THE ESSENTIAL OIL OF SEQUOIA SEMPERVIRENS

A thesis submitted in partial satisfaction of the requirements for the degree of Master of Science at the University of California by

HAYWARD MERRIAM SEVERANCE

April 1912

[Degree conferred, Dec. 1914. J. B. R.]
My dear Mr. Russell,

The Thesis of Mr. Severance has been approved and I understand is in your possession.

Edmund C. Weiss

Dec. 15, 1914
THE ESSENTIAL OIL OF SEQUOIA SEMPERVIRENS

No work has been done on this oil, so far as known, with the exception of that of B. R. Bowron, California '02, whose results were presented in a thesis for the bachelor's degree April 1902. So far as he was able to ascertain "no attempts have been made up to this time (1902) to investigate this oil." No mention of it has been found in the literature since that date.

The Sequoia genus comprises only two surviving species; (1) the Bigtree, Sequoia gigantea Dec. (Washingtoniana, Wellingtoniana) growing only on the western slope of the Sierra Nevada in California; (2) the Redwood, Sequoia sempervirens, growing only in a narrow belt along the Californian coast. The essential oil of the Bigtree was described by Lunge and Steinkauler in 1880 (Berichte, XIII, 1656 b, XIV 2202 b). They obtained the oil from small trees growing in Zurich, Switzerland. Their results are dis-
No work has been done on this as yet as far as I know, with the exception of that by Mr. Potter Cellarini's work being presented in a lecture to the Institute's Society April 12th. So far as I can make out no satisfactory researches have been made up to this time (1923) to investigate the site of it. No mention of it has been found in the historical literature.

The position seems completely lost again.

The Province seems complete only to meagre疯

The species: 1. the Pithecanthropus, Pittingtonense Dec.

Western slope of the Taurus Mts, remaining only on the

(2) the Heidelberg, Sedgwick specimens, remaining only in a narrow belt along the Callapatain coast. The steep

site off of the Pithecanthropus geologically far more

published in 1888 (Refael, XIII, 126, p. 1285) that a portion of the off from small pieces from

the in situ, Palaeontop. Brit. Museum we are the
cussed below. This work, quoted by Rollins, soil scientist and Hoffman, is the only one found on the oil of the Big Tree.

The trees used in this work [Redwood] were all young growth, largely stump cut, age of 30 to 20 years, and were cut in cut over forest near Fort Bragg, Mendocino co., Cal. the last week in February 1912. A previous shipment cut during a personal visit to the woods was lost in transit. The weather conditions here (and in general along the coast) are a temperature of about 60°F and a moist atmosphere most of the time. During the two days spent at Fort Bragg a light rain fell almost continuously. This may have been partly to blame for the rapid loss of the oil from the trees after cutting and spring storage in the basement of the Chemistry Building of Pacific.

Apparatus—the oil was extracted in a steam still, shown in attached grins. The still is of copper, the upper part having a perforated bottom on which the material extracted neste. The lower part contains a steam coil attached to the University Heating system. Water is supplied in the lower part, heated by the coil, and steam generated
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Apparatus--The oil was extracted in a steam still, shown in attached print. The still is of copper, the upper part having a perforated bottom on which the material extracted rests. The lower part contains a steam coil attached to the University heating system. Water is poured in the lower part, heated by the coil, the steam generated
The trees near in this wood (Redwood) are
still young enough to make a stump enough of 10 to
80 acres, and we cut in our own forest next
Friday. These Monstrosities call the last week in
February 1915, a brain fever epidemic cut down a
bent-rail which is the fawn was lost in its tent an
The weather conditions here (and in General stone
the coast) the temperature of about 60° F and a
mohat steamy prey at the time. A point that
two days spent at Fort Bluff a light rain fell
almost continually. The may have been pretty
fine after cutting any cutting steve in the
trees after cutting any cutting steve in the
beech of the beech family and beech

Appertaining--The off was extracted in a steam
still, * still, snow in a scattered place, the still is of
steel. The upper part is being a beehive of copper.
The upper part remains a beehive effect to the
lower part containing a steam coil attached to the
university testing settee. Water is pumped to the
lower part toward the coil, the steam generated
passing upward through the holes in the plate on which the material rests. In starting a run the water was also heated by a Bunsen burner until water began to come through the condenser, after which the steam coil furnished heat enough to keep a small stream of water dripping from the outlet.

The four joints of the apparatus; (1) between the top of the still and the head, (2) between the two parts of the still, (3) between head and cross piece and (4) between crosspiece and condenser, were all packed with gaskets cut from asbestos reinforced with fine wire mesh ("gas engine packing"), between brass collars tightened by brass screws. The lower side of each ring was coated with white lead and the upper with graphite. This did away with the necessity of cutting fresh rings after each run.

At the start of each run the still was filled with water to about one inch in the gauge glass. The water which distilled over was withdrawn from under the oil by a siphon and returned to the still. The oil floated on the water in the receiving bottle and was withdrawn from time to time with a pipette. In some cases a slight
Producing moistue resulting the proper in the plate on

which the material resists in stretching a any the

wet surface coagulated by a pronounced purple

diff water began to come through the condenser

after which the stream will intimated near enough

to keep a small stream of water dripping from

the collector.

(1) pe-

The four joints of the apparatus: (2) "one-

between the top of the still and the head,

between the two parts of the still,

between any one piece of (x) between opposite

and condenser were still connected with exekets cut

from the receiver containing with the water near

between piece coils" (between piece coils

stretched on piecealore the lowe side of each

piece were covered with white lead and the upper

with exekets. The air is easy with the necessary

of cutting these lines after each run.

At the start of each run the still was

little with water to about one inch in the column.

The water which collected over was with-

drawn from beneath the oil on a siphon and returned

to the still. The oil is fed on the water in

the receiving potteray was withdrawn from time

to time with a pipette in some cases a slight

The collector...
additional amount of oil separated from the milky water in the large bottle after standing overnight at the conclusion of a run and was also withdrawn. The oil was immediately transferred to a flask, kept tightly corked in the dark in a basement room.

Yield--The oil as it came over had a golden yellow color and the odor of the fresh leaves. It was nearly clear but a turbidity developed on standing.

It was impossible to make a satisfactory determination of the yield owing to several circumstances. The first of these was a delay of a week--ten days after cutting--before the still was available. The first run was interrupted by a leak in the still around the heating coil, causing another delay. The solubility of the oil in water caused a considerable loss, especially on the first run.

The first run was started March 7. Subsequent runs were made March 20, 22, 26, 27, and 29, and April 12. The rapid decline in yield showed that this was obviously and unfair test. The odor from the trees which was very pronounced at first, declined proportionately to the yield and appeared to concentrate lower down in the branches. As the
of theencentration of a new and was also without

Yield--The soil as it came over had a yellow color and the color of the leaf lesions. It was needly clean but a part of the growth developed on a staning

It was impossible to make a satisfactory growth.

mission of the armyön to several ollowances

The trial of these was a hefty of a week--ten days after cutting--before the stilt was available. The trial was interrupted by a lack in the soil around the peeling coat causing another failure. Difficulty of the soil in which caused a contract

For the first time we started Mission A and

male were made

April 15. The third season in which showed that these were obtained and with some taste from the trees which were very promising at that time.

offered boardersinstrn for the help and assistance.

to concentrate lower down in the parishes. The
trees began to dry, the pleasant aromatic odor disappeared, except on breaking a twig 1-2" or more in diameter, and another quite different one took its place. There was no change in the oil except a possible slight darkening. (Owing to its being spread out in a thin layer it was impossible to determine this.)

Branches were cut off the trees as needed, up to a diameter of about ½" and including all of the growth of the last year. The terpene odor was strongest in the tops of the trees, especially the new growth of the main trunk.

Fractionation--The first fraction was distilled again from a 20cc flask. (There was not enough to use a column.) The oil distilled with 7000 grams. The other runs were made on smaller quantities up to 4600g. with the idea of hastening the time of extraction. This appeared to be complete in two to three hours in all cases except the first. When this work is resumed a quantitative determination of the yield from fresh foliage will be made.

Purification of the oil--In this way about 150cc of oil were collected (not including the oil dissolved in the water). This was rectified by distillation with steam, the oil coming over being collected fractionally in four portions of about 25cc each. The water was removed by a
The pleasant atmosphere of all parts except the garage and the areas around the garage were immaculate. There were no cracks in the tiles except outside the garage. The absence of algae was remarkable. Coming from the pen, I was impressed by the germinating Ging.

Knowing were one of the trees in need,
up to a number of about 20 and including all
of the growth of the last year. The results of
were astounding in the tops of the trees, especially
the new growth of the main trunk.

The soil was hotted slightly on the site to
with 9000 square. The next time were made on
smaller dimensions up to 8000. With the idea of
preventing the time of excretion, the spores
to be concentrated in two to three homes in all cases
except the little. When the work is done or
during the germination of the after from
the seed lots will be made.

Petition of the off. In this way:

Food of off were collected (not in the
off associated in the water). There we're collecting
0% of excretion with steam. The off coming over
per cent collected immediately in their bottle
of about 500 each. The water was removed by a
separating funnel and the oil dried by sodium sulphate. The first fraction after being so treated was clear and colorless, with the same odor as that of the original oil but more delicate—evidently a terpene hydrocarbon. The second fraction had a light yellow green tinge, the two following a deeper color. After four fractions had been collected, the oil ceased to come over with the water and distillation was stopped.

Fractionation—The first fraction was distilled again from a 20cc flask. (There was not enough to use a Hempel column.) The oil distilled almost completely at 157–160. With about 1cc remaining the thermometer rose above 162° and the residue turned greenish yellow. The flame was removed at this point. No carbonization or decomposition was evident from the appearance or odor of the residue.

The second, third, and fourth fractions from the steam distillation were distilled again. The distillate was collected as the first fraction to 160°, the second to 165°. The temperature then rose rapidly to 190° at which most of the remainder passed over. This fraction
Separating furnace and the oil grate by a sloping surface. The first section after being treated was clean and colorless, with the same aspect as that of the original oil put more after.

After treatment had a light yellow green tinge.

The two following a deeper color. After hom treatment had been collected, the oil ceased to come over with the water and distillation was stopped.

Distillation

The first section was the volume to see a yellow color. This oil distilled almost completely at 195-200°. With spot test to be-

maintained the thermometer rose space 175°, and the temperature at the bottom of the column.

No condensation or flow

position was evident from the appearance of color.

The second, third, and fourth sections.

From the steam distillation were hailing.

The oil, after treatment as collected, was the first section to 195°, the second to 200°, the firm.

Because these lose rapidly to 100° at first.
evidently suffered some decomposition. At 198°C no more passed over and the temperature dropped. The residue (about 2cc) solidified on cooling.

The first fraction, constituting the greater part of the oil, was distilled again and constants determined as follows:

Boiling point 157°C (Stem exposed above 540)
Specific gravity (capillary pyrometer) $d_{150} = 0.831$
Refractive index (Abbe') $n_{18.50} = 1.473$

There was no action on the oil by freshly cut sodium. The odor resembles that of the entire oil but is not so strong and each distillation appeared to diminish it slightly.
specific gravity (sp. gr.)

\[ \frac{0.831}{b} \]

refractive index (n \_D)

[1.475]

Polarization

Schmidt & Hessen polarizer

\[ D = \frac{5400}{290} \]

There was no reaction on the end of the test. The color of the solution was not so strong as expected.

Attention suggested to the inspection of affinity.
This suggests that the odor may come from a trace of high boiling aldehyde or ester.

Ultimate analysis—0.3669g. of oil was burned in a combustion analysis, resulting as follows:

<table>
<thead>
<tr>
<th>Found</th>
<th>Calculated for C_{10}H_{16}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 87.085</td>
<td>88.20</td>
</tr>
<tr>
<td>H 11.73</td>
<td>11.80</td>
</tr>
</tbody>
</table>

The low yield of carbon is apparently a result of the large quantity taken and of a slightly rapid current of oxygen and air through the tube, causing incomplete absorption of the CO_2. To drive off all moisture in the tube it was heated to the safe limit of the glass for an hour and cooled with a slow stream of purified air passing through.

Comparison with terpene from Bigtree—Lunge and Steinkauler report as their first compound from the oil of Sequoia washingtoniana a colorless oil, b. p. 155°, d_{150} 0.8522; vapor density (Victor Meyer in diphenyl amine) 69.67 (C_{10}H_{16} = 68) Rotation (Wild Polaristrobometer) (α) = 23.8

<table>
<thead>
<tr>
<th>Found</th>
<th>Calculated C_{10}H_{16}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 86.09</td>
<td>87.90</td>
</tr>
<tr>
<td>H 12.68</td>
<td>1230</td>
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<tr>
<td></td>
<td>11.80</td>
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The following data are from a Grace ultimate instability.

<table>
<thead>
<tr>
<th>Ultimate Instability</th>
<th>0.899e-01</th>
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| *One test of material testing as follows:*
| Formulated for 0.10%    |
| 58.20                |
| 51.72                |

According to oxydern G. E. is 81.2, 0.8388; these percent.

For the first time of the I. H. so not and according with a flow stream of printing at press.

Calculated for 0.10%:

| 58.20 |
| 51.72 |

...
Addition of Bromine—Two cc of hydrocarbon were dissolved in four volumes of alcohol and four of ether, the solution cooled by ice and distilling, it was transferred to a boiling point salt and bromine added drop by drop. Complete discoloration resulted, indicating unsaturation. Bromine was added until a yellow color appeared.

On standing in ice a short time the color disappeared and a few more drops of bromine were added, shaking after each addition. When the yellow color reappeared the tube was left in ice until the ice melted but no crystals appeared. The tube was then exposed to the air. After approximately a third of the solution had evaporated a layer with a slight yellow tint appeared at the bottom. At room temperature this was slightly turbid, but cleared on warming to about 25°. After three days the solvent was driven off as much as possible by surrounding with water which was gradually brought to boiling.

There still remained a volume of solvent approximately that of the oil below. The upper layer was pipetted off, some of the lower removed and placed in a clean tube, a few drops of ligroin added and the tube cooled and allowed to stand 24 hours. The oil again separated as a turbid liquid, clearing on gently warming.
Agitation of Promine--Two or three preliminary
were giving me in lower volumes at school and
from of these, the solution coated on ice and
self and Promine spread on an object. Complete
neutralization sewage. Neutralizing, neutralizing neutralization
Promine was mixed with a yellow color substitute.

On standing in the form time the color of the
substance and a few more days Promine were
seemed smoky after each application. The
yellow color began to disappear the substance wax felt in
the milk. The milk wax then exposed to the art.

After approximately a third of the solution and
well as pretty uniform, put on a great deal
were slightly turbid, 10% coated on waiting to

After three days the solution was

was expanded, but the solution with
water, which was expanded to point to pollution.
These with remaining a volume of solution supply
inertly just at the oil before the upper layer
were bleached off. Some of the lower remains and
placed in a green glass a few drops of Lead
bathed the Fine coated and allowed to stand

In order, to ensure on receipt waiting,
As the quantity of brominated oil on hand was not sufficient to attempt a purification by distilling, it was transferred to a boiling point apparatus and the sulphuric acid bath slowly heated. The oil gradually darkened, indicating a separation of bromine. At $50^\circ$ it was red (the color of dilute ferric sulphocyanate) and at $100^\circ$ almost black. At $157^\circ$ fumes of bromine and hydrobromic acid came off copiously and the oil distilled into the reservoir above the air chamber. After cooling the liquid remained black, slightly more viscous and with a changed odor, but not one suggesting carbonization.

Addition of Iodine—About 1cc of oil was dissolved in an equal volume of absolute alcohol and a saturated solution of iodine in alcohol added drop by drop with shaking. No visible discoloration followed. The mixture was allowed to stand for two days and the excess alcohol was then driven off by immersing the bottle in water which was brought to a boil. The liquid which remained had a color not quite as dark as ordinary iodine tincture and a peculiar odor resembling that of anethol. Owing to lack of time work was discontinued at this point. An attempt
As the density of the current on the wing was not sufficient to support a balloon in a vertical ascent, we were transferred to a smaller boat. The oil was at a temperature of 60°, and on the center of the oil rest, 1.240 times, 0.350, and the oil was finally poured into the boat. A natural space filled with the oil provided a natural space, and with a opened oil, not in one successful attachment of the pipe.

Addition of a pipe--Pour 100 oil on oil we issued, in an empty volume of a proper size, and a separate addition to that in progress of a pipe to the oil, not in an oil, or a pipe in the oil. The mixture was allowed to stand for two years, and the excess stood by the cold, with a separate addition of a pipe to the oil. The filling method was examined with a separate addition to the oil, and a separate addition to the oil, with a separate addition of a pipe to the oil, and a separate addition to the oil.
to form an iodine addition compound will be made later.

Residue of the original oil--The residue which remained in the flask on the rectification by distillation with steam was separated from the water by a separating funnel and allowed to stand until the emulsion layer and presumably impurities carried over from the original distillation had settled. This left a yellow oil, thicker than the original oil as obtained from the still and with nearly the same odor. This oil was filtered through cotton, coming through perfectly clear. On heating it was found to contain a large percentage of water. Granulated calcium chloride was added and the oil allowed to stand two days with occasional shaking. A considerable amount of water separated out below the oil. An attempt was then made to distill the oil. This was a total failure under atmospheric pressure. Decomposition (and probably formation of resins) occurred before any vapor passed over. The quantity of unheated oil on hand was not sufficient for a distillation under reduced pressure and that is also deferred.
It was found to contain a large percentage of water. Gradually, some oil floated and some took and the oil allowed to stand two days with occasional stirring. A considerable amount of water separated.

It was then removed from the mixture, and the oil was a solid fat. It was a good material for margarine, and proved to be a good source of fat for the manufacture of margarine. The quantities of the material and water were balanced on the scale, and the mixture and water were then combined to form a gelled mass.
pending a new supply of foliage.

Products from the Bigtree—As the only closely allied botanical species, the Sequoia oils give an indication of possible products to expect from the redwood. Lunge and Steinkauler report the following, besides the hydrocarbon already referred to:

(2) A colorless oil turning yellow on long keeping, odor reminding of peppermint. Boiling point 227--230°, d 1.045, n about --6.

(3) In very small amount a heavy yellow oil, boiling point 280--290°.

(4) A solid body "Sequojen" with melting point 105°, boiling point 290-300°. White leaflets with weak bluish fluorescence.

This study was begun at the suggestion of Mr. Carl A. Kupfer, Forest Assistant, United States Forest Service, San Francisco, to whom I am indebted for kind assistance at several stages of the work. Acknowledgments are also due to President Johnson and other officers of the Union Lumber Co., San Francisco, for assis-
(2) A collection of turning yellow on line.

(3) In very small amount a very yellow oil.

(4) A slightly color "redating" with water.


The study was begun at the suggestion of Mr. Fleet, Assistant, U.S.I. and Mr. Fleet, Assistant, New California, to whom the author's thanks are expressed for the work's encouragement and other offices of the Union Pacific Co. New California, 49 State.

(6)
ance in securing material and to Dr. C. E. Burke of the College of Chemistry, University of California for many suggestions and aids in the analysis. To all of these, my most cordial thanks.

The work will be continued.

Chemistry Building, University of California,

Berkeley, Cal.,

April, 1912.
The work will be continued.

Chemistry Building, University of California

Henry E. Gilman

April 13, 1913
Sprout growth from Redwood stump. Material of character used in this work.

(Photo by Forest Service.)