(74) McKee, R. H., and Salls, C. M., Ind. Eng. Chem., **16**, 279, 351 (1924).
(75) Marvel, C. S., and co-workers, *J. Am. Chem. Soc.*, **56**, 1815 (1934); **57**, 1691, 2311 (1935); **58**, 2047 (1936); **59**, 707, 1014 (1937); **60**, 1450, 2622 (1938); **61**, 1603, 2709, 2710, 2714 (1939).
(76) Mellor, J. W., "Treatise on Inorganic and Theoretical Chemistry", Vol. X, p. 657, London, Longmans, Green and Co., 1930.
(77) Meyer, R. F., U. S. Patent 1,730,584 (Oct. 8, 1929).
(78) Neumann, B., and Kunz, H., *Z. angew. Chem.*, **42**, 1085 (1929).
(79) *Oil, Paint, Drug Reptr.*, Dec. 15, 1941.
(80) Paine, H. S., Thurber, F. H., Balch, R. T., and Richee, W. R., Ind. Eng. Chem., **30**, 1331 (1938).
(81) Peniakoff, D. A., Brit. Patents 20,604 (1893); 22,037 (1895).
(82) Percival, J. O., Dyer, C. P., and Taylor, M. H., Ind. Eng. Chem., **33**, 1529 (1941).
(83) Powell, A. R., *Ibid.*, **31**, 795 (1939).
(84) Pratt, L. A., *Ibid.*, **16**, 676 (1924).
(85) Ralston, O. C., U. S. Bur. Mines, *Bull.* **260** (1927).
(86) Riess, German Patent 15,277.
(87) Rosebaugh, T. W., *Refiner Natural Gasoline Mfr.*, **17**, 245, 288 (1938).
(88) Ross, John, Percy, J. H., Brandt, R. L., Gebhart, A. I., Mitchell, J. E., and Yolles, Seymour, Ind. Eng. Chem., **34**, 924 (1942); Ross, Brandt, and Percy (to Colgate-Palmolive Peet Co.), U. S. Patent 2,245,721 (June 17, 1941).
(89) Ruff, O., *Ber.*, **34**, 3509 (1901).
(90) Seyer, W. F., and co-workers, *J. Am. Chem. Soc.*, **55**, 3140 (1933); **58**, 996 (1936); Ind. Eng. Chem., **29**, 91 (1937).
(91) Shatenshtein, A. I., and co-workers, *Acta Physicochim. U. S. S. R.*, **7**, 401, 883 (1937); *J. Phys. Chem.* (U. S. S. R.), **10**, 766 (1937), **11**, 18 (1938).
(92) Silberrad, C. A., *J. Soc. Chem. Ind.*, 45, 55 (1926).
(93) Smith, A. K., and Max, H. J., Ind. Eng. Chem., **34**, 817 (1942).
(94) Snow, R. D., and Frey, F. E., *Ibid.*, **30**, 176 (1938).
(95) Spangler, S. F., *Chem. & Met. Eng.*, 42, 139 (1935).
(96) Staudinger, M., and Ritzenthaler, B., *Ber.*, **68B**, 455 (1935).
(97) Terres, E., and Overdick, F., *Gas- u. Wasserfach*, **71**, 49, 81, 106, 130 (1928).
(98) Tomlinson, G. H. and Wilcoxson, L. S., *Paper Trade J.*, **110**, No. 15, 31 (1940).
(99) U. S. Dept. of Commerce, Biennial Census of Manufacturers, 1933–1939.
(100) U. S. Dept. of Interior, Minerals Yearbook, 1933–1941.
(101) Voss, W., and Blanke, E., *Ann.*, **485**, 258 (1931).
(102) Wardlaw, W., Carter, S. R., and Clews, F. H., *J. Chem. Soc.*, **117**, 1241 (1920).
(103) Waterman, H. I., and co-workers, *Verfkroniek*, **13**, 130, 180 (1940).
(104) Weeks, E. J., *Chem. News*, **144**, 50 (1932).
(105) Weidmann, H., and Roesner, G., *Metallges. Periodic Rev.*, No. 11 (1935).
(106) Weldon, W., Brit. Patent 134 (1867).
(107) Wells, A. E., U. S. Bur. Mines, *Bull.* **133**, (1917).
(108) Wickert, K., *Z. anorg. allgem. Chem.*, **239**, 89 (1938).
(109) Wickert, K., *Z. Electrochem.*, **44**, 410 (1928).
(110) Wood, W. R., and Storrs, B. D., *Refiner Natural Gasoline Mfr.*, **17**, 234 (1938).
(111) Wyld, W., "Raw Materials for Manufacture of Sulphuric Acid and Sulphur Dioxide", p. 436, London, Gurney and Jackson, 1923.
(112) Young, S. W., *Trans. Am. Inst. Chem. Engrs.*, **8**, 81 (1915).
(113) Yushkevitch, N. F., and co-workers, *J. Chem. Ind.* (U. S. S. R.), **8**, No. 1, 3; No. 2, 109; Nos. 11–12, 1053; No. 14, 1 (1931); **9**, No. 3, 17 (1932).
(114) *Ibid.*, **11**, No. 2, 33 (1934).
(115) Zawadski, J., Ostrouch S., and Kwiecinski, G., *Przemysl Chem.*, **22**, 558 (1938).

