

So far as the previous use of hydrocarbons of the methane series is concerned mixtures only have been employed. The heptane from both the Digger's and Jeffrey pines appears to be devoid of isomers and homologues and the small amount of impurities present in the natural products can be removed by a variety of new ways, as has been ascertained in the preliminary survey already alluded to. In heptane, a distinctively chemical unit, capable of a high degree of purity, is now made available; hence not only more satisfactory qualitative work can be done, but, what is possibly more important, quantitative work as well.

Heptane is not only volatile, but its boiling point lies very close to that of water, the most common solvent used. Moreover, its boiling point lies only twenty degrees higher than that of alcohol, the most common of the organic solvents employed in chemical work.

A disadvantage of the heptane, namely, its highly selective solvent property, frequently turns out an advantage, for it is remarkable how many substances can be prepared in this solvent by the precipitation method. Indeed, in many of the innumerable organic reactions performed, the writer was again and again reminded of his early chemical work in qualitative inorganic analysis. So simple were many of the reactions that the writer has referred to his work as "playing" at chemistry. This does not imply, however, that many of the precipitates are as simple as at first supposed. Indeed, much painstaking detail work will have to be done in order that the secrets of this chemistry of the heptane solution may be properly revealed.

CHEMISTRY OF THE HEPTANE SOLUTION.

BY EDWARD KREMERS.

2. REVISION OF THE PHYSICAL CONSTANTS OF HEPTANE.

BY ROLAND E. KREMERS.

The physical constants for normal heptane, so painstakingly determined by Thorpe for the hydrocarbon obtained from the Digger's pine, are possibly among the most accurate on record for a hydrocarbon of the methane series. However, if one stops to consider that the hydrocarbon so carefully investigated physically by Thorpe had an optical rotation of $6.9'$, it becomes apparent at once that the material examined by him must have been impure. Normal heptane should be optically inactive. The angle of rotation can readily be accounted for by assuming that in the collection of the oleoresin, the collector did not discriminate sufficiently between *Pinus sabiniana* and other species of pine yielding pinene, *e. g.*, *Pinus ponderosa*.¹ That such mistakes have been made has since then been demonstrated repeatedly. Thus, *e. g.*, an oleoresin presumably from Jeffrey pine, which likewise produces heptane in place of pinene, contained about one-third or more of the oleoresin of *Pinus ponderosa*, with which this species is readily confounded by the workmen. This oleoresin was distilled and the oil examined in this laboratory by R. J. Harnon.² In like manner the admixture of a pinene oleoresin with the oleoresin of *Pinus sabiniana* has since then been observed in the Forest Products Laboratory.³ Hence, with an unusually pure heptane at our disposal, it seemed highly desirable to re-determine the physical constants and to compare them with those of Thorpe.

Material.—The material used in this investigation was obtained in January, 1913, through the kind coöperation and liberality of the Forest Products Laboratory at Madison, Wisconsin. It consisted of fifteen five-gallon cans of oleoresin of Digger's pine or *Pinus sabiniana*. The oleoresin is obtained by boxing and was collected in Sierra National Forest, California.⁴ Some of the cans were labeled "second grade," one "poor grade." The assumption is that the remaining cans were to be considered as first grade.

The oleoresin as received was a viscous semi-liquid.

Distillation of the Oleoresin.—This was distilled during the week beginning December 29, 1913, in the 60-liter Lentz still of the Department. The distillation was effected by passing steam into the oleoresin as well as into the jacket space of the still. The oil separated rapidly from the water of the distillate and a rough separation was effected by means of a separatory funnel. The oil from each can was united, but kept separate from the rest. The aqueous distillate was reserved for cohobation. The contents of one can were found to make a convenient charge. Five cans was the maximum amount handled in a seven-hour day. When the volatile oil about ceased to distil, the distillation was stopped, the residue allowed to settle, whereupon the resin rose to the surface, and the water was largely decanted into the cans. The resin, while hot, was emptied into wooden boxes and upon further cooling solidified.

On February 2, 1914, the cohobation of the aqueous distillate was commenced. About forty liters were emptied into the still as a single charge. Steam was passed into the water only until distillation had begun, whereafter the heat from the jacket alone sufficed. When the aromatic odor of the distillate became somewhat less pungent, distillation was stopped and the residue discarded. In this manner about 45 liters were collected. These were again cohobated and the first 8 to 10 liters collected. At first the distillate was milky, later it cleared with a slight separation of an oil on the surface. This oil was collected separately.

The following table records the description of the crude material, the amount of oil obtained, and the density of the oil at 20° as determined by means of a Mohr-Westphal balance:

Experiment.	Description of oleoresin.	Amount of oil.	Cc.	Sp. gr. at 20° C.
1. Dec. 29.	"Second grade"	1750		0.686
2. Dec. 29	"A"	2090		0.685
3. Dec. 30	"A"	2300		0.685
4. Dec. 30	"A No. 5"	2390		0.685
5. Dec. 30	"A No. 5"	2240		0.685
6. Dec. 30	"A No. 4"	1950		0.685
7. Dec. 30	"A No. 5"	2500		0.685
8. Dec. 31	"A No. 3."	1875		0.685
9. Dec. 31	"A No. 3"	2170		0.685
10. Dec. 31	"A No. 4"	2725		0.685
11. Jan. 2	"A No. 2"	2415		0.686
12. Jan. 2	"A"	2440		0.685
13. Jan. 2	"No. 8, second grade"	1110		0.685
14. Jan. 2	"No. 7, second grade"	1725		0.685
15. Jan. 2	"Poor grade"	1451		0.685

Total 31,131

Assuming the total weight of oleoresin approximately to have been 600 lbs., 1 gallon of 8 pints with a density of 1.00,⁵ the average yield of oil may be assumed to be approximately 7.8 percent. The best yield (Experiment 10) on the same assumption, is 9.4 percent, the poorest yield (Experiment 13) 4.2 percent. A comparison of these yields with those obtained by previous investigators is afforded by the data recorded in the following table:

Investigator.	Yield, percent.
Rabak ⁶	7.3
Schorger ⁷	11.4
R. E. K. ⁸	7.8

Fractionation of the Oil.—With the exception of the small amount of oil obtained by the cohobation of the aqueous distillation, all of the fifteen oils obtained by the steam distillation of the oleoresin were united and fractionated by steam. For the greater part of the distillation the heat of the steam jacket sufficed. The residue was driven over by passing steam into it, hence was distilled with water vapor, and the oil thus obtained separated in the usual manner. The bulk of the oil, distilled by itself, was collected in liter fractions, thirty-one such fractions, all colorless, being obtained. Fraction 32 consisted of about 100 Cc. of a mobile yellow oil of an agreeable odor and was obtained by separation from the aqueous distillate as already indicated. In the following table the densities of these fractions, as determined with the aid of a Mohr-Westphal balance, are recorded:

Fraction.	Sp. gr. at 20°.	Fraction.	Sp. gr. at 20°.	Fraction.	Sp. gr. at 20°.	Fraction.	Sp. gr. at 20°.
1	0.6835	9	0.684	17	0.684	25	0.685
2	0.684	10	0.6835	18	0.684	26	0.6845
3	0.684	11	0.684	19	0.684	27	0.685
4	0.684	12	0.684	20	0.684	28	0.685
5	0.684	13	0.684	21	0.6845	29	0.685
6		14	0.684	22	0.684	30	0.685
7		15	0.684	23	0.684	31	0.7081
8		16	0.684	24	0.685	32	0.8300

Purification of Heptane.—Although the density of most of the fractions of the Digger's pine oil revealed that they consisted of an unusually pure heptane, a chemical purification seemed desirable for a revision of the physical constants of this natural hydrocarbon. For this purpose a liter fraction of the oil was thoroughly shaken with 100 Cc. of concentrated sulphuric acid. While the acid darkened readily, no appreciable amount of heat was evolved. The dark colored acid was removed and a second 100 Cc. were employed. For a third shaking a like amount of fuming sulphuric acid was used. After these three treatments, the oil had a decided odor of sulphur dioxide which was removed by shaking the oil with a solution of sodium carbonate. This having been separated, the oil was shaken vigorously with a one percent solution of permanganate, a few Cc. being used at a time, until the permanganate color was no longer destroyed. The heptane thus purified was distilled, a small first fraction and a small last fraction being kept separate from the bulk of the distillate.

Fractions 1, 5 and 10 of the Digger's pine oil were thus purified. The loss involved in the purification of Fraction 10 of 1056 Cc. amounted to 24 Cc., hence was less than 2.5 percent. By way of control a few of the physical constants were determined. Thus it was desirable to ascertain before proceeding further whether the fractions contained any appreciable amount of optically active ter-

pene. The circular rotation for fraction 1 was found to be 0.10° in a mm. tube. The specific gravity of Fraction 5, as determined by a Mohr-Westphal balance, was found to be 0.6838 at 20° ; the index of refraction of Fraction 10, as determined at 20° by means of an Abbé refractometer, was 1.3880.

In spite of the purification, or possibly because of the nature thereof, all three fractions when thus purified had a decided spicy odor. Attributing this to the presence of small amounts of oxygenated compounds that had either not been destroyed by the purifying agents or had been produced by them, metallic sodium in the form of wire was added and the contents of each bottle shaken from time to time. Although a large number of extremely minute bubbles were formed at first, the surface of the sodium wire remained essentially unchanged, so small was the action. Nevertheless, the spicy odor did not disappear entirely. The index of refraction of Fraction 10 of the purified oil, after the treatment with sodium, was 1.3895 at 20° .

For the more careful determination of the physical constants, the fraction or fractions used were subjected to a final purification in the fractional distillation which they underwent in the determination of the boiling point.

Physical Constants.—The following physical constants were determined in the laboratory for Physical Chemistry. The writer wishes to acknowledge his indebtedness to the kind assistance and supervision of Professor J. H. Mathews in this work.

Boiling Point.—The boiling point was determined in connection with the final purification by distillation. Electrical heating was secured by passing a current through a platinum spiral that was immersed in the heptane. The thermometer employed was graduated to 0.5° C., and had been standardized by the Reichs Anstalt. In the course of an hour and a quarter the temperature rose from 96.0° to 96.4° under a barometric pressure of 739 mm. The further determinations were made on the distillate which amounted to some 300 Cc. after a "Vorlauf" of several Cc. had been set apart. A residue of about 600 Cc. became necessary because the platinum coil became exposed. Corrected according to the following expression:

$$C = 0.00012(760 - b)(273 + t),$$

where C is the correction, b the observed barometric pressure, and t the observed degrees, on the centigrade scale, the boiling point under 760 mm. becomes 97.33° C.

Optical Rotation.—As a check upon the purity a determination of the optical rotation was made. The polarimeter employed was of the usual laboratory type made by Schmidt and Haensch. To insure monochromatic light a bichromate cell was used. Within the limits of error of the instrument the optical rotation at 20° C. was found to be zero.

Density.—By means of a large pyknometer a determination of the density was made at two temperatures.

$$d_{20^\circ} = 0.68288$$

$$d_{40^\circ} = 0.66623$$

Surface Tension.—The surface tension was computed by the expression:

$$\gamma = \frac{1}{2} g r h d$$

the cathetometer employed was one constructed by the "Geneva Society for the

Construction of Physical Instruments," Geneva, Switzerland. The radius of the tube was found to be 0.0360 cm. This value represents the average result of five independent observers. The average of the elevations was found to be:

$$h_{200} = 1.6425 \text{ cm.}$$

$$h_{400} = 1.5569 \text{ cm.}$$

The computation gave the following values:

$$\gamma_{200} = 19.80 \text{ ergs.}$$

$$\gamma_{400} = 18.316 \text{ ergs.}$$

Index of Refraction.—By Abbe refractometer:

$$n_{200} = 1.3895.$$

BIBLIOGRAPHY.

1. Oleoresin of Some Western Pines, A. W. Schorger. *Bull.* 119, Forest Service.
2. See letter of C. Stowell Smith to E. Kremers, also laboratory notes of R. J. Harnon.
3. Personal Communication.
4. See letter from C. Stowell Smith to E. Kremers, Dec. 2, 1912.
5. Schorger, *Bull.* 119, Forest Service.
6. *Pharm. Rev.*, vol. 25.
7. *Bulletin* 119, Forest Service.
8. Inasmuch as some of the cans were not very carefully sealed, the average yield may have been lowered somewhat by evaporation.

THE INFLUENCE OF HYDROCHLORIC ACID ON CINCHONA PREPARATIONS.*

BY WILBUR L. SCOVILLE.

It has been observed that in the extraction of cinchona with acidulated menstrua, erratic results are sometimes obtained. In some instances the alkaloids are extracted rapidly and in others very slowly, and that under seemingly parallel circumstances. While the very slow extractions are comparatively rare, they are frequent enough to warrant an investigation. The following experiments were therefore undertaken.

Five hundred grammes of cinchona calisaya assaying 7.1 percent of alkaloids by the U. S. P. process, was percolated with a neutral menstruum consisting of 4 volumes of alcohol with 1 volume of water, and another portion of 500 grammes was percolated at the same time with an acidulated menstruum of the same alcoholic strength but containing 50 mils of diluted hydrochloric acid in the first 500 mils of menstruum. Percolation was conducted as evenly as possible and the percolates received in 400 mil, then 500, 500, and 500-mil portions. Each fraction was then assayed for alkaloidal strength, and the results are as follows:

	Neutral menstruum.		Acid menstruum.	
	Gm. per 100.	% of exhaustion.	Gm. per 100.	% of exhaustion.
First 400 mils.	4.2	47.5	5.0	56.5
First 500 mils.	1.4	19.77	1.7	24.0
Second 500 mils.	0.65	9.25	0.61	8.64
Third 500 mils.	0.25	3.53	0.26	3.7
Fourth 500 mils.	0.112	1.58	0.110	1.55
Totals.		81.63		94.39

*Read before Scientific Section, A. Ph. A., City of Washington meeting, 1920.