

AN ATTEMPT TO RECOVER CEDARWOOD OIL FROM
WESTERN JUNIPER BY DESTRUCTIVE DISTILLATION

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INTRODUCTION

The western juniper (*Juniperus occidentalis* Hook.) grows in great profusion in arid parts of the western states. It occurs in pure forest form in areas of central and eastern Oregon. It is a tree of low stature with thick, twisted trunk that tapers rapidly, with limbs commencing near the ground level. The juniper has pronounced deficiencies in requirements for conventional utilization. Of these deficiencies the short, gnarled trunk, the deep lobes of the trunk, and the profuse center rot are perhaps the most important. These factors make high-quality lumber production almost impossible and seriously limit the possibilities for peeled or sliced veneer. At the present time the two primary uses of juniper are for fence posts because of the natural resistance to decay of the heartwood, and for novelties where the seasoned wood finds a ready market because of the color and grain variation.

Although it is known that the wood contains cedarwood oil, previous investigators (7, p.23) deemed the quantity available insufficient for commercial recovery by steam distillation. The heartwood portion is most productive

of the volatile oil, but profuse attacks by the fungus Fomes juniperinus (v. Schr.) Sacc. & Syd., reduce this source of the oil. If the oil could be obtained by a means that would produce other products which might defray the cost of production, the utilization of the juniper would be more economically feasible.

OBJECTIVES

It is known that destructive distillation yields many products, some of which have economic value (12, pp.684-685). Therefore, this process was selected as one likely to make the chemical utilization of juniper profitable. Since cedarwood oil is normally obtained by a process of steam distillation, a possibility exists that during the initial stages of destructive distillation when the greater percentage of the condensate is water, this water would carry with it some cedarwood oil from the wood. If such is the case this would be a preliminary steam distillation in the destructive-distillation process.

With samples already available, there existed an opportunity to ascertain the quantity of cedarwood oil that could be recovered by the conventional steam-distillation process. With this in mind the following objectives for the study were established:

1. determine by steam distillation the cedarwood-oil content of a wider selection of juniper-wood samples,
2. determine the possibility of recovering the cedarwood oil through the destructive-distillation of wood and bark,

3. analyze the charcoal and any other products readily identifiable that would supplement the yield of primary product and thus contribute to economic possibilities of utilization through destructive distillation.

With the exception of the steam distillation samples no attempt was made to separate the bark from the wood. All reference to wood in destructive-distillation procedure refers to both wood and bark.

HISTORICAL

There is no record of the actual beginning of the wood-distillation industry, although the production of charcoal has existed for hundreds of years. Charcoal has always been the primary product of the process. Acetic acid and methanol are also recovered in some hardwood-distillation operations. Only recently, because of the decline in use of charcoal, has there been an active interest in the development of recovery processes and uses for other by-products of destructive distillation (9, p.378).

Primarily, destructive distillation of wood consists of heating the wood in a retort or furnace in the absence of air. The elevated temperature brings about a breakdown of the complex wood structure. Of the products recovered, charcoal is the only one that is directly marketable. Other than charcoal, the chemically valuable products of destructive distillation are contained in the volatile vapors given off during the charring process. These vapors are channeled from the retort or furnace through a condenser. After condensation they separate into two layers, a crude pyroligneous acid and a heavy tar. The pyroligneous acid consists primarily of water, methanol, acetic acid, and dissolved

tar-forming materials. The tar was formerly used as a fuel, but its value is increasing as a chemical raw material. At one time acetone was a valuable product from destructive distillation, but it is presently produced more cheaply by other means.

Raw material and product recovery naturally separate the wood-distillation industry into two types, hardwood distillation and softwood distillation. The two processes are similar, with initial carbonization and subsequent refining procedures to recover the volatile products. The principal marketable products from hardwood distillation include charcoal, acetic acid and methanol. The principal products from softwood distillation (pitchy southern pine) include turpentine, pine tar, pine oil, and various types of specialty oils. A typical procedure for the distillation of hardwood and the byproducts obtained is shown in Figure 1 (2, p.51).

The method of recovery of by-products in this study has been modified, since the primary interest lies in the recovery of the volatile oil. It more nearly parallels resinous-wood distillation.

