THE PRODUCTS OF
THE DESTRUCTIVE DISTILLATION OF LARIX AMERICANA

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The Larix Americana, commonly called tamarack, is a tree growing abundantly in Wisconsin and neighboring states. It is found in cold, deep swamps which are designated tamarack swamps, but is occasionly found on dry land. It is a tree 50 to 60 feet high, trunk 18 to 20 inches in diameter; small horizontal branches forming during the early life of the tree a narrow regular pyramidal head always characteristic of this tree when crowded in the forest, but in the open sweeping out in graceful curves, often becoming contorted and pendulus and forming a broad, open frequently picturesque head, and slender leading brachlets often covered at first with a glaucous bloom, becoming light orange brown during their first winter and conspicuous from the small globose, dark red, lustrous buds. Leaves linear, triangular, rounded above, prominently keeled on their lower surface, 3/4 to 1 1/4 inches long, bright green, conspicuously stomatiferous when they first appear; turning yellow anf falling in September or October. Flowers: staminate, subglobose and sessile, pale yellow; pistillate, oblong, with light colored bracts produced into elongated green tips, and nearly orbicular, rose red scales. Fruit: on stout incurved stems, oblong rather obtuse, 1/2 to 3/4 in. long, composed of about 20 scales slightly erose

on their nearly entire margins, rather longer than broad and twice as long as their bracts, bright chesnut brown at maturity, usually falling during the second year; Seeds: 1/8 in. long, about one third as long as their chestnut brown wings broadest near the middle and obliquely rounded at the apex. Bark of the trunk 1/2 to 3/4 of an inch thick, separating into thin closely oppressed, rather bright reddish brown scales. Wood heavy, hard, very strong, rather coarsely grained, very durable, light brownish yellow, sapwood nearly white, very resinous. Used for the upper knees and other ship timbers of small vessels, fence posts, telegraph poles, and railway ties.

As far as can be found no one has ever made a study of the products of destructive distillation of the tamarack.

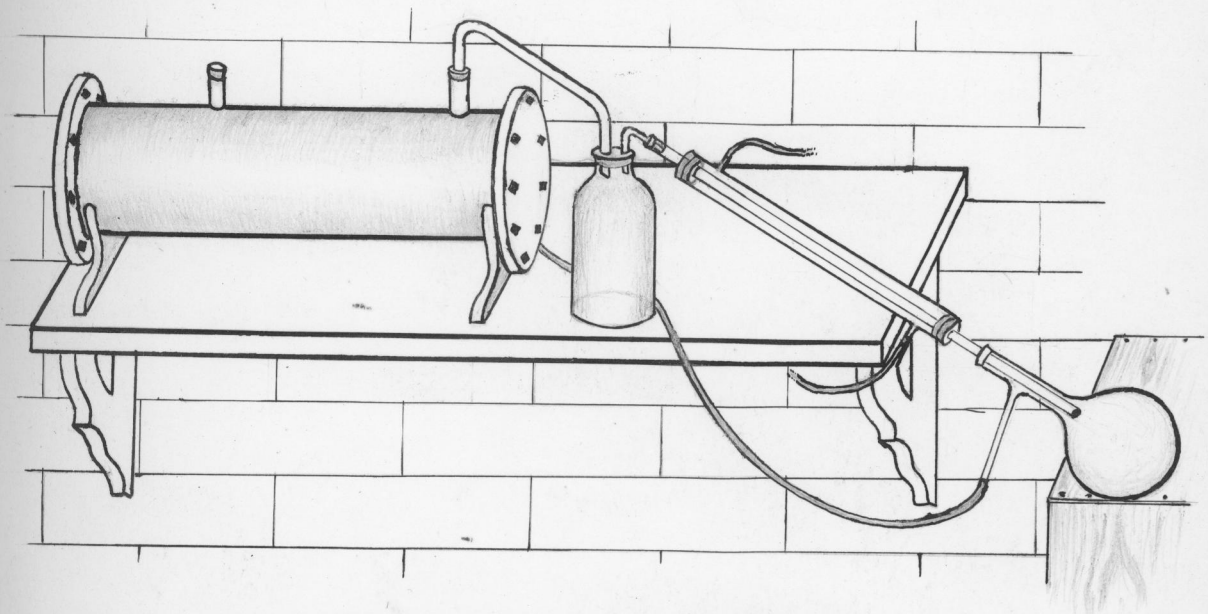
The material for this work was kindly supplied by Mr. Benjamin Walther of Helenville, Wisconsin. The tree was about 10 inches in diameter, forty feet high and was collected in the month of January. The bark was carefully stripped from the wood and a separate study made of it. The heart wood of the trunk seemed to be the most resinous even occasionally containing a clear, light straw colored

