lactone, the free fatty acids and a blue oil "Azulene" were exceedingly small.

TOKYO, JAPAN.

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, ENGINEERING COLLEGE, IMPERIAL UNIVERSITY OF JAPAN.]

ESSENTIAL OIL OF FORMOSAN HINOKI (*Chamaecyparis obtusa,* S. et Z.) WOOD.

BY SO UCHIDA.

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The Hinoki tree (*Chamaecyparis obtusa,* S. et Z.), which is extensively grown in Japan, furnishes a valuable timber wood of superior quality and is likewise prized for the manifold uses to which the wood is well adapted. In the mountain districts (5000–7000 ft.) of Formosa, Hinoki trees thrive most wonderfully, forming a splendid virgin forest. The present paper is concerned with the results obtained in experiments on the composition of Formosan Hinoki wood oil. A sample of the crude oil obtained by the dry distillation of wood was forwarded in 1912 from the Forest office of Arisan Mountains, Formosa. The yield of the crude oil was reported to be 2.4% of the wood. On examination of the sample, it was a reddish brown, mobile liquid possessing a woody and empyreumatic smell and contained some tarry matter.

Rectification of the Crude Oil.—A quantity of the crude oil weighing 780 g. was first rectified by distillation with steam and 700 g. of the rectified oil were obtained which amounted to 89.9% of the crude oil or 2.16% of the weight of wood. The quantity of the distilled water used in rectification was 8 l. The oil thus obtained was mobile, lemon-yellow in color and possessed a Hinoki wood odor. To remove the pyrogenous acids which it still contained, it was subsequently treated with dilute sodium carbonate solution, washed with water and dried with anhydrous sodium sulfate. The oil, thus rectified, has a density $d_{15.5} = 0.8821$; the refractive index $n_D^{18.5} = 1.4990$, and $[\alpha]_D = +50.37°$ in a 10% chloroform solution.

Fractional Distillation of the Oil.—A quantity of the rectified oil weighing 448 g. was distilled fractionally under atmospheric pressure, and began to boil at 157° and continued to distil until the temperature rose to 270°. It was resolved into the following three fractions, a reddish brown, resinous substance amounting to 1.5% of the oil employed remaining in the distilling flask:

I, 157–200°; II, 200–240°; III, 240–270°.

Identification of α-Pinene.—Fraction I (157–200°). This fraction, which was by far the largest obtained, representing 68.7% of the whole of the oil used, was mobile and almost colorless. When heated with metallic sodium, it was practically unacted on. The substance was, therefore, submitted to repeated distillation over sodium under ordinary pressure until the metal remained quite unaltered. The oil, thus purified, passed over chiefly at 155–160° and a smaller fraction was collected at 160–165°. The chief fraction, when redistilled, boiled mainly at 156–157°. It has a specific gravity $d\,^{15.5}_{15.5} = 0.8616$; the rotatory power $[\alpha]_D = +44°\ 42'$; and the refractive index $n_D = 1.4662$. It possesses a turpentine-like odor and is mobile and colorless. It was diluted with an equal volume of dry ether, cooled with a mixture of ice and salt and dry hydrogen chloride was passed in it. On evaporating off the diluent, a crop of crystalline substance separated which was collected, drained on a porous tile and recrystallized from alcohol. Since the repeated recrystallization from ethyl alcohol seemed to be insufficient for the purification of the substance, it was finally rectified by sublimation. This product forms white, feathery crystals, smells like camphor and is volatile at ordinary temperature. When pressed, the crystals cling together forming a sticky mass. It melts constantly at 132.5–133.5° (corr.). The crystals thus rectified by sublimation were again recrystallized three times from alcohol but the melting point of the crystals remained unchanged after each recrystallization.

0.2291 g. gave 0.1892 AgCl. Cl = 20.44%. $C_{10}H_{16}.HCl$ requires Cl = 20.54%.

According to Wallach,[1] pure pinene has the following constants:

$$\text{B. p.} = 155\text{–}156°;\ d_{20} = 0.858;\ n^{21}_D = 1.46553.$$

Flawitzky[2] gave the physical properties of *d*-pinene obtained from the leaves of *Pinus cembra* as follows:

$$\text{B. p.}_{753} = 156°;\ d^{20}_4 = 0.8585;\ [\alpha]_D = +45.04°.$$

Wallach[3] described pinene hydrochloride as follows:

> "Reines Pinenhydrochlorid lässt sich so gut wie unzersetzt destillieren und siedet bei 207° bis 208°. Der sehr schwer genau zu bestimmende Schmelzpunkt liegt gegen 125°. Aus Alkohol krystallisirt das Chlorid in gefiederten Krystallen, welche die unangenehme Eigenschaft besitzen, beim Trocknen zu einer sehr klebrigen, an allen Gegenständen sehr haftenden Masse zusammen zu sintern,......... Das schon bei gewöhnlicher Temperatur sehr flüchtige Chlorid verhält sich wie eine völlig gesättigte Verbindung."

According to J. H. Long[4] pinene hydrochloride melts at 131° and not at 125°.

The physical properties of this fraction coincide fairly well with those of pure pinene as given by Wallach and Flawitzky, and, further, this fraction affords a crystalline monohydrochloric addition product (of all terpenes ever known, pinene is the only one which gives a crystalline monohydrochloric addition product), the properties of which coincide entirely with

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[1] *Ann.*, **258**, 344.