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Developments in Terpene Chemicals

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Turpentine and its related terpenes are the raw materials for a number of industrial chemicals. The manufacture of the better known products, such as terpineol and camphor, is reviewed. A number of new developments are described. These include the chemical separation of steam-distilled pine oil into its principal components anethole, camphor, fenchone, and terpineol, as well as the synthesis of pine oil from turpentine.

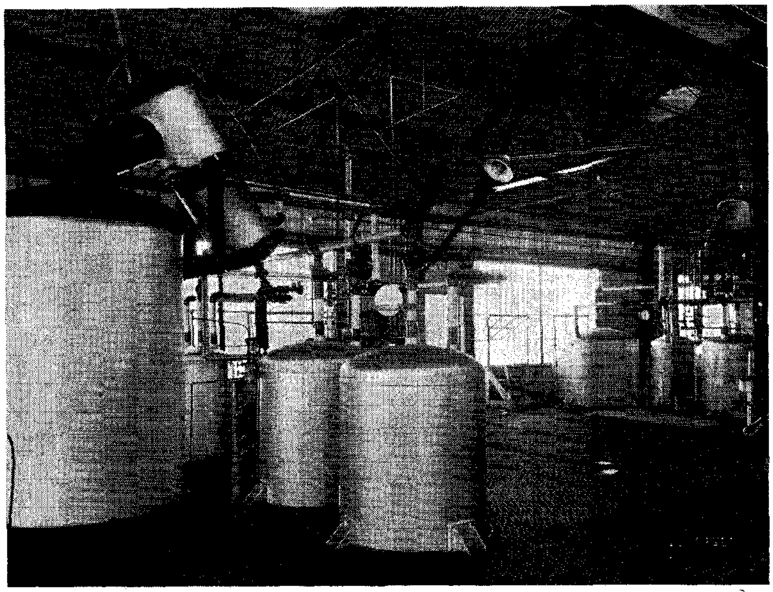
Terpene hydrocarbons are the raw materials for valuable resins. The monocyclic terpene hydrocarbons are also converted to *p*-cymene and *p*-menthane. Cymene is further processed to yield α-methyl-*p*-methylstyrene or its parent, carbinol, and the corresponding ketone. Cumic acid is a by-product. Isoprene will also be produced commercially from terpenes.

THE fact that the chemical literature on terpenes is voluminous is shown by the classical works of Semmler, Wallach, Gildermeister and Hoffman, the more modern books of Brooks or Parry, or, more recently and probably most comprehensive of all, Simonsen's two volumes and the numerous papers in current scientific journals of the world. The astonishing thing is that in this era of industrial chemistry the applied chemical reactions involving terpenes have been almost insignificant in relation to the data available.

There has been considerable speculation regarding the actual original chemical from which the terpenes are derived in plants. Read's theory (*16*) advanced in 1929 that geraniol, an unsaturated acyclic alcohol, is the plant parent of all terpenes is often quoted. Hall (*10*) elaborated on this a few years later and ingeniously showed that many of the exceptions to Read's theory could be explained if four theoretically possible glycols of geraniol were formed; he argued for this theory by counting the actual number of occurrences together in plants of the various groups that could be derived from any one of these glycols.

The most widely distributed of all the terpenes is α-pinene, and it is the one most abundantly recovered for industrial use as oil of turpentine. It is found in the wood of many coniferous trees although in widely varying amount. Wherever it is found in the wood, it is also always a substantial portion of the oleoresin produced in the pathological process of resin formation, as in the so-called chipping methods.

The value of turpentine as a solvent led to its widespread use, particularly in the manufacture of protective coatings. But even though the supply was plentiful and the product easy to obtain, there was no great incentive to find chemical uses for it. Lack of economic control of production led to widely fluctuating prices, and this condition was not encouraging to its use as a chemical raw material. Yet this lack of control of turpentine prices was finally the cause of sufficiently permanent prices at levels low enough to make turpentine an attractive chemical raw material. Each recurrent high price period introduced new and greater volumes of competitive cheaper substitutes, until even in low production years a surplus of turpentine was made. There was also another and an important factor that played its part in creating an additional supply of terpenes. This was the rapidly increasing production of turpentine and other terpenes from wood and wood waste during the last twenty-five years, not only from stumps and other wood waste by steam and solvent extraction processes but also the oils recovered as by-products from the kraft pulp mills.


Stills and Receivers for the Production of Camphor, Anethole, and Terpineol from Pine Oil

Synthetic Camphor

Probably the earliest effort to use turpentine for an industrial chemical process was in the manufacture of camphor. Brooks (*8*) states that the first commercial attempt to manufacture synthetic camphor from turpentine was at Niagara Falls in 1900. This process consisted of a fusion of the oil with oxalic acid to convert the pinene directly to bornyl oxalate and formate. The esters were saponified to give the secondary alcohol, borneol, and this was oxidized by chromic acid to camphor. Even though turpentine was then available at 35 cents a gallon, which had considerable influence on initiating this venture, it failed because of very low yield. Again, during the first World War an effort was made to solve this problem commercially. This was also a period of low-priced turpentine and high-priced natural camphor. In general, the process followed more nearly the classical synthesis. Pinene was converted to its hydrochloride which, on reaction with alkali, yielded camphene. The camphene was esterified with an organic acid, and the ester of borneol thus formed was hydrolyzed to obtain the borneol which, in turn, was oxidized to camphor. This process had more steps than the earlier Niagara plant, but the final oxidation was better controlled and the yields were notably higher. However, after the war ended, turpentine took one of its upward price surges, and coupled with ample supplies of cheap natural camphor at a price pegged by the Japanese Camphor Monopoly Board, the operation of this plant was stopped and was never resumed.