resin, in narrow pits which varied from one half to two inches in length. These pits were not of a sufficient number to allow any appreciable amount of the resin to be collected.

Before subjecting the bark to destructive distillation, it was distilled with steam, in order to determine the presence of any volatie oil. One hundred and twenty five pounds of bark were distilled and about fifteen gallons of aqueous distillate was collected. No volatile oil was obtained, although the distillate had the characteristic fragrant odor of the bark. Nothing further was attempted with the distillate.

The dried bark was then distilled by destructive distillation, using a cylindrical iron still as shown in the accompanying illustration. The still was connected by a delivery tube to a water cooled condenser, which was connected with a large Emery distilling flask used as a receiver; through the outlet of the flask the gas was conducted back to the still where it was used as fuel. An attempt was made to collect and determine the weight of the gas obtained for every distillation, but this was found impracticable because of the quantities of gas generated. The supply of gas was sufficient to keep a large Bunsen burner burning with a large flame through the entire

distillation.



The distillate consisted of a reddish colored aqueous part and a dark brown oily layer which was very thick and hard to separate completely from the aqueous part. The following table shows the results obtained:

Destructive distillation of the bark of Larix Americana.

Distillations	Wt. of the bark used.	Wt. of total dist.	Percentage yield	Wt. of the charcoal. *
First Distillation	5000 gms.	2700 g.	54.0 p.c.	1900 gms.
Second Distillation	5000 "	2475 "	49.5 p.c.	1900 "
Third Distillation	5000 "	2450 "	49.0 p.c.	1900 "
Fourth Distillation	5600 "	2660 "	47.5 p.c.	1900 "
Fifth Distillation	5600 "	2270 "	40.35p.c.	1900 "

* The weight of the charcoal as given in the table for any one distillation is the average of all the distillations.

The entire distillate being strongly acid, was neutralized with sodium carbonate thus liberating any oil held in solution by the free acetic acid. The oily layer could then be much more easily separated from the aqueous layer, which was accomplished by means of an ordinary separatory funnel. The total weights of the products obtained in all of the above distillations taken together, is

as follows:

Weight of the bark used.....	26200 grams.	
Weight of the oil obtained.....	610 "	or 2.32 p.c.
Weight of the aqueous distillate..	11945 "	or 47.91 p.c.
Weight of the charcoal	10120 "	or 38.62 p.c.
Loss in gas, e tc....	3525 "	or 11.15 p.c.
	26200 gms.	100.00 p.c.

Distillation of the Wood.

The wood of Larix americana was cut in suitable lengths, then split in thin pieces about the size of a lath, in order to facilitate thorough carbonization.

Distillation began fifteen minutes after the application of heat to the still. The greater part of the oily distillate passed over during the early part of the distillation, appearing as light yellow colored vapors, but after being cooled and condensed soon turned to a dark brown color, and sank to the bottom of the receiver. As obtained directly from the still the aqueous portion of the distillate was of a light yellow color, but upon neutralizing the pyroligneous acid with sodium carbonate, the aqueous layer turned red, and the thick oily portion rose to the surface. The following table shows the results of the distillations and percentages of products obtained:

Distillation of the Wood of Larix Americana .

Distillations.	Wt. of Wood used.	Wt. of Distillate.	Percent	Wt. of Charcoal	Percent.	Loss in Gas.	Percent.
1	6000 g.	3065 g.	51.08	2315 g.	38.58	620 g.	10.34
2	6000	2905	48.41	2200	36.66	895	14.93
3	6000	3005	50.08	2210	36.83	785	13.09
4	6000	2580	43.00	2180	36.33	1240 *	20.67
5	6000	2960	49.33	2260	37.66	780	13.01
6	6000	2805	46.75	2630	43.83	565	9.42
7	6000	2420	40.33	2690	44.83	890 *	14.84
8	6000	2925	48.75	2300	38.11	775	13.14
9	6000	2860	47.66	2300	38.11	840	14.23

* In the fourth and seventh distillations a leakage in the still caused a loss of vapors and a consequent inaccuracy of results.

The total weights and percentages of the products obtained in all of the foregoing distillations taken together is as follows:

Wt. of wood used.....54000 gms.
Wt. of distillate obtained.....25525 " or 47.26%
Wt. of charcoal.....21085 or 39.04%
Loss in gas, etc.....7390 or 13.70%

After neutralizing the entire distillate with sodium carbonate the oily potrion cound be easily separated from the aqueous part, and this was accomplished by means of a large separatory funnel. The following table shows the weights of the products of distillation then obtained:

Wt. of wood used.....54000 gms.
Wt. of oily distillate.....2440 " or 4.51 %.
Wt. of aqueous distillate.....23085 or 42.75 %.
Wt. of charcoal.....21085 or 39.04 %.
Loss in gas, etc.....7390 or 13.70 %.

A comparison of the results obtained in the distillation of the bark with those obtained when the wood was distilled, shows that the wood yields about twice as

much oil as the bark, the latter yielding 2.32 percent of oil while the wood yielded 4.51 percent. This was to be expected from the fact that the wood appeared much more resinous, even containing resin ducts. The percent of charcoal obtained in the two cases was almost the same, while the bark yielded a greater percent of aqueous distillate.

An experiment was made in the sixth distillation to determine the effect of a larger or smaller amount of heat on the quantity of the oil produced. About two thirds of the number of burners used in the preceding distillations were used, with the result of an increase of only fifteen grams of crude oily distillate after separating from the aqueous portion. The gas percentage was reduced but the charcoal percentage was increased; while the time required for complete charring of the wood was eight hours being almost double that of the foregoing distillations, which was four and one half hours.

Although one would expect to obtain a greater percentage of yield of oil, when the distillation was conducted at more moderate temperatures, it was not possible with apparatus used to obtain results which corresponded with this. On account of the great radation of heat from the apparatus, no distillation whatever, came over

when the number of burners was diminished below the number used in Exp. No. 6. With the increase of the number of burners, however, the time of distillation was decreased, but the percent of oil remained almost constant.

The bark required a much longer period of heating, than did the wood, eight hours being necessary for complete distillation.

Rectification of the Oil from the Bark.

The crude oily distillate from the bark consisted of two portions, a hydrocarbon oil and a phenol oil. To separate the non-phenol or hydrocarbon oil from the phenol oil, the crude mixture was shaken in a separatory funnel with a three percent solution of potassium hydrate (commercial potash) until alkaline, and the aqueous portion drawn off and reserved. The oily portion remaining in the separatory funnel was washed with a dilute solution of hydrochloric acid until neutral, then distilled by steam distillation. About thirty cc. of a clear oil were obtained, of a dark red color and a strongly empyreumatic odor.

This was rectified by the process of the United States Pharmacopoeia of 1900 for Oleum Terebinthina

Rectificatum, by mixing with an equal volume of sodium hydrate solution, then distilling with steam until the greater part of the oil had passed over. The oil distilled quite readily and was collected in a separatory funnel used as a receiver, and by means of which the oil was easily separated from the aqueous distillate without the usual small loss in volume incurred by changing from a receiver to a separatory funnel. Twenty five cubic centimeters of product were obtained, of a lemon green color which upon standing soon changed to a dark bronze color; odor empyreumatic, slightly terebinthinate; specific gravity at 25°C. = 0.8830, index of refraction= 1.49165, optically inactive.

This oil was then distilled by direct distillation. On account of the small amount of oil worked with, separation into fractions was useless; the variation in the boiling point was therefore simply noted. Distillation commenced at a temperature of 65° C. with a steady rise in temperature to 165°C. Only a small quantity of the distillate had passed over up to this point. From 170° to 180° about one fourth of the entire amount of oil had passed over, the temperature rising steadily to 186° where one half of the oil used came over. From 186° the rise was

steady, with a constant decrease in the volume of distillate, until at 240° distillation ceased. The distilled product was of a light lemon yellow color, empyreumatic, terebinthinate odor, and a burning taste.

The oil evidebtly contains no pinene as is shown by the fact that practically no oil distills below 170°, and also by the fact that the oil is optically inactive.

A comparison of the physical constants of the oil with the physical constants of known terpenes whose boiling points fall within the boiling point of the oil, are shown in the following table:

Terpene	Sp. Gr.	α_D	Index of Refraction.
Dipentene	0.845	Inactive	N_c = 1.47308
Sylvestrene	0.8510	+66.32°	N_c = 1.47468
Terpinene	0.847	Inactive	N_d = 1.48458
Oil from Bark of Larix americana.	0.8830	Inactive	1.49165

Phenol Oil from the Bark.

The reserved aqueous potassium hydrate solution from the saponification of the non-phenol oil, containing the phenol oil in solution was treated with hydrochloric acid until the solution was slightly acid, in order to precipitate the phenols. A thick, brownish black precipitate resulted which was filtered out by means of a wetted filter. This precipitate was placed in the distilling bulb of a diminished pressure apparatus and distilled under diminished pressure. The first fraction of distillate which passed over at a temperature of 45° and a pressure of three mm. consisted entirely of water. The following table shows the results obtained.

Fractions.	Temperature.	Pressure.	Wt. of Distillate.
1 - Fraction	120°-135°	77.5 mm.	5.1 gms.
2 - Fraction	135°-170°	77.5 mm.	14.6 gms.
3 - Fraction	170°-205°	117 mm.	14.0 gms.
4 - Fraction	205°-270°	172 mm.	17.0 gms.

The greater part of the third fraction passed over at 200°; and in the fourth fraction the greater portion passed ov er at 245°. The phenol appeared as a clear, thick, almost colorless liquid which soon changed to a deep red color; readily soluble in potassium hydrate solution and in alcohol.

50.7 gms. of entire product was obtained, corresponding to 8.36 % of phenols in the crude oily distillate from the bark, and 0.1946 % of phenol in the bark proper.

Residue left in the distilling flask was black in color and almost solid.

Rectification of the Crude Oil from the Wood.

The crude oil from the wood of Larix americana evidently consisted of a mixture of a hydrocarbon oil and a phenol oil. The non-phenol or the hydrocarbon oil was separated by the same method as engaged in the rectification of the oil from the bark, by treating with a five percent sodium hydrate solution. The greater portion of the crude oil seemed to be of a phenol nature, as it was soluble in the alkali and formed a dark red-brown solution. The entire mixture was placed in a copper still and distilled with steam. The non-phenol oil distilled over as a light straw-colored oil, witha empyreumatic odor and a burning taste; the odor however, was much less strongly empyreumatic than that of the similaroil obtained from the bark.

The non-phenol distillate obtained, which had a strong basic odor, was shaken with a five percent solution of hydrochloric acid in order to remove any basic principles present in the oil, and the acid solution then allowed to evaporate spontaneously to dryness. Only about 0.75 grams of residue were obtained ,,of an amorphous nature dark brown in color, and a pungent odor.

The oil, now free from basic principles, was rectified by the process of the United States Pharmacopoeia of 1900 by shaking with an equal volume of sodium hydrate solution and distilling with steam. The oily distillate thus obtained was of a light straw color, slightly empyreumatic odor; specific gravity at 27° C.= 0.9278; the specific rotatory power was then taken, using a 100 mm. tube, and the angle was found to be less than a half of a degree dextrogyrate; index of refraction 1.49552; volume obtained 75.0 cc.

