that a careful study of each of the chief components of these forest products will yield information which may aid in uncovering industrial uses for a large amount of available and valuable material which is now being wasted.  $\alpha$ -Pinene is one of the stable components which is easily obtained; thus it was decided to begin the work by making a study of this compound.

#### SOURCES OF $\alpha$ -PINENES

$\alpha$ -Pinene is the chief constituent of turpentine. It is a hydrocarbon with the empirical formula  $C_{10}H_{16}$  and contains one double bond. Turpentine then may be defined as an oil which is the chief product of the distillation of the resinous exudations of several species of Pinus. It is a thin colorless liquid, occasionally slightly greenish or yellowish in color and possesses a characteristic odor. At a pressure of 760 mm. Hg. turpentine oil begins to boil at a temperature ranging from  $152^{\circ}$  to  $156^{\circ}C$ . The oil is optically active. The American oil usually has a specific rotation of  $0^{\circ}$  to  $+40^{\circ}$  while the specific rotation of the laevo variety varies from  $0^{\circ}$  to  $-35^{\circ}$ . The European

turpentine oils are usually laevogyrate while the oil from American sources as well as that from Greece, Algiers, and Provence is dextrogyrate,  $+38^{\circ}$  to  $+41^{\circ}$ .

The production of turpentine in America up to the year 1830 was restricted to the southern states: North and South Carolina, Georgia, Alabama, and Virginia. At the present time the production of turpentine in the various states is as follows: Texas, 7 per cent; Mississippi, 9 per cent; Alabama, 12 per cent; Louisiana, 15 per cent; Georgia, 19 per cent; Florida, 37 per cent. The supplies of North and South Carolina, where formerly large quantities were produced, are now less than 1 per cent.

American turpentine is obtained from various species, but chiefly from *Pinus palustris*, Mill., the long-leaf pine, and *Pinus Caribaea*, Morelet, the slash pine. In addition, *Pinus echinata* Miller, the short-leaf pine, *Pinus taeda*, the loblolly pine.

Turpentine oil is produced commercially in France, India, Spain, Portugal, Greece, Italy, Russia, Mexico, and Central America.

The oil is obtained in Oregon from two main sources, namely: Port Orford Cedar wood oil, *Chamaecyparis lawsoniana* (Murr.) Parlatores, and Oregon Balsam obtained from Douglas Fir, *Pseudotsuga taxifolia* (Lamarck) Britton. Other sources for the oil are Larch, *Larix occidentalis*, Nuttall; *Abies fraseri* (Pursh) Poiret; *Abies canadensis*, Mill.; *Abies*

Cophalonica, Loudon, and many other sources throughout the world.

The oil is extracted by one of three methods: first, the destructive distillation of wood containing the oil; second, the steam distillation of resinous exudations from any of the trees mentioned; and third, the steam distillation of lumber waste such as sawdust and chips.

#### WORK OF PREVIOUS INVESTIGATIONS

The constants for pinene obtained from Port Orford Cedar oil, *Chamaecyparis lawsoniana* (Murr.) Parlatores, given by Schorger (2) were:

B.p.	.....	156°-156.1° C
$d_{15}$	.....	0.8631
$n_D^{15}$	.....	1.4684
$\alpha_D^{20}$	.....	+51.52°

This  $\alpha$ -pinene was obtained by the steam distillation of cedar waste and was an old sample.

The work was repeated by Thurber and Roll (3) on pinene from the same source with the following results:

B.p.	.....	155°-156.5° C
$d_{20}$	.....	0.8584
$n_D^{20}$	.....	1.4608
$\alpha_D^{20}$	.....	+53.01°

The oil was obtained from a fresh sample of cedar wood waste from the mills in southern Oregon. The Port Orford Cedar oil had the following composition:  $d$ - $\alpha$ -pinene

45.7%, d-limonene 3.2%, d-borncol 26%, d-cadinene 21%, and l-cadinol 3.9%. The d-a-pinene fraction was collected between the temperatures of 155° -159°C.