About 1931 one of the largest users of camphor (for celluloid and smokeless powder manufacture) again felt the desirability of being permanently independent of the Japanese monopoly, and synthetic camphor production was revived. Turpentine was again available at a reasonable cost and for the first time appeared to have a fair chance of continuing so. A great many details of the original synthesis were revised and perfected. Technically pure pinene became available for the first time which in itself meant higher yield. The final conversion step from borneol to camphor was replaced by a process that was a decided technical advance over the former methods. No very accurate figures are available, but it is a safe assumption that the use of chemically made camphor considerably exceeded the natural even before December 7, 1941. The availability of the technically pure α-pinene has more recently brought about another shortening of the process. It is understood that the direct production of camphene by the vapor-phase catalytic rearrangement of pinene is now entirely successful. This chemical use of α-pinene is apparently permanently established.

Terpineol from Pinene

One other chemical use for turpentine, known for many years, has been to a large extent independent of fluctuations in turpentine prices. This is the manufacture of the perfume base, terpineol. The process is a two-step synthesis. Pinene is first hydrated to terpinol hydrate, and the hydrate is gently dehydrated so as to stop at the tertiary alcohol, terpineol, instead of completing the dehydration to the monocyclic terpene hydrocarbons which readily occurs unless the reaction is carefully controlled. Actually the partial dehydration of the hydrate yields several isomeric alcohols which give the oil its fine lilac odor, although α-terpineol predominates.

Substantial amounts of terpineol are still made from turpentine, but a new source of this product was made available with the growth of the steam and solvent naval stores plants. The high-boiling oil naturally present in southern pine stumps, commonly known as steam-distilled pine oil, was found to contain a large amount of α-terpineol and was used for the recovery of this terpene alcohol as early as 1917–18. Steam-distilled pine oil has continued to be an important if not a principal source of the perfume grade terpineol, which is largely used as a soap fragrance. The chemical reactions involved are, in general, the same as those starting with turpentine, although the operating conditions in the first step are different. Terpineol is hydrated to terpinol hydrate and the solid hydrate is then dehydrated in exactly the same manner as in the process using pinene as the base.

Phytosynthesis of Pine Oil

The pine oil occurring in old pine stumps is an interesting mixture. It is a striking example of a natural essential oil whose constituents can probably be traced to a common parent, and which it has been possible to duplicate not only in the laboratory but also on a commercial scale. The synthesis of camphor from pinene through camphene and the esters of borneol normally produces only monocyclic terpene hydrocarbons as by-products. The direct conversion, however, of α-pinene as well as β-pinene to the bornyl ester of an organic acid is nearly always accompanied by the formation of the corresponding ester of fenchol, another secondary alcohol, in substantial amount. Monocyclic hydrocarbons are also produced. This is apparently exactly what happens in the processing that has taken place in the old wood of a pine stump, where the simple organic acids are the most probable reagents. Almost no trace of β-pinene remains, although large amounts of α-pinene are still present. β-Pinene would appear to be selectively reacted on but cannot be the sole source of all the products other than pinene. The beta isomer will not average more than 30 per cent of the total oil in oleoresin, while at least 50 per cent of the total oil recoverable by extraction of old wood is no longer pinene. Also, β-pinene is readily isomerized to the alpha form.

The composition of steam-distilled pine oil can be traced through several types of reaction. In one case there has probably been a selective hydration to isomeric tertiary alcohols (terpineols), with the α-terpineol predominating, apparently without going through the hydrate. At least terpinol hydrate has been found in old wood only rarely. The presence of the oxide, 1,4-cineole, however, indicates some hydration to terpinol hydrate, since this oxide has been produced only by the dehydration of terpinol. All of the isomeric monocyclic hydrocarbons, dipentene, the terpinenes, and terpinolene are present. They may have been formed either by the breaking of the inner ring of bicyclic pinene or by the complete dehydration of the tertiary alcohols. Another reaction may have produced the secondary alcohols borneol and fenchol, probably through their simple organic acid esters and subsequent hydrolysis, but no intermediate products are left to trace the exact course of the reaction with any degree of definiteness. Camphor is a positive constituent so the oxidation of one of the secondary alcohols must occur. The mechanism is unknown. The pine oil group of terpenes also includes a phenol ether, methylchavicol, which cannot be traced to pinene or any of its reaction products. Recent researches indicate a probable source of this terpene ether in the fragmentary degradation of lignin. The chemistry of the formation of pine oil as it occurs in the plant can, therefore, be rather well outlined in some such way.

