An attempt to separate from petroleum spray oils the portion which is injurious to plants

by Jesse R Green

A THESIS Submitted In partial fulfillment of the requirements for the Degree of Master of Science In Chemistry Montana State College
Montana State University

Abstract:
The purpose of this Investigation Is stated In the title. It has been conducted on the hypothesis that some portion of petroleum spray oils is especially injurious to plants. On account of the great number of compounds in petroleum and their close similarity, the identification and separation of any portion la difficult. The complexity of the reactions of the compounds of petroleum with those of the plant has made it almost impossible to solve the problem by purely scientific method#. Thus, in the absence of strictly scientific means, the cut and try method was used with the aid of whatever scientific knowledge or methods that were available.

There has been considerable speculation regarding the compounds that cause plant injury. The blame has largely been placed on the unsaturated compounds, but there are other possibilities. Sulfur and nitrogen compounds may be responsible for injury, but it has been shown in a former Investigation that the part that nitrogen plays must be very small(l). The oxygen compounds in petroleum are also among those that may be considered. Hoerner(2) has proposed the use of sulfonated oxidation products as insecticides and gives data showing practically no injury to typical plants. It la generally conceded that these compounds are efficient insecticides, but their effect on plants is still an open (1)Green, Jesse, Chemical and Physical Properties of Petroleum Spray Oils. Accepted for publication by J. of Agr. Res. 1932.

(2)Hoerner, John L., A Report of Progress on the Testing of Sulfonated Oxidation Products of Petroleum for Their Insecticidal Properties. Vd.

Agr. Expt. Sta. Bui. 310, 1929.

question. Until more Knowledge Is gained regarding petroleum compounds and their exact physiological effect it is best to with-hold opinions.

The causes and nature of plant injury have been discussed by Kelley (1), Swingle end Snapp(2) and Knight, Chamberlin and Samuels(3).

In the course of the work oils were treated by over 120 different processes and then applied to barley seedlings to determine the Injury they would cause. The barley seedling method of testing spray oils was devised and used in a previous work(4). It is carried out by applying the oil to be tested to 10 barley seedlings that have been grown in quarts send with nutrient solution In a small earthenware jar. several more than 10 seeds are planted and when the seedlings are 6 to 8 cm. high they are thinned out leaving 10 that are uniform and that are near the height of the seedlings in the other jars.

The oil ie applied to both sides of the seedlings with a camel's hair brush. At the end of 3 days the seedlings are cut and weighed.

Their weight Is subtracted from the same number of control seedlings and the difference in weight is

computed to percentage of the weight of the controls and called injury.

(1)Kelley, Victor K., Effect of Certain Hydrocarbon Oils on the Respiration of Foliage and Dormant Twigs of the Apple. 111. Agr. Expt. ate. Bui. 348, 1830.

(2)Swingle, H.S., and Snapp, 0. I., Petroleum Oile and Oil Emulsions as Insecticides, and Their Uae Against San Jose scale on ,each Trees of the South. U. S. Deptl of Agr. Pul. 253, 1831.

(3)Knight, Hugh, Chamberlin, Joseph C., and Samuels, C. D., Some Limiting Factors in Uie Use of Saturated Petroleum Oile as Insecticides. Plant Physiology, 4 : 288-381, 1928.

(4)Green, Jesse, Chemical and Physical Properties of Petroleum Spray Oils. Accepted for publication by J. of Agr. Res. 1832.

AN ATTEMPT TO SEPARATE FROM PETROLEUM SPRAY OILS THE PORTION WHICH IS INJURIOUS TO PLANTS

BY

JESSE R. GREEN

A THESIS

Submitted in partial fulfillment of the requirements
for the Degree of Master of Science in Chemistry

MONTANA STATE COLLEGE

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Bozeman, Montana
June, 1932

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There has been considerable speculation regarding the compounds that cause plant injury. The blame has largely been placed on the unsaturated compounds, but there are other possibilities. Sulfur and nitrogen compounds may be responsible for injury, but it has been shown in a former investigation that the part that nitrogen plays must be very small(1). The oxygen compounds in petroleum are also among those that may be considered. Hoerner(2) has proposed the use of sulfonated oxidation products as insecticides and gives data showing practically no injury to typical plants. It is generally conceded that these compounds are efficient insecticides, but their effect on plants is still an open

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In the course of the work oils were treated by over 120 different processes and then applied to barley seedlings to determine the injury they would cause. The barley seedling method of testing spray oils was devised and used in a previous work(4). It is carried out by applying the oil to be tested to 10 barley seedlings that have been grown in quartz sand with nutrient solution in a small earthenware jar. Several more than 10 seeds are planted and when the seedlings are 6 to 8 cm. high they are thinned out leaving 10 that are uniform and that are near the height of the seedlings in the other jars.

