

PHYTOCHEMICAL NOTES.*

From the Laboratory of Edward Kremers.

82. The Oleoresin and Oil of *Pinus jeffreyi*.

BY L. J. OSTLUND.

An oil from *Pinus jeffreyi* was examined by Venable¹ in 1880, who supposed it to be an oil from *Pinus sabiniana*, but Wenzell² later (1904) showed that it was from the related California species.

In 1901 Blasdale³ re-examined the oil for heptane and identified the latter by its boiling point and behavior toward sulphuric acid.

A material supplied by the Forest Products Laboratory was examined in 1913 by R. J. Harnon⁴ and was found to consist in part (about two-fifths) of terpenes. The oleoresin from Jeffrey pine had evidently been mixed with that from the western yellow pine, *Pinus ponderosa*, in the gathering.

Schorger,⁵ while he discussed the heptane situation, did not examine the oleoresin from Jeffrey pine, but expressed the hope "that this may be done later" (p. 18).³

Through the kind coöperation of the Forest Service and that of Mr. F. D. Fryer of Santa Rosa, Cal., a barrel of Jeffrey pine oleoresin was collected during the summer of 1915, in the collection of which special care was taken not to allow any admixture of oleoresin from other species. Leaves and cones submitted by Mr. Fryer were identified by Professor R. H. Denniston as those of *Pinus jeffreyi*. A sample of oil distilled by himself was also sent for examination.

Acid and Saponification Values of Oleoresin.—The acid and saponification values of the oleoresin collected in 1915 by Fryer were determined according to the directions of the U. S. P. (eighth revision) for Acid Number of Resins (p. 535) and Saponification Value of Fats and Oils (p. 535). Duplicate determinations were made. The following results were obtained:

Expt.	Acid value.	Sap. value.
I.....	140.0	166.0
II.....	140.5	166.5

Preliminary Distillation.—500 Gm. of the oleoresin, as received, were subjected to ordinary steam distillation in a glass flask, the steam being generated in a tin can. This yielded 43 Gm. or 8.6 percent of oil which had a specific gravity of 0.697 at 20°.

Another 500 Gm. of oleoresin were saponified in five separate portions with a

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

¹ Berichte, 13, 1649.

² Pharm. Rev., 22, 413.

³ J. Am. Chem. Soc., 23, 162.

⁴ Unpublished results in the possession of E. K.

⁵ "An Examination of the Oleoresins of Some Western Pines," Bull. 119, of the Forest Service, U. S. Dept. of Agr., 1913.

slight excess of sodium hydroxide, the saponification value of the oleoresin having previously been determined as 166.0 and 166.5, respectively. The amounts and percentage yields are herewith tabulated.

Expt.	Amt. of oleoresin.	Amt. of oil.	Percentage of oil.
1.....	112 Gm.	9.9 Gm.	8.9 percent
2.....	115 Gm.	10.1 Gm.	8.8 percent
3.....	125 Gm.	11.5 Gm.	9.2 percent
4.....	116 Gm.	10.3 Gm.	8.9 percent
5.....	105 Gm.	9.3 Gm.	8.9 percent
Total.....	573 Gm.	51.1 Gm.	8.92 percent (Average)

Hence it becomes apparent that the percentage yield of oil can be increased but little by saponification of the resin acid previous to the steam distillation.

The only reference to the yield of heptane in the oleoresin of Jeffrey pine is found in the article of Blasdale, previously referred to, who obtained "about three percent" from material "collected at Lake Tahoe from stumps of recently cut trees."¹ The larger yield recorded above is unquestionably due to the fact that the oleoresin collected by Mr. Fryer was obtained by the boxing method whereas that distilled by Blasdale had been exposed in such a manner that much of the heptane had evaporated. Hence the percentage of heptane agrees fairly well with that obtained from the oleoresin of Digger's pine.

