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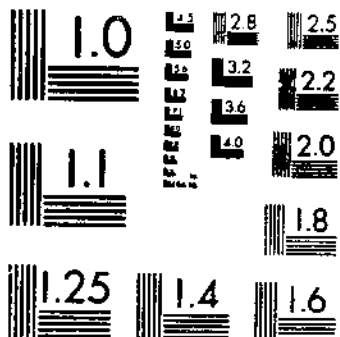
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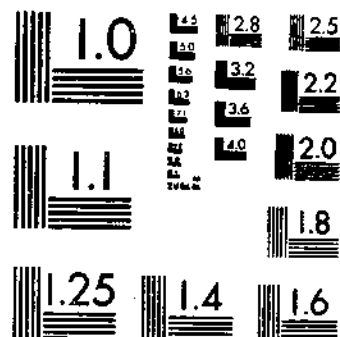
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COMPOSITION OF GUM TURPENTINES OF PINES

by N. T. MIROV

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Part 1. Introduction

In America, the term "gum turpentine"¹ is used to designate the volatile part of an oleoresinous exudate of conifers, chiefly of pines. In pines, oleoresin droplets may be found in any living parenchyma cells, but most oleoresin is produced in the thin-walled epithelial cells surrounding the resin ducts or canals. When a pine is wounded, the resin ducts are severed. The oleoresin, squeezed from the epithelial cells into the resin canals, may be gathered in receptacles attached below the wound. When obtained in this way the oleoresin is called pine gum.

Oleoresin can be separated into two components: rosin and turpentine. Generally, turpentine is removed from oleoresin by steam distillation, and rosin remains in the still as a non-volatile residue. Rosin consists mostly of rosin acids having an empirical formula $C_{20}H_{30}O_2$. Rosin also includes a small amount of substances (varying from one species to another) other than rosin acids; these are loosely called resenes. The chemical nature of resenes is little known. In some pines at least, this unsaponifiable material includes many compounds of the sesquiterpene and diterpene series. Technically, these sesqui- and diterpenes could be classified with the volatile part of oleoresin; in practice they are not removed in the process of steam distillation, but remain in the non-volatile residue or rosin, rendering it soft and tacky.

The steam-volatile part of the oleoresin, i.e., turpentine, is not a chemically pure substance. It consists generally, but not always, of cyclic hydrocarbons, or terpenes, of an empirical formula $C_{10}H_{16}$. There is almost always an admixture of sesquiterpenes ($C_{15}H_{24}$) and sometimes of nonterpene substances. The components of pine gum turpentines are listed in Appendix 1, p. 143.

In the course of normal growth of a pine, the inner parts of the sapwood are gradually converted into heartwood. The oleoresin which is found in heartwood, and chiefly in stumps, can be recovered. The wood is chipped, the chips are extracted with some appropriate solvent, and the oleoresin distilled much like gum.

Turpentine obtained from the wood in this manner is called wood turpentine; its composition often differs from that of gum turpentine of the same species, although the chief ingredients of both are usually the same. (Cf. p. 81.)

Sulfate turpentine is obtained as a byproduct from the pulping of pine. During the digestion, turpentine vaporizes and is collected. The chemical composition of sulfate turpentines is not considered in this publication.

¹ For explanation of technical terms see Glossary, Appendix 3, p. 156.

HISTORY OF TURPENTINE ANALYSIS

The word "turpentine" (old "terebenthyno") is derived from the Greek word "terebenthina." This word originally meant oleoresin of a Mediterranean shrub, *Pistacia terebinthus* of the Cashew family (Anacardiaceae). Later, the oleoresin of pines also became known as turpentine, and even now the term "crude turpentine" is occasionally used instead of "oleoresin." The volatile part of oleoresin, or turpentine, is still known commercially as "oil of turpentine" or even as "spirits of turpentine."

Early researches on the composition of turpentine were concerned only with commercial products obtained in the United States from *Pinus elliotii* and *P. palustris*, and in France from *P. pinaster*. Later, Herty (67, 68, 69)² and his coworkers analyzed turpentines of three other American pines: *P. taeda*, *P. echinata*, and *P. serotina*.

In France, much work was done with turpentines of European pines other than *Pinus pinaster* by Dupont and his associates, especially by Mlle. Marcelle Barraud. In Russia, where the chief source of turpentine is *P. sylvestris*, a great deal of work on composition of turpentines was done by B. A. Arbutov (7, 8, 9) and recently by Burdyshev and his coworkers (13, 14, 15, 16, 17, 18).

In Indonesia, turpentine research has dealt exclusively with *Pinus merkusii*.

In India, early in this century, Simonsen and his associates analyzed turpentines of several Asiatic pines. Although at the beginning Simonsen's interest in the subject was purely technological, his later work was of a highly fundamental nature. His "Terpenes" (150) is a classical treatise on the subject.

Simonsen (152) discovered in *Pinus longifolia* (now called *P. roxburghii*) a new bicyclic terpene, Δ^2 -carene, which had been overlooked by earlier investigators of pine turpentines, and a sesquiterpene, which he called longifolene. In *P. excelsa*, now known as *P. griffithii*, Simonsen found a paraffin hydrocarbon, *n*-undecane (151).

In 1872 Wenzell (165) published a startling report that some California pines yield an unusual turpentine consisting not of terpenes, but of a hydrocarbon named abietene. Later it was shown that abietene was *n*-heptane (29, 136).

In 1911 the U.S. Forest Service (28) conducted a series of experiments to determine suitability of Western pines as a source of Naval Stores. The fieldwork was done by George Hunt; the laboratory phase of the project was done by A. W. Schorger, at the U.S. Forest Products Laboratory, Madison, Wis. (136). In those days, fractional distillation apparatus was rather primitive; Schorger had at his disposal merely a 12-inch-long tube known as a Hempel column. But even with this equipment, he was able to contribute a great deal to the knowledge of American turpentines.

Schorger verified previous reports that the turpentine of two California pines, *Pinus Jeffreyi* and *P. sabiniana* consisted almost entirely of a paraffin hydrocarbon, *n*-heptane, instead of the usual terpenes; he was the first to report that *P. contorta* turpentine consisted almost entirely of β -phellandrene—a monocyclic terpene

² Italic numbers in parentheses refer to Literature Cited, p. 134.

commonly found in the essential oils of Umbelliferae, the carrot family, and also in essential oils of some eucalypts (12). Schorger also reported the presence of eadinene in *P. edulis* (136) and in *P. monophylla* (135) turpentine, and he found camphene in the turpentine of *P. clausa* (134).

Schorger suggested (138) that in reporting the composition of any turpentine, it is important to know exactly the biological source of the material; that there is a possibility of existence of stable varieties within a species, each variety possessing its peculiar turpentine; that there is always a possibility of finding in the woods a "bastard pine" whose turpentine differs considerably from the general run. The idea of an existence of stable chemical varieties within a species has been more fully developed by Penfold and his associates, working with Australian essential oils (124, 125).

Some research on the composition of turpentines has also been conducted in Spain, Yugoslavia, Poland, the Philippines, Japan, and Mexico. These studies dealt primarily with turpentine as a commercial product. Nevertheless, much valuable biological information can be obtained from the published results of these investigations.

Dr. P. A. Foote and I published the first analytical paper on the composition of gum turpentine (of *Pinus monticola*) in 1933 (54). After a long interval, my studies of turpentines were resumed and two papers were published: one in 1946 on composition of turpentine of *P. coulteri* (95) and one in 1947 of *P. muricata* (96).

In 1946 Dr. A. J. Haagen-Smit, professor of Bio-organic Chemistry at the California Institute of Technology, was invited to participate in the project of studying composition of pine turpentine. During 1947, 1948, and 1949, the analytical work was done at the Institute under his direction and with the assistance of C. T. Redemann and T. H. Wang. Turpentine samples of 17 pine species were analyzed; Δ^3 -carene and longifolene were first reported to be components of turpentines of New World pines. In *Pinus albicaulis* were discovered a new sesquiterpene, albicaulene; a new sesquiterpene alcohol, albicaulol; and a diterpene, cembrene. Diterpenes had never been reported in turpentines before. We found cembrene, albicaulene, and albicaulol in several Asiatic pines.

In 1950 and 1951 I continued the project alone, working chiefly with Mexican pines. From 1952 through 1955 the project was supported by the Rockefeller Foundation, and most of the laboratory work was done by Dr. P. M. Hoff, Jr. Although the project was officially closed early in 1956, I completed analyses of *Pinus patula*, *P. tenuifolia*, *P. serotina*, and *P. yunnanensis*, and wrote the concluding remarks in 1957.

During the progress of the research reported here, nearly 30 analytical papers were published in the Journal of American Pharmaceutical Association, Scientific Edition, under the general title "Composition of Gum Turpentine of Pines." However, many data included in this bulletin have never been published before.

Including reliable information of previous investigators for 18 species, knowledge of turpentine composition is now available for all but a few controversial species, such as *Pinus kwantungensis* and several varieties of different pines. Because turpentine composition

is a little-explored field, information for some pines is rather sketchy, especially for the pines of China (for instance, *P. tabulaeformis*).

STABILITY OF TURPENTINE COMPOSITION

It has often been reported that the composition of turpentine of a pine varies considerably. The nature, extent, and causes of this variability have been little understood and seldom discussed. For a better understanding of the chemistry of pine turpentines, it is necessary to discuss briefly what is known about stability and variability of their composition. To begin with, three questions will be considered:

1. Does turpentine composition of an individual tree change during the growing season?

2. Does the composition change when a pine is planted outside its natural range?

3. Does a change of environment in a given region affect the composition of turpentine of a pine?

To study variability in physical properties—and thus the variability in chemical composition—investigators often select optical rotation of turpentine. Variability of optical rotation depends on three factors: (a) different amounts of levorotatory and dextrorotatory terpenes in a turpentine, (b) different amounts of the levorotatory and the dextrorotatory antipodes of the same terpene, and (c) different amounts of an optically active compound and an optically inactive compound.

Herty (67) investigated optical variability in turpentine samples obtained throughout two seasons from several individual *Pinus elliotii* and *P. palustris* trees. He found considerable variation among individual trees, but very little within an individual tree. Herty's investigation was followed by similar experiments of the French workers, Dupont and Barraud (43), who studied a European pine, *P. nigra*. They found that although the rotatory power of the composite samples varied with the method of obtaining the oleoresin and with the time of the year, the chemical composition of the turpentine remained about the same. Here follow some examples of variability of optical rotation of *P. nigra* turpentine:

	Sample 10	Sample 11	Sample 12
3d gathering.....	-42.36°	-39.90°	-46.63°
4th gathering.....	-33.90°	-40.45°	-41.75°
5th gathering.....	-25.35°	-29.98°	-48.00°

Although the optical rotation of the samples (more than 40) varied considerably (from -25° to -48°), all of them were levorotatory.

Oudin (119), working with *Pinus pinaster* turpentine, found that the optical rotation of commercial lots was -30° , and varied only within one degree. In individual trees, the optical rotation varied from $+16.20^{\circ}$ to -41.0° : that is, some trees possessed dextrorotatory and other trees levorotatory turpentine. In individual trees, variations from one year to another, and from one gathering of the oleoresin to another, were relatively small. Oudin's "dextrorotatory pines" were less frequent than the "levorotatory pines." There were no morphological differences between the two.

Black and Thronson (24), studying six *Pinus elliottii* and six *P. palustris* trees, found that during a single season the optical properties of turpentines of individual trees of both species did not follow any orderly course. Optical rotation of turpentine of one slash pine actually changed for 2 weeks from minus to plus, but later returned to the original levorotatory state.

As the result of an inquiry into seasonal variability of *Pinus ponderosa* turpentine in the Sierra Nevada of California, I found considerable difference in the optical rotation of individual trees (fig. 1). Also, this character varied little throughout a growing season, and, as in Black and Thronson's experiment, the variation did not follow any orderly course. A clear-cut decision cannot be made as to whether the observed variation was attributable to experimental error. However, an estimate of the variability due to technique was obtained by doing three rotation readings from turpentine obtained at one time from one tree. The variation observed in these 3 readings was greater than the average within-tree variation for the 11 trees of the study. Statistical analysis of the data indicated that the variation is not linearly associated with date of instrument reading, and is not different from tree to tree.

To sum up, all evidence seems to indicate that turpentine composition varies little throughout a growing season, in individual trees, and especially in composite lots of turpentine (i.e., obtained from many trees) because here individual differences are likely to balance themselves.

Then does the chemical composition of turpentine change when a pine is planted outside its natural range? Scheuble (133) reported that *Pinus jeffreyi*, a California pine whose turpentine consists chiefly of *n*-heptane, also yields chiefly *n*-heptane when cultivated in Austria. In my experience, *P. contorta* turpentine consists chiefly of *l*- β -phellandrene both in the United States and when planted in New Zealand. *P. pinca* terpene fraction consists fully of *l*-limonene both in Italy, where it is native, and in California, where it is cultivated in parks. Examples of this stability in turpentine composition are numerous; these three are sufficient to demonstrate that composition of turpentine is a genetically fixed character.

Finally, when one physiological form³ of a pine grows under different ecological conditions within its habitat, the chemical composition of its turpentine remains unchanged. Krestinsky and his coworkers (83) found that *Pinus sylvestris* turpentine obtained from different ecological types of a forest in the same locality possessed the same physical properties and the same chemical composition. Apparently these workers dealt with the same physiological form of *P. sylvestris*. On the other hand, Penfold (124) was able to distinguish in one locality several physiological forms of *Eucalyptus*.

SPECIFICITY OF TURPENTINES

Some closely related pines may possess turpentines of different composition; on the other hand, it is known that two species

³The term "physiological form" was suggested by Penfold (124) to denote subspecific entities having the same morphological appearance but differing in chemical composition of essential oils.

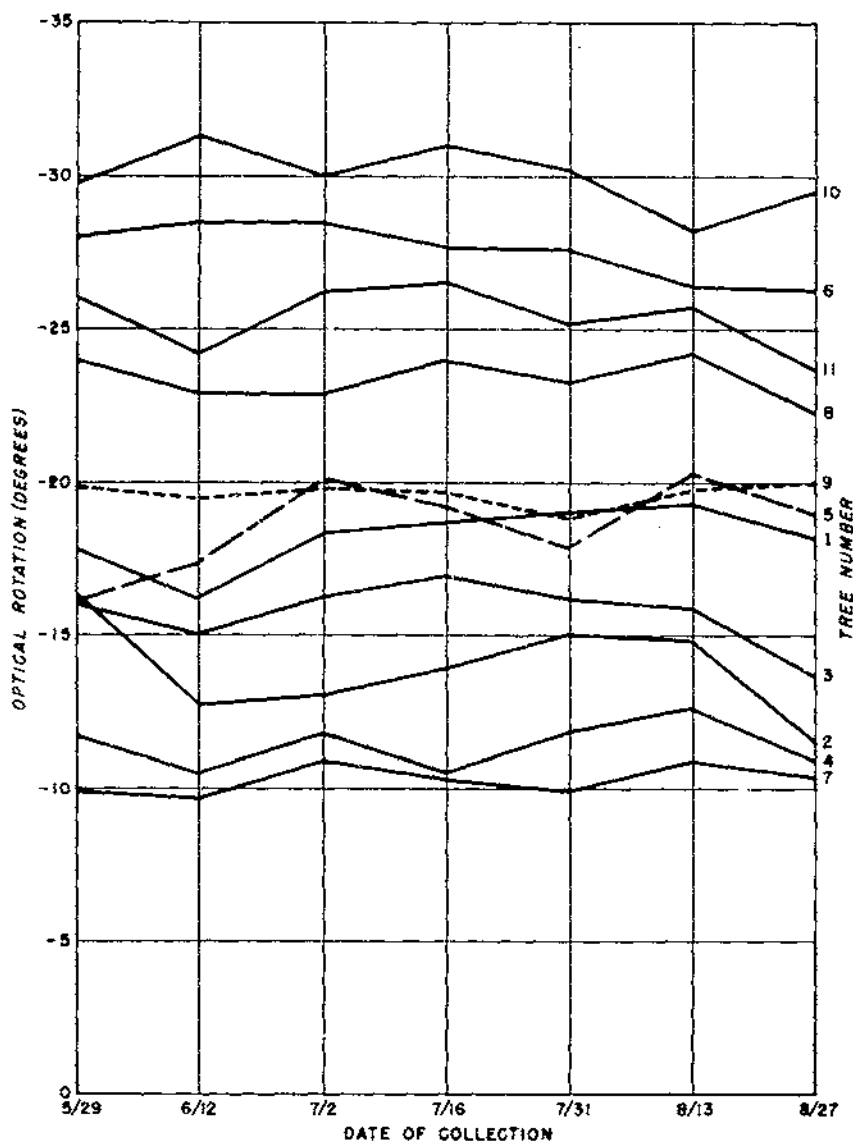


FIGURE 1.—Seasonal variability of optical rotation in several individual trees of *Pinus ponderosa*.

taxonomically remote have turpentines of almost identical composition. The high-boiling sesquiterpene fractions from such pines may differ, but knowledge of the composition of these fractions is still too meager to permit any conclusions.

The chemical composition of turpentine is not always correlated with the taxonomic position of a pine. One reason for absence of relationship is incomplete knowledge of chemical composition of pine

turpentines. Another reason is that there is still a great deal of disagreement among botanists as to the classification of pines. A natural taxonomic system for the genus *Pinus* has not been developed. Some botanists (131) maintain that pines really belong to four different genera: *Strobus*, *Apinus* (white pines), *Pinus* (hard or yellow pines) and *Caryopitys* (pinyon pines).

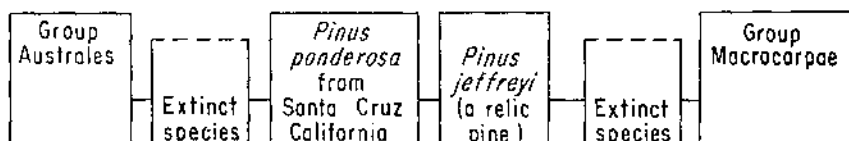
Evolutionary development may also explain certain absences of relationship. Most likely, morphological and chemical characters have followed different paths of evolution.

In correlating the composition of turpentine with the taxonomic position of a pine, one should remember that the genus *Pinus* of today is different from the genus of the Tertiary Period. The oldest living species is probably not older than Miocene. The chemical relationship of pines that existed during the Jurassic was most likely different from what it is now. During the evolution of the genus, many ancient species became extinct and many new species appeared. At present we have merely patches of an old biochemical pattern. Some of these patches are difficult to fit into the present structure of the genus; others fit very well and are useful in understanding the relationship of living pines.

An interesting example of this relationship is *Pinus jeffreyi*, a relic pine of California (94) whose turpentine consists almost entirely of *n*-heptane with a small addition of aliphatic aldehydes. In some morphological characters, this pine resembles *P. ponderosa*, which belongs to the group Australes. The two pines hybridize naturally, and the hybrids are fertile (93). Many botanists have considered *P. jeffreyi* as a variety of *P. ponderosa* (142).

Yet in the chemistry of its turpentine, *Pinus jeffreyi* is related not to Australes but to a distant group of Macrocarpae. This group consists of three pines, *P. sabiniana*, *P. coulteri*, and *P. torreyana*, all containing *n*-heptane and aliphatic aldehydes. It has been found that *P. jeffreyi* crosses naturally with *P. coulteri*, and the hybrids between the two pines are also fertile (128).

There is evidence that the present taxonomic position of *Pinus jeffreyi* had an intermediate place between the two groups: the older group Macrocarpae and the more recent group Australes, perhaps having been closer to the former. Turpentine of the group Macrocarpae contains chemical compounds simpler (more primitive) than terpenes, i.e., *n*-heptane and *n*-undecane. The group Australes, with the exception of one variety of *P. ponderosa* from the Santa Cruz Mountains of Coastal California, does not contain paraffin hydrocarbons. In the course of evolution, intermediate links between the two groups disappeared, and *P. jeffreyi* is now the only pine (except perhaps the Santa Cruz variety of *P. ponderosa*) that reminds us of their former relationship. The relationship may be represented like this:



There is also evidence other than presence of heptane that *P. jeffreyi* is an older species than *P. ponderosa*. This evidence is based on the degree of unsaturation of seed oils of the two pines (94).

Difficulties in correlating taxonomy with chemistry of turpentines occur:

(a) When a complex botanical species, such as *Pinus ponderosa* or *P. sylvestris*, contains several varieties, each possessing its own specific turpentine.

(b) When a valid species is erroneously included in another species. A good example is *Pinus engelmannii* which until recently was considered as a synonym of *P. ponderosa*. Chemically the two pines are quite different (102).

(c) When chemical mutants, or abnormal trees, are encountered within a species.

(d) When two species naturally cross.

The last two statements require some amplification.

Chemical mutants have occasionally been found among pines. In 1930 two Russian investigators (82) reported an unusual turpentine obtained from an individual tree of *Pinus sylvestris*. The turpentine lacked completely the usual Δ^3 -carene; it consisted of α -pinene, camphene, and *l*- β -phellandrene.

Schorger's (138) "bastard" *Pinus ponderosa* apparently was a chemical mutant differing radically from the general composition of ponderosa pine turpentine in the same locality. I found a *P. monticola* tree in northern Idaho which appeared to be a chemical mutant; its turpentine contained an unusually high proportion of *l*-limonene, as revealed by an unusually high levorotatory rotation. (See *P. monticola* No. 10, table 2, p. 10.) The occurrence of chemical mutants in populations of pines has not yet been systematically studied.

Natural hybridization among pine species has been observed rather frequently, although seldom studied thoroughly. Artificial crossings have been made between many pine species, sometimes between species belonging to quite distant groups. Our experience with *Pinus contorta* \times *banksiana* indicates that when two pine species are crossed, the turpentine in the F_1 hybrids is composed of the terpenes of both parents. The bicyclic pinenes of *P. banksiana* predominate over the monocyclic phellandrene of *P. contorta* (104). The two pines also hybridize naturally, forming a hybrid swarm in Alberta, Canada. Chemical composition of turpentine samples taken from individual trees in that locality, as could be expected, varied from pure *P. contorta* to pure *P. banksiana*. Many trees were intermediate, possessing a mixture of *P. banksiana* pinenes and *P. contorta* phellandrene in different proportions. Morphology and chemistry of the individual trees of the swarm were not always correlated (table 1).

At present it would be futile to develop a natural classification of pines based on their chemical characters. We can merely claim now that chemistry and taxonomy of pine species often coincide, and that when morphological characters are ambiguous, a knowledge of chemistry of the turpentines may be useful.

TABLE 1.—*Distribution of experimental trees from the Alberta lodgepole-jack pine overlap area, by morphological and chemical characters*

Morphological character	Chemically jack pine		Chemically intermediate forms		Chemically lodgepole pine		Total	
	No.	Percent	No.	Percent	No.	Percent	No.	Percent
Jack pine.....	21	28.8	0	0	0	0	21	28.8
Intermediate.....	3	4.1	14	19.2	0	0	17	23.3
Lodgepole pine.....	3	4.1	17	23.3	15	20.5	35	47.9
Total.....	27	37.0	31	42.5	15	20.5	73	100.0

VARIABILITY IN TURPENTINE COMPOSITION WITHIN A SPECIES

When the physical characters (which reflect the chemical composition) even of composite samples of turpentine are studied, it is easy to notice that some species vary but little throughout their environmental range, whereas others vary a great deal. *Pinus merkusii*, which grows over a wide range in Burma and in Indonesia, is rather uniform in the physical characters of its turpentine (97). Turpentine of this pine collected in different localities of its range is always dextrorotatory, varies from $+29^{\circ}$ to $+37^{\circ}$ in optical rotation, and always consists predominantly of α -pinene.

On the contrary, another widely distributed pine, *Pinus ponderosa*, varies widely in physical characters and chemical composition of its turpentine. Several physiological varieties of *P. ponderosa* have been identified. There is no doubt that when two varieties hybridize, the change from one variety to another is gradual, with many intermediate forms.

Within a species, the optical rotation of some populations is rather uniform, but in other populations it is rather variable (table 2). As was mentioned before, this variability is caused either by the presence of different antipodes of the same terpene or by different amounts of dextrorotatory and of levorotatory terpenes. For instance, some individual trees of *Pinus washoensis* contain turpentine that is composed predominantly of dextrorotatory Δ^3 -carene; others contain more levorotatory β -pinene. Incidentally, the chemical composition of *P. washoensis* turpentine is still very puzzling. Most likely, the species originated as a chemical mutant of *P. ponderosa*, or is a result of hybridization between two varieties of *P. ponderosa*, at least one of which is extinct.

Apparently individual variability in composition of turpentine is sometimes caused by hybridization of two pine species or varieties. This situation was clearly demonstrated by the study of turpentine from individual trees of the hybrid swarm in Alberta, Canada (104). On the other hand, in a pine forest composed of only one species where there is no possibility of interspecific hybridization, the variability in chemical characters of individual trees is apparently caused by crossing

TABLE 2.—Optical rotation ($\alpha_{578}^{25} m \mu$) of turpentine obtained from individual trees of several pine species

Tree No.	<i>P. engelmanni</i> Arizona	<i>P. washingtonis</i> Nevada	<i>P. parryana</i> California	<i>P. monticola</i> N. Idaho	<i>P. ponderosa</i> Sierra-Nevada, Calif.	<i>P. ponderosa</i> SW Utah	<i>P. ponderosa</i> Priest River, Idaho	<i>P. ponderosa</i> McNary, Ariz.	<i>P. ponderosa</i> Santa Cruz, Calif.	<i>P. ponderosa</i> Manitou, Colo.
1	+27.5	-1.6	+5.3	-30.2	-9.1	-17.7	+2.5	+11.3	-12.5	+7.7
2	+18.7	-6.6	+23.5	-18.8	-11.2	+16.3	+4.5	+11.3	-32.3	+8.0
3	+12.7	+1.0	+27.7	-33.7	-12.2	+10.3	+1.0	+11.0	-19.0	+3.0
4	+7.0	+8.1	+20.2	-16.0	-12.5	+9.0	+4.2	+14.4	-20.2	+5.5
5	+1.0	+10.1	+8.5	-23.3	-12.7	+23.3	-6.0	+16.0	-17.0	+5.3
6	-1.0	+4.4	+26.0	-29.7	-13.9	+20.8	-2.7	+10.3	-21.8	+5.3
7	-2.3	+6.8	+22.5	-29.2	-15.2	+14.2	-4.0	+11.0	-18.8	+4.2
8	±0.0	+1.7	+28.3	-29.3	-16.0	-4.5	-3.0	+10.5	-19.7	+10.2
9	0	+8.0	+15.2	-27.8	-16.1	-16.0	-10.2	+16.2	-16.7	+7.8
10	0	+7.9	+23.8	-69.0	-17.7	+17.2	+4.2	+26.8	-19.3	+1.3
11	+5.0	0			-18.7	+8.7	-10.7			-2.5
12	+8.7	-9.7			-19.7	+3.3	-6.0			-2.8
13	+10.0	+1.3			-19.8	+3.5	-5.1			-3.5
14	+8.0	+3.7			-20.5	+1.9	-13.2			-6.2
15	+6.0	+3.4			-21.2	+6.2				-13.4
16	+4.0	+4.2			-21.2	+7				-1.5
17	+1.4	+3.1			-22.7	-7.3				
18	+8.0	+8.4			-22.8	+1.5				
19	+18.0	+4.8			-24.3	0				
20	+30.4				-25.5	-3.0				
21	+40.7				-25.6	+22.8				
22	+47.0				-26.7	-27.2				
23	+49.0				-27.1	+9.0				
24	+46.0				-29.9	+19.5				
25	+49.0				-30.9	+2.7				
26	+46.0				-33.5	-13.0				
27	+49.6				-39.1	+13.8				

among individual members of the population, with the occasional mutations superimposed. On the whole, individual variation in turpentine chemistry is only one manifestation of variability among the individual trees of a forest. This ever-present variability in a population of forest trees is of prime importance in development of subspecific taxa as well as in the evolution of the genus. It is not the species or varieties that hybridize naturally or are hybridized artificially; it is the individual trees that cross one with another.

METHODS OF ANALYSIS

Because there are many different ways to tap pines for oleoresin and many different ways of extracting and analyzing the turpentine, the field and laboratory practice used in our work is explained here. One purpose is to demonstrate how the job has been done; another is to suggest to future workers what methods may be used in order to obtain comparable results.

Above all, the researcher should satisfy himself regarding the authenticity of his source of turpentine. Each oleoresin sample should be collected by a person familiar with botany of pines, and it should *always* be accompanied with herbarium specimens of the same trees from which it was obtained. The information accompanying an oleoresin sample should include geographical location, altitude, ecological description of the area, age of the tapped trees, and a note concerning the presence or absence of other pine species in the locality.

Among the causes of discrepancies in reporting turpentine analysis of the same species by different investigators are differences in techniques of obtaining oleoresin samples, in ways of separating turpentine from the rosin, and in methods of distillation.

Collecting Oleoresin

Oleoresin may be obtained from a tree either by using the open-face method and an open receptacle or by boring holes in a tree and using air-tight receptacles, such as test tubes or vials. The open-face method lets some turpentine be evaporated and lost, especially when the turpentine consists of compounds possessing a high vapor pressure. But as most turpentines are obtained by the open-face technique,⁴ this method has been used in all our work and in the work of our collaborators.

Separating Turpentine From Oleoresin

There are several methods of removing turpentine from oleoresin. In commerce the usual way is to blow more or less superheated steam through a batch of oleoresin. Turpentine is volatile with the steam; the rosin remains as a pot residue.

In early analytical work, the steam distillation method was also commonly used. This method has the disadvantage of being very slow

⁴ For the technique of obtaining oleoresin from trees see U.S. Naval Stores Handbook (161).

in a laboratory. From 3 to 4 hours are usually required to expel most of the turpentine. To distill off all the high-boiling substances, such as sesquiterpene derivatives or diterpenes, would require a much longer time. Frequently these substances are not completely removed from oleoresin by steam distillation.

In almost all of our work, we used vacuum distillation methods for the recovery of turpentine. The procedure is to charge a large Claisen flask (3-liter flask with glass joints was usually used) about half full with oleoresin, apply vacuum (about 100 mm. pressure at the beginning), and heat the flask gradually (fig. 2).

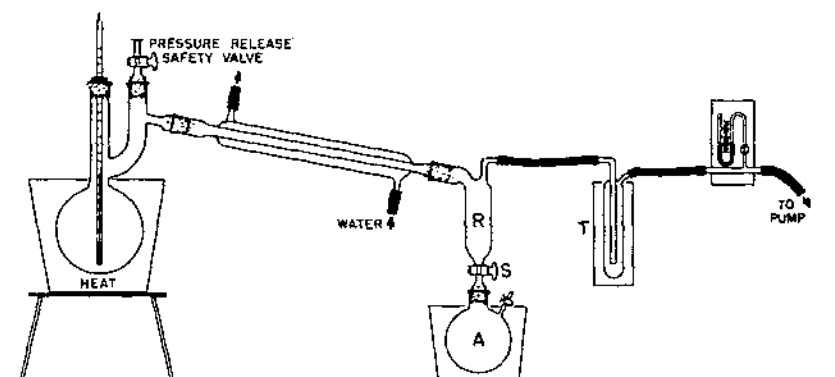


FIGURE 2.—A convenient assembly for vacuum distillation of turpentine from oleoresin.

Under these conditions most of the turpentine, i.e., the terpene fraction proper, can generally be safely distilled. When low-boiling hydrocarbons are suspected, as in oleoresin of hybrids between a heptane pine and a terpene pine, extreme caution should be exercised to prevent loss of the low-boiling compound. Two dry-ice traps (*T*, fig. 2) should be used instead of one, and the receiver (*R*) should also be chilled with dry ice. When the terpene fraction is removed, the receiving flask (*A*) should be changed or the stopcock (*S*) between the receiving flask and the upper receiving tube (*R*) should be turned off. The pressure in the system then can be reduced gradually; 1 mm. to 0.5 mm. of pressure would suffice in most distillations, and the temperature in the distilling flask can be gradually increased. The upper limit of temperature inside the flask varies with the oleoresin.

In some pines lacking a sesquiterpene fraction, all turpentine is removed at 180° C. (and even lower) and 1 mm. of pressure. In other species, the flask has to be heated as much as 200° to 210° C. (at 1 mm. to 0.5 mm. of pressure) to expel all, or almost all high-boiling components of turpentine. As a criterion of the completion of the process, we used an arbitrary method: when cooled rosin is not sticky but can be crushed to dry white powder by pressure of the fingers, the distillation was considered completed although some small quantity of volatile oil might still remain in the flask residue. This distillation method has proved satisfactory and is recommended for future work with pine oleoresins.

In countries with summer rains, there always will be some water in the oleoresin. At the beginning of the distillation, this water will co-distill with turpentine, following the law of boiling two immiscible liquids.⁵ If the amount of water is great, this stage of vacuum distillation can be rather violent.

Turpentine is separated from water by means of a separatory funnel. Traces of water in the distilled samples of turpentines are removed by adding a small quantity of anhydrous sodium sulfate.

The percentage of turpentine in the oil is determined on the weight of pure oleoresin, that is, after the weight of impurities and of water is subtracted. In experimental (not commercial) samples of oleoresin, the amount of impurities—needles, pieces of bark, and occasional insects—is usually very small.

Determining Physical Properties of Turpentine

Before a sample of turpentine is subjected to further investigation, its physical properties are determined. The most commonly determined physical properties are: density, index of refraction, and optical rotation.

Density of turpentine refers to its weight per unit volume. Specific gravity is the ratio of the density of turpentine to the density of water. For practical purposes there is very little difference between specific gravity and density. For fundamental distinction between the two, consult Guenther (59, v. 1, pp. 236-43). In our work, we expressed density by the symbol d_t^t , where t is the temperature at which the observation is made, and the figure 4 refers to the centigrade temperature of water, taken for comparison. We used tube pycnometers 0.2 to 0.3 ml. capacity. Other investigators sometimes used density of water at temperatures other than 4° C.; hence, the symbols d_{15}^t or d_{20}^t . Some authors do not indicate temperature.

Index of refraction is designated with the symbol n_D^t , where t is the temperature of the substance at the time of observation and D is the wavelength of light, that is, the D line of sodium, equivalent to 589 μ . The index of refraction is most conveniently determined by means of an Abbé refractometer; this instrument is provided with a compensator so that the values corresponding to the wavelength of the D line of sodium can be obtained by using an ordinary source of light. With few exceptions, individual trees of pine species show considerable variability in densities and in indexes of refraction. Causes of variability of physical constants within pine species have already been discussed (p. 9).

Sometimes, to compare densities and indexes of refraction of different samples of turpentine, it is necessary to adjust the observed data to uniform temperature, usually 25° C. (157), by using correction factors. For density, for each degree we have used a factor of 0.0008; for index of refraction, 0.00045. We have found that in turpentines these factors give satisfactory results, although the practice of using them has not been considered advisable in determining the qualities of essential oils (59). Turpentines are generally much more uniform and much less complex than many essential oils.

⁵ Consult any text on physical chemistry.

Sutherland (157), using indexes of refraction as the abscissa and densities as the ordinate, both at 25° C., and plotting data for different pure terpenes (fig. 3), showed how useful this type of diagram can be

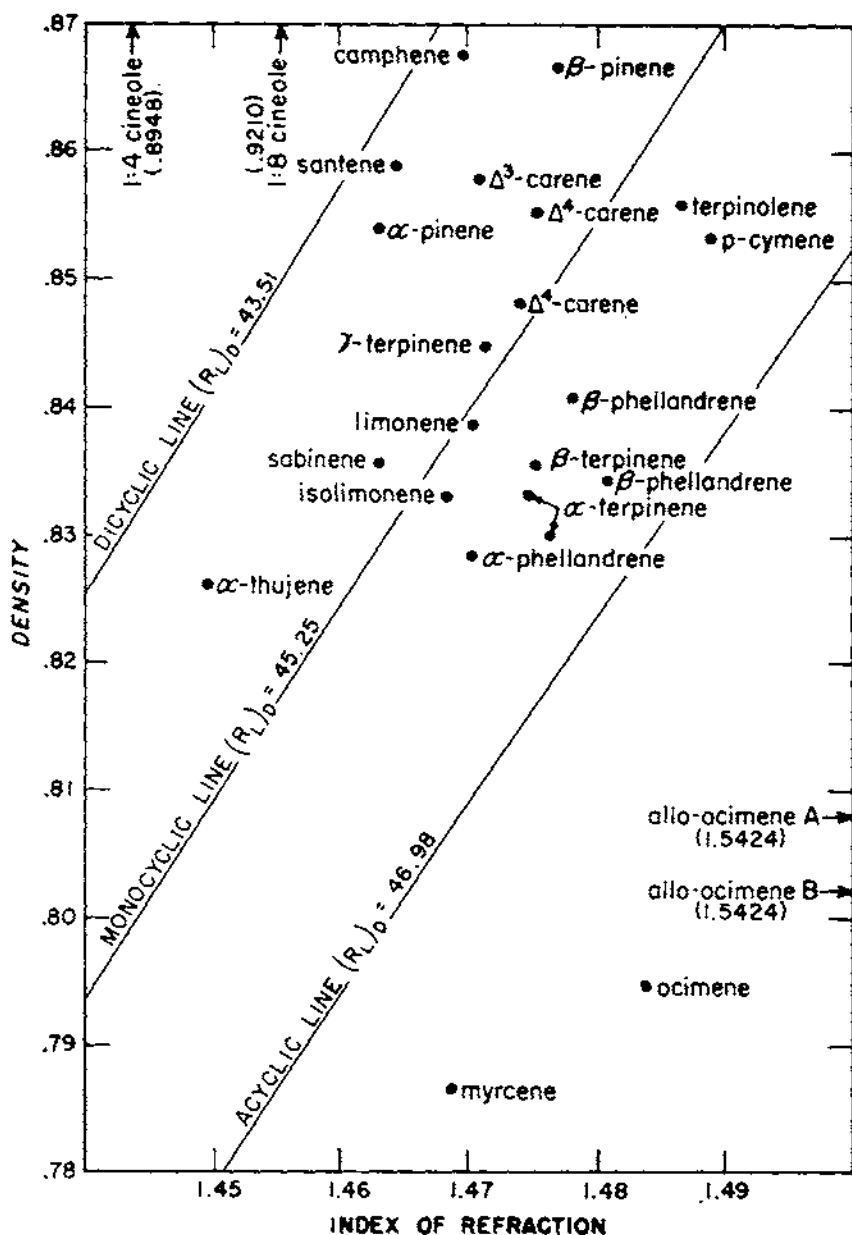


FIGURE 3.—Densities and indexes of refraction of terpenes. After Sutherland (157).

in studying turpentine composition. Figures 4, 5, and 6 illustrate how such diagrams aid in differentiation between species of pines and between turpentines of parent species and the hybrids.

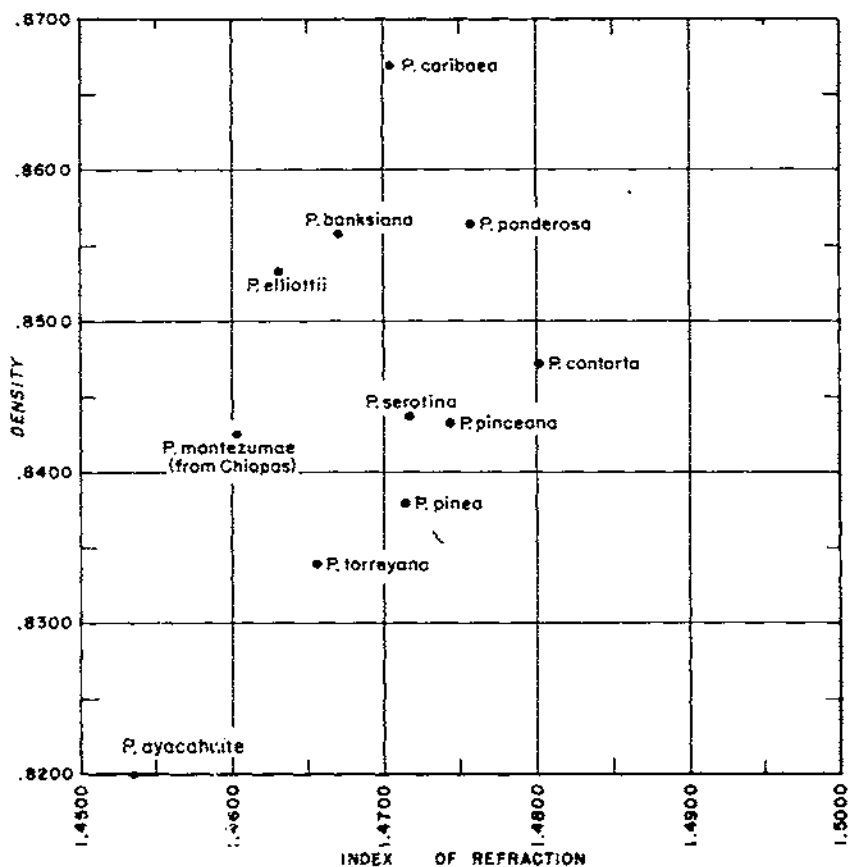


FIGURE 4.—Densities and indexes of refraction of turpentines of several pines. *Pinus elliotii* and *P. banksiana* are α - and β -pinene pines; *P. caribaea*, besides α -pinene, contains some Δ^2 -carene, some β -phellandrene and large amounts of a sesquiterpene, longifolene; *P. ponderosa* always possesses large quantities of Δ^2 -carene; *P. contorta* is a β -phellandrene pine; *P. serotina*, *P. pinceana*, *P. pinea*, and *P. torreyana* contain large amounts of limonene. *P. montezumae* from Chiapas and *P. ayacahuite* turpentine contain an admixture of a paraffin hydrocarbon, *n*-heptane.

Optical rotation of turpentine is usually determined in a tube 10 cm. long and about 10 mm. inside diameter; for small samples we used tubes 5 cm. long having only 6 mm. and 2 mm. inside diameters. As a source of light, a sodium lamp is commonly used. It gives the D line equivalent to a wavelength of 589 μ . In our studies, we used either a sodium lamp or more often a mercury lamp equipped with light filters No. 3480 and No. 4303, which produced light of wavelength = 578 μ . French investigators' "j-line" (jaune, i.e., yellow) has the same wavelength of 578 μ .

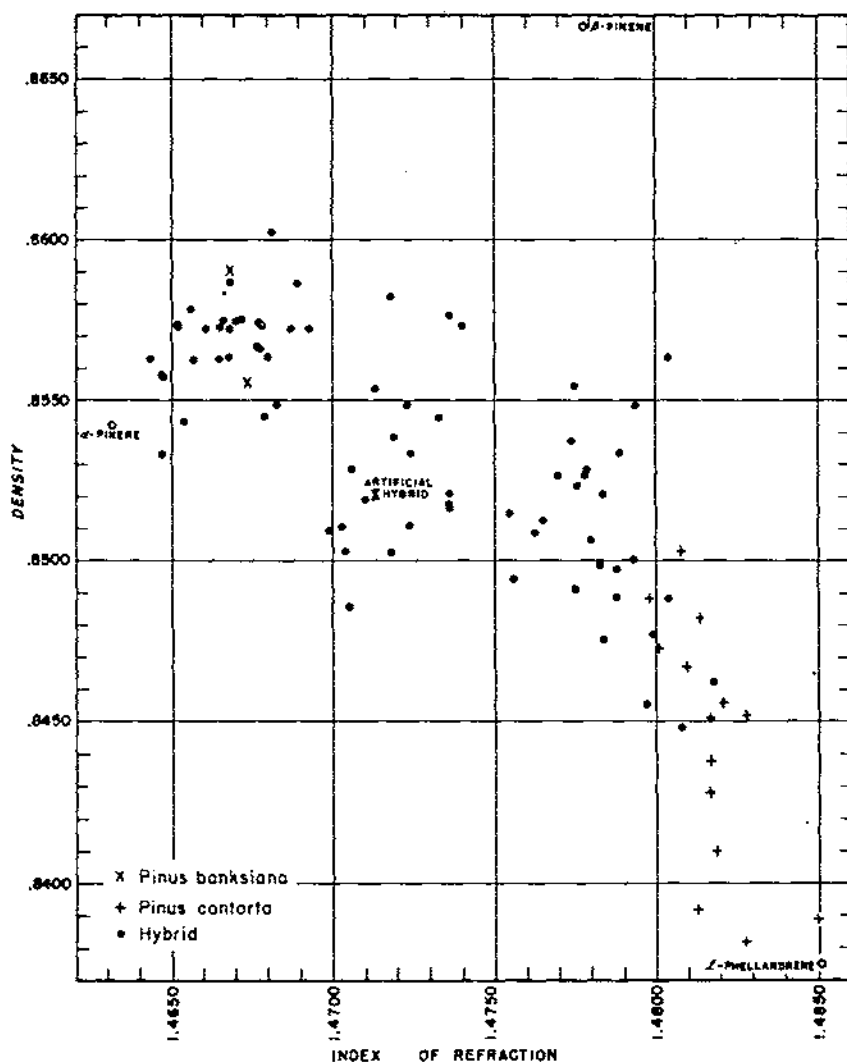


FIGURE 5.—Densities and indexes of refraction of turpentines of *Pinus banksiana* and *P. contorta*, and of the hybrids between the two pines.

Optical rotation is designated by the symbol α_D (or α_D , or $\alpha_{578 m\mu}$). Specific rotation $[\alpha]_D$ is optical rotation divided by the density of the sample, d . Determinations of optical rotation accurate to 0.1 of a degree are satisfactory, because pure substances are not dealt with.

The optical rotation of a turpentine sample has good diagnostic value. For instance, composite *Pinus elliotii* turpentine is levorotatory, whereas composite *P. palustris* turpentine is dextrorotatory. When a sample of crude turpentine possesses a very high rotation to the left, for instance, *P. pinceana*, $[\alpha]_D = -100.6$, or *P. pinca*, $[\alpha]_D = -118.0$, it is an indication of a high percentage of *l*-limonene.

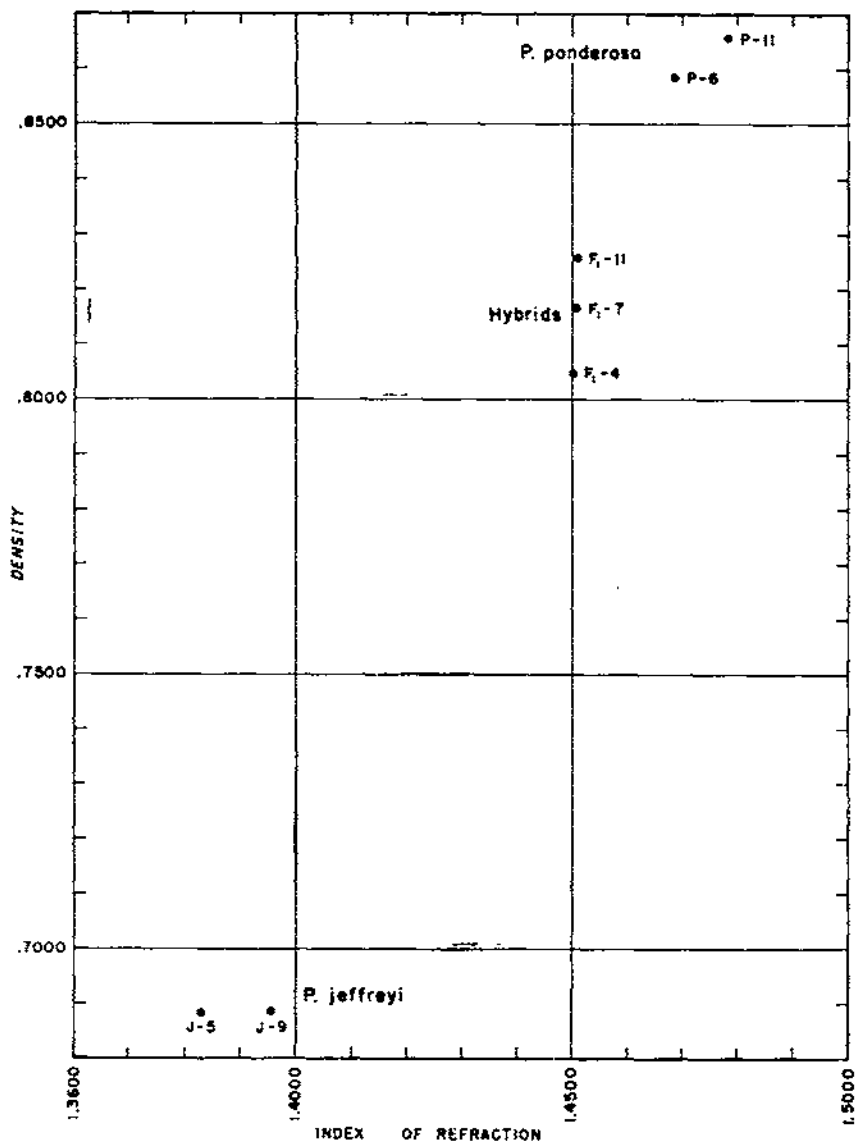


FIGURE 6.—Densities and indexes of refraction of turpentines of *Pinus jeffreyi* and *P. ponderosa*, and of the hybrids between the two pines.

On the other hand, rotation of a turpentine sometimes might be rather misleading. Optical inactivity of a turpentine might indicate a complete absence of optically active components, as for instance in the turpentine of heptane-bearing *Pinus jeffreyi*. But optical inactivity might also be caused by compensating effects of dextro-rotatory and levorotatory terpenes, as exemplified by the optically

inactive turpentine of tree No. 11 of *P. washoensis* (table 2, p. 10); it consisted chiefly of a mixture of α - Δ^3 -carene and *l*- β -pinene.

When a composite sample of pine turpentine is designated as either dextrorotatory or levorotatory, it may be that all individual trees of the locality are either dextrorotatory or levorotatory. Or, again it may be that the sample includes some trees with dextrorotatory and others with levorotatory turpentine. This often unpredictable and little studied variability in optical properties of individual trees is clearly demonstrated by *Pinus ponderosa* from different localities (table 2).

Molecular refraction (MR_D) has been used in our work solely for studies of the sesquiterpenes. (For particulars see a laboratory manual, such as that of McElvain (92), or Guenther (59, v. 1, p. 242).

Fractionating the Turpentine

After the physical characteristics are determined, raw turpentine is subjected to fractional distillation. This procedure separates the turpentine into its components. The boiling points of some components of pine turpentines lie very close to one another (table 3). Therefore, an efficient fractionating apparatus is needed for satisfactory separation of the turpentine components. Inaccurate results of some earlier research can be attributed to poor equipment; during recent years fractional distillation apparatus has been greatly improved.

It should be noted that if a turpentine sample is not appropriately dehydrated, there might be some water distilled over with the first fraction of the turpentine. This water may contain some acids, chiefly acetic and formic (123).

TABLE 3. --Boiling temperatures of some components of pine turpentines

Component	Boiling temperature	Component	Boiling temperature
	°C.		°C.
<i>n</i> -heptane	98	β -terpineol	209-210
α -thujene	150-152	Borneol	212
α -pinene	155-156	Methyl chavicol	213-215
Camphene	160-161	α -terpineol	218-219
β -pinene	164-166	α -terpinyl acetate	220
β -myrcene	166-167	Nerol	224
β -phellandrene	170-172	Bornyl acetate	225-226
Δ^3 -carene	170-173	Bornyl formate	225-230
<i>n</i> -octylaldehyde	171-173	Sesquiterpene range in general; approx.	230-277
<i>p</i> -cymene	175-176	Longifolene	260-261
Limonene	175-176	Cadinene	274-275
Ocimene	176-178	Sesquiterpene alcohols in general; approx.	275-295
Terpinolene	186-187	Diterpenes; approx.	295-310
<i>n</i> -undecane	195-196		
Linalool	198-199		
<i>n</i> -decylaldehyde	207-209		

We have used a column 90 cm. long equipped with a heated jacket and a stillhead permitting a suitable reflux ratio, usually 10 to 1. When preliminary fractionation of a small sample of turpentine indicated that no appreciable amounts of sesquiterpene fractions were present and that easily polymerized terpenes were absent, then the fractionation was performed under atmospheric pressure, which (at Berkeley) usually fluctuates between 755 mm. and 762 mm. But where the presence of high boiling substances had been revealed or suspected, the fractionation was performed at reduced pressure, usually 14 mm. or 15 mm. of mercury. To catch highly volatile substances, such as *n*-heptane, a dry-ice trap was placed between the column and the vacuum pump. Fractions (cuts) were usually taken at 1° intervals. In some pines possessing turpentine of a simple composition, the number of fractions is small. For instance, in *Pinus cooperi* turpentine only four fractions were obtained (table 4). Turpentines of other species had to be separated into many fractions—54 in *Pinus edulis*.

TABLE 4.—Fractional distillation of *Pinus cooperi* turpentine, (to illustrate a turpentine of simple composition)

Fraction	Pressure	Boiling range	Dis-tilled	Density d ₄ ²⁵	Index of refraction n _D ²⁵	Specific rotation [α] _D ²⁵
	mm.	° C.	Percent			Degrees
1	759	155 -157	56.2	0.8576	1.4691	+10.0
2	759	157 -158.2	22.7	.8602	1.4718	-0.2
3	759	158.5-160	8.3	.8617	1.4742	-8.8
4	759	160 -161	7.5	.8632	1.4760	-14.6
Pot residue		+161	4.2			
Losses			1.1			

Even a cursory inspection of a fractional distillation sheet may reveal some interesting information about the turpentine under investigation. Consider, for example, the data on fractionation of *Pinus edulis* (table 5 and fig. 7). Fractions 1 and 2 made up more than 43 percent of the oil; they consisted of a strongly dextrorotatory component. Its density and index of refraction (table 5) suggested that the component perhaps was *d*-α-pinene. The negative rotations of fractions 7, 8, 9 suggested the possible presence of a very small quantity of *l*-β-pinene. The low density of fraction 10 seemed to indicate β-myrcene. The higher densities, positive rotation, and sweet odor of fractions 12 and 13 indicated Δ³-carene. Then, densities began to decrease and reached a minimum at fraction 17. Because the odor of this fraction resembled the odor of ocimene, a search was made there for this hydrocarbon.