Oregon Balsam oil was first mentioned by Rabak in 1904. (4) When distilled with steam it yields 22-25% a-pinene which is laevogyrate and according to Frankforter (5) has the following constants:

$d_{20}$	.....	0.8621
$n_D^{20}$	.....	1.47299
$a_D^{20}$	.....	-47.2

From the oleoresin of *Pseudotsuga taxifolia*, W. C. Blasdale (6) obtained 9% a-pinene with the following constants:  $d_{20}$  0.8593,  $n_D^{20}$  1.4754,  $a_D^{20}$  -41.21', and distilled principally between the temperatures of 157° to 160°C.

According to Rabak, Oregon Balsam oil distills over between the temperatures of 150° to 160°C.,  $d_{20}$  0.822 to 0.882, and  $a_D^{20}$  -34° to -40°. Frankforter observed the following constants:  $d_{20}$  0.8621,  $n_D^{20}$  1.47299, and  $a_D^{20}$  -47.2°. Rabak claims that Oregon Balsam oil consists mainly of l-a-pinene. (m.p. of nitroso chloride 106°C.)

Pinenes and their chemical properties have been studied quite extensively by many investigators. One particularly convenient method of identification and purification of this terpene is to prepare the nitroso chloride and then to regenerate the a-pinene with an organic base such as anilino. This in turn gives a pure product. This pure regenerated a-pinene can then be studied to determine its optical ac-

tivity, specific gravity, boiling point, refractive index, preparation of the  $\alpha$ -pinene hydrochloride, melting point, and optical activity of the hydrochloride.

$\alpha$ -Pinene forms a number of well-defined crystalline compounds. Of these, one of the best known is the nitroso chloride. This body is formed by treating  $\alpha$ -pinene with nitrosyl chloride and consists of the addition of NOCl to the double bond of the pinene molecule forming a compound with the formula  $C_{10}H_{16}NOCl$ .

The nitroso compounds, characterized by the group  $-N=O$ , were first prepared by Cahours in 1842 (7), by Tilden in 1875 (6), and by other investigators who have published papers on the subject from time to time. (9) (10) (11) (12) (13) Tilden found that nitroso compounds could be prepared by addition to unsaturated compounds.  $\alpha$ -Pinene is one of these substances that forms a nitroso derivative by addition of the nitroso group to its double bond. The nitroso derivatives have been shown by a number of investigators to be isonitroso in character, that is, the  $-N=O$  group readily changes to the  $=N-OH$  group in compounds of this nature. The following investigators have submitted evidence to bear out this fact: Goldschmidt (14), Kremers and Urban (15), Meyer (16), and Kremers and Head (17). They have also shown that the isonitroso compounds are colorless while the true nitroso compounds are blue in color. Kremers (18) and Baeyer (19) have shown that nitroso compounds appear to exist in the bisnitroso form characterized by the structure  $R'-N_2O_2R'$ .

In this case R' denotes the pinene molecule  $C_{10}H_{16}$ . The blue colored compounds have been shown to be true nitroso in character by Wallach (20), Baeyer (21), Thiele (22) Chapman (23), Piloty (24), Kremers and Schreiner (25), Schmidt (26), Piloty and Steinbock (27), Schmidt (28), and that these compounds readily change to isonitroso and bis-nitroso isomers, Kremers and Schreiner (29). In 1891, Kremers (30) noticed a wide difference in yield in the nitroso chloride from pinene of different sources, and in 1892, (31) he showed that the yield of pinene nitroso chloride varied with the optical rotation of the pinene employed. This has been confirmed by other investigators: Fox (32), Tilden (33), Gildemeister and Kohler (34), Schimmel and Company (35), Lynn (36), Brandel and Bandt (37). To account for the variation in the yield of pinene nitroso chloride the following facts must be considered:

1. The nitroso chloride obtained was always inactive.
2. Pinene of high optical activity gave a small yield of the nitroso chloride.
3. The mother liquor remained blue for some time after the inactive nitroso chloride was filtered off.
4. There was frequently a wide difference in solubility between the inactive and active modifications of nitroso derivatives (38).
5. There was an increase in yield of the nitroso chloride by treating mixtures of dextro and laevo pinenes. (39) Tilden (40) decided that the poor yield from  $\alpha$ -pinene

of a high optical rotation was due to the destructive effects of the heat generated in the inversion of one half of the product as soon as it was formed.