[2] *J. prakt. Chem.*, **45**, II, 115.

[3] *Ann.*, **239**, 4.

[4] THIS JOURNAL, **21**, 637 (1899).

those of pinene monohydrochloride described by Wallach. Thus, there is no doubt that this fraction consists of α-pinene. It is worth noting here that pinene hydrochloride melts constantly at 132.5–133.5 (corr.), and neither at 125° (Wallach) nor at 131° (J. H. Long).

Fraction 160–165°. This fraction has a density $d\,^{15.5}_{15.5} = 0.8642$; the refractive index $n^{20}_{D} = 1.4672$, and the rotatory power $[\alpha]_D = 46° 27'$. It also furnishes a crystalline monohydrochloride which melts at 132.5–133.5° (corr.). Thus, this fraction also consists chiefly of α-pinene.

Fraction II (200–240°). This fraction was relatively small in amount, representing 8.0% of the oil used, and on redistillation it chiefly separated into fractions boiling above 240° and below 200°. Thus this fraction is apparently a mixture of the preceding and the following fraction with some oxygenated compounds.

Identification of Cadinene.—Fraction III (240–270°). This fraction, amounting to 21.8% of the whole of the oil employed, was a slight yellow, viscous liquid possessing a Hinoki wood odor. It was found to give only a slight action with sodium and hence consisted almost entirely of hydrocarbons which, from their boiling point, seemed to be sesquiterpenes. When purified by repeated distillation over sodium under ordinary pressure, it boiled chiefly between 260–270° and especially at 267–268°. The fraction collected at 267–268° during the distillation has the density $d\,^{22.8}_{22.8} = 0.9204$ and the refractive index $n^{18}_{D} = 1.5040$.

0.1522 g. gave 0.4897 CO_2 and 0.1614 H_2O. C = 87.74; H = 11.79. $C_{15}H_{24}$ requires C = 88.16; H = 11.84.

It was a colorless, somewhat viscous liquid and had a characteristic odor. When a few drops of this fraction were dissolved in a few cc. of glacial acetic acid and shaken with one drop of concentrated sulfuric acid, the liquid assumed a feeble reddish color which turned to red with violet shade and on standing overnight it finally developed a brownish red color.

Preparation of Hydrochloride.—A hydrochloride was prepared by passing dry hydrogen chloride in a well-cooled solution of the substance in twice its volume of ether. The gas was readily absorbed and the liquid became brown. After saturation, it was kept four hours and on evaporating the ether crystals separated, which, after washing with glacial acetic acid, were recrystallized from acetic ether. The crystals, thus obtained, formed white needles, having a radial aggregation and melting at 117–118°.

0.2903 g. gave 0.2986 AgCl. Cl = 25.45%. $C_{15}H_{24}.2HCl$ requires Cl = 25.59%.

Preparation of Hydrobromide.—The fraction was dissolved in twice its volume of glacial acetic acid and well cooled. A cold, saturated hydrogen bromide solution in glacial acetic acid was added in it and well shaken, when a crop of white, needle-like crystals separated which were washed with glacial acetic acid, drained on a porous tile, and finally recrystallized from acetic ether. It melted at 124–125°. Thus the identification of this fraction with cadinene was confirmed.

From the results of this investigation, the following conclusion may be drawn:

The Formosan Hinoki wood oil consists chiefly of *d*-α-pinene and cadinene, with a small amount of oxygenated compounds. The amount of terpenes is about 70% and that of sesquiterpenes is about 24%.

Pinene hydrochloride may advantageously be purified by sublimation and it melts sharply at 132.5–133.5° (corr.).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF VANDERBILT UNIVERSITY.]

ORGANIC MOLECULAR COMPOUNDS.

BY JAMES F. NORRIS.

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In a paper published sometime ago by Norris, Thomas, and Brown[1] it was shown that tetraphenylethylene dichloride, $(C_6H_5)_2CCl.ClC(C_6H_5)_2$, formed well-characterized molecular addition products with chloroform and with carbon tetrachloride. Since organic molecular compounds have been little investigated, it seemed advisable to study such compounds more fully in order to determine, if possible, the conditions necessary for their formation. It is evident that a satisfactory theory of valency must be susceptible of explaining the atomic relationships in molecular compounds; for these substances are as definite in their composition as the simpler compounds, which are explicable with our present inadequate views; and, moreover, certain so-called molecular compounds are known which are more stable than many possessing a simple atomic structure. Our present theories of valency, as applied to organic chemistry, do not cover the case of molecular compounds, and we cannot, therefore, predict what atomic conditions are necessary for the formation of a compound as the result of the union of two molecules. The field of organic chemistry is the best available for the investigation of these atomic conditions, since slight and graded changes in the combining power which holds the atoms together can be made by introducing into the molecule one or more groups the nature of which can be changed at will.

The results described below were obtained in a preliminary study of this problem. Work is actively in progress to determine, if possible, the causes that affect the mutual affinity between atoms in organic molecules, and the relationship between these affinities and the phenomenon of the formation of molecular compounds.

As has been emphasized of late, the bonds which unite atoms in an organic compound are markedly affected by the nature of the surround-

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[1] *Ber.*, 43, 2940 (1910).