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THE INFLUENCE OF METHODS OF DISTILLATION ON THE COMMERCIAL VALUE OF OIL OF AMERICAN WORMSEED.

BY G. A. RUSSELL.

INTRODUCTION.

Within the past few years considerable difficulty has been experienced by the trade in securing wormseed oil that conforms to the U. S. P. specifications. Whereas small lots of oil have been secured in quantities to meet the spot demand to a greater or less degree, the supply left in the hands of the producers has been of relatively large magnitude. This oil was probably, without exception, of such character that it did not test up to the U. S. P. requirements, and this condition of affairs appears to have grown more and more acute until at the present time it is stated that more than 50 percent of the crop is still in the hands of the producers.

Such a condition would naturally point to three possible explanations: (*a*) adulteration, (*b*) a change in the character of the oil brought about by long and intensive cultivation and selection of the plants, or (*c*) a change in the method of distillation at the distilling plants.

It is believed that no instances of adulteration have been disclosed by the offices charged with the enforcement of the Food and Drugs Act, and thus the first supposition is at once eliminated. While it is perhaps true that long and intensive cultivation, accompanied by seed selection, or type selection, would influence the character of the oil to some extent, to prove this would require study over a period of years, and there is no evidence that such a study has been made. There remains, then, the third supposition that the method of distillation at the distilling plants might produce changes in the oil which would cause it to be rejected as not up to specifications.

In 1908 Schimmel and Company[1] pointed out that the distillation of Chenopodium herb must be accomplished by the exercise of certain precautions in order that an oil might be secured which would conform to the standards of that time. Later Nelson[2] laid emphasis on the method of distillation, stating, ".....the valuable and chief ingredient, is unstable, and is decomposed gradually on boiling with water. Consequently, the distillation must be carried on rapidly with steam at a good pressure, the condenser kept warm and the warm distillation water separating from the oil in the receiver, discarded."

The second precaution mentioned by Nelson has no effect on the composition of the oil but does tend to effect a better separation of the oil in the receiver. The densities of warm water and warm wormseed oil vary by a greater degree than do

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[1] Schimmel and Company, "Semi-Annual Report," April 1908, p. 109.

[2] E. K. Nelson, "The Composition of Oil of Chenopodium from Various Sources," *J. Am. Chem. Soc.*, 42, 1204, 1920.

those of cold water and cold oil. The third precaution is not applicable at present, for no producer of wormseed oil is returning distillate water to the retorts. However, this is a point that needs emphasis since the custom of returning distillate water is quite general in the practice of distilling volatile oils and its adoption in wormseed distillation may be a future possibility.

U. S. P. SPECIFICATIONS FOR OIL OF CHENOPODIUM.

In Edition IX of the U. S. Pharmacopoeia the oil of Chenopodium, or Oil of American Wormseed, is described as a volatile oil distilled from *Chenopodium Ambroisioides Anthelminticum* Linné (Fam. Chenopodiaceae), which is colorless, or pale yellow in color, soluble in 8 volumes of 70 percent alcohol and varying in specific gravity from 0.955 to 0.980 at 25° C. The optical rotation varies between minus 4° and minus 10° in a 100 millimeter tube at 25° C. These limits were established only after the examination of a great number of samples of oil obtained at the source of production and represent the minimum and maximum as found.

Of late years, more especially 1920 and 1921, the producers and dealers in Chenopodium oil have argued that the U. S. P. standards should be lowered. They base their argument on the fact that authentic oils secured at the stills do not have a specific gravity of even 0.955 and that they are not soluble in 8 volumes of 70% alcohol. In this respect the contention of the producers and dealers appears sound and reasonable. However, as has been pointed out by Nelson,[1] the lower the specific gravity the less ascaridole present in the oil. If, then, the oil of low specific gravity is allowed to enter the market, lower therapeutic activity may be expected. It would seem rational, therefore, to look for a reason or reasons why the oil which is produced now should vary so much from the oils produced when the standards were formulated.

In view of the results obtained by Schimmel and Nelson it might be expected that the oils of low specific gravity and solubility were not distilled by proper methods. A study of the methods of distillation now in common use has shown that on the whole the conditions under which American oil of wormseed is distilled are unfavorable to the production of a marketable oil which satisfies the U. S. P. requirements.

LABORATORY INVESTIGATIONS.

In 1921 some first-hand information was obtained on the behavior of Chenopodium oil under various conditions of distillation. A plat of the so-called "Tall variety" of Chenopodium was grown on the heavy clay soil at the Government Experimental Farm, Arlington, Va. Plants were not set out, as is done in Maryland, but seed was sown direct in the row. An excellent stand of uniform growth was secured. During the growing season the plants received the necessary attention as to cultivation and hoeing. The herb was harvested on September 12 and allowed to "cure" in the field until September 16, when it was distilled. During the curing period no rain fell and the days were unusually warm for that season of the year. The cured herb was collected on canvas sheets, to prevent loss of seed through shattering, and divided into two equal portions. These portions were then distilled and the oils analyzed.

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[1] *Loc. cit.*

OIL A. (RAPID DISTILLATION WITH CONDENSER WARM.)

Weight of herb distilled	150 kilograms
Weight of oil secured	275 grams
Yield of oil	0.183%
Steam pressure at inlet to retort	60 pounds
Temperature of cooling water entering condenser	18° C.
Temperature of cooling water leaving condenser	72–85° C.
Temperature of distillate	60–74° C.
Time of distillation	30 minutes

The capacity of the condenser was limited so that 3.65 pounds of steam per minute was the maximum that could be condensed and cooled to not over 74° C. The distillate water weighed approximately 110 pounds. The oil was removed from the receiver at once and allowed to cool. It was then dried with anhydrous calcium chloride and filtered.

OIL B. (SLOW DISTILLATION WITH CONDENSER COLD.)

Weight of herb distilled	150 kilograms
Weight of oil secured	185 grams
Yield of oil	0.123%
Steam pressure at inlet to retort	60 pounds
Temperature of cooling water entering condenser	18° C.
Temperature of cooling water leaving condenser	35° C.
Temperature of distillate	22° C.
Time of distillation	60 minutes

The steam flow through the herb was regulated to 1.82 pounds per minute. The distillate water weighed approximately 110 pounds. Oil B was treated in the same manner as Oil A.

The oils were then analyzed and the results obtained are given in Table I.

TABLE I.

Oil.	Color.	Odor and Taste.	Sp. Gr. at 25° C.	Angle Rotation in 100 Mm. Tube at 25° C. Minus.	Solubility in 70% Alcohol.	Ascaridole (1) Percent.
A	Light yellow	Characteristic	0.9631	5°30′	8 vols.	73
B	Light yellow	Characteristic	0.9338	6°55′	Insoluble	60

[1] E. K. Nelson, "A Rapid Assay Method for the Determination of Ascaridole in Oil of Chenopodium," JOUR. A. PH. A., 10, 836, 1921.

In reviewing these results it at once becomes apparent that the method of distillation is a factor which causes great change in the oils. With rapid distillation, that is, with a good flow of steam, an oil was secured which passed all the U. S. P. requirements and contained a high percentage of ascaridole, hence its therapeutic value would without doubt be higher than the oil secured by slow distillation, in which the ascaridole content was only 60 percent and the physical constants too low to fulfil the minimum U. S. P. requirements. These results confirm the previous statements found in the literature respecting the technique of distillation of this oil.

In addition to the variation in the physical constants and ascaridole content of these oils a marked difference in the percentage of yield is also to be noted. This

difference amounts approximately to an increase of 48 percent in the yield obtained by distillation with a good flow of steam. Such a large increase is not due wholly to the loss of ascaridole, which is broken down into water-soluble products by boiling water, but to other factors which are not at present explainable. Some variation in yield is to be expected from two apparently uniform lots of herb but not to the extent found in these experiments. This variation in yield can therefore be accounted for only in part.

FIELD INVESTIGATION.

Having demonstrated by experiment that the flow of steam, or, in other words, the rate of distillation, was the main if not the only factor which caused the low-grade oil, a brief field investigation was undertaken for the purpose of studying methods of distillation and to obtain some data on the oil as it was produced at the distilling plant.