Methods for the preparation of  $\alpha$ -pinene nitroso chloride have been proposed by Wallach (41), Rape and Löffl (42), and Ehestadt (43). These methods were found to be inadequate by Lynn (44), who suggested a new modification. In the course of our work, Lynn's method was also found to be inadequate and was revised during the course of the investigation.

The hydrochloride of  $\alpha$ -pinene has also been the subject of much speculation. It is an important method for the identification of  $\alpha$ -pinene and was once known as artificial camphor. The melting point for this compound given by most textbooks on essential oils is  $127^{\circ}\text{C}$ . A survey of the literature, however, shows that the melting point for  $\alpha$ -pinene hydrochloride ranges from the temperatures of  $118^{\circ}$  to  $133^{\circ}\text{C}$ . The optical activity of  $\alpha$ -pinene hydrochloride has been a subject of much speculation. Wallach, Lynn, and many other investigators, maintain that the hydrochloride of *d*- $\alpha$ -pinene is inactive, and all investigators agree that the hydrochloride of *l*- $\alpha$ -pinene is laevo rotatory. Long (46) has shown that the hydrochloride of *d*- $\alpha$ -pinene is dextro rotatory, giving a specific rotation of  $+33^{\circ}$ . This was confirmed by Tsakalotos and Papaconstantinou (47), who obtained a sample with a specific rotation

of  $+33.4^\circ$ . Flawitzky (48) obtained values of  $+24^\circ$  and  $+30^\circ$ . Marsh and Gardner (49) obtained specific rotations of  $+3^\circ$  and  $+5^\circ$ .

## EXPERIMENTAL PART

d-a-Pinene - This product was prepared by the fractionation of cedar oil over sodium hydroxide, and the fraction distilling between the temperatures 155° and 159°C. was collected and subjected to still further purification by repeated fractionation over metallic sodium. The final fraction was collected between the temperatures 155° and 156.5°C.

l-a-Pinene - This compound was prepared by the steam distillation of Douglas Fir balsam. The distillate was subjected to three fractional distillations over metallic sodium and the final fraction was collected between the temperatures of 155° and 156°C.

a-Pinene from American turpentine - This product was obtained by the fractionation of American turpentine oil over metallic sodium. It was not necessary to have a very pure a-pinene from this source since it was used in the preparation of inactive a-pinene nitroso chloride.

The fractionation of each of the above mentioned samples was carried out in an efficient fractionating column filled with short sections of glass tubing. The column as well as the distillation flask was covered with insulating material.

Preparation of ethyl nitrite - This compound was prepared by adding 70 g. of sodium nitrite and 350 cc. water to 35 cc. ethyl alcohol (95%) in a 1 liter distillation

flask. A mixture of 350 cc. water, 55 cc. of concentrated sulphuric acid and 55 cc. ethyl alcohol was mixed at 0°C. and then added drop by drop through a dropping funnel. The reaction mixture was maintained at a temperature of 40°C. and the vapors of ethyl nitrite were condensed in a long Liebig condenser. The distillate was caught in a bottle surrounded by ice and salt. The yield was approximately 40 to 50 cc.

As was mentioned before, the method proposed by Lynn (44) was found to be inadequate for the preparation of the active nitroso chloride of  $\alpha$ -pinene. It was necessary, therefore, to study the conditions whereby the active  $\alpha$ -pinene nitroso chlorides could be formed. The method developed is outlined below.