An experimental procedure for small-scale destructive distillation was developed by Subba Ratnum

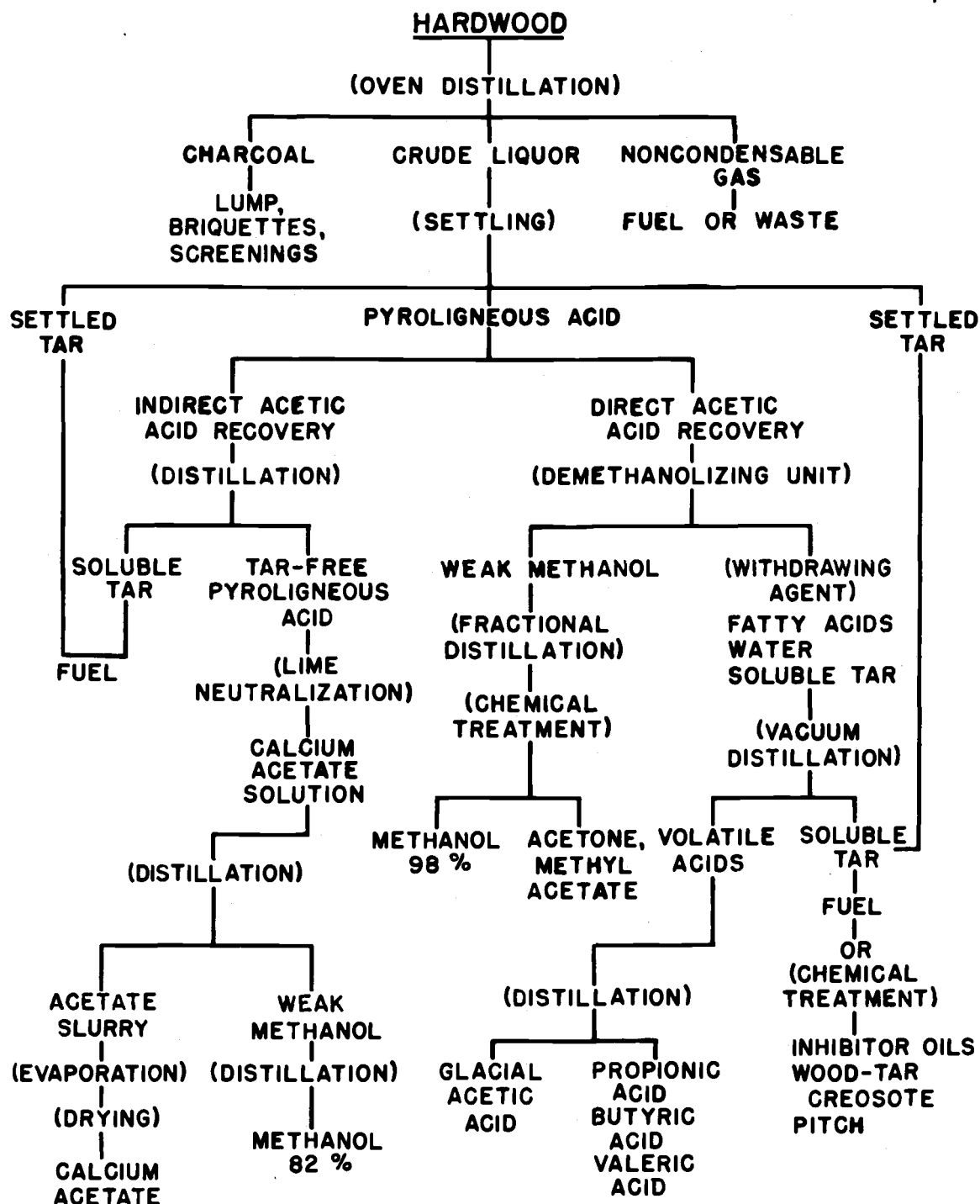


FIGURE 1. PROCEDURES COMMONLY APPLIED FOR THE DISTILLATION OF HARDWOODS AND PRINCIPAL BYPRODUCTS OBTAINED.

in an investigation of Douglas-fir bark (11, pp.20-21). This general procedure has been followed in the carbonization of juniper wood.

Little work has been done on the chemical analysis of western juniper. Lynn and Fischer (8) reported on the chemical analysis of the oil from fresh leaves and twigs. Lackey (7) determined the constituents of the petroleum-ether extractives from the wood. He reported that volatile oil occurred in the whole wood to the extent of one per cent of the acetone extract of whole wood. Rootwood oil was 49.3 per cent cedrene, 17.8 per cent cedrol and the balance unidentified. Kurth and Lackey (5) report that volatile oil from the acetone extract of the bole of the tree yields almost pure cedrol in an amount of 0.9 to 1.25 per cent of the weight of the wood. They also report that oil from stumpwood and rootwood was 49.3 per cent cedrene. Kurth (6) has reported on the chemical composition of juniper wood.

EXPERIMENTAL PROCEDURE

Raw Materials

The material for this study was collected from the vicinity to the southwest and southeast of Prineville, Oregon. The material was classified before collection into three arbitrary types according to the area in which it grew. Type 1 was taken from the dry desert area southwest of Prineville. Type 2 was from moist, valley bottom-land southeast of Prineville. Type 3 was taken from the high desert area between Prineville and Burns, where it grew under arid conditions but in a loose, lava-ash type soil, and at a higher elevation than Type 1. The material was collected in December 1951.

Preparation of Samples

Five trees approximately 16 inches in diameter at a point two feet above the ground were collected from each of the three areas. Two sections were then cut from each tree; one a two-foot section ranging downward from a six-inch top, the other a two-foot section ranging upward from a point one foot above ground level. The five, top sections within each type were then combined

to form a composite sample of the five trees from that type. The same procedure was followed with the butt sections, giving six composite samples in all. Identification hereafter will be by type number and respective top or butt section.

Determination of Cedarwood Oil Content of Wood by Steam Distillation

With the samples of juniper wood available, there existed an opportunity to determine the cedarwood oil content over a wider selection of wood samples than had been done previously. Since the samples were divided into three groups with a further separation of butt and top within these groups, the same classification was retained for the determination of cedarwood oil.

From each composite sample of juniper wood, bark excluded, a sample of ground wood was prepared for direct steam distillation by grinding in a Wiley mill to pass a 28-mesh screen. The distillation apparatus consisted of a 500-ml Erlenmeyer flask with a ground-glass joint. Connected to this flask was a modified Clevenger trap for volatile oils with a specific gravity less than 1.0. Volatile oil was collected in this trap where the volume was read directly to the nearest one-tenth milliliter. Steam distillation was continued until there was no visible evidence of further oil recovery. In most samples

this was accomplished in twenty-four hours. Weight of the oil was calculated on a specific gravity of 0.93 (3, p.118). Percentages were based on the oven-dry weight of the wood. The volatile-oil content of the wood ranged from 1.01 to 1.14 per cent in the top sections of the trees, while the wood from the butt sections yielded oil ranging from 2.01 to 2.43 per cent. The averaged yield was 1.67 per cent. Qualitative tests described later give conclusive evidence of the presence of cedrene and cedrol, the main constituents of cedar-wood oil.

Destructive-distillation Procedure

Since removal of the bark would not be feasible in an economic operation, no attempt was made to remove the bark in the laboratory. To insure representative quantities of bark, sapwood, and heartwood for each charge, each piece in each composite sample was split into pie-shaped sections. These pie-shaped sections were then split into small pieces approximately 12 inches long and ranging in cross-sectional dimension from one half to one and one quarter inches. Random sampling of these pieces was effected for each charge.

Apparatus for distillation consisted of an electric muffle furnace, a cartridge of such dimensions that it

fitted snugly into the opening of the furnace, a time-clock switch to control the heating current going to the furnace, and a condensing train of two flasks in a cold-water bath. A vertical condenser was placed in the second flask. The non-condensable gasses were passed through a wash solution of 10 per cent sodium carbonate before entering the "Precision" wet-test meter. The muffle furnace temperature was controlled by the timeclock setting. Temperatures were read from an automatic potentiometer coupled with an iron-constantan thermocouple placed in the center of the cartridge. The pieces of wood were stacked horizontally into the cartridge, the cover bolted on, and the cartridge placed in the muffle furnace.

Conditions of carbonization were arbitrary. An ultimate temperature of 1100 deg F and a distillation period of eight and one half hours were sought. The actual distillation time varied from eight hours to eight hours and forty minutes. The final distillation temperature ranged from 1060 deg F to 1150 deg F. The muffle furnace was operated at full capacity until the temperature of exothermic reaction was reached, at which point the time of heating was reduced and controlled according to the rise in temperature.

The condensate from the destructive-distillation charges separated into two fractions, pyroligneous acid and tar, with the tar settling to the bottom of the flask.

Products from Destructive Distillation

Separation of the distillate was effected as shown in Figure 2. The crude liquor was first subjected to steam distillation to separate the volatile oils and volatile acids from the tar. Approximately seven liters of distillate were required to remove all but a trace of the volatile oil. The oil was removed from the aqueous distillate in a separatory funnel, the aqueous distillate was then washed with ether, and the ether removed from this solution with a small fractionating column over a steam cone. The two fractions of oil were combined, weighed, and recorded as the volatile-oil content of that particular charge. The aqueous non-volatile acid solution was removed from the non-volatile tar under partial vacuum provided by a water aspirator and heated over a steam cone. The weight of the dried tar residue was recorded. The total dissolved acid was computed as acetic acid. It was titrated against standard base, using phenolphthalein as indicator. The weight was calculated and recorded. The charcoal was allowed to cool for twelve hours in the cartridge before weighing. The non-condensable

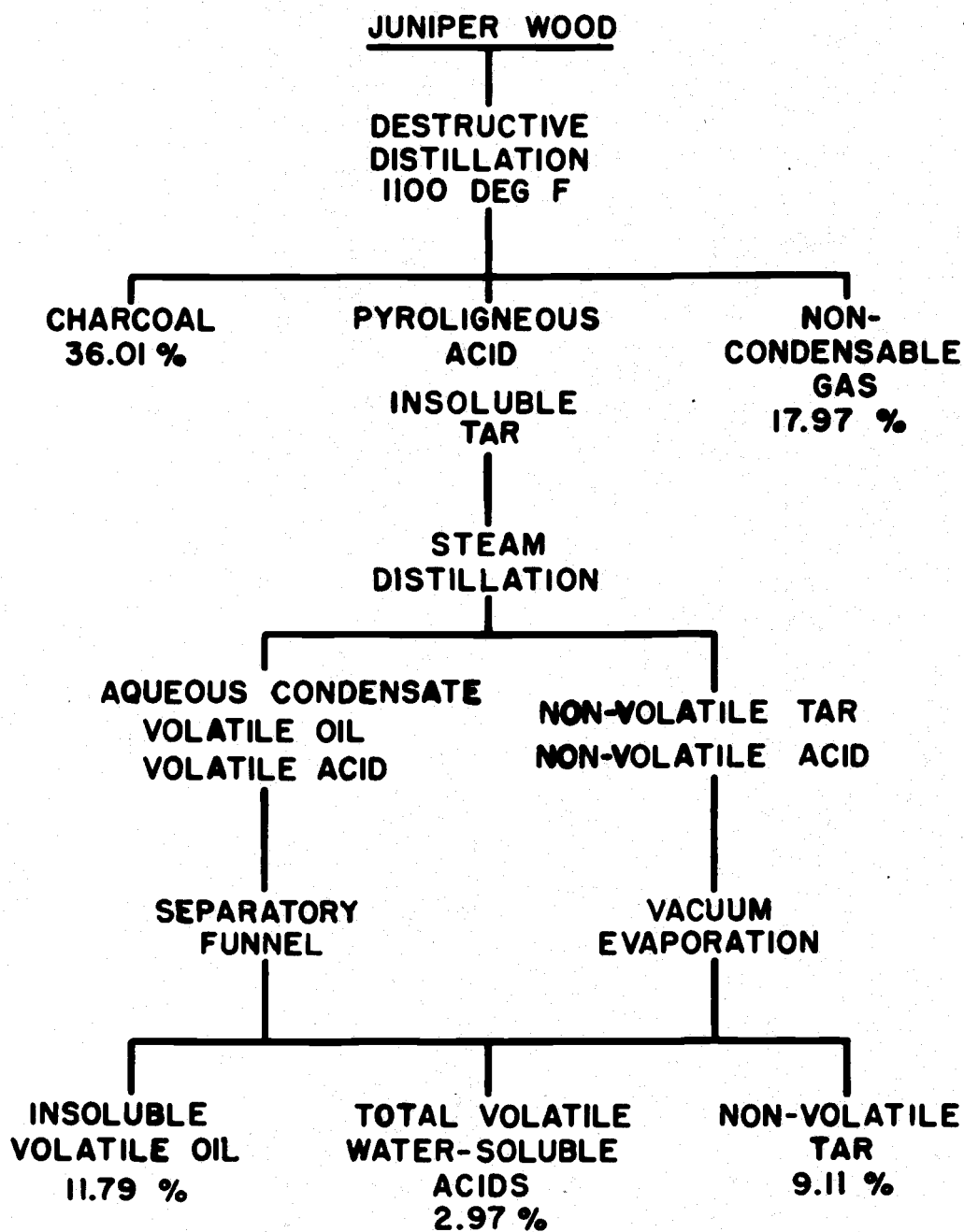


FIGURE 2. RECOVERY OF DESTRUCTIVE-DISTILLATION PRODUCTS.

gas volume was read directly from the wet-test meter, corrected to standard conditions, and the weight calculated on the basis of 0.04 pounds per cubic foot of gas. The yield of products is tabulated in Table 1.

Table 1. Destructive-distillation Products from Western Juniper in Percentages of Oven-dry Weight of Wood and Bark.

Wood :		Products				
	:	Charcoal :	Volatile :	Non-vol-:	Non-con-:	Total
	:	:	Oil :	atile :	densable:	Acid
	:	:	:	Tar :	Gas :	:
1	Top	33.91	2.96*	9.76	17.89	3.36
	Butt	36.66	14.35	7.74	18.46	2.81
2	Top	36.24	10.39	7.90	17.23	3.03
	Butt	36.63	11.83	9.81	16.78	2.69
3	Top	38.18	11.70	8.89	19.72	3.13
	Butt	34.47	10.69	10.53	17.71	2.82

* The moisture content of this charge at the time of carbonization was 25.4 per cent, approximately twice that of the other charges.

Charcoal Analysis

A composite sample of charcoal from the six charges was ground to pass a 60-mesh screen and analyzed for purity according to ASTM procedure (1, pp.20-24). Determinations were made for moisture, ash, and volatile matter, and the carbon content was calculated by

difference. The moisture content was determined by drying a one-gram sample in an electric oven at 104 deg C for one hour. The sample was removed from the oven, cooled in a dessicator over sulphuric acid and weighed. The moisture content was 1.668 per cent. This percentage was used to calculate the other results to a dry basis. For the determination of ash a one-gram sample was heated to constant weight at 750 deg C. The ash content was 1.448 per cent. The volatile matter was determined by heating a one-gram sample in a covered platinum crucible for seven minutes at 950 deg C. The loss of weight minus moisture equals the volatile matter. This was calculated to be 13.610 per cent. The percentage carbon by difference was 82.274 per cent.

Volatile Oil Analysis

The crude volatile oil recovered by steam distillation from the liquor of the six destructive distillation runs was combined to form a composite sample for further analysis. A 25-ml portion was taken from the composite sample. It boiled between 67 and 262 deg C, at which point decomposition started. There was still considerable residue left in the distillation flask.

A solubility test of the crude oil proved inconclusive. The oil was completely soluble in ether, alcohol,

hexane (a slight cloudiness was in evidence in the hexane), and was insoluble in water.

Chemical separation of the oil was then tried, using a 25-ml sample. The oil was diluted with three volumes of ether, and then extracted successively with 5 per cent solutions of sodium bisulfite, sodium bicarbonate, and potassium hydroxide, until a clear extract was obtained from each. These separations were effected to remove the aldehydes, acids, and phenols respectively. The remaining extracted oil was considered as neutral. The oil contained 5.836 per cent aldehydes, 5.940 per cent acids, 29.099 per cent phenols, and 51.529 per cent neutrals by weight. The balance of 7.596 per cent was lost in the various extraction processes.

For analysis of the presence of cedrene and cedrol, 255 ml of the crude volatile oil were treated with dilute potassium hydroxide to remove all acids and phenols. Three successive 400-ml portions of 5 per cent potassium hydroxide solution were required to remove all reactive groups from the neutral oil. The phenol-acid extract was acidified with dilute (3:1) sulphuric acid. The volatile oil was removed from this solution by washing with successive portions of ether. The ether solution was then separated in a separatory funnel and the ether removed with a short Vigreux fractionating column over

a steam cone. Boiling range of this phenol-acid fraction was from 90 to 133 deg C at 20 mm of mercury. Fourteen ml of the oil had been removed between 80 and 100 deg C at atmospheric pressure. No further identification of the phenol fraction was attempted.

The volatile oil remaining from the potassium hydroxide extraction was considered to be neutral oil. This is the fraction that would contain both cedrene and cedrol. The neutral volatile oil was subjected to vacuum fractional distillation. Reduced pressure was supplied by an oil pump with a flutter valve to control the pressure at any desired level. The oil was placed in a round-bottom 500-ml flask with pointed medical-applicator sticks added to prevent bumping. This flask was connected to a 24- by 204-mm Vigreux fractionating column and condenser by means of standard taper glass joints. Heat was supplied by an oil bath. Six fractions were collected from this distillation, a total of 81.4 per cent by weight. Five fractions were collected over a boiling range from 31 to 116 deg C at a pressure of approximately 8 mm of mercury. The fraction that distilled at a temperature of 85 to 95 deg C was redistilled at a pressure of 42 mm of mercury. The entire volume distilled between 147 and 155 deg C. This fraction was near the experimental results as determined

by Lackey (7, p.20) for cedrol. The atmospheric boiling point of this fraction was 234 deg C. Repeated attempts to crystallize by dissolving in hot methanol and cooling (3, p.284) were unsuccessful.

That portion of the original fractional distillation which distilled between 95 and 116 deg C was redistilled at a pressure of 17 mm of mercury. Approximately half of the original volume distilled at a temperature range of 127 to 134 deg C. This compared favorably with the experimental values for cedrene as determined by Lackey (7, p.20). However, the atmospheric boiling point was 230 to 235 deg C as compared with the value of 264 deg C for cedrene (3, p.118). This fraction of the oil was subjected to a color-reaction test for cedrene (4). One ml of a dilute solution of the oil in 95 per cent ethanol was placed in a test tube. The solution was diluted to five ml with ethanol. Five ml of a freshly prepared solution containing one-tenth gram vanillin in 100 ml of concentrated hydrochloric acid was added. A red-violet color is positive for cedrene. The color test on this fraction was negative. It is concluded from the above that neither cedrene nor cedrol is present in the volatile oil obtained by destructive distillation of western juniper.

DISCUSSION AND SUMMARY

An attempt was made to recover cedarwood oil from western juniper by destructive distillation.

The presence of cedarwood oil in juniper wood was determined by steam distillation of a ground-wood sample from each of six composite samples. Oil content ranged from 1.0 to 2.4 per cent of the dry weight of the wood, with the butt sections giving a higher yield of oil than the top sections. Oil yields are considerably greater than those reported by Lackey (7, p.25) and Kurth and Lackey (5, p.2207). Some correlation can be found in that the oil yield from the top portion of trees in this study approximates the yield from the butt section of trees in Kurth's study. Diameters of these respective sections were about eight inches and would probably contain equivalent amounts of sapwood and heartwood. Higher oil yields from the butt sections in this study are probably due to the greater percentage of heartwood in this section of the tree. Lackey stated that the volatile oil content of the whole wood was one per cent of the petroleum ether extract of the whole wood, which would be considerably less than one per cent of the weight of the wood. However, his study of juniper wood was limited to one log approximately eight inches in

diameter at the stump. Therefore it would seem that varying results could be attributed to environmental factors and sampling technique.

Six charges of juniper wood, bark included, were destructively distilled for a period of eight and one half hours to an average final temperature of 1100 deg F. Final temperatures ranged from 1060 to 1150 deg F. Charcoal thus obtained was quite tough, and had split but little during the process of carbonization. The yield of charcoal ranged from 33.9 to 38.2 per cent with an average yield of 36.0 per cent based on the oven-dry weight of the wood and bark. The charcoal contained 82 per cent carbon. Because literature records seldom give the conditions of carbonization it is very difficult to compare the yields obtained in this study with those of other species. The yield of charcoal obtained from juniper is apparently close to that obtained from spruce and pine (12, pp.689-690), and considerably higher than that obtained from Douglas-fir (11, p.9). Lackey (7, p.5) has determined that the lignin content of juniper wood is approximately 5 to 7 per cent over the value for most softwoods. This may account for the higher charcoal yield for juniper.

The volatile oil from destructive distillation was obtained by steam distillation of the crude liquor. The

average yield was 10.32 per cent of the dry weight of the wood and bark. Chemical separation was effected to obtain the neutral portion of volatile oil. This neutral oil was fractionally distilled at reduced pressure.

Boiling points and qualitative tests failed to reveal the presence of either cedrol or cedrene, the two principal constituents of cedarwood oil. The components were not identified. Steam distillation tests gave conclusive evidence that cedarwood oil exists in the wood. It is believed that the initial heat of distillation caused the cedrol to dehydrate to cedrene.

Cedrene in turn was apparently broken down in structure into other compounds. Inclusion of the bark with the wood in destructive distillation may have resulted in a higher yield of volatile oil than would have been obtained with wood alone.

In view of the fact that no positive identification was made of any of the volatile products from destructive distillation, and that these products occur in fairly large amounts, further work would be justified for their identification. Some of the volatile oil fractions were aromatically pleasant. These and other of the lighter oils may have economic value.

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