SOIL ALDEHYDES.*

A SCIENTIFIC STUDY OF A NEW CLASS OF SOIL CONSTITUENTS UNFAVORABLE TO CROPS, THEIR OCCURRENCE, PROPERTIES AND ELIMINATION IN PRACTICAL AGRICULTURE.¹

BY

JOSHUA J. SKINNER, Ph.D.

INTRODUCTION.

THE isolation and identification of definite organic compounds from soils has stimulated investigations pertaining to the physiological effect of various organic compounds on plants. The chemical composition of the organic matter of soils concerns every investigator of soil problems: it may be the physicist, the chemist, the bacteriologist, the physiologist, or the agronomist. The quantity of organic matter in the average soil is considerable. The average content in the soils of the United States is 2.06 per cent., and of the subsoils, 0.83 per cent. (11).² The organic compounds which have been found to occur in soil organic matter affect plants differently: some are beneficial to plant life, others are inimical to proper plant development, and still others have no effect on growth. In every soil there exists a balance of these two contesting influences, the good and the bad. The decreased soil fertility, in so far as it is due to the chemical composition of its organic matter, as a single factor, is due to the preponderance of that type of biochemical action which will result in the accumulation of harmful compounds; increase in soil productivity, on the other hand, is due to favorable biochemical action resulting in the accumulation of compounds beneficial to plants. Whether one or the other predominates is due to soil conditions, drainage, composition, plant occupation, etc., which can be influenced by soil management, such as tillage, cultivation, drainage, liming, fertilization, and by crop rotation, all of which influence the biochemical factors in soils and, through them, soil fertility.

* Communicated by Dr. Oswald Schreiner.

¹ Contribution from the Laboratory of Soil Fertility Investigations.

² Refers to literature citation in Bibliography appended.

During the last ten years a large number of organic compounds have been isolated from soils by Schreiner and his co-workers, Shorey, Walters, Lathrop, and Wise, of the Laboratory of Soil Fertility Investigations. Previous to that time the constituents of the organic matter of soils were practically unknown. The individual compounds isolated are agroceric acid (46), agrostol (46), arginine (49), acrylic acid (61), adenine (61), benzoic acid (62), α -crotonic acid (82), creatinine (60), cyanuric acid (85), choline (61), cytosine (49), dihydroxystearic acid (46, 48), glycerides (49), guanine (42), hentriacontane (49), histidine (49), hypoxanthine (49), lignoceric acid (49), lysine (61), monohydroxystearic acid (49), metahydroxytoluic acid (62), mannite (61), nucleic acid (61), paraffinic acid (49), peptones (81), proteoses (81), pentosan (49), pentose (49), phytosterol (49), picoline carboxylic acid (47, 48), oxalic acid (61), rhamnose (61), resin (49), resin acids (49), resin esters (49), saccharic acid (61), salicylic aldehyde (61), succinic acid (61), sulphur (61), trimethylamine (61), tetracarbonimid (63), tri-thiobenzaldehyde (61), vanillin (62), and xanthine (49).

From this list it is seen that the compounds represent a great variety of chemical classes: there are paraffinic hydrocarbons, hydroxy fatty acids, and other organic acids, organic bases, esters, alcohols, aldehydes, carbohydrates, hexone bases, pyrimidine derivatives, purine bases, pyridine derivatives, organic sulphur compounds, organic phosphorous compounds, and nitrogenous compounds.

Especially interesting, in passing, are the groups of nitrogenous compounds. Some of these are beneficial and others harmful to plant growth; they are absorbed by plants as such, enter into the cell, and react with the protoplasm, causing effects either beneficial or detrimental, as the case may be. Among the beneficial compounds of this class which have been found in soils are creatinine (64, 65), creatine (64, 65, 10), hypoxanthine (54, 56), xanthine (54, 56), nucleic acid (54, 56), guanine (54, 10), histidine (54, 66), arginine, (54, 66), and choline (54). Other nitrogenous compounds reported as beneficial are acetamide (25), alanine (54, 25, 24, 31, 10), allantoin (54, 31), amygdaline (31), asparagine (54, 31, 24, 10), betaine (30), formamide (25), glycocoll (54, 25, 24, 31), and leucine (54, 31).

Not all nitrogenous compounds are beneficial, as is shown by

the following presentation: Guanidine (54, 55, 10), a nitrogen-containing body, is very harmful to plants. It is especially interesting in that it produces effects similar to those produced by plant diseases, manifesting itself by bleached spots on the leaves, which spread, cause wilting and final collapse. The effect is accentuated by nitrate, and is less observable in the total absence of nitrate. The striking difference between effects of the two closely related nitrogenous compounds, glycooll and methