[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

AN INVESTIGATION OF WOOD TAR FROM THE DOUGLAS FIR, "PSEUDOTSUGA TAXIFOLIA."[1]

BY H. G. BYERS AND PAUL HOPKINS.

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THE Douglas fir, better known as Oregon Pine, grows only upon the humid western slopes of the Cascade range. Its great size and its value as a source of timber makes it an important part of the natural wealth of the northwest. A number of attempts have been made to make use of the waste products in the mills of this state but without very marked success. The quantity of material destroyed by our mills is enormous. There are mills on Puget Sound which have been burning their waste for thirty years and during all that time the fires have not been out.

In view of these facts and because of almost numberless requests for information concerning the products of distillation of fir wood we decided to make some little investigation upon that subject in order to get data that would afford a comparison between our wood and that used in distillation processes in other places.

The Rainier Tar Company, of Seattle, kindly placed at our disposal a large steel retort capable of holding about three-fifths of a cord of wood. In this retort two carefully regulated runs were made. The products of the distillation were condensed in a 4-inch copper worm 125 feet in length, surrounded by cold water. All the products were carefully measured except the gas, which was estimated by difference.

The material used in the distillation was partially seasoned fir wood taken from the "butt cuts" of trees. It was cut into 2-foot lengths, weighed, and placed in the retort, which was held at as constant a temperature as possible. Not having a pyrometer at our disposal we arrived at an approximation of the temperature by means of small bars of metals placed within the retort so that the maximum temperature could be determined. In the case denominated "low run" in the following discussion at no time did the temperature rise above 420° C., the melting-point of zinc, while in

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[1] *Pseudosuga mucronata* (Sargent's *silva*).

the "high run" the temperature never exceeded 700°, the melting-point of aluminum.

The time required to complete the distillation of a charge was about twelve hours, and the quantity used was about half a cord and weighed 2,500 pounds.

The results of these distillations are as follows:

	High run.	Low run.
Pyroligneous acid	34.0	47.5
Tar	17.7	7.5
Charcoal	29.0	30.0
Gas	19.3	15.0
Total	100.0	100.0

The high percentage of tar in the high run was due to the fact that it contained an abnormal quantity of water which in the course of several weeks settled out gradually. Referring the weight of water-free tar to the wood we have 6.37 per cent. for the high run and 6.00 for the low run.

PYROLIGNEOUS ACID.

The pyroligneous acid produced in the distillation was of a rich red color, that from the low run being slightly the darker. The specific gravity of the low run was 1.025; that of the high run was 1.020. The methyl alcohol was determined by conversion into methyl iodide by means of phosphorus tri-iodide. The percentages were: for the high run 2.95; for the low run 4.16 per cent. (volume). The percentage of acetic acid was determined by direct titration and found to be 2.90 per cent. for the high run and 3.47 for the low run.

TAR.

The tar was fractionated and the oil which distilled below 150°, the light oil, was investigated a little more fully than the other portions. A discussion of its constituents will be found at the close of this article. The creosote oil boiling between 150° and 250° was separated and the residue weighed as pitch.

The results of this separation are as follows:

	High run.	Low run.
Specific gravity	1.060	1.075
Watery distillate (pyroligneous acid)	64.0	20.0
Light oil	8.0	18.0
Creosote oil	10.0	23.0
Pitch	18.0	39.0

Because of the great amount of water in the one sample a more accurate comparison of the composition may be gained by referring these values to water-free tar as:

	High run.	Low run.
Light oil	22.2	22.5
Creosote oil	27.8	28.7
Pitch	50.0	48.8

The creosote in the creosote oil was separated in the usual way and found to be 17 per cent. of the oil or 5 per cent. of the tar. The percentage of guaiacol in the creosote was also determined and found to be about 9.5 per cent.; the method used was that given in Allen's "Commercial Organic Analysis," Vol. II, Part II, p. 284. The creosote is almost colorless, has a smoky aromatic odor and a specific gravity of 1.065. It seems almost identical with the product of beech-wood tar. The pitch from the tar is black or very dark brown and resembles closely in appearance coal-tar pitch but has not the same odor or taste.

Since great quantities of Stockholm tar are imported for the local market and it commands a high price, it seemed worth while to compare our product with that and also with pine tar. We found that by removing the water and a certain amount of the light oil, a tar could be obtained which resembles Stockholm tar very closely. The color suffers somewhat in the redistillation yet the tar as obtained can not be otherwise distinguished from Stockholm tar, even by the tests usually given for identification of the latter.[1] A fair idea of the variations may be gained from the following table:

	Fir tar.	Stockholm tar.	Pine tar.
Color	Black (almost).	Brownish black.	Brown.
Odor	Smoky but characteristic.	Smoky.	Resinous.
Consistency	Sirupy.	Sirupy.	Viscid.
Specific gravity	1.100	1.090	1.110
	Per cent.	Per cent.	Per cent.
Light oil	3	3	5
Creosote oil	34	30	40
Pyroligneous acid	4	5	2
Pitch	59	62	53
Hardness of pitch	Brittle.	Less brittle.	Soft.
Color of pitch	Black.	Black.	Brown.