Further analyses also indicated the presence of small quantities of *l*,*dl*-limonene in fractions 15 to 19. Fraction 20 had the physical properties of terpinolene. Fractions 23 and 24 possessed an extremely

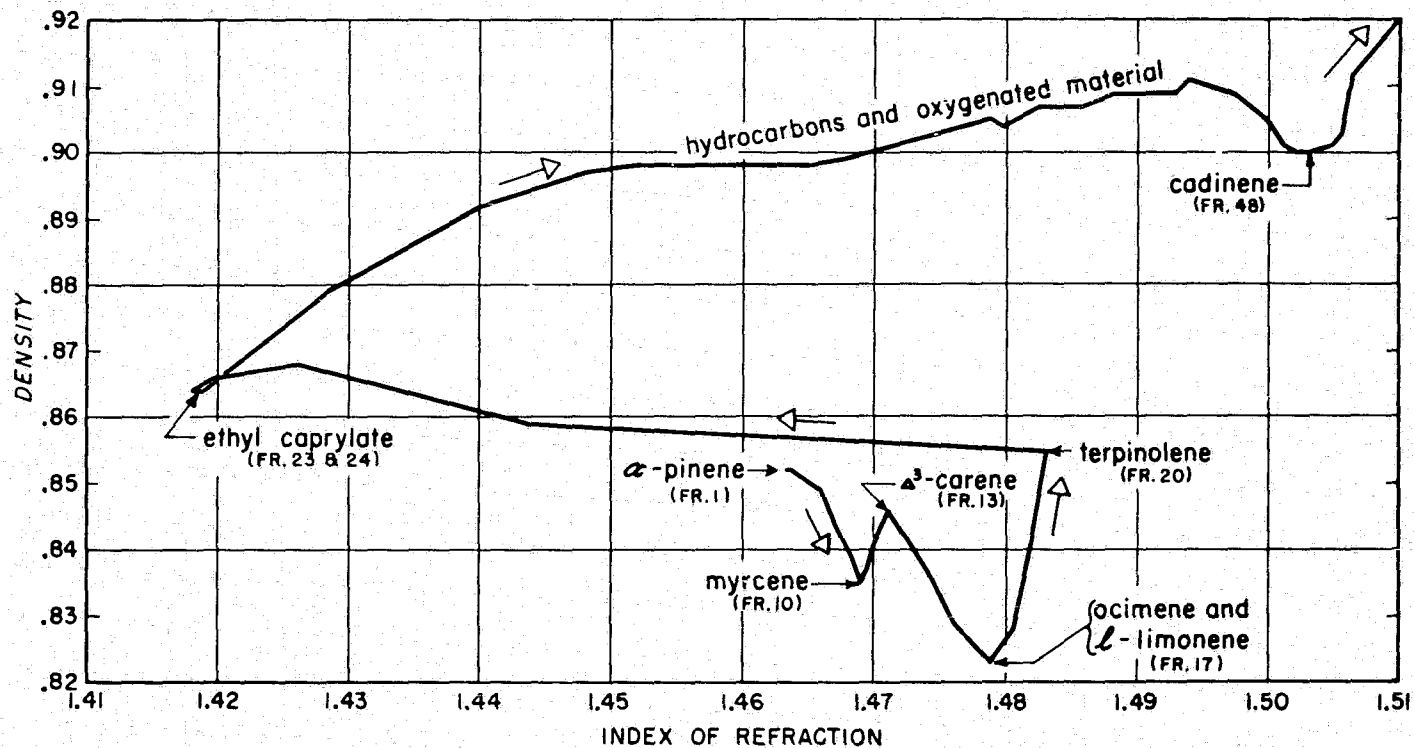


FIGURE 7.—Results of fractional distillation of *Pinus edulis* turpentine plotted according to Sutherland (157).

fragrant odor, which could not be identified with any other essential oil component. The physical properties of these fractions indicated the possible presence of an aliphatic ester. All the way to fraction 43, the fractions (except fractions 27, 28, and 29) were dextrorotatory. Judging from their physical characters, these fractions contained oxygenated terpene compounds. Fractions 44 to 50 were levorotatory; and the last fractions, 51 to 54, were again dextrorotatory. The fractions from 44 to 54 possessed the characteristics of sesquiterpenes.

TABLE 5.—*Fractional distillation of turpentine of Pinus edulis (to illustrate a turpentine of complex nature)*

Fraction	Pressure	Boiling range	Distillate	Density d_4^{20}	Index of refraction n_D^{20}	Specific rotation $[\alpha]_D^{20}$
	<i>mm.</i>	$^{\circ}$ C.	<i>Percent</i>			<i>Degrees</i>
1.....	13	43-43	23.97	0.854	1.4643	+46.8
2.....	13	43-44	19.54	.854	1.4646	+46.9
3.....	13	44-45	1.84	.853	1.4653	+30.4
4.....	13	45-46	1.70	1.852	1.4658	+15.0
5.....	13	46-47	1.90	1.851	1.4665	+5.5
6.....	13	47-49	1.85	.851	1.4672	+2.8
7.....	13	49-51	1.77	.846	1.4678	-10.4
8.....	13	51-53	.43	.843	1.4687	-15.9
9.....	13	53-54	.39	.841	1.4692	-16.4
10.....	13	54-55	.87	.837	1.4699	-8.3
11.....	13	55-56	1.52	.839	1.4703	+2.6
12.....	13	56-57	4.66	.843	1.4708	+10.7
13.....	13	57-58	.86	.848	1.4720	+9.3
14.....	13	58-59	.66	.845	1.4731	+3.6
15.....	13	59-61	.42	.839	1.4750	-1.9
16.....	13	61-63	.40	.831	1.4771	-6.8
17.....	13	63-66	.67	.825	1.4798	-7.0
18.....	13	66-68	.42	.830	1.4815	-3.1
19.....	13	68-70	.67	.843	1.4829	-1.0
20.....	13	70-71	.40	.857	1.4840	+7
21.....	13	71-86	1.07	.861	1.4447	0
22.....	13	86-88	.46	.870	1.4271	0
23.....	13	88-89	1.03	1.868	1.4208	+7
24.....	13	89-90	3.80	.866	1.4190	+7
25.....	13	90-93	.74	.866	1.4196	+9
26.....	13	93-97	.38	.881	1.4291	+4
27.....	13	98-101	.29	.894	1.4410	-2
28.....	13	101-103	.30	.899	1.4490	0
29.....	13	103-106	.29	.900	1.4532	0
30.....	13	106-108	.32	.900	1.4574	+1.4
31.....	13	108-110	.48	.900	1.4624	+4.0
32.....	13	110-111	.27	.900	1.4659	+4.0
33.....	13	111-112	.47	.901	1.4687	+5.6
34.....	13	112-114	1.13	.903	1.4722	+7.8
35.....	13	114-115	.72	.905	3.4760	+10.6
36.....	13	115-116	1.00	.907	1.4797	+11.7
37.....	13	116-116	1.64	.906	1.4808	+11.7
38.....	13	116-117	1.00	.909	1.4837	+14.1
39.....	13	117-118	.99	.909	1.4866	+14.0
40.....	13	118-119	.66	.911	1.4892	+13.9

See footnote at end of table.

TABLE 5.—Fractional distillation of turpentine of *Pinus edulis* (to illustrate a turpentine of complex nature)—Continued

Fraction	Pressure	Boiling range	Distillate	Density d_4^{25}	Index of refraction n_D^{25}	Specific rotation $[\alpha]_D^{25}$
	mm.	° C.	Percent			Degrees
41-----	13	119-120	0.93	0.911	1.4920	+8.6
42-----	13	120-121	1.27	.911	1.4935	+2.2
43-----	13	121-122	1.11	.913	1.4947	+7.7
44-----	13	122-124	.53	.911	1.4982	-5.1
45-----	13	124-126	.67	.907	1.5008	-23.6
46-----	13	126-127	.74	.903	1.5021	-39.0
47-----	13	127-129	1.11	.902	1.5031	-49.2
48-----	13	129-130	2.20	.902	1.5042	-56.6
49-----	13	130-132	2.62	.903	1.5059	-42.5
50-----	13	132-133	1.90	.905	1.5065	-8.5
51-----	13	133-134	2.39	.911	1.5069	+20.2
52-----	13	134-135	1.44	.912	1.5072	+56.2
53-----	13	135-136	1.07	.914	1.5074	+76.8
54-----	13	-----	1.26	.922	1.5109	+41.5
Pot residue and loss-----	-----	-----	3.78	-----	-----	-----

† Estimated.

When fractionation is done carefully, and densities and indexes of refraction of each cut are determined accurately, it is expedient to plot the data on the Sutherland diagram, on which the densities and indexes of refraction of the most common pure terpenes are already shown. Because the two physical characteristics of pure terpenes are given by Sutherland (157) at 25° C., it is necessary to use correction factors if the properties were taken at different temperatures (see p. 13).

French and Russian research workers usually present the results of fractional distillation of their turpentine samples as a set of curves showing densities, indexes of refraction, optical activities, and boiling points of all fractions. The quantity of the distilled turpentine is plotted along the abscissa, and the physical properties are plotted along the ordinate (fig. 8).

IDENTIFYING TURPENTINE COMPONENTS

After the physical properties of the fractions are determined and studied, the suspected components of the turpentine are identified in most cases by preparation of crystalline derivatives.⁶ Using modern methods of determining infrared spectra of the fractions, the components can be identified much faster.

A simple method of ascertaining the approximate composition of a turpentine after it has been fractionated, is to construct a bar diagram with the boiling range plotted along the abscissa and the percent of distillate along the ordinate. Such a diagram for *Pinus chihuahuana*

⁶ Except paraffin hydrocarbons and those new or little known sesquiterpenes and their derivatives, which do not yield known crystalline compounds.

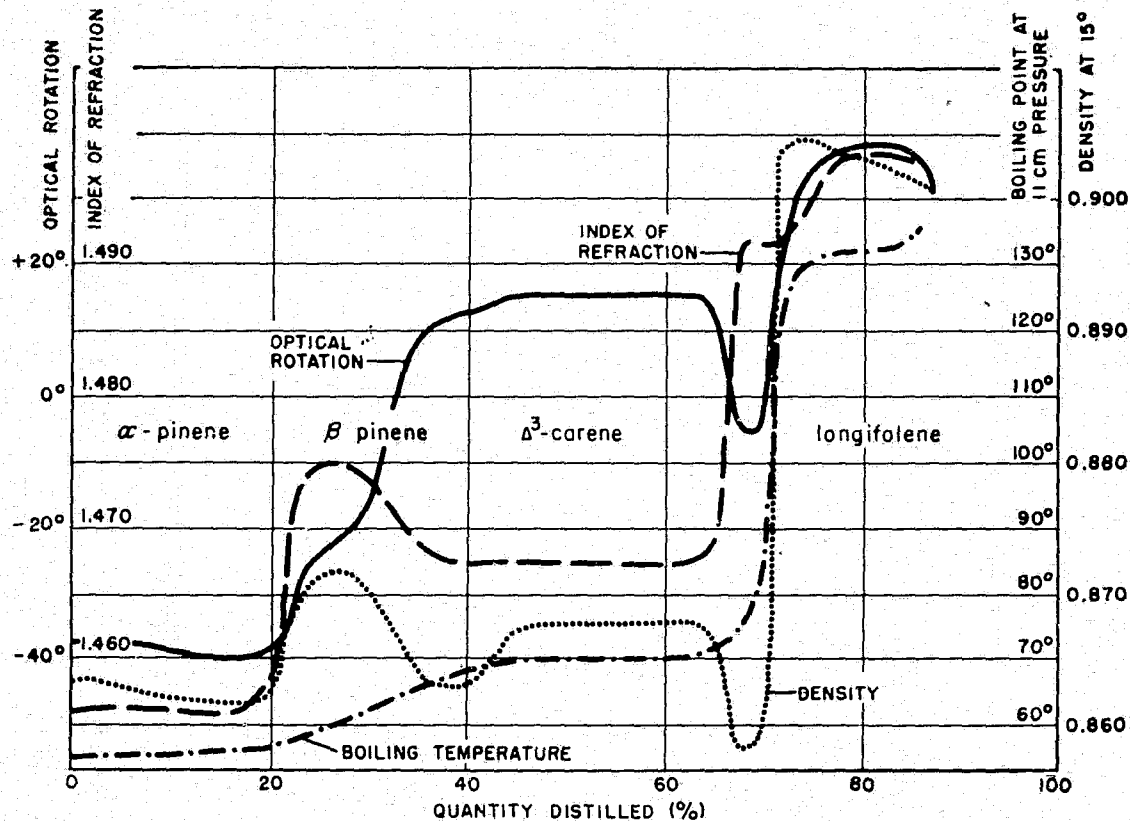


FIGURE 8.—Curves showing results of fractional distillation of *Pinus longifolia* (*P. roxburghii*) turpentine. After Dupont and Uzac (51).

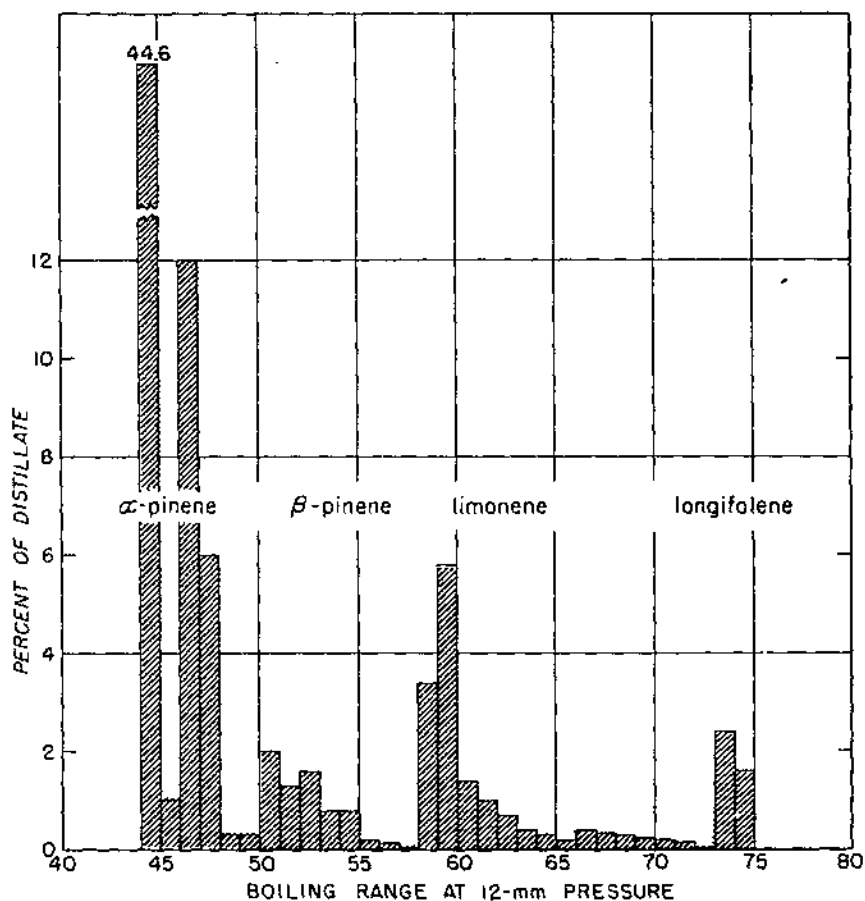


FIGURE 9.—Results of fractional distillation of *Pinus chihuahuana* turpentine.

reveals four major components, represented by the longer bars, in the turpentine (fig. 9). Of course, bar diagrams merely indicate the amount of material distilled at a given range of temperature. When a fractionation is done throughout under atmospheric pressure, the bar diagram gives a good idea of the composition of a turpentine. But when the distillation is started under atmospheric pressure and later continued under reduced pressure, the diagram is rather difficult to interpret. Conversion of boiling points of turpentine components from one pressure to another is a tedious and not too accurate job.

Vapor chromatography is very useful in the analysis of turpentines. For the theory of the method and a description of the apparatus, the reader is referred to some convenient text, such as Keulemans, A.I.M. Gas Chromatography. (Reinhold Pub. Corp. 217 pp. N.Y. 1957.)

The method of vapor chromatography consists essentially of forcing, by means of a stream of inert gas, a small sample of the volatile oil that is to be analyzed, through a column packed with

an adsorbent and maintained at a constant temperature. Components separate according to their volatility partition coefficients as well as adsorptive effects. A resistance device placed at the end of the column detects the arrival of each component and transmits the results to a continuous recorder. The apparatus is rather expensive, and if it is used in turpentine analysis the recorder must be standardized against known pure ingredients of turpentine. A vapor chromatography assembly became available to us only when our project was almost completed, and we applied the method to ascertain the composition of turpentine of *Pinus patula*.

The methods we used to identify the components of turpentines by means of preparation of crystalline derivatives are fully explained in Guenther's *The Essential Oils* (59, v. 1 and 2). For those rare cases when the methods of identification are not described by Guenther, as in the case of ethyl caprylate, we have reported our methods under the particular species in which the compound was found.

Part II. Composition of Gum Turpentine of Pines

COMPONENTS OF PINE GUM TURPENTINES

We have found that pine gum turpentine contains at least 30 different named components, that is, those which have been already reported in literature as ingredients of essential oils. Besides these known compounds, pine turpentine contains at least as many, and probably more, ingredients whose physical properties are not exactly known. Most of these unknown compounds, sesquiterpenes and their oxygenated derivatives, are found in the high-boiling fractions and generally in very small amounts. All told, there are perhaps more than a hundred organic substances in pine gum turpentine.

The components of gum turpentine of pines are listed in Appendix I, p. 143. Structural formulas are given there when known. For sesquiterpenes that appeared to be new, melting points of their hydrochloride are cited. A few sesquiterpenes have not yielded solid derivatives. Some sesquiterpenes and oxygenated compounds were found in such small quantity that it was impossible to identify or to describe them. There is evidence that some oxygenated terpene derivatives occasionally reported as components of gum turpentine are of a secondary origin.

SYSTEMATIC DESCRIPTION OF TURPENTINES

In this publication are listed 92 species and 2 varieties of pines (table 6). Of these 94, turpentine of 76 were analyzed in our laboratory. For the other 18, results obtained by earlier investigators were considered reliable and included in this publication without verification. The pines listed in table 6 do not include many varieties, such as the varieties of *Pinus sylvestris*, *P. nigra*, and *P. pseudostrobus*. These varieties are usually mentioned in the systematic description of the pines.

Essentially, the species are arranged according to the system used in Shaw's monograph of 1914 (142) which contained 66 species. Since that time, Shaw's treatment of the genus *Pinus* has somewhat changed. Several new pines have been described—for instance, Nos. 46, 56, 66, 69 in table 6—and some 20 pines have been elevated from varietal to species rank.

In the light of recent investigations⁷ I prefer, instead of the highly heterogeneous *Pinus chinensis* (142), to use the name *P. tabulaeformis*.

⁷ WE, CHENG-LWEN. THE PHYTOGEOGRAPHIC DISTRIBUTION OF PINES IN CHINA. 77 pp., map. 1947. [M.S. thesis. Copy on file at Yale Univ. School of Forestry, New Haven.]

TABLE 6.—Species of the genus *Pinus* included in this publication¹

SUBGENUS HAPLOXYLON	
Group Cembrae	Group Strobi—Continued
1. <i>P. koraiensis</i> Sieb. & Zucc.	14. <i>P. monticola</i> Dougl.
2. <i>P. cembra</i> L.	15. <i>P. strobus</i> L.
3. <i>P. sibirica</i> Mayr.	Group Gerardianae
4. <i>P. pumila</i> Regel.	16. <i>P. bungeana</i> Zucc.
5. <i>P. albiculis</i> Engelm.	17. <i>P. gerardiana</i> Wall.
Group Flexiles	Group Balfourianae
6. <i>P. flexilis</i> James	18. <i>P. balfouriana</i> Crev. & Balf.
7. <i>P. reflexa</i> Engelm.	19. <i>P. aristata</i> Engelm.
8. <i>P. armandi</i> Franchet	Group Cembroides
Group Strobi	20. <i>P. cembroides</i> Zucc.
9. <i>P. ayacahuite</i> Ehrenb.	21. <i>P. edulis</i> Engelm.
10. <i>P. lambertiana</i> Dougl.	22. <i>P. quadrifolia</i> Parl.
11. <i>P. parviflora</i> Sieb. & Zucc.	23. <i>P. monophylla</i> Torr. & Frém.
12. <i>P. pruce</i> Griseb.	24. <i>P. pinceana</i> Gordon
13. <i>P. griffithii</i> McClelland	25. <i>P. nelsonii</i> Shaw
SUBGENUS DIPLOXYLON	
Group Longifoliae	Group Australes—Continued
26. <i>P. longifolia</i> Roxb. (<i>P. roxburghii</i>)	57. <i>P. palustris</i> Mill.
27. <i>P. canariensis</i> Smith	58. <i>P. caribaea</i> Morelet
Group Leiophyllae	59. <i>P. elliottii</i> Engelm. var. <i>elliottii</i>
28. <i>P. leiophylla</i> Schiede & Deppe	60. <i>P. elliottii</i> Engelm. var. <i>densa</i> Little & Dorman
29. <i>P. chihuahuana</i> Engelm.	61. <i>P. taeda</i> L.
30. <i>P. lumholtzii</i> Rob. & Fern.	62. <i>P. cchinata</i> Mill.
Group Pineae	63. <i>P. lawsonii</i> Roehl
31. <i>P. pinca</i> L.	64. <i>P. teocote</i> Schl. & Cham.
Group Macrocarpae	65. <i>P. montezumae</i> Lamb.
32. <i>P. jeffreyi</i> Crev. & Balf.	66. <i>P. durangensis</i> Martinez
33. <i>P. torreyana</i> Parry	67. <i>P. hartwegii</i> Lindl.
34. <i>P. coulteri</i> D. Don	68. <i>P. rudis</i> Endl.
35. <i>P. sabiniana</i> Dougl.	69. <i>P. cooperi</i> Blanco
36. <i>P. oaxacana</i> Mirov	70. <i>P. michoacana</i> Martinez
Group Lariciones	71. <i>P. engelmannii</i> Carr.
37. <i>P. resinosa</i> Ait.	72. <i>P. pseudostrobus</i> Lindl.
38. <i>P. tropicalis</i> Morelet	73. <i>P. tenuifolia</i> Benth.
39. <i>P. massoniana</i> Lamb.	74. <i>P. occidentalis</i> Swartz
40. <i>P. densiflora</i> Sieb. & Zucc.	75. <i>P. glabra</i> Walt.
41. <i>P. thunbergii</i> Parl.	Group Insignes
42. <i>P. sylvestris</i> L.	76. <i>P. pringlei</i> Shaw
43. <i>P. montana</i> Miller	77. <i>P. oocarpa</i> Schiede
44. <i>P. luchuanensis</i> Mayr.	78. <i>P. oocarpa</i> var. <i>bifoliata</i> Martinez
45. <i>P. taiwanensis</i> Hayata	79. <i>P. halepensis</i> Miller
46. <i>P. huananensis</i> Hsia	80. <i>P. brutia</i> Ten.
47. <i>P. merkusii</i> DeVries	81. <i>P. pilyusa</i> Steven
48. <i>P. insularis</i> Endlich	82. <i>P. pinaster</i> Ait.
49. <i>P. khasya</i> Royle	83. <i>P. virginiana</i> Mill.
50. <i>P. yunnanensis</i> Franchet	84. <i>P. clausa</i> (Chapm.) Vasey
51. <i>P. nigra</i> Arnold	85. <i>P. rigida</i> Mill.
52. <i>P. heldreichii</i> Christ.	86. <i>P. scrotina</i> Michx.
53. <i>P. tabulaeformis</i> Carriere	87. <i>P. pungens</i> Lamb.
Group Australes	88. <i>P. banksiana</i> Lamb.
54. <i>P. ponderosa</i> Laws.	89. <i>P. contorta</i> Dougl.
55. <i>P. arizonica</i> Engelm.	90. <i>P. greggii</i> Engelm.
56. <i>P. washcoensis</i> Mason & Stockwell	91. <i>P. patula</i> Schl. & Cham.
	92. <i>P. muricata</i> D. Don
	93. <i>P. attenuata</i> Lemm.
	94. <i>P. radiata</i> D. Don

¹ The common names of species listed here are given in Appendix 2, p. 153.

I considered *Pinus jeffreyi* and *P. oaxacana*³ as valid species and moved them from the group *Australes* to the group *Macrocarpae*. Then I moved the whole group *Macrocarpae* from the end of Shaw's classification closer to the head of the subgenus *Diploxylon*, so that instead of Shaw's classification: *Leiophyllae*, *Longifoliae*, *Pineae*, *Lariciones*, *Australes*, *Insignes*, and *Macrocarpae*, I arranged the *Diploxylon* pines in the following order: *Longifoliae*, *Leiophyllae*, *Pineae*, *Macrocarpae*, *Lariciones*, *Australes*, and *Insignes*.

Such a rearrangement of the pines is not as drastic as it may appear. As a whole Shaw's system has been retained, but the rearrangement places all aliphatic hydrocarbon pines together, and closer to the monospecific group *Pineae*. *Pinus pinea* of this group has morphological characters and chemical composition of turpentine similar to those of *P. torreyana* of the group *Macrocarpae*. Shaw's arrangement of the subgenus *Haploxylon*, Nos. 1 to 25, has not been changed.

The geographic distribution of the 94 pines (fig. 10) shows that they are restricted to the Northern Hemisphere, where they grow from the Arctic regions to the Equator, jumping it in one place on Sumatra. Of the 94, 62 are found in the New World and only 32 in the Old World. The highest concentration of pines is in California and in Mexico.

Subgenus Haploxylon

Group Cembrae

1. *Pinus koraiensis* Sieb. & Zucc.

Reference (75)

(Fl. Jap. ii, 28. 1842)

Pinus koraiensis grows in the Amur and Maritime provinces of Russia; in Manchuria and Korea, and in the central part of the Japanese island of Honshu. The samples of oleoresin of this pine were obtained from Seoul.

The volatile oil was obtained in two steps. The lower boiling fraction distilled below 190° C. at 0.1 mm. of mercury. This fraction, which amounted to 18 percent of the weight of the oleoresin, comprised the light oil. When the temperature was increased to 200° and pressure reduced to 0.05 mm. of mercury, a heavy oil started to distill. Some of it solidified in the condenser. The heavy oil amounted to 8 percent of the weight of the oleoresin; the total volatile oil amounted to 26 percent. Physical properties of both light and heavy oils are given in table 7.

TABLE 7.—Physical properties of turpentine of *Pinus koraiensis*

Fractions	Yield percent	Density d_4	Index of refraction n_D	Specific rotation $[\alpha]_{25}$
Light oil.....	18	0.8634 ²⁵	1.4730 ²⁵	-11.6°
Heavy oil.....	8	.9300 ²⁵	1.5213 ²⁰	+119.0°

³ In Shaw's monograph *Pinus jeffreyi* is included in *P. ponderosa*; *P. oaxacana*, under the name of *P. apulcensis*, is included in *P. pseudostrobus*; in 1957 I proposed that it be considered as an independent species, *P. oaxacana* (105).

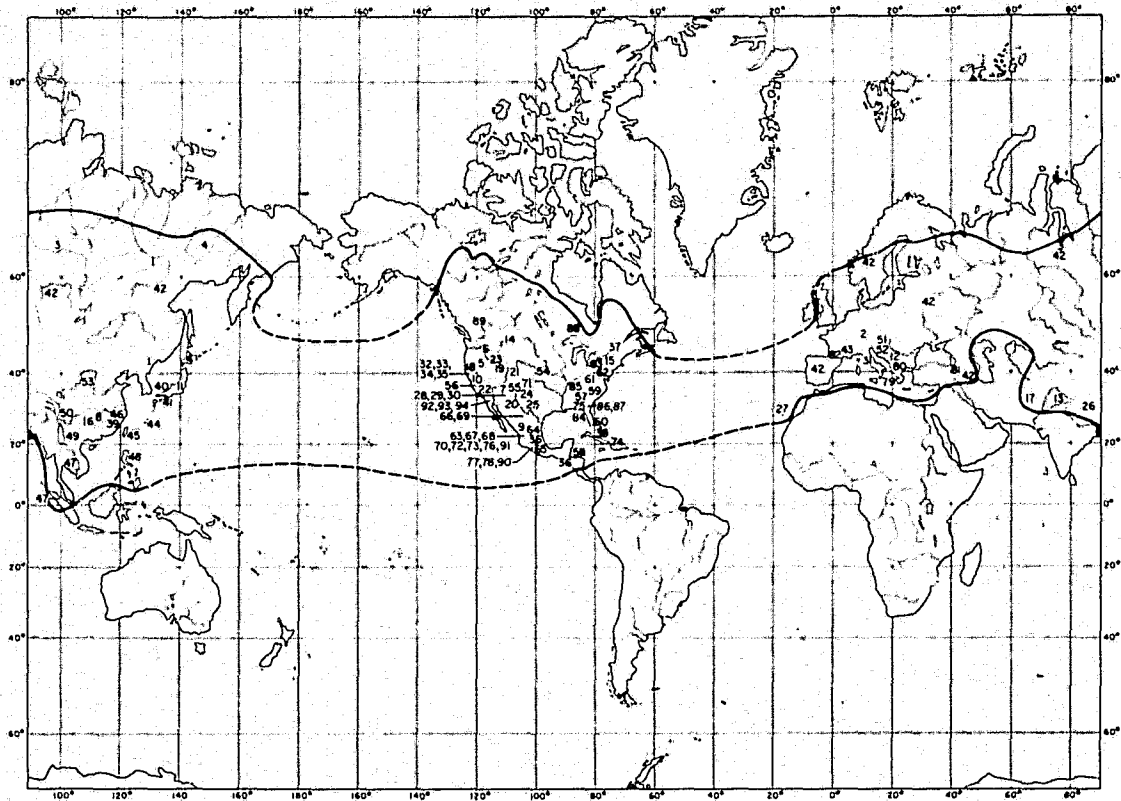


FIGURE 10.—Geographic distribution of pines. Numbers are those under which pines are listed in table 6.

The light oil of *Pinus koraiensis* contained:

Compound:	Percent
<i>l, dl</i> - α -pinene.....	44
<i>l</i> - β -pinene.....	22
α - Δ^3 -carene.....	11
<i>l, dl</i> -limonene.....	8.5
<i>n</i> -undecane (table 8).....	.5
<i>l, dl</i> -bornyl acetate.....	3.0
Sesquiterpenes, mostly <i>d</i> -longifolene.....	7.4

The heavy oil of this pine contained:

Compound:	Percent
Sesquiterpenes.....	12
Diterpenes, mostly cembrene with some diterpene, that yielded a maleic anhydride adduct, m.p. 148°-149° C.....	60-61
Oxygenated compounds.....	3

As a whole, turpentine of *Pinus koraiensis* (i.e., both light and heavy oils combined) had the following composition:

Compound:	Percent
<i>l, dl</i> - α -pinene.....	29.0
<i>l</i> - β -pinene.....	15.0
α - Δ^3 -carene.....	7.0
<i>l, dl</i> -limonene.....	6.0
<i>n</i> -undecane (table 8).....	0.5
<i>l, dl</i> -bornyl acetate.....	2.0
Sesquiterpenes, mostly longifolene.....	9.0
Diterpenes, mostly cembrene with some of those which yielded a maleic anhydride adduct, m.p. 148°-149° C.....	20.5
Oxygenated compounds.....	1.0

TABLE 8.—Physical constants of *n*-undecane

Constant	<i>n</i> -undecane from <i>Pinus koraiensis</i>	<i>n</i> -undecane ¹
Boiling point.....	196°-197° C.....	195.8° C.
Index of refraction, n_D	1.4167 ^{23, 24}	1.41902 ²⁰
Density, d_47364 ²⁵7404 ²⁰

¹ Egloff, G., *Physical constants of hydrocarbons*. Vol. 1, Amer. Chem. Soc. Monog. 78, p. 76. Reinhold Pub. Corp., N.Y. 1939.

Analysis of undecane from *P. koraiensis*: Anal.—Calcd. for $C_{11}H_{22}$: C, 84.52; H, 15.48. Found: C, 84.98; H, 15.15.

2. *Pinus cembra* L.

Reference (116)

(Sp. Pl. 1000: 1753)

Pinus cembra is known in America as Swiss stone pine. It grows at high altitudes in the Alps, eastward to the Carpathian Mountains. The oleoresin sample was collected for us in the forest reserve Paal bei Murau, Obersteiermark, Austria, elevation about 5,500 feet. The turpentine was distilled from the oleoresin under reduced pressure, so that at the end of distillation the pot temperature was 200° C. and pressure was 0.05 mm. of mercury. Under these conditions all

volatile substances were removed. The yield of turpentine was 21.4 percent; its characteristics were as follows:

Density, $d_4^{20} = 0.8522$
 Index of refraction, $n_D^{20} = 1.4654$
 Specific rotation, $[\alpha] = +13.53^\circ$

The turpentine contained:

Compound:	Percent
<i>d</i> - α -pinene.....	85
<i>l</i> - β -pinene.....	9
Residue and losses.....	6

It differed from *Pinus sibirica*, No. 3, turpentine by the complete absence of Δ^3 -carene.

3. *Pinus sibirica* Mayr.

References (18, 132)

(Fremdl. Wald - & Parks. 388: 1906)

Pinus sibirica is considered by Shaw as a synonym of *P. cembra*. It occupies an area entirely different from that of *P. cembra* (fig. 11). This species grows in plains, river valleys, and in the mountains of the northern part of European Russia; in Siberia it is replaced by *P. pumila*, No. 4, and in the east by *P. koraiensis*, No. 1. Russians call *P. sibirica* cedar. In the Transbaikal region and in the Sayan Range of Eastern Siberia as well as in the Altai Mountains of Western Siberia there grows a pine, *P. coronans* Litv., which apparently is a mountain variety of *P. sibirica*.

Schkateloff (132) partially analyzed old oxidized oleoresin of *Pinus sibirica*; the turpentine had a density of 0.865 at 15° C., and contained presumably 20 percent of *d*- α -pinene.

Bardyshev and his coworkers (18) investigated *Pinus sibirica* from the Altai Mountains. Possibly it was the above mentioned *P. coronans*. Physical characteristics were:

Density, $d_4^{20} = -0.8600$
 Index of refraction, $n_D^{20} = 1.4706$
 Specific rotation, $[\alpha]_D = +3.09^\circ$

The composition was:

Compound:	Percent
<i>d</i> - α -pinene.....	69
<i>l</i> - β -pinene.....	7
<i>d</i> -terpene (unknown).....	11
Δ^3 -carene.....	8
<i>l</i> -limonene and dipentene.....	2
Residue and losses.....	3

It is seen that the chemical composition of *Pinus sibirica* differs considerably from that of *P. cembra*. Unfortunately the sesquiterpene fraction of the turpentine was not explored. The chemical characteristics of *P. sibirica* turpentine are closer to those of some other Asiatic and of western American pines than to those of the European *P. cembra*.

4. *Pinus pumila* Regel.

Reference (*Unpub. orig. data*)

(Index Sem. Hort. Petrop. 23. 1858)

Pinus pumila is a very small tree, more often a creeping shrub, growing in the northeastern part of Siberia and in alpine parts of Japan and Manchuria. It is closely related to *P. sibirica*. Some

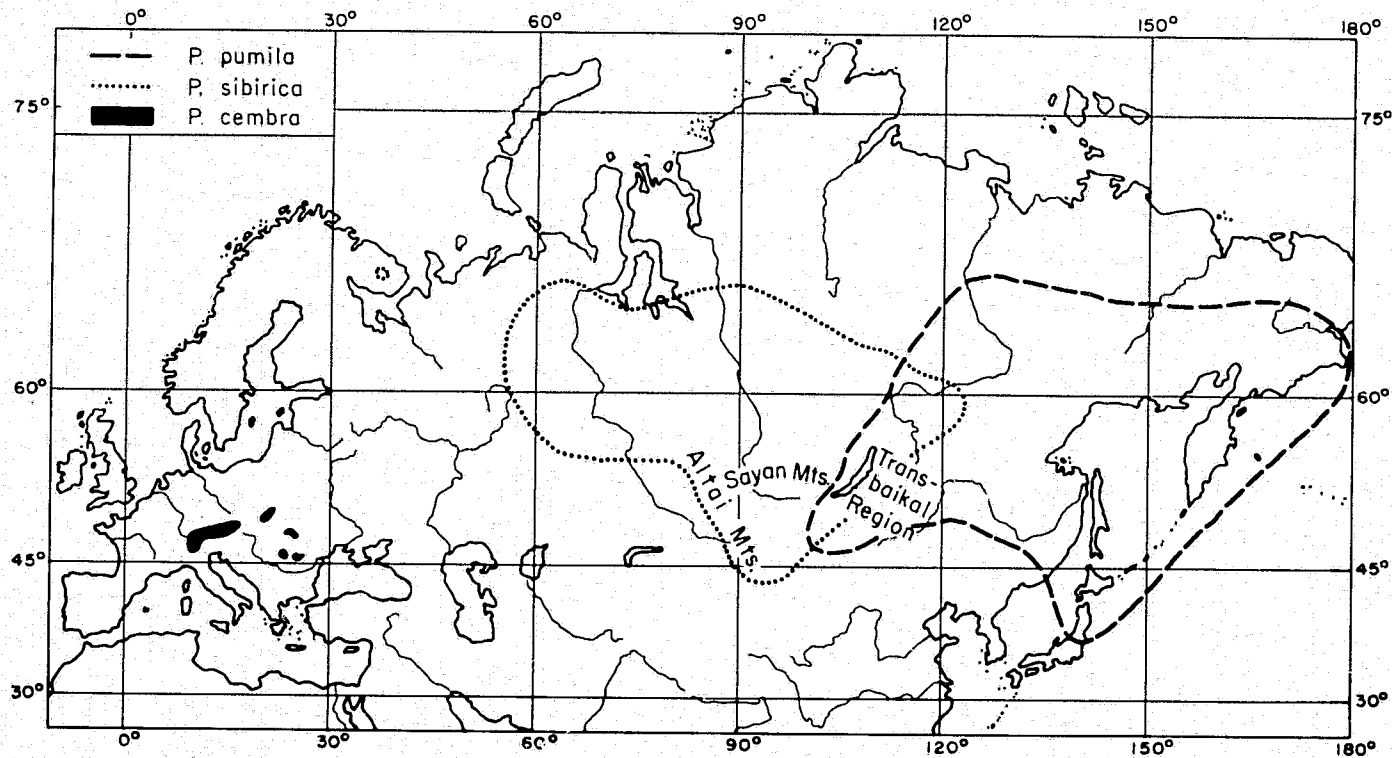


FIGURE 11.—Distribution of three related pines: *P. cembra*, No. 2, *P. sibirica*, No. 3, and *P. pumila*, No. 4.

botanists say that it is merely a dwarf variety of *P. sibirica*; others maintain that it deserves the rank of an independent species.

Because of the small size of *Pinus pumila*, it is rather difficult to obtain a sufficient amount of its oleoresin for analysis. To get some idea of the chemical composition of its turpentine, we obtained from Professor Nobukiyo Takahashi, Yamabe, Sorochi, Hokkaido, a sample of its steam-distilled wood turpentine. Our main purpose was to find out whether the sample contained Δ^3 -carene and thus whether the species was chemically related to *P. sibirica*. We knew that if this terpene were found in large amounts in the wood turpentine of the pine, the terpene would also be present in its gum turpentine (cf. *P. ponderosa*, No. 54).

The physical properties of *Pinus pumila* wood turpentine were these:

Density, d_4^{20} = 0.8855
 Index of refraction, n_D^{25} = 1.4815
 Optical rotation, α_{589}^{25} = +7.34°

Upon fractionation, only 45.5 percent of the oil distilled below 174° C.

Judging from the physical characteristics of the fractions boiling below 173° C., these contained:

Compound:	Percent
<i>d</i> - α -pinene about	25
<i>l</i> - β -pinene about	10
Δ^3 -carene	20

Presence of Δ^3 -carene was verified by preparation of nitrosate which melted at 142°–143°. The remaining 45 percent of the turpentine apparently contained a good deal of secondary oxygenated compounds, not commonly found in large quantities in gum turpentine (however see No. 43). Because the high-boiling compounds of steam-distilled wood turpentine were beyond the scope of the study, they were not analyzed. The most important information gained from the analysis of *Pinus pumila* turpentine was proof of the presence of large quantities of Δ^3 -carene, which ties this pine chemically to its nearest relative, *Pinus sibirica*, No. 3.

5. *Pinus albicaulis* Engelm.

Reference (62)

(Acad. Sci. St. Louis, Trans. 2:209. 1863)

The range of *Pinus albicaulis*, or whitebark pine, extends from British Columbia to the mountains of northern California and the Sierra Nevada. This pine occurs in the Rocky Mountains in Idaho, Montana, and northern Wyoming. It is an alpine tree, often assuming a shrublike form.

The oleoresin examined was collected by the author near Mt. Rose, Nev., elevation 9,000 feet. The volatile oil was separated by heating the oleoresin so that at the end of distillation its temperature reached 200° C. and pressure was reduced to 0.01 mm. of mercury. The last 10 percent of the distillate had the consistency of glycerol. The yield of turpentine was 31.15 percent.

Physical properties of the turpentine were as follows:

Density, d_4^{20} = 0.8979
 Index of refraction n_D^{25} = 1.4971
 Specific rotation, $[\alpha] = -25.1^\circ$

The turpentine was found to contain approximately:

Compound:	Percent
<i>d</i> - Δ^3 -carene (table 9)	32
α -terpinyl acetate	3
<i>l</i> -cadinene	10
Albicaulene	42
Albicaulol	0.2
Cembrene (a diterpene)	2.5

Later, albicaulene and albicaulol were identified in other white pines. Dauben⁸ determined the structure of albicaulol (from *Pinus armandi*, No. 8) and proposed a structural formula for it.

TABLE 9.—Identification of Δ^3 -carene in *Pinus albicaulis* turpentine

Property	Δ^3 -carene ¹	Fractions 2 and 3
Boiling point	168°–171° C. at 1 mm.	165°–169° C. at 740 mm.
Density	d_4^{25} , 0.8668	d_4^{25} , 0.8625
Refractive index	n_D^{25} , 1.4675	n_D^{25} , 1.4700
Molecular refraction	$M R_D$, 43.5	44.0
Carbon, percent	88.23 ²	88.46
Hydrogen, percent	11.77 ²	12.03
Melting point of nitro-sate	146° C. ³	146°–147° C.

¹ Dupont, *C. Ann. Chim.*, 1, 184. 1924.

² Calculated.

³ Aschan, *O. Ann.*, 461, 20. 1928.

Group Flexiles

6. *Pinus flexilis* James

Reference (61)

(Exp. Rocky Mts. 2: 27, 35. 1823)

Pinus flexilis, commonly known as limber pine, grows in the Rocky Mountains from Alberta and southeastern British Columbia to the Trans-Pecos region of Texas, in northern Mexico, and from California to Nebraska.

An oleoresin sample was collected by the author from the White Mountains, lying between the Owens Valley of California and the deserts of Nevada, at an elevation of 10,000 feet. In distilling the oleoresin of limber pine, great difficulties were experienced in expelling the higher boiling fractions of volatile oil (these hardly could be called turpentine). At 0.05 mm. of pressure with the flask temperature reaching 210° C., the residue (rosin) still was rather soft. This property seemed to indicate that some high-boiling volatile substances remained in the residue. Apparently these substances are of the nature of diterpenes, similar to cembrene of *Pinus albicaulis*, No. 5.

Twenty percent of turpentine was obtained. It possessed the following characteristics:

Density, d_4^{25} = 0.8606
 Index of refraction, n_D^{25} = 1.4707
 Specific rotation, $[\alpha]_{D}^{25}$ = +41.2°

⁸ William G. Dauben, Professor of Organic Chemistry, Univ. Calif., Berkeley. Personal communication.

The turpentine was found to be composed mainly of the following ingredients:

Compound:	Percent
<i>d,l</i> - α -pinene	80
Albicanlene	17
Bicyclic sesquiterpene of unknown structure	3

The diterpenes remained in the flask residue and were not investigated.

7. *Pinus reflexa* Engelm.

Reference (101)

(Bot. Gaz. 7:4. 1882)

Pinus reflexa grows in the mountains of southeastern Arizona, southwestern New Mexico, and northern Mexico (Sonora and south to Sinaloa, Durango, Zacatecas, and Nuevo Leon, and especially in Chihuahua and Tamaulipas).

The synonymy of this pine is confusing. Some botanists call it *Pinus strobiformis* Engelm. (156); others prefer to call it *P. ayacahuite* var. *brachyptera* (142). Still others believe that the proper name for this pine should be *P. flexilis* var. *reflexa* (86). Another group of botanists, including such authorities as Standley (154) and Martinez (88) believe that this pine is different from both *P. flexilis* and *P. ayacahuite* and call it *P. reflexa*.

Samples of oleoresin were collected in July and August 1951 on the Apache Indian Reservation, Ariz., near the logging town of Maverick, at an elevation of 8,100 feet. The turpentine was separated from the rosin under reduced pressure. At the end of the distillation, the pot temperature was 190° C. and the vacuum gage indicated 3 mm. of pressure. Turpentine amounted to 17.7 percent. Its physical characteristics were:

Density $d_4^{20} = 0.8456$
 Index of refraction, $n_D^{20} = 1.4669$
 Specific rotation, $[\alpha]_{D^{20}} = 0.0^\circ$

Its composition was:

Compound:	Percent
<i>n</i> -heptane	5
<i>d,l</i> - α -pinene	75
Δ^3 -carene	5
<i>d</i> -terpinolene	5
<i>n</i> -undecane	2-3
A bicyclic sesquiterpene possessing two double bonds, possibly eadinene	5

It is seen that the turpentine of *Pinus reflexa* differs considerably from the turpentine of *P. flexilis*, No. 6. On chemical grounds alone, the two pines should be considered as different species (101).

The procedure used in identification of *n*-heptane in the turpentine of *Pinus reflexa*, was as follows: Fraction 1 was repeatedly shaken with fuming sulfuric acid; the unreacted part of the oil was washed with sodium carbonate and dried over anhydrous sodium sulfate. The oil was optically inactive; d_4^{22} , 0.6826; n_D^{23} , 1.3868; b.p., 98.4° C. The respective values for *n*-heptane⁹ are d_4^{20} , 0.68368; n_D^{20} , 1.38764;

⁹ ROSSING, ET AL. SELECTED VALUES OF PROPERTIES OF HYDROCARBONS. [U.S.] Natl. Bur. Standards Cir. 461, p. 39. 1947.

b.p., 98.42°. (Anal.-Calcd. for C_7H_{14} : C, 83.91; H, 16.09. Found: C 84.32; H, 15.89)

8. *Pinus armandi* Franchet References (Dauben, *Int.* 8, p. 34; 111)
(Nouv. Arch. Mus. Paris, ser. 2, vii, 95, 96, t. 12. 1884)

Pinus armandi is a native of China. It is of wide distribution, scattered over a vast but ill-defined range. It is found in Shensi, Hupeh, Szechuan, Kweichow, southwest Kansu, and in other adjacent provinces of central and southwestern China. It also occurs in Burma, in southern Japan, in Formosa, and on the Island of Hainan. A sample of oleoresin was obtained from Formosa, where this pine is known as *P. armandi* var. *mastersiana* Hyata.

In the process of separating the volatile oil from the rosin, 32 percent of oil was obtained at 150° to 170° C. and 10 mm. of pressure, mercury. This part of the distillate was designated as light oil. Its characteristics were these:

Density, $d_4^{20} = 0.8635$
Index of refraction, $n_D^{20} = 1.4701$
Specific rotation, $[\alpha]_{D,20} = -31.3^\circ$

When the temperature was increased to 210° C. and the pressure reduced to 2 mm. of mercury, 7 percent more of volatile oil was obtained; this oil had the consistency of castor oil and was of a yellowish color. It possessed high density and high index of refraction. Owing to the formation of crystals in the oil, exact measurements of its physical properties were not taken.

The light oil of *Pinus armandi* had the following composition:

Compound:	Percent
<i>l</i> , <i>dl</i> - α -pinene.....	53.5
<i>l</i> -camphene.....	3
<i>l</i> - β -pinene.....	5
<i>l</i> -limonene.....	21
<i>n</i> -undecane (table 10).....	0.7
<i>l</i> -bornyl acetate.....	5.5
A bicyclic sesquiterpene with two double bonds, b_{70}^{20} , 116°-118° C.....	2.4
A bicyclic sesquiterpene related to cadalene.....	3
Pot residue and loss.....	5.0

TABLE 10.—Properties of a saturated hydrocarbon, *n*-undecane, from *Pinus armandi*

Property	<i>n</i> -undecane from <i>P. armandi</i>	<i>n</i> -undecane ¹
Index of refraction, n_D	1.4166 ^{22.5}	1.4190 ²⁰
Density, d_47362 ²³7404 ²⁰
Boiling point, b_{760}	196°-197° C.....	195.8° C.

¹ Ealovv, G., *Physical constants of hydrocarbons*. Vol. 1, Amer. Chem. Soc. Monog. 78, p. 76. Reinhold Pub. Corp., New York, 1939.

Composition of the heavy oil was estimated to be:

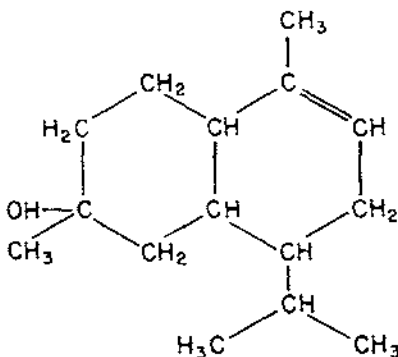
Compound:	Percent
<i>l</i> -bornyl acetate.....	12.5
A bicyclic sesquiterpene (b_{12} , 116°-118° C., with two double bonds, same as in the light oil, but in larger quantity and of higher purity).....	8-9
A bicyclic sesquiterpene related to cadalene.....	36
A sesquiterpene alcohol, albicaulol (See No. 5).....	8
Cembrene.....	25
A diterpene which gave a maleic anhydride adduct.....	5
Pot residue and loss.....	5

Composition of the total oil of *Pinus armandi*, both light and heavy, was found to be approximately as follows:

Compound:	Percent
<i>l</i> , <i>dl</i> - α -pinene.....	44
<i>l</i> -camphene.....	2
<i>l</i> - β -pinene.....	4
<i>l</i> -limonene.....	17.5
<i>n</i> -undecane.....	1
<i>l</i> -bornyl acetate.....	6.5
A bicyclic sesquiterpene, having two double bonds and boiling at 12 mm. pressure at 116° to 118° C.....	3.5
A bicyclic sesquiterpene, related to cadalene.....	9
A sesquiterpene alcohol, albicaulol, originally found in turpentine of <i>Pinus albicaulis</i> (See No. 5).....	1.5
Cembrene, a diterpene also first found in <i>P. albicaulis</i> turpentine.....	4.5
A diterpene which gave a maleic anhydride adduct.....	1
Pot residue and loss.....	5.5

The sesquiterpene alcohol (albicaulol) of *Pinus armandi* was further studied by Dauben.¹⁰ A sample of oleoresin received from Formosa for his work contained less albicaulol and more cembrene than the sample just discussed; it was obtained in a different locality. Dauben found that albicaulol had a cadinane [2,8-dimethyl-5-isopropyl-bicyclo-(4,4,0)-decane] skeleton, a hydroxyl group and a carbon-carbon double bond. The most probable location of the double bond was found to be between carbon atoms 7 and 8. The hydroxyl group is apparently of the tertiary nature and the carbon atom 2 appears to be the most probable location of the hydroxyl.

Dauben proposed the following structural formula of albicaulol:



¹⁰ See footnote 8, p. 34.

Group *Strobi*9. *Pinus ayacahuite* Ehrenb.

Reference (100)

(Linnaea xii, 492. 1838)

Pinus ayacahuite is a noble Mexican pine, possessing morphological characters similar to those of *P. lambertiana*, *P. flexilis*, and *P. strobus* (88). It grows over an extensive area from the northern States of Sonora and Chihuahua to Chiapas. It is also found in the Santa Barbara Mountains of Honduras (6), and in the highlands of Guatemala (139). Martinez (88) distinguishes three varieties of *P. ayacahuite*:

(1) Typical,¹¹ which is found in the southern part of Mexico and in Central America. In Chiapas it is called Pinabete (a name commonly applied to *Abies*) or sometimes pino de azucar, i.e., sugar pine.

(2) Var. *veitchii* of the central part of the country (Puebla and adjacent States).

(3) Var. *brachyptera* of the north (Chihuahua, Sonora, Sinaloa, Durango, and northern part of Zacatecas.)

Because the author collected his oleoresin sample of this pine in the State of Chiapas, it can be classified as coming from typical *Pinus ayacahuite*.