Commercial Separation of Pine Oil Constituents

Pine oil is at present the commercial source of its main constituents. The tertiary alcohols are separated either as the α-terpineol or as the mixed alpha and other isomeric terpineols which have the fine floral essence that makes it of special value as a perfume base. α-Terpineol can be obtained by fractional crystallization (melting point, 35° C.), but to obtain commercially the perfume grade known as β-terpineol, the operation involves the complete hydration of the tertiary alcohol naturally present in the pine oil under carefully controlled conditions. Sulfuric acid is used as the catalyst. After the acid is removed, all of the pine oil not reacted on is separated from the terpinol hydrate by steam distillation; care must be taken to control the pH on the alkaline side during steaming. The conditions are then changed to the acid side, and the terpinol is dehydrated to a crude terpineol which is then carefully refined by severe fractional distillation over caustic alkali under very high vacuum (*2*). This yields the commercial β-terpineol.

The portion unaffected by hydration, which has been steam-distilled from the terpinol, is then treated with concentrated caustic at temperature conditions that will isomerize the phenol ether, methylchavicol, to its useful isomer, anethole (*3*). The boiling point of the ether is so near that of some of the alcohols it cannot be isolated by fractional distillation, but its isomer, anethole, boils about 18° C. higher and can, therefore, be easily separated in that way. The crude anethole is chemically treated to ensure the absence of phenols and is then redistilled under high vacuum to give the refined product (*4*). The aromatic chemical, anethole, has an extremely sweet licorice taste and is widely used as a flavor in confections and also in chewing tobacco.

The treatment so far described has in no way injured the two remaining components of the original pine oil that are of any commercial importance. These are the secondary alcohols, fenchol and borneol, which have now been recovered as a cut in the fractional distillation of anethole. They are, however, of value only as potential sources of their corresponding ketones. The next step in the process is their oxidation which is carried out as a liquid-phase atmospheric-pressure catalytic dehydrogenation (*5*). This is accomplished by boiling the oil under reflux with about 2 per cent by weight of nickel, or copper carbonate, or a mixture of the two for several hours.

The reaction must be and is 100 per cent of theoretical, since the secondary alcohols cannot be separated from the ketones by distillation. After the hydrogen is removed, the oil is distilled again under high vacuum, and pure fenchone is separated as the lower boiling fraction. The camphor cut may be somewhat less pure, as camphor is readily and finally purified to its U. S. P. specification melting point by fractional crystallization from alcohol. The camphor produced in this way from pine oil has a positive optical rotation, while synthetic camphor from pinene is optically inactive. The most probable cause of this difference is the presence of some natural camphor in pine oil which is recovered unchanged with the camphor synthesized from the borneol. The latest edition of the U. S. Pharmacopoeia modified its definition of synthetic camphor over earlier volumes as regards the optical properties because of this peculiarity of camphor derived from pine oil.

Synthetic Pine Oil from Turpentine

As long as a decade ago the producers of steam-distilled pine oil were engaged in intensive research to find outlets for this product. The successful separation into its ingredients or their more salable derivatives, just described, was one result of these studies. There were also several equally as successful and important developments. The chemistry of the pine oil as formed by nature from pinenes was, as previously mentioned, sufficiently understood in the laboratory, so it was not surprising that the commercial synthesis of pine oil from the pinenes was undertaken when the demand exceeded that being supplied from its normal sources. Pine oil made from turpentine is not a new development but has been made in substantial volume for several years. All reagents do not act exactly alike on terpenes, so it may be expected that synthetic pine oils may differ somewhat in their composition depending on the process employed. There are a number of possible reagents and considerable latitude of operating conditions from which a process may be selected.

Terpene Resins

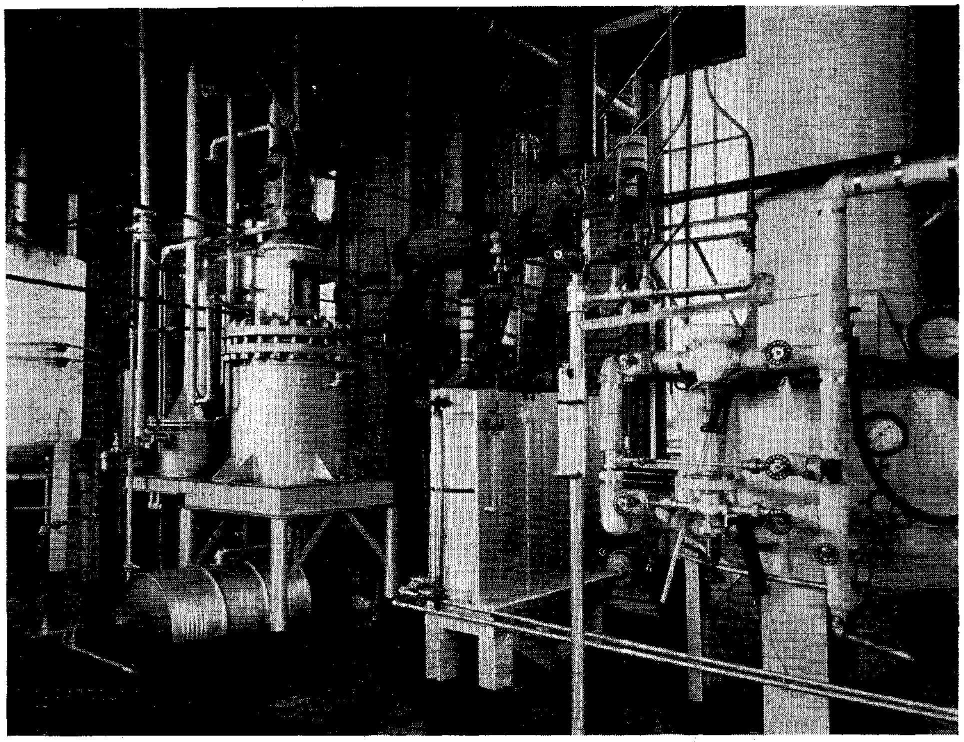
A more recent development utilizing bicyclic terpene hydrocarbons should be mentioned, as it may, conceivably, rank eventually with the leading chemical uses of turpentine. It has long been known that the unsaturated character of the terpenes lends itself readily to polymerization reactions as well as to condensations. There is a little patent literature on the subject, but outside of a paragraph or so in such works as Ellis' "Chemistry of Synthetic Resins", almost no mention is made of the possible formation of useful resins from terpenes. Such resins are now being made commercially and in rapidly increasing quantity. The processes are new and details have not been divulged.

Two types of resins are being made from terpenes. One is a substituted phenolic which, on condensation with formaldehyde, gives either thermosetting or thermoplastic resins of good melting point and excellent color stability, depending on how the aldehyde reaction is conducted. The other type, which is the more recent development and has perhaps the greatest possibility of growth, is a neutral hydrocarbon resin. This is obtained by catalytic polymerization. These resins are available in a range of melting point and color grades comparable to the older and somewhat better known cumar resins, but the terpene products seem to have somewhat greater usefulness. They not only have satisfactory initial color but good color stability. They are also soluble in a variety of solvents. Resins can be made from monocyclic terpene hydrocarbons as well as the bicyclic, but so far the pinenes seem to be preferred.

Monocyclic Terpene Hydrocarbons

The developments so far described have related almost entirely to the primary terpenes present in turpentine or pine oil—that is, the bicyclic pinenes and the tertiary and secondary terpene alcohols. There is, however, another group of terpenes obtainable from the dead wood. Their importance is greater when it is realized that these terpenes not only occur in the essential oils of many other plants than the pine tree, but can also be readily produced chemically from either pinene or terpineol. These are the various isomeric monocyclic hydrocarbons limonene or its optically inactive form dipentene, terpinolene, and the various terpinenes. Dipentene can be isomerized to terpinolene and terpinolene, in turn, to terpinene; there are many ways of accomplishing these rearrangements. It is often difficult to prevent the isomerization and to control it, and these structural changes are not reversible.

Until substantial amounts of these monocyclic hydrocarbons began to be produced by the extraction of pine wood waste, probably not enough was being recovered from the other essential oils to warrant concerted effort to find any uses for these terpenes, let alone chemical uses. As was only natural, the wood extraction industry was the first to undertake investigation of possible markets for these hydrocarbons, particularly as production increased. It was soon found that these oils possessed different and superior solvent properties compared to turpentine. This was happily coincident with a tremendous development in phenol-base varnish resins which were, in general, more difficultly soluble than those made from the oleoresinous bases. These terpenes had by then become known commercially as "dipentenes" (generally a misnomer chemically), and they found a ready sale because of their special solvent properties. Until recently there have been



Semicommercial Units in Terpene Chemical and Isoprene Development Laboratory

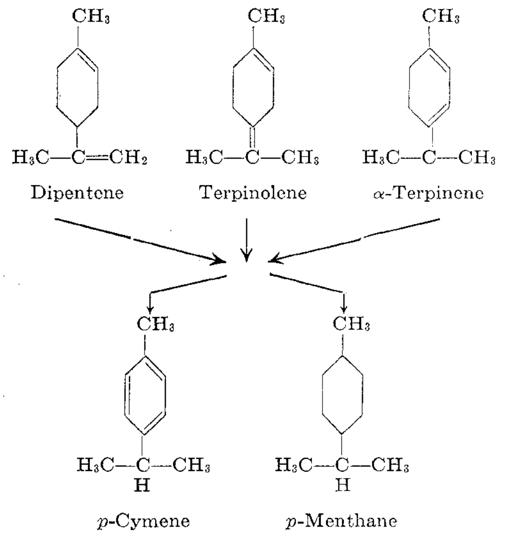


FIGURE 1. STRUCTURAL RELATIONS OF MONOCYCLIC TERPENES WITH p-CYMENE AND p-MENTHANE

	p-Cymene	p-Menthane
Specific gravity (15.5/4° C.)	0.8612	0.8130
Refractive index (20° C.)	1.4905	1.4480
Boiling range, ° C.	177–178	171–172

no real chemical developments that utilize the so-called, dipentenes.

p-Cymene and p-Menthane

The kinship of the $C_{10}H_{16}$ monocyclic terpene configuration to p-menthane $C_{10}H_{20}$, and also to the aromatic benzoid $C_{10}H_{14}$, more commonly known as cymene, can be readily seen. As early as 1909 limonene had been catalytically reduced to p-menthane. Both p-menthene, $C_{10}H_{18}$, and menthane, $C_{10}H_{20}$, have been identified in steam-distilled wood turpentine, and the presence of cymene is possible though not necessarily so. Cymene is also a by-product of the sulfite pulp process by dehydrogenation of the terpenes, and has been found in Swedish and Russian turpentine oils.

The benzene nucleus of p-cymene is suggestive of so many possible chemical derivatives that the conversion of the terpene hydrocarbons to cymene and its possible recovery in high technical purity at reasonable cost has been thoroughly studied. There are several references in the chemical literature to vapor-phase dehydrogenation of limonene or dipentene, but for the most part the decomposition is not readily controlled. Losses as tar may be excessive or the dehydrogenation is so incomplete that it is not possible to separate the cymene from unreacted terpenes without resorting to expensive additional steps. An entirely practicable method has now been developed, and any of the monocyclic terpene hydrocarbons may be used with equal success (*12*). Figure 1 shows the structural relation of the monocyclic terpene hydrocarbons with p-cymene and p-menthane. The process consists in a liquid-phase catalytic disproportionation at atmospheric pressure with practically 100 per cent theoretical yield.

The catalyst is copper-nickel formate with a metal ratio of three copper to one nickel, which is best prepared by reacting the metal carbonates with formic acid. The dried, powdered, mixed formate, equal to about 2 per cent by weight of the oil, is gradually fed into the boiling terpene hydrocarbon connected to a reflux condenser and a water trap. About 8 hours are usually required to complete the reaction. For every three parts of starting terpenes there are produced two parts of cymene containing two less hydrogens and one part of p-menthane containing four more hydrogens than the starting oil. By careful vacuum fractionation these products can be completely separated. Two terpene chemicals are thus provided at sufficiently low cost and high purity that they immediately become interesting raw materials for further processing. Typical constants of the cymene and menthane made by the process are shown in the caption to Figure 1.

Cymene Acids

The conversion of cymene to its monobasic acid, toluic acid, by the oxidation of the isopropyl group is not new. The dibasic acid, terephthalic acid, involving the oxidation of the p-methyl as well as the isopropyl group, is also possible. Both of these acids were made by Senseman and Stubbs (*17*) by a liquid-phase reaction. It was an unexpected result to find that the p-methyl group could be exclusively and selectively oxidized to give the corresponding isopropylbenzoic acid, cumic acid (*13*).

A number of oxygen-containing compounds of the many metals have been found to be satisfactory catalysts. A mixture of powdered dehydrated manganese and lead acetates gives good results. The oxidation can be conducted simply by blowing air through the cymene in which about 2 per cent by weight of the catalyst is suspended. A wide range of temperatures below the boiling point of cymene is operative. The lower temperatures give a better control of the reaction, and from 30° to 50° C. is usually sufficient. Time and temperature are, of course, functional. After 72 hours at 30° C. as much as 40 per cent of the cymene reacted on may be converted to cumic acid.

The acid is washed out of the reaction mass with alkali and then recovered by acid precipitation; refinement is conventional, such as by distillation and crystallization from a solvent. Cumic acid can thus be readily obtained in technical purity. It is a colorless needle crystal (melting at 116° C.) and can be substituted for benzoic acid for a number of uses. It is believed that this homolog of benzoic acid will have a wider usefulness in organic reactions than toluic acid.

Dimethyltolylcarbinol

Another new product that will be made from cymene is a tertiary alcohol, dimethyltolylcarbinol; it is produced by the controlled catalytic liquid-phase oxygenation of the cymene (*14*). Except for the fact that the starting material has a benzene nucleus rather than a terpene, the product would be α-terpineol. The physical properties of this carbinol are quite different from those of terpineol. It has a high gravity (around 0.98 compared to 0.936 for terpineol) and a high index of refraction (1.52 compared to 1.485 for the terpene alcohol). The wetting properties are good. It has a pleasant odor and may readily be used as a substitute for pine oil wherever a high alcohol content is required. The boiling range is about 10° C. higher than that of terpineol. This carbinol differs from terpineol in a lack of stability when heated to its boiling point at atmospheric pressure.

p-Methyl-α-methylstyrene

The hydrocarbon produced when the alcohol is dehydrated is perhaps the most interesting chemical produced in this series of products. It is still unsaturated in the side chain, which becomes a methyl-substituted vinyl group. This hydrocarbon is, therefore, the p-methyl homolog of α-methylstyrene. A large-scale manufacture of this new chemical from terpenes is of considerable interest and is a noteworthy development for several reasons. The foremost of these becomes apparent when it was discovered during the course of these researches that the α-substituted styrenes, while not polymerizable alone by means of heat as are the vinylbenzenes themselves, are readily copolymerizable with the styrenes in molar proportions or less to yield colorless resins. This property is not confined to the styrenes but includes other polymerizable materials having the diene structure. Pure α-styrene hydrocarbons have never been available commercially, and the many new compounds made possible by a supply of this terpene derivative have hardly been touched upon. Typical physical constants of *p*-methyl-α-methylstyrene are: specific gravity at 15.5/4° C., 0.9038; index of refraction at 20° C., 1.5329; boiling range, 190–191° C.

Methylacetophenone

From a practicable operative standpoint it is more convenient to carry out the oxygenation of the cymenes under conditions that produce some dehydration of the unstable carbinol, and the α-styrene hydrocarbon thus formed is unavoidably oxidized to the ketone. The ketone and the tertiary alcohol cannot be separated by fractional distillation so the carbinol is recovered containing some ketone. After the dehydration step to produce *p*-methyl-α-methylstyrene and the separation of the hydrocarbon by fractional distillation, methylacetophenone remains as a residue and is recovered as one of the by-products. The manufacture of this ketone is therefore one of the new terpene chemicals produced in this series. It is widely used as a soap perfume and for other purposes. It is a colorless, high-boiling oil (boiling point about 225° C.) and has a specific gravity of slightly over 1.0. It is anticipated that it will find numerous industrial uses. This material has not been available heretofore in any quantity but only as an expensive aromatic chemical.