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[1] Allen's "Commercial Organic Analysis."

The light oil which is separated from the tar by this redistillation has a specific gravity of 0.945 and when freshly distilled is of a clear amber color but darkens markedly on standing.

THE CHARCOAL.

There was no attempt made to distinguish between the samples of charcoal made at the different temperatures. The quantities were nearly the same and they were similar in appearance. The coal is soft and retains the porous structure of the wood. It is, however, remarkably free from ash.

THE GAS.

No attempt was made to analyze the gas given off in this distillation and its amount was determined by difference. This gas is, however, utilized in the processes of the refining of the wood products. It is non-illuminating and hence cannot be used directly as an illuminant, except in Welsbach burners, in which it gives an excellent light. A series of tests was made on this subject in the city of Tacoma and a sample of the gas was sent us for analysis. The temperature at which it was produced was much higher than those of our experiments and the retort was arranged to decompose almost totally all the tar produced. The results are as follows:

	Per cent.
Light hydrocarbons	6.3
Heavy hydrocarbons	0.0
Methane	7.3
Carbon monoxide	28.8
Hydrogen	30.6
Carbon dioxide	12.3
Nitrogen	14.7

THE LIGHT OIL.

In addition to the foregoing experiments we decided to compare our light oil with that obtained from hard woods as given in an investigation by G. S. Fraps.[1]

This was not fully carried out by reason of lack of time but a few points of interest were developed. Only that portion of the oil boiling below 140° was used. Fifteen liters of the light oil were first fractioned into six fractions—below 75°; 75°-90°; 90°-105°; 105°-120°; 120°-135°; 135°-150°. These portions were then

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[1] *Am. Chem. J.*, **25**, 26.

fractioned, through a Hempel tube, five times and the fractions collected for every five degrees.

It was found that a small portion passed over before 50° was reached and indeed a little before 40° but this is included in the portion 40°-50°. The following table shows the result of this fractionation in percentage of total oil:

Fraction.	Per cent.	Fraction.	Per cent.
40°- 50°	0.37	105°-110°	0.87
50°- 55°	0.47	110°-115°	0.43
55°- 60°	0.77	115°-120°	0.53
60°- 65°	0.55	120°-125°	0.40
65°- 70°	0.62	125°-130°	0.37
70°- 75°	0.70	130°-135°	0.002
75°- 80°	0.57	135°-140°	0.73
80°- 85°	0.93	40°-140°	13.68
85°- 90°	0.94		
90°- 95°	1.40		
95°-100°	1.37		
100°-105°	0.97		

The table shows five points of accumulations of distillate but they are not so marked nor is the percentage of oil coming over below 140° nearly so great as in the oil investigated by Mr. Fraps. The color of the oily distillates varied from colorless to almost black and always darkened upon standing, but the change was not regular.

SOLUBILITY.

The solubility of the fractions was determined by shaking 2 cc. of the oil in a graduated pipette with 10 cc. of water, and determining the loss of volume. The results follow:

Fraction.	Solubility. Per cent.	Fraction.	Solubility. Per cent.
40°-50°	55	85°-90°	30
50°-55°	52	90°-95°	27
55°-60°	50	100°-105°	20
60°-65°	44	105°-110°	16
65°-70°	40	110°-115°	12
70°-75°	35	115°-120°	12
75°-80°	34	120°-125°	10
80°-85°	32	125°-130°	10
		130°-135°	9
		135°-140°	9

It will be noticed that the solubility of this oil is greater for corresponding fractions than in the hard wood oil.

KETONES AND ALDEHYDES.

The ketones and aldehydes were removed from each fraction by shaking with a concentrated solution of acid sodium sulphite, keeping the mixture cool during the reaction. The crystalline precipitates were filtered by suction through muslin, and dried. A second precipitation with sulphite was always attempted. As in the hard oil, the precipitates from the lower fractions were distinctly crystalline and became more gelatinous with the higher fractions, but, curiously, when the higher fractions were reached, *viz.*, from 100° upward, the precipitates became crystalline again. In filtering the lower fractions a strong odor as of acrolein was developed.

The precipitates contained very small quantities of aldehydes. Assuming that half the weight of the dried precipitate is the volume of the ketone the following approximation is reached.