The turpentine was distilled from the oleoresin *in vacuo*. At the beginning of the distillation, some volatile oil was obtained at room temperature under 40 mm. of pressure. Towards the end, the temperature of the oleoresin was increased to 200° C., and the pressure was reduced to 1 mm.

Yield of the turpentine was 17 percent of the weight of the oleoresin. The turpentine had the following characteristics:

Density, $d_4^{20} = 0.8194$
 Index of refraction, $n_D^{20} = 1.4528$
 Specific rotation, $[\alpha]_D^{20} = +7.93^\circ$

It is seen from these data that the turpentine possessed a lower density and a lower index of refraction than most turpentines. (See fig. 4, p. 15).

The composition of the turpentine was as follows:

Compound:	Percent
<i>n</i> -heptane (table 11)	20
<i>d</i> - α -pinene	70
terpinolene, about	5
Possibly a small amount of unidentified oxygen-containing derivatives; and a bicyclic sesquiterpene	3

The sesquiterpene possessed two double bonds; the melting point of its hydrochloride was 108° C.

¹¹ According to the rules of the International Code of Botanical Nomenclature, adopted in 1950, the correct name of this variety should be: *P. ayacahuite* var. *ayacahuite*.

TABLE 11.—Constants of combined purified fractions 1 and 2 of *Pinus ayacahuite* turpentine and those of *n*-heptane

Property	Fractions 1 and 2	<i>n</i> -heptane ¹
Density, d_{20}^{20}	0.6746 ²⁵	0.684 ²⁰
Index of refraction, n_D^{20}	1.3867 ²³	1.3867 ²³
Boiling point.....	98° C. at 764 mm.....	98.52° C. at 760 mm.
Carbon, percent.....	83.49.....	83.91
Hydrogen, percent.....	16.23.....	16.09

¹ *Handbook of chemistry and physics*. Ed. 27, pp. 810-811. Chem. Rubber Pub. Co., Cleveland, Ohio. 1943.

10. *Pinus lambertiana* Dougl.

References (108, 136)

(Trans. Linn. Soc. Lond. 15: 500. 1827)

Pinus lambertiana, or sugar pine, is the most majestic of all pines, reaching a height of 225 feet and a diameter of 10 feet. It grows from southern Oregon to the Mexican State of Baja California, in mixture with other conifers at middle elevations of mountain ranges.

In 1913, turpentine of sugar pine growing at an elevation of 5,800 feet was obtained by steam distillation and analyzed by Schorger (136) with the following results:

Yield of turpentine=16.4 percent
 Density, d_{15}^{15} =0.8663
 Index of refraction, n_D^{15} =1.4728
 Specific rotation, $[\alpha]_D^{25}$ =+10.42°

Composition of the turpentine was reported to be as follows:

Compound:	Percent
<i>d</i> - α -pinene.....	70-75
β -pinene.....	about 5
Probably phellandrene.....	2-3
Probably aliphatic hydrocarbon.....	2-3
A sesquiterpene of aromadendrene type.....	10-12

In 1947, a sample of oleoresin was obtained under the author's supervision in the Sierra Nevada at an elevation of about 3,500 feet. Twenty trees yielded, in 2 months, about 10,000 grams of honeylike oleoresin that remained liquid after a prolonged storage. In some samples, rosin acids precipitated reluctantly; in others they did not precipitate at all. Turpentine was obtained by distilling the oleoresin under reduced pressure. Toward the end of the distillation, the temperature inside the flask was 200° C. and the pressure was 0.02 mm.

A measure of 5,690 grams of oleoresin yielded 18.4 percent turpentine, having the following characteristics:

Density, d_4^{20} =0.8669
 Index of refraction, $n_D^{27.5}$ =1.4753
 Specific rotation, $[\alpha]_D^{27.5}$ =-7.46°

The specific rotation $[\alpha]$ of 15 turpentine samples, obtained from individual trees, varied from -18.25° to -1.35° .¹²

The turpentine was distilled at atmospheric pressure until the temperature reached 187° C. Finally the pressure was reduced to 0.1 mm., and the distillation was discontinued when the temperature reached 200° . The turpentine contained:

Compound:	Percent
<i>l</i> - α -pinene.....	65
<i>l</i> - β -pinene.....	13
An unidentified monocyclic terpene possessing two double bonds, about.....	2
A bicyclic sesquiterpene of cadalene type possessing two double bonds.....	10
A sesquiterpene alcohol $C_{15}H_{26}O$, m.p. 133°	2
An unidentified diterpene, about.....	2
Residue and losses.....	6

Attempts to prepare crystalline derivatives with the methods used for the identification of dipentene, terpinene, and carene were unsuccessful.

It is noteworthy that the sesquiterpene alcohol of *Pinus lambertiana* possessed about the same melting point (133° C.) as the sesquiterpene alcohol of *P. albicaulis*, No. 5 (135°).

Results of our investigation are at variance with those obtained by Schorger. The discrepancy in optical rotation perhaps could be easily explained (see table 2, p. 10) in light of our present knowledge of the variability of optical properties of pine turpentines.

The presence of α and β -pinene has been verified; possibly, small amounts of phellandrene were present but not identified; aliphatic hydrocarbons were not detected; the sesquiterpene fraction was more fully explored. Later work with turpentines of white pines indicates that it is advisable to repeat the analysis of turpentine of this pine.

11. *Pinus parviflora* Sieb. & Zucc.

Reference (61)

(Fl. Jap. 2 : 27 t. 115. 1842)

Pinus parviflora is the Japanese white pine. Its common name is Himekomatsu. It grows in the mountains of central Japan, and it includes several varieties. The northern variety, extending to Hokkaido is known as *P. pentaphylla* or Goyomatsu. A variety growing on Formosa is known as *P. morrisonicola* Hayata or *P. formosana* Hayata. Variety *fenzeliana* Hand.-Mazz., reported from the Island of Hainan, is apparently the same pine as *P. kwangtungensis*, which grows on the mainland (see fig. 13, p. 72). Wu¹³ thinks that the original home of *P. parviflora* is southern China. These notes emphasize some of the nomenclature difficulties encountered in reporting turpentine composition of a pine.

The sample of oleoresin used in our work came from typical *Pinus parviflora* from near the village of Andon, Nagano prefecture, Japan, elevation 3,000 feet. The oleoresin was distilled so that towards the end of the operation the pressure was reduced to 0.2 mm. and pot temperature reached 175° C.; under these conditions, the residue was still soft. With an increase of temperature to 210° , more volatile oil

¹² In some populations of sugar pine, turpentine is predominantly dextrorotatory.

¹³ See footnote 7, p. 26.

was obtained; this part of the turpentine had the consistency of castor oil. The total volatile oil amounted to 28 percent of the weight of the oleoresin.

Physical characters of the turpentine were:

Density, $d_4^{20} = 0.8880$
 Index of refraction, $n_D^{20} = 1.4858$
 Specific rotation, $[\alpha]_D^{20} = +17.66$

The turpentine contained the following substances:

Compound:	Percent
<i>l,d,l</i> - α -pinene.....	50
Acetic acid ester of a terpene alcohol.....	2
A bicyclic sesquiterpene, possessing two double bonds (its dihydrochloride melted at 107° to 108° C.).....	25
Cadinene (table 12).....	8
Albicaulene, together with another sesquiterpene, which upon dehydrogenation, gave azulene (C ₁₅ H ₁₃) (table 13).....	15

TABLE 12.—Constants of fraction 21 of *Pinus parviflora* turpentine and cadinene

Property	Fraction 21	Cadinene †
Boiling point.....	265°–266° C. at 740 mm. 134°–136° C. at 16 mm.	134°–136° C. at 11 mm.
Density.....	d_4^{20} , 0.9154.....	d_4^{20} , 0.9189
Index of refraction.....	n_D^{20} , 1.5038.....	n_D^{20} , 1.5079
Molecular refraction.....	65.97.....	66.13
Analysis.....	Pct. C, 87.29 } found..... Pct. H, 12.06 }	Pct. C, 88.23 } calcd. for Pct. H, 11.77 } C ₁₅ H ₂₄
Melting point of dihydrochloride.....	117°–118° C.....	117° C.
Melting point of dihydrochloride of Fr. 21 mixed with cadinene dihydrochloride.....	117°–118° C.....	

† Henderson and Robertson. Amer. Chem. Soc. Jour., 125: 1992. 1924.

TABLE 13.—Constants of albicaulene and fraction 22 of *Pinus parviflora*

Property	Albicaulene †	Fraction 22
Boiling point.....	180° C. at 20 mm.....	136°–138° C. at 0.5 mm.
Density, d_4^{20}	0.9195.....	0.9125
Index of refraction, n_D^{20}	1.5190.....	1.5150
Molecular refraction.....	67.96.....	67.42
Molecular refraction calcd. for C ₁₅ H ₂₄	67.86.....	
Pierate of dehydrogenation product, melting point.....	113° C.....	113° C.
Maleic anhydride addition product: Melting point.....	149° C.....	150° C.
Mixed melting point.....	150° C.....	

† Haagen-Smit, Wang, and Mirov (62).

12 *Pinus peuce* Griseb.

Reference (75)

(Spicil, Fl. Rumel. 2, 349. 1844)

Pinus peuce is a rare pine of southeastern Europe, morphologically similar to *P. griffithii* (*P. excelsa*) of India, No. 13. *P. peuce* grows in a few places in the mountains of southern Yugoslavia and in the adjacent parts of Albania, Bulgaria, and Greece at elevations from 2,500 to 6,000 feet (fig. 12).

An oleoresin sample of *Pinus peuce* was obtained in 1954 through the courtesy of Prof. Dr. Branislav Pejoski of the University of Macedonia, Skopje, Macedonia, Yugoslavia. Pejoski himself had already investigated the oleoresin of this pine (personal communication, 1954). His steam-distilled turpentine had the following characteristics:

Yield=32.4 percent
 Density, $d_{20}^{20}=0.861$ to 0.866
 Index of refraction, $n_D^{20}=1.462$ to 1.463
 Specific rotation, $[\alpha]_D^{20}=-13.33^\circ$ to -29.36°

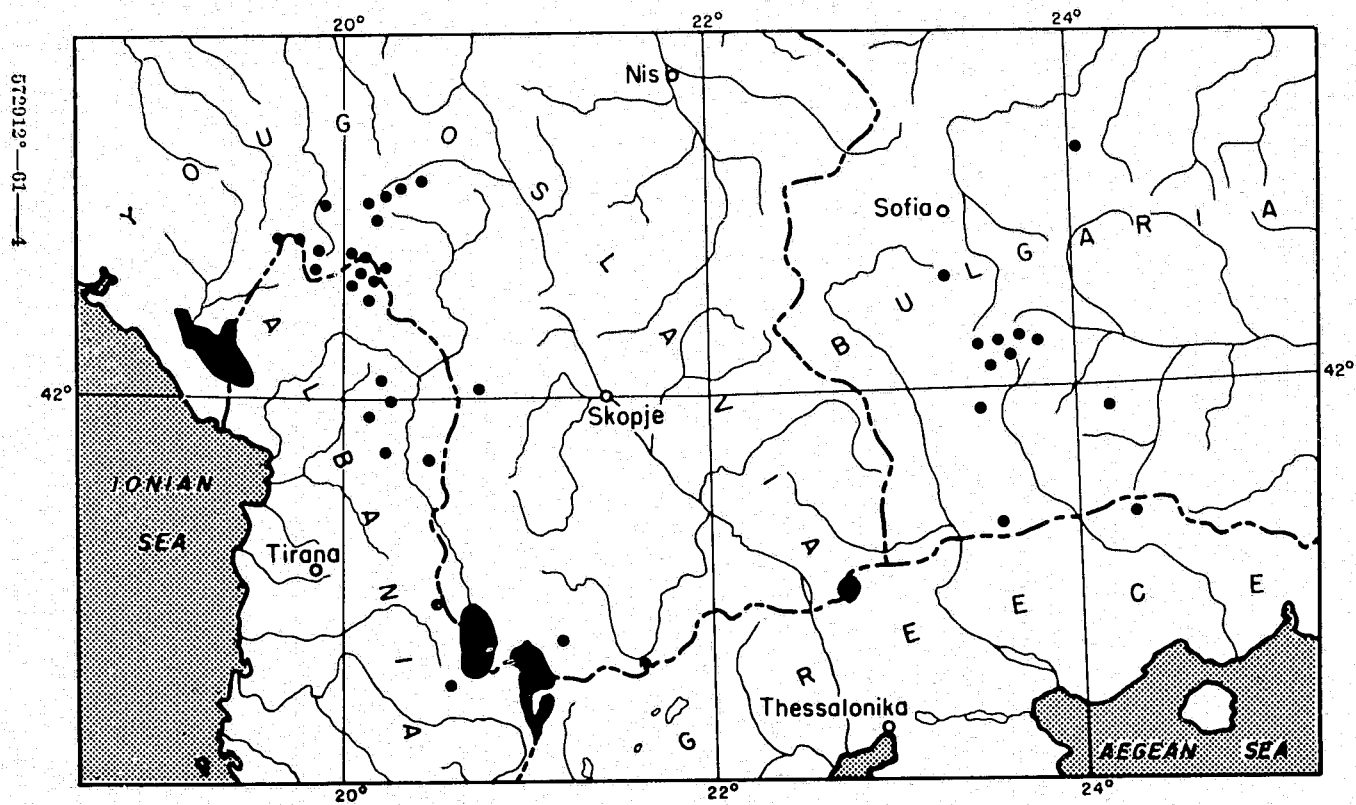
The oleoresin we used (75) was heated under reduced pressure. At a maximum temperature of 180°C . and a pressure of 0.5 mm. of mercury, 23.3 percent of turpentine distilled over. This was designated as portion 1. After this operation, the pot residue (rosin) was still very soft on cooling. When temperature was increased to 200° to 205° and pressure reduced to 0.05 mm., about 9.5 percent more distillate was obtained. This was designated as portion 2. It had the consistency of castor oil and was of yellowish color and faint fragrance. Similar behavior in distillation had been experienced with the oleoresins of *Pinus albicaulis*, No. 5, *P. parviflora*, No. 11, *P. koraiensis*, No. 1, *P. armandi*, No. 8.

Physical characteristics of *Pinus peuce* turpentine, if one could call the second portion of the distillate by this name, are given in table 14 separately for each portion of distillate. Pejoski's data are given for comparison. It should be noted that when Pejoski used steam distillation for obtaining turpentine, apparently only the first portion was distilled over; the second one remained in the still.

The light oil of *Pinus peuce* oleoresin contained: *dl,l*- α -pinene, 71 percent; *l*- β -pinene, 9 percent; β -myrcene, 2 percent; terpinolene, 1.5

TABLE 14.--Physical characteristics of the low-boiling and high-boiling portions of *Pinus peuce* turpentine

Portions	Percent of weight of oleoresin	d_4	n_D	$[\alpha]_D^{20}$
Portion 1, 160° - 180°C . at 0.5 mm. (light oil).	23.1	0.8628 ²¹	1.4717 ²³	-16.2°
Portion 2, 200° - 205°C . at 0.5 mm. (heavy oil).	9.4	.9280 ^{22,5}	1.5200 ²³	+113.0°
Pejoski's data for steam-distilled turpentine.	19-22	.861 to .866	1.462 to 1.463	-13.33° to -29.36°

FIGURE 12.—Geographical occurrence of *Pinus peuce*.

percent; *l,dl*-bornyl acetate, 2 percent; sesquiterpenes, 7.4 percent, mainly consisting of two sesquiterpenes, one of which is a cadalene-type sesquiterpene and the other unidentified. It did not give a crystalline hydrochloride and it gave no aromadendrene color test. Pot residue and loss amounted to 7.1 percent.

The heavy oil of *Pinus peuce* contained sesquiterpenes, 10 percent; diterpenes, mainly cembrene (with a small amount of diterpene, maleic anhydride adduct melting at 148° to 149° C.), 59 to 60 percent; oxygenated compounds, probably diterpene alcohols, 6 percent; residue and loss, 24 percent.

As a whole, turpentine of *Pinus peuce*, i.e., both light and heavy oil combined, had the following composition:

Compound:	Percent
<i>dl</i> ,- α -pinene	50
<i>l</i> - β -pinene	6
β -myrcene	2
terpinolene	1
<i>l,dl</i> -bornyl acetate	1
Two sesquiterpenes, one of which is of a cadalene type	9
Diterpenes, mainly cembrene	17
Oxygenated compounds, probably diterpene alcohols	2
Residue and loss	12

13. *Pinus griffithii* McClelland

References (151, 50)

(In Griffith, Notul. Pl. Asiat.

4, 17; Icon. Pl. Asiat. t. 365. 1854)

Pinus griffithii is an Indian white pine, also known as *P. excelsa*. It grows with some interruptions along the Himalayas from Afghanistan to Bhutan, at 6,000 to 12,000 feet above sea level. It occurs also in upper Burma and adjacent parts of Yunnan, China. The turpentine of *P. griffithii* was investigated by Simonsen and Rau (151), who reported the yield as 2 gallons per maund (about 82 pounds) of resin. The physical properties of the turpentine were as follows:

Density, $d_{20}^{20} = 0.857$

Index of refraction, $n_D^{20} = 1.4627$

Specific rotation, $[\alpha]_D^{20} = +40.42^\circ$

The turpentine consisted of the following ingredients: *d*- α -pinene, 87.9 percent; *d*-terpineol, percent not given; *n*-undecane, a small quantity; a bicyclic sesquiterpene, percent not given.

The sesquiterpene, when dissolved in acetic anhydride and treated with a drop of concentrated sulfuric acid, developed a pale pink color that slowly became magenta. This sesquiterpene had the following constants:

Boiling point at 34 mm., 145° to 146° C.

Density, $d_{20}^{20} = 0.8954$

Index of refraction, $n_D^{20} = 1.486$

Specific rotation, $[\alpha]_D^{20} = +26.25^\circ$

Molecular refraction, $MR_D = 65.4$

Pinus griffithii turpentine was also analyzed in 1926 by Dupont and Soum (50). The turpentine was obtained from a commercial distillery located at Jallo, Punjab, India. Dupont and Soum were able to identify only α -pinene; there was no β -pinene, limonene, carene, or bornyl acetate. There was apparently a sesquiterpene in

the higher boiling fraction, but "as usual with pine sesquiterpenes, no crystalline hydrochloride was obtained."¹¹

14. *Pinus monticola* Dougl.

References (54, 109)

(Lambert, Deser. Gen. Pin. Ed. 3, V. 2. 1832)

Pinus monticola is commonly called western white pine. It is found in western Montana and northern Idaho. In Idaho it reaches its best development; hence, it is often called Idaho white pine. It extends to Washington and southern British Columbia and southward to Oregon, central California and adjacent parts of Nevada. A sample of the oleoresin of this pine was obtained in 1929 by the writer from the Warner Mountains of northeastern California. The trees were tapped at an elevation of 7,400 feet in a locality separated from the more northern forests of this species by arid, treeless stretches of land. The turpentine was obtained by steam distillation. Yield of the turpentine was 18.2 percent (54).

The turpentine had the following constants:

Density, $d_{20}^{20} = 0.6891$
 Index of refraction, $n_D^{20} = 1.4646$
 Optical rotation, $\alpha_D^{20} = +20.59^\circ$

The turpentine contained:

Compound:	Percent
<i>d</i> - α -pinene.....	60
<i>l</i> - β -pinene.....	26
<i>n</i> -undecane.....	1-2

No oxygenated compounds were detected; *l*-limonene and sesquiterpenes were suspected, but not identified by preparation of crystalline derivatives. Because turpentine was obtained by steam distillation, the low-boiling heads may have been lost during the operation.

Twenty-five years later we obtained oleoresin of *Pinus monticola* from Priest River, northern Idaho, and investigated its turpentine (109). The turpentine was obtained by heating the oleoresin under reduced pressure; at the end of distillation, the pot temperature reached 180° C. and the pressure was reduced to 0.1 mm. of mercury. Yield of turpentine was 20 percent. At the beginning of the process some oil was carried over to the dry-ice trap, indicating the presence of a low-boiling substance.

Physical properties of the turpentines were:

Density, $d_{20}^{20} = 0.8500$
 Index of refraction, $n_D^{20} = 1.4687$
 Specific rotation, $[\alpha]_D^{20} = -23.8^\circ$

The composition of the turpentine was:

Compound:	Percent
<i>n</i> -heptane (table 15).....	2
<i>l,dl</i> - α -pinene.....	32
<i>l</i> - β -pinene.....	45
<i>l</i> -limonene.....	7
<i>n</i> -undecane (table 15).....	2
Bornyl acetate.....	2
Sesquiterpenes.....	4
Pot residue and losses.....	6

¹¹ Generally, we have had no difficulties in preparing crystalline sesquiterpene hydrochlorides.

TABLE 15.—Properties of *n*-heptane and *n*-undecane from *Pinus monticola* turpentine

Property	<i>n</i> -heptane from <i>P. monticola</i>	<i>n</i> -heptane ¹
Density, <i>d</i>	0.6807 ²¹	0.6873 ²⁰
Index of refraction, <i>n</i> _D	1.3881 ²²	1.3876 ²⁰
Boiling point, ° C.....	98.5 ²²	98.4 ²⁰
	<i>n</i> -undecane from <i>P. monticola</i>	<i>n</i> -undecane ²
Density, <i>d</i>	0.7394 ²	0.7404 ²⁰
Index of refraction, <i>n</i> _D	1.4181 ^{20, 2}	1.4190 ²⁰
Boiling point, ° C.....	197 ²²	195.8 ²⁰

¹ Rossini, et al. *Selected values of properties of hydrocarbons*. U.S. Natl. Bur. Standards Cir. 461, p. 39. 1947.

² Egloff, G. *Phys. constants of hydrocarbons*. V. 1, Amer. Chem. Soc. Monog. 78, p. 76. Reinhold Pub. Corp., N.Y. 1930.

The sesquiterpenes found were one monocyclic, whose hydrochloride in the form of plates melted at 75° to 79° C., and the other bicyclic; its hydrochloride, which was in form of needles, had a melting point of 117°. It is possible that the two sesquiterpenes were bisabolene and cadinene, as these frequently occur together and have hydrochlorides which melt at 79° and 118.5°, respectively. Lack of material prevented further investigation.

The difference in chemical composition of the two samples—one from the outskirts of the *Pinus monticola* range and the other from the center of its distribution—could perhaps be explained partly by some geographic variability within the species and partly by the better methods of fractionation of the Idaho samples.

The most important feature of the earlier analysis was the discovery of *n*-undecane in the California sample. It was the first reporting of this hydrocarbon in American pines. Undecane had been discovered in an Indian pine, *P. griffithii*, No. 13, by Simonsen and Rau. Later we found *n*-undecane in several pines (See Nos. 1, 7, 33, 34, 36, 54).

15. *Pinus strobus* L.

Reference (116)

(Sp. Pl. 1001. 1753)

Pinus strobus is commonly known in America as eastern white pine. Its range extends from Newfoundland to central Ontario, to south-eastern Manitoba, southward through northern and eastern Minnesota, Iowa, Illinois, Indiana, Ohio, Pennsylvania, and New Jersey, and south to western North Carolina, northern Georgia, and Tennessee. It is local in western Kentucky.

A variety of *Pinus strobus*, called *chiapensis*, grows in southern Mexico in the States of Veracruz, Puebla, Oaxaca, and Chiapas. It forms extensive forests in Guatemala, and it was reported from one locality in Honduras (6). In my opinion, var. *chiapensis* is an independent species, perhaps related more closely to *P. monticola* than to *P. strobus*.

The oleoresin of typical *Pinus strobus* used in our work was collected in the Chippewa National Forest, northern Minnesota. The turpentine was distilled under reduced pressure; toward the end of the distillation, the temperature inside the flask reached 205° C. and the pressure was reduced to 0.05 mm. Yield of turpentine was 25 percent; it had the following characteristics:

Density, d_4^{20} = 0.8611
 Index of refraction, n_D^{20} = 1.4714
 Specific rotation, $[\alpha]_D^{20}$ = -0.75°

The turpentine of *Pinus strobus* had the following composition:

Compound:	Percent
<i>dl</i> - α -pinene	75
<i>l</i> - β -pinene	15
Oxygenated compounds	4
A tricyclic sesquiterpene	0.3

Tests for Δ^3 -carene were negative; fractions 12 to 15 contained small amounts of oxygenated compounds, possibly alcohols and ketones (table 16). Fraction 16 consisted of a sesquiterpene. After distillation over sodium, the physical constants of the fraction were d_4^{20} , 0.9131; n_D^{20} , 1.4913; boiling point, 110° to 115° C. at 27 mm. Molecular refraction, MR_D was 64.83; calculated for a sesquiterpene (C₁₅H₂₄) with one double bond, it would be 64.40. This indicated the presence of a tricyclic sesquiterpene.

The turpentine of *Pinus strobus* var. *chiapensis* has not yet been analyzed.

TABLE 16.—Analytical data of several fractions of *Pinus strobus* turpentine¹

Compound	Fraction	Carbon	Hydrogen	Determined by Zerewitinoff method ²	
				Active hydrogen	Carbonyl group
		Percent	Percent	Mol.	Mol.
α -pinene	3	87.94	12.28		
β -pinene	6	88.35	11.79		
Oxygenated compounds	12	87.30	11.81	0	0.2
	15	84.24	11.57	0.2	.4
Sesquiterpene	16	88.06	12.11		

¹ Calculated: for C₁₀H₁₆ or C₁₅H₂₄: C = 88.17 percent; H = 11.83 percent; for C₁₀H₁₆: C = 78.91 percent; H = 10.58 percent.

² Soltys, Arnulf. *Die microanalytische Bestimmung der aktiven Wasserstoffes nach L. Tschugaeff und Th. Zerewitinoff*. Mikrochemie 20: 107. 1936.

Group Gerardianae

16. *Pinus bungeana* Zucc.

Reference (111)

(Endlicher, Syn. Conif. 166. 1847)

Pinus bungeana is a rare mountain pine of central China; it is found naturally in a few spots in Shansi, Hupeh, and south Kansu.

It is a picturesque pine, with sycamorelike, peeling bark. The Chinese plant it near temples and in cemeteries.

It was impossible to get oleoresin of *Pinus bungeana* from China, so we obtained a sufficient amount of it from trees cultivated in California. We had previously found that chemical composition of turpentine does not change when a pine is transplanted from one part of the world to another.

The turpentine was distilled from the oleoresin under reduced pressure so that at the end of the operation the temperature was 190° C. and the pressure was 0.1 mm. of mercury. The pot residue (rosin) was very hard and brittle, showing that all volatile fractions (including possible sesquiterpenes) had been removed. Physical characteristics of the turpentine samples are shown in table 17.

TABLE 17.—Physical characteristics of *Pinus bungeana* turpentine

Origin of sample	Yield of turpentine	Density $d_4^{23.5}$	Index of refraction n_D^{25}	Specific rotation $[\alpha]_{D^{25}}$
	Percent			Degrees
Chico, Calif. ¹	25	0.8625	1.4730	-7.0
Placerville, Calif.....	27	.8627	1.4745	-11.0

¹Thanks are due to Mr. L. E. Jolley, in charge of Chico Plant Introduction Garden for furnishing the material.

The physical constants of *Pinus bungeana* turpentine obtained from the two different localities, whose seeds most likely came from two different sources, were almost identical. The turpentine contained:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	60-65
<i>l</i> - β -pinene.....	30-35
Sesquiterpenes.....	2-3

Because of insufficient material, sesquiterpenes have not been investigated. *P. bungeana* occurs in the same part of China as *P. armandi*, No. 8, yet chemistry of the turpentines of the two pines is very different.

17. *Pinus gerardiana* Wall.

Reference (148)

(Lambert, Deser. Gen. Pinus Ed. 3 V. 2 t. 79. 1832)

Pinus gerardiana grows in dry rocky valleys of northeastern Afghanistan and the northwestern Himalayas. Commercial turpentine of this species was analyzed by Puran Singh and reported by Simonsen (148). The turpentine had the following physical constants:

Density, d_{20}^{20} = 0.8658
 Index of refraction, n_D^{20} = 1.468
 Specific rotation, $[\alpha]_D^{20}$ = +18.4°

The composition was reported to be as follows:

Compound:	Percent
<i>d</i> - α -pinene.....	78
<i>d</i> - β -pinene.....	7
Sesquiterpene with a small amount of sesquiterpene alcohol.....	12

This is one of a few cases when β -pinene obtained from pine turpentine was reported to be dextrorotatory. However, it appears from the description of the experimental technique and from the fractionation data that the β -pinene was levorotatory, as it generally is in most pines.

Tests for phellandrene, dipentene, terpinene, and terpineol were negative.

Group Balfourianae

18. *Pinus balfouriana* Grev. & Balf.

Reference (61)

(Murray, Bot. Exp. Ore. (Rpt. 8) No. 618. 1853)

Pinus balfouriana, or foxtail pine, is a rare alpine white pine. Apparently it once occupied a large area, but since the late Pliocene it separated into two isolated localities. It now grows in northern California on several mountain ranges at an elevation of 7,000 to 8,000 feet (Scott Mts., Marble Mts., Salmon Mts., Trinity Alps, and Yolla Bolly Mts.). In the southern Sierra Nevada it grows mainly at the sources of the Kings and the Kern Rivers. The two localities are separated by a distance of at least 300 miles in which no *P. balfouriana* has been found.

Oleoresin from the northern location was collected in the Scott Mountains, about 7 miles south of the town of Callahan, at an elevation of 7,500 feet. The oleoresin yield was poor. All together, 5,170 grams of oleoresin was gathered in 3 weeks from 70 trees. Oleoresin from the southern location was collected on the east side of the Sierra Nevada, at an elevation of 9,000 feet, just above the town of Independence and below the Kearsarge Pass. Twenty trees hucked during July 1948 yielded 1,600 grams of oleoresin. The physical characteristics of the turpentines from the two localities were these:

	Northern	Southern
Yield of turpentine (percent)	28.3	25.8
Density (d_4^{20})8570	.8612
Index of refraction (n_D^{20})	1.4643	1.4642
Specific rotation ($[\alpha]_D^{20}$)	-11.05°	+24.33°

Chemical composition of the two samples of turpentine was as follows:

Compound:	Northern (percent)	Southern (percent)
α -pinene	90 (l,dl)	98 (d,dl)
β -pinene	2	0
Limonene	2	0
Bornyl acetate	0	1
A tricyclic sesquiterpene	4	1

Bornyl acetate was identified in the turpentine from the southern location, in fraction 14 distilling at 106° to 110° C. at 17 mm. A saponification test was applied with a positive result. Upon distillation of the saponified liquid, droplets of oil could be observed in the distillate; from this oil a derivative, 3,5-dinitrobenzoate, melting at 154°, was prepared. It gave no depression in melting point when added to known borneol 3,5-dinitrobenzoate, which has a melting point of 154° (11).

After the volatile alcohol was distilled off, the saponified liquid was acidified with sulfuric acid and again distilled. The distillate was acidic to litmus; it was neutralized with NaOH solution and evaporated to dryness. From the residue *p*-phenylphenacyl ester was prepared; after being purified by passing through a chromatographic column (81), flaky colorless crystals were obtained. These crystals melted at 109° to 110° C. and gave no depression in melting point when mixed with an authentic sample of *p*-phenylphenacyl acetate, melting at 111° (36). Thus the acid was acetic acid and the ester in fraction 14 was bornyl acetate.

Physical characters of the higher boiling fractions of the *Pinus balfouriana* turpentine from the northern location, were compared with those of aromadendrene (table 18).

These fractions possessed characteristic constants of a sesquiterpene; but they did not form solid hydrochloride. The percentage composition of carbon and hydrogen agreed well with those of C₁₅H₂₁, and molecular refraction indicated that this was a tricyclic sesquiterpene with one double bond. The sesquiterpene fraction of *Pinus balfouriana* turpentine from the southern location had a molecular refraction of 63.1, indicating that the sesquiterpene also was tricyclic with one double bond. It formed no solid hydrochloride. Apparently it is a sesquiterpene identical to that in the turpentine from the northern location.

19. *Pinus aristata* Engelm.

Reference (61)

(Am. J. Sci. & Arts, Ser. 2, 34: 331. 1862)

Pinus aristata is commonly called bristlecone pine. It is very local and widely scattered in the high mountains of Colorado, Utah, Nevada, and northern New Mexico; it is also found in one locality near Flagstaff, Ariz., and in two localities of southeastern California. A sample of oleoresin of *P. aristata* was collected by the author with some difficulties (this pine is a very poor producer of oleoresin) in the White Mountains, Calif., at an elevation of 10,000 feet above sea level. The yield of turpentine was 24 percent of the weight of the oleoresin. The turpentine had the following physical characteristics:

Density, $d_4^{25} = 0.8649$
 Index of refraction, $n_D^{25} = 1.4656$
 Specific rotation, $[\alpha]_D^{25} = +25.21^\circ$

Composition of the turpentine of *Pinus aristata* was found to be:

Compound:	Percent
<i>d,d,l</i> pinene.....	96
A tricyclic sesquiterpene.....	4

The sesquiterpene possessed one double bond and formed a hydrochloride melting at 80° to 80.5° C.

Group *Cembroides*

All six pines of this group are inhabitants of the desert mountains of southwestern United States and Mexico. They are known by the Spanish name piñones. In the United States they are known as pinyon pines. Their seeds (or pine nuts) are edible.

TABLE 18.—*Constants of fractions 16 to 18 of Pinus balfouriana turpentine, from northern location, and of aromadendrene*

Property	Fraction 16	Fraction 17	Fraction 18	Aromadendrene ¹
Boiling point-----	145°-154° C. at 75 mm.	154°-156° C. at 75 mm.	156°-159° C. at 75 mm.	121° C. at 10 mm.
Density, d_4 -----	0.9214 ²⁵	0.9171 ²⁵	0.9161 ²⁵	0.9116 ²⁰
Index of refraction, n_D -----	1.4940 ²⁵	1.4962 ²⁵	1.4985 ²⁵	1.4978 ²⁰
Molecular refraction, MR_D -----	64.45	65.000	65.30	65.58
Percent of carbon-----	85.32	{-----	85.45	83.23 } calcd. for
Percent of hydrogen-----	11.90 } found		12.04 } found	

¹ Briggs, L. H., and W. E. Short. Amer. Chem. Soc. Jour. 2524-29. 1928.

20. *Pinus cembroides* Zucc.

Reference (100)

(Abh. Akad. Wiss. Munch. 1: 392. 1832)

Pinus cembroides is predominantly a Mexican pinyon. In Coahuila it is called pino prieto. It is scattered over the desert ranges of the northern Mexican plateau, as far south as the States of Tlaxcala and northern Puebla. It is also found in Baja California. In the United States it occurs in southwestern New Mexico and southeastern Arizona.

An oleoresin sample was collected under the author's supervision in a desert range, Sierra Garambullo, not far from Parras, Coahuila, Mex. Turpentine was obtained from the oleoresin at reduced pressure; at the end of the distillation the temperature reached 170° C. and the pressure was reduced to 2 mm. of mercury. The turpentine comprised 26.2 percent of the weight of the oleoresin and possessed the following characteristics:

Density, d_4^{20} = 0.8471
 Index of refraction, n_D^{20} = 1.4680
 Specific rotation, $[\alpha]_{D^{20}}$ = +45.2°

Chemical composition of *Pinus cembroides* turpentine was found to be:

Compound:	Percent
<i>d</i> - α -pinene.....	92
<i>l,dl</i> -limonene.....	4
A sesquiterpene, <i>d</i> -longifolene.....	2
Residue and losses.....	2

21. *Pinus edulis* Engelm.

References (113, 136, 143)

(Wisliz. Mem. Tour. North. Mex. 88. 1848)

Pinus edulis is called pinyon or Colorado pinyon. It grows in the Rocky Mountain region from Utah and Colorado to Arizona, New Mexico, and the Trans-Pecos region of Texas. It also occurs sporadically in southwestern Wyoming, northwestern Oklahoma, and southeastern California, and in the northern States of Mexico—Chihuahua (86) and Baja California (88).

Pinus edulis turpentine obtained from southwestern Colorado was analyzed by Schorger in 1913 (136), and reported to have the following composition:

Compound:	Percent
<i>d</i> - α -pinene.....	70-75
<i>l</i> - β -pinene.....	5
<i>d</i> -cadinene.....	15-20

The extremely fragrant odor of *Pinus edulis* turpentine was ascribed by Schorger to cadinene.

Oleoresin samples of *Pinus edulis* used in this study were collected under the author's supervision in Arizona on the Fort Defiance plateau, elevation 6,800 to 7,400 feet, Navajo Indian Reservation. The oleoresin was distilled under reduced pressure, so that at the end of distillation the temperature reached 203° C. at 4 mm. of mercury. Yield of turpentine was 24 percent of the weight of the oleoresin. The turpentine had the following characteristics:

Density, d_4^{20} = 0.8708
 Index of refraction, n_D^{20} = 1.4728
 Specific rotation, $[\alpha]_{D^{20}}$ = +17.9°

In the process of fractional distillation (cf. table 5, p. 21, and fig. 7, p. 20), fractions 23 and 24, having a boiling temperature of 88° to 90° C. at 13 mm. of mercury, attracted our attention because of the pleasant odor. The fractions were, in fact, responsible for the fragrance of *Pinus edulis* turpentine.

Physical properties of fraction 24 were:

Density, $d_4^{20} = 0.866$
 Index of refraction, $n_D^{20} = 1.4190$
 Specific rotation, $[\alpha]_D^{20} = +0.7^\circ$

These properties suggested the possible presence of an aliphatic ester.

One gram of this fraction was treated with benzylamine according to the procedure of Dermer and King (34). The amide (428 mg., m.p. 62° to 63.5° C.) was recrystallized from diluted ethanol to a constant melting point at 65° to 66°. By the same procedure, benzyl amide (m.p. 63° to 64.5°) was prepared from known caprylic acid. The white crystals of the amide were recrystallized to a constant melting point of 65.5° to 66.5°. Results of analysis were these: Calculated for $C_{15}H_{25}ON-C$, 77.20 percent; H, 9.94 percent; found—C, 77.06 percent; H, 9.28 percent.

This derivative was not previously reported. A mixture of the authentic benzyl amide of caprylic acid with the derivative from fraction 24 melted at 65.5° to 66.5° C.

Two milliliters of fraction 24 were treated according to the method shown in Vogel's textbook (163, p. 387) with 2 drops of concentrated sulfuric acid and 1.5 g. of 3,5-dinitrobenzoic acid. After one recrystallization of the crude product from ethanol, 431 mg. of needles, m.p. 89° to 93° C., were obtained. After two more crystallizations, 203 mg. of derivative, melting at 92.5° to 93.5°, were obtained. When mixed with authentic ethyl 3,5-dinitrobenzoate, the derivative showed no depression of melting point. Thus the acid portion of the ester was caprylic acid and the alcohol portion was ethanol. Therefore, the ester was ethyl caprylate.

A fraction boiling between 135° and 136° C. at 13 mm. of pressure and redistilled at reduced pressure over sodium gave a heart cut with the following properties:

Boiling point at 10 mm. of pressure = 133° to 134° C.
 Density, $d_4^{20} = 0.9131$
 Index of refraction, $n_D^{20} = 1.5078$
 Specific rotation, $[\alpha]_D^{20} = +78.4^\circ$

A 0.74-g. sample of a hydrochloride was prepared from 3 ml. of the heart cut. The hydrochloride melted at 118° to 119° C.; it did not depress the melting point of cadinene dihydrochloride. The optical rotation (α_D^{20}) was -36.8° ; $c = 28.8$ in chloroform.¹⁵ The positive rotating fraction 53 gave a hydrochloride of negative rotation as does canadene (143), but the fraction had considerably higher rotation and lower density than canadene. Canadene is a structural isomer of *l*-cadinene; its physical characteristics (143) are:

Density, $d_4^{20} = 0.928$
 Index of refraction, $n_D^{20} = 1.4954$
 Optical rotation, $\alpha_{D,28} = +33.73^\circ$

¹⁵ c is concentration of solution expressed as the number of grams of active substance in 100 cc. of solution.

As a whole, turpentine of *Pinus edulis* contained:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	46
Unidentified terpenes.....	1
β -myrcene.....	2
<i>d</i> - Δ^2 -carene.....	6
<i>dl</i> -limonene.....	1
Terpinolene.....	1
Ethyl caprylate.....	6
Unidentified mixture of oxygenated compounds and hydrocarbons.....	12
Sesquiterpenes related to cadinene.....	16
Residue and loss.....	9

It is seen from these results that the chemical composition of *Pinus edulis* turpentine is much more complex than reported by Schorger. The exquisite fragrance of the turpentine is to a large extent due to the presence of ethyl caprylate. Ethyl caprylate has never been reported before as a constituent of turpentine. Webb, Kepner, and Ikeda (164) found (in 1952) 0.6 percent of ethyl caprylate in fusel oil of grape brandy. Caprylic esters were also reported in Palestine orange oil (59).

22. *Pinus quadrifolia* Parl.

Reference (73)¹⁶

(Sudw., USDA, Div. For. Bul. 14: 17. 1897)

Pinus quadrifolia is a rare pinyon pine. It occurs in dry, almost desert, localities of southern California and of the northern part of Baja California, Mex.

The oleoresin sample of this pine was obtained in Riverside County, Calif., near a place called Anza, at an elevation of about 4,000 feet. Eleven trees were tapped. Yield (average of 11 samples) of turpentine was 23.5 percent of the weight of the oleoresin.

Physical characteristics of the turpentine samples obtained from an individual tree varied within these limits:

Density, d_{20}^{20} , from 0.8609 to 0.8668
 Index of refraction, n_D^{20} , from 1.4732 to 1.4787
 Specific rotation, $[\alpha]_{D}^{25}$, from $+6.2^\circ$ to $+32.7^\circ$

The mixed turpentine had the following characteristics:

Density, d_{20}^{20} , 0.8629
 Index of refraction, n_D^{20} , 1.4742
 Specific rotation, $[\alpha]_{D}^{25}$, $+24.8^\circ$

The composite sample of *Pinus quadrifolia* turpentine contained:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	62
Ocimene.....	3.8
Intermediate unidentified fractions.....	1.6
Sesquiterpenes.....	16.8
Residue and losses.....	15.8

The sesquiterpene fraction consisted of two bicyclic sesquiterpenes (13.8 percent) that yielded crystalline cadinene hydrochloride. It also contained a cadalene-type sesquiterpene (3.0 percent); this sesquiterpene, possibly monocyclic, was in the fraction boiling between 131° and 132° C. at 12 mm. of pressure. Its characteristics were these:

¹⁶ In the work cited, the paragraphs containing information on *Pinus quadrifolia* were intermingled by mistake with information on *P. caribaea*.

Density, $d_4^{20.5} = 0.8990$
 Index of refraction, $n_D^{20} = 1.5065$
 Specific rotation, $[\alpha]_D^{20} = +26.5^\circ$
 Molecular refraction, $MR_D = 67.4$

Four grams of oil from this fraction were mixed with 1.88 g. of sulfur and dehydrogenated according to the method of Ruzicka and Meyer (130). The oil received was distilled at reduced pressure. The distillate was treated with 1 g. of trinitrobenzene dissolved in hot alcohol. The mixture was warmed on the steam bath until the reactants were dissolved, and on cooling 1.6 g. of yellow crystals were received. After two recrystallizations from hot alcohol, the crystals melted at 111° to 112° C., and further recrystallization did not change the melting point. Admixture with authentic cadalene trinitrobenzene adduct caused no change of melting point. The fraction showed strong absorption maxima in the infrared region at $1,651 \text{ cm.}^{-1}$ and at 883 cm.^{-1} . This was interpreted as indicating the presence of an $R_1R_2C=C(H_2)$ group. The average value for $C=C(H_2)$ is 1,653 and for $C-H$ out-of-plane wagging is 890 (144). Judging from this evidence, fraction 18 contained a cadalene-type sesquiterpene possessing an $R_1R_2C=C(H_2)$ group.

23. *Pinus monophylla* Torr. & Frém.

Reference (135)

(Frem. Rep. Explor. Exped. Rocky Mts. 319)

Pinus monophylla is commonly known as singleleaf pinyon; unlike all other pines, it bears solitary, round needles. *P. monophylla* grows in dry, desert ranges of southern Idaho, western Utah, Nevada, eastern California, northwestern Arizona, and Baja California, Mex. Turpentine of this pine was examined by Schorger (135) in 1913. The yield was 19 percent. The physical properties of several samples were these:

Density, d_4^{20} from 0.8721 to 0.8733
 Index of refraction, n_D^{20} from 1.4732 to 1.4733
 Specific rotation, $[\alpha]_D^{20}$ from -14.4° to -17.3°

The composition of the turpentine was found to be as follows:

Compound:	Percent
<i>d</i> - α -pinene	85
<i>l</i> - <i>l</i> -limonene	4-5
Sesquiterpene fraction, reported as cadinene	4-6

Because *Pinus monophylla* turpentine has a fragrance similar to that of the closely related *P. edulis*, No. 21, it is possible that it also contains Δ^3 -carene, β -myrcene, and ocimene, and particularly ethyl cuprylate. It is advisable to repeat the analysis of turpentine of *P. monophylla*, using modern fractionation apparatus.

24. *Pinus pinceana* Gordon

Reference (100)

(Pinetum 204. 1858)

Pinus pinceana is a very rare pine growing in dry ravines of desert ranges in the southeastern part of the State of Coahuila, Mex., possibly in the adjacent parts of Nuevo León, and (subject to verification) near Camargo, Hidalgo. This pine is grouped by Shaw (142) with the pinyons, that is, desert pines having edible nuts.

Oleoresin of *Pinus pinceana* was collected in 1950 under the author's supervision from trees near the village of Garambullo, Coahuila,

about 5 or 6 miles south of the station El Fraile of the Coahuila and Zacatecas Railroad. It was gathered through the courtesy of the Madero Agricultural Company of Parras, Coahuila.

The oleoresin was subjected to distillation under reduced pressure so that when all turpentine was removed, the temperature inside the flask was 195° C. and the pressure was 10 mm.; 17.7 percent of turpentine was obtained. The rosin was very brittle.

The turpentine had the following characteristics:

Density, $d_{20}^{20} = 0.8434$
 Index of refraction, $n_D^{20} = 1.4753$
 Specific rotation, $[\alpha]_{D}^{20} = -100.6^{\circ}$

Pinus pinceana turpentine was found to contain:

Compound:	Percent
<i>d</i> - α -pinene.....	5
<i>l</i> -limonene ($[\alpha]_D = 134.25$).....	80
A new bicyclic sesquiterpene.....	5

The new sesquiterpene was named maderene; it possessed two double bonds; its hydrochloride had a melting point of 67° to 68° C.

25. *Pinus nelsonii* Shaw Reference (*Unpub. orig. data*)
 (Gard. Chr. Ser. 3. 36, 122. Fig. 49. 1904)

Pinus nelsonii is a small bushy tree with long, pliant branches, gray bark, and sparse gray-green foliage (88); three cohering needles give the impression of a single needle. It is a very rare pine, growing in a few restricted localities in the desert ranges of the Mexican States of Tamaulipas, Nuevo León, Coahuila, and San Luis Potosí. This pine is closely related to *P. pinceana*.

A 580-g. sample of oleoresin of this pine was sent to our laboratory through the courtesy of Sr. Don Erasmo Cerda of Aramberri, Nuevo León, Mex., and was accompanied by branches and cones collected from the trees from which the oleoresin was procured. The trees were growing at an elevation of 8,000 feet, near a place called Valle Hermoso, Niquihuana, Tamaulipas.

Turpentine was distilled under reduced pressure. At the end of the operation, the pressure was reduced to 2 mm. and the temperature reached 215° C. The last portions of the volatile oil solidified in the condenser.

Yield of the turpentine was 27.8 percent; its physical characteristics were:

Density, $d_{20}^{20} = 0.8557$
 Index of refraction, $n_D^{20} = 1.4711$
 Specific rotation, $[\alpha]_{D}^{20} = -38.5^{\circ}$

No further work was done with turpentine of this pine.

Subgenus Diploxylon

Group Longifoliae

26. *Pinus longifolia* Roxb. References (51, 56, 118, 152, 158)
 (Lambert. Descr. Genus Pinus 1: 29 t. 21. 1803)

Pinus longifolia has been known under this name for a long time (142). Recently, however, it was renamed *P. roxburghii* Sarg. According to a change in the International Code of Botanical Nomen-

elature adopted in 1930, the name *P. longifolia* should be rejected as a later homonym. However, proposals to permit retention of old names of important economic species such as this are pending.

In this publication the name *Pinus longifolia* is retained, chiefly because one of the most important sesquiterpenes of the genus *Pinus*, longifolene, was discovered in this pine.

Turpentine of *Pinus longifolia* was analyzed by Simonsen and Rau in 1920-23 (152). Composition of the turpentine was as follows:

Compound:	Percent
<i>l</i> - α -pinene	about 25
A new terpene named Δ^2 -carene	about 40
<i>l</i> - β -pinene	about 10
A new tricyclic sesquiterpene, longifolene	10

Dupont and Uzac (51) also analyzed *Pinus longifolia* turpentine. It possessed the following constants:

Density, $d_{20} = 0.8750$
 Index of refraction, $n_D^{20} = 1.4797$
 Specific rotation, $[\alpha]_D = -1.51^\circ$

The turpentine composition was:

Compound:	Percent
<i>l</i> - α -pinene	24
<i>l</i> - β -pinene	9.7
A <i>d</i> -terpene together with Δ^2 -carene	37.6
A <i>l</i> -terpene	1.7
<i>d</i> -longifolene and oxygenated products	20.3
Residue and losses	5.9

The structural formula of longifolene has been a matter of controversy. In 1953 Naffa and Ourisson (118) proposed the structural formula of longifolene as it appears in the appendix of this publication. Ghatgey and Bhattacharyya (56), working with large quantity of longifolene, reported that besides longifolene proper there are two other sesquiterpenes closely related to longifolene. Physical constants of the three sesquiterpenes are shown in table 19.

TABLE 19.—*Sesquiterpenes of Pinus longifolia*¹

Sesquiterpenes	Boiling temperature at 9 mm. of pressure	Density d_4^{20}	Index of refraction n_D^{25}	Specific rotation $[\alpha]_D$
	$^\circ\text{C}$			Degrees
Longifolene	113	0.9328	1.5002	+37.8
β -longifolene	126-128	.9153	1.5025	+28.9
γ -longifolene	116-117	.9247	1.5007	-3.68

¹ After Ghatgey and Bhattacharyya (56).

In 1956 Sutherland and Wells (158) reported results of analyses of *Pinus longifolia* turpentine. Its constants were:

Density, $d_4^{25} = 0.8631$
 Index of refraction, $n_D^{25} = 1.4735$
 Specific rotation, $[\alpha]_D = +0.9^\circ$

Besides the presence of major components reported by previous investigators, Sutherland and Wells found in the turpentine minute quantities of α -thujene, β -myrcene, *l*-limonene, and terpinolene.

Longifolene also occurs in 4 other Asiatic pines besides *Pinus longifolia*. We have found longifolene in turpentine of 17 American and Mexican pines.

27. *Pinus canariensis* Smith

Reference (68)

(Buch. Canar. Ins. 159. 1825)

Pinus canariensis is a subtropical tree native to the Canary Islands; in Tenerife, La Palma, and Grand Canary it grows on dry exposed slopes at elevations of 3,700 to 6,600 feet. It has been planted as an ornamental tree in the warmer parts of the United States. Oleoresin of this pine was obtained by the author from 25-year-old planted trees on the University of California campus, Berkeley, Calif. The oleoresin was heated at a pressure of 0.01 mm. until the bath temperature reached 200° C. Yield of turpentine was 27 percent; it possessed the following characteristics:

Density, $d_4^{20} = 0.8552$
 Index of refraction, $n_D^{20} = 1.4637$
 Specific rotation, $[\alpha]_D^{20} = +0.91^\circ$

The components of the turpentine were:

Compound:	Percent
<i>dl</i> - α -pinene.....	94
<i>l</i> -limonene.....	2
Esters of borneol, chiefly bornyl formate.....	1.5
An unidentified dextrorotatory sesquiterpene.....	.5

The fraction in which esters were found boiled between 116° and 118° C. at 23 mm., and had the following properties:

Density, $d_4^{20} = 0.952$
 Index of refraction, $n_D^{20} = 1.4782$
 Specific rotation, $[\alpha]_D^{20} = +2.27^\circ$

When this fraction was saponified, a solid substance with an odor like that of borneol was obtained from the steam distillate of the alcohol portion. This substance, when treated with 3,5-dinitrobenzoyl chloride in pyridine solution, gave a crystalline 3,5-dinitrobenzoate melting at 152°–153° C.; *d*-borneol 3,5-dinitrobenzoate is reported (11) to melt at 154°. The 3,5-dinitrobenzoate obtained from *Pinus canariensis* did not change the melting point of an authentic specimen of *d*-borneol 3,5-dinitrobenzoate. After removal of the alcohol by steam distillation, the presence of formic acid among the volatile acids was demonstrated, indicating that the ester present in the fraction consisted of *d*-bornyl formate. The physical constants of the ester fractions indicated the possibility of the presence of esters of higher acids.

Group *Leiophyllae*

28. *Pinus leiophylla* Schiede & Deppe

References (77, 99)

(Linnaea 6: 354. 1831)

Pinus leiophylla is a Mexican pine, found in the States of Chihuahua and Durango and as far south as Veracruz and Oaxaca. Generally it grows in dry localities at high elevations, but occasionally it occurs

at lower altitudes. A sample of commercial, steam-distilled turpentine of *P. leiophylla* from Uruapan, Michoacan, had been previously analyzed by Iriarte (77). The yield was 26.3 percent and the physical characteristics were:

Density, $d_{20}^{20} = 0.8640$
 Index of refraction, $n_D^{20} = 1.4633$
 Specific rotation, $[\alpha]_D^{20} = +38.9^\circ$

The turpentine was found to contain 95 percent of *d*- α -pinene. Oleoresin for our studies was collected by the author at a turpentine operation, also near Uruapan, Michoacan.

