

SCIENTIFIC SECTION, AMERICAN PHARMACEUTICAL ASSOCIATION

PHYTOCHEMICAL NOTES.*†

From the Laboratory of Edward Kremers.

81. The Oil of *Pinus sabiniana*.

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That the oleoresin of the Digger's pine of California does not, upon distillation, yield a turpentine oil but a product that bears resemblance to some of the lower fractions of American petroleum was observed during the seventies of the past century.¹ That it might be used for similar purposes as those to which petroleum benzine had been put is indicated by the trade name "erasine" under which, for a time, it appeared in the California market.

The identity of the bulk of this oil with normal heptane was established physically by Thorpe² in 1879, and chemically by Schorlemmer and Thorpe³ in 1882. That the oil contains substances other than heptane, though in but small amount, is indicated by its odor and by the synonym "aurantine," under which it likewise appeared in the California market. Whereas the striking occurrence of heptane, as a product of a conifer, attracted the attention of chemists to this hydrocarbon, the one or two percent of non-heptane constituents of the oil are of equal interest to the phytochemist. Rabak⁴ in 1904 endeavored to ascertain something about these other constituents but did not have sufficient material at his disposal to identify any of them. Hence, when a larger amount became available, this was one of the first problems to suggest itself for at least a partial solution.

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 about 6.9' it becomes apparent that it could not have been absolutely pure. Normal heptane should be optically inactive.

* The publication of these notes, which has been interrupted for several years, is herewith resumed. Since the publication of the revised list (JOUR. A. PH. A., 2, 724), the following numbers have been published in this Journal:

1912

73. R. C. Roark, "Oil from *Mentha citrata*," JOUR. A. PH. A., 2, 839.
78. R. C. Roark, "An Unusual Oil of Wormwood," JOUR. A. PH. A., 2, 841.
79. O. A. Beath, "Oleoresin of *Pseudotsuga taxifolia*," JOUR. A. PH. A., 2, 303 and 1566.
80. O. A. Beath, "A Crystalline Resin Acid from *Pinus sabiniana*," JOUR. A. PH. A., 2, 303 and 1569.

† Read in abstract before Scientific Section, A. Ph. A., Atlantic City meeting, 1916.

¹ Wenzel, Am. Journal of Pharmacy, 1872, 92.

² Chem. Soc. Journal, Trans., 35, 296.

³ Annalen, 217, 149.

⁴ Pharm. Review, 25, 212.

The slight angle of rotation can readily be accounted for by assuming that in the collection of the oleoresin, the collector did not discriminate sufficiently between the *Pinus sabiniana* and other species of pine yielding pinene, e. g., *Pinus ponderosa*.⁵ That such mistakes have been made has since then been demonstrated repeatedly. Thus, e. g., an oleoresin 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.⁶ 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.⁷ Hence, with an unusually pure heptane at our disposal it seemed highly desirable to redetermine the physical constants and to compare them with those of Thorpe.

The chemical identification of heptane from Digger's pine by Schorlemmer and Thorpe involved the repetition of Schorlemmer's classical experiments on the constitution of the methane hydrocarbons. The chlorination, esterification, saponification and oxidation experiments involved, ought to find a place in the laboratory courses for organic chemistry. Though chlorine substitution is mentioned in the textbook as one of the characteristic reactions of the methane hydrocarbons, yet not a single laboratory manual calls for this experiment for the simple and sufficient reason that no sufficiently pure hydrocarbon of this series has thus far been available. With the availability of heptane, it seemed desirable to work out the conditions under which the experiments referred to above could be made laboratory exercises in elementary organic chemistry.

The three problems thus indicated are those, the partial solution of which has been attempted. Well-nigh innumerable other problems in organic, physical and analytical chemistry and even in chemical technology, that are suggested by the possible supply of heptane on a commercial scale, cannot here be considered, but may receive consideration later.

The present report, however, deals only with the distillation of the oil and its fractionation. Already work has been done on the purification of the heptane thus obtained and the redetermination of its physical constants. These, together with the physical constants of heptane prepared from Jeffrey pine, will be made the subject of a separate report. Work has also been done on the higher boiling oxygenated constituents of both oils. The results of this work, which may point the way to an understanding of the genesis of the heptane in these pines, will also appear in a separate report. Finally, it may be pointed out that part of the work done by O. A. Beath on the resin acids of Digger's pine has already been reported (see Phytochemical Notes, No. 80 in JOUR. A. PH. A., 2, 1569). Further reports on this work may be expected.

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 was obtained by boxing and

⁵ "Oleoresin of Some Western Pines," Bull. 119, Forest Service.

⁶ See letter of C. Stowell Smith to E. K.; also lab. notes of R. J. H.

⁷ Personal communication.

was collected in the Sierra National Forest, Cal.⁸ 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 semiliquid.

Distillation of the Oleoresin.—This was distilled during the week beginning December 29, 1913, in the 60-liter Lentz still of the Chemical Laboratory. The distillation was effected by passing steam into the oleoresin as well as into the jacket 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 water rose to the surface and was largely decanted into the cans. The resin, while hot, was emptied into wooden boxes and upon further cooling solidified.

After an interruption in the work, the cohobation of the aqueous distillate was commenced on February 2, 1914. 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 of first cohobate 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:

Expt.	Description of oleoresin.	Amount of oil.	Sp. gr. at 20°.
1 Dec. 29.....	"Second grade"	1750 Cc.	0.6861
2 Dec. 29.....	"A"	2090 Cc.	0.685
3 Dec. 30.....	"A"	2300 Cc.	0.685
4 Dec. 30.....	"A No. 5"	2390 Cc.	0.685 +
5 Dec. 30.....	"A No. 5"	2240 Cc.	0.685 +
6 Dec. 30.....	"A No. 4"	1950 Cc.	0.685
7 Dec. 30.....	"A No. 5"	2500 Cc.	0.685 +
8 Dec. 31.....	"A No. 3"	1875 Cc.	0.685
9 Dec. 31.....	"A No. 3"	2170 Cc.	0.685
10 Dec. 31.....	"A No. 4"	2725 Cc.	0.685
11 Jan. 2.....	"A No. 2"	2415 Cc.	0.686
12 Jan. 2.....	"A"	2440 Cc.	0.685
13 Jan. 2.....	"No. 8, second grade"	1110 Cc.	0.685
14 Jan. 2.....	"No. 7, second grade"	1725 Cc.	0.685
15 Jan. 2.....	"Poor grade"	1451 Cc.	0.685
Total.....		31,131 Cc.	

Assuming the total weight of oleoresin approximately to have been 600 lbs., the average yield of oil may be assumed to be approximately 7.8 percent. The

⁸ See letter from C. Stowell Smith to E. Kremers, Dec. 2, 1912.

best yield (Expt. 7) on the same assumption is 9.4 percent, the poorest yield (Expt. 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.
Rabak ¹	7.3 percent
Schorger ²	11.4 percent
R. E. K. ³	7.8 percent

FRACTIONATION OF THE OIL.

With the exception of the small amount of oil obtained by the cohobation of the aqueous distillates, 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 these fractions and their densities, as determined with the aid of a Mohr-Westphal balance, are recorded:

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

The densities recorded above show quite clearly that most of the fractions consisted of relatively pure heptane. Practically all of the material obtained has been utilized in a variety of experiments. As already indicated, several fractions were purified and used for a redetermination of the physical constants. A considerable number were used in chlorination experiments and the subsequent conversion of the chlorides to acetates of the corresponding alcohols. Still others were used as solvent in a variety of phytochemical investigations.

Finally, it may be mentioned that the presence of an aldehyde in the highest fractions has been indicated by the formation of its sodium acid sulphite addition product. Reports on all of these aspects of the work will follow later.