The rectified product was then distilled by direct distillation, and found to distill at a temperature of 150°C. The temperature gradually rose to 170°, about 20 cc. having passed over up to this point. At 180° about one half of the entire volume had passed over; at 200° about four fifths of the entire volume had distilled, and at 220° almost the entire bulk had passed over and distillation was discontinued. About 70.0 cc. of product was obtained, which was of a light lemon yellow color, terebinthinate slightly empyreumatic odor, and a burning taste.

The non-phenol oil from the wood boiled at somewhat lower temperature than that from the bark, a considerable portion coming over at a temperature which would

indicate pinene. A comparison of the constants of the two oils is given in the following table:-

Non-phenol Oil	Boiling point.	Sp.Gr.	a_D	Index of refraction.
From Bark	-170°	0.8830	Inactive	1.49165
	170°-186°-1/4 of oil			
	186° - 1/2 of oil			
	186°-240°			
From Wood	150°-170° -1/4 of oil.	0.9278	+0.5°	1.49552
	170°-180° -1/2 of oil			
	180°-220°			

Phenol Oil from the Wood.

The alkaline residue from the steam distillation of the crude oil, containing the phenol oil in solution, was acidified with hydrochloric acid thus precipitating the phenols contained. The black precipitate was separated by filtering through a wetted filter, and distilled under diminished pressure.

The phenol distillate was clear, thick and almost colorless but soon changed to a deep red color. The greater part of the distillate passed over between the temperature of 225° and 260°.

Four hundred grams of product was obtained, corresponding to 16.39 % of phenol in the crude oil, and 7.4 % in the wood proper.

The residue left in the flask was black, solid and very brittle.

The following table shows the results obtained:

Fractional Distillation of Phenol from the Wood.

Fraction.	Temperature.	Pressure.	Wt. of Distillate.
No. 1	90°-125°	374 mm.	10 grams.
No. 2	125°	83 mm.	20 "
No. 3	125°-150°	83 "	10 "
No. 4	150°-160°	79 "	25 "
No. 5	160°-225°	75 "	45 "
No. 6	225°-235°	75 "	120 "
No. 7	235°-260°	75 "	130 "
No. 8	260°-278°	75 "	40 "

The wood of the Tamarack, as is shown by the results obtained, contained almost thirty nine times as much phenol as the bark; the former containing 7.4 percent and the la tter 0.1946 percent. The production of hydrocarbon or non-phenol oil was more nearly the same in each case, the bark producing 0.084 percent of rectified oil, and the wood 0.127 percent. These results were contrary to expectation, as it was thought the wood of the Tamarack would produce a much larger percentage of non-phenol oil and a smaller percentage of phenol than was actually found.

Sodium Acetate.

The oily and aqueous distillates of both bark and wood were of decided acid character, from the acetic acid formed. This pyroligneous acid was neutralized with sodium carbonate, forming sodium acetate in solution.

The oily portion was separated from the neutral aqueous portion, which was of a reddish brown color and empyreumatic odor, and the aqueous portion evaporated to a small volume, filtered while hot, and allowed to crystallize out.

On evaporating, when the heat was first applied, vapors passed off which had an ethereal odor and caused smarting of the eyes; this was probably wood alcohol in the solution.

Ten liters or 10500 gms. of aqueous solution (Sp Gr. 1.05 at 20°C.) upon evaporation and crystallization produced 600 gms. of crude sodium acetate, after being freed from the tar which separated from the mother liquid upon cooling. This crude sodium acetate was dissolved, filtered and recrystallized from cold water, thus removing much of the dark, reddish black gummy material. 500 grams of sodium acetate were obtained. This corresponded

to 500 grams of free acetic acid or 4.76 percent of acetic acid in the original aqueous distillate.

A test was made on the crude salt of the solvent action of alcohol and water, to determine the practibility of partially purifying the salt by washing with each menstruum to remove the coloring matter etc. Alcohol removed the coloring matter better than water, and also exerted a much less solvent action on the salt; the salt being soluble in 30 parts of alcohol and in 1.4 parts of water. Even the alcohol however did not remove enough of the coloring and organic material to be made of practical use.

Approved..... L. W. Brandt .....

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