The turpentine was distilled from the oleoresin under reduced pressure; at the end of the distillation, flask temperature was 165°C . and the pressure was 0.5 mm. Under these conditions all turpentine was expelled from the oleoresin. The yield of turpentine was 29.6 percent; the constants were as follows:

Density, $d_{20}^{20} = 0.8515$
 Index of refraction, $n_D^{20} = 1.4662$
 Specific rotation, $[\alpha]_D^{20} = +23.0^\circ$

The turpentine contained:

Compound:	Percent
<i>d</i> - α -pinene.....	90
Δ^2 -carene.....	8
Unidentified high-boiling fractions.....	0.5
Pot residue and losses.....	1.5

29. *Pinus chihuahuana* Engelm.

Reference (109)¹⁷

(Wisliz. Mem. Tour North Mex. 103. 1848)

Pinus chihuahuana is essentially a Mexican pine. It grows chiefly in the States of Chihuahua, Sonora, and Durango. Southward it extends to Nayarit, Zacatecas, and the northern part of Jalisco. In the north it occurs in the desert mountains of southeastern Arizona and southeastern New Mexico. After its discovery in 1848, for more than 60 years this pine was considered as a valid species. In 1909 Shaw (141) designated it as a variety of *P. leiophylla*, No. 28. Recently Martinez (88) elevated it again to a specific rank. It is possible that the two pines cross and produce natural hybrids.

The oleoresin used in our work was obtained from El Salto, Durango, Mex. The yield of turpentine was 20 percent of the weight of the oleoresin.

Physical characteristics of the turpentine were:

Density, $d_4^{20} = 0.8646$
 Index of refraction, $n_D^{20} = 1.4730$
 Specific rotation, $[\alpha]_D^{20} = -25.5^\circ$

Composition of the turpentine was:

Compound:	Percent
<i>l</i> - α -pinene.....	60
<i>l</i> - β -pinene.....	10
<i>l</i> -limonene.....	15
<i>d</i> -longifolene.....	5

Tests for Δ^2 -carene were negative.

¹⁷ Attention is called to an error in this reference. In the composition of *Pinus chihuahuana* turpentine, limonene was identified in Fraction 12, not in Fraction 15 as reported; longifolene was identified in Fraction 16 instead of Fraction 20.

30. *Pinus lumholtzii* Rob. & Fern.

Reference (73)

(Proc. Am. Acad. 30:122. 1894)

Pinus lumholtzii is a picturesque Mexican pine with bright-green drooping foliage and cinnamon-red sheaths of needle fascicles. Local people call it pino triste (sad pine) or pino barba caída (drooping beard pine). It grows in the western part of Mexico from southern Chihuahua to Jalisco (88).

A sample of oleoresin of this species was obtained at an elevation of 8,500 feet, not far from El Salto, Durango. Yield of turpentine was 18 percent. Physical characteristics were:

Density, $d_{20}^{20} = 0.8455$
 Index of refraction, $n_D^{20} = 1.4723$
 Specific rotation, $[\alpha]_{D_{25}}^{25} = -81.3^\circ$

The turpentine contained:

Compound:	Percent
<i>d,l</i> - α -pinene	16
<i>l</i> -limonene $[\alpha]_{D_{25}}^{25} = -124.0$	75
Methyl chavicol	2-3
Unidentified sesquiterpenes	2
Pot residue and losses, about	5

Group *Pinaceae***31. *Pinus pinea* L.**

References (41, 85, 110, 120)

(Sp. pl. 1000. 1753)

Pinus pinea is native to the Mediterranean region, from Portugal to Syria. Its northern limits are in southern France and northern Italy. *P. pinea* has been widely planted for centuries, and it is difficult to say whether the stands in some localities are natural or artificial (83). This species does well in California.

In 1917 Paluzzo (120) fractionated a batch of *Pinus pinea* commercial turpentine; it began to boil at 162° to 163° C. and 75 or 80 percent of it distilled between 163° and 178°. (Possibly the head fraction contained minute quantities of α -pinene.) Under laboratory conditions, using steam at 2 to 3 atmospheres of pressure, Palazzo obtained turpentine with the characteristics (average of eight samples) shown in table 20. Only 1.04 percent of the turpentine distilled below 173°; 90 percent of it distilled below 180°. No α -pinene was reported; the oil apparently consisted almost entirely of *l*-limonene. The sesquiterpene fraction was very small (probably less than 5 percent), and it was not investigated.

Lacrué (85) also reported characteristics of *Pinus pinea* turpentine (table 20) which indicated the presence of large amounts of *l*-limonene.

Dupont and Barraud (41) analyzed commercial, steam-distilled turpentine obtained in the province of Granada, Spain. Yield of turpentine was 16 to 18 percent; its characteristics are given in table 20. Purified *l*-limonene, obtained by fractional distillation of the crude turpentine, possessed specific rotation $[\alpha]$, equal to -123.7° . The composition of the turpentine was:

Compound:	Percent
<i>l</i> - α -pinene	16.7
<i>l</i> -limonene	75.4
Sesquiterpene	6.6

TABLE 20. - Physical characteristics of *Pinus pinea* turpentine

Author	Origin of turpentine	Density d	Index of refraction n_D	Specific rotation $[\alpha]$
Palazzo (120)	Italy	0.8473 ¹⁵ to 0.8514 ¹⁵	1.4731 to 1.4751 ²⁰	-93.80° to -97.30° (D line)
Dupont and Barraud (71)	Spain	.8506 ¹⁵	1.4700 ²⁵	-84.53° (j line)
Audrain ¹	do	.8513 ¹⁷	1.4769 ¹⁵	-82.62° (D line)
Laerue (87)	do	.8435 to .8498 ¹⁵	1.4750 to 1.4775 ¹⁷	-92.68° to -96.69° (D line)
Berkel (personal communication)	Turkey	.8400 to .8440 ²⁰	1.4740 to 1.4770 ²⁰	-118.7° to -119.3° (D line) ²
Mirov and Hoff (110)	California	.8393 ¹¹	1.4723 ²¹	-118.0° (j line)

¹ Quoted by Laerue (85).

² Of the main fraction.

Laerue (85) questioned the presence of α -pinene in turpentine of *Pinus pinea*. He said the sample analyzed by Dupont and Barraud contained an admixture of *P. maritima* turpentine, which is rich in α -pinene. The sesquiterpene was optically inactive, having density, $d^{15}_4 = 0.9157$ and index of refraction, $n_D^{20} = 1.4983$. No crystalline derivatives (nitroschloride, nitrosite, nitrosate, bromide) were obtained.

Professor Adnan Berkel, University of Istanbul wrote to me in 1953 that he had analyzed Turkish *Pinus pinea* turpentine. Physical characters of this turpentine are given in table 2). Initial boiling point of the turpentine at 760 mm. was 172°-173° C. Only 0.09 percent distilled above 181°. About 90 percent distilled between 175° to 177°, and the specific rotation of this fraction was: $[\alpha]_D^{20} = -118.7^\circ$ to -119.3° . Hence there was very little, if any, α -pinene and very little sesquiterpene.

To sum up, past investigations have shown that *Pinus pinea* turpentine, obtained throughout its natural range, consisted almost entirely of *l*-limonene; α -pinene apparently was either completely lacking or was found in minute quantities.

Oleoresin for the present study was obtained in the summer of 1953 from five 25-year-old planted trees at the Institute of Forest Genetics, Placerville, Calif. The trees were grown from seeds received from Italy.

The turpentine was expelled from the oleoresin under vacuum; at the end of the operation the pot temperature was 190° C. and the pressure was 0.5 mm. The yield of turpentine was 18.5 percent; its physical characteristics are given in table 20.

Chemical composition of the turpentine was:

Compound:	Percent
<i>l</i> -limonene	95
A bicyclic sesquiterpene with two double bonds	4

The limonene possessed a specific rotation of -118.0° ; the sesquiterpene yielded crystalline hydrochloride having a melting point of 67.5° to 68.5° C.

The sesquiterpene was apparently the same as in the turpentine of *Pinus pineana* of Mexico (table 21). Presence of α -pinene was doubtful. It is evident that turpentine from *P. pinea* grown in its Mediterranean home and in California has the same composition: it consists mostly of *l*-limonene. This finding indicates that despite a change of environment, chemical composition of the turpentine does not change. The presence of large quantities of limonene suggest that this pine is related to *P. torreyana*, No. 33, of the group *Macrocarpae* and to *P. pineana*, No. 24, of the group *Cembroides*. The latter relationship is also supported by the presence of apparently the same sesquiterpene in *P. pinea* and *P. pineana*.

Group *Macrocarpae*

According to Shaw (142), the group *Macrocarpae* (that is, the group with large-sized cones) is composed of three pines: *Pinus torreyana*, *P. sabiniana*, and *P. coulteri*. I believe that there are sufficient reasons, biochemical as well as morphological and genetic, to include *P. jeffreyi* in this group. *P. oaracana* is also included in this group because of its morphological and biochemical characters.

Chemically, group *Macrocarpae* is characterized by the presence of aliphatic hydrocarbons—either heptane or undecane.

32. *Pinus jeffreyi* Grev. & Ball. References (29, 53, 134, 135)¹⁸

(A. Murray, Bot. Exp. Ore. Rpt.

No. 8; 2 pl. 1853)

Pinus jeffreyi, commonly known as Jeffrey pine, is essentially a California species. In the north it extends to Oregon; in the east to adjacent parts of Nevada; and in the south, to the Mexican State of Baja California.

Since the days of the Civil War, the turpentine obtained from Jeffrey pine had been known to possess unusual properties. Early information on this subject was described by Guy Carruthers (29). Briefly, it was found that Jeffrey pine turpentine consists almost entirely of a paraffin hydrocarbon, *n*-heptane.

In 1913 Schorger (135) reported that the yield of Jeffrey pine turpentine varied from 8.81 to 11.25 percent, the average being 9.96 percent, and that physical characteristics of the turpentine were:

Density, d_4^{20} = 0.6951 to 0.7100

Index of refraction, n_D^{20} = 1.3927 to 1.4060

Specific rotation, $[\alpha]_D^{20}$ = 0.0°

Schorger concluded that the previous findings were correct and that the turpentine consisted principally of *n*-heptane. In the higher boiling fractions of Jeffrey pine turpentine, Schorger suspected citro-

¹⁸ Also ZOBEL, BRUCE JOHN. THE NATURAL HYBRID BETWEEN COULTER AND JEFFREY PINES. 114 pp. 1951. [Ph. D. thesis. Copy on file at Univ. of California, Berkeley.]

TABLE 21.—Physical characteristics of sesquiterpenes from turpentine of *Pinus pineana* and *P. pinea*

Species	Density d	Index of refraction n	Optical rotation α	Boiling range	Molecular refraction MR_{25}^{25}	Melting point of hydrochloride
<i>P. pineana</i> (Mirov, 100).	0.9117 ₄ ²³ -----	1.500 ₁₅ ²⁷ -----	Slightly negative-----	259°-60° C. at 760 mm.	65.8	67°-68° C.
<i>P. pinea</i> (Dupont and Barraud, 41).	0.9157 ¹⁵ -----	1.4965 ₁₅ ²³ -----	Inactive-----	128.5°-9° C. at 13 mm.	65.2	(¹).
<i>P. pinea</i> (Mirov and Hoff, 110).	0.9037 ₄ ²³ -----	1.4993 ₁₅ ²³ -----	do-----	110° C. at 4 mm-----	66.3	67.5°-68.5° C.

¹ Not prepared.

nellal. He compared physical properties of the fractions with those of citronella oil. The results were:

	Citronella oil	High-boiling fractions of Jeffrey pine turpentine
Boiling range	205 ² 208 ² C.	200 ² -215 ² C.
Density d_{20}	0.8567	0.8578
Index of refraction n_D^{20}	1.4478	1.4570
Optical rotation α	-3 ²	-2.5 ²
Melting point of semicarbazone	96 ² C.	91 ² -92 ² C.

In 1915 Schimmel & Co. chemists (134) analyzed Jeffrey pine turpentine and found that it consists chiefly of *n*-heptane with small amounts of *n*-decyl aldehyde, linalool, and methyl chavicol.

Foote (53) identified in the tails of *Pinus jeffreyi* turpentine: *n*-octyl, *n*-nonyl, and *n*-decyl aldehydes.

Occurrence of large quantities of *n*-heptane in Jeffrey pine turpentine has been verified repeatedly in our laboratory.

Jeffrey pine occasionally crosses with *ponderosa* pine, No. 54 (93). Turpentine of the hybrid consists of a mixture of *n*-heptane (about 25 percent) and of terpenes (about 75 percent).¹⁹ Jeffrey pine also occasionally crosses with Coulter pine, No. 34, in nature; but the composition of turpentine in hybrids has not been studied. It appears however, from the determination of physical properties of Jeffrey \times Coulter hybrids by Zobel (166) that the chemical composition of turpentine of the hybrids is also intermediate between that of the parents.

33. *Pinus torreyana* Parry

Reference (60)

(Carr. *Traité Gén. Conif.* 326. 1855)

Pinus torreyana, or Torrey pine, is a rare western American pine. It occupies a small patch on a headland near San Diego, Calif., and it occurs on the island of Santa Rosa near the coast of California.

A quantity of oleoresin of Torrey pine was obtained by the author from old planted trees at Golden Gate Park, San Francisco, Calif. The turpentine was obtained by heating the oleoresin under reduced pressure, so that at the end of the distillation temperature reached 200² C. and the pressure was reduced to 0.01 mm. Yield of the turpentine was 17 percent of the weight of the oleoresin. The turpentine possessed the following physical constants:

Density, d_{20}^{20}	0.8360
Index of refraction, n_D^{20}	1.4656
Specific rotation, $[\alpha]_D^{20}$	-118.12 ²

Further analysis was done at California Institute of Technology under direction of Dr. A. J. Haagen-Smit. The turpentine was found to consist of the following ingredients:

Compound:	Percent
<i>l</i> -limonene	75
<i>n</i> -decyl aldehyde	10
<i>n</i> -undecane	5
Lauroal (<i>n</i> -dodecyl aldehyde)	0.2
Longifolene	.4
An unidentified C ₂₀ carbonyl compound	.2

¹⁹ L. F. HAWLEY AND E. BEGLINGER. THE ANALYSIS OF OLEORESIN SAMPLES. U.S. Forest Serv., Forest Prod. Lab., Madison, Wis. 1929. (Unpublished report.)

In the low-boiling fraction, small quantities (less than 0.1 percent each) of *n*-heptane and *n*-nonane were detected by mass spectroscopy.

The following methods were used for the identification of the aldehydes in the Torrey pine turpentine:

(1) Presence of *n*-decyl aldehyde was established by preparation of 2,4-dinitrophenylhydrazones and by measurement of the physical properties of the appropriate fractions. The experimental evidence for the identity of these fractions is summarized in table 22. Each derivative was prepared by adding 100 mg. of 2,4-dinitrophenylhydrazine to 100 mg. of the oil, and adding just enough boiling glacial acetic acid to effect complete solution of the reagent. The solution was permitted to cool slowly to room temperature, whereupon the 2,4-dinitrophenylhydrazone separated. The product was twice recrystallized from 95-percent ethyl alcohol before analysis. Inasmuch as a mixture of the 2,4-dinitrophenylhydrazones of fractions 19 and 20 showed no change in melting point, the two were assumed identical.

TABLE 22. *Identification of n-decyl aldehyde in Torrey pine turpentine*

Property	<i>n</i> -decyl aldehyde	Fraction 19	Fraction 20
Boiling point.....	207°-209° C. at 760 mm. ¹	83°-93° C. at 21 mm.	93°-97° C. at 21 mm.
Density.....	d_4^{20} , 0.850 ²	$d_4^{20.5}$, 0.807.....	$d_4^{20.5}$, 0.840.
Index of refraction.....	n_D^{20} , 1.4287 ²	$n_D^{20.5}$, 1.4283.....	$n_D^{20.5}$, 1.4357.

RESULTS OF ANALYSIS OF 2,4-DINITROPHENYLHYDRAZONES

Melting point, ° C.:			
2,4-dinitrophenyl- hydrazone.	104 ³	104.....	104.
2,4-dinitrophenyl- hydrazone mixed with authentic 2,4-dinitro- phenylhydrazone.	104.....	104.....	104.
Crystallization habit.....	Yellow needles ³	Yellow needles.....	Yellow needles.
Carbon, percent.....	57.14 ⁴	57.17.....	57.17.
Hydrogen, percent.....	7.19 ⁴	7.24.....	7.24.
Nitrogen, percent.....	16.66 ⁴	16.53.....	16.53.

¹ Stephan (155).

² Uhl (100).

³ Allen (5).

⁴ Calculated.

(2) Dodecyl aldehyde was identified as a minor constituent of fraction 23 by preparing its 2,4-dinitrophenylhydrazone. One gram of fraction 23 and 100 mg. of 2,4-dinitrophenylhydrazine were dissolved on 10 ml. of glacial acetic acid heated to boiling. As the solution cooled, a mass of yellow needles formed. These crystals were filtered off, the filtrate was brought to a boil, and an additional 100 mg. of 2,4-dinitrophenylhydrazine was dissolved in the hot filtrate. On cooling, only crystals of the reagent separated. This observation indicates that the initial precipitate represented most of the aldehyde present in fraction 23.

The yellow precipitate of this 2,4-dinitrophenylhydrazone was dissolved in 40 ml. of benzene and adsorbed on a 20 mm. by 130 mm. column of "Aloreo" F-20 grade, 80-mesh activated alumina. After development with 110 ml. of benzene, a minor band 2 mm. wide appeared 11 mm. beneath the top of the column. Directly beneath this was the main, 50-mm.-wide brown band.

The column packing was extruded and the lower, main band cut apart from the remainder of the material. The desired compound was eluted from the alumina with 20 ml. of a mixture of equal volumes of ethyl ether and ethyl alcohol. The eluate was evaporated to dryness, and the residue recrystallized twice from 96 percent ethyl alcohol. The resultant yellow needles melted at 106° to 107° C. Dodecyl aldehyde 2,4-dinitrophenylhydrazone is reported to melt at 106° (5).

Analysis: Calcd. for $C_{15}H_{25}N_2O_4$: C, 59.32; H, 7.74.

Found: C, 59.66; H, 7.71.

The identity of this compound with dodecyl aldehyde 2,4-dinitrophenylhydrazone was confirmed by the observation that a mixture of the two compounds showed no change in melting point.

34. *Pinus coulteri* D. Don

Reference (95)

(Linn. Soc. London Trans. 17: 440. 1836)

Pinus coulteri grows in the dry coastal mountains of central and southern California, and in the northern part of Baja California, Mex. Oleoresin of this pine was collected by the author in 1945 from 18-year-old planted trees at the Eddy Arboretum, Institute of Forest Genetics, Placerville, Calif.

The turpentine was obtained by steam distillation of the oleoresin. The yield of the turpentine was about 17 percent. Its physical constants were:

Density, $d_4^{20} = 0.8505$

Index of refraction, $n_D^{20} = 1.4767$

Specific rotation, $[\alpha]_D^{20} = -15.21^\circ$

Composition of the turpentine was as follows:

Compound:	Percent
<i>n</i> -heptane.....	5
<i>l</i> - α -pinene.....	30-35
<i>l</i> - β -phellandrene.....	30-35
<i>n</i> -undecane.....	10

The sesquiterpene portion of the turpentine was small: it was not further investigated. Subsequent tests (unpublished) showed the presence of an aldehyde—probably *n*-decyl, but because of the small quantity of material no further identification of this component was made.

35. *Pinus sabiniana* Dougl.

References (136, 160)

(Lamb. Descr. Gen. Pinus Ed. 3(8°) v. 2, pl. 80. 1832)

Pinus sabiniana is commonly called Digger pine. It is a native of dry foothills of California. Early investigations of the composition of *P. sabiniana* turpentine have been summarized by Schorger (136). All these investigations indicated that *P. sabiniana* turpentine consisted

of a paraffin hydrocarbon, *n*-heptane. Schorger (136) determined properties of the turpentine.

The yield of turpentine was 11.4 percent; the physical constants were:

Density, $d_{15}^{15}=0.6961$
 Index of refraction, $n_D^{15}=1.3903$
 Optical rotation, none

Schorger verified the report of previous investigators that turpentine of *P. sabiniana* contained 95 percent *n*-heptane. The tails of *P. sabiniana* turpentine were analyzed by Uhl (160), and found to consist of four normal aldehydes: octyl, nonyl, decyl, myristyl ($C_{14}H_{28}O$), probably dodecyl ($C_{12}H_{24}O$), and possibly small quantities of other aldehydes possessing a larger number of carbon atoms.

Occurrence of large quantities of *n*-heptane in Digger pine turpentine has been verified repeatedly in our laboratory.

36. *Pinus oaxacana* Mirov

Reference (70)

(Madroño, 14: 145-150. 1958)

This pine, formerly called *Pinus pseudostrobus* var. *oaxacana*, is a pine of tropical highlands of southern Mexico and Central America. It grows in the States of Mexico, Puebla, Guerrero, Veracruz, Oaxaca, and Chiapas. It also occurs in the highlands of Guatemala, adjacent to Chiapas, and in Honduras. Martinez (88) places this pine under *P. pseudostrobus*, but it differs so much in its chemical and morphological characters (especially in the shape and structure of the cone) from *P. pseudostrobus*, that I elevated it to the rank of an independent species. Dr. Martinez concurred in this change. Apparently it crosses on the one hand with *P. pseudostrobus*, No. 72, and on the other with *P. montezumae*, No. 65.

An oleoresin sample of *Pinus oaxacana* was collected in Chiapas under the author's supervision. The turpentine was separated from the oleoresin *in vacuo*; at the end of the distillation, the temperature inside the flask was 180° C. and pressure was 3 mm. The yield of the turpentine was 17 percent of the weight of the oleoresin.

The physical characteristics of the turpentine were:

Density, $d_{15}^{15}=0.7920$
 Index of refraction, $n_D^{20}=1.4445$
 Specific rotation, $[\alpha]_{D}^{20} = -10.5^{\circ}$

The density and index of refraction were thus considerably lower than the values for most turpentines. The turpentine was found to contain:

Compound:	Percent
<i>n</i> -heptane.....	21
<i>d,dl</i> - α -pinene.....	51
<i>l,dl</i> -limonene.....	15-16
<i>n</i> -undecane.....	1.3
Longifolene.....	7.5

Tables 23, 24, and 25 present data dealing with the identification of *n*-heptane and *n*-undecane in the turpentine of *Pinus oaxacana*.

TABLE 23.—Identification of *n*-heptane in *Pinus oaxacana* turpentine

Heptane from <i>P. oaxacana</i>	<i>n</i> -heptane ¹	
Index of refraction, n_D 1.3865 ²³	1.38764 ²⁰	1.38517 ²⁵
Density, d 0.6805 ²⁴	0.68368 ²⁰67947 ²⁵
Boiling point, 98°-98.5° C.....	98.428° C.....	

¹ Rossini, F. D., Pitzer, K. S., Taylor, W. J., and others. U.S. Natl. Bur. Standards Cir. 461, 472 pp. 1947.

TABLE 24.—Identification of *n*-undecane in *Pinus oaxacana* turpentine

Property	<i>n</i> -undecane from <i>P. oaxacana</i>	<i>n</i> -undecane ¹
Index of refraction, n_D	1.4165 ^{22,23}	1.41902 ²⁰
Density, d7374 ²⁴7404 ²⁰
Boiling point, b_{760}	196°-197° C.....	195.8° C.

¹ Egloff, G. *Physical constants of hydrocarbons*. Vol. 1, Amer. Chem. Soc. Monog. 78, p. 76. Reinhold Pub. Corp., New York. 1939.

TABLE 25.—Absorption maxima in the infrared region for *n*-heptane and *n*-undecane fractions of *Pinus oaxacana*¹

<i>n</i> -heptane, A.P.I. infrared spectrum #637	Maxima in wave numbers		
	<i>n</i> -heptane from <i>P. oaxacana</i>	<i>n</i> -undecane A.P.I. infrared spectrum #391	<i>n</i> -undecane from <i>P. oaxacana</i>
723.....	723	721	719
739.....	739	761	761
774.....	773	780	778
833.....	832	826	824
864.....	867	843	-----
876.....	877	890	888
901.....	902	906	904
931.....	933	948	945
961.....	961	960	-----
990.....	-----	1010	1002
1022.....	1022	1076	1076
1039.....	1077	1094	1095
1067.....	1140	1135	1134
1209.....	1210	1180	1179
1235.....	1238	1206	1206
1280.....	1282	1241	1243
1302.....	1303	1270	1272
1342.....	1344	1303	1303
1380.....	1382	1342	1343
		1354	1353
		1379	1379
		1467	1465

¹ Rossini, Frederick D., et al. *Catalog of selected infrared absorption spectrograms*. Amer. Petrol. Inst. Res. Proj. 44, U.S. Nat. Bur. Standards. 1946-51.

Group Lariciones

All species of the group Lariciones are of the Old World, except *Pinus resinosa*, No. 37, and *P. tropicalis*, No. 38. The group includes some variable species, which perhaps should be designated as complexes, No. 42, No. 51, No. 53. My treatment of this group, at times, is at variance with Shaw's (142) classification. For instance, I omitted *P. sinensis* and put in its place *P. tabulaeformis*. *P. yunnanensis* is included in this publication as a valid species. The taxonomy of Chinese pines of the group Lariciones is still very confusing.

37. *Pinus resinosa* Ait.

Reference (101)

(Hort. Kev. 3: 367. 1789)

Pinus resinosa is commonly called red pine or Norway pine (after the town of Norway, Maine, U.S.A.). Its range is from Nova Scotia to northern Ontario, to southern Manitoba, southward through Massachusetts, Pennsylvania, West Virginia, central Michigan, Wisconsin, and northeastern Minnesota.

Frankforter (55) reported that steam-distilled turpentine of *Pinus resinosa* possessed the following characteristics:

Boiling point (presumably, initial), 153°-154° C.

Density, $d_{20}^{20} = 0.8626$ Index of refraction, $n_D^{20} = 1.47127$ Specific rotation, $[\alpha]_D^{20} = +17.39^\circ$

No further inquiry into the composition of the turpentine was made.

The oleoresin used in our investigation came from the U.S. Forest Service office at Rhinelander, Wis. The turpentine was distilled so that at the end of the operation the pot temperature reached 180° C. and pressure was reduced to 4 mm. Yield of turpentine was 20 percent of the weight of the oleoresin. The turpentine had the following properties:

Density, $d_{20}^{20} = 0.8571$ Index of refraction, $n_D^{20} = 1.4668$ Specific rotation, $[\alpha]_{573m\mu}^{20} = +10.0^\circ$

The turpentine contained:

Compound:	Percent
<i>d,l</i> - α -pinene.....	92
<i>l</i> - β -phellandrene (possibly).....	3
An unidentified dextrorotatory sesquiterpene.....	1

The fraction in which phellandrene was suspected, when redistilled over metallic sodium, had these constants:

Density, $d_{20}^{20} = 0.8571$ Index of refraction, $n_D^{20} = 1.4760$ Specific rotation, $[\alpha]_D^{20} = -3.0^\circ$

When 1 g. of oil of this redistilled fraction was mixed with 5 cc. of petroleum ether and 2 cc. of glacial acetic acid with the subsequent addition of 2 cc. of saturated solution of sodium nitrite, a precipitate of nitrosite was formed. Because of the small quantity of material, further purification of the nitrosite was unsuccessful, and its melting point could not be determined. Therefore, although it appears that *Pinus resinosa* oil contains a small amount of phellandrene, its presence still needs verification.

38. *Pinus tropicalis* MoreletReference (113)²⁰

(Rev. Hart. Cote d' Or 1. 105. 1851)

Pinus tropicalis grows at sea level in Cuba and on the nearby island, Isla de Pinos. A sample of oleoresin was obtained for our studies under supervision of a trained forester at the property of Minas de Matahambre S.A. The sample was accompanied with herbarium specimens of cones and foliage of the trees from which oleoresin was obtained.

Turpentine was separated from the oleoresin under reduced pressure. At the end of distillation, pressure was 9 mm. and temperature of the batch was 200° C. Rosin remaining in the distilling flask on cooling became very hard and brittle, showing that all volatile oil had been expelled. Yield of turpentine was 23.7 percent.

The turpentine had the following physical characteristics:

Density, d_4^{20} : 0.8566
 Index of refraction, n_D^{20} : 1.4658
 Specific rotation, $[\alpha]_D^{20}$: +36.6°

The turpentine contained:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	96
An unidentified terpene, probably <i>l</i> - β -pinene.....	1
<i>d,dl</i> -limonene.....	1-2

The fraction in which limonene was detected was redistilled over sodium and yielded a heart cut with the following properties:

Boiling point at 16 mm., 58°-60° C.
 Density, d_4^{20} , 0.842
 Index of refraction, n_D^{20} , 1.4751
 Specific rotation, $[\alpha]_D^{20}$, +24.9°

From 2 g. of the heart cut, 0.33 g. of crude tetrabromide was prepared. After three recrystallizations from cold ethyl acetate 53 mg. of crystals melting at 124° to 124.5° were received. Admixture with an authentic sample of *dl*-limonene tetrabromide did not depress the melting point.

This was one of the two exceptional cases when limonene was detected in a dextrorotatory fraction. Usually pine limonene is strongly levorotatory (Nos. 24, 28, 30, 31).

39. *Pinus massoniana* Lamb.

Reference (19)

(Descr. Gen. Pinus 1: 17. t. 12. 1803)

Pinus massoniana is the Chinese red pine. It grows over a large area of southeastern China (fig. 13). Barraud (19) said, without reference to the original work and without further elaboration, that turpentine of *P. massoniana* is composed almost entirely of *d*- α -pinene. I was unable to find the original source of Barraud's information, which is obviously incomplete.

²⁰ In the original article (110) fractions 5, 6, and 7, were erroneously designated as fractions 10, 11, and 12, respectively.

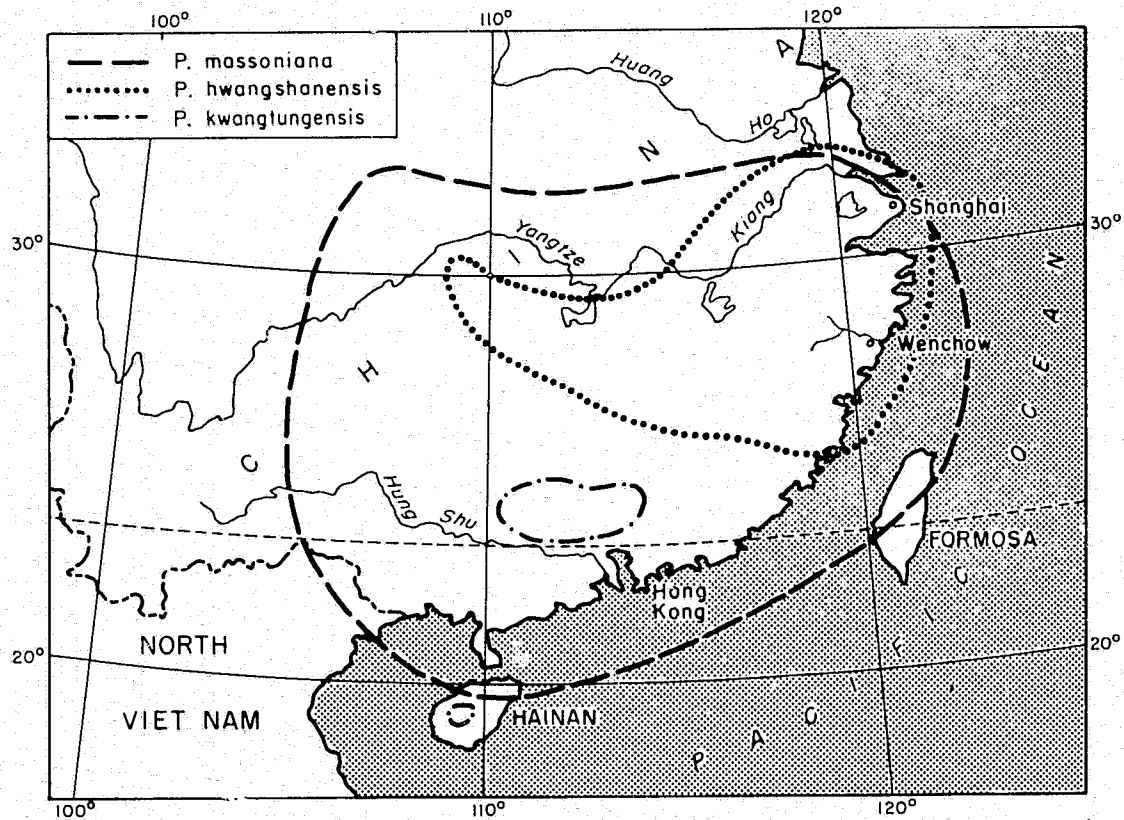


FIGURE 13.—Approximate distribution of *Pinus massoniana*, *P. hwangshanensis*, and *P. kwangtungensis*.

40. *Pinus densiflora* Seib. & Zucc. Reference (*Unpub. orig. data*)
(Fl. Jap. 2: 22-112. 1842)

Pinus densiflora is the Japanese red pine, locally called Akamatsu. It occurs in all three large islands of Japan proper, but it is absent in the northern island of Hokkaido. It also occurs in Korea and in Kiangsu and Shantung provinces of China.

Turpentine of this pine was analyzed by Dr. Kunisuke Horioka, and his results were transmitted to us in 1950. The information was incomplete. The turpentine was reported to contain:

Compound:	Percent
<i>l</i> - α -pinene	58.3
<i>l</i> - β -pinene	18.4
Fractions boiling between 172° and 187° C.	7.4
Residue, probably containing considerable quantities of sesquiterpenes.	15.9

41. *Pinus thunbergii* Parl. References (44, 145)
(DC. Prodrômus 16.2. 388. 1868)

Pinus thunbergii is the Japanese black pine or Kuramatsu. It has been cultivated for such a long time that its original geographic range is difficult to define. Its steam-distilled turpentine was analyzed in 1918-19 by Shinosaki (145). The yield of turpentine was 22.92 percent; its physical characteristics were:

Density, d_4^{25} 0.8740
Index of refraction, n_D^{25} 1.4738
Optical rotation, α_D^{25} -19.17°

The turpentine contained *d*- α -pinene, 73 percent; camphene, probably less than 5 percent, and a tricyclic sesquiterpene were found in a fraction 104° to 107° C. at 2.5 mm. The sesquiterpene had the following physical characteristics:

Density, d_4^{25} 0.9370
Index of refraction, n_D^{25} 1.5005
Optical rotation, α_D^{25} +43.5°

Dihydrosesquiterpene prepared by hydrogenation of the above described sesquiterpene possessed these characteristics:

Boiling point at 2.3 mm., 98°-99° C.
Density, d_4^{25} 0.9294
Index of refraction, n_D^{25} 1.4959
Optical rotation, α_D (in chloroform solution), -25.5°

Dupont and Barraud (44) also analyzed a sample of turpentine of *Pinus thunbergii*. Its physical characteristics were:

Density, d_{15}^{25} 0.8661
Index of refraction, n_D^{25} 1.4629
Specific rotation, $[\alpha]_D^{25}$ -33.46°

The turpentine contained:

Compound:	83
<i>l</i> - α -pinene	10
<i>l</i> - β -pinene, <i>l</i> , <i>l</i> -limonene and two unidentified compounds (terpenes?) ..	1
A terpene alcohol, nerol	5
A sesquiterpene	1
Unidentified oxygenated compounds	

The fraction in which nerol was found boiled between 85° and 100° C. at 10 mm.; the fraction contained both an acetic acid ester and an alcohol (calculated as C₁₀H₁₆O).

The alcohol obtained after acetylation and saponification of the whole fraction possessed the following characteristics: index of refraction, n_D^{25} , 1.4790; specific rotation, $[\alpha]_D$, -7.38° . Treated with diphenylcarbonyl chloride, the alcohol formed diphenylurethane, which melted at 52.5° C. This is the only instance of reporting nerol in pine turpentine.

The sesquiterpene, redistilled over sodium had the following constants:

Boiling point at 10 mm. = 130° C.
 Density, d_4^{25} 0.929
 Index of refraction, n_D 1.4980
 Specific rotation, $[\alpha]_D$ $+42.67^\circ$
 Melting point:
 Hydrobromide $+70^\circ$ C.
 Hydrochloride $+60^\circ$ C.

The sesquiterpene was named "thumbergilene." From the data given above, it is apparent that the sesquiterpene was longifolene.

42. *Pinus sylvestris* L.

References (7, 13, 14, 15, 17, 27, 45, 58, 82, 126, 140)

(Sp. Pl. 1000. 1753)

Pinus sylvestris is called in English, Scotch or Scots pine. On the Continent it is known under many different names. It occupies an area larger than any other pine; longitudinally it grows from Scotland to the Pacific coast of Siberia; latitudinally, from Finland to Spain and from the arctic Siberia to Turkey and to Mongolia (fig. 14). It is natural to expect that this species has many varieties, because it grows over such a large area and under so many different environmental conditions. In fact, *P. sylvestris* is a complex composed of several pines. Some botanists call these pines species; others designate them as varieties, while still others (140) designate the whole complex as a single species, *P. sylvestris*.

It is therefore also natural to expect that turpentine of *Pinus sylvestris* obtained from different places would differ considerably in chemical composition. In 1926 Dupont and Barraud (45) reported on the composition of *P. sylvestris* turpentine from France. Physical constants were:

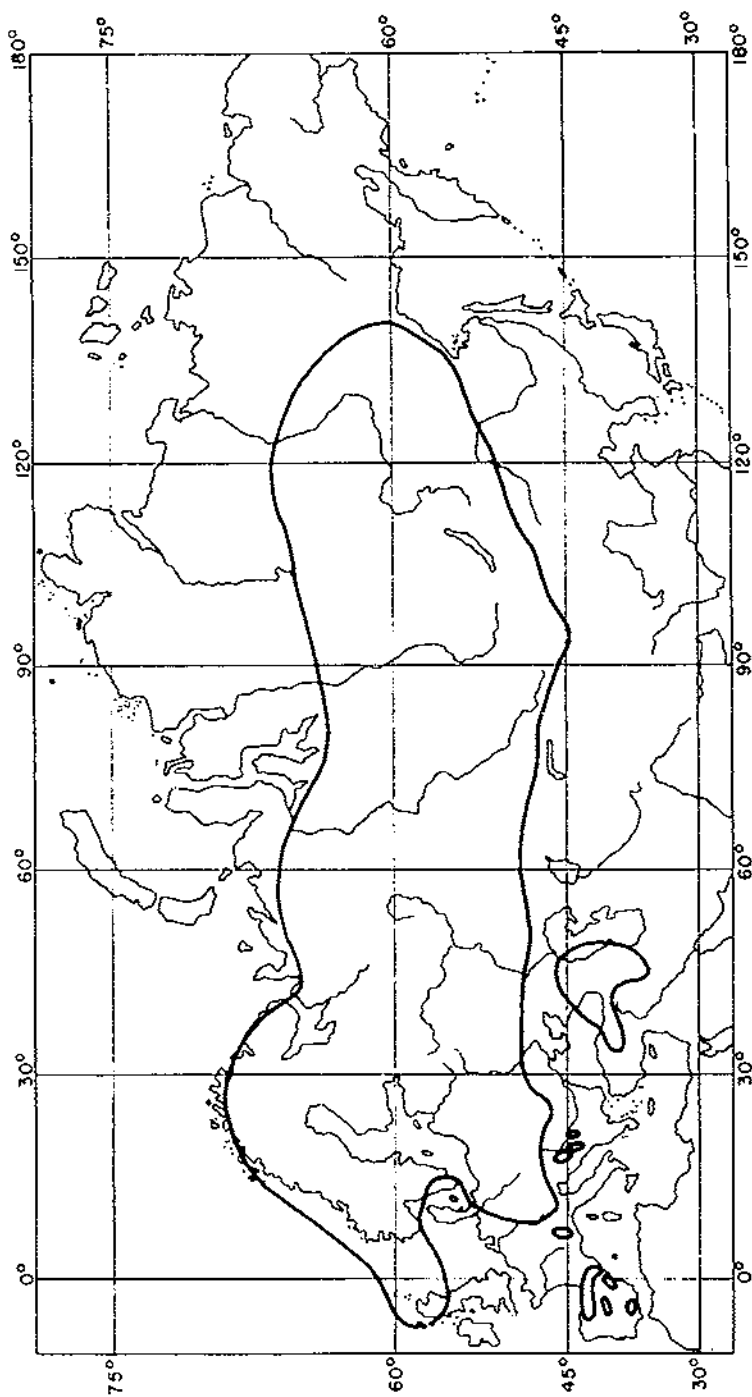
Density, d_4^{25} 0.8614
 Index of refraction, n_D^{25} 1.4666
 Specific rotation, $[\alpha]_D$ $+3.97^\circ$

The turpentine was composed of:

Compound:	Percent
<i>d</i> - α -pinene.....	60.6
β -pinene.....	17.4
<i>d</i> - Δ^3 -carene.....	16.9
Sesquiterpene.....	5.1

The sesquiterpene, redistilled over sodium, possessed the following characteristics: density, d_{15}^{25} 0.918, index of refraction, n_D^{25} 1.4980. No crystalline derivatives of this sesquiterpene were obtained.

Arbuzov (7) analyzed a sample of *Pinus sylvestris* turpentine from the upper Volga Region (Kazan) Russia. The density, d_4^{15} , was 0.856; specific rotation, $[\alpha]_D^{15}$ $+25.6^\circ$. The turpentine contained: *d*- α -pinene, 76 percent; *d*- Δ^3 -carene, 14 percent; an unidentified levorotatory terpene, 7 percent; higher fractions, 1 percent. In 1948 Bardyshev and Bardysheva (15) showed that the unidentified

FIGURE 14.—Geographical distribution of *Pinus sylvestris*.

levorotatory component of *P. sylvestris* turpentine was a mixture of *l*-limonene, dipentene, and an unknown hydrocarbon. Bukala and Kuczynski (27) reported on the composition of *P. sylvestris* turpentine from Poland. Both gum turpentine and wood turpentine were investigated. The two kinds of turpentine contained:

Compound:	Gum turpentine (Percent)	Wood turpentine (Percent)
<i>d</i> - α -pinene.....	46.79	55.79
<i>l</i> - β -pinene.....	8.59	3.87
<i>d</i> - Δ^3 -carene.....	36.24	30.68
Limonene.....	(<i>l</i> -) 2.88	(<i>dl</i> -) 1.51
Terpinolene.....	4.08	0
A monocyclic terpene with two double bonds.....	.35	.48
Terpene alcohol and sesquiterpene fraction.....	1.07	7.48

In 1947 Bardyshev and his coworkers (17) investigated *Pinus sylvestris* turpentine from the Altai Mountains of southern Siberia. The turpentine contained:

Compound:	Percent
<i>d</i> - α -pinene.....	62.68
<i>l</i> - β -pinene.....	6.36
Δ^3 -carene.....	21.82
<i>l,dl</i> -limonene.....	3.73
An unidentified dextrorotatory compound, tentatively designated as terpene.....	2.71
Higher fractions.....	2.70

An important finding of all these studies of *Pinus sylvestris* turpentine is a high percentage of Δ^3 -carene. It seems entirely possible that Δ^3 -carene will be found in all composite samples of *P. sylvestris* turpentine obtained from any place in its extensive range. This terpene also occurs in some pines of the group *Insignes* of the eastern Mediterranean region where there is a contact between *Insignes* pines and *P. sylvestris* (see *P. brutia*, No. 80).

In 1930 two Russian investigators (82) described an unusual turpentine obtained from an individual tree of *Pinus sylvestris*. It was levorotatory ($\alpha_D = -6.01^\circ$) and it was composed of α -pinene, 69 percent; camphene, 5 percent; and *l*- β -phellandrene, 1.5 percent. The usual Δ^3 -carene was absent. Apparently it was a case of a chemical mutant—a phenomenon that occasionally can be observed in studying turpentine composition of individual trees in a population (cf. No. 14).

From the data of different investigators, it is evident that the composition of *Pinus sylvestris* turpentine is not yet completely known. For instance, the sesquiterpene has not yet been identified. Judging from the Rau and Simonsen report (126) on cadinene found in *P. sylvestris* needle oil, it is possible that the sesquiterpene of the gum turpentine of this pine is also cadinene.

The mystery of the frequently mentioned unidentified terpene found in *Pinus sylvestris* gum turpentine was solved in 1950 by Bardyshev (13). He proved beyond any doubt that this compound, which occurs in the fractions immediately following β -pinene, is an aliphatic terpene, β -myrcene.

In 1955 Bardyshev (14) reported the presence of about 1 percent of *p*-cymene in gum turpentine of *Pinus sylvestris*. It was identified

in a fraction having density, d_4^{20} , 0.8460 and optical rotation $\alpha_D = -39^\circ$.

The fraction was treated with 2 percent potassium permanganate in order to remove terpenes, redistilled over metallic sodium, and purified by means of silica gel. This fraction had the following characteristics:

Density, $d_4^{20} = 0.8550$
 Index of refraction, $n_D^{20} = 1.4911$
 Optical rotation, $d_D = 0.0^\circ$
 Molecular refraction, $MR_D = 45.47$

It was oxidized to *p*-hydroxyisopropylbenzoic acid which possessed a melting point of 155° to 156° C. An addition of authentic *p*-hydroxyisopropylbenzoic acid did not change the melting point. This is the only instance in which *p*-cymene was found in gum turpentine, although it is found in some steam-distilled wood turpentines (58). Semmler and Schiller (140) reported that *Pinus sylvestris* turpentine, obtained by steam distillation of stump wood, had the following composition: *d*- α -pinene, very little; *d*- β -pinene, very little; *d*- Δ^3 -carene, chiefly; *d*- Δ^1 -carene, little; α -terpinolene, very little.

Semmler and Schiller's findings as well as the results of Bukala and Kuczynski (27) are of considerable importance for evaluating the nature of pine gum turpentines; turpentine obtained from cut wood and dead stumps, and from the oleoresin of living trees, had considerable amounts of Δ^3 -carene.

43. *Pinus montana* Miller

Reference (*Unpub. orig. data*)

(Gard. Diet. Ed. 8. 1768)

Pinus montana ranges from central Spain through the Pyrenees, Alps, and Appenines to the Balkan Mountains. Its three major varieties are: *nughus*, *uncinata*, and *pumilio*; there are many horticultural forms. In the lower altitudes of its range, it intermingles and possibly crosses with *P. sylvestris* (22, pp. 431-432). We obtained a sample of oleoresin of *P. montana* var. *uncinata* from the communal Forest of Bolguere, Pyrenees Orientales, France. The oleoresin was collected at an elevation of 5,575 feet. The flow of oleoresin was enhanced by spraying 50 percent sulfuric acid over the wound. A batch of 2,000 grams of the oleoresin was heated under reduced pressure so that at the end when all turpentine was distilled, the temperature of the pot contents was 180° C. and the pressure was 0.6 mm. The turpentine amounted to 27 percent of filtered oleoresin.

The turpentine emitted a strong odor of sulfur dioxide and was of a reddish color and muddy appearance. Filtered turpentine possessed the following characteristics:

Density, $d_4^{20} = 0.8700$
 Index of refraction, $n_D^{20} = 1.4774$
 Specific rotation, $[\alpha]_D^{20} = -10.0^\circ$

Fractional distillation under atmospheric pressure showed that 73 percent distilled under 179° C.; the remaining 27 percent consisted of higher boiling, extremely pungent residue.

Apparently the residue contained a great deal of oxidized or polymerized material. In the head fractions, *l,dl*- α -pinene was identified by preparing pinene nitrosochloride which, after several recrystalli-

zations from chloroform by means of cold methanol, melted at 105° to 106° C. An addition of a known pinene nitrosochloride did not change the melting point. *l*- β -pinene was identified in fractions boiling between 163° and 168°; nopinic acid prepared from the fraction boiling at 164° to 166° possessed a melting point of 127°.

Attempts to identify Δ^3 -carene in fractions boiling at 170° to 172° C. were not successful. Limonene also was apparently absent. The rest of the oil, boiling above 179°, was not analyzed.

At the Institute of Forest Genetics, Placerville, Calif., there are several shrubby trees of *Pinus montana* var. *uncinata*. A small amount of oleoresin was obtained from these trees and distilled at reduced pressure; at the end of the distillation, the temperature was 180° C. and the pressure was 1 mm. The turpentine amounted to 22 percent of the oleoresin and had the following characteristics:

Density, d_4^{25} = 0.8659
 Index of refraction, n_D^{25} = 1.4741
 Specific rotation, $[\alpha]_{D^{25}}^{25}$ = -11.5°

These characteristics were very similar to those obtained with the Pyrences turpentine.

A batch of 9 grams of the turpentine was carefully distilled in a 50 cc. flask equipped with a Vigreux column 12 inches long. Results of this distillation are shown in table 26.

TABLE 26.—Fractional distillation of 9 grams of *Pinus montana* turpentine

Fraction	Pressure	Boiling range	Distillate	Density d_4^{25}	Index of refraction n_D^{25}	Optical rotation $[\alpha]_{D^{25}}^{25}$
	<i>Mm.</i>	<i>°C.</i>	<i>Percent</i>			
1	760	155-160	10.0	0.8559	1.4666	-14.0
2	760	160-164	32.1	.8526	1.4864	-10.6
3	760	164-167	16.2	.8543	1.4700	-4.0
4	760	167-168	14.4	.8550	1.4710	0.0
5	8	60-66	10.0		1.4749	+1.0
6	8	66-100	2.0			
Residue			11.1			
Losses			4.2			

l,dl- α -pinene was identified in fraction 1 by preparing a nitrosochloride having a melting point of 105° to 106° C.; *l*- β -pinene was identified in fraction 2 by preparing nopinic acid which possessed a melting point of 127° to 128°. Because fractions 5 and 6 were small, no crystalline derivatives were prepared.

The amount of higher boiling fractions, apparently containing a great deal of oxygenated terpene compounds, was rather high—probably up to 15 percent.

It appears very desirable to repeat analyses of *Pinus montana* turpentine and to ascertain whether or not Δ^3 -carene is present. Results of such an ascertainment would contribute to a better understanding of the relationship between *P. montana* and *P. sylvestris*. An analysis of the higher boiling fractions of *P. montana* turpentine

also promises very interesting results, because there are very few pines possessing such a large percentage of high-boiling, fragrant, presumably oxygenated compounds.

44. *Pinus luchuensis* Mayr. References (4; unpub. orig. data)
(Bot. Centralb. 58: 149. 1894)

Pinus luchuensis is an East Asiatic pine native to Okinawa and adjacent islands of the Riu-Kyu group. Its turpentine was examined by Akiyoshi (4), who obtained a 22.6-percent yield of turpentine with these physical constants:

Density, $d_4^{20} = 0.8583$
Index of refraction, $n_D^{20} = 1.4681$
Specific rotation, $[\alpha]_D^{20} = -24.2^\circ$

The composition was reported to be: *l*- α -pinene, more than 90 percent; small amounts of β -pinene, dipentene, phellandrene (?) and dodecaldehyde, commonly called laural or lauraldehyde.

We received in 1952 a sample of oleoresin of *Pinus luchuensis*, collected on Okinawa by the Riu Kyu Forestry Bureau. Yield of the turpentine amounted to 24 percent. The turpentine possessed the following characteristics:

Density, $d_4^{20} = 0.8536$
Index of refraction, $n_D^{20} = 1.4650$
Specific rotation, $[\alpha]_D^{20} = -24.5^\circ$

About 92 percent consisted of *l*- α -pinene; the presence of small quantities of β -pinene, dipentene, and an aldehyde was confirmed. Presence of an aldehyde is especially significant; aldehydes (chiefly decyl) have been found in four California pines (*Pinus jeffreyi*, *P. sabiniana*, *P. torreyana* and *P. coulteri*). Lauraldehyde also was identified in *P. torreyana* turpentine.

45. *Pinus taiwanensis* Hayata Reference (79)

(Jour. Coll. Sci. Tokyo 30: 307. 1911)

Pinus taiwanensis grows in the mountains of Formosa (Taiwan). Shaw does not mention this pine in his 1914 monograph (142). Morphologically, this pine is related to *P. luchuensis*, No. 44, and Wu²¹ considers it a variety of *P. luchuensis*.

Turpentine of *Pinus taiwanensis* was analyzed by Kafuku, Ichikawa, and Kato (79); physical constants were:

Density, $d_4^{20} = 0.8664$
Index of refraction, $n_D^{20} = 1.4725$
Specific rotation, $[\alpha]_D^{20} = -4.8^\circ$

The turpentine contained:

Compound:	Percent
<i>l</i> - α -pinene.....	73
<i>d</i> -limonene and bornyl acetate, small amounts.....	—
<i>d</i> -longifolene.....	13

It is seen from the above that the chemical composition of *Pinus taiwanensis* turpentine differs considerably from that of *P. luchuensis*. I am inclined to consider the two pines as independent species.

²¹ See footnote 7, p. 26.