Practically all the oil of wormseed produced comes from Carroll County,

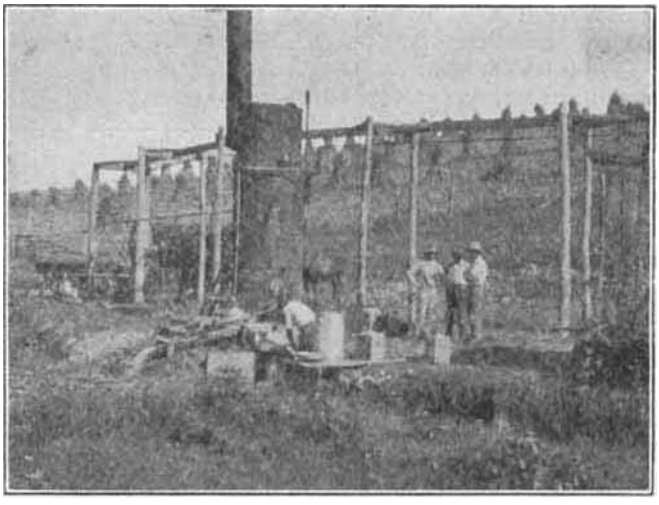

Fig. 1.—A Typical Distilling Plant for the Production of Oil of Wormseed in Carroll County, Maryland.

Maryland. From twelve to fifteen distillers operate there, the number working depending upon local conditions. The retorts are usually processing kettles such as are used in canning factories. The steam is usually generated in a stationary boiler, as shown in Figure 1, and in some instances in the boiler of a threshing engine, as shown in Figure 2. The condensers are uniformly of one type and consist of straight pipes laid in a trough of running water and connected to the retort in a suitable manner just under the cover. Each distilling outfit is set up near a small stream so that by building a dam across the stream the water can be diverted to the condenser trough and an abundant supply be assured at all times. These condensers are very efficient since no limit need be set as to the length of pipe through which the steam from the retort must pass.

From the study of the method, or technique, of distilling as practiced at one still where the oil produced in 1921 was of uniformly high grade, the figures given

in Table II were secured. At this particular distilling plant the herb was distilled in an average time of not over 12 minutes, and during this period approximately 250 pounds of steam were passed through the retort.

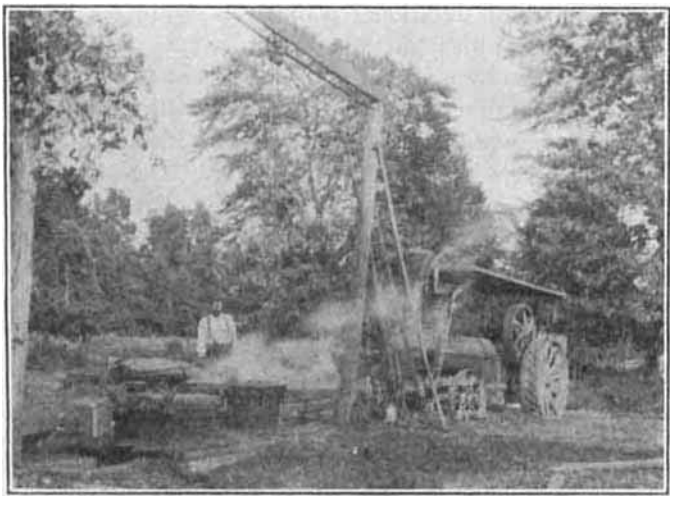

Fig. 2—A Distilling Plant for the Production of Oil of Wormseed, Using a Threshing Engine for the Steam Generator.

The figures in Table II require some explanation. In Oils 1 and 2, a slight variation was made in the steam pressure and the effect on the yield and specific gravity of the oils observed. No differences were noted. Oil 3 was obtained in two portions, the first 10 minutes' run being 64 ounces, and the second 10 minutes' run 4 ounces, the steam pressure being cut down to not over 60 pounds. It will

TABLE II.

No. of Oils.	Time of Distillation (Minutes).[1]	Steam Pressure at Retort (Pounds).	Sp. Gr. of Oils at 25° C.	Solubility of Oils in 70% Alcohol.
1	9	80	0.974	8 vols.
2	8	100	0.974	"
3	10	40 to 60	0.9735	"
	10	40 to 60	0.9710	"
4	12	100	0.974	"
5	11	100	0.968	"
6	10	100	0.968	"
7	8	100	0.962	"
	10	100	0.9615	"
8	12	100	0.968	"
9	12	100	0.974	"
10	12	100	0.960	"
11	12	100	0.956	"

[1] Time taken from appearance of distillate at discharge end of condenser.

be noted that the specific gravity of these oils was lowered, noticeably so in the 4 ounces obtained during the latter part of the run. Oils 1 to 4, inclusive, were distilled from herb grown by a farmer on $^1/_2$ acre of so-called good wormseed land.

Oils 5 and 6 were regular distillations, whereas Oil 7 was collected in fractions and obtained by slow distillation. In distilling this oil the inlet valve at the retort was cracked and 8 minutes elapsed before the steam appeared in the condenser. At the end of 8 minutes' further distilling 4 pounds of oil had been secured, and in the next 10 minutes an additional pound was distilled. The specific gravity of these oils was lowered by the method of distillation. Oils 5 to 7 inclusive were distilled from herb grown by a farmer on $^1/_2$ acre of so-called good wormseed land, this farm being some distance from the one first mentioned. Oil 8 was distilled from herb grown in Howard County, Oil 9 from herb grown in Carroll County, and Oil 10 from herb grown in Frederick County. The last three oils were produced by the regular method of distillation as conducted at this particular distilling plant. Oil 11 was distilled from sweepings around the retorts, plus a considerable amount of emulsion which is always present in the receiving can. This emulsion accumulates and is usually redistilled whenever advisable. The oil obtained from this miscellaneous lot of material barely passed the lower limit specified by the U. S. Pharmacopoeia.

The apparatus in use at the distilling plant where the figures in Table II were obtained was similar to that in all the distilling plants producing wormseed oil, with the exception of the steam pipe from the boiler to the retort, which pipe was of considerably larger diameter. This large steam pipe permitted a large volume of steam per minute to pass through the retort—at this plant about 20 pounds. No difficulty was experienced in condensing since the condenser pipes lay in running water and could be extended indefinitely, or until the proper condensation was effected. At all the other distilling plants visited the feed steam pipe was of small diameter and quite often of considerable length before entering the retort. In addition to the lack of sufficient steam many operators admit the steam slowly and thus "cook" the herb for a considerable time before the steam begins to pass into the condenser.

The field investigation was further extended to a distilling plant where the volume of steam passed through the retort per minute was considerably less than 20 pounds. In fact, about 5 pounds of steam per minute was the usual rate of distilling. The figures given in Table III were obtained at this distilling plant.

TABLE III.

No. of Oils.	Time of Distillation (Minutes).	Steam Pressure at Retort (Pounds).	Sp. Gr. of Oils at 25° C.	Solubility of Oils in 70% Alcohol.
12	30	About 40	0.938	Turbid in 8 vols.
13	30	"	0.950	Soluble 0.946
14	30	"	0.946	"
15	30	"	0.946	"
16	$12^1/_2$	"	0.965	"
	$12^1/_2$	"	0.955	"

The steam pressure at the retort could not be accurately determined owing to the fluctuations in pressure at the boiler. However, the pressure, as stated in Table III, may be taken as the average for the period of distillation. Oils 12 to 15, inclusive, were of the general run secured at this distilling plant. Oil 16 was distilled from a lot of well-cured herb and was distilled without the previous warming or "cooking" that was the usual method of procedure. This oil was collected

in two fractions, the first weighing 80 ounces and distilling off in 12½ minutes, the second weighing 6 ounces and distilling off in the same length of time. After examining the results given in Table III it at once becomes apparent that long distillation, in which a great portion of time is taken up by the preliminary warming or "cooking," affects the oil secured to such an extent that it does not meet the official requirements.

In view of the results given above it appears that the agitation to have the requirements for oil of wormseed changed so as to admit oils of lower specific gravity than are admitted in Edition IX of the U. S. Pharmacopoeia is not warranted. Lowering the standards would admit oils of low ascaridole content and consequently of lower therapeutic value. Moreover, the changing of the U. S. P. requirements is unnecessary since by following a few simple directions each producer can distill oil of high grade and one which will answer all the present required tests.

SUGGESTED MODIFICATIONS IN DISTILLING PLANTS.