Active  $\alpha$ -pinene nitroso chloride - Forty cc. of dry, purified  $\alpha$ -pinene together with 40 cc. 90% methyl alcohol (36 cc. absolute methyl alcohol and 4 cc. water) were placed in a suitable reaction bottle. The mixture was cooled to -12°C. and 40 cc. ethyl nitrite were added. The apparatus was provided with an efficient mechanical stirrer and thermometer suitable for measuring low temperatures. The reaction mixture was maintained at this temperature during the addition of the theoretical amount of hydrochloric acid. The hydrochloric acid solution was prepared by passing dry hydrogen chloride in to 90% methyl alcohol until an approximately 5 normal solution was obtained. This solution was titrated with standard base, and the amount of hydrochloric

acid to be used was calculated. The hydrochloric acid was slowly added through a dropping funnel, the delivery tube so arranged that the acid was cooled to the temperature of the ice and salt bath before it was admitted to the reaction mixture. The time required was approximately two and one-half hours. A bluish green solution was obtained at the end of the reaction. Two hundred cc. of 90% methyl alcohol, cooled to  $-12^{\circ}\text{C}$ . were added to the solution, and the resulting mixture was allowed to stand for 24 hours at a temperature of  $-20^{\circ}\text{C}$ . White needle-like crystals of the active nitroso chloride of d-a-pinene began to crystallize out when the cold methyl alcohol was added. At the end of 24 hours the product was filtered and the crystals were washed with 90% methyl alcohol. A yield of 2 to 3 g. was obtained. The crystals must be kept at a temperature of  $-20^{\circ}\text{C}$ . to prevent decomposition.

The same conditions were used in the preparation of l-a-pinene nitroso chloride, except that at the end of the reaction there was a precipitate of the inactive a-pinene nitroso chloride together with a small amount of the active nitroso chloride. It was necessary to filter off this precipitate before the 200 cc. of 90% methyl alcohol were added. As before, at the end of 24 hours the needle-like crystals of the active pinene nitroso chloride had precipitated. The crystals of l-a-pinene nitroso chloride were filtered and stored at a temperature of  $-20^{\circ}\text{C}$ . One to one and one-half g. of the nitroso chloride were obtained in

each run.

The yield in both cases is dependent upon the optical activity of the pinene employed. The higher the specific rotation of the pinene used in the preparation, the higher will be the yield of the active nitroso chloride obtained. In contrast, the lower optical rotation of the pinene used, the higher will be the yield of the inactive nitroso chloride. The pinene, therefore, used in the preparation of the inactive nitroso chloride, was a sample of pinene from American turpentine oil of a low optical activity.

Inactive  $\alpha$ -Pinene Nitroso Chloride - The method proposed by Wallach (41) was used in this preparation. A mixture of 50 g. each of pinene, glacial acetic acid, and ethyl nitrite were cooled in a freezing mixture of salt and ice. Fifteen cc. of 33% hydrochloric acid were then added drop by drop. The temperature was not allowed to rise above 0°C. The crystals of the inactive nitroso chloride were filtered off at the end of the run and washed with 90% methyl alcohol. A yield of 8 to 12 g. was obtained. Runs were made on each of the nitroso chlorides obtained. The next step in this investigation was to regenerate the pinene from the nitroso chloride.

Regenerated  $\alpha$ -pinene - The regeneration was accomplished by the method proposed by Tilden (40) in which the nitroso chloride is split off by the use of di-methyl aniline. Wallach in 1888 (41) suggested the use of aniline in splitting of the nitroso chloride, but in this investi-