46. *Pinus hwangshanensis* Hsia

References (19, 146)

(Apud Tsong in Contr. Inst. Bot. Nat. Acad. Peiping, 4: 155. 1936)

Pinus hwangshanensis is a pine of southern China; its distribution is very spotty. Approximately, it occurs between 121° and 108° east longitude and between 24° and 32° north latitude. It is related to *P. taiwanensis* of Formosa. Would it be possible that "L'essence de pin chinois" briefly mentioned by Barraud (19, p. 94) with reference to Shinosaki and Ono (146) was obtained from *P. hwangshanensis*?

The oleoresin used by Shinosaki and Ono, designated merely as "a Chinese pine from Wenchow," came from a region occupied by only two species of pines: *Pinus massoniana* (No. 39) and *P. hwangshanensis* (fig. 13, p. 71).

Because *Pinus massoniana* yields a dextrorotatory turpentine, and its turpentine consist "almost entirely of α -pinene" (Cf. No. 39), we tentatively concluded that "the Chinese pine from Wenchow" is not *P. massoniana* but *P. hwangshanensis*. This conclusion needs verification.

According to Shinosaki and Ono (146), turpentine of *Pinus hwangshanensis* possessed the following physical characteristics:

Density, d_{20}^{20} = 0.8670
 Index of refraction, n_D^{20} = 1.4711
 Specific rotation, $[\alpha]_D^{20}$ = -34.41°

The turpentine contained L - α -pinene, 85 percent; dipentene, a trace; and a tricyclic sesquiterpene, apparently longifolene, because its hydrochloride melted at 58° to 59° C.

47. *Pinus merkusii* DeVriese

References (1, 10, 21, 33, 149, 153)

(P. Nov. Ind. Bat. 5, t. 2, 1845)

Pinus merkusii is a native of the Philippines (Luzon and Mindoro), Sumatra, Lower Burma, Siam, and western Viet Nam. In Siam it is a common tree at an altitude of 1,500 feet (33, p. 415). In Burma it occupies low hills and spurs at elevations of 500 to 2,500 feet. Its southernmost occurrence is in central Sumatra, Barisan Range, 2° 6' southern latitude on Mt. Penawar near Lake Kerintji, at 4,900 to 6,600 feet of altitude.

Turpentine of *Pinus merkusii* has been analyzed by several investigators. The first was Armstrong (10), who reported in 1896 that *P. merkusii* turpentine was dextrorotatory ($\alpha = +31^{\circ}45'$) and that its density was 0.8610. His purpose was to compare commercial possibilities of Burmese turpentines (of *P. merkusii* and *P. khasya* No. 49) with those of American and French turpentines. In 1923 Simonsen (149) reported the results of a more complete analysis of *P. merkusii* turpentine from Burma; the physical constants were these:

Density, d_{20}^{20} = 0.8575
 Index of refraction, n_D^{20} = 1.4653
 Specific rotation, $[\alpha]_D^{20}$ = +28.67°

The turpentine was composed of:

Compound:	Percent
<i>d</i> - α -pinene	78
<i>d</i> - β -pinene	7
<i>d</i> - Δ^3 -carene	10
<i>d</i> -longifolene	5

The presence of dextrorotatory β -pinene is unusual; in almost all pines this terpene is levorotatory. It is possible that the presence of large quantities of strongly dextrorotatory α -pinene caused the β -pinene fraction to be dextrorotatory. (Cf. No. 49.)

In 1930 Spoon (153) reported physical constants of several samples of *Pinus merkusii* turpentine (table 27). These samples were obtained from a commercial distillery, located at Atjeh, North Sumatra.

TABLE 27.—Physical constants of *Pinus merkusii* turpentine from Atjeh, Sumatra¹

Samples	Density d_{4}^{25}	Index of refraction n_D^{25}	Optical rotation α_D
1924:			
1.....	0.8628	1.4665	+35.8°
2.....	.8636	1.4678	+35.4°
3.....	.861	1.470	+36.4°
4.....	.862	1.4680	(?) +31.0°
1930:			
5.....	.8675	1.4675	+35.68°
6.....	.8660	1.4677	+35.8°
7.....	.8661	1.4680	+35.6°
8.....	.8648	1.4680	+35.4°

¹ After Spoon (153).

Also in 1930, Barraud (21) analyzed a sample of *Pinus merkusii* turpentine from Caha (in former Annam, now Viet Nam). This turpentine possessed the following physical characteristics:

Density, $d_{4}^{25} = 0.8625$
 Index of refraction, $n_D^{25} = 1.4672$
 Specific rotation, $[\alpha]_D = -5.7^\circ$

Its composition was:

Compound:	Percent
α -pinene and β -pinene, approx.....	45
Δ^3 -carene with admixture of a levorotatory hydrocarbon, approx.....	55

That same year an anonymous author of the Colonial Institute of Amsterdam (1) reported that a sample of *Pinus merkusii* turpentine from northern Sumatra (Atjeh) possessed the following constants:

Density, $d_{4}^{25} = 0.865$
 Index of refraction, $n_D^{25} = 1.468$
 Optical rotation, $\alpha = +35.6^\circ$

The turpentine included:

Compound:	Percent
<i>d</i> - α -pinene.....	85-90
Δ^3 -carene.....	4
Sesquiterpene.....	0.15

To sum up, all turpentine samples of *Pinus merkusii* contained large amounts of *d*- α -pinene; β -pinene was found in varying quantities; *d*- Δ^3 -carene was found in all samples. The sesquiterpene fraction in all samples apparently consisted of longifolene. Barraud's sample

from Annam (Viet Nam) was unique in that it was levorotatory (because of large percentage of *l*- α -pinene); it contained an unusually large percentage of *d*- Δ^3 -carene; its β -pinene was levorotatory.

48. *Pinus insularis* Endlich

References (35, 74, 80, 127)

(Syn. Conif. 157. 1847)

Pinus insularis is a pine of Philippine Islands. It is closely related to *P. khasya* (No. 49) of Burma. *P. insularis* has been tapped for turpentine and rosin for a long time, and its turpentine has been investigated by several men.

In 1909, Richmond (127) investigated possibilities of producing turpentine from this pine. The yield was 23.4 percent, and the physical constants were:

Density, d_{20}^{20} = 0.8593
 Index of refraction, n_D^{20} = 1.4656
 Optical rotation, α_D = +26.5°
 Specific rotation (calcd.), $[\alpha]_D$ = +30.8°

Ninety-six percent of the turpentine distilled between 154° and 165.5° C.

In 1931 deSantos, West, and Fontana (35) reported results of their researches on *Pinus insularis* turpentine. The yield was from 15.33 to 17.23 percent; physical constants are shown in table 28. Further analysis of turpentine was limited only to the identification of α -pinene by preparing pinene hydrochloride. The authors estimated that the turpentine contained from 30 to 52 percent of *d*- α -pinene.

Koolhaas and DeVos in 1935 (80) investigated steam-distilled turpentine of *Pinus insularis* obtained from young planted trees in Java. The constants they obtained were:

Density, d_4^{20} = 0.8508
 Index of refraction, n_D^{20} = 1.4702
 Optical rotation, α_D = +33°
 Specific rotation (calcd.), $[\alpha]_D$ = +38°

The initial boiling point of turpentine was 154° C.; 94 percent of the turpentine distilled below 170°.

TABLE 28.—Physical properties of several samples of *Pinus insularis* turpentine

Tree No.	Density d	Index of refraction n_D	Specific rotation $[\alpha]$
3	0.8475	1.4650	Degrees +30.20
5	.8473	1.4644	+32.10
9	.8480	1.4665	+27.05
18	.8488	1.4650	+32.07
Mixed samples of many trees	}	1.4653	+29.65
		1.4668	+28.02
		1.4716	+22.75

We used *Pinus insularis* oleoresin received (together with herbarium specimens) in 1952 from Dr. Florencio Tamesis, Director of the Philippine Forestry Bureau. A batch of 2,000 g. of oleoresin was

distilled under reduced pressure. At the end of the operation, temperature of the oleoresin was 190° C. and pressure was 3 mm. Rosin remaining in the pot was very hard and brittle. The amount of turpentine in the oleoresin was 20.0 percent.

The turpentine had the following characteristics:

Density, $d_4^{20} = 0.8586$
 Index of refraction, $n_D^{20} = 1.4685$
 Specific rotation, $[\alpha]_D^{25} = +31.2^\circ$

Chemical composition of the turpentine was as follows:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	74
<i>l</i> - β -pinene.....	3
<i>l</i> - β -phellandrene.....	7
Tails, including a sesquiterpene, whose hydrochloride had a melting point of 47° to 48° C.....	7
Polymerized pot residue (probably mostly polymerized phellandrene).....	5

It was not surprising to find a small amount of β -pinene in the turpentine of *Pinus insularis* because this terpene very often accompanies α -pinene; but the presence of *l*- β -phellandrene was unexpected. β -phellandrene has never been reported in Asiatic pines; so far it has been detected in five New World species, Nos. 34, 37, 58, 89, and 91. In all these pines β -phellandrene, too, is found in its levorotatory form.

In table 29 the properties of a fraction of *Pinus insularis* turpentine in which phellandrene was identified are compared with the literature values for pure *l*- β -phellandrene.

TABLE 29.—Physical properties of β -phellandrene from *Pinus insularis* turpentine and from Canada balsam

Property	β -phellandrene fraction of <i>P. insularis</i>	β -phellandrene ¹ from Canada balsam
Index of refraction, n_D^{20}	1.4819.....	1.4851
Density, d_4^{20}8389 ²8375 ²
Specific rotation, $[\alpha]_D$	-13.5°.....	-2.86°
Boiling point.....	57°-58° C. at 11 mm.....	70° C. at 20 mm.

¹ Davenport, J. B., Sutherland, M. D., and West, T. F. Jour. Appl. Chem. 1, p. 528. 1951.

49. *Pinus khasya* Royal²²

Reference (147)

(DC., Prodr. 16:2390. 1868)

Pinus khasya is a native of northern Burma, occurring in the Khasia Hills, Shan Hills, and the Hills of Martaban. This species is also found in the adjacent parts of India. It grows at elevations from 3,000 to 7,000 and occasionally to 10,000 feet.

Turpentine of this pine, distilled in a commercial plant at Jallo, India, was analyzed by Simonsen and Rau (147). It had the following physical characteristics:

²² The name of this pine is spelled in several different ways: Khasya, Kasia, Kescyn, Kasya, Khasyana, Khasia.

Density, $d_{20}^{20} = 0.8633$
 Index of refraction, $n_D^{20} = 1.4765$
 Specific rotation, $[\alpha]_D^{20} = +32.83^\circ$

The turpentine contained the following:

Compound:	Percent
<i>d</i> - α -pinene.....	70
<i>d</i> - β -pinene.....	10
<i>d</i> -longifolene.....	10

This is one of the few instances in which dextrorotatory β -pinene had been reported in pine turpentines. However, the original report did not give enough detail to be absolutely sure if it is really *d*- β -pinene.

50. *Pinus yunnanensis* Franchet Reference (*Unpub. orig. data*)
 (Jour. de Botanique 13: 253. 1899)

Pinus yunnanensis was described in 1899 by Franchet as an independent species. Shaw (142) placed it as a synonym under *P. sinensis*. Lately, however, the name *P. sinensis* has to a certain degree been replaced by *P. tabulaeformis*, No. 53, while *P. yunnanensis* became again an independent species (Dr. Hui-Lin Li, personal communication). Chung-Lwen Wu,²³ working with herbarium material available in American institutions, concluded that *P. yunnanensis* and *P. insularis* are one species.

Pinus yunnanensis occupies the whole of Yunnan province, except the alpine zone; it also grows in the southwestern part of Kweichow province, in Upper Burma, in northern Viet Nam, and in a narrow belt of northern India.

Because it was difficult to obtain oleoresin of this pine from its native land, I tapped a few planted trees in the Eddy Arboretum, Institute of Forest Genetics, Placerville, Calif. A little more than 30 g. of turpentine was obtained by heating the oleoresin under reduced pressure. At the end of distillation, the temperature was 180° C. and the pressure was 1 mm. Under these conditions the remaining rosin was hard and brittle, showing that all volatile oil had been recovered. The yield of turpentine was 22.6 percent; its physical characteristics were:

Density, $d_{17.5}^{21.5} = 0.8591$
 Index of refraction, $n_D^{20} = 1.4663$
 Specific rotation, $[\alpha]_D^{20} = -44.3^\circ$

The turpentine consisted of:

Compound:	Percent
<i>l</i> - α -pinene.....	87
<i>l</i> - β -pinene.....	3
An oxygenated dextrorotatory ingredient, about.....	5

The appearance of the residue did not suggest any appreciable amounts of sesquiterpenes.

51. *Pinus nigra* Arnold References (16, 42, 48, 78)
 (Reise nach Mariaz. 8, t. 1785)

Pinus nigra is a pine widely and unequally distributed in central and southern Europe and in Asia Minor. Sometimes it is called *P.*

²³ See footnote 7, p. 26.

laricio Poir. Within the species several varieties are recognized: *pallasiana* Lamb., native to Crimea; *austriaca* Endlich., of Austria; *calabrica* Loud., of Italy; *corsicana* Loud., of Corsica, and some others.

Turpentine of *Pinus nigra* has been studied by several investigators. It appears from their data (table 30) that the composition of *P. nigra* turpentine from different parts of its extensive range, except perhaps Bulgaria, is about the same. Apparently camphene, β -myrcene and *l*-limonene are found in all varieties in small amounts. In earlier reports these substances had been overlooked, probably because the old methods of fractional distillation were rather primitive.

52. *Pinus heldreichii* Christ.

Reference (87)

(Verh. Nat. Gez. Basel 3:549. 1863)

Pinus heldreichii was described in 1863 as an independent species. In 1914, Shaw (142) placed it within *P. nigra*. In this publication, *P. heldreichii* is considered as a valid species. *P. heldreichii* grows in northeastern Greece and Albania, and in the adjacent parts of Yugoslavia. Information regarding the chemical composition of turpentine of this pine was obtained through the courtesy of Professor Branislav Pejovski (private correspondence) of the University of Skopje, Yugoslavia. The analysis of the turpentine was apparently performed by Dr. B. Okrajnov-Rotovic. Results of the fractional distillation were reported as:

	Fractions		
	1	2	3
Density, d_{20}	0.8598	0.8468	0.8467
Index of refraction, n_D	1.4696	1.4715	1.4724
Optical rotation, α_D	-72.60°	-91.30°	-103.56°
Percent.....	21.5	25.4	40.6

The approximate composition of the turpentine was reported as follows:

Compound:	Percent
<i>l</i> - α -pinene.....	30.14
<i>l</i> -limonene.....	57.39
Oxidation products, pot residue, and losses.....	12.47

It is seen that turpentine of *Pinus heldreichii* differs from the turpentine of *P. nigra* by the presence of large quantities of limonene. Unfortunately the nature of the sesquiterpene fraction of turpentine of this pine is still unknown.

Composition of turpentine of *Pinus heldreichii* var. *leucodermis* (Antoine) Markgraf was reported in 1954 by Lombard and Rotovic (87). The turpentine was levorotatory; its components were:

Compound:	Percent
α -pinene.....	2
<i>l</i> -limonene, ($\alpha_D = -103.56^\circ$).....	27
High-boiling fractions.....	27

It is seen that although the variety *leucodermis* also contained a considerable amount of *l*-limonene, the percentage of higher boiling fractions of this variety was higher than in typical *Pinus heldreichii*.

TABLE 30.—Physical characteristics and chemical composition of several varieties of *Pinus nigra* turpentine

Variety and source of material	Percent of turpentine	Density d_4	Index of refraction n_D	Optical rotation	Composition of turpentine
				Degrees	Percent
<i>corsicana</i> , Corsica (48) <i>austriaca</i> , France (42)	23	0.8580 ²⁵	1.4631 _j	-31.09 _D	<i>l</i> - α -pinene, 87; β -pinene, little. <i>l</i> - α -pinene, 94; β -pinene, trace; a <i>d</i> -terpene, 1; a sesquiterpene, 1 (m.p. hydrochloride 115°-115.5); tails, 4.
<i>austriaca</i> , Ukraine (16)	12-27	0.856-0.861 ²⁰	1.4662-1.4710 _D ²⁰	+2-47 _D	<i>l</i> - α -pinene, 85; camphene, 1; β -pinene, 2; β -myrcene, 1; <i>l</i> -limonene, 3; tails, 7.
<i>pallasiana</i> , Ukraine (16)	30	0.8570-0.870 ²⁰	1.4668-1.4730 _D ²⁰	-13--56 _D	<i>l</i> - α -pinene, 87.2; camphene, 1; β -pinene, 2.3; β -myrcene, 1; <i>l</i> -limonene, 1.4; higher fractions, 7.
<i>nigricans</i> , Bulgaria (78)		0.8635 ²⁰	1.470 _D ²⁰	-20.96 _D	<i>l</i> - α -pinene, 53; <i>l</i> - β -pinene, 38; <i>l,dl</i> -limonene, 6.
prob. <i>hispanica</i> , Spain (42).					<i>l</i> - α -pinene, 90; <i>l</i> -limonene, 4; a sesquiterpene, 1.5; tails, 4.5.

53. *Pinus tabulaeformis* Carriere Reference (*L'apub. orig. data*)
(*Frait. Conif. ed. 2: 510. 1867*)

In Shaw's monograph (142), *Pinus tabulaeformis* is called *P. sinensis*. It occupies an enormous area of northern and north-central China. Its habitat extends from southern Manchuria to Kansu and to Yunnan. In Yunnan it crosses with *P. yunnanensis*. The result of this cross apparently is *P. densata* Masters.²⁴

Pinus tabulaeformis is a species for which several varieties are recognized:

Variety:	Habitat
<i>mukdensis</i> Uyeki.....	Extreme East
<i>rubescens</i> Uyeki.....	Do.
<i>pseudosylvestris</i> Wu.....	Desert ranges of southern part of outer Mongolia.
<i>leucosperma</i> Max.....	Alpine region of W. Kansu
<i>wilsoni</i> Wu.....	Northwestern Szechwan and extreme eastern Sikang.
<i>wilsoni</i> , forma <i>tokunagii</i> Wu.....	Ninghsia, Jehol, Hopei
<i>grandifolia</i> Wu.....	Scattered over the Provinces of Kansu, Shansi, and Hopei.

To my knowledge, the chemical composition of *Pinus tabulaeformis* turpentine has never been reported before. In 1956 a few 30-year-old trees of this pine, planted at the Institute of Forest Genetics, Placerville, Calif., were tapped, and a small amount of oleoresin was obtained. The oleoresin was heated under reduced pressure; at the end of the operation when all volatile oil was expelled, the temperature was 205° C. and pressure was 0.5 mm. The last part of the volatile oil had the consistency of castor oil.

The yield of turpentine was 31 percent; its physical characteristics were:

Density, $d_{20}^{20} = 0.8936$
Index of refraction, $n_D^{20} = 1.4741$
Specific rotation, $[\alpha]_{D20} = +11.2^\circ$

The high density indicated the presence of substances other than the usual terpenes, perhaps sesquiterpenes and sesquiterpene alcohols. Fractional distillation of 30 g. of the oil gave the following results:

Fractions	Boiling range, ° C. (760 mm.)	Percent of total oil
1.....	155-160.....	23.0
2.....	161-170.....	11.4
3.....	171-190.....	2.0
4.....	191-210.....	1.0
5.....	211-260.....	7.2
6.....	261-285.....	11.5
7.....	285-300.....	17.6
8.....	301-308.....	11.3
Residue.....	Solid.....	15.0

²⁴ See footnote 7, p. 26.

No further work has been done with the sample. It appears that at least 25 percent of the turpentine consisted of α -pinene; the presence of β -pinene is possible. The sesquiterpene and diterpene fractions of the turpentine were unusually large, amounting to about 50 percent of the total oil. The residue appeared to contain some polymerized substances. It is highly desirable to analyze larger quantities of turpentine of *Pinus tabulaeformis* and its numerous varieties, especially because the other *Diploxyylon* pines of China possess turpentines of a relatively simple composition (cf. Nos. 39, 45, 46, 50).

Group Australes

54. *Pinus ponderosa* Laws. References (58, 63, 72, 98, 112, 114, 136)
(Agr. Man. 354. 1836)

Pinus ponderosa, or ponderosa pine, is an American pine of wide distribution. Its range extends from British Columbia to the Mexican border. Possibly it occurs in adjacent parts of Mexico. Longitudinally, its range extends from the Pacific coast eastward to the Dakotas, western Nebraska, Colorado, northwestern Oklahoma, New Mexico, and the Trans-Pecos region of western Texas.

Earlier investigations of *Pinus ponderosa* turpentine were conducted by Schorger (136) at the beginning of this century. At that time, the most important ingredient of *P. ponderosa* turpentine, Δ^3 -carene, had not yet been discovered,²⁵ and Schorger did not report it.

According to Schorger, the Pacific coast form of *Pinus ponderosa* possessed turpentine decidedly levorotatory because of the predominance of *l*- β -pinene, whereas the Arizona turpentine was decidedly dextrorotatory because it consisted largely of *d*- α -pinene. This difference caused Schorger to generalize that the Pacific coast form possesses levorotatory turpentine, but that the Rocky Mountain form, called by some botanists *P. ponderosa* var. *scopulorum* Engelm. (86, p. 270), always yields dextrorotatory turpentine.

Samples of *Pinus ponderosa* turpentine from 12 localities of its extensive range were analyzed in the project reported here. These investigations showed that only in Arizona, where Schorger obtained his turpentine, did all individual trees yield dextrorotatory turpentine. In California (Santa Cruz Mountains and the west slope of the Sierra Nevada) all individual trees yielded levorotatory turpentine. In all other places, including the east side of the Sierra Nevada, some trees yielded dextrorotatory and others levorotatory turpentines.

Table 31 shows the physical characteristics of *Pinus ponderosa* turpentine obtained from the 12 localities of the entire range of this pine. Table 32 shows the chemical composition of turpentine from the 12 localities. Only the Arizona and southwestern Utah samples contained considerable amounts of *d*- α -pinene, which in combination with *d*- Δ^3 -carene, was responsible for the dextrorotatory nature of the turpentine. Turpentine from all other localities contained very little α -pinene, and this terpene was always in a *l*- or *dl*-form.

²⁵ Δ^3 -carene was discovered in 1920 by Simonsen in *Pinus longifolia* (No. 26) turpentine. The credit of discovering Δ^3 -carene in *P. ponderosa* goes to Dr. A. J. Haagen-Smit of California Institute of Technology.

TABLE 31.—Physical characteristics of *Pinus ponderosa* turpentine from 12 localities of its range

Region	Locality ¹ and elevation	Density d ₄	Index of refraction n _D	Specific rotation [α]	Yield of turpentine, percent of weight of oleoresin	Variability of optical rotation	Variability of density	Variability of index of refraction
Pacific coast-----	1. Near Santa Cruz, Calif. (1,550 ft.)	0.8459 ²⁵	1.4749 ²⁵	Degrees -23.2	19.5	Degrees -12.5 to -32.5	0.8532 to 0.8685	1.4732 to 1.4782
Sierra Nevada, west slope.	2. Near Placerville, Calif. (2,700 ft.)	.8594 ²²	1.4756 ²⁵	-29.0	15.0	-9.1 to -39.1		
Northern Idaho..	3. Priest River Expt. Sta. (2,850 ft.)	.860 ²²	1.4741 ²⁵	-2.7	22.0	² +4.5 to -13.3		
Southwestern Utah.	4. Panguitch Lake (8,500 ft.)	.8611 ²³	1.4711 ²⁴	+6.0	26.5	³ +23.3 to -17.6		
Southern Rocky Mountains	5. Beulah (SW of Pueblo, Colo., 7,500 ft.)	.8661 ²²	1.4747 ²²	+1.8	20.0			
East central Arizona.	6. Near McNary, Ariz. (Apache Indian Res., 8,200 ft.)	.8701 ^{22,5}	1.4721 ²³	+13.7	22.0	⁴ +10.5 to +16.3		
Northwestern Nebraska.	7. Near Chadron, Nebr. (3,500 ft.)	.8695 ²⁴	1.4777 ²⁴	+ .9	18.9			
Central Montana.	8. Near White Sulphur Springs, Mont. (5,000 ft.)	.8614 ²²	1.4747 ²²	- .9	17.7			
Southeastern Wyoming.	9. Esterbrook Ranger Station (6,500 ft.)	.8673 ²⁴	1.4768 ²⁵	+1.5	22.0			
Southwestern Idaho.	10. Idaho City Expt. Forest (near Boise, 4,070 ft.)	.8563 ²²	1.4745 ²²	-7.2	19.7			
Central Rocky Mountains.	11. Manitou Expt. Forest (west of Colorado Springs, 7,600 ft.)	.8692 ²³	1.4770 ²³	-2.1	19.0	-9.3 to +9.0		
Black Hills, South Dakota.	12. Near old Pactola Ranger Station (4,600 ft.)	.8648 ²³	1.4752 ^{22,5}	+1.2	20.0	-8.0 to +10.0		

¹ Figures refer to the locations shown on map, figure 15.² 14 trees.³ 17 trees.⁴ 10 trees.

TABLE 32.-- Composition of turpentine of *Pinus ponderosa* from 12 localities of its range

Region	Locality ¹ and elevation	α -pinene	<i>l</i> - β -pinene	<i>d</i> - Δ^2 -carene	<i>l</i> -limonene	Terpinolene	β -myrcene	<i>n</i> -undecane	Camphene	Longifolene	Unidentified sesquiterpene	Aldehydes	Methyl chavicol	β -phellandrene
		Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.
Pacific coast	1. Near Santa Cruz, Calif. (1,550 ft.).	² 6 (<i>l</i>)	43	25	10	0	2	0.2	2.5	0	2.0	Positive reaction	0	2(?)
Sierra Nevada, west slope.	2. Near Placerville, Calif. (2,700 ft.).	1 (<i>l</i>)	50	30	4-5	0	3	0	3	0	1	Negative reaction	0	0
Northern Idaho	3. Priest River Expt. Sta. (2,850 ft.).	1-2 (<i>dl</i>)	12	64	5	0	5	0	2.5	0	2.0	do.	2	0
Southwestern Utah.	4. Panguitch Lake (8,500 ft.).	45 (<i>d</i>)	³ 0	40	2-3	³ 0	³ 0	0	0	10	0	do.	0	0
Southern Rocky Mtn.	5. Beulah (SW of Pueblo, Colo., 7,500 ft.).	5 (<i>dl</i>)	17	40	15	0	5	0	0	8	0	do.	0	0
East central Arizona.	6. Near McNary, Ariz. (Apache Indian Res., 8,200 ft.).	34 (<i>d</i>)	14	31	4	0	³ 0	0	0	4	4-5	do.	0	0
Northwestern Nebraska.	7. Near Chadron, Nebr. (3,500 ft.).	2 (<i>dl</i>)	32	38	7	0	3	0	4	12	0	do.	0	0
Central Montana.	8. Near White Sulphur Springs, Mont. (5,000 ft.).	3 (<i>l</i>)	25	47	6	4	5	0	5	2	0	do.	0	0
Southeastern Wyoming.	9. Esterbrook Ranger Station (6,500 ft.).	2 (<i>l</i>)	31	40	4	1	4	0	5	10	0	do.	0	0
Southwestern Idaho.	10. Idaho City Expt. Forest (near Boise, 4,070 ft.).	6 (<i>dl</i>)	30	40	10	2	3	0	0.5	0	0	do.	0	0
Central Rocky Mountains.	11. Manitou Expt. Forest (west of Colorado Springs, 7,600 ft.).	2-3	30	47	0	2-3	0	0	1	8	0	do.	1	0
Black Hills South Dakota.	12. Near old Pactola Ranger Station (4,600 ft.).	2 (<i>dl</i>)	38	37	0	3	0	0	0	13	1	do.	1-2	0

¹ Figures refer to location shown on map, figure 15.

² Letters *l*, *d* or *dl* in this line refer to dextrorotatory or levorotatory nature of the α -pinene fraction. These are earlier findings; possibly small quantities are found.

β -pinene was found in practically all samples in large amounts (from 12 to 50 percent) but was not detected in the Utah sample, probably because of faulty technique. Δ^3 -carene truly is the specific terpene of *Pinus ponderosa*. It was found in large quantities (from 25 to 64 percent) in all samples throughout the range of the species. The presence of Δ^3 -carene gives to this turpentine a specific sweet odor that distinguishes it from the turpentines of all other Australes pines of the United States.²⁶

Minor constituents of *Pinus ponderosa* turpentine have a very interesting distribution (fig. 15, table 31). Limonene, which is the only monocyclic terpene in the first seven localities shown in the table, is accompanied (in southwestern Idaho, southeastern Wyoming and central Montana) by another monocyclic terpene, terpinolene. In Manitou, Colo., and in the Black Hills, S. Dak., limonene is completely replaced by terpinolene. Myrcene was found in all samples except those from Manitou, Colo., and the Black Hills, S. Dak.

The distribution of the two *Pinus ponderosa* sesquiterpenes, cadinene and longifolene, is also interesting. In trees of the Pacific coast we have found only cadinene; in those of several other localities we found both sesquiterpenes; and in turpentine from the Black Hills, S. Dak., from southeast Colorado, from the Apache Indian Reservation, Ariz., and from southwest Utah, longifolene replaced cadinene entirely.

Samples of turpentine from Santa Cruz on the coast of California had the most unusual composition. The turpentine, besides containing α - and β -pinenes, Δ^3 -carene, and limonene, gave a positive test for aldehydes and contained a small quantity of *n*-undecane and apparently some phellandrene. This unusual composition suggests an affinity of the coastal ponderosa pine to *P. coulteri*, No. 34, which grows not far from the coast. At some time in the past these two pines may have intercrossed. It is of interest that the western pine beetle (*Dendroctonus brevicornis*) normally attacks only two species of pine: *Pinus ponderosa* and *P. coulteri*.²⁷

Goldblatt and Burgdahl (58) reported the composition of *Pinus ponderosa* turpentine obtained from stump wood and from lumber by acetone extraction (table 33). The data presented in table 33 are important to an understanding of the stability of turpentines. Although small quantities of ingredients not found in gum turpentine of *P. ponderosa* were detected, nevertheless the most important component of the wood turpentine was the same Δ^3 -carene that is also the prominent component of gum turpentine of this pine.

²⁶ Cf. *Pinus arizonica* (No. 55) and *P. washoensis* (No. 56); these two pines are closely related to *P. ponderosa* and they both contain Δ^3 -carene. I consider these pines as belonging to the *P. ponderosa* complex.

²⁷ Compare with entomological relations of *Pinus halepensis*, No. 79, and *P. brutia*, No. 80.

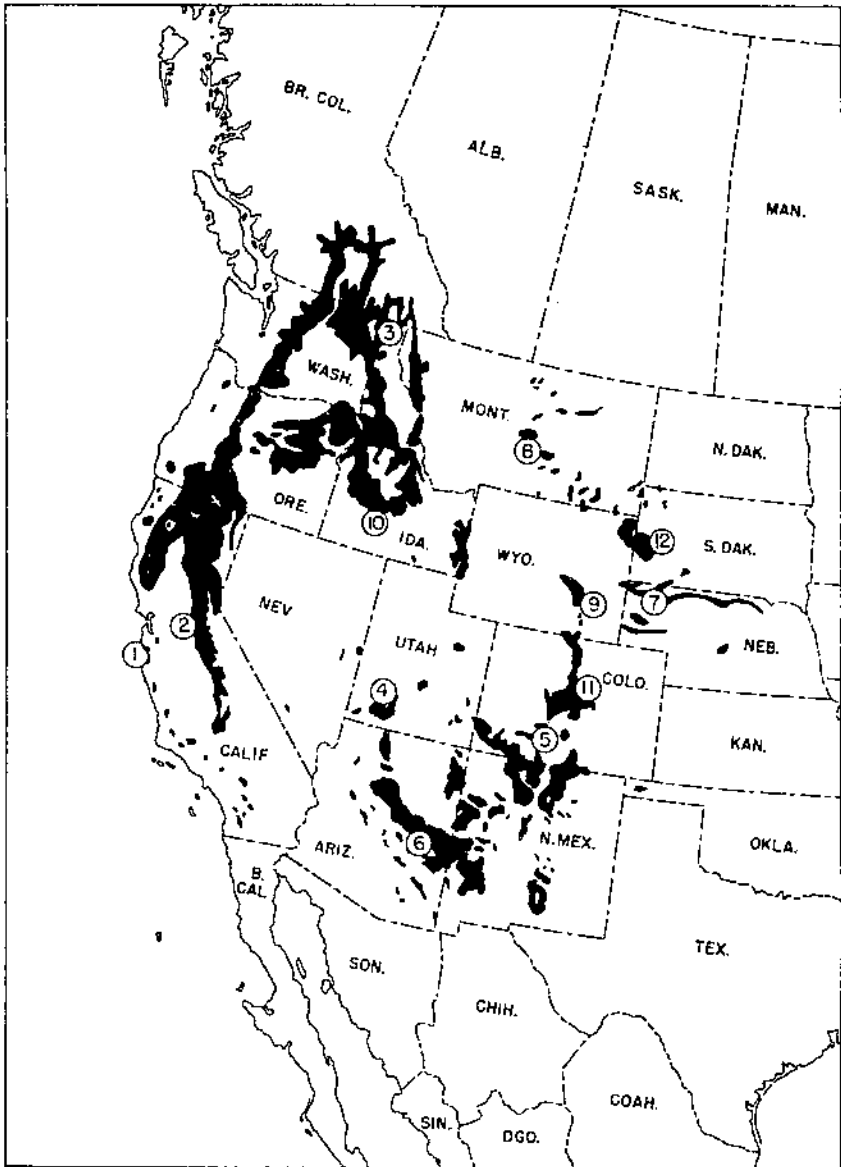


FIGURE 15.—Geographical distribution of *Pinus ponderosa*. Numbers in circles show places where turpentine samples were obtained.

TABLE 33.—Approximate composition of turpentine from *Pinus ponderosa* stump wood and lumber

Component	Weight of oil from the—	
	Stump wood	Lumber
Acetone (solvent).....	Percent 0.5	Percent (¹)
Benzaldehyde.....	(²)	(¹)
<i>dl,l</i> - α -pinene.....	8.0	7
<i>l</i> -camphene.....	.5	1
<i>l</i> - β -pinene.....	6.0	7
β -myrcene.....	8.0	8
<i>d</i> - Δ^2 -carene.....	70.0	65.0
<i>d</i> -terpinene.....	1.5	1
<i>p</i> -cymene.....	.5	1
<i>dl,l</i> -limonene.....	1.5	3
Terpinolene.....	1.0	2
Loss and unidentified.....	2.5	4

¹ Less than 1 percent.² Less than 0.1 percent.

Source: Goldblatt and Burgdahl (58).

55. *Pinus arizonica* Engelm.

Reference (76)

(U.S. Geogr. Surv. West 100th Merid. Rep. 6: 26. 1878)

Pinus arizonica, or Arizona pine, was discovered in Arizona, but its main range is in the Mexican States of Sonora, Chihuahua, and Durango. Its form *stermitae* Martinez occurs in the desert mountains of Coahuila and adjacent parts of Nuevo Leon (88). Martinez considers Arizona pine as a valid species (88), but Shaw (142) places it under *P. ponderosa*. Little (86) designates this pine as a variety of *P. ponderosa*.

Oleoresin used in our investigations was received through the courtesy of Sr. Mario González Múzquiz of the Aserraderos González Ugarte S. A. Thanks are due to Ing. Alfredo Parra R. for supervising the collection of this oleoresin sample, which was accompanied by branches, pieces of bark, and cones. These were deposited in our herbarium. The oleoresin was collected at El Retiro, near San Juanito, Chihuahua, at an altitude of 8,250 feet above sea level.

A batch of the oleoresin weighing 3,628 g. was heated under reduced pressure so that at the end, when all turpentine was distilled off, the pressure was 2 mm. and temperature reached 180° C. The remaining rosin was hard and brittle. Turpentine obtained by this means amounted to 908 g., or 25 percent of the weight of the oleoresin.

The turpentine of *Pinus arizonica* had the following characteristics:

Density, d_4^{20} = 0.8585Index of refraction, n_D^{20} = 1.4690Specific rotation, $[\alpha]_D^{20}$ = +9.7°

A batch of 882 g. of the turpentine was distilled through a 90 cm. long, 25-mm. inside diameter, Todd column, packed with 3/32-inch single-turn glass helices, and equipped with magnetic control of reflux. A reflux ratio of 10 to 1 was maintained.

The turpentine of Arizona pine contained:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	60
<i>l</i> - β -pinene.....	29
<i>d</i> - Δ^3 -carene.....	5
Tails.....	4.2
Pot residue and loss.....	1.8

Presence of *d*- Δ^3 -carene in Arizona pine turpentine seems to indicate that this pine is closely related to *Pinus ponderosa*, No. 54. I therefore concur with Little (86) that *P. arizonica* may be considered a variety of *P. ponderosa*. Of interest is the resemblance of this pine to *P. ponderosa* from southwestern Utah and from Arizona, which also contains large amounts of α -pinene (see table 32, p. 89). It appears that *P. ponderosa* in the south merges into *P. arizonica*.

56. *Pinus washoensis* Mason & Stockwell References (63, 90)
(Madroño 8: 61-63. 1945)

Pinus washoensis was discovered in the upper reaches of Galena Creek in the Sierra Nevada, east of Lake Tahoe, at an elevation of 7,000 to 8,500 feet (90). Before exploration of the West this pine had apparently been rather abundant, but towards the end of the Nineteenth century, it became almost completely exterminated, having been logged to supply lumber for the development of Nevada silver mines. It resembles very closely *P. ponderosa* in all morphological characters, but the small cones look like miniature *P. jeffreyi* cones. Some botanists have expressed verbally their opinion that *P. washoensis* was a result of hybridization between *P. jeffreyi* and some other pine.

To obtain a sample of oleoresin from this pine, nineteen 50- to 60-year old trees were tapped under the author's supervision near Mt. Rose, Nev., about 15 miles southwest from Reno, at an elevation of 7,000 feet. Oleoresin was gathered from each tree separately. At the end of each distillation, the temperature reached 190° C. and pressure was reduced to 0.5 mm. On the average, turpentine content in the oleoresin was 19.4 percent; it varied from 18 to 22 percent.

Physical characters of turpentine samples taken from the individual trees showed the following range (also see table 2, p. 10):

Density, d_4^{20} , from 0.8522 to 0.8613
Index of refraction, n_D^{20} , from 1.4750 to 1.4777
Specific rotation, $[\alpha]_D^{20}$, from +11.7 to -11.4°

The turpentine samples were found to consist largely of *d*- Δ^3 -carene in varying quantities. In the turpentines of some trees with low carene content, *l*- β -pinene was found in large quantities. In the trees of high carene content, β -pinene was almost entirely absent. Small quantities of dipentene, *d*- α -pinene, and an unidentified sesquiterpene were found in all 19 samples. No heptane or aldehydes (that is, *Pinus jeffreyi*, No. 32, turpentine ingredients) were found in any samples.

Judging by the morphological characters of this pine, and by the chemical composition of its turpentine, I am inclined to consider *Pinus washoensis* as a variety or a mutant of *P. ponderosa*. There is no chemical evidence that this pine is a product of hybridization between *P. jeffreyi* and some other pine.

57. *Pinus palustris* Mill.

References (30, 47)

(Gard. Diet. Ed. 8. *Pinus* No. 14. 1768)

Pinus palustris is the longleaf pine of the Southeastern United States. It grows on the coastal plains from southeastern Virginia to central Florida and west to eastern Texas. Together with slash pine, No. 59, it is the chief source of American commercial gum turpentine. The yield of turpentine of longleaf pine is 2½ to 23 percent.

In 1929 Dupont and Barraud (47) examined gum turpentine of longleaf pine that they obtained from the Hercules Powder Company. The physical characteristics of the turpentine were as follows:

Density, $d_{20}^{20} = 0.8618$
 Index of refraction, $n_D^{20} = 1.4657$
 Optical rotation, $\alpha_D^{20} = +7.89^\circ$

Chemical composition of the turpentine was:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	64.3
<i>l</i> - β -pinene.....	31.1
Tails.....	4.6

Chadwick and Palkin (30), using large quantities of commercial longleaf pine turpentine, reported on the composition of its heads and tails. The heads (substances boiling below α -pinene) amounted to less than 0.07 percent of the turpentine. No heptane was found there. The tails (substances boiling above β -pinene) comprised 7.7 percent of the turpentine. The tails contained chiefly the following compounds: dipentene, terpinolene, bornyl acetate, and methyl chavicol. No sesquiterpenes were detected, even when large quantities of material were analyzed.

58. *Pinus caribaea* MoreletReference (73)²⁸

(Rev. Hort. Cote D'Or. 1, 105: 1851)

Pinus caribaea grows in the Bahama Islands, Western Cuba, Honduras, Guatemala and Nicaragua, British Honduras, and in a few places in the southeastern part of Quintana Roo, Mex. Until recently the southeastern slash pine, whose official name is now *Pinus elliottii*, No. 59, was also known by this name.

A small sample of oleoresin of *Pinus caribaea* was obtained through the courtesy of Professor James J. Parsons of the University of California. The sample was collected in April 1953 at Karawala, near the mouth of the Rio Grande, about 50 miles north of Bluefields, Nicaragua. The turpentine had the following properties:

Density, $d_{20}^{20} = 0.8670$
 Index of refraction, $n_D^{20} = 1.4708$
 Specific rotation, $[\alpha]_D^{20} = -20.6^\circ$

The turpentine consisted of:

Compound:	Percent
<i>l,d,l</i> - α -pinene.....	59-60
<i>l</i> - β -phellandrene.....	5
<i>d</i> - Δ^3 -carene.....	10
<i>d</i> -longifolene (about).....	13
Polymerized pot residue and losses.....	11

²⁸ In the work cited, the description and analysis of *Pinus caribaea* were somewhat mixed up typographically. The beginning of the part dealing with *P. caribaea* is at the end of the article (p. 741); its continuation is in the middle of col. 1, p. 740.

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USDA TECHNICAL BULLETINS

UPDATA

COMPOSITION OF GUM TURPENTINES OF PINES

MIRY, N. I.

2 OF 2

An analysis of a larger sample of *Pinus caribaea* turpentine would be desirable.

59. *Pinus elliottii* Engelm. var. *elliottii* References (30, 47, 57, 121)
(Acad. Sci. St. Louis. Trans. 4: 186. pl. 1-3, 1880; Jour. For. 50:
918-923, 1952)

Pinus elliottii, or slash pine, is a chief source of American gum turpentine. This pine has been known for some time as *P. caribaea*. Originally it was named *P. elliottii*, and at one time it was known as *P. heterophylla* Sudw. and *P. caribaea* Mor. In 1952 it became known again as *P. elliottii*. This species now is subdivided into *P. elliottii* var. *elliottii*—the familiar naval stores tree of Southeastern United States, and *P. elliottii* var. *densa* of southern Florida, No. 60. The name *P. caribaea*, No. 58, was retained only for the slash pine growing in the West Indies and Central America.

There are ample morphological justifications for segregating slash pine into the above three entities. The chemical characters of these three pines, Nos. 58, 59, 60, also are different.

The yield of turpentine of *Pinus elliottii* var. *elliottii* is generally about 22 percent of the weight of the oleoresin.

Turpentine of *Pinus elliottii* var. *elliottii* (referred to as *P. heterophylla* Sudw.) was analyzed in 1929 by Dupont and Barraud (47). The product was obtained from the Hercules Powder Company. Physical constants of the turpentine were these:

Density, $d_{25}^{25} = 0.8533$
Index of refraction, $n_D^{25} = 1.4631$
Optical rotation $\alpha_D = -30.78^\circ$

The turpentine contained:

Compound:	Percent
<i>l</i> - α -pinene.....	75.6
<i>l</i> - β -pinene.....	21.2
Tails.....	3.2

In 1932 Palkin (121) reported the following data for freshgum (Gum dip 8) slash pine turpentine:

Density, $d_{15}^{15} = 0.8657$
Index of refraction, $n_D^{15} = 1.4694$
Optical rotation, $[\alpha]_D = -22.58^\circ$

The composition of this turpentine was as follows:

Compound:	Percent
<i>l</i> - α -pinene.....	61
<i>l</i> - β -pinene.....	33.7
Tails.....	5.3

Chadwick and Palkin (30) reported that the tails of slash pine turpentine contained dipentene, methyl chavicol, and very little of alcohols, esters, and others other than methyl chavicol.

For a more complete treatment of American turpentine obtained from *Pinus elliottii* var. *elliottii*, No. 59, and from *P. palustris*, No. 57, consult Goldblatt (57).

60. *Pinus elliotii* var. *densa* Little & Dorman Reference (113)
(Jour. Forestry 50: 921, figs. 1, 2. 1952)

Pinus elliotii var. *densa* was described by Little and Dorman in 1952. This pine grows on the lower Florida Keys and in southern Florida and north along the coasts to central Florida.

A sample of oleoresin was obtained through the courtesy of the U.S. Forest Service Southeastern Forest and Range Experiment Station from its South Florida Experimental Area near Ft. Myers, Fla. A 3,694 g. batch of the oleoresin was heated under reduced pressure so that when all turpentine was distilled off, the vacuum gage showed pressure of 2 mm. of mercury and the temperature reached 190° C. Yield of turpentine amounted to 19 percent.

The turpentine had the following physical characteristics:

Density, $d_4^{20} = 0.8532$
Index of refraction, $n_D^{20} = 1.4709$
Specific rotation, $[\alpha]_{D}^{20} = -38.6^\circ$

The turpentine contained:

Compound:	Percent
<i>l,l</i> α pinene.....	71
<i>l</i> - β pinene.....	3-4
An unidentified terpene, possibly α phellandrene.....	1-2
<i>l</i> - β phellandrene.....	19
Methyl chavicol.....	3

The unidentified terpene was detected in the fraction boiling at 62° to 63° C. at 17 mm. pressure. The characteristics of the fraction were:

Density, $d_4^{20} = 0.833$
Index of refraction, $n_D^{20} = 1.4808$
Specific rotation, $[\alpha]_{D}^{20} = -25.5^\circ$

61. *Pinus taeda* L. References (116, 68, 158)
(Sp. Plant. 1000. 1753)

Pinus taeda is the loblolly pine of Southeastern United States. It occurs from southern New Jersey to central Florida and from the Atlantic to eastern Texas, southeastern Oklahoma, southeastern Arkansas, and southern Tennessee.

Loiblolly pine turpentine was investigated by Herty,²⁰ who found a yield of the turpentine at 19.29 percent; the physical characteristics are given below.

Density, $d = 0.8525$
Index of refraction, $n_D = 1.4700$
Optical rotation, $\alpha = +46.2^\circ$

Fractionation yielded the following results:

Boiling range (° C.):	Percent
160-165.....	9.3
165-167.....	38.0
167-172.....	37.5
172-180.....	12.5
Above 180.....	2.7

From these results it was concluded that the loblolly pine turpentine was a mixture of pinene and limonene, with the latter probably in

²⁰ Unpublished Forest Service report, 1906.

excess. No identification of the components was made. In a later note, Herty and Dixon (68) stated that loblolly pine turpentine consists chiefly of pinene.

Oleoresin of loblolly pine used in the investigation reported here (116) was sent by Mr. Keith W. Dorman, of the U.S. Forest Service Southeastern Forest Experiment Station, Lake City, Fla. Upon distillation under 0.05 mm. vacuum, the oleoresin yielded 18.6 percent of turpentine. The relatively low yield may be explained by the loss of some volatile oil from a jar broken in transit. The turpentine had the following constants:

Density, $d_4^{20} = 0.8570$
 Index of refraction, $n_D^{20} = 1.4675$
 Specific rotation, $[\alpha]_D^{20} = +20.17^\circ$

Chemical composition of the turpentine was *d*- α -pinene, 85 percent, and *l*- β -pinene, 12 percent.

In 1956 Sutherland and Wells (158) reported the results of analysis of *Pinus taeda* turpentine "supplied by Mr. W. Langdale of Florida, U.S.A." Because of damage to the container, some liquid part of the oleoresin was lost in transit and accordingly, the yield of turpentine was only about 14 percent. The constants of the turpentine were these:

Density, $d_4^{20} = 0.8592$
 Index of refraction, $n_D^{20} = 1.4683$
 Specific rotation, $[\alpha]_D^{20} = +24.1^\circ$

They found the turpentine contained:

Compound:	Percent
<i>d</i> - α -pinene.....	71
<i>l</i> - β -pinene.....	22
Methyl chavicol.....	1
Unsaturated ketone.....	0.5
Myrcene, limonene, and <i>p</i> -cymene.....	1
An unidentified sesquiterpene, about.....	1
Other unidentified substances.....	3 or 4

62. *Pinus echinata* Mill.

References (68, 98)

(Gard. Dict. Ed. 8. *Pinus* No. 12. 1768)

Pinus echinata is commonly known as shortleaf pine. It grows from New York to Florida and west through West Virginia, southwestern Illinois, and eastern Tennessee to southern Missouri, Arkansas, Oklahoma, and eastern Texas.

This pine has been considered a poor source of commercial oleoresin products, and consequently its turpentine has not been thoroughly investigated. There is in the Forest Service files, however, a typewritten office report by Herty, dated 1906, on composition of shortleaf pine turpentine. The oleoresin used by Herty was collected in northern Florida. Herty obtained the following data for two samples of crude shortleaf pine turpentine:

Turpentine, 16.27 and 20.00 percent
 Density (no temperature given) 0.8452 and 0.8464
 Index of refraction (no temperature given) 1.4728 and 1.4723
 Optical rotation $+103^\circ 49'$ and $+123^\circ 48'$ ³⁰

³⁰ Note very strong dextrorotatory power of the crude turpentine; this was undoubtedly an error.

A rather low specific gravity of the turpentine caused Herty to suggest that it consists of a mixture of limonene and pinene, the former being the greater share. Fractional distillation of 100 cc. of two samples combined gave the following results:

Boiling range (° C.):	Percent
172-175.....	77
175-177.....	10
177-187.....	10
Residue above 187.....	3

The boiling range is that of limonene.

In a later publication, Herty and Dixon (68) stated that "the chief constituent [of shortleaf pine turpentine] is pinene." There is one pine in northern Florida—*Pinus serotina*, No. 86—whose turpentine contains 90 percent of *l*-limonene. Would it be possible that what Herty reported as *P. echinata* turpentine was actually that of *P. serotina*?

The oleoresin used in the present investigation was obtained through the courtesy of Keith W. Dorman, of the U.S. Forest Service. It was collected at Bent Creek Experimental Forest, near Asheville, N.C. Turpentine was obtained from the oleoresin under reduced pressure; at the end of distillation the temperature inside the flask was 150° C. and pressure was 0.1 mm. The pot residue (rosin) was hard and brittle. The yield of turpentine amounted to 21.4 percent. Physical characteristics of the turpentine were:

Density, d_4^{20} = 0.8575
 Index of refraction, n_D^{20} = 1.4685
 Specific rotation, $[\alpha]_D^{20}$ = + 9.9°

Chemical composition of turpentine was as follows:

Compound:	Percent
<i>d</i> - α -pinene.....	85
<i>l</i> - β -pinene.....	11

63. *Pinus lawsonii* Roehl

Reference (112)

(Gordon, Pinet. Suppl. 64. 1862)

Pinus lawsonii is a subtropical pine growing in central and western Mexico (States of Jalisco, Michoacan, Morelos, Mexico, Puebla, Guerrero, Oaxaca). A sample of oleoresin of this pine was collected for us by Ing. Mario Avila González near Ciudad Hidalgo, Michoacán, at an elevation of 7,540 feet, and sent to us through the courtesy of M. Louis Huguét, Forester for the Food and Agriculture Organization, United Nations. The sample was accompanied by herbarium material.

A batch of the oleoresin was heated under reduced pressure; towards the end of distillation, the temperature was increased to 195° C. and pressure was reduced to 1 mm. Yield of turpentine amounted to 20.8 percent of the weight of the oleoresin. The remaining rosin was hard and brittle, indicating that all volatile ingredients had been removed from the oleoresin. The turpentine had the following physical properties:

Density, d_4^{20} , 0.8627
 Index of refraction, n_D^{20} , 1.4725
 Specific rotation, $[\alpha]_D^{20}$, + 24.0°

The turpentine contained:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	55
Δ^2 -carene.....	31
<i>l,dl</i> -limonene.....	2-3
Terpinolene.....	2
Methyl chavicol.....	2
<i>d</i> -longifolene.....	2

64. *Pinus teocote* Schl. & Cham.

Reference (115)

(*Linnaea* 5: 76. 1830)

Pinus teocote is a widely distributed pine of Mexico. It grows from Coahuila (and possibly from southern Chihuahua) to Chiapas (88). A sample of oleoresin of this pine was collected for us at El Salto, Durango, under the supervision of an expert on Mexican pines, Forest Engineer Cenobio E. Blanco.

The oleoresin was distilled at reduced pressure; at the end of distillation, the temperature in the flask reached 203° C. and the pressure was 0.8 mm.

Yield of turpentine was 24.2 percent; it had the following physical characteristics:

Density, $d_4^{25} = 0.8578$
 Index of refraction, $n_D^{25} = 1.4669$
 Specific rotation, $[\alpha]_D^{25} = +7.6^\circ$

The turpentine contained:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	92
Sesquiterpenes, mostly longifolene.....	3

65. *Pinus montezumae* Lamb.