It is believed that if the distilling plants in Carroll County, Maryland, will change the steam lines so that a larger volume of steam per minute can be passed through the retorts a high-grade oil will result. Most of the distilling plants possess sufficient boiler capacity and the only change required would be in the supply steam lines. These should not be less than two inches in diameter from boiler to retort and with a one-inch pipe distributing the steam through a "spider" in the retort. The two-inch line should be as short as possible, that is, the retorts should be placed as near the boiler as is convenient and the steam line should be insulated. If the two-inch pipe is not too long and has the minimum number of bends necessary to lead it from the boiler to the retort, a steam pressure of 80 pounds at the boiler gauge will be sufficient to provide a good pressure at the retort.

At some distilling plants a preliminary "warming up" is given each charge. This is done by admitting the steam slowly and allowing it to work its way gradually up through the packed herb. This practice should be discontinued since it tends only to break down the ascaridole in the oil into water-soluble constituents and thus affects the quality of the finished product. The placing of water in the bottom of the retort should likewise be avoided and the retorts should be drained after each charge is distilled, if this is found necessary. Steam should be admitted promptly and at the full capacity of the one-inch inlet pipe. If a pipe of sufficient size leads from the retort to the condenser and the pipes of the latter are kept free from obstruction no pressure will develop in the retort.

The condensers now in use are probably of sufficient capacity to condense the steam which will be passed into them if the suggestion as to steam supply is adopted. If not, the capacity can readily be enlarged by lengthening the condenser tubes. The condensate, a mixture of water and oil, should flow out at a relatively high temperature. To cool the distillate too much causes a loss of oil which is carried away by the overflow, the oil and water being relatively nearer the same density when cold than when warm.

The receiver in use at present could readily be modified into a "florentine flask"-like type and the excessive "churning" of the oil and hot water avoided. By placing two receivers in series the second would act as a trap to collect any oil carried over mechanically from the first.

The distiller should provide himself with a specific gravity apparatus calibrated at 25° C. The hydrometers now in general use throughout the distillation district are calibrated at 60° F. (15.5° C.), whereas they should be calibrated at 77° F. (25° C.). A distiller who tests his patron's oil at 60° F. and finds it just within the lower limit for specific gravity is much disgruntled when he discovers that the dealer or broker refuses to accept the oil, because it is not up to "gravity." As a matter of insurance to themselves brokers and dealers in volatile oils should see to it that the producer is equipped with proper instruments for testing his oils as they are distilled.

SUMMARY.

Producers of Oil of Wormseed, U. S. P., favor a change in the requirements of this oil, specifically a lowering of the minimum limit for specific gravity. Such a change is believed to be unwarranted, in view of the results herewith presented.

Oil of Wormseed can be produced that will meet all the U. S. P. requirements by distilling the herb with a large volume of steam during a relatively short period of time. It is recommended that with the apparatus now in use not less than 20 pounds of steam per minute be passed through the retort and that the distillation time does not exceed 15 minutes.

"Warming up" of the charge to be distilled is not necessary, in fact it is bad practice, and water should not be added to the retorts. These should be drained of condensed steam whenever necessary.

Changes in the present distilling outfits can be effected at small cost and without complicating the routine of distillation whatever.

BUREAU OF PLANT INDUSTRY,
U. S. DEPARTMENT OF AGRICULTURE.

DETECTION OF DIETHYLPHTHALATE IN WHISKY.

BY A. B. LYONS.

A special denatured alcohol (Formula 39 B) for use in perfumery is now obtainable at a moderate price, offering a new temptation to the bootlegging fraternity. A sample of whisky was recently brought to me for examination, said to have caused "sickness" in those who had sampled it. I examined it with reference to the presence of the usual denaturants. When tested for acetone in the usual manner with iodine and sodium hydroxide, distinct milkiness appeared in the solution tested within a minute at room temperature, increasing in density on shaking up to a certain point. The odor of iodoform was distinctly recognizable. After an hour or two the solution had become quite transparent, with a scanty, pale yellow deposit, which showed under the microscope hexagonal plates. The reaction was obtained both in the sample and in a distillate therefrom. It was also obtained from a dilute hydroalcoholic solution of diethylphthalate, and in denatured alcohol, Formula 39 B. From the scantiness of the precipitate in the latter cases, it may be inferred that the reaction is due to an impurity present only in small proportion and so has no practical importance.

A distillate from the sample was diluted with water and tested for methyl alcohol by the modified Hehner test, with unsatisfactory results. A color was produced, having a purplish shade, but the indications of the test were inconclusive, and further experiment showed that I was on the wrong track.