Methylstyrene

One additional series of reactions was carried through in this investigation but will not be included in the commercial plant. The *p*-methyl-α-methylstyrene is readily oxidized to the corresponding ketone, methylacetophenone. This ketone may then be reduced to a secondary alcohol which, on dehydration, gives *p*-methylstyrene. This vinyltoluene has the identical polymerizing properties of styrene which yields the tough colorless resins being developed with such rapidity in this era of plastics.

Figure 2 shows the series of reactions from cymene to cumic acid, or through the alcohol to the methyl-substituted styrene and ketone, and also indicates how the ketone may be converted to methylstyrene.

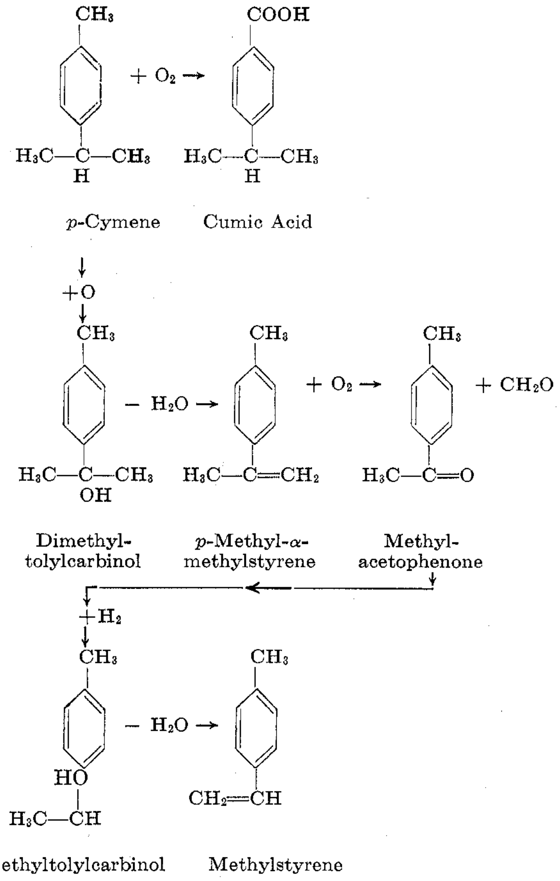


FIGURE 2. SERIES OF REACTIONS FROM CYMENE TO METHYLSTYRENE

p-Menthane Products

The process of oxidizing cymene is adaptable to the treatment of *p*-menthane with slight modification. The products are in each case the hexahydro modifications of the corresponding cymene derivatives. Hexahydrocumic and toluic acids are closely related to (in fact, are isomeric with) the naphthenic acids. The corresponding alcohol is dihydroterpineol. It has a pleasant odor and could no doubt be used for many of the same purposes as pine oil where a terpene alcohol is the important and desirable constituent. The saturated ketone has not been isolated or investigated. *p*-Menthane itself is also of commercial interest as a solvent because of its extremely narrow boiling range and the fact that it is chemically saturated.

Acyclic Terpene Hydrocarbons

Aliphatic terpene hydrocarbons can be readily produced by rupturing the pinene ring. The two hydrocarbons of particular interest are myrcene and the isomer ocimene or rather its transformation product allo-ocimene. These unusual products were discovered many years ago (1895) as constituents of the essential oils of bay, verbina, and other plants. It was many years later that Arbuzov (*1*) discovered the isomer of ocimene, allo-ocimene, in the vapor-phase pyrolysis products of pinene. He believed that both α- and β-pinene gave the same results.

In the course of an investigation of methods of producing other types of products from wood turpentine which contains only α-pinene, a novel process of producing allo-ocimene in a liquid-phase reaction was developed (*15*). The method has not yet been commercialized, pending the completion of other research. β-Pinene was also studied but, contrary to Arbuzov, did not produce allo-ocimene. This result was confirmed by Goldblatt and Palkin (*9*) who were experimenting with vapor-phase reactions; they made the very interesting discovery that β-pinene yielded principally myrcene. Ocimene is so easily converted to allo-ocimene by even moderate heat that it is not surprising the former is never found in the pyrolysis products of α-pinene.

It is well within commercial possibility that allo-ocimene and perhaps myrcene may become available as industrial chemicals. Their great interest lies in a triple unsaturation and, therefore, their adaptability to many reactions. Myrcene has one conjugated double linkage, and allo-ocimene has the unusual structure of two conjugated double bonds. Both are capable of the Diels-Alder reaction with maleic anhydride, which makes possible a large number of complex esters. This interesting field has not yet been explored.

Allo-ocimene readily polymerizes by oxidation to a dry resinous film without the aid of a catalyst. In the presence of a little ordinary varnish oil drier, the drying characteristics are rapid. The film retains moderate flexibility for some time but finally becomes brittle. Numerous other uses for these unusual terpenes of even greater interest seem possible. The conversion of α- and β-pinene to allo-ocimene and myrcene, respectively, is shown in Figure 3.