References (71, 77, 99)

(*Descr. Gen. Pinus* Ed. 3. 1. 39, t. 22. 1832)

Pinus montezumae is a complex species; Shaw (142) was well aware of it when he wrote that "a monograph of this species . . . would be a valuable contribution to science." Since Shaw's time, a great deal of work has been done in studying the *P. montezumae* complex. Several pines that in Shaw's "Genus *Pinus*" (142) were found under *P. montezumae* have been elevated to the rank of a species—such as *P. hartwegii*, No. 67, *P. rudis*, No. 68, *P. michoacana*, No. 70.

Pinus montezumae is a Mexican pine, growing from Coahuila in the north, through Jalisco and Michoacán and south to Chiapas. It also occurs in Guatemala and Honduras.

In 1946 Iriarte (77) reported the composition of *Pinus montezumae* turpentine obtained from a commercial distillery located near Uruapan, Michoacán. The yield of the steam-distilled turpentine was 22.7 percent. Physical constants were:

Density, $d_4^{25} = 0.8757$
 Index of refraction, $n_D^{25} = 1.4656$
 Specific rotation, $[\alpha]_D^{25} = +36.5^\circ$ ³¹

The composition of the turpentine was reported to be *d*- α -pinene, 96 to 97 percent.

Five years later Mirov (99) published data on *Pinus montezumae* turpentine from the same locality. The oleoresin was collected in

³¹The minus sign before the specific rotation value in Iriarte's paper was obviously a typographical error, since all his fractions had plus signs.

the woods from well-identified trees. The turpentine was removed under reduced pressure; at the end of distillation, the pot temperature was 165° C. and the pressure was 0.5 mm. The yield of turpentine, 27.6 percent, was higher than in Iriarte's tests. Physical constants were:

Density, $d_4^{20} = 0.8563$
 Index of refraction, $n_D^{20} = 1.4655$
 Specific rotation, $[\alpha]_{D, 20}^{20} = +47.7^\circ$

The turpentine consisted almost entirely of *d*- α -pinene (97 or 98 percent).

Loff and Mirov (71) reported composition of turpentine of *Pinus montezumae* from the most southern Mexican State of Chiapas (fig. 16). The trees were selected and identified by Mirov. Conditions at the end of distillation were as follows: temperature, 175° C.; pressure 5 mm. The yield of the turpentine was 25 percent of the weight of the oleoresin.

The physical constants were as follows:

Density, $d_4^{20} = 0.8441$
 Index of refraction, $n_D^{20} = +1.4612$
 Optical rotation, $[\alpha]_{D, 20}^{20} = +19.2^\circ$

Composition of the turpentine was:

Compound:	Percent
<i>n</i> -heptane (table 34)-----	8
<i>d, dl</i> - α -pinene-----	72
<i>l, dl</i> -limonene-----	6-7
<i>d</i> -longifolene-----	8
Oxygenated terpene derivatives-----	1-2

Judging by the differences in chemistry of the turpentines of *Pinus montezumae* from the two localities, it appears that *P. montezumae* of Michoacán and *P. montezumae* of Chiapas are at least two different varieties. There is a possibility that the Chiapas *P. montezumae* is a result of hybridization with *P. oaxacana*, No. 36.

TABLE 34.—Identification of *n*-heptane in the Chiapas variety of *Pinus montezumae*

Property	<i>n</i> -heptane from head fraction of <i>P. montezumae</i> from Chiapas	<i>n</i> -heptane ¹
Index of refraction, n_D -----	1.3868 ^{22, 5}	0.38764 ²⁰
Density, d_4 -----	.6807 ²³	.68368 ²⁰
Boiling point (°C.), 760 mm-----	97-98	98.428

¹ Rossini, et al. *Selected values of properties of hydrocarbons*. U.S. Natl. Bur. Standards Cir. 461, p. 39. 1947.

66. *Pinus durangensis* Martínez

Reference (71)

(Annal. Inst. Biol. 13: 1, 23, Mexico. 1942)

In 1938, Cenobio E. Blanco described a majestic pine, "un pino real," growing in the State of Durango and possessing six, sometimes seven and eight, needles in a fascicle (25).

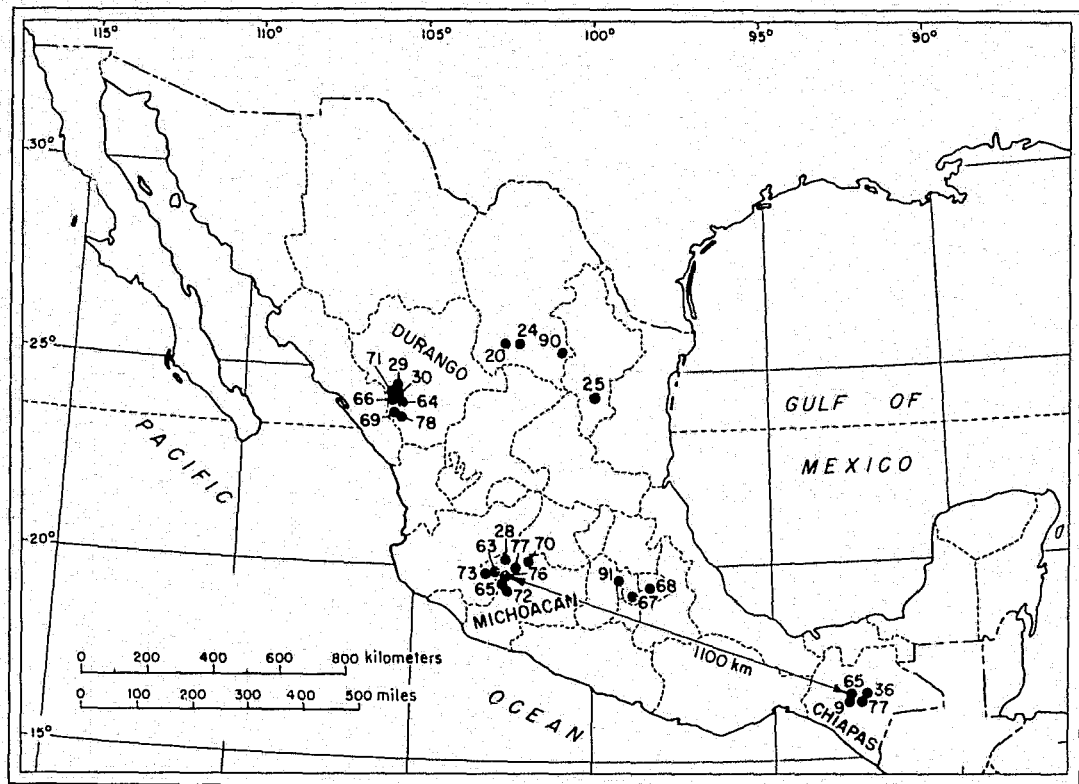


FIGURE 16.—Location of Mexican pines from which samples of turpentine were obtained for analysis. (Numbers refer to the list of pines, p. 27.)

Shaw had been aware of the existence of this pine. In "The Pines of Mexico" (141) he included this pine in *Pinus montezumae*, but later, in his "Genus Pinus" (142), he designated this pine as *P. ponderosa*, mentioning however that "Fuscicles of 6 and 7 are sometimes found and specimens that I have collected in Sandia, Durango (issued by Pringle through misunderstanding, under the name of *P. roseana* ined.) show such fuscicles on the fertile branches."

Pinus durangensis resembles *P. montezumae*, but its cones are comparatively small, and its needles are more delicate. It also resembles *P. ponderosa*, but it lacks sharp prickles on the cone scales. I believe that *P. durangensis* as well as *P. engelmannii*, No. 71, and *P. cooperi*, No. 69—located between the areas of *P. ponderosa* on the north and *P. montezumae* on the south—do not belong to either of the two complexes, but rather are independent species. The chemical composition of *P. durangensis* turpentine seems to support this belief.

A batch of oleoresin of *Pinus durangensis* (received from Señor Blanco) was distilled under reduced pressure. At the end of the distillation, the pot temperature was 180° C. and pressure was 2 mm. Based on the trash-free weight of the oleoresin, 25 percent of turpentine was obtained.

Physical characteristics of the turpentine of *Pinus durangensis* were:

Density, $d_4^{20} = 0.8566$
 Index of refraction, $n_D^{20} = 1.4702$
 Specific rotation, $[\alpha]_D^{20} = +15.4^\circ$

The turpentine was estimated to contain:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	71
<i>l</i> - β -pinene.....	19
<i>d</i> -cadinene.....	3
Unidentified components, residue and losses.....	7

67. *Pinus hartwegii* Lindl.

References (74, 77)

(Bot. Reg. 25. Misc. 1839)

Pinus hartwegii is a Mexican pine which is placed by Shaw (142) under the name of *P. montezumae*. Standley (154) and Martínez (88), however, consider it as an independent species. It grows in the State of Mexico and adjacent States and also has been reported from Veracruz, Oaxaca, and Chiapas. It grows at higher elevations than any other pine of the world, being found in its upper limit near the line of permanent snow, higher than 13,100 feet (4,000 meters). On the slopes of the two famous Mexican volcanoes, Popocatepetl and Ixtaccihuatl, *P. hartwegii* forms pure stands at elevations ranging from 8,400 feet to 11,500 feet.

Turpentine of *Pinus hartwegii* was previously investigated by Iriarte (77). The source of the oleoresin was Rio Frio in the Valle de Mexico on the slope of the volcano Popocatepetl. The turpentine yield, obtained by steam distillation of oleoresin, was 27.7 percent. Physical characteristics of the turpentine were:

Density, $d_4^{20} = 0.8637$
 Index of refraction, $n_D^{20} = 1.4653$
 Specific rotation, $[\alpha]_D^{20} = +2.5^\circ$

The turpentine was fractionated in a 15-cm. column and contained at least 65 percent of *d,dl*- α -pinene, and a small amount of *l*-limonene.

A sample of oleoresin analyzed in our laboratory had been collected by Jesse P. Perry, Jr., of the Rockefeller Foundation, Mexico City, in a pure stand of *Pinus hartwegii* near timberline on the slopes of Popocatepetl. The oleoresin was heated under reduced pressure; at the end of distillation the temperature reached 180° C. and pressure was 0.5 mm. By this means 29.7 percent turpentine was obtained. The turpentine possessed the following characteristics:

Density, $d_4^{20} = 0.8480$
 Index of refraction, $n_D^{20} = 1.4705$
 Specific rotation, $[\alpha]_D^{20} = -48.7^\circ$

Composition of the turpentine was:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	28
β -myrcene.....	1
<i>d</i> - Δ^3 -carene.....	5
<i>l</i> -limonene.....	56
Methyl chavicol.....	3
<i>d</i> -longifolene.....	1-2

The chemical composition of turpentine of *Pinus hartwegii* is so different from that of *P. montezumae* (No. 65) that I am inclined to agree with Martínez and Standley in considering *P. hartwegii* an independent species.

68. *Pinus rudis* Endl.

Reference (74)

(Syn. Conifer. 151. 1847)

Pinus rudis, in the classification of Shaw (142), is called *P. montezumae*. Martínez (88), however, considers it to be a separate species. I have observed this pine in Mexico and am inclined to accept its specific rank. *P. rudis* and *P. montezumae* are related and apparently they hybridize naturally; both species and many intermediate forms are often found in the same locality. *P. rudis* grows over a large territory from Coahuila and Tamaulipas to Michoacán and farther east to Puebla, Oaxaca, and apparently to Chiapas. It extends even farther south and has been reported (139) as growing in the mountains of Guatemala, adjacent to the Mexican State of Chiapas.

The oleoresin sample of this pine was collected for us by Jesse P. Perry, Jr., Rockefeller Foundation, Mexico City, along the Texcoco-Veracruz Highway, on the border between the States of Mexico and Tlaxcala.

A batch of oleoresin was distilled under reduced pressure; at the end of distillation, the temperature was 183° C. and the pressure was 0.5 mm. of mercury. The turpentine obtained in this manner amounted to 22.7 percent of the weight of the oleoresin.

The turpentine of *Pinus rudis* had the following physical characteristics:

Density, $d_4^{20} = 0.8627$
 Index of refraction, $n_D^{20} = 1.4734$
 Specific rotation, $[\alpha]_D^{20} = -11.1^\circ$

It consisted of:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	32
<i>l</i> - β -pinene.....	62
Dipentene.....	1
Higher boiling substances.....	1

69. *Pinus cooperi* Blanco

Reference (70)

(Annal. Inst. Biol. 20: 185-7, Mexico. 1949)

Pinus cooperi is a newly discovered pine. It was originally described by Blanco in 1940 as *P. lutea*, probably because it is known as pino amarillo, that is yellow pine (88). As the name *P. lutea* had been given in 1788 to loblolly pine (No. 61), Blanco (26) decided in 1949 on the suggestion of Dr. Elbert L. Little, Jr., to change its name from *P. lutea* to *P. cooperi*. Martinez (88) places this pine near *P. rudis* (No. 68).

Pinus cooperi grows in the mountain ranges of Durango, Mex. At El Salto, Durango, it occurs at elevations of 8,200 to 9,000 feet. In the same locality grows a variety of this pine (*P. cooperi* var. *ornelasi*) characterized by coarser bark, longer needles, larger cones, and whiter wood than *P. cooperi* proper. Local people also distinguish these two pines and call the *ornelasi* variety not pino amarillo, but albacarroto.

Oleoresin of *Pinus cooperi* was collected at El Salto, Durango, Mex., under the supervision of Sr. Cenobio E. Blanco. Turpentine was distilled under reduced pressure. At the end of distillation, the pressure was 4 mm. and the temperature was 180° C. Yield of turpentine was 25 percent.

The crude turpentine of *Pinus cooperi* had the following physical characteristics:

Density, $d_4^{20} = 1.4705$
 Index of refraction, $n_D^{20} = 0.8580$
 Specific rotation, $[\alpha]_{D,20}^{20} = +2.9^\circ$

Its composition was:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	56
<i>l</i> - β -pinene.....	39-40
Pot residue, boiling above 161° C. at 759 mm. (not investigated).....	4.2

70. *Pinus michoacana* Martinez

Reference (76)

(Annal. Inst. Biol. 14: 1, Mexico. 1944)

Pinus michoacana is a part of that complex which Shaw (142) designated in 1914 as *P. montezumae*. *P. michoacana* was described by Martinez in 1944. This species includes two varieties and two forms. Its typical form occurs in Michoacán, Jalisco, Oaxaca (88). In Michoacán it can be found growing together with *P. montezumae*; possibly these two pines intercross.

A sample of oleoresin of this pine was sent to us in 1954 from Mexico by M. Louis Hugnet, a French forester of the Food and Agriculture Organization of the United Nations. The turpentine was distilled from the oleoresin under reduced pressure; at the end of distillation, the pressure was 5 mm. and temperature was 190° C. Yield of turpentine was 30 percent of the weight of oleoresin. The turpentine possessed the following physical characteristics:

Density, $d_4^{20} = 0.8657$
 Index of refraction, $n_D^{20} = 1.4760$
 Specific rotation, $[\alpha]_{D,20}^{20} = -8.4^\circ$

It contained:

Compound:	Percent
<i>d,dl-α-pinene</i>	29
<i>l-β-pinene</i>	60
<i>l,dl-limonene</i>	1-2
Methyl chavicol.....	2-3
<i>d-longifolene</i>	3

71. *Pinus engelmannii* Carr.

Reference (109)

(Wisliz., Mem. Tour North Mex. 103. 1848)

Pinus engelmannii is also known as *P. mayriana* Sudw., *P. latifolia* Sarg., *P. macrophylla* Engelm., and *P. apachea* Lemm. All these names indicate that this pine is believed by some botanists to be a valid species. Others, like Shaw (142), consider that all these names are mere synonyms of *P. ponderosa*, No. 54. In the United States, this pine has the common name Apache pine.

Pinus engelmannii grows in southern Arizona and in southwestern and north-central New Mexico. It extends into northern Mexico.

The oleoresin used in the investigation reported here was collected in the southern fork of Cave Creek Canyon, Chiricahua Mountains, Coronado National Forest in southeastern Arizona, at an elevation of 5,200 feet. The turpentine was obtained by heating a batch of oleoresin under reduced pressure; at the end of the distillation, the pressure was 0.1 mm. and the pot temperature reached 210° C. The yield of turpentine was 22.5 percent.

The gum turpentine of *Pinus engelmannii* had the following physical characteristics:

Density, d_4^{20} = 0.8648
 Index of refraction, n_D^{20} = 1.4695
 Specific rotation, $[\alpha]_D^{20}$ = +42.0°

It contained:

Compound:	Percent
<i>d,dl-α-pinene</i>	80
<i>l-β-pinene</i>	2
Dipentene.....	2
<i>α-longifolene</i>	12
An unidentified solid component, apparently a sesquiterpene alcohol, a trace	--

The apparent sesquiterpene alcohol distilled at a temperature slightly above 121° C. at 14 mm. of pressure; it solidified in the condenser, forming white crystals. After several resublimations, the crystals melted at 103° to 105°. An analysis showed the crystals were 81.49 percent carbon and 11.48 percent hydrogen. Calculated for a sesquiterpene alcohol $C_{15}H_{26}O$, the composition would be C, 80.98 percent; H, 11.78 percent.

72. *Pinus pseudostrobus* Lindl.

Reference (77)

(Bot. Reg. 25. Misc. 63. 1839)

Pinus pseudostrobus is a pine of subtropical regions of Mexico and Central America. In Mexico it grows from Jalisco to Chiapas. In Central America it occurs in Guatemala and Honduras. It is an extremely variable, complex species. Martínez (88) distinguishes, besides the typical *P. pseudostrobus*, several varieties of this species. Possibly the different varieties of *P. pseudostrobus* intercross. This

situation makes identification of pines of the *Pseudostrobus* complex extremely difficult.

Pinus pseudostrabus var. *oaxacana* of Martínez is considered to rank as a species (105), and the composition of its turpentine has been already discussed in this publication, under No. 36, p. 67.

Iriarte (77) in 1946 reported on the composition of steam-distilled turpentine of *Pinus pseudostrabus* (typical form) from Uruapan, Michoacán. The yield was 21.3 percent of the weight of the oleoresin, and the physical constants of the turpentine were:

Density, $d_{25}^{25} = 0.8672$
 Index of refraction, $n_D^{25} = 1.4624$
 Specific rotation, $[\alpha]_D^{25} = +31.5^\circ$

The turpentine was fractionated under a pressure of 23 mm., more than 90 percent distilling between 55° and 57° C. This fraction had specific rotation $[\alpha]_D = -34.5^\circ$ and consisted of *l*- α -pinene. Its nitrosochloride had a melting point of 102° to 103° . The flask residue was also dextrorotatory, $[\alpha]_D = +10^\circ$.

The oleoresin used in the work reported here also came from Uruapan, Michoacán, Mex., courtesy of M. Louis Huguet, a forester for the United Nations Food and Agricultural Organization in Mexico. Upon receipt at Berkeley, Calif., the oleoresin was heated under reduced pressure. When all the turpentine had been expelled, the pressure was 1 mm. and the temperature was 210° C. Yield of turpentine was 19 percent of the oleoresin. The turpentine possessed the following physical characteristics.

Density, $d_{25}^{25} = 0.8581$
 Index of refraction, $n_D^{25} = 1.4720$
 Specific rotation, $[\alpha]_D^{25} = -16.67^\circ$

No further work has been done with this sample of turpentine, because of an accident. The data presented above seem to indicate that *Pinus pseudostrabus* did not contain any low-boiling components, such as *n*-heptane (cf. *P. oaxacana*, No. 36, p. 67.)

73. *Pinus tenuifolia* Benth.

Reference (106)

(Pl. Hartw. 92. 1839)

Pinus tenuifolia is a pine of the subtropical regions of Mexico. It grows in the States of Jalisco, Michoacán, Sinaloa, and Guerrero. It also grows in Oaxaca and Chiapas and in the adjacent parts of Guatemala. *P. tenuifolia* is closely related to *P. pseudostrabus*; Shaw (142) considered it a variety of *P. pseudostrabus*.

A sample of oleoresin was collected for us in Michoacán by M. Louis Huguet, forester for the Food and Agriculture Organization, United Nations. The turpentine was obtained under reduced pressure; at the end of the distillation, temperature reached 180° C. and the pressure was reduced to 2 mm. The yield of the turpentine was 27.1 percent.

The turpentine had the following characteristics:

Density, $d_{25}^{25} = 0.8600$
 Index of refraction, $n_D^{25} = 1.4672$
 Specific rotation, $[\alpha]_D^{25} = +25.0^\circ$

Its composition was:

Compound:	Percent
<i>d</i> - α -pinene.....	77
<i>l</i> - β -pinene.....	6-7
<i>d</i> - Δ^2 -carene.....	8
Terpinolene.....	1-2
Dipentene, indicated by physical constants, but not identified by preparation of crystalline derivatives.....	3
Linalool, approx.....	1
Methyl chavicol (possibly), less than.....	1
Sesquiterpenes.....	1

74. *Pinus occidentalis* Swartz

(Nov. Gen. & Sp. Pl. 103. 1788)

Pinus occidentalis is a pine confined to San Domingo, Haiti, and eastern Cuba. It is one of the few pines whose turpentine has not been analyzed. *P. cubensis* Griseb. is considered by Shaw (142) as a synonym of *P. occidentalis*. Possibly it is an independent species.

75. *Pinus glabra* Walt.

Reference (115)

(Fl. Carol. 237. 1788)

Pinus glabra is the spruce pine of the Southeastern United States. Its range lies in the coastal plains of South Carolina, northern Florida, and west to southeastern Louisiana. In South Carolina it is called king's tree; in Florida, poor pine, which shows the inconsistency of common names. Spruce pine attains its largest size—up to 120 feet in height—in northwestern Florida.

Oleoresin was collected by John K. Gross, U.S. Forest Service, from five trees growing in the DeSoto National Forest, Perry County, Miss. A 3,500-g. batch was distilled under reduced pressure. Toward the end of distillation, the temperature of the oleoresin was 150° C. and pressure was 0.05 mm. The yield of turpentine was 22.3 percent.

The turpentine possessed these characteristics:

Density, d_{20}^{20} = 0.8599
 Index of refraction, n_D^{20} = 1.4735
 Specific rotation, $[\alpha]_D^{20}$ = -4.65°

The turpentine contained:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	45
<i>l</i> - β -pinene.....	45
<i>l</i> -limonene.....	8
A sesquiterpene, whose hydrochloride had a melting point of 48° to 49° C., less than.....	1

Group Insignes

76. *Pinus pringlei* Shaw

Reference (77)

(In Sargent, Trees & Shrubs. 1,211. Pl. 100. 1905)

Pinus pringlei is a subtropical Mexican pine growing in the States of Michoacán, Mexico, Guerrero, and Oaxaca, at altitudes of 5,750 to 6,600 feet. According to Martínez (88), it is closely related to *P. occarpa*.

A sample of oleoresin of *Pinus pringlei* was sent to us from Uruapan, Michoacán, through the courtesy of M. Louis Huguet, forester of the United Nations Food and Agriculture Organization. A batch of 2,989 g. was heated under reduced pressure; at the end of distillation,

the temperature reached 190° C. and the pressure was 2 mm. The yield of turpentine was 19.7 percent.

Crude turpentine of *Pinus pringlei* had the following characteristics:

Density, d_4^{20} = 0.8642
 Index of refraction, n_D^{20} = 1.4721
 Specific rotation, $[\alpha]_D^{20}$ = +39.5°

It contained:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	73
<i>l</i> - β -pinene.....	2
<i>d</i> - Δ^3 -carene.....	11
Terpinolene.....	1
Methyl chavicol.....	2.5
<i>d</i> -longifolene.....	6

Physical characteristics of terpinolene are shown in table 35; the melting point of terpinolene hydrochloride was 115° to 116° C. Slight optical activity (+2.6°) of the terpinolene fraction was probably caused by slight admixture of *d*- Δ^3 -carene.

TABLE 35.—*Fraction of Pinus pringlei* turpentine in which terpinolene was found

Property	Fraction in which terpinolene was found	Terpinolene ¹
Boiling point.....	72°-78° C. (15 mm.)	185° C. (760 mm.)
Index of refraction, n_D	1.4871 ²³	1.4864 ²⁵
Density, d_4860 ²³	.8560 ²⁵
Specific rotation, $[\alpha]_{D58}$	+2.6°	.0

¹ Sutherland, M. D. Queensland Univ. Papers, Dept. Chem. 1, 34. 1948.

77. *Pinus oocarpa* Schiede

References (71, 99)

(Linnaea 12: 491. 1838)

Pinus oocarpa is a variable, generally five-needled pine of Mexico and Central America. Besides its typical form, four varieties are recorded (88):

1. *microphylla*, possessing very short fine foliage;
2. *manzanoti*, which has asymmetrical cones with very short peduncules;
3. *trifoliata*, characterized by three needles in a fascicle;
4. *ocholerenai*, distinguished by its slender cones, which are not as heavy as those of the typical form.

We have investigated turpentine composition of *Pinus oocarpa* (typical form) and *P. oocarpa* var. *trifoliata*, No. 78. Oleoresin samples of *P. oocarpa* (typical form) were collected by the author in the States of Chiapas and Michoacán, Mex. The Chiapas turpentine was separated from the oleoresin under reduced pressure; at the end of distillation, temperature was 190° C. and the pressure was 4 mm. Yield of the turpentine was 22 percent of the weight of the oleoresin. The physical characteristics of the turpentine were:

Density, d_4^{20} = 0.8562
 Index of refraction, n_D^{20} = 1.4684
 Specific rotation, $[\alpha]_D^{20}$ = +25.4°

Composition of the turpentine was:

Compound:	Percent
<i>d,dl-α-pinene</i>	68
<i>l,dl-limonene</i>	22
<i>d-longifolene</i>	7

The Michoacán sample of *P. oocarpa* oleoresin was heated *in vacuo*; at the end of the distillation, temperature was 165° C. and pressure was 0.5 mm. Yield of the turpentine was 24.8 percent; it possessed the following physical characteristics:

Density, $d_4^{20} = 0.8569$
 Index of refraction, $n_D^{20} = 1.4656$
 Specific rotation, $[\alpha]_{578}^{20} = +47.5^\circ$

The turpentine contained *d-α-pinene*, 97 to 98 percent.

78. *Pinus oocarpa* var. *trifoliata* Martinez Reference (71)

(Annal. Inst. Biol. 17, 297. 1945)

This pine differs from typical *Pinus oocarpa* Schiede by having three needles in each bundle instead of five. The three-needled form apparently occurs only in the mountains of the State of Durango, where it grows in pure stands. It was discovered by Cenobio E. Blanco and described by Martinez.

The oleoresin of this pine came from Sr. Blanco. It was distilled under reduced pressure; at the end of the operation, temperature reached 170° C. and the pressure was reduced to 0.2 mm. The yield of turpentine was 23.0 percent. The turpentine possessed the following physical characteristics:

Density, $d_4^{20} = 0.8588$
 Index of refraction, $n_D^{20} = 1.4682$
 Specific rotation, $[\alpha]_{578}^{20} = +39.8^\circ$

Its composition was:

Compound:	Percent
<i>d,dl-α-pinene</i>	87
Unidentified terpenes.....	5
<i>d-longifolene</i>	4.5

A fraction with these characteristics—density, $d_4^{25} = 0.8524$; index of refraction, $n_D^{25} = 1.4693$; specific rotation, $[\alpha]_{578}^{25} = -19.0^\circ$ —was re-fractionated in a 12-inch glass helix-packed column. The boiling range of 155° to 170° C. at 760 mm. and other physical characteristics of the refraction indicated that it contained *α-pinene* and some higher boiling terpene, possible Δ^1 -carene. No nitrosate was formed when an attempt was made to identify Δ^3 -carene in this fraction.

The fraction characterized by density, $d_4^{25} = 0.8548$; index of refraction, $n_D^{25} = 1.4806$; specific rotation, $[\alpha]_{578}^{25} = -11.7^\circ$ —when re-distilled over sodium, boiled at 180° to 185°, and its index of refraction, n_D^{25} , was 1.4799. A bromide was prepared by adding bromine to an alcohol-ether solution of this fraction. After two recrystallizations from alcohol, the bromide melted at 113° to 113.5° C. On admixture with terpinolene tetrabromide, the melting point was depressed below 108°.

79. *Pinus halepensis* Miller References (97, 84, 110, 162)

(Gard. Diet. Ed. 8. 1768)

Pinus halepensis grows in parts of southern Europe, Asia Minor,

and northern Africa, adjacent to the Mediterranean Sea. It crosses naturally with *P. brutia*, No. 80, (122).

Veze and Dupont (162) investigated turpentine of *Pinus halepensis* obtained from Provence, France. The yield was 26.98 percent from the first gathering of the oleoresin and 20.7 from the fourth gathering: in other words, it decreased somewhat with the advance of the summer. The physical constants were:

Density, $d_{25}^{25} = 0.8550$ to 0.8580
Optical rotation, $\alpha_D = +41.92^\circ$ to $+41.29^\circ$.

The composition was reported as *d*- α -pinene, 95 percent; higher boiling fractions, 5 percent. Later, Dupont (37) investigated the higher boiling fractions (tailings). These fractions contained bornyl acetate, 1.14 percent of the total oil, and a monocyclic sesquiterpene having two double bonds, 3.8 percent. The physical constants of the sesquiterpene were as follows:

Density, $d_{20}^{20} = 0.9056$
Index of refraction, $n_D^{20} = 1.4977$
Optical rotation, $\alpha_D = -7.24^\circ$
Molecular refraction, $MR_D = 66.02$ (calculated, 66.14)

Laerué (84) analyzed many samples of *Pinus halepensis* turpentine from several localities in Spain and compared these with samples obtained in Algeria, Italy, and Greece. Physical characteristics of these samples were:

Density, $d_{11}^{11} = 0.8561$ to 0.8590
Index of refraction, $n_D^{11} = 1.4661$ to 1.4669
Specific rotation, $[\alpha]_D^{11} = +42.83$ to $+48.52^\circ$

Thus, all samples of *P. halepensis* turpentine collected in different localities were dextrorotatory, and their specific rotation varied in rather narrow limits from $+42.83^\circ$ to $+48.52^\circ$. Laerué stated that the older data, giving specific rotation values for this pine of -8.73 , $+2.84$, $+1.61$, and $+0.28$, were incorrect, because they referred to commercial mixtures of dextrorotatory turpentine of *P. halepensis* and levorotatory turpentine of *P. nigra*.

In 1955, *Pinus halepensis* turpentine was analyzed in our laboratory (110). The oleoresin was obtained through the courtesy of Dr. D. Y. Goor, Conservator of Forests, State of Israel. The oleoresin was collected in the summer of 1953 in Israel on the slopes of Mt. Carmel.

The oleoresin was distilled under reduced pressure; at the end of the distillation, the pot temperature was 180°C . and the pressure was 0.1 mm. Yield of the turpentine was 20 percent of the weight of the oleoresin.

The turpentine possessed the following physical characteristics:

Density, $d_{15}^{15} = 0.8575$
Index of refraction, $n_D^{15} = 1.4658$
Specific rotation, $[\alpha]_D^{15} = +41.25^\circ$

It contained:

Compound:	Percent
<i>d,d</i> - α -pinene.....	87
β -myrcene.....	2
Sesquiterpenes.....	4

80. *Pinus brutia* Ten.

References (2, 3, 110)

(Cat. Hort. Neap. Appx. 1, 75. 1815)

Pinus brutia has a more restricted range than *P. halepensis*, No. 79. It grows in the Italian province of Calabria (ancient Brutium),³² in Syria, Turkey, Greece, and on the islands of Chios, Rhodes, Crete, and Cyprus. Some botanists consider *P. brutia* as a variety of *P. halepensis* (28); others believe that the two names are synonyms (142). *P. brutia* is immune to *Matsucoccus* infestation, while *P. halepensis* is susceptible to the attacks of this scale insect. *P. brutia* crosses naturally with *P. halepensis* (122).

Very little had been known about the chemical composition of *Pinus brutia* turpentine. An anonymous author (2, 3) described commercial turpentine obtained from "*P. halepensis*" from Cyprus (that is, of *P. brutia*, because *P. halepensis* does not occur on that island). The turpentine was found to be levorotatory (-20.2 ; -32.5). Only α -pinene was identified; it amounted to 55 percent of the total turpentine. Fractions boiling above 160° C. were not investigated.

A sample of *Pinus brutia* oleoresin came to us through the courtesy of Mr. D. F. Davidson, Conservator of Forests, Government of Cyprus. It was collected in the Dhiorios Forest, Cyprus. The oleoresin was distilled under the same conditions as that of *P. halepensis*. The yield of turpentine was 20 percent.

The crude turpentine had the following physical characteristics:

Density, $d_4^{20} = 0.8571$
 Index of refraction, $n_D^{20} = 1.4612$
 Specific rotation, $[\alpha]_D^{20} = -28.7^{\circ}$

It was composed of:

Compound:	Percent
<i>l,l</i> - α -pinene	62
β -pinene	17
Δ^2 -carene	13
Terpinolene (see table 36)	2
Sesquiterpenes	4.6

The chemical composition of the turpentine of *Pinus brutia* differs so much from that of *P. halepensis* that I am inclined to consider the two pines as separate species.

TABLE 36.—Physical properties of terpinolene and of fraction 14 of *Pinus brutia* turpentine

Property	Fraction 14	Terpinolene ¹
Density, d_4^{20}	0.8600 ²³	0.8560 ²⁵
Index of refraction, n_D^{20}	1.4351 ²²	1.4864 ²⁵
Specific rotation, $[\alpha]_D^{20}$0 ²⁴	.0 ²⁵

¹ Sutherland, M. D. Queensland Univ. Papers, Dept. Chem. 1, 34. 1948.

³² It is not certain whether *Pinus brutia* is native in Calabria or was planted there a long time ago.

81. *Pinus pityusa* Steven

Reference (9)

(Bul. Soc. Nat. Mose 11: 49. 1838)

Pinus pityusa was described in 1838 from near Pitsunda (ancient Pityum) on the east coast of the Black Sea. Later, this pine was found on the island of Prinkipo near Istanbul, in Thraee, in Anatolia, and in Syria. Apparently, the pine growing on the island Thasos, near the coast of eastern Thraee, is also *P. pityusa* (122).

Shaw (142) considered this pine to be *Pinus halepensis*. It is very closely related to *P. brutia*. Turpentine of this pine was analyzed by Arbuzov and his coworkers (9). The only physical constant of the crude turpentine given was $[\alpha]_D$, which was -5.33° . They reported the composition of the turpentine to be:

Compound:	Percent
<i>l</i> - α -pinene	69.8
<i>d</i> - Δ^1 -carene	23.6
An unidentified component boiling at 73° to 78° C. at 14.5 mm.	1.0
Unidentified higher boiling fractions	5.0

Arbuzov's technique of obtaining the turpentine was rather unusual and interesting: the crystallized part of the oleoresin was separated from the uncrystallized part by means of a Buchner funnel; the remaining turpentine was removed from the crystalline part by steam distillation; the noncrystalline part was also steam distilled. The results were as follows:

	Percent
Turpentine	33.67
Crystalline rosin acids	35.89
Noncrystalline, nonvolatile with steam	30.00

82. *Pinus pinaster* Ait.

References (38, 39, 40, 46, 49, 52, 117)

(Hort. Kew 3: 367. 1789)

Pinus pinaster (or *P. maritima*) is called French maritime pine. Its area extends from southwestern France and Portugal through Spain, Italy, and the Dalmatian coast of Yugoslavia to Greece. It also grows in a few places in Morocco and Algeria. Because this pine is extensively planted in France for obtaining oleoresin, the chemistry of its turpentine has been well studied. Dupont (40) determined the composition of *P. pinaster* turpentine both by applying Darinois' method³³ of estimating its composition by the optical rotation of different fractions and by conventional methods of chemical analysis (38).

The composition of *Pinus pinaster* turpentine was:

Compound:	Percent
<i>l</i> - α -pinene	63
<i>l</i> - β -pinene	26.5
Tails	10.5

³³ Darinois, optical method of determining percentage of α -pinene and β -pinene in a turpentine is based on the Biot relationship:

$$X_1 = \frac{\alpha_0 - \alpha_2}{\alpha_1 - \alpha_2}$$

for any given fraction containing the two terpenes.

X_1 = the proportion of α -pinene

α_0 = observed optical rotation of the fraction

α_1 = rotation of pure α -pinene

α_2 = rotation of β -pinene

This method is used only when the bulk of the turpentine consists of two components, such as in French maritime pine—for details see Palkin (121).

Dupont added an important note to the data, stating that the tails do not represent entirely the products of post-distillation oxidation of the main fractions, but that some oxygen-containing substances may be present in small amounts as such in the crude turpentine.

In a later paper Dupont (39) reported on the composition of the tails of *Pinus pinaster* turpentine. The tails contained: a dextrorotatory sesquiterpene, which yielded a nitrosite ("belles aiguilles bleues") with melting point of 109° to 110° C. Besides the sesquiterpene, there were some oxygenated compounds: pinol and pinol hydrate, a ketone, some terpenes, chiefly dipentene, and an unidentified dextrorotatory monocyclic terpene with two double bonds. In 1927 Dupont and Barraud (46) inquired into the nature of the dextrorotatory terpene. It proved to be *d, dl*-limonene.

In 1948 Dupont, Dulou, and Naffa (52) reported that the sesquiterpene fraction of the *Pinus pinaster* turpentine contained two sesquiterpenes: caryophyllene, melting point of its dihydrochloride being 69° to 70° C., and longifolene, melting point of monohydrochloride, 59° to 60°. These two sesquiterpenes made up 87 percent of the total sesquiterpene fraction. In 1949, Naffa (117) reported that besides caryophyllene and longifolene, the sesquiterpene fraction of *P. pinaster* turpentine contained: (1) a mixture of a tricyclic sesquiterpene, isomeric with copaene, and a tricyclic hydrocarbon related to azulene; these two amounted to 10 percent of the sesquiterpene fraction; and (2) cadinene, which amounted to 3 percent of the fraction, together with a little cadinol.

Dupont and Soum (49) analyzed commercial turpentine of *Pinus pinaster* from near Avila, Spain (about 4,000 to 4,600 feet of altitude). The physical constants of the turpentine were:

Density, d_4^{20} 0.8705
 Index of refraction, n_D^{20} 1.4723
 Optical rotation, $[\alpha]_D^{20}$ +29.26°

The turpentine consisted of:

Compound:	Percent
<i>l</i> - α -pinene.....	79
An unidentified terpene, very small amounts.....	
<i>l</i> - β -pinene.....	10.73
Tails, (which as a whole had a much simpler composition than the tails of the above described French turpentine), about.....	10

The chief component of the tails was a sesquiterpene. The sesquiterpene was colorless, had a boiling point of 258° C. at 760 mm., and possessed the following physical characteristics:

Density, d_4^{20} 0.8704
 Specific rotation, $[\alpha]_D^{20}$ +28.25°
 No index of refraction was reported

When one drop of concentrated sulfuric acid was added to the sesquiterpene diluted with acetic acid, an intense rose color developed which, appropriately enough, changed to "Bordeaux red." No crystalline derivatives of this sesquiterpene were obtained. Dupont and Soum suggested that the sesquiterpene was different from that found previously in French turpentine.

83. *Pinus virginiana* Mill.

Reference (116)

(Gard. Dict. Ed. 8, Pinus No. 9. 1768)

Pinus virginiana, called both Virginia pine and scrub pine, grows in eastern United States from New Jersey and southeastern Virginia to Florida. Recently this pine attracted the attention of naval stores producers by a report of Hepting (65) who found that a fungus of the genus *Fusarium* caused an excessive flow of oleoresin but did not change oleoresin composition. Experiments have been conducted in inoculating healthy pines with the fungus in order to increase the flow of gum. Apparently these experiments were not conclusive.

Oleoresin used in the present tests was received from Dr. Hepting, from Asheville, N.C. The oleoresin represented a mixed sample obtained from nine trees inoculated with the fungus and from two untreated trees. Upon distillation under reduced pressure, 23 percent of turpentine was obtained, with the following characteristics:

Density, $d_4^{20} = 0.8563$
 Index of refraction, $n_D^{20} = 1.4657$
 Specific rotation, $[\alpha]_D^{20} = -3.83^\circ$

The turpentine consisted of α -pinene, 98 percent.

84. *Pinus clausa* (Chapm.) Vasey

Reference (137)

(Gard. Monthly and Hort. 18: 151. 1876)

Pinus clausa, commonly called sand pine, is a native of Florida. Westward it extends to extreme southern Alabama. Its turpentine was analyzed by Schorger in 1915 (137).

The yield of turpentine was 18.93 percent. Two samples of the turpentine had the following properties:

Density, $d_4^{20} = 0.8723$ and 0.8725
 Index of refraction, $n_D^{20} = 1.4767$ and 1.4768
 Observed rotation $\alpha_D^{20} = -22.80$ and -22.49°

Composition of the turpentine was:

Compound:	Percent
<i>l</i> - α -pinene.....	10
<i>l</i> -camphene.....	10
<i>l</i> - β -pinene.....	75

This is the only pine in which camphene is found in relatively large amounts.

85. *Pinus rigida* Mill.

Reference (98)

(Gard. Dict. Ed. 8 Pinus No. 10. 1768)

Pinus rigida Mill. is commonly known as pitch pine. Its range extends from New Brunswick and southern Ontario south to Georgia and Tennessee.

The oleoresin sample from pitch pine was collected in 1949 by Keith W. Doran near Asheville, N.C., and analyzed in our laboratory. The turpentine was obtained by heating the oleoresin under reduced pressure; at the end of distillation, the temperature of the oleoresin was 200° C., and pressure was 0.1 mm. Turpentine yield amounted to 23 percent of the weight of the oleoresin and possessed the following physical characteristics:

Density, $d_4^{20} = 0.8560$
 Index of refraction, $n_D^{20} = 1.4701$
 Specific rotation, $[\alpha]_D^{20} = -0.6^\circ$

The turpentine contained:

Compound:	Percent
<i>l</i> - α -pinene.....	65
<i>l</i> - β -pinene.....	20
<i>l</i> , <i>dl</i> -limonene.....	10

Sesquiterpenes apparently were not present.

86. *Pinus serotina* Michx.

Reference (106)

(Fl. Bor.-Amer. 2: 205. 1803)

Pinus serotina, or pond pine, sometimes is described as a subspecies (31) or a variety of *Pinus rigida*. Shaw (142) and Little (86) consider this pine an independent species. It grows on the coastal plains from southern New Jersey to central and northwestern Florida and Alabama.

Pinus serotina turpentine was analyzed in 1908 by Herty and Dixon (69). The steam-distilled turpentine had these physical characteristics:

Density, d_{20}^{20} = 0.8478
Index of refraction, n_D^{20} = 1.4734
Specific rotation, $[\alpha]_D^{20}$ = -105° 36'

The turpentine began to boil at 172° C. In the fraction boiling at 175° to 176°, Herty and Dixon identified *l*-limonene by preparation of tetrabromide. No other components were identified, although a small amount of sesquiterpenes was suspected. Herty and Dixon reported that 90 percent of the turpentine consisted of *l*-limonene.

In 1954 we received a sample of pond pine oleoresin from the Olustee Experimental Forest, northern Florida. The turpentine was obtained by heating the oleoresin under reduced pressure; at the end of the operation, the pot temperature reached 212° C. and the pressure was reduced to 2 mm. Yield of the turpentine was 19 percent of the weight of the oleoresin.

The physical characteristics of the turpentine were:

Density, d_{20}^{20} = 0.8437
Index of refraction, n_D^{20} = 1.4716
Specific rotation, $[\alpha]_D^{20}$ = -83.7°

During the fractionation of the turpentine, it was noticed that fraction 17 was extremely fragrant. There was a great deal of limonene in that fraction, but there was also apparently an admixture of an oxygenated compound. This fraction was redistilled to remove most of the limonene. The higher boiling part of the fraction (1.3 g.) was oxidized to homoanisic acid; we used the same procedure as for identification of methyl chavicol in *Pinus lumholtzii* turpentine (73). Recrystallized from hot *n*-hexane, the homoanisic acid possessed a melting point of 85° to 86° C. The homoanisic acid was further oxidized to anisic acid by the action of chromic anhydride. The acid, recrystallized from *n*-hexane, had a melting point of 183.7° to 184.6°. There was no change in melting point upon admixture of authentic anisic acid.

Turpentine of *Pinus serotina* contained:

Compound:	Percent
<i>l</i> - α -pinene.....	5
<i>l</i> -limonene.....	90
Methyl chavicol ¹	1
Unidentified sesquiterpene.....	2 or 3

¹ Thanks are due Dr. Gene Kritchevsky for identification of methyl chavicol.

87. *Pinus pungens* Lamb.

Reference (115)

(Ann. Bot. 2: 198. 1805)

Pinus pungens (Table-Mountain pine) is a tree which in the forest occasionally reaches 60 feet in height and 2 to 3 feet in diameter: when open-grown, it is rather scrubby—20 to 30 feet high, with a short, thick trunk. *P. pungens* grows on dry gravelly slopes and ridges of the Appalachian Mountains from southern Pennsylvania to North Carolina, eastern and middle Tennessee, and Georgia.

A sample of oleoresin from this species was collected for us by U.S. Forest Service personnel in Buncombe County, N.C., at an elevation of 2,400 feet. Unfortunately, some of the liquid part of the oleoresin was lost in transit, and thus the yield of turpentine was rather low—only 14.5 percent. The turpentine was separated from the oleoresin under reduced pressure; at the end of the distillation the temperature was 170° C. and pressure was 1 mm. The turpentine possessed the following characteristics:

Density, $d_{20}^{20} = 0.8564$
 Index of refraction, $n_D^{20} = 1.4682$
 Specific rotation, $[\alpha]_{D}^{20} = -23.7^\circ$

The turpentine consisted of:

Compound:	Percent
<i>dl,l</i> - α -pinene	70
<i>l</i> - β -pinene	20
<i>l</i> -limonene	8-9

The polymerized residue amounted only to 1 percent of the weight of the turpentine.

88. *Pinus banksiana* Lamb.

Reference (68)

(Deser. Gen. Pinus 1: 7 pl. 3. 1803)

Pinus banksiana, or jack pine, grows farther north than any other American pine. In the MacKenzie River Valley it occurs near the Arctic Circle. Its range extends from Nova Scotia and central Quebec, west to northern Saskatchewan and the Northwest Territory, south to central Alberta and southern Manitoba. It grows in North-eastern United States—in Minnesota, Wisconsin, Michigan, Maine, Vermont, New Hampshire, and in the northern parts of New York, Illinois, and Indiana. In Alberta it crosses naturally with *P. contorta*, No. 89 (104).

We obtained a sample of jack pine oleoresin through the courtesy of the U.S. Forest Service Lake States Forest Experiment Station, St. Paul, Minn. The oleoresin was collected from 35-year-old pines in the Chippewa National Forest, northern Minnesota, in the summer of 1946. All together, about 7,000 g. of oleoresin was obtained. The oleoresin was heated under reduced pressure; at the end of the distillation, when all turpentine had been expelled, the pot temperature was increased to 185° C. and the pressure was reduced to 0.5 mm. The yield of turpentine was 21 percent.

The turpentine had the following properties:

Density, $d_{20}^{20} = 0.8595$
 Index of refraction, $n_D^{20} = 1.4670$
 Specific rotation, $[\alpha]_{D}^{20} = +9.75^\circ$

The turpentine consisted of:

Compound:	Percent
<i>d,dl</i> - α -pinene.....	85
<i>l</i> - β -pinene.....	10
Residue and losses.....	5

Jack pine turpentine received from Nicolet National Forest, Wis., had a yield of 14.5 percent with the following characteristics:

Density, $d_4^{20} = 0.8555$
 Index of refraction, $n_D^{20} = 1.4674$
 Specific rotation, $[\alpha]_D^{20} = +2.2^\circ$

A sample from Ontario, Canada, had the following constants:

Density, $d_4^{20} = 0.8590$
 Index of refraction, $n_D^{20} = 1.4668$
 Specific rotation, $[\alpha]_D^{20} = -16.3^\circ$

The chemical composition of hybrids between *Pinus banksiana* and *P. contorta* is considered under *P. contorta*, No. 89.

89. *Pinus contorta* Dougl. References (136; unpub. orig. data)
 (Loud. Arb. Frut. Brit. 4: 2292. 1838)

Pinus contorta, commonly known as lodgepole pine, grows over a very wide range. It is found from Alaska and the Yukon Territory to Baja California, Mex., and from the Pacific coast to the Rocky Mountains, where it grows at elevations up to 11,000 feet above sea level. It also occurs in the Black Hills of South Dakota and in southwestern Saskatchewan.

Botanists distinguish between a coastal and an inland form of lodgepole pine. The Pacific coast form is designated as *Pinus contorta* proper, whereas the inland form, both of the Sierra Nevada of California and the American Rockies, is known as *P. contorta* var. *latifolia* Engelm., *P. contorta* var. *murrayana* (Grev. & Balf.) Engelm., or *P. murrayana* Grev. & Balf. A scrubby form of this pine grown on the Mendocino coast of California is called *P. contorta* var. *bolanderi*. In British Columbia the coastal form and the inland form merge, and farther north both have the name of *P. contorta*. In Alberta, *P. contorta* overlaps the area of *P. banksiana*, No. 88. The two pines intercross there, forming a rather confusing hybrid swarm (104).

Critchfield (32) studied variability of *Pinus contorta* throughout its range and concluded that this species can be divided into four subspecies: (1) *P. contorta contorta* of the Pacific coast, (2) *P. contorta bolanderi* found in only one locality, called White Plains, in Mendocino County, Calif., (3) *P. contorta murrayana* of the Sierra Nevada of California, and (4) *P. contorta latifolia* of the Rocky Mountains.

The chemical composition of *Pinus contorta* turpentine was first reported by Schorger in 1913 (136). The yield of turpentine was 14.7 percent of the weight of the oleoresin. Physical characteristics of the turpentine (obtained by steam distillation) were these:

	1910 sample	1911 sample
Density, d_4^{20}	0.8549	0.8518
Index of refraction, n_D^{20}	1.4860	1.4862
Specific rotation, $[\alpha]_D^{20}$		-20.12°

Upon analyzing the turpentine, Schorger concluded that it consisted almost entirely of *l*- β -phellandrene. No other terpenes were detected.

In 1948 I compared steam-distilled gum turpentines of the *contorta*, *murrayana*, and *bolanderi* varieties of *Pinus contorta* and found these to be very similar (table 37). In 1949 I collected a sample of oleoresin of var. *murrayana* from the same locality as shown in table 37. The turpentine was distilled by one of Dr. Hagen-Smit's students at California Institute of Technology (unpublished report).

The pressure at the end of the distillation was reduced to 2 mm. Yield of turpentine was 15 percent of the weight of the oleoresin, and the physical characteristics of the turpentine were as follows:

Density, $d_4^{20} = 0.8389$
 Index of refraction, $n_D^{20} = 1.4818$
 Specific rotation, $[\alpha]_D^{20} = -12.14^\circ$

The turpentine was reported to contain *l*- β -phellandrene.

Later, we made numerous analyses of *Pinus contorta* turpentine samples, but the results have not been published. The physical constants of some of these samples are given in table 38. All the samples listed in the table were obtained by heating the oleoresin under reduced pressure; at the end of the operation, the temperature reached 180° C. and the pressure was 1 mm. Under these conditions, the pot residue (i.e., the rosin) was hard and brittle, showing that almost all volatile ingredients of the oleoresin had been recovered.

All samples of *Pinus contorta* turpentine analyzed in our laboratory possessed about the same composition as reported by Schorger (136). The bulk of the turpentine consisted of *l*- β -phellandrene. The heads contained varying but generally very small amounts of *l*- α -pinene. In some samples α -pinene was completely lacking.

Pinus contorta oleoresin obtained from Lake Tahoe Valley, Calif., behaved somewhat differently. When distilled at 1 mm. pressure and a final temperature of 180° C., the 15-percent yield of turpentine had the usual *P. contorta* characteristics:

Density, $d_4^{20} = 0.8650$
 Index of refraction, $n_D^{20} = 1.4877$
 Specific rotation, $[\alpha]_D^{20} = -14.1^\circ$

The turpentine, however, consisted entirely of *l*- β -phellandrene, and the remaining pot residue (the rosin) was very soft.

When the temperature was increased to 200° C., or when the pressure was reduced to 0.5 mm., an additional 11 percent of oil was obtained. The oil had the consistency of castor oil, and part of it solidified in the condenser. This fraction of the volatile oil, which hardly could be called turpentine, was strongly dextrorotatory ($\alpha_D = +34.5$). The substance was apparently a mixture of a sesquiterpene-aldehyde and a sesquiterpene-ketone. No further work was done with it.

In Alberta, Canada, *Pinus contorta* crosses naturally with *P. banksiana* (No. 88). Turpentine composition of individual trees in that area was studied by Mirov (104). *P. contorta* turpentine contained only *l*- β -phellandrene. Neither α -pinene nor sesquiterpenes nor sesquiterpene derivatives were present. The turpentine of *P. banksiana* consisted of α -pinene with an admixture of β -pinene. Turpentine of the hybrids contained a mixture of α - and β -pinenes and *l*- β -phellandrene, the pinenes predominating. Morphology and composition of turpentine in the hybrids were not always correlated.

TABLE 37.—Characteristics of three varieties of *Pinus contorta turpentine* ¹

<i>Pinus contorta</i> variety	Locality	Initial boiling point at 28 mm.	Final boiling point at 28 mm.	Density d_4^{25}	Index of refraction n_D^{25}	Specific rotation $[\alpha]_D^{25}$
		° C.	° C.			Degrees
<i>Murrayana</i>	Sierra Nevada.....	73	76	0.8400	1.4804	-15.0
<i>Contorta</i>	California Coast.....	73	78	.8368	1.4802	-14.1
<i>Bolanderi</i>	do.....	75	77	.8358	1.4817	-16.1

¹ β -phellandrene was identified in all three varieties (unpublished data).