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(3)Knight, Hugh, Chamberlin, Joseph C., and Samuels, C. D., Some Limiting Factors in the Use of Saturated Petroleum Oils as Insecticides. Plant Physiology, 4 : 299-321, 1929.

(4)Green, Jesse, Chemical and Physical Properties of Petroleum Spray Oils. Accepted for publication by J. of Agr. Res. 1932.

Consideration of Error in Method

There is obviously a large error in the barley seedling method, but it has served a useful purpose in estimating the injurious qualities of the oils to plants.

Figures 1 and 2 show the effect of processed oils. They represent tests Nos. 73, 74, 75 and 76 considered in the discussion of table VIII. The first three are extreme cases in which there was complete killing of the plants. A more typical example is shown in figure 3, which is a close-up view of test No. 76 and the control plants. The mere retardation in the growth of the treated seedlings as compared with the controls is the usual effect.

Figure 4 shows the samples reported in table VI after they were cut and ready to weigh. Figure 5 shows a close-up view of test No. 55 in which there was severe injury.

The largest error is, of course, the lack of uniformity of samples. In order to show the limits of this error the weights of 8 average samples of 10 seedlings each are reported in table I. The variation from the mean is given and in this trial the maximum positive variation was 12.7 per cent and the maximum negative variation was 8.4 per cent.

The amount of oil applied to the seedlings influences the amount of injury. It is believed to be of less importance than it might appear to be. The amount of oil remaining on the seedlings when they are weighed is of greater importance. With a very viscous oil a great deal is required to completely cover the seedlings and there is practically no volitilization or run-off during the test.

Table I. Showing Variation of Control Samples Used in Barley Seedling Test

Controls	Weight of 10 seedlings	Variation from average	Percentage variation from average
	grams	grams	
1 (no treatment)	0.790	+0.004	+0.5
2 " "	0.720	-0.066	-8.4
3 " "	0.790	+0.004	+0.5
4 " "	0.720	-0.066	-8.4
5 " "	0.890	+0.104	+12.7
6 " "	0.790	+0.004	+0.5
7 " "	0.780	-0.006	-0.8
8 " "	0.810	+0.024	+3.1
Average	0.786		

Ordinary methods of observation are perhaps just as useful as a comparison of the weights of the plants, and have been used in estimating the injury in every case. There is, however, practically no means of recording and presenting the data of analyses made by observation.

A study of the various tables will show that there is a wide variation in the degree of injury reported. This is due largely to the growing conditions which prevailed during the test. If conditions were good the control plants made rapid progress and left the injured ones far behind, thus showing a large amount of injury. If growing conditions were poor a smaller amount of injury would be caused by the same oil. For these reasons it is necessary to examine the data in each table as a unit. All the tests made in any single table were made at the same time and are comparable with each other.

Oils Used

A series of 13 oils were used in a former investigation, and

from this group the oils for this work were selected. Considerable data were obtained in the earlier study and are attached to this report as an appendix. The relative injury as determined in the former work is also given in the appendix. The laboratory numbers of the original oils are 3, 4, 5, 8, 12, 13, 15, 16, 20, 21, 22, 24, and 28. These numbers should not be confused with the barley seedling test numbers, or the processed oils which bear the same number as the test in which they were used. The original or non-treated oil is designated as "normal oil".

Distillation of Oils

The first attempt to separate the injurious portion from the oil was by distillation. A bead tower was used and was wrapped with an electrical heating element and asbestos insulation. The complete apparatus is shown in figure 6. A certain amount of fractionation was accomplished in the bead tower, and all the distillations were made at an absolute pressure of approximately 10 cm. of mercury.

The different oils were distilled into 3 fractions each. A given amount of oil was placed in the still and the first fraction consisted of one-third of the total, the second fraction one-third, and the residue remaining in the still of one-third. These samples were applied to barley seedlings and the results reported in table II.

There was more or less cracking or breaking down of the oils during distillation. Darkening of the residue, sudden changes in temperature and increases in sulfonatable portion are the evidences supporting this statement. The variations in temperature from one fraction to another were caused by the releasing of the vacuum and cooling down of the still to change the receiver between fractions.