Fraction.	Ketones. Per cent.	Fraction.	Ketones. Per cent.
40°-50°	2.2	95°-100°	1.1
50°-55°	5.7	100°-105°	1.1
55°-60°	9.7	105°-110°	1.0
60°-65°	6.3	110°-115°	2.5
65°-70°	2.2	115°-120°	2.2
70°-75°	3.9	120°-125°	1.7
75°-80°	2.2	125°-130°	1.4
80°-85°	2.1	130°-135°	1.0
85°-90°	4.3	135°-140°	4.4
90°-95°	1.6		

It will be seen that while there is not nearly so large a percentage of ketones in the fir as in the hard oil yet there are marked accumulations at 55°-60° (this is probably acetone), at 70°-75°, at 85°-90°, and at 135°-140°. We attempted to separate the ketones from the sulphite fractions, but the quantities were too small to be of use in further investigation. However, in the fraction 125°-130° a test was made for mesityl oxide which was not found by Mr. Fraps in the hard oil. The solution was distilled with strong caustic soda and a strong odor of peppermint was developed, showing the possible presence of mesityl oxide.

ETHEREAL SALTS.

The residual oil after removal of the ketones was dried and fractionated. The fractions were shaken with a caustic soda solution (1:4) for fifteen to twenty hours. To accomplish this the glass-stoppered bottles were fastened to the face of a wooden pulley about 8 inches in diameter which made nine revolutions per minute. The oils were measured before and after saponification and the loss in volume was considered to be due to the saponification of ethereal salts. This loss was for each fraction as follows:

Fraction.	Per cent.	Fraction.	Per cent.
40°-50°	20	90°-95°	18
50°-55°	23.5	95°-100°	20
55°-60°	27	100°-105°	19
60°-65°	24	105°-110°	13.9
65°-70°	25	110°-115°	17.6
70°-75°	25	115°-120°	15.6
75°-80°	18.5	120°-125°	20.7
80°-85°	31	125°-130°	38.5
85°-90°	15.5	130°-135°	25.4
		135°-140°	27.1

It will be observed that there are marked accumulations at certain temperatures and also that there is no marked decrease in the amount of oil saponified as the boiling-point of the fraction rises. In the higher boiling fractions a gummy solid of a yellow color was formed, which while insoluble in water dissolved easily to a purple solution in nitric, hydrochloric, or sulphuric acids. This color was not destroyed by boiling but disappeared on standing and on addition of water. No attempt to discover its nature was made.

The caustic soda solutions of the ethereal salts were distilled to remove alcohols. No odor of ammonia was developed.

The alcoholic distillates were all found to contain methyl alcohol by the test of Mulliken and Scudder.[1] The alcoholic distillates were also treated with iodine and caustic potash and always gave a decided test for ethyl alcohol.

The acids were now freed by addition of sulphuric acid and distilled.

The silver salts precipitated from the fraction boiling at 40°-50° gave 68.74 per cent. silver. Calculated percentage of silver in silver formate is 70.59; in silver acetate 64.66. The acid was therefore probably a mixture of the two, since methyl formate boils at 30.4° and some of the oil passed over before that temperature was reached. The silver salt of the 50°-55° fraction gave:

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[1] *Am. Chem. J.*, **24**, 444.

	Found.	Formic acid.	Acetic acid.
Percentage of silver	65.44	70.59	64.66

This result we take to indicate the presence of ethyl formate (54.9°) and methyl acetate (57.3°).

The silver salt from fraction 55°-60° gave 64.99 per cent. of silver (calculated for acetic acid, 64.66). It hence consisted almost entirely of methyl acetate (57.3°).

The presence of acetic acid was also indicated by qualitative tests in fraction 70°-75°. Satisfactory results from the silver salt were not obtained because of the small quantity at our disposal.

The same statements apply to fractions 75°-80° in which the boiling-point and odor indicate the presence of methyl propionate (79.5°).

From the fraction 102°-105°, by acidifying with sulphuric acid, an oil separated which was by odor butyric acid and indicates the presence of methyl butyrate (102.3°).

The investigation was necessarily interrupted at this point but will probably be taken up at some future date.

There seems to be enough of interest in the wide difference between this oil and that from other varieties of wood to warrant further investigation.

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INVESTIGATION OF THE OIL OF THE RED ELDERBERRY, "SAMBUCUS RACEMOSA ARBORESCENS."

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ON the western slopes of the Cascade Mountains and on the lowlands about Puget Sound grow great quantities of a red elderberry which, by reason of its large size, is denominated a variety of the species *racemosa.* The berries are a bright crimson and serve as food for birds but because of an unpleasant odor and the presence in them of a considerable quantity of a yellow oil are not used by the people as food nor are they converted into wine.

An investigation of this oil was made with the following results. From about 10 gallons of the berries it was possible to get about 500 cc. of the oil by pressing the juice from berries and ex-