TABLE 38.—Physical constants and chemical composition of *Pinus contorta turpentine* samples from different localities

Locality	Yield of turpentine	Density d_4^{25}	Index of refraction n_D^{25}	Specific rotation $[\alpha]_D$	Components other than β -phellandrene ¹
	Percent			Degrees	
Minturn, Colo.....	18.6	0.8473	1.4801	-11.8	No sesquiterpene compounds; 3 to 4 percent <i>l</i> - α -pinene.
Kananaskis, Alberta, Sample No. 1.....	13.0	.8484	1.4798	-14.7	} No α -pinene and no sesquiterpene compounds.
Kananaskis, Alberta, Sample No. 2.....	12.5	.8489	1.4796	-15.9	
Kamloops, British Columbia.....	14.2	.8452	1.4828	-17.3	5 percent <i>l</i> - α -pinene.
New Zealand (planted trees).....	15.0	.8410	1.4819	-15.5	} No α -pinene; no sesquiterpene compounds.
New Zealand (planted trees).....	13.0	.8451	1.4817	-15.0	
Priest River, Idaho.....	11.0	.8514	1.4808	-19.1	

¹ This terpene formed the bulk of all samples.

To sum up, most of the analyzed samples of *Pinus contorta* turpentine consisted predominantly of *l*- α -phellandrene, some with a small admixture of *l*-pinene; turpentine of one variety (possibly Critchfield's *contorta murrayana*) was found to contain 15 percent of the usual *l*- β -phellandrene and about 11 percent of sesquiterpene-carbonyl compounds. Future work on these interesting compounds is desirable.

90. *Pinus greggii* Engelm.

Reference (*Unpub. orig. data*)

(Ex. Parlatore. DC. Prodr. 16-2, 396. 1868)

Pinus greggii occurs in the northeastern part of Mexico, namely, in southeastern Coahuila and in adjacent parts of Nuevo León and farther south in San Louis Potosí and in Hidalgo. Morphologically, it is closely related to *P. patula*, No. 91, but it can be distinguished by its shorter, coarser, erect, rather than drooping, needles.

A small sample of oleoresin of *Pinus greggii* came, through the courtesy of Professor Jose de la Puente, from near Saltillo, Coahuila. The turpentine was obtained by heating the oleoresin under reduced pressure; at the end of distillation, the pot temperature was 190° C. and the pressure was 1 mm. Yield of turpentine was 15.2 percent.

Physical characteristics of the turpentine were:

Density, d_4^{25} = 0.8650

Index of refraction, n_D^{25} = 1.4826

Specific rotation, $[\alpha]_{D^{25}}$ = -30.0°

A batch of 97 g. of the turpentine was subjected to fractional distillation in a 90 cm. Todd distilling column. The operation met with an accident and was not completed. Results of this partial fractional distillation are given in table 39.

TABLE 39.--Results of fractional distillation of *Pinus greggii* turpentine

Fractions	Boiling range ¹	Distillate	Density d_4^{25}	Index of refraction n_D^{25}	Specific rotation $[\alpha]_D$
	°C.	Percent			Degrees
1	153-155	2.56	0.8508	1.4645	-8.00
2	155-157	.71	.8522	1.4650	-----
3	157-160	1.02	.8564	1.4659	-----
4	160-165	2.15	.8584	1.4689	-9.82
5	165-166	1.02	.8544	1.4704	-----
6	166-168	1.33	.8505	1.4715	-11.40
7	168-169	2.05	.8502	1.4725	-13.00
8	169-170	1.43	.8538	1.4735	-14.66
9	170-171	1.74	.8517	1.4745	-16.50
10	171-172	4.92	.8582	1.4749	-20.66
11	172-173	13.94	.8438	1.4759	-25.66

¹ Pressure, 760 mm.

The three head fractions were composed of *l*- α -pinene. Fractions 4 to 8, inclusive, consisted mainly of *l*- β -pinene. The undistilled

residue, which possessed the consistency of a heavy syrup, amounted to 68.13 percent. It is possible that the syrupy residue contained *l*- β -phellandrene, together with *l*-limonene, and some sesquiterpenes. Turpentine of *Pinus greggii* should be reexamined.

91. *Pinus patula* Schl. & Cham. Reference (*Unpub. orig. data*)
(*Linnaea*, 6, 354)

Pinus patula is a Mexican pine of a rather limited distribution. It grows in the subtropical parts of the country at elevations ranging from 1,600 to 3,000 meters (about 5,250 to 9,800 feet) above sea level where the climate is cool and humid. This pine occurs in the States of Querétaro, Hidalgo, Mexico, Puebla, and Veracruz. It has been reported to grow in one locality in the State of Tamaulipas (66). It has been planted for ornamental purposes in the warmer parts of California.

Oleoresin for the present study was collected from 30-year-old planted trees growing at the Eddy Arboretum, Institute of Forest Genetics, Placerville, Calif. Yield of the turpentine, because of very hot and dry California summers and the nature of the volatile oil, was very small—only 15 percent of the weight of the oleoresin. When oleoresin was collected in air-tight containers, the yield of turpentine was 27 percent.

The turpentine was obtained by heating the oleoresin under reduced pressure; at the end of distillation, the pot temperature reached 212° C. and the pressure was reduced to 1 mm.

The turpentine possessed a sweet odor, suggesting not only the presence of phellandrene but also of some other sweet-smelling substances, perhaps oxygenated compounds.

Physical characteristics of the turpentine were these:

Density, $d_4^{20} = 0.8591$
Index of refraction, $n_D^{20} = 1.4885$
Specific rotation, $[\alpha]_D^{25} = -5.24^\circ$

The turpentine was fractionated in a 90-cm. Vigreux column, 20-cm. diameter, equipped with heated jacket. A reflux of 10:1 was maintained; the results and physical characteristics of the fractions are shown in table 40.

Physical properties of the fractions plotted according to Sutherland (157) suggested that the fractions boiling below 170° C. contained two main ingredients: *dl*- α -pinene and *l*- β -phellandrene (fig. 17). These two terpenes were duly identified by preparation of crystalline derivatives.

Pinene nitrosochloride (melting point 105° C.) was prepared from the material of fraction 1, and phellandrene nitrosite (melting point 102°) from the oil of fractions 10, 11, and 12. Tests for presence of limonene and Δ^3 -carene were negative.

When the distillation temperature reached 175° C., the oil remaining in the flask became polymerized to the consistency of castor oil. A 120 cc. measure of this partly polymerized flask residue was fractionated under reduced pressure in a 12-inch long, 1-inch diameter column, filled with glass helices. The results are given in table 41.

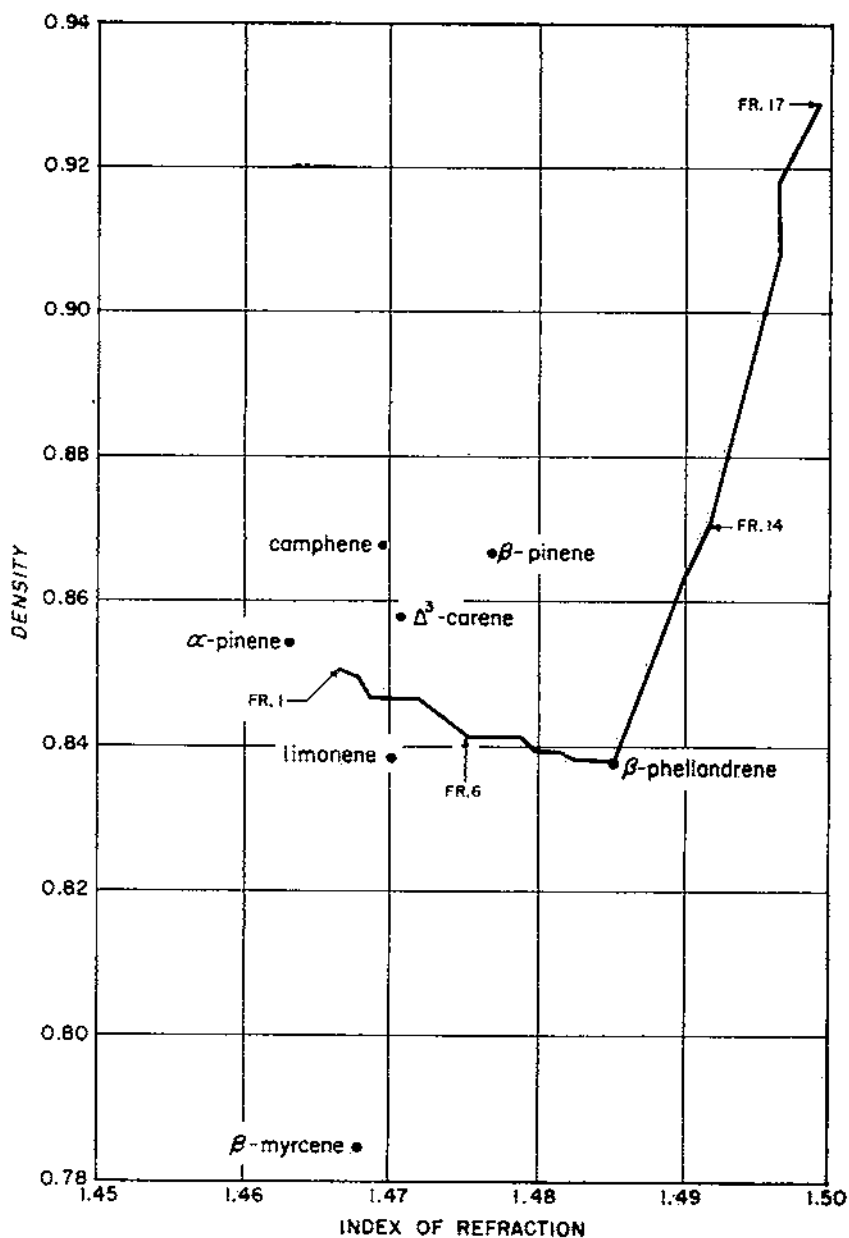


FIGURE 17.—Sutherland diagram of fractionated *Pinus patula* turpentine.

TABLE 40.—Fractional distillation of 200 g. of *Pinus patula* turpentine—pressure 762 mm.

Fractions	Pressure	Boiling range	Distillate	Density d_{20}^{20}	Index of refraction n_D^{20}	Specific rotation $[\alpha]_{D,20}^{20}$
	mm.	Degrees	Percent			Degrees
1	760	158-159	0.9	0.852	1.4665	-7.7
2	760	159-161	1.8	.851	1.4679	-10.1
3	760	161-162	2.8	.847	1.4690	-10.9
4	760	162-163	1.0	.847	1.4706	-13.9
5	760	163-164	2.4	.847	1.4721	-14.9
6	760	164-169	2.8	.843	1.4755	-15.7
7	760	169-171	5.3	.843	1.4779	-18.2
8	760	171-172	1.9	.841	1.4799	-17.5
9	760	172-173	1.8	.841	1.4814	-17.8
10	760	173-174	4.6	.840	1.4826	-18.3
11	760	174-175	12.0	.840	1.4841	-18.8
12	760	175-176	4.4	.840	1.4846	-18.0
13	2	54-66	13.0	.842	1.4861	-18.0
14	2	66-73	4.0	.876	1.4921	-17.0
15	2	73-78	2.0	.908	1.4965	-1.0
16	2	78-85	3.0	.917	1.4966	+15.4
17	2	85-90	4.5	.926	1.4989	+31.3
Pot residue ¹ and loss			31.8			

¹ After cooling, 63.6 g. of pot polymerized residue solidified into an amber-colored mass.

TABLE 41.—Fractional distillation of higher fractions of *Pinus patula* turpentine

Fractions	Pressure	Boiling range	Distillate	Density d_{20}^{20}	Index of refraction n_D^{20}	Specific rotation $[\alpha]_{D,20}^{20}$
	mm.	° C.	Percent			Degrees
1	2	54-66	21.8	0.8421	1.4861	-21.3
2	2	66-73	3.4	.8759	1.4921	-17.0
3	2	73-78	6.7	.9084	1.4965	-1.1
4	2	78-85	5.0	.9175	1.4966	+16.8
5	2	85-90	7.5	.9258	1.4989	+33.8

Fraction 13 also consisted predominantly of *l*- β -phellandrene. Fraction 15 was tested for methyl chavicol; the results were positive. Fraction 17 was tested for sesquiterpenes by preparing hydrochloride: 5 g. of the oil were dissolved in 40 cc. of absolute ether and treated with dry HCl gas for 30 minutes. Abundant crystals of hydrochloride were formed after the treated oil had remained in the

refrigerator for 50 days. The hydrochloride was recrystallized three times from glacial acetic acid. Its melting point, 59° to 60° C., was not changed by addition of known longifolene hydrochloride.

The composition of *Pinus patula* turpentine was also determined by means of vapor chromatography. Previously the apparatus had been calibrated by using known α -pinene and β -phellandrene. From the results shown in figure 18, it is seen that the two major components of the terpene fraction of *P. patula* turpentine are α -pinene and β -phellandrene. Besides these two terpenes, a very small amount of another compound was present, probably methyl chavicol.

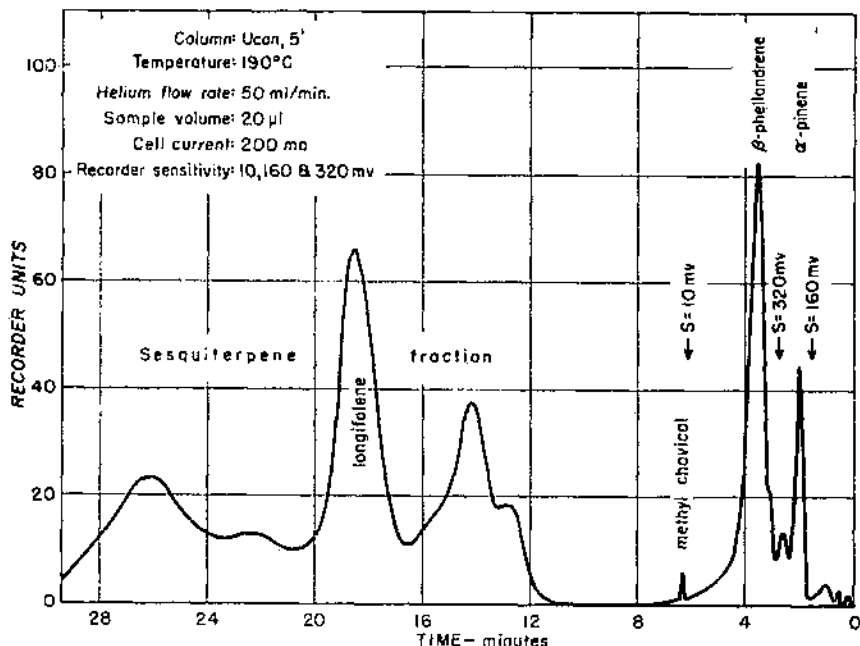


FIGURE 18.—Vapor chromatography chart of *Pinus patula* turpentine.

The sesquiterpene part of the chart shows three major peaks. One of these peaks represents longifolene, already identified by its hydrochloride. The other two peaks possibly are β -longifolene and γ -longifolene. These two sesquiterpenes had been found by Ghatgey and Bhattacharyya (56) in *Pinus longifolia*, No. 26, turpentine.

To sum up, turpentine of *Pinus patula* contained:

Compound:	Percent
<i>dl</i> - α -pinene.....	5
<i>l</i> - β -phellandrene.....	70-80
Methyl chavicol.....	5
Sesquiterpenes, chiefly longifolene.....	10

The high content of *l*- β -phellandrene in *P. patula* turpentine can be compared only with that of *P. contorta*, No. 89. The two pines in Shaw's botanical classification (142) stand very close to one another. A reexamination of the turpentine of this interesting pine is advised.

92. *Pinus muricata* D. Don References (96; unpub. orig. data)
(Linn. Soc. London. Trans. 17: 441. 1936)

Pinus muricata is a California species, commonly called bishop pine. It grows along the coast of northern and central California. It also occurs in the Mexican State of Baja California and on the islands of Cedros and Guadalupe, near the coast. Duffield,³⁴ who studied variability of *P. muricata*, proposed that this species be divided into four varieties: (1) *borealis* of the north; (2) *muricata* of the south (mainland); (3) *remorata* of Santa Cruz and Santa Rosa Islands; and (4) *cedrosensis* Howell (of Cedros Island).

In 1945 I obtained a sample of *Pinus muricata* oleoresin from near Fort Bragg, on the Mendocino coast, Calif. Turpentine was obtained by steam distillation, and the yield was 22.4 percent of the weight of the oleoresin. The physical characteristics of the turpentine were these:

Density, $d_4^{20} = 0.8610$
Index of refraction, $n_D^{20} = 1.4693$
Specific rotation $[\alpha]_D^{20} = +11.6^\circ$

The turpentine consisted almost entirely of *d,dl*- α -pinene (98 to 99 percent), and less than 1 percent camphene. Apparently there were no sesquiterpenes. Dr. Sutherland of the University of Queensland, Brisbane, Australia, wrote me that he suspected small amounts of α -tujene in the turpentine of this pine.

For an investigation of the variety *remorata*, originally known as *Pinus remorata* Mason (89), we obtained five small samples of turpentine from Santa Cruz Island and two samples from Santa Rosa Island. The samples had optical rotation, α_D , varying within narrow limits from -43.00° to -45.5° , as compared with $\alpha_D = +9.98^\circ$ of *P. muricata* var. *borealis*.

93. *Pinus attenuata* Lemm. Reference (107)
(Mining and Sci. Press 64:45. 1892)

Pinus attenuata, knobcone pine, is a Pacific coast species, growing in widely scattered places at medium altitudes, often on rocky slopes, of both the Coast Ranges and the Sierra Nevada from southwestern Oregon to southern California. It is also found in Baja California, Mexico.

Oleoresin of knobcone pine was collected in the summer of 1945 near Kelsey, El Dorado County, Calif., at an elevation of 1,500 to 1,800 feet. The trees were overmature, of poor growth, and of rather grotesque appearance. The site was extremely dry and poor. Twenty trees were tapped.

The oleoresin was heated in a 2-liter Claisen flask in an oil bath under reduced pressure; the temperature of the bath toward the end of distillation reached 200° C. and the pressure was reduced to 0.05 mm. Yield of the turpentine was as follows:

Date of oleoresin collection:	Turpen- tine (percent)
June 9.....	24.2
June 27.....	23.4
July 24.....	23.8
August 25.....	24.0

³⁴ DUFFIELD, JOHN WARREN. INTERRELATIONS OF THE CALIFORNIA CLOSED-ONE PINES WITH SPECIAL REFERENCE TO *PINUS MURICATA* D. DON. 85 pp. 1951. [Ph. D. thesis. Copy on file Univ. Calif., Berkeley.]

The turpentine (combined from all four gatherings) had the following characteristics:

Density, $d_4^{20} = 0.8520$
 Index of refraction, $n_D^{20} = 1.4652$
 Specific rotation, $[\alpha]_D^{20} = +17.1^\circ$

The turpentine was 98 percent *d*- α -pinene.

94. *Pinus radiata* D. Don References (8, 20, 91, 116)
 (Linn. Soc. London. Trans. 17: 442. 1836)

Pinus radiata is the Monterey pine of the California coast south of San Francisco Bay, particularly of the Monterey peninsula. It also grows on nearby islands. It has been planted extensively in the warmer parts of the world, especially in the Southern Hemisphere. In Australia and New Zealand, where it is known as *P. insignis* Dougl., it has become a commercial source of lumber. Turpentine of Monterey pine was investigated first by Barraud in 1928 (20). She worked with two samples of turpentines. Physical characteristics of the samples were as follows:

	Planted trees	
	France	Portugal
Yield of turpentine, percent.....	22	20
Density, d_4^{15}	0.8685	0.8700
Index of refraction, n_D^{15}	1.4690	1.4712
Rotation, α	-10.88°	-11.20°

Apparently both samples were fractionated together. The turpentine contained:

Compound:	Percent
<i>l, dl</i> - α -pinene.....	34.3
<i>l</i> - β -pinene.....	64.4
Dipentene.....	1.6
Tails.....	1.7

No crystalline tetrabromide was obtained to verify the presence of dipentene. Alcohols were suspected but not identified. A sesquiterpene was apparently present, but no crystalline derivatives were obtained.

McCombs (91) in 1931 analyzed Monterey pine turpentine obtained in New Zealand from planted trees. The characteristics of this turpentine were: Density, $d = 0.872$ to 0.874 ; observed rotation, $\alpha = -12.4^\circ$

The composition:

Compound:	Percent
<i>l</i> - α -pinene.....	24
<i>l</i> - β -pinene.....	75
Tails.....	1

In 1932 Arbuzov and his coworkers (8) reported their work on turpentine obtained from planted Monterey pines in southern Russia.

Physical characteristics:

Density, $d_4^{17.5} = 0.8685$
 Index of refraction, $n_D^{17.5} = 1.4776$
 Specific rotation, $[\alpha]_D = -3.25^\circ$

The composition was:

Compound:	Percent
<i>d, dl</i> - α -pinene.....	40.6
<i>l</i> - β -pinene.....	56.4
Camphene.....	.3
Higher boiling fractions (unidentified).....	2.7

Monterey pine turpentine investigated in our laboratory (116) was distilled from oleoresin collected from 20-year-old planted trees at the Institute of Forest Genetics, Placerville, Calif. Yield of oleoresin was very poor. The oleoresin was heated under reduced pressure; at the end of the distillation, pot temperature reached 190° C. and pressure was reduced to 1 mm.

The yield of turpentine was 16.8 percent. It possessed the following physical characteristics:

Density, $d_4^{20} = 0.8596$
 Index of refraction, $n_D^{20} = 1.4727$
 Specific rotation, $[\alpha]_D^{20} = -5.85^\circ$

The turpentine contained:

Compound:	Percent
<i>l, dl</i> - α -pinene.....	75
<i>l</i> - β -pinene.....	22
The tails, amounting to 3 percent, were not examined.....	

Part III. Conclusion

SUMMARY OF FINDINGS

This investigation has broadened our knowledge of the composition of pine gum turpentine, their variability and inheritance, and the distribution of their components among the species of the genus *Pinus*.

We have found that paraffin hydrocarbons are not as rare in pine gum turpentine as had been thought before. Previously, *n*-heptane (C_7H_{16}) was reported only in two California pines, *Pinus jeffreyi* and *P. subiniana*. We have found *n*-heptane in six other pines: *P. reflexa*, *P. ayacahuite*, *P. monticola*, *P. torreyana*, *P. oaxacana*, and *P. montezumae*. *n*-undecane ($C_{11}H_{24}$) discovered in 1922 by Simonsen and Rau in *P. excelsa* (*P. griffithii*) has also been found in the following pines: *P. koraiensis*, *P. reflexa*, *P. armandi*, *P. monticola*, *P. torreyana*, *P. coulteri*, and *P. oaxacana*, and in one variety of *P. ponderosa*. An unidentified nonane (C_9H_{20}) was detected by means of a mass spectroscopy in the turpentine of *P. torreyana*, No. 33. It is possible that minute quantities of other low-boiling paraffin hydrocarbons could be found in other pine turpentine.

An aromatic hydrocarbon, *p*-cymene, previously reported (14) in *Pinus sylvestris* turpentine, was not found in any other pine gum turpentine. After our work had been completed, however, Sutherland and Wells (158), using ultraviolet absorption technique, reported minute quantities of *p*-cymene in turpentine of *P. taeda*.

Olefinic open chain terpenes of the general formula C_nH_{2n-4} are represented in gum turpentine by only two compounds: β -myrcene and ocimene. Myrcene had been previously reported in turpentine of *Pinus sylvestris*, *P. longifolia*, and *P. nigra*. Later it was found in the turpentine of five additional pines: *P. peuce*, *P. edulis*, *P. ponderosa*, *P. taeda*, and *P. halepensis*. Ocimene, never before reported as a component of gum turpentine, was detected in *P. edulis* and *P. quadrifolia*.

Among monocyclic terpenes, limonene was found in 30 pines—predominantly in its *l-dl* form, in some pines probably as a pure levorotatory antipode. In *Pinus lumholtzii*, *l*-limonene possessed a very high rotatory power of -124 . An inert form of limonene, commonly known as dipentene, is found in turpentine of eight, possibly nine pines, in very minute quantities. A dextrorotatory limonene was found, also in minute quantities, in turpentine of *P. pinaster*, by Dupont and Barraud (16); we recorded it in turpentine of *P. tropicalis*.

Another monocyclic terpene, terpinolene, had been previously reported in *Pinus sylvestris* (No. 42) turpentine and in minute amounts in the tails of *P. palustris* turpentine. We found this terpene in tur-

pentines of five additional pines, Nos. 9, 12, 21, 76, and 80, and in some eastern forms of *P. ponderosa*, No. 54.

A third monocyclic terpene, β -phellandrene, previously reported in *Pinus contorta* turpentine (186) and in a mutant of *P. sylvestris* (82), has been found in our laboratory in turpentines of several other pines: *P. coulteri*, *P. resinosa*, *P. insularis*, *P. ponderosa*, *P. patula*, *P. caribaea*, and *P. elliotii*. In all these cases, β -phellandrene was levorotatory, its specific rotation being in the neighborhood of -15° .

Five bicyclic terpenes are found in pine gum turpentines: α -pinene, β -pinene, Δ^2 -carene, camphene, and α -thujene. α -pinene in either a dextrorotatory or a levorotatory form, proved to be, as expected, the most common of all terpenes in pines. If it were not lacking in turpentines of six pines, *Pinus albicaulis*, *P. pinea*, *P. jeffreyi*, *P. torreyana*, *P. sabiniana*, *P. washoensis*, and in some varieties of *P. contorta*, it could have been called the generic character of pines.

β -pinene, almost always in its levorotatory form, was found in fifty or so pine species. This terpene generally, but not always, occupies a subordinate position in the composition of pine turpentines.

A bicyclic terpene, Δ^2 -carene, originally detected by Simonsen in *Pinus longifolia* and reported to be an ingredient of four more Asiatic pines, *P. sibirica*, *P. sylvestris*, *P. merkusii*, and *P. pityusa*, was rather common in the turpentines of American pines. Some varieties of *P. ponderosa* contain 50 to more than 60 percent of this terpene in their turpentines. Δ^1 -carene was suspected but not identified in turpentine of *P. oocarpa* var. *trifoliata*.

Camphene, which had been previously reported in *Pinus nigra*, *P. clausa*, and rarely in *P. sylvestris* turpentine, was detected in our laboratory in the turpentine of only two additional pines: *P. armandi* and *P. muricata*.

A bicyclic terpene, α -thujene, was suspected by Sutherland (personal communication) as occurring in minute quantities in turpentine of *Pinus muricata* and was definitely found by Sutherland and Wells (158) in minute quantities in turpentine of *P. longifolia*. We have not detected this terpene in any other pines.

In the sesquiterpene group, cadinene had been reported in *Pinus pinaster* and in two pinyon pines, *P. edulis* and *P. quadrifolia*. In several additional pines, we found either cadinene, or cadinenelike sesquiterpenes, yielding crystalline cadinene dihydrochloride.

A tricyclic sesquiterpene, longifolene, which had been discovered by Simonsen in *Pinus longifolia*, was identified in our laboratory in 17 pine species. Counting previous findings, this sesquiterpene is in the turpentines of 24 pines, often in large quantities. For instance, ponderosa pine turpentine from the Black Hills of South Dakota contained 13 percent longifolene. Thunbergine, reported by Dupont and Barraud in the turpentine of *P. thunbergii*, no doubt was longifolene.

A bicyclic sesquiterpene, named albicaulene by Haugen-Stuit, was found in three pines: *Pinus albicaulis*, *P. flexilis*, and *P. parviflora*. A bicyclic sesquiterpene which I detected in turpentine of *P. pinceana* and named maderene is apparently a new sesquiterpene. Later we found a sesquiterpene with similar properties in *P. pinea* turpentine. Both *P. pinceana* and *P. pinea* are predominantly limonene pines. We also found several sesquiterpenes whose crystalline hydrochlorides we were not able to prepare. The sesquiterpenes of five pines yielded

cadalene. *P. parviflora* turpentine contained a sesquiterpene which on dehydrogenation gave azulene.

Diterpenes were found in turpentines of five pines, *Pinus koraiensis*, *P. albicaulis*, *P. armandi*, *P. lambertiana*, and *P. peuce*.

Aliphatic terpene alcohols are very rare in pine gum turpentines. Besides nerol, found by Dupont and Barraud in turpentine of *Pinus thunbergii*, we detected linalool in turpentine of *P. tenuifolia*. Possibly linalool is also found in turpentine of *P. jeffreyi*.

Cyclic terpene alcohols are almost never found in gum turpentines. Simonsen reported terpineol in *Pinus griffithii* turpentine; we have never encountered this substance.

A sesquiterpene alcohol, cadinol, had been reported by Naffa (117) in the cadinine fraction of *Pinus pinaster* turpentine. We found albicaulol in three or possibly four pines, Nos. 5, 8, 10, 11, and two other sesquiterpene alcohols, one in *P. lambertiana* and another in *P. engelmannii*.

A diterpene alcohol was apparently present in the turpentine of *Pinus peuce*, No. 12.

In the distribution of aliphatic aldehydes, we have found little that is new: only decyl and lauryl aldehydes in turpentine of *Pinus torreyana*, and the indicated presence of aldehydes in turpentines of *P. coulteri* and the Santa Cruz variety of *P. ponderosa*.

The presence of lauryl aldehyde in turpentine of *Pinus luchuensis*, No. 44, reported by Akiyoshi (4), is of utmost significance, because it ties California pines with pines of Eastern Asia.

Apparently small amounts of ketones occur in turpentine of *Pinus strobus*; a C_{10} carbonyl compound in *P. torreyana*, and a sesquiterpene aldehyde with a sesquiterpene ketone in *P. contorta*. Unidentified oxygenated compounds were detected in turpentines of several pines.

A phenol ether, methyl chavicol, had been previously reported in turpentine of *Pinus jeffreyi*, and in tails of turpentines of *P. palustris* and *P. elliotii* var. *elliottii*. We found methyl chavicol in three U.S. pines: *P. ponderosa*, *P. elliotii* var. *densa*, and *P. serotina*, and in five Mexican pines: *P. luhholtzii*, *P. hartwegii*, *P. michoacana*, *P. pringlei*, and *P. patula*.

We found an aliphatic ester, ethyl caprylate, in the turpentine of *Pinus edulis*. This ester had been found previously in small quantity (0.6 percent) in fusel oil of grape brandy.

Only three terpene esters have been found in pine turpentines: bornyl formate in *Pinus canariensis*, terpinyl acetate in *P. albicaulis*, and bornyl acetate which, though found in large quantities in pine needle oil of many pines, proved rather rare in pine turpentine. We found bornyl acetate in only six pines, *P. koraiensis*, *P. armandi*, *P. peuce*, *P. monticola*, *P. balfouriana*, and *P. taiwanensis*, and it has been reported in the tails of *P. palustris* turpentine (30).

APPLICATION OF RESULTS

In taxonomic studies, especially when morphological characters are not too clear, a knowledge of chemical composition of the turpentines may be helpful. A good example of how chemical composition of turpentine may serve taxonomic purposes is the relationship of

Pinus halepensis and its supposed variety *P. brutia*. In the light of chemical differences of their turpentines, these two pines appear to be separate species. This conclusion has been supported by independent morphological studies (122) and by entomological evidence (103).

Knowledge of the chemical composition of turpentines often is useful in untangling difficult problems in tree breeding, especially when taxonomic status of the parent trees is not certain. For instance, Righter and Duffield (129) in 1951 described a hybrid obtained by crossing *Pinus ponderosa* and *P. engelmannii*. The hybrid possessed several advantageous characters, such as a long taproot and rapid growth. The taxonomic status of the parents was not certain, because their relationship was far from being settled.

Some botanists (142) consider *Pinus engelmannii* merely a variety of *ponderosa* pine. From their point of view, the hybrid *P. engelmannii* \times *P. ponderosa* is, then, the product of an intraspecific hybridization of two varieties of the same species. Others (156) believe that the two pines are distinct species; the hybrid then would be considered the result of an interspecific hybridization.

Pinus ponderosa is generally recognized as a valid species. Some botanists recognize several varieties within the species, such as variety *scopulorum*. Others do not believe that these taxa merit a varietal status.

The status of *Pinus engelmannii*, however, is more complicated. This pine has been described by various botanists as a distinct species (*P. macrophylla* Engelm., 1887; *P. latifolia* Surg., 1889; *P. apachea* Lemm., 1894; *P. mayriana* Surtw., 1897). All these names signify that it may be entitled to the rank of a species. On the other hand, Shaw (142) does not consider this pine distinct from *ponderosa* pine and places the above listed names in synonymy under *P. ponderosa*. In the Forest Service Check List of the Trees of the United States (36), it is listed as *P. engelmannii*.

Herbarium specimens of *Pinus engelmannii* and *P. ponderosa* are very similar in appearance. But foresters, and those botanists who are familiar with the two pines growing under natural conditions, are aware of many distinguishing characters in *P. engelmannii*: long, lush-green foliage; deep taproot of seedlings; a seedling "grass stage" similar to that of *P. palustris* and (in lesser degree) of *P. montezumae*; red-brown color of bark scales, and others. It is on these characters that *P. engelmannii* was considered to be a distinct species.

Our investigations of the turpentines furnished additional information on the relationship of the two. All the investigated varieties of *Pinus ponderosa*--from California, northern Idaho, the Black Hills of South Dakota, Colorado, Utah, and Arizona--may be characterized by the presence in their turpentines of large quantities of a terpene, Δ^3 -carene. This terpene may be thus considered as a specific character of *ponderosa* pine throughout its range. On the contrary, turpentine of *P. engelmannii* does not contain any Δ^3 -carene. Thus, taking into consideration its chemical characters, it should be classified as a distinct species and not as a variety of *P. ponderosa*, and the hybrid between the two pines should be considered as an interspecific rather than an intraspecific hybrid.

If the chemical composition of turpentines of two pines is sufficiently distinct, it is easy to identify natural hybrids by their turpentines.

Such are hybrids between *Pinus jeffreyi* and *P. ponderosa*, or between *P. banksiana* and *P. contorta*.

The data presented in this publication may also be of value to industry. Some pines have turpentines consisting almost entirely of α -pinene. Some species contain an abundance of *l*-limonene. Turpentine of two California pines consists chiefly of *n*-heptane; large quantities of this hydrocarbon were obtained as a chemically pure product from *Pinus jeffreyi* in the 1930's when antiknocking motor fuels were developed (29).

Δ^3 -carene is a relatively new terpene (discovered in 1922). Its industrial possibilities are less known than, say, those of α -pinene. We have found Δ^3 -carene in several American pines—sometimes in large quantities (more than 60 percent of the total weight of the turpentine). Perhaps this terpene may be industrially important.

Knowledge of turpentine composition may be useful in entomological studies concerned with insect-repellent or insect-attractive constituents of oleoresins. Knowledge of the effect of different constituents of turpentine on fungi or bacteria might be profitable in pathological work.

Terpenes of certain pines have been employed in the preparation of liquid scintillators for studies of C^{14} distribution in nature (64). An inventory of the occurrence of different terpenes among the pines throughout the world proved to be very useful for this purpose.

SUGGESTIONS FOR FURTHER RESEARCH

Investigation of the chemical nature of pine turpentines is far from being completed. The information contained in this publication covers most, but not all species. In many species only one sample of turpentine was available for analysis; occasionally a sample received was of such poor quality that the results cannot be considered as final.

There are pines whose botanical status is uncertain. Such pines as *Pinus densata*, and *P. kwangtungensis* of southwestern China, or *P. douglasiana*, are apparently valid species, but they are not included in this publication. Their turpentines should be studied. The same applies to what appeared to be an inland form of *P. caribaea* which I observed in the mountains of Honduras; and to *P. cubensis*, which is placed by Shaw (142) under *P. occidentalis*. Turpentine of *P. occidentalis* has not been analyzed.

A study of the occurrence of chemical mutants among the pines promises interesting results.

In the course of our project we have inquired into the composition of turpentines of pine hybrids, both natural and artificial (104). As more and more pine hybrids are found in nature and more artificial hybrids are created by tree breeders, there should be more studies of the chemical composition of turpentine of the hybrids. A study of the mode of inheritance of terpenes in the genus *Pinus* might be very useful, in both science and practice.

Our work with *Pinus ponderosa* has shown that several chemical varieties may exist within a pine species. Penfold (124) calls these varieties physiological forms. Many other pine species, such as *P. pseudostrabus*, *P. nigra*, *P. sylvestris*, and *P. tabulaeformis*, are com-

posed of several varieties. Turpentine composition of these varieties should be carefully studied. Further studies of individual variability in composition of turpentine within a pine population also are very desirable.

The high-boiling fractions of turpentines contain, besides sesquiterpenes, small quantities of oxygenated terpene and sesquiterpene compounds. These high-boiling fractions should be more carefully studied. New methods of analysis, such as infrared spectroscopy or vapor chromatography will be indispensable in such studies.

Because Δ^3 -carene is more widespread in pine turpentines than formerly thought, it should be intensively studied. Structural formulae of the sesquiterpene compounds reported in this publication should be determined. Biogenesis of terpenes and of nonterpene constituents of turpentines should be studied. Especially intriguing is the biogenesis of paraffin hydrocarbons.

It is hoped that information presented in this publication will stimulate further research in the field of turpentines.

Literature Cited

- (1) ANONYMOUS.
1930. ATJEH-TERPENTIJN (VAN PINUS MERKUSII), AMSTERDAM KOLONIAL INSTITUTE. Afd. Handelsmuseums 9: 31-35.
- (2) ————
1938. PINUS HALEPENSIS OLEORESIN FROM CYPRUS. [London] Imp. Inst., Bul. 36: 157-162.
- (3) ————
1939. PINUS HALEPENSIS OLEORESIN FROM CYPRUS. [London] Imp. Inst. Bul. 39: 104-106.
- (4) AKIYOSHI, SAHURU.
1937. TURPENTINE OILS OF JAPAN AND HER NEIGHBOURING COUNTRIES. Imp. Indus. Res. Inst. Rpt., Osaka, Japan, 17: 1-102.
- (5) ALLEN, CHARLES F. H.
1930. THE IDENTIFICATION OF CARBONYL COMPOUNDS BY USE OF 2,4-DENITROPHENYLDRAZINE. Amer. Chem. Soc. Jour. 52: 2955-2959.
- (6) ALLEN, PAUL H.
1955. THE CONQUEST OF CERRO SANTA BARBARA, HONDURAS. Ceiba 4: 253-270.
- (7) ARBUZOV, B. A.
1934. A NOTE ON COMPOSITION OF RUSSIAN GUM TURPENTINE. Zhur. Prikl. Khimii 7: 757-759.
- (8) ARBUZOV, B., ABRAMOV, A., AND VALITOVA, F.
1932. A STUDY OF COMPOSITION OF OLEORESIN OF PINUS INSIGNIS. Zhur. Obshch. Khimii 2: 376-387.
- (9) ————, BASTANOVA, L., IVANOVA, E., AND OTHERS.
1933. COMPOSITION OF GUM TURPENTINE OF PINUS PETHYUSA. Zhur. Prikl. Khimii 5: 787-789.
- (10) ARMSTRONG, HENRY E.
1896. PRELIMINARY REPORTS ON TWO BURMESE TURPENTINES. Pharm. Jour. [London] 56: 370.
- (11) ASAHINA YASUHIKO, MORIZO ISHIDATE, AND TUNEITI SANO.
1936. ZUR BORNEOL-ISOBORNEOL-PRAGE. Ber. der Deut. Chem. Gesell. 69: 343-348.
- (12) BAKER, RICHARD T., AND SMITH, HENRY G.
1902. A RESEARCH ON THE EUCALYPTUS ESPECIALLY IN REGARD TO THEIR ESSENTIAL OILS. [N.S. Wales] Technol. Mus. Tech. Ed. Ser. 18, 295 pp., illus.
- (13) BARDYSHEV, I. I.
1950. β -MYRCENE—A COMPONENT OF TURPENTINES OF COMMON PINE (PINUS SILVESTRIS). Dokl. Akad. Nauk. USSR 71: 675.
- (14) ————
1955. THE PRESENCE OF p-CYMOL IN GUM TURPENTINE OF PINUS SILVESTRIS. Dokl. Akad. Nauk. USSR 101(2): 263-264.
- (15) ———— AND BARDYSHEVA, K. B.
1948. ON THE NATURE OF l-COMPONENT OF RUSSIAN GUM TURPENTINES. Zhur. Obshch. Khimii 18: 1475-1479.
- (16) ———— AND BARDYSHEVA, K. B.
1952. COMPOSITION OF TURPENTINE OF PINUS NIGRA. Zhur. Prikl. Khimii 25: 1095-1098, 1231-1232.
- (17) ————, PIRIATINSKI, A. L., BARDYSHEVA K. B., AND CHERNIAEVA, O. I.
1947. ON OCCURRENCE OF β -PINENE IN GUM TURPENTINE OF COMMON PINE. Zhur. Prikl. Khimii 20: 1308-1319.
- (18) ————, PIRIATINSKI, A. L., BARDYSHEVA K. B., AND CHERNIAEVA, O. I.
1950. COMPOSITION OF TURPENTINE OF SIBERIAN CEDAR (PINUS CEMBRA L.). Zhur. Prikl. Khimii 25: 1095-1098.

- (19) BARRAUD, MARCELLE.
1929. L'ETAT DE NOS CONNAISSANCES SUR LA COMPOSITION DES ESSENCES DE TÉRÉBENTHINE. *Bul. de L'Inst. du Pin* 58: 93-97.
- (20) ————
1930. COMPOSITION DE L'ESSENCE DE TÉRÉBENTHINE DE PINUS INSIGNIS. *Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1927-28*, pp. 70-74.
- (21) ————
1930. CONTRIBUTION À L'ÉTUDE DE L'ESSENCE DE TÉRÉBENTHINE DE PINUS MERKUSII. *Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1927-28*, pp. 74-76.
- (22) BEISSNER, L.
1909. *HANDBUCH DER NADELHOLZKUNDE*. 742 pp., illus. Berlin.
- (23) BETTS, H. S.
1912. POSSIBILITIES OF WESTERN PINES AS A SOURCE OF NAVAL STORES. *U.S. Dept. Agr. Forest Serv. Bul.* 116, 23 pp., illus.
- (24) BLACK, A. P., AND THRONSON, S. M.
1934. OLEORESIN FROM INDIVIDUAL TREES OF SLASH AND LONGLEAF PINES. *Indus. and Engin. Chem.* 26: 66-69.
- (25) BLANCO, CENOBIO E.
1935. LOS FINOS DE MEXICO. [*Mex.*] *Dept. Forest. Bol.* 3, 248 pp.
- (26) ————
1949. PINUS COOPERI BLANCO, SP. NOVA. *Ann. del Inst. de Biol.* 20: 185-187.
- (27) BUKALA, MIŁCZYSLAW, AND KUCZYNSKI, HENRIK K.
1952. STUDIES ON THE COMPOSITION OF THE POLISH TURPENTINES OBTAINED FROM PINUS SILVESTRIS. [*In Polish.*] *Rocz. Chem.* 26: 58-84.
- (28) CARRIÈRE, E. A.
1867. PINUS PYRENAICA. [*Paris*] *Rev. Hort.* 38: 150-152.
- (29) CARRUTHERS, GUY.
1956. OUR STRANGE DEBT TO THE "GASOLINE TREE." *Westways* 48: 14-15.
- (30) CHADWICK, T. C., AND PALKIN, S.
1941. COMPOSITION OF AMERICAN GUM TURPENTINE EXCLUSIVE OF THE PINENES. *U.S. Dept. Agr. Tech. Bul.* 749.
- (31) CLAUSEN, ROBERT T.
1939. CONTRIBUTION TO THE FLORA OF NEW JERSEY. *Torreya* 39: 126-132.
- (32) CRITCHFIELD, WILLIAM B.
1957. GEOGRAPHIC VARIATION IN PINUS CONTORTA. *Maria Moors Cabot Found. Pub.* 3. Harvard University, Cambridge, Mass.
- (33) DALLMORE, W., AND JACKSON, A. BRUCE.
1923. A HANDBOOK OF CONIFERS. 670 pp. Longmans, Green and Co., N. Y. (Single-leaf pines, see pp. 383, 425, and 453; *P. pinea*, see p. 437.)
- (34) DERMER, O. C., AND KING, JACK.
1943. N-BENZYLAMIDES AS DERIVATIVES FOR IDENTIFYING THE ACYL GROUP IN ESTERS. *Jour. Organic Chem.* 8: 168-173.
- (35) DE SANTOS, IRENE, WEST, AUGUSTUS P., AND FONTANA, J.
1931. PHILIPPINE TURPENTINE FROM PINUS INSULARIS. *Philippine Jour. Sci.* 45: 233-238.
- (36) DRAKE, NATHAN L., AND BRONITSKY, JACK.
1930. PARA-PHENYLPHENACYL BROMIDE, A REAGENT FOR IDENTIFYING ORGANIC ACIDS. *Am. Chem. Soc. Jour.* 52: 3719-3720.
- (37) DUPONT, GEORGE.
1922. LES CONSTITUANTS DE LA GEMME DE PIN D'ALEP. *Chem. et Indus.* 8: 320-321.
- (38) ————
1924. SÉPARATION DES CONSTITUANTS DE L'ESSENCE DE TÉRÉBENTHINE DE BORDEAUX. *Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1921-22*, pp. 10-18.

- (39) DUPONT, GEORGE.
1924. SUR LES CONSTITUANTS DE L'ESSENCE DE TÉRÉBENTHINE *PINUS MARITIMA*. CONSTITUANTS AUTRES QUE LES PINÈNES. Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1921-22, pp. 40-44.
- (40) ————
1926. LES ESSENCES DE TÉRÉBENTHINE. 332 pp., illus. Paris.
- (41) ———— AND BARRAUD, M.
1924. SUR LA COMPOSITION DE L'ESSENCE DU PIN PIGNON (*PINUS PINEA*). Soc. Chim. de France Bul. [4] 35: 625-631.
- (42) ———— AND BARRAUD, M.
1924. COMPOSITION DES ESSENCES DE TÉRÉBENTHINE DU PIN LARICIO D'AUTRICHE (*P. LARICIO AUSTRIACA*) ET DU PIN LARICIO D'ESPAGNE. Soc. Chim. de France Bul. 35: 784-792.
- (43) ———— AND BARRAUD, M.
1925. SUR L'ESSENCE DE TÉRÉBENTHINE DU PIN NOIR D'AUTRICHE (*P. LARICIO AUSTRIACA*). Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1923-24, pp. 6-12.
- (44) ———— AND BARRAUD, M.
1927. CONTRIBUTION OF L'ETUDE DE L'OLÉRESINE DU *PINUS THUNBERGII*. Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1925-26, pp. 131-136.
- (45) ———— AND BARRAUD, M.
1928. COMPOSITION DE L'ESSENCE DE PIN SYLVESTRE (*P. SYLVESTRIS*). Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1926-27, pp. 111-116.
- (46) ———— AND BARRAUD, M.
1928. SUR LA NATURE DE CONSTITUANT D'EXTROGYRE DES QUEUES D'ESSENCE DE TÉRÉBENTHINE DE BORDEAUX. Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux. Année 1926-27, pp. 164-167.
- (47) ———— AND BARRAUD, M.
1930. SUR LA COMPOSITION DE L'ESSENCE DE TÉRÉBENTHINE AMÉRICAINE. Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1928-29, pp. 15-20.
- (48) ———— AND LIPARO.
1926. L'ESSENCE DE TÉRÉBENTHINE DU PIN LARICIO DE CORSE. Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux Année 1924-25, pp. 9-11.
- (49) ———— AND SOUM, M.
1926. SUR L'ESSENCE DE TÉRÉBENTHINE DU PIN MARITIME D'ESPAGNE. Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1924-25, pp. 6-58.
- (50) ———— AND SOUM, M.
1926. SUR LA COMPOSITION DE L'ESSENCE DE TÉRÉBENTHINE DU *PINUS EXCELSA*. Chimie & Indus. [Paris] 16: 595-596.
- (51) ———— AND UZAC, R.
1925. SUR LA COMPOSITION DE L'ESSENCE DE TÉRÉBENTHINE INDIENNE (*PINUS LONGIFOLIA*). Procès-verbaux Soc. Sci. Phys. et Natur. de Bordeaux, Année 1922-23, pp. 83-88.
- (52) ———— DULOU, R., AND NAFFA, P.
1948. LES CONSTITUANTS SESQUI-TERPÉNIQUES DE L'ESSENCE DE TÉRÉBENTHINE DE PIN MARITIME: CARYOPHYLLENE ET LONGIFOLENE. Soc. Chim. de France Bul. 15: 990-994.
- (53) FOOTE, P. A.
1929. PHYTOCHEMICAL NOTES, NO. 102. THE NON-HEPTANE CONSTITUENTS OF JEFFREY PINE. Amer. Pharm. Assoc. Jour. 28: 350-353.
- (54) ———— AND MIROV, N. T.
1933. A PHYTOCHEMICAL INVESTIGATION OF THE OLBORESIN OF *PINUS MONTICOLA* DOUGL. Amer. Pharm. Assoc. Jour., Sci. Ed. 22: 829-834.
- (55) FRANKFOTER, G. B.
1906. THE PITCH AND THE TURPENTINES OF THE NORWAY PINE AND THE DOUGLAS FIR. Amer. Chem. Soc. Jour. 28: 1467-1472.

- (56) GHATGEY, B. B., AND BHATTACHARYYA, S. C.
1950. LONGIFOLENE FRACTION OF INDIAN TURPENTINE OIL. *Perfumery and Essential Oil Rec.* 47: 122-127.
- (57) GOLDBLATT, LEO A.
1952. AMERICAN TURPENTINES. In "The essential oils," by Ernest Guenther. v. 6: 253-308. New York.
- (58) ——— AND BURCD AHL, A. C.
1952. TURPENTINE FROM PONDEROSA PINE. *Indus. and Engin. Chem.* 44: 1634-1636.
- (59) GUENTHER, ERNEST.
1948. THE ESSENTIAL OILS. 6 v., illus. 1954. New York.
- (60) HAAGEN-SMIT, A. J., REDEMANN, C. T., AND MIROV, N. T.
1947. COMPOSITION OF GUM TURPENTINE OF TORREY PINE. *Amer. Chem. Soc. Jour.* 69: 2014.
- (61) ——— WANG, TIAO-HSIN, AND MIROV, N. T.
1950. COMPOSITION OF GUM TURPENTINE OF PINUS ARISTATA, P. BALFOURIANA, P. FLEXILIS, AND P. PARVIFLORA. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 39: 254-259.
- (62) ——— WANG, T. H., AND MIROV, N. T.
1951. COMPOSITION OF GUM TURPENTINES OF PINES. XIII. A REPORT ON PINUS ALDICAULIS. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 40: 557-559.
- (63) ——— REDEMANN, C. T., WANG, T. H., AND MIROV, N. T.
1950. COMPOSITION OF GUM TURPENTINES OF PINES: A REPORT ON PINUS PONDEROSA, P. BANKSIANA, P. CANARIENSIS, AND P. WASHOENSIS. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 39: 260-265.
- (64) HAYES, F. N.
1956. LIQUID SCINTILLATORS: ATTRIBUTES AND APPLICATIONS. *Internat. Jour. Radiation and Isotopes* 1: 46-56.
- (65) HEPTING, GEORGE H.
1947. STIMULATION OF OLEORESIN FLOW IN PINES BY A FUNGUS. *Science* 105: 209.
- (66) HERNANDEZ, EFRAIM X., CRUM, HOWARD, FOX, WM. B., AND SHARP, A. J.
1951. A UNIQUE VEGETATIONAL AREA IN TAMAULIPAS. *Torrey Bot. Club Bul.* 78: 458-63.
- (67) HERTY, CHAS. H.
1908. THE OPTICAL ROTATION OF SPIRITS OF TURPENTINE. *Amer. Chem. Soc. Jour.* 30: 863-867.
- (68) ——— AND DIXON, W. S.
1908. THE VOLATILE OILS FROM PINUS TAEDA AND P. ECHINATA. *Science* 27: 327.
- (69) ——— AND DIXON, W. C.
1908. THE VOLATILE OILS OF PINUS SEROTINA. *Amer. Chem. Soc. Jour.* 30: 872-874.
- (70) ILOFF, P. M., JR., AND MIROV, N. T.
1953. COMPOSITION OF GUM TURPENTINES OF PINES. XVI. A REPORT ON PINUS OCCARPA AND P. PSEUDOSTROBUS VAR. OAXACANA FROM CHIAPAS AND P. COOPERI FROM DURANGO. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 42: 46-49.
- (71) ——— AND MIROV, N. T.
1953. COMPOSITION OF GUM TURPENTINES OF PINES. XVII. A REPORT ON PINUS MONTEZUMAE FROM CHIAPAS AND P. OCCARPA VAR. TRIFOLIATA AND P. DURANGENSIS FROM DURANGO, MEXICO. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 42: 464-467.
- (72) ——— AND MIROV, N. T.
1954. COMPOSITION OF GUM TURPENTINES OF PINES. XIX. A REPORT ON PINUS PONDEROSA FROM ARIZONA, COLORADO, SOUTH DAKOTA, AND NORTHERN IDAHO. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 43: 374-378.
- (73) ——— AND MIROV, N. T.
1954. COMPOSITION OF GUM TURPENTINES OF PINES. XXI. A REPORT ON PINUS QUADRIFOLIA FROM SOUTHERN CALIFORNIA, PINUS LUMHOLTZII FROM DURANGO, MEXICO, AND PINUS CARIBAEA FROM NICARAGUA. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 43: 738-741.