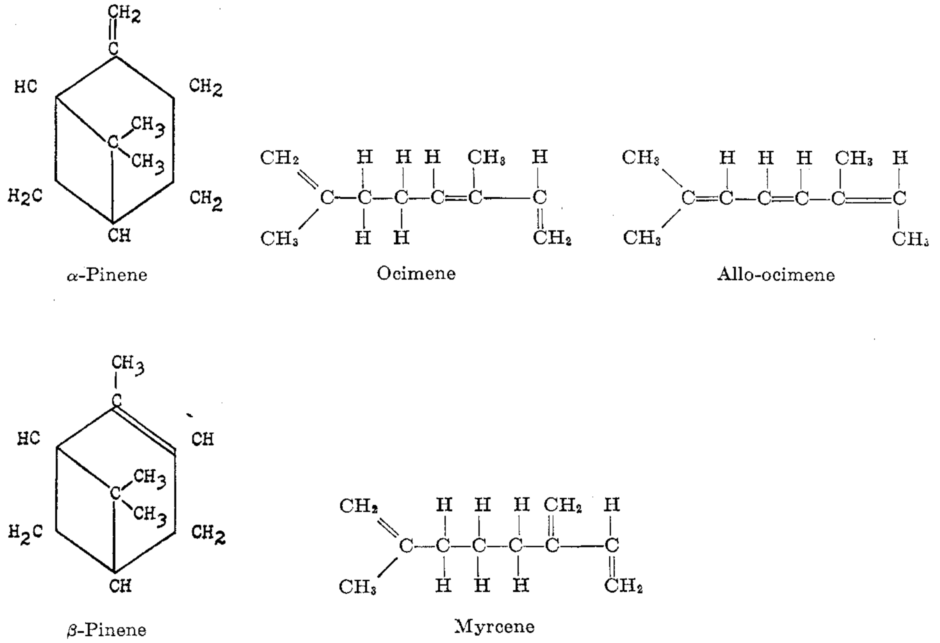


FIGURE 3. CONVERSION OF α- AND β-PINENE TO ALLO-OCIMENE AND MYRCENE

Isoprene

Probably the first chemical ever made from turpentine excited the liveliest interest at the time and has continued to do so ever since. Hlasiwetz (*11*) passed turpentine through a red-hot iron tube packed with broken porcelain and obtained a number of new products. They were not actually identified until Tilden (*18*) repeated this work and proved that isoprene was formed in this manner. Williams (*19*) had made isoprene many years earlier from rubber; Tilden's work took on added significance because Bouchardat had noted (*7*) that when obtained from rubber this same material could be repolymerized to a rubberlike body only a few years before Tilden found isoprene in the pyrolysis of turpentine.

The production of isoprene from terpenes has, until recently, never been commercialized. A unique process has now been developed that ensures the maximum yields at all times (*6*). A pilot plant has already produced several tons. It is expected that a large-scale plant will be in operation in a few months.

It has been found possible to make isoprene of very high purity by this process. A study has also been made of the by-products of the isoprene process, which are unavoidably formed. These have been shown to consist of aromatic hydrocarbons of the benzene, toluene, xylene series as well as some terpenes which have escaped the pyrolysis; but as they are mixed with cyclic hydrocarbons of the same boiling range and contain also terpene decomposition products, they are of more interest for use as solvents than to be recovered for recycling. A neutral, high-boiling, polymerlike material is also formed which is sufficiently unsaturated to dry readily by oxidation to a hard film.

The new terpene chemicals considered here embrace only a limited survey of the subject. But even with these few new developments there can no longer be doubt that the ultimate goal of a well-established terpene chemical industry is not some far distant possibility but is well within sight.

Literature Cited

(1) Arbuzov, B. A., *Ber.*, **67**, 563 (1934).
(2) Bibb, C. H., U. S. Patent 2,052,743 (1936).
(3) *Ibid.*, 2,052,744 (1936).
(4) *Ibid.*, 2,052,745 (1936).
(5) *Ibid.*, 2,052,746 (1936).
(6) *Ibid.*, patent allowed.
(7) Bouchardat, *Compt. rend.*, **89**, 361, 1117 (1879).
(8) Brooks, B. T., "Chemistry of the Non-benzenoid Hydrocarbons", New York, Chemical Catalog Co., 1922.
(9) Goldblatt, L. A., and Palkin, S., *J. Am. Chem. Soc.*, **63**, 3517 (1941).
(10) Hall, J. A., *Chem. Rev.*, **13**, 479–99 (1933).
(11) Hlasiwitz, *Ber.*, **9**, 1991 (1876).
(12) Palmer, R. C., and Bibb, C. H., U. S. Patent 2,211,432 (1940).
(13) *Ibid.*, patent pending.
(14) *Ibid.*, patent pending.
(15) *Ibid.*, patent pending.
(16) Read, J., *Chem. Rev.*, **7**, 1–50 (1930).
(17) Senseman, C. E., and Stubbs, J. J., IND. ENG. CHEM., **23**, 1129 (1931).
(18) Tilden, *J. Chem. Soc.*, **45**, 410 (1884).
(19) Williams, Geville, *Trans. Roy. Soc.* (London), **150**, 254 (1860).

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