gation it was found that Tilden's method was more suitable. A typical preparation is described below. Twenty g. of the  $\alpha$ -pinene nitroso chloride are placed in a round-bottom flask and two molecular proportions of di-methyl aniline in three volumes of 95% ethyl alcohol are added. The flask is fitted with a reflux condenser and the reaction mixture is heated gently over a steam bath until the reaction begins. The heating is then discontinued. When properly heated the mixture reacts gently until all of the nitroso chloride has been decomposed. A beautiful green solution results. An excess of glacial acetic acid is then added to neutralize the unused dimethyl aniline. This mixture is then steam distilled until no more crude pinene comes over. The crude pinene is separated from the distillate in a separatory funnel and this oil washed several times with dilute hydrochloric acid solution until it is almost colorless. The oil is then washed with a sodium carbonate solution to neutralize the hydrochloric acid. The resulting pinene is then dried over metallic sodium for a short time, and finally distilled over metallic sodium, the fraction distilling over between  $155^{\circ}$  and  $157^{\circ}\text{C}$ . being collected. A yield of 9 cc. of  $\alpha$ -pinene is obtained from 20 g. of the nitroso chloride. This corresponds to approximately 70% of the theoretical yield. The above described procedure was carried out for each of the three samples of nitroso chloride, namely: d- $\alpha$ -pinene nitroso chloride, l- $\alpha$ -pinene nitroso

chloride, and dl- $\alpha$ -pinene nitroso chloride. Nine cc. of each of the corresponding  $\alpha$ -pinenes were obtained.

Preparation of  $\alpha$ -Pinene Hydrochloride. - Three cc. of each of the regenerated  $\alpha$ -pinenes were used in the preparation of the hydrochloride. Three cc. of  $\alpha$ -pinene were saturated with dry hydrogen chloride at a temperature of from 10° to 15°C. The semi-solid mass was then allowed to stand for one hour at a temperature of -5°C. The crystalline  $\alpha$ -pinene hydrochloride was filtered by suction and was then recrystallized from five times its weight of absolute methyl alcohol. The recrystallized mass was dried by suction, and its physical constants were determined immediately. These properties are tabulated on page 19 and 20.

Physical Constants. - The remainder of the regenerated pinene was used in the determination of the refractive index, the determination of the specific gravity, the determination of the boiling point, and the determination of the specific rotation. The specific rotation was determined using pure pinene without a solvent, and was also determined using alcohol as a solvent.

The refractive index of each of the five samples of  $\alpha$ -pinene was determined at a constant temperature, 20°C., with an Abbé refractometer. The specific gravity was determined at 20°C. by means of a small specific gravity tube. The neck was of fine capillary tubing so that the amount of liquid taken in each case was always the same. The boiling point of each sample of  $\alpha$ -pinene was obtained by taking the

constant boiling temperature during the distillation process. The thermometer used in the determination was accurately calibrated against a standard thermometer. The specific rotation was determined by using a standard polarimeter. The determination was carried out at 20°C., and the D line of sodium light was used. The determination of the specific rotation of the oil without a solvent required a special polarimeter tube for holding small quantities of liquid. The tube was 2.95 cm. in length and had a capacity of 1 cc. The specific rotation was also determined by using a 1 dm. tube and by using alcohol as a solvent.

The physical constants were also determined on each of the three samples of the  $\alpha$ -pinene nitroso chloride. One run for the preparation of the nitroso chloride of each pinene was made to obtain material for the determination of the melting point and the specific rotation for each sample. The  $\alpha$ -pinene nitroso chloride was crystallized three times by saturating pure chloroform with the material and then adding two volumes of absolute methyl alcohol and cooling the resulting solution to -10°C. After the nitroso chloride crystallized it was filtered by suction and washed with cold methyl alcohol. The melting point for each sample was determined by the capillary tube method; that is, a small amount of the material was placed in the sealed end of a capillary tube and fastened to a calibrated thermometer which was suspended in a sulphuric acid bath. The bath was

carefully heated and the temperature was recorded at which the crystals and the liquid phase were in equilibrium. The recrystallized nitroso chlorides were used in the determination of the specific rotation. Benzene was used as a solvent in this determination.

A molecular weight determination was also carried out on each sample of the nitroso chloride for the purpose of checking the results of Baeyer (19) who claimed that the nitroso chlorides of various terpenes existed in the bimolecular state. His determination was carried out in a benzene solution on limonene nitroso chloride but not for  $\alpha$ -pinene nitroso chloride. Various solvents were used in this determination, namely: benzene, nitro benzene, and ethylene dibromide. The method employed was the cryoscopic or freezing point depression method.

Another determination was carried out to determine whether an increased yield of the inactive nitroso chloride would be obtained when an inactive mixture of d- $\alpha$ -pinene and l- $\alpha$ -pinene was treated by the method previously outlined.

## RESULTS AND DISCUSSION

Refractive index of samples of  $\alpha$ -pinene was carried out at 20°C. and is as follows:

Port Orford $\alpha$ -pinene (b.p. 155° - 156.5°) ...	1.4670
Oregon Balsam 1- $\alpha$ -pinene (b.p. 155° -156°) ..	1.4676
dl- $\alpha$ -pinene (regenerated) .....	1.4664
d- $\alpha$ -Pinene (regenerated) .....	1.4663
l- $\alpha$ -Pinene (regenerated) .....	1.4662

It is noticed from these results that the  $\alpha$ -pinene from Port Orford Cedar oil and the  $\alpha$ -pinene from the Oregon Balsam vary a trifle from that of the three regenerated  $\alpha$ -pinenes in refractive index. This is to be expected because it seems logical to expect that although they have a narrow boiling point range they probably contain slight amounts of impurities which cannot be separated by distillation processes. On the other hand, the refractive indices of the pure regenerated  $\alpha$ -pinenes are all the same within the limits of experimental error.

The specific gravity determination was carried out at both 20°C and 25°C. and are as follows:

sample	$d_{20}$	$d_{25}$
Port Orford d- $\alpha$ -pinene	0.8617	0.8598
Oregon Balsam 1- $\alpha$ -pinene	0.8598	0.8581
Regenerated d- $\alpha$ -pinene	0.8592	0.8567
Regenerated 1- $\alpha$ -pinene	0.8591	0.8567
Regenerated dl- $\alpha$ -pinene	0.8590	0.8571

The specific gravities of the three samples of synthetic  $\alpha$ -pinenes at both 20° and 25°C. are the same within the limits of experimental error.

The boiling points for the samples (760 mm. Hg.) are as follows:

Port Orford d- $\alpha$ -pinene .....	155°-156.5°C.
Oregon Balsam l- $\alpha$ -pinene .....	155°-156°C.
d- $\alpha$ -Pinene (synthetic) .....	155°-156°C.
l- $\alpha$ -Pinene (synthetic) .....	155°-156°C.
dl- $\alpha$ -Pinene (synthetic) .....	155°-156°C.

The boiling points of all five samples are the same. This would indicate that chemically they should all have the same constitution. The d- $\alpha$ -pinene used by Lynn (44) had a boiling point range from 155° to 159°C. This undoubtedly was not as pure a sample as that used in this investigation.

The results of the study of the optical activity of the samples of  $\alpha$ -pinene are found below.

Specific rotation at 20°C and D line of sodium light.	
Port Orford d- $\alpha$ -pinene .....	+51.81°
Oregon Balsam l- $\alpha$ -pinene .....	-42.63°
d- $\alpha$ -Pinene (synthetic) (regenerated) .....	+51.14°
l- $\alpha$ -Pinene (regenerated) .....	-51.28°
dl- $\alpha$ -Pinene (regenerated) .....	0.00°

Results when alcohol (95%) was used as a solvent are:

Regenerated d- $\alpha$ -pinene .....	+53.91°
Regenerated l- $\alpha$ -pinene .....	-54.04°
Regenerated dl- $\alpha$ -pinene .....	0.00°

It is of interest to note that the rotations for the dextro and laevo  $\alpha$ -pinenes are the same within the limits of experimental error, the dextro variety exhibiting a specific rotation of  $+51.14^\circ$  and the laevo  $-51.28^\circ$ . This would indicate that the synthetic pinenes are pure products and that pinene in the pure state, that is, composed entirely of one of its optical isomers, should exhibit a specific rotation of  $+51.28^\circ$ . It is possible that the specific rotation of the synthetic d- $\alpha$ -pinene should be  $+51.28^\circ$  as for the l- $\alpha$ -pinene because the mean of three readings was taken as the initial rotation, while the three readings for the laevo pinene were all the same. The specific rotations obtained in the alcoholic solution were somewhat higher, but as before were equal and opposite in sign. In both cases the rotation of the synthetic or regenerated dl- $\alpha$ -pinene was zero. This should be the case because the synthetic dl- $\alpha$ -pinene would be an equal mixture of pure d- $\alpha$ -pinene and l- $\alpha$ -pinene. The value obtained for the specific rotation of the regenerated d- $\alpha$ -pinene obtained by Lynn (44) from  $\alpha$ -pinene from Port Orford Cedar oil was reported as  $+47.7^\circ$ . His sample of the laevo variety was too small to obtain any constants.

The following melting points were obtained for the active and inactive  $\alpha$ -pinene nitroso chlorides:

dl- $\alpha$ -Pinene nitroso chloride .....	115 $^\circ$ C. corr.
d- $\alpha$ -Pinene nitroso chloride .....	89.5 $^\circ$ C "
l- $\alpha$ -Pinene nitroso chloride .....	90.0 $^\circ$ C."

The melting point given for the inactive  $\alpha$ -pinene nitroso chloride according to Parry (50) is  $115^{\circ}\text{C}$ . This is identical with that obtained in this investigation. The melting point given by Lynn (44) for d- $\alpha$ -pinene nitroso chloride is  $81^{\circ}$  to  $81.5^{\circ}\text{C}$ . This product was evidently not as pure as that obtained in this work.

The specific rotation of the nitroso chlorides prepared was as follows:

dl- $\alpha$ -Pinene nitroso chloride .....	$0.00^{\circ}$
d- $\alpha$ -Pinene nitroso chloride .....	$+396.2^{\circ}$
l- $\alpha$ -Pinene nitroso chloride .....	$-366.8^{\circ}$

These values were obtained by using benzene as a solvent. The specific rotation obtained by Lynn (44) was  $-322^{\circ}$  for d- $\alpha$ -pinene nitroso chloride when alcohol was used as a solvent. He did not get a value for the active laevo variety because of the limited amount of material which was prepared.

The melting point of the hydrochloride of pinene has been the subject of much speculation as has been previously stated, and the results of different investigators vary considerably. The melting points for this compound, as reported in the literature, range from  $118^{\circ}$  to  $133^{\circ}\text{C}$ . In this investigation the melting point of the hydrochloride of several pinenes was carefully determined and the results are here tabulated.

$\alpha$ -Pinene hydrochloride from Port Orford Cedar .. 127°C.  
 $\alpha$ -Pinene hydrochloride from Oregon Balsam ..... 127°C.  
 $\alpha$ -Pinene hydrochloride from reg. d- $\alpha$ -pinene .... 132°C.  
 $\alpha$ -Pinene hydrochloride from reg. l- $\alpha$ -pinene .... 132°C.  
 $\alpha$ -Pinene hydrochloride from reg. dl- $\alpha$ -pinene ... 132°C.

The hydrochloride in each case was recrystallized from five times its weight of absolute methyl alcohol and the melting point immediately determined. It was found that if the hydrochloride were allowed to stand, even in a desiccator, the crystals change to a gummy mass which has a melting point of 125°C. Perhaps this accounts for the variance in the results of previous investigations on the melting point of  $\alpha$ -pinene hydrochloride. It is interesting to note that the melting points of each of the three regenerated samples are exactly the same.

As has been mentioned previously in this discussion, the hydrochloride of d- $\alpha$ -pinene has, with the exception of four investigations, always been reported as inactive. The hydrochloride of l- $\alpha$ -pinene, on the other hand, has always been reported as optically active. Both should be active or both should be inactive, according to our present conception of optically active derivatives. This was carefully investigated and found to be true. The specific rotations of each of the hydrochlorides are tabulated below.

d- $\alpha$ -Pinene hydrochloride (regenerated) ..... +35.52°  
 l- $\alpha$ -Pinene hydrochloride (regenerated) ..... -33.24°  
 dl- $\alpha$ -Pinene hydrochloride (regenerated) ..... 0.00°

The specific rotation was determined using alcohol as a solvent. The rotations are very nearly equal and opposite in sign. The hydrochloride of d- $\alpha$ -pinene is optically active as it should be, and it rotates polarized light in the same direction as the pinene from which it is prepared. The conclusion may be drawn, then, that the hydrochlorides of  $\alpha$ -pinene behave normally.

No consistent results were obtained in the molecular weight determination of the nitroso chloride of any of the samples. The values obtained varied from two hundred to thirteen hundred for the molecular weight.

An experiment was carried out to determine accurately the increase in yield of the nitroso chloride from an inactive mixture of d- $\alpha$ -pinene and l- $\alpha$ -pinene. Twenty cc. of the dl- $\alpha$ -pinene were used and the nitroso chloride was prepared by the method previously outlined. A yield of 6 g. of the inactive nitroso chloride was obtained. Twenty cc. of l- $\alpha$ -pinene were treated under the same conditions. Two and two tenths g. of the inactive material and 0.71 g. of the active laevo nitroso chloride were obtained. Twenty cc. of the dextro variety gave 1.5 g. of  $\alpha$ -pinene nitroso chloride. The significance of these results could not be ascertained; however, no active nitroso chloride was obtained when the dl- $\alpha$ -pinene was treated in the usual manner. This might indicate that dl- $\alpha$ -pinene was simply a mixture of the dextro and laevo isomers, and that the inactive nitroso

chloride was a compound formed from equal amounts of laevo  
and dextro  $\alpha$ -pinenes.

## SUMMARY

As was previously mentioned in this investigation, the purpose of this study is to show that the pinenes from Oregon sources are identical chemically as well as physically with the pinenes from any other source. This has been found to be true. After the regeneration of the  $\alpha$ -pinenes from the nitroso chlorides, it was found that they had the same properties, within the limits of experimental error. The boiling points in every case were the same, the specific gravities, and the refractive indices were the same within the limits of experimental error. The constants for  $\alpha$ -pinene from Port Orford Cedar oil, Oregon Balsam  $\alpha$ -pinene, and the  $\alpha$ -pinene from American turpentine oil are not the same as the constants for the regenerated  $\alpha$ -pinenes. This may be accounted for by the fact that the original pinenes may contain small amounts of impurities which cannot be separated from the pinene by fractional distillation. There is the possibility that other oils present might form constant boiling solutions with  $\alpha$ -pinene. However, these impurities would be present only in very small amounts. Probably the main objection to the use of Oregon pinenes is the fact that they do not have the odor of ordinary turpentine oil obtained from sources elsewhere. Port Orford pinene has the odor of the original Cedar oil, while the pinene from Oregon Balsam has the odor of the Balsam pitch. This,

however, does not alter its chemical properties and therefore this pinene is not inferior to that obtained from other sources.

In the course of this investigation several very theoretical problems presented themselves such as the fact that the hydrochloride of dextro pinene has always been reported in the literature as being optically inactive. It was definitely shown that this is not true. The hydrochloride of d- $\alpha$ -pinene is optically active and its specific rotation is exactly opposite to that obtained for the hydrochloride of laevo  $\alpha$ -pinene. It was found that the hydrochloride of  $\alpha$ -pinene decomposes rapidly into a gummy mass with a decrease in melting point. This explains the fact that the melting points given for  $\alpha$ -pinene hydrochloride in the literature vary within the wide limits of  $118^{\circ}$  to  $133^{\circ}\text{C}$ .

There are almost unlimited supplies available in Oregon of both the active  $\alpha$ -pinenes discussed. At the present time they have no great use commercially. The experimental work accomplished during the course of this investigation indicates that  $\alpha$ -pinenes from Oregon sources are not inferior to  $\alpha$ -pinenes from other sources. Chemically and physically they are identical.

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