- (74) LLOFF, P. M., JR., AND MIROV, N. T.
1954. COMPOSITION OF GUM TURPENTINES OF PINES. XXII. A REPORT ON PINUS RUDIS AND P. HARTWEGII FROM MEXICO AND P. INSULARIS FROM PHILIPPINES. Amer. Pharm. Assoc. Jour., Sci. Ed. 43: 742-745.
- (75) ——— AND MIROV, N. T.
1956. COMPOSITION OF GUM TURPENTINES OF PINES. XXV. A REPORT ON TWO WHITE PINES: PINUS KORAIENSIS FROM KOREA AND P. PEUCE FROM MACEDONIA. Amer. Pharm. Assoc. Jour., Sci. Ed. 45: 77-81.
- (76) ——— AND MIROV, N. T.
1956. COMPOSITION OF GUM TURPENTINE OF PINES. XXVII. A REPORT ON THREE MEXICAN PINES: PINUS PRINGLEI AND P. MICHUACANA FROM MICHUACÁN AND P. ARIZONICA FROM CHIHUAHUA. Amer. Pharm. Assoc. Jour., Sci. Ed. 45: 167-170.
- (77) IRIARTE, JOSE.
1946. ESTUDIO DE LOS AGUARRASES MEXICANOS. Quimica (Mexico) 4: 117-119.
- (78) IVANOV, D., AND IVANOV, C.
1950. ANALYSE DE L'ESSENCE DE TÉRÉBENTHINE DU PINUS NIGRICANS, DE L'ESSENCE DE BOIS ET DES COLOPHANES D'ORIGINE BULGARE. Compt. Rend. Acad. Bulgar. Sci. Sec. Mat. et Nat. 3: 17-20.
- (79) KAFUKU, KINZO, NORIYOSHI ICHIKAWA, AND RYO KATO.
1934. ROSIN AND GUM TURPENTINE FROM PINUS TAIWANENSIS, HAYATA. Chem. Soc. Japan Jour. 55: 185-189.
- (80) KOOLHAAS, R., AND DEVOS, I.
1935. ONDERZOEK VAN VALSEM VAN PINUS INSULARIS EN P. MERKUSII VERKREGEN DOOR TAPPEN VAN EEN PROEFAANPLANT OP JAVA. Tectona. Boschbouw. Tijdschr. 28: 595-605.
- (81) KIRCHNER, J. G., PRATER, ARTHUR N., AND HAAGEN-SMIT, A. J.
1946. SEPARATION OF ACIDS BY CHROMATOGRAPHIC ABSORPTION OF THEIR P-PHENYLPHENACYL ESTERS. Indus. and Engin. Chem. 18: 31-32.
- (82) KRESTINSKY, V., AND BAZHENOVA-KOZLOVSKAIA, L.
1930. ON LAEVO-ROTATORY GUM TURPENTINE FROM PINUS SILVESTRIS. Zhur. Prikl. Khimii 3: 681-689.
- (83) ——— MALEVSKAIA, S., AND SOLODKY, F.
1932. ON INFLUENCE OF GEOGRAPHY FACTORS AND FOREST TYPES ON COMPOSITION OF GUM TURPENTINE OF PINUS SILVESTRIS. Zhur. Prikl. Khimii 3: 681-689.
- (84) LACRUÉ, MARIANO TOMEO.
1928. EL AGUARRÁS ESPAÑOL DE PINO DE ALEPO. Inst. Forest. de Invest. y Exper. Año 1, Vol. 2: 116-119.
- (85) ———
1928. EL AGUARRÁS ESPAÑOL DE PINO PIÑONERO. Inst. Forest. de Invest. y Exper. Año 1, Vol. 2: 120-125.
- (86) LITTLE, ELBERT L., JR.
1953. CHECK LIST OF NATIVE AND NATURALIZED TREES OF THE UNITED STATES. U.S. Dept. Agr., Agr. Handb. 41, 472 pp.
- (87) LOMBARD, RENÉ, AND ROTOVIC, B.
1954. L'OLEORÉSINE DE PINUS LEUCODERMIS. Compt. Rend. Acad. Sci. 238: 1670-1672.
- (88) MARTINEZ, MAXIMUNO.
1948. LOS PINOS MEXICANOS. 368 pp., illus. Ed. 2. Ediciones Botas.
- (89) MASON, HERBERT L.
1930. SANTA CRUZ ISLAND PINE. Madroño 2: 8-10.
- (90) ——— AND STOCKWELL, W. PALMER.
1945. A NEW PINE FROM MOUNT ROSE, NEVADA. Madroño 8: 61-63.
- (91) MCCOMBS, T. H.
1931. TURPENTINE FROM PINES OF NEW ZEALAND. Jour. Sci. Techn. 12: 333.
- (92) McELVAIN, SAMUEL M.
1949. THE CHARACTERIZATION OF ORGANIC COMPOUNDS. 282 pp., illus. New York.

- (93) Mirov, N. T.
1932. A NOTE ON JEFFREY AND WESTERN YELLOW PINE. *Jour. Forestry* 30: 93-94.
- (94) _____
1938. PHYLOGENETIC RELATIONS OF *PINUS JEFFREYI* AND *P. PONDEROSA*. *Madroño* 4: 169-171.
- (95) _____
1940. COMPOSITION OF GUM TURPENTINE OF COULTER PINE. *Indus. Engin. Chem.* 38: 405-408.
- (96) _____
1947. COMPOSITION OF GUM TURPENTINE OF BISHOP PINE. *Jour. Forestry* 45: 659-660.
- (97) _____
1948. THE TERPENES (IN RELATION TO THE BIOLOGY) OF GENUS *PINUS*. *Ann. Rev. Biochem.* 17: 521-540.
- (98) _____
1951. COMPOSITION OF GUM TURPENTINES OF PINES: A REPORT ON *PINUS ECHINATA*, *P. RIGIDA*, AND *P. PONDEROSA* FROM UTAH. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 40: 410-413.
- (99) _____
1951. COMPOSITION OF GUM TURPENTINES OF PINES. XII. A REPORT ON *PINUS MONTEZUMAE*, *P. OCCARPA*, AND *P. LEIOPHYLLA*. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 40: 550-551.
- (100) _____
1951. COMPOSITION OF GUM TURPENTINES OF PINES. XIV. A REPORT ON THREE MEXICAN PINES: *PINUS AYACAHUITE*, *P. CEMBROIDES*, AND *P. PINCHEANA*. *Amer. Pharm. Assoc. Jour., Sci. Ed.*, 41: 673-676.
- (101) _____
1952. COMPOSITION OF GUM TURPENTINES OF PINES. XV. A REPORT ON *PINUS RESINOSA* AND *P. REFLEXA*. *Amer. Pharm. Assoc. Jour., Sci. Ed.*, 41: 677-679.
- (102) _____
1954. APACHE PINE AND ITS RELATIONSHIP TO PONDEROSA PINE. *Madroño* 12: 251-252.
- (103) _____
1955. RELATIONSHIP BETWEEN *PINUS HALEPENSIS* AND OTHER INSIGNES PINES OF THE MEDITERRANEAN REGION. *Israel Res. Council Bul.* 5D: 65-72.
- (104) _____
1956. COMPOSITION OF TURPENTINE OF LODGEPOLE X JACK PINE HYBRIDS. *Canad. Jour. Botany* 34: 443-457.
- (105) _____
1958. *PINUS OAXACANA*, A NEW SPECIES FROM MEXICO. *Madroño* 14: 145-150.
- (106) _____
1958. COMPOSITION OF GUM TURPENTINES OF PINES. XXX. A REPORT ON *PINUS SEROTINA*, *P. TENUIFOLIA*, AND *P. YUNNANENSIS*, AND CONCLUDING REMARKS. *Amer. Pharm. Assoc. Jour., Sci. Ed.* 47: 410-413.
- (107) _____ AND HAAGEN-SMIT, A. J.
1949. COMPOSITION OF GUM TURPENTINE OF KNOBCONE PINE. *Jour. Forestry* 47: 721-722.
- (108) _____ HAAGEN-SMIT, A. J., AND THURLOW, JAMES.
1949. COMPOSITION OF GUM TURPENTINE OF *PINUS LAMBERTIANA*. *Amer. Pharm. Assoc. Jour., Sci. Ed.*, 38: 407-408.
- (109) _____ AND LOFF, P. M., JR.
1954. COMPOSITION OF GUM TURPENTINES OF PINES. XX. A REPORT ON *PINUS CHIHUAHUANA* FROM DURANGO, *P. APACHECA* FROM ARIZONA, AND *P. MONTICOLA* FROM NORTHERN IDAHO. *Amer. Pharm. Assoc. Jour., Sci. Ed.*, 43: 378-381.
- (110) _____ AND LOFF, P. M., JR.
1955. COMPOSITION OF GUM TURPENTINES OF PINES. XXIII. A REPORT ON THREE MEDITERRANEAN SPECIES: *PINUS PINEA* (CULTIVATED IN CALIFORNIA), *P. HALEPENSIS* (FROM ISRAEL) AND *P. BRUTIA* (FROM CYPRUS). *Amer. Pharm. Assoc. Jour., Sci. Ed.*, 43: 378-381.

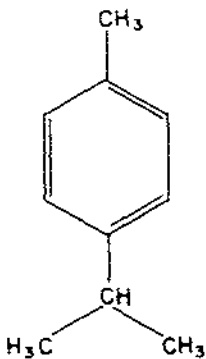
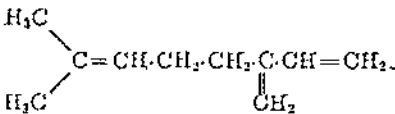
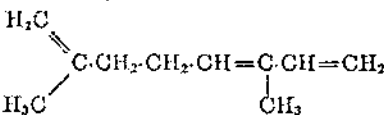
- (111) MIROV, N. T., AND ILOFF, P. M., JR.
1955. COMPOSITION OF GUM TURPENTINE OF PINES. XXIV. A REPORT ON TWO ASIATIC PINES: *PINUS ARMANDI* AND *P. BUNGEANA*. Amer. Pharm. Assoc. Jour., Sci. Ed., 44: 424-427.
- (112) ——— AND ILOFF, P. M., JR.
1956. COMPOSITION OF GUM TURPENTINES OF PINES. XXVI. A REPORT ON *PINUS LAWSONI* AND *P. HERRERAII* FROM MICHOCACÁN, MEXICO, AND *P. PONDEROSA* FROM THE CALIFORNIA COAST. Amer. Pharm. Assoc. Jour., Sci. Ed., 45: 153-156.
- (113) ——— AND ILOFF, P. M., JR.
1956. COMPOSITION OF GUM TURPENTINES OF PINES. XXVIII. A REPORT ON *PINUS EDULIS* FROM EASTERN ARIZONA, *P. TROPICALIS* FROM CUBA, AND *P. ELLIOTTI* VAR. *DENSA* FROM FLORIDA. Amer. Pharm. Assoc. Jour., Sci. Ed., 45: 629-634.
- (114) ——— AND ILOFF, P. M., JR.
1958. COMPOSITION OF GUM TURPENTINES OF PINES. XXIX. A REPORT ON *PINUS PONDEROSA* FROM SOUTHEASTERN COLORADO, CENTRAL IDAHO, NEBRASKA, WYOMING, AND MONTANA. Amer. Pharm. Assoc. Jour., Sci. Ed., 47: 404-409.
- (115) ——— ILOFF, P. M., JR., AND GORDON, L. B.
1954. COMPOSITION OF GUM TURPENTINE OF PINES. XVIII. A REPORT ON *PINUS PUNGENS*, *P. GLABRA*, AND *P. TECOTE*. Amer. Pharm. Assoc. Jour., Sci. Ed., 43: 13-15.
- (116) ——— WANG, T. H., AND HAAGEN-SMIT, A. J.
1949. CHEMICAL COMPOSITION OF GUM TURPENTINES OF PINES; A REPORT ON *PINUS STROBUS*, *P. CEMBRA*, *P. TAEDA*, *P. RADIATA*, AND *P. VIRGINIANA*. Amer. Pharm. Assoc. Jour., Sci. Ed., 38: 403-407.
- (117) NAFFA, P.
1951. LES CONSTITUENTS SESQUITERPÉNIQUES DE L'ESSENCE DE TÉRÉBENTHINE DE PIN MARITIME (2^e COMMUNICATION). Soc. Chim. de France Bul. 18: 753-755.
- (118) ——— AND OURISSON, G.
1953. CHEMICAL APPROACH TO THE STRUCTURE OF LONGIFOLENE. Chem. and Indus. 35: 917-918.
- (119) OUDIN, A.
1939. LES VARIATIONS DU POUVOIR ROTATOIRE DE L'ESSENCE DE TÉRÉBENTHINE DU PIN MARITIME ET LA NOTION D'INDIVIDUALITÉ CHIMIQUE. Assoc. France, pour l'Avanc. des Sci. Rap. et Comm. sur pin Marit. 62 Cong. Archaron, 22-27 Sept. 1938, pp. 123-125.
- (120) PALAZZO, F. C.
1917. SOPRA L'OLIO ESSENZIALE DALLA TREMENTINA DI *PINUS PINEA* (L.). Ann. del R. Inst. Super. Forest. Naz. 2: 157-181 (Anno 1916-17). Firenze.
- (121) PALKIN, S.
1932. THE FRACTIONATION OF AMERICAN GUM SPIRITS OF TURPENTINE AND EVALUATION OF ITS PINENE CONTENT BY OPTICAL MEANS. U.S. Dept. Agr. Tech. Bul. 276, 14 pp.
- (122) PAPAIOANNOU, JOHANNES.
1936. ÜBER ARTRASTARDE ZWISCHEN *PINUS BRUTIA* TEN. AND *P. HALEPENSIS* MILL. Forstwiss. Abh. 58: 194-205.
- (123) PARKER, E. D., AND GOLDBLATT, L. A.
1952. ACID COMPOSITION OF GUM SPIRITS OF TURPENTINE AND LOW WINES. Indus Engin. Chem. 44: 2211-2213.
- (124) PENFOLD, A. R.
1935. THE PHYSIOLOGICAL FORMS OF THE EUCALYPTS AS DETERMINED BY THE CHEMICAL COMPOSITION OF THE ESSENTIAL OILS AND THEIR INFLUENCE ON THE BOTANICAL NOMENCLATURE. Australasian Jour. Pharm. 16: 168-171.
- (125) ———
1950. AUSTRALIAN EUCALYPTUS OILS. In Guenther's "The essential oils," 4: 437-482.
- (126) RAU, SANJIVA B., AND SIMONSEN, JOHN LIONEL.
1925. THE OCCURRENCE OF SYLVESTRENE. [London] Chem. Soc. Jour. 127: 2494-2499.

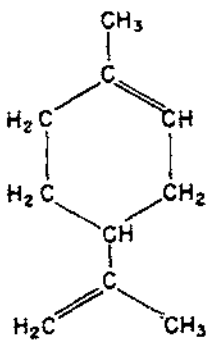
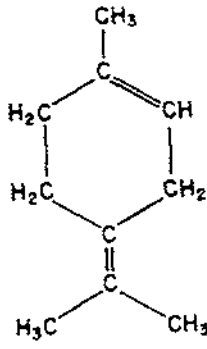
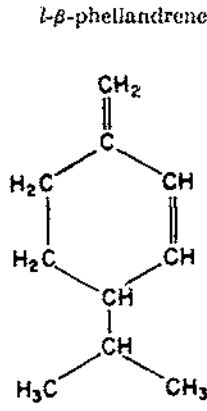
- (127) RICHMOND, G. F.
1909. PHILIPPINE TURPENTINE. *Philippine Jour. Sci.* 4: (a) 231-232.
- (128) RICHTER, F. I.
1915. PINUS: THE RELATIONSHIP OF SEED SIZE AND SEEDLING SIZE TO INHERENT VIGOR. *Jour. Forestry* 43: 134-137.
- (129) ——— AND DUFFIELD, J. W.
1951. HYBRIDS BETWEEN PONDEROSA AND APACHE PINE. *Jour. Forestry* 49: 345-9.
- (130) RUZICKA, L., AND MEYER, JULES.
1921. UBERFUHRUNG DES CADINENS IN EINEN NAPHTALINCOHLENWASSERSTOFF. *Helvetica Chim. Acta.* 4: 505-510.
- (131) RYDBERG, P. A.
1922. FLORA OF THE ROCKY MOUNTAINS AND ADJACENT PLAINS. Ed. 2. 1110 pp. New York.
- (132) SCHKATELOFF, M. W.
1908. SUR LES PROPRIÉTÉS DE LA RÉSINE DES DIFFÉRENTS CONIFERES. *Mon. Sci. Doct., Quesneville* 22: 217-227.
- (133) SCHEUBLE, RUDOLF.
1942. DIE UNGEWÖHNLICHE ZUSAMMENSETZUNG DER TERPENTINÖLE VON PINUS SABINIANA UND JEFFREYI. Ein Beitr. z. Klärung des Gegenstandes. *Centbl. f. das Gesam. Forstw.* 58: 64-69.
- (134) SCHIMMEL AND CO.
1915. REPORT. Oct. 1914-April 1915. 45 pp.
- (135) SCHORGER, A. W.
1913. THE OLEORESIN OF JEFFREY AND SINGLELEAF PINES. *Indus. Engin. Chem.* 5: 971-973.
- (136) ———
1913. AN EXAMINATION OF THE OLEORESINS OF SOME WESTERN PINES. U.S. Dept. Agr. Forest Serv. Bul. 119, 36 pp.
- (137) ———
1915. THE OLEORESIN OF SAND PINE. *Indus. Engin. Chem.* 7: 321-322.
- (138) ———
1916. CHEMISTRY AS AN AID IN THE IDENTIFICATION OF SPECIES. *Soc. Amer. Foresters Proc.* 11: 33-39.
- (139) SCHWERDTFEGER, FRITZ.
1953. LOS PINOS DE GUATEMALA. Informe FAO/ETAP 202, 68 pp., illus. Rome.
- (140) SEMMLER, F. W., AND VON SCHILLER, H.
1927. BEITRÄGE ZUR KENNTNISS DES ÄTHERISCHEN ÖLES AUS DEN KIEFERNSTÄMMEN UND WURZELN VON PINUS SILVESTRIS (KIEFERNWURZELÖL) UND SEIN VERGLEICH MIT STAMMUND NADELÖLEN DIESER PINUS-ART. *Ber. der Deut. Chem. Gesell.* 60: 1591-1607.
- (141) SHAW, GEORGE RUSSELL.
1909. THE PINES OF MEXICO. *Arnold Arboretum Pub.* 1, 29 pp., illus.
- (142) ———
1914. THE GENUS PINUS. *Arnold Arboretum Pub.* 5, 96 pp., illus.
- (143) SHAW, A. C.
1951. THE ESSENTIAL OIL OF TSUGA CANADENSIS (L.) Carr. *Amer. Chem. Soc. Jour.* 73: 2859-2861.
- (144) SHEPPARD, NORMAN, AND SIMPSON, DELIA M.
1952. THE INFRA-RED AND ROMAN SPECTRA OF HYDROCARBONS. Pt. 1. ACETYLENES AND OLEFINS. [*London*] *Chem. Soc. Quart. Rev.* 6: 1-33.
- (145) SHINOSAKI YEINOSUKE.
1919. ESSENTIAL OIL OF PINUS THUNBERGH PARL. *Chem. Soc. Japan Jour.* 21: 31-33; 22: 451-454.
- (146) ——— AND TETSUJI ONO.
1920. CHINESE PINE RESIN AND ITS ESSENTIAL OIL. *Chem. Soc. Japan Jour.* 23: 45-56.
- (147) SIMONSEN, JOHN LIONEL, AND MADYAR GOPAL RAJ.
1922. THE ESSENTIAL OIL FROM THE OLEORESIN OF PINUS KHASYA. *Indian Forest Rec.* 9 (Pt. 4): 112-115.
- (148) ———
1922. THE ESSENTIAL OIL FROM THE OLEORESIN OF PINUS GERARDIANA WALL. *Indian Forest. Rec.* 9 (Pt. 4): 345-348.

- (149) SIMONSEN, JOHN LIONEL, AND MADYAR GOPAL RAU.
1923. THE CONSTITUENTS OF SOME ESSENTIAL OILS. PT. 12. THE ESSENTIAL OIL FROM THE OLEORESIN OF *PINUS MERKUSII*. Indian Forest Rec. 10 (Pt. 4): 51-57.
- (150) ——— AND OWEN, L.
1947-57. THE TERPENES. Ed. 2, rev. 5 v. (Ed. 1 [2 v.] by Simonsen alone, pub. 1931-32.)
- (151) ——— AND MADYAR GOPAL RAU.
1922. THE ESSENTIAL OIL FROM OLEORESIN OF *PINUS EXCELSA*. Indian Forest Rec. 9 (Pt. 4): 116-122.
- (152) ——— AND MADYAR GOPAL RAU.
1920-23. THE CONSTITUENTS OF INDIAN TURPENTINE FROM *PINUS LONGIFOLIA ROXB.* [London] Chem. Soc. Jour. Pt. 1. 117: 570-578 (1920); Pt. 2. 123: 549-560 (1923); Pt. 3. 123: 2642-2666 (1923).
- (153) SPOON, W., JR.
1930. ATJER-TERPENTIJN. TEGENWOORDIGE KWALITEITEN EN NIEUWE BEORDEELINGEN BERICHTEN VAN DE AFDELING HANDELSMUSEUM VAN DE KON. Ver. Kolon. Inst. 57, 30 pp. Amsterdam.
- (154) STANDLEY, PAUL CARPENTER.
1920-25. TREES AND SHRUBS OF MEXICO. U.S. Natl. Mus. Contrib. U.S. Natl. Herbarium 23: Pts. 1-5 (1920-25); Pt. 1 (1920).
- (155) STEPHAN, KAHL.
1900. UEBER SÜESSES PONERANZEN-SCHALENOL. Jour. f. Prat. Chem. 62: 523-535.
- (156) SUDWORTH, GEORGE B.
1917. PINE TREES OF THE ROCKY MOUNTAIN REGION. U.S. Dept. Agr. Bul. 460: 33-35.
- (157) SUTHERLAND, MAURICE D.
1948. A REVIEW OF THE DENSITIES AND REFRACTIVE INDICES OF THE TERPENES. Queensland Univ. Papers, Dept. Chem. 1, 34: 1-21.
- (158) ——— AND WELLS, J. W.
1956. A REEXAMINATION OF INDIAN AND LOBLOLLY TURPENTINES. Jour. Organic Chem. 21: 1272-1276.
- (159) ——— AND WILSON, MISS S. J.
1950. THE PHYSICAL PROPERTIES OF PURE TERPENES. PT. I. MYRCENE. Queensland Univ. Papers, Dept. Chem. 1, 38: 1-3.
- (160) UHL, ARTHUR H.
1935. NON-HEPTANE CONSTITUENTS OF DIGGER PINE (*PINUS SABINIANA*). Amer. Pharm. Assoc. Jour. 24: 380-382.
- (161) U.S. FOREST SERVICE, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AND BUREAU OF PLANT INDUSTRY.
1935. A NAVAL STORES HANDBOOK DEALING WITH THE PRODUCTION OF PINE GUM OR OLEORESIN. U.S. Dept. Agr. Misc. Pub. 209, 201 pp., illus.
- (162) VEZES, M., AND DUPONT, G.
1922. LES CONSTITUANTS DE LA GEMME DE PIN D'ALEP. Chem. et Indus. 8: 318-319.
- (163) VOGEL, A. I.
1948. A TEXTBOOK OF ORGANIC CHEMISTRY. 1012 pp. New York.
- (164) WEBB, A. DINSMOOR, KEFNER, RICHARD E., AND IKEDA, ROBERT.
1952. COMPOSITION OF TYPICAL GRAPE BRANDY FUSEL OIL. Analyt. Chem. 24: 1944-1949.
- (165) WENZEL, W. T.
1872. ABIEtene, A NEW HYDROCARBON. Amer. Jour. Pharm. 44: 97-100.
- (166) ZOBEL, BRUCE JOHN.
1951. THE NATURAL HYBRID BETWEEN COULTER AND JEFFREY PINES. Evolution 5: 405-413.

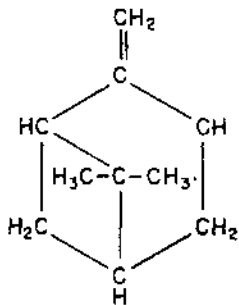
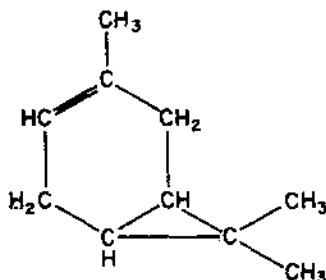
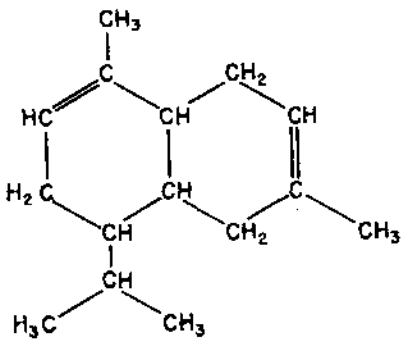
Appendix 1

CHEMICAL COMPOUNDS FOUND IN PINE GUM TURPENTINES

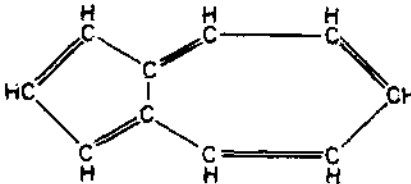
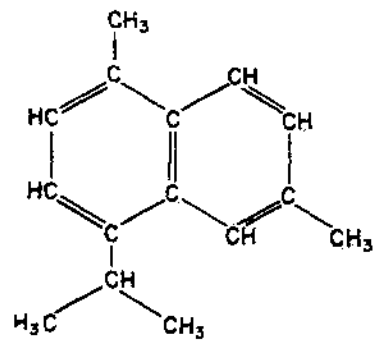
Compound	Pine in which found, by number as listed in text
<i>Paraffin hydrocarbons</i> (C_nH_{2n+2}): <i>n</i> -heptane (C_7H_{16})	7, 9, 14, 32, 33 (less than 0.1 percent), 347, 35, 36, 65 (possibly as a result of hybridization)
An unidentified nonane (C_9H_{20}) <i>n</i> -undecane ($C_{11}H_{24}$)	33 (less than 0.1 percent) 1, 7, 8, 13, 14, 33, 34, 36, 54 (one variety)
<i>Aromatic hydrocarbons</i> <i>p</i> -cymene ($C_{10}H_{14}$)	42, 61 (by ultraviolet absorption only; minute quantities)
	
<i>Olefinic open chain terpenes</i> (C_nH_{2n-4}): β -myrcene ($C_{10}H_{16}$)	12, 21, 42, 51, 54, 61, 79
	
Ocimene ($C_{10}H_{16}$)	21, 22; 23 (possibly)
	

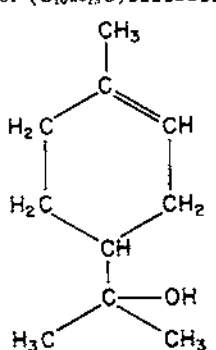
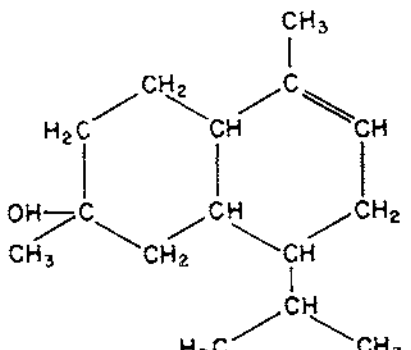
Compound	Pine in which found, by number as listed in text
<p><i>Monocyclic terpenes:</i> Limonene (C₁₀H₁₆) Predominantly <i>l,dl</i>-----</p>	<p>1, 3, 8, 14, 18, 20, 21, 23, 24, 26, 27, 29, 30, 31, 33, 36, 41, 42, 45, 52, 54, 61, 65, 67, 70, 75, 77, 85, 86, 87</p>
<p><i>d,dl</i>----- <i>dl</i>-limonene (dipentene)-----</p> 	<p>38, 82 44, 45, 46, 51, 56, 57 and 59 (in tails), 68, 73 (possibly)</p>
<p>Terpinolene (C₁₀H₁₆)-----</p>	<p>9, 12, 21, 26, 42, 54, 57 (in tails), 73, 76, 80</p>
	<p>34, 37 (possibly), 42 (rarely), 44 (possibly), 48, 54 (possibly), 58, 60, 89, 91</p>
<p><i>l</i>-β-phellandrene (C₁₀H₁₆)-----</p> 	

Compound	Pine in which found, by number as listed in text
<p><i>Bicyclic terpenes:</i> α-thujene ($C_{10}H_{16}$)</p>	<p>26 (minute quantity); suspected by Sutherland in 92 (personal communication)</p>
<p>Camphene ($C_{10}H_{16}$)</p>	<p>8, 42 (rarely), 51, 84, 94 (trace)</p>
<p>α-pinene ($C_{10}H_{16}$)</p>	<p>In all pines except 5, 31, 32, 33, 35, 56; 74 has not been investigated.</p>

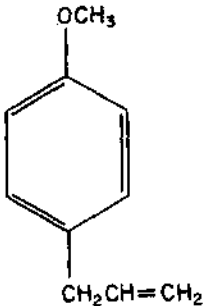
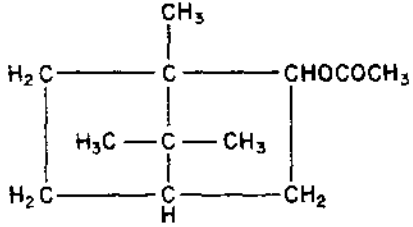
Compound	Pine in which found, by number as listed in text
<p><i>Bicyclic terpenes</i>—Continued β-pinene (nopinene) ($C_{10}H_{16}$)-----</p> 	<p>1, 2, 3, 4, 8, 10, 12, 14, 15, 16, 17, 18, 25 (possibly), 26, 29, 37 (possibly), 38 (possibly), 40, 42, 43, 44, 47, 48, 49, 51, 53 (probably), 54, 55, 56, 57, 59, 60, 61, 62, 66, 68, 69, 70, 71, 73, 75, 76, 79, 80, 82, 84, 85, 87, 88, 90, 91, 94</p>
<p>Δ^3-carene ($C_{10}H_{16}$)—always in a d-form-----</p> 	<p>1, 3, 4, 5, 7, 21, 26, 28, 42, 47, 54, 55, 56, 58, 63, 67, 73, 76, 80, 81 NOTE: Δ^4-carene was suspected, but not positively identified in turpentine of <i>P. oocarpa</i> var. <i>trifoliata</i>, No. 78</p>
<p><i>Sesquiterpenes</i> ($C_{15}H_{24}$): Cadinene and cadinenelike sesquiterpenes, yielding crystalline cadinene dihydrochloride m.p. 117.5°–118.5° C.</p>	<p>5, 7 (possibly), 8, 11, 14?, 21, 22, 23, 42 (possibly), 54, 66, 82 (reported as isocopaene)</p>
 <p>Cadinene (according to Campbell and Soffer)</p>	

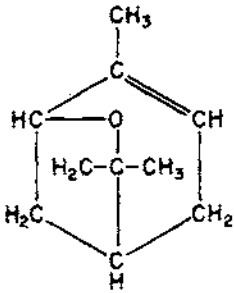
Compound	Pine in which found, by number as listed in text
<i>Sesquiterpenes (C₁₅H₂₄)—Continued</i>	
<p>Cadinene dihydrochloride (according to Soffer) Reference: Guenther (50, v. 2, p. 91)</p>	
<p>Longifolene (C₁₅H₂₄), always in dextro-rotatory form</p>	<p>1, 20, 26, 29, 30, 33, 36, 41, 45, 46, 47, 49, 54, 58, 63, 64, 67, 70, 71, 76, 77, 78, 82, 91</p>
<p>(After Ghatgey and Bhattacharyya, 50)</p>	
<i>Caryophyllene (C₁₅H₂₄)</i> -----	82
<i>Albicaulene (C₁₅H₂₄)</i> -----	5, 6, 11
<i>Canadene (C₁₅H₂₄)</i> -----	Suspected in 21
<i>Sesquiterpenes that yielded crystalline hydrochlorides, and m.p. of hydrochloride (°C.)</i>	
A bicyclic sesquiterpene, 47°-49°-----	48, 75
A bicyclic sesquiterpene, 67°-68.5°-----	24, 31
A monocyclic sesquiterpene, possibly bisabolene, 75°-79°-----	14
A tricyclic sesquiterpene, 80°-80.5°-----	19
A bicyclic sesquiterpene, 85°-87°-----	8
A bicyclic sesquiterpene, 107°-108°-----	9, 11
Possibly endinene, 117°-----	14
A monocyclic sesquiterpene, 120°-130°-----	54

Compound	Pine in which found, by number as listed in text
<i>Sesquiterpenes, which upon dehydrogenation gave azulene (C₁₅H₁₀)</i>	11
<i>Azulenelike sesquiterpene</i> -----	82
	
Parent substance of azulenes, a bicyclic hydrocarbon C ₁₀ H ₈ See Guenther (59, v. 2, p. 128)	
<i>Unidentified sesquiterpenes whose hydrochlorides were not prepared</i>	17, 27, 37, 53, 56, 70, 80, 86, 90
<i>A tricyclic sesquiterpene with one double bond</i> -----	15
<i>A tricyclic sesquiterpene with one double bond, possibly aromadendrene</i>	18
<i>A bicyclic sesquiterpene of unknown structure</i> -----	6, 13
<i>Sesquiterpenes of the cadalene type (i.e., those which on dehydrogenation gave cadalene, C₁₅H₁₀)</i>	6, 8, 10, 12, 22
	
Cadalene See Guenther (59, vol. 2 p. 82)	
<i>Diterpenes:</i>	
<i>Cembrene</i> -----	1, 5, 8, 12
<i>A diterpene forming a maleic anhydride adduct of m.p. 148°-149° C.</i>	1
<i>An unidentified diterpene</i> -----	10

Compound	Pine in which found, by number as listed in text
<p><i>Aliphatic terpene alcohols:</i> $C_{10}H_{18}O$ Linalool (3,7-Dimethyl-1, 6-octadien-3-ol)-----</p> $\begin{array}{c} H_3C \\ \diagdown \\ C=CH-CH_2-CH_2-C-OH \\ \diagup \\ H_3C \end{array} \begin{array}{c} OH \\ \\ CH_3 \end{array} \begin{array}{c} CH=CH_2 \end{array}$ <p>For details see Guenther (59, v. 2, p. 167)</p>	73, 32 (possibly).
<p>Nerol (2, 6-dimethyl-1, 6-octadien-8-ol)-----</p> $\begin{array}{c} H_2C \\ \diagdown \\ C-CH_2-CH_2-CH_2-C-CH_3 \\ \diagup \\ H_3C \end{array} \begin{array}{c} HO-H_2C-C-H \\ \\ O \end{array}$ <p>For details see Guenther (59, v. 2, p. 174)</p>	41
<p><i>Cyclic terpene alcohols:</i> α-terpineol ($C_{10}H_{18}O$)-----</p> 	Reported in 13.
<p><i>Sesquiterpene alcohols:</i> Cadinol ($C_{15}H_{26}O$)----- Albicaulol ($C_{15}H_{26}O$)-----</p>	82 (very little) 5, 8, (and probably in 10 reported as lambertol)
	
<p>Structural formula of albicaulol (δ-cadinol or pilgerol) according to Prof. William G. Dauben (see footnote 8, p. 34).</p>	

Compound	Pine in which found, by number as listed in text
<i>A sesquiterpene alcohol, m.p. 133° C.</i> -----	10
<i>A sesquiterpene alcohol</i> -----	71 (possibly)
<i>Diterpene alcohols</i>	
<i>A diterpene alcohol</i> -----	12 (possibly)
<i>Aliphatic aldehydes:</i>	
Octyl $\text{CH}_3(\text{CH}_2)_6\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{C} \\ \text{=O} \end{array}$	32
Nonyl $\text{CH}_3(\text{CH}_2)_7\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{C} \\ \text{=O} \end{array}$	32
Deoyl $\text{CH}_3(\text{CH}_2)_8\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{C} \\ \text{=O} \end{array}$	32, 33, 34 (possibly)
Laural (<i>n</i> -dodecyl) $\text{CH}_3(\text{CH}_2)_{10}\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{C} \\ \text{=O} \end{array}$	33, 35 (possibly), 44
Citronellal	
$\begin{array}{c} \text{H}_2\text{C} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H}_3\text{C} \end{array} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{C} \\ \text{=O} \end{array}$	32 (possibly)
For details see Guenther (59, v. 2, p. 336)	
<i>Unidentified C₁₀ carbonyl compound</i> -----	33 (traces)
Myristyl (tetradecyl) $\text{CH}_3(\text{CH}_2)_{12}\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{C} \\ \text{=O} \end{array}$	35
<i>Ketones:</i>	
Unidentified ketones 1 or 2 percent-----	15
An unidentified C ₁₀ carbonyl compound, probably a ketone	33
A sesquiterpene ketone apparently with a sesquiterpene aldehyde	89
<i>Unidentified oxygenated compounds</i> -----	1, 9, 15, 21, 50

Compound	Pine in which found, by number as listed in text
<i>Phenol ethers</i> Methyl eubaycol $C_{10}H_{12}O$	30, 32, 54, 57 and 59 (in tails),
	60, 61, 67, 70, 73 (possibly), 91
<i>Aliphatic esters</i> Ethyl caprylate $C_7H_{14}-CO-O-C_2H_5$	21
<i>Terpene esters:</i> Bornyl formate $C_{11}H_{18}O_2$	27
Bornyl acetate $C_{12}H_{20}O_2$	1, 8, 12, 14, 18, 45, 57 (in tails)
 <p style="text-align: center;">Bornyl acetate</p>	
α -terpinyl acetate $C_{10}H_{17}-O-CO-CH_3$	5

Compound	Pine in which found, by number as listed in text
<p><i>Oxides</i></p> <p>Small quantities of pinol ($C_{10}H_{16}O$) and pinol hydrate were reported by Dupont in No. 82. It appears, however, that the oxide and its hydrated form are secondary products formed by oxydation of terpenes and not found in the freshly distilled material.</p> <div style="text-align: center;">  </div> <p>Reference: Guenther (59, v. 2, p. 713)</p>	82

Appendix 2

INDEX—BOTANICAL AND COMMON NAMES OF PINE SPECIES MENTIONED IN THIS REPORT

<i>Botanical name</i>	<i>Common name</i>	<i>No.</i>	<i>Page</i>
<i>P. albicaulis</i>	Whitebark pine	5	33
<i>P. apachea</i> = <i>engelmanni</i>	Apache pine	71	105
<i>P. aristata</i>	Bristlecone pine	19	50
<i>P. arizonica</i>	Arizona var. of ponderosa pine	55	92
<i>P. armandi</i>	Armand pine	8	36
<i>P. attenuata</i>	Knobcone pine	93	125
<i>P. ayacahuite</i>	Mexican white pine	9	38
<i>P. halfouriana</i>	Foxtail pine	18	49
<i>P. banksiana</i>	Jack pine, Banks pine	88	116
<i>P. bolanderi</i> = <i>contorta</i>	Lodgepole pine	89	117
<i>P. brutia</i>	Calabrian pine	80	111
<i>P. bungeana</i>	Lacebark pine	16	47
<i>P. canariensis</i>	Canary pine	27	58
<i>P. caribaea</i>	Slash pine	58	94
<i>P. cembra</i>	Swiss stone pine	2	30
<i>P. cembroides</i>	Mexican pinyon	20	52
<i>P. chihuahuana</i>	Chihuahua pine	29	59
<i>P. clausa</i>	Sand pine	84	114
<i>P. contorta</i>	Lodgepole pine	89	117
<i>P. cooperi</i>	Pino amarillo (Durango)	69	104
<i>P. coronans</i> (var. of <i>P. sibirica</i>)	Locally known as Siberian cedar	3	31
<i>P. coulteri</i>	Coulter pine	34	66
<i>P. cubensis</i> (see <i>P. occidentalis</i>)	Cuban pine	74	107
<i>P. densata</i> (see <i>P. tabulaeformis</i>)	Possibly a hybrid	53	86
<i>P. densiflora</i>	Japanese red pine, Akamat- su	40	72
<i>P. durangensis</i>	Pino real (Durango)	66	100
<i>P. echinata</i>	Shortleaf pine	62	97
<i>P. edulis</i>	Pinyon	21	52
<i>P. elliottii</i> var. <i>elliottii</i>	Slash pine	59	95
<i>P. elliottii</i> var. <i>densa</i>	So. Florida slash pine	60	96
<i>P. engelmannii</i>	Apache pine	71	105
<i>P. excelsa</i> (see <i>P. griffithii</i>)	Himalayan pine	13	44
<i>P. fenzliana</i>	Closely related to <i>P.</i> <i>kwantungensis</i>	---	---

Botanical name	Common name	No.	Page
<i>P. flexilis</i>	Limber pine	6	34
<i>P. formosana</i>	A variety of or closely related to <i>P. parviflora</i>	---	---
<i>P. gerardiana</i>	Chilghosa pine	17	48
<i>P. glabra</i>	Spruce pine	75	107
<i>P. greggii</i>	Gregg pine—Pino prieto	90	120
<i>P. griffithii</i>	Himalayan pine	13	44
<i>P. halepensis</i>	Aleppo pine	79	109
<i>P. hartwegii</i>	Hartweg pine	67	102
<i>P. heldreichii</i>	Heldreich pine	52	84
<i>P. hwangshanensis</i>	Hwangshan pine	46	79
<i>P. insignis</i> (see <i>P. radiata</i>)	Monterey pine	94	126
<i>P. insularis</i>	Luzon pine	48	81
<i>P. jeffreyi</i>	Jeffrey pine	32	62
<i>P. khasya</i>	Khasya pine	49	82
<i>P. koraiensis</i>	Korean pine	1	28
<i>P. kwangtungensis</i>	A little-known white pine of S.W. China	---	---
<i>P. lambertiana</i>	Sugar pine	10	39
<i>P. laicio</i> (see <i>P. nigra</i>)	Austrian pine	51	83
<i>P. lawsonii</i>	Lawson pine	63	98
<i>P. leiophylla</i>	Pino chino (Michoacán); in U.S., it is called chihua-hua pine	28	58
<i>P. leucodermis</i> (see <i>P. heldreichii</i>)	Palebark pine	52	84
<i>P. longifolia</i>	Chir pine	26	56
<i>P. luchuensis</i>	Luchu pine, Okinawa pine	44	78
<i>P. lumholtzii</i>	Lumholtz pine, Pino triste (Durango)	30	60
<i>P. massoniana</i>	Masson pine	39	70
<i>P. merkusii</i>	Merkus pine, Tenasserim pine	47	79
<i>P. michoacana</i>	Michoacán pine, Pino lacio	70	104
<i>P. monophylla</i>	Singleleaf piñon	23	55
<i>P. montana</i>	Swiss mountain pine	43	76
<i>P. montezumae</i>	Montezuma pine	65	99
<i>P. monticola</i>	Western white pine	14	45
<i>P. morrisonicola</i>	A Formosan pine, related to <i>P. parviflora</i>	---	---
<i>P. muricata</i>	Bishop pine	92	125
<i>P. murrayana</i> (see <i>P. contorta</i>)	Lodgepole pine	89	117
<i>P. nelsonii</i>	Nelson pine	25	56
<i>P. nigra</i>	Austrian pine	51	83
<i>P. oaxacana</i>	Oaxaca pine	36	67
<i>P. occidentalis</i>	Cuban pine	74	107
<i>P. oocarpa</i>	-----	77	108
<i>P. oocarpa</i> var. <i>trifoliata</i>	-----	78	109
<i>P. palustris</i>	Longleaf pine	57	94
<i>P. parviflora</i>	Japanese white pine, Hime-komatsu	11	40

Botanical name	Common name	No.	Page
<i>P. patula</i>	Jelicote pine	91	121
<i>P. pentaphylla</i>	A variety of <i>P. parviflora</i> , Goyomatsu	11	40
<i>P. peuce</i>	Balkan white pine	12	42
<i>P. pinaster</i>	Cluster pine (Pin maritime)	82	112
<i>P. pinceana</i>	Pince's pine	24	55
<i>P. pinea</i>	Italian stone pine	31	60
<i>P. pityusa</i>	Pitsunda pine	81	112
<i>P. ponderosa</i>	Ponderosa pine	54	87
<i>P. pringlei</i>	Pringle pine	76	107
<i>P. pseudostrobus</i>	False Weymouth pine is a book name. Very mis- leading. Locally this pine is known under many different names. In Central America and adjacent parts of Mexico it is called pinabete, a name generally used for fir (<i>Abies</i>).	72	105
<i>P. pumila</i>	Japanese stone pine	4	31
<i>P. pungens</i>	Table-Mountain pine	87	116
<i>P. quadrifolia</i>	Parry pinyon	22	54
<i>P. radiata</i>	Monterey pine	94	126
<i>P. reflexa</i>	-----	7	35
<i>P. resinosa</i>	Norway pine	37	69
<i>P. rigida</i>	Pitch pine	85	114
<i>P. rudis</i>	-----	68	103
<i>P. sabiniana</i>	Digger pine	35	66
<i>P. serotina</i>	Pond pine	86	115
<i>P. sibirica</i>	Siberian white pine (Sibe- rian cedar)	3	31
<i>P. strobus</i>	Eastern white pine	15	46
<i>P. sylvestris</i>	Scots (Scotch) pine ("Com- mon pine" of Europe)	42	73
<i>P. tabulaeformis</i>	Chinese pine	53	86
<i>P. taeda</i>	Loblolly pine	61	96
<i>P. taiwanensis</i>	Formosa pine	45	78
<i>P. tenuifolia</i>	-----	73	106
<i>P. teocote</i> ¹	Teocote, Octoe, Aztec pine (U.S.)	64	99
<i>P. thunbergii</i>	Japanese black pine	41	72
<i>P. torreyana</i>	Torrey pine	33	64
<i>P. tropicalis</i>	-----	38	70
<i>P. virginiana</i>	Virginia pine	83	114
<i>P. washoensis</i>	Washoe pine	56	93
<i>P. yunnanensis</i>	Yunnan pine	50	83

¹ Teocote is an Aztec word meaning "Pine of the Gods." Only the Aztec nobles were permitted to use the resin of this pine for incense in worship.

Appendix 3

GLOSSARY OF SOME TERMS USED IN THE TEXT

Most of the terms used in commercial turpentine production in the United States are explained in "Standard Definitions of Terms Relating to Naval Stores and Related Products," issued by the American Society for Testing Materials under "ASTM designation D804-52." The ASTM definitions are generally followed in this glossary, except where a definition suitable for use in the Naval Stores industry cannot be extended to all species of pine. An example is the ASTM definition of turpentine as "The volatile oil consisting primarily of a number of terpene hydrocarbons"; some pine turpentines do not contain any terpenes at all. Also, where a reader could be confused by ambiguous or erroneous definitions of terms found in some dictionaries, the author has considered it necessary to explain the discrepancies. For instance, there is a great difference between the crude turpentine and the sap of trees.

Abietene. Proprietary name of *Pinus jeffreyi* turpentine. It consisted of *n*-heptane with an admixture of aliphatic aldehydes.

Balsam. A viscous substance obtained from many different plants; sometimes a synonym of oleoresin (which see). This name should not be used to designate pine oleoresins.

Composite sample of turpentine. Obtained from not one but several trees.

Face. A part of a pine trunk from which the bark only or bark and part of the sapwood is removed, and from which oleoresin exudes.

Gum. A commonly used name in trade for pine oleoresin that is obtained from a living tree or that exudes from a face. Chemically speaking it is a misnomer. True gums are composed of uronic acids and hexose or pentose.

The term gum is firmly established in American Naval Stores (which see) industry, as a synonym of oleoresin. The term is used in this sense by the author.

Gum turpentine. This term is used to distinguish the volatile oil obtained from oleoresin of pines from that distilled from wood or stumps. The oil is composed of different terpenes and sesquiterpenes, sometimes with admixture of nonterpene compounds. Gum turpentine of some pines consists of one terpene only, and in rare instances, pine gum turpentine does not contain terpenes at all. Although several different methods are used to obtain turpentine from oleoresin, the usual method is steam distillation.

In this publication gum turpentine or turpentine is used to designate the volatile part of pine oleoresin obtained by wounding the living tree.

J-line. (For jaune, i.e., yellow). A wave length of 578 m μ . "J-line" is used by French investigators in determining optical rotation of turpentine.

Naval stores. ASTM defines this term as "Chemically reactive oils, resins, tars, and pitches derived from oleoresin contained in, exuded, or extracted from trees, chiefly of the pine species (genus *Pinus*) or from the wood of such trees."

Naval Stores is an old colonial name for the resinous products of pines used in wooden ships of the British Royal Navy.

Oil of turpentine. A pharmaceutical name for turpentine. Sometimes used in old literature as a synonym of turpentine, especially when the term turpentine is used for oleoresin.

Oleoresin. In pines, oleoresin originates in living cells of the sapwood and flows from resin canals or ducts when these are severed. Commonly called gum, pitch, or even sap. (See Pitch.)

ASTM defines oleoresin as "pine gum, the nonaqueous secretion of resin acids dissolved in a terpene hydrocarbon oil which is (1) produced in or exuded from the intercellular resin ducts of a living tree, (2) accumulated, together with oxidation products, in the dead wood of weathered limbs and stumps."

It should be noted that "resin acids" are not always dissolved in "terpene hydrocarbon oil." Sometimes the solvents are other substances, such as paraffin hydrocarbons, *n*-heptane, and to a lesser degree *n*-undecane, and even benzene derivatives.

Pitch. Commonly a dark, viscous substance obtained as a residue by distilling wood tar or petroleum; also occurs naturally as asphalt. The name is occasionally used instead of oleoresin; hence—pitch pine.

Oxford University Dictionary, Ed. 3, 1955, defines pitch as "a tenacious resinous substance obtained as a residuum from the boiling of tar, also from distillation of turpentine" (they meant oleoresin).

The American College Dictionary (Harper, 1953) defines pitch as "any of various resins" and as "the *sap* (sic!) or crude turpentine which exudes from the bark of pines." (See Sap.)

ASTM restricts trade use of the term pitch to the "solidified material . . . obtained by distilling off . . . the volatile oil from a retort pine tar."

Resenes. ASTM defines the term "as applied to naval stores, those constituents of rosin which cannot be saponified with alcoholic alkali, but which contain carbon, hydrogen, and oxygen in the molecule." We found in several pines some unsaponifiable components of rosin which did not contain oxygen; such were diterpenes of pine Nos. 1, 5, 8, and 12. We discussed these as ingredients of the volatile part of oleoresin.

Resin. A generic name for many organic products, including oleoresin.

Rosin. ASTM definition of rosin is "a specific kind of natural resin obtained as a vitreous water insoluble material from pine oleoresin by removal of volatile oils." Rosin, thus, is the residue remaining in a pot after all or almost all of the turpentine and resenes have been removed. Rosin is composed chiefly of rosin acids, C₂₀H₃₀O₂,

possessing a decahydrophenantrene ring structure, and generally a small amount of unsaponifiable matter.

In some pines, rosin obtained by conventional steam distillation processes is very soft and tacky, and contains a large percentage of unsaponifiable substances. (*See Resenes.*)

Sap. Watery solution (juice) contained in plants. Popularly, any fluid secretion of plants. (*See Pitch*, as defined by the American College Dictionary.) The term sap should never be used to designate oleoresin or turpentine.

Spirits of turpentine. Pharmaceutical or trade name for turpentine. Same as oil of turpentine or turpentine (which see).

Sulfate wood turpentine. A product obtained in sulfate (kraft) pulping process. During digestion of pine pulp, the turpentine vaporizes and is collected.

Taxon (pl. taxa). A general term applied to any taxonomic element, population, or group irrespective of its classification level. (*See* George H. M. Lawrence, *Taxonomy of vascular plants*, footnote 8, p. 53, and p. 772. New York, 1951.)

Terebenthine. Obsolete name of oleoresin.

Terpene. The ASTM definition is "Unsaturated organic compound having the empirical formula $C_{10}H_{16}$, occurring in most essential oils and oleoresins of plants." Some pine turpentines do not contain terpenes, but such instances are rare.

Turpentine. Volatile oil obtained by distillation of either oleoresin (*see* Gum turpentine) or wood (*see* Wood turpentine).

Turpentine, Canada. Same as Canadian balsam (*see* Balsam).

Turpentine, crude. In European literature this term is sometimes used for oleoresin. In this publication the term crude turpentine is used for the volatile part of oleoresin previous to fractionation.

Turpentine, stump. *See* Wood turpentine.

Turpentine, sulfate. *See* Sulfate wood turpentine.

Wood turpentine. ASTM distinguishes three kinds: (1) "Steam distilled wood turpentine obtained from the oleoresin within the wood of pine stumps or cuttings, either by direct steaming of mechanically disintegrated wood or after solvent extraction of the oleoresin from the wood. (2) Sulfate wood turpentine recovered during the conversion of wood to paper pulp by the sulfate process. (3) Destructively distilled wood turpentine, obtained by fractionation of certain oils recovered by condensing the vapors formed during the destructive distillation of pine wood."

END