Distillation of Oleoresin.—The bulk of the oleoresin was then subjected to steam distillation in the 60 liter Lentz still of the laboratory, about one-eighth being taken as a charge. This task was kindly performed by Professor E. R. Miller. Of the careful manner in which the distillation was conducted he states:

"In any given distillation the greater part of the oil, probably 80–90 percent, was driven over in half an hour, but in every case the distillation was continued at least five hours and in some cases as long as eight hours, in order to obtain as much as possible of the higher boiling oil. Even in the case of the longest period of distillation small amounts of oil were still obtained during the last hour."

A total of 21.95 liters of oil was thus obtained, the specific gravities of the several distillates determined at 20° being herewith recorded.

1.....	0.6963	5.....	0.6976
2.....	0.6963	6.....	0.6976
3.....	0.6976	7.....	0.6976
4.....	0.6974	8.....	0.6976

Cohobation of the Aqueous Distillate.—"In separating the oil from the resin about 70 gallons of aqueous distillate were obtained. With the exception of 8 to 10 gallons which were lost, this distillate was distilled by means of the steam-jacket until a little more than one-fourth of it had passed over. The portion in the still was rejected. The distillate thus obtained was in like manner distilled, recovering about one-third of it and rejecting the remainder. Finally, the distillate was cohobated, the process having been continued until about one-half (2¹/₂ gal.) of the distillate had passed over. In all these distillations small quantities of oil were obtained, the total yield of oil recovered being 92 Gm. The color of the oil was decidedly brownish yellow."

Fractionation of the Oil.—"After reserving about two ounces of each sample

¹ Comp. also Gildemeister, "Die aeth. Oele," Bd. II, p. 100.

(the eight portions) the remainder of the mixed oil (about 21¹/₂ liters) was fractionated with steam. Twenty fractions of one liter each were obtained. All these volatilized very rapidly. The first nineteen were colorless; the twentieth had only a trace of color. The twenty-first fraction measured 500 Cc., fraction No. 22, 110 Cc. and fraction No. 23, 22 Cc. Fraction No. 21 had a slight yellowish color, fraction No. 22 was very noticeably colored and fraction No. 23 was yellow with a tinge of green."

The specific gravity of these fractions was taken at 20° with a Mohr-Westphal balance and the results are herewith tabulated:

Fraction.	d ₂₀ °.	Fraction.	d ₂₀ °.
1.....	0.6855	12.....	0.6860
2.....	0.6865	13.....	0.6875
3.....	0.6865	14.....	0.6985
4.....	0.6865	15.....	0.6879
5.....	0.6864	16.....	0.6879
6.....	0.6864	17.....	0.6888
7.....	0.6865	18.....	0.6896
8.....	0.6865	19.....	0.6980
9.....	0.6870	20.....	0.782
10.....	0.6870	21.....	0.863
11.....	0.6860	22.....	0.9014

The constancy of the density of fractions No. 1 to 19 certainly speaks not only for the uniformity in composition, but also speaks well for the absence of terpenes, the absence of which in turn reveals the absence of oleoresins from terpene-producing pines. Whether there is any probability of admixture of oleoresin from *Pinus sabiniana* does not become apparent from these data.

COHOBATION OF AQUEOUS DISTILLATE OBTAINED BY FRACTIONATION OF THE OIL.

Inasmuch as steam was used in the fractionation of the oil, the aqueous distillate might be assumed to have retained at least a part of the more water-soluble constituents of the oil. The amount of aqueous distillate being about 38 liters and that of the fractionated oil 21 liters, the ratio of water to heptane is roughly 2 : 1.

These 10 gallons were cohobated twice, yielding all told 12 g. of oil.

NOTE.—The heptane material thus obtained will be used in part for the revision of the physical constants of this hydrocarbon. The percentage of higher boiling non-heptane constituents appears to be larger than in the case of the oil from the Digger's pine. That aldehydes or ketones are present is indicated by the formation of a solid sodium acid addition product. The regenerated aldehyde or ketone yields a crystalline condensation product with *p*-nitrophenyl hydrazine. The presence of esters is also indicated by the saponification values of certain fractions. Optically active substances are also present in these higher fractions. A joint report of these oxygenated constituents together with those found in the Digger's pine oil will be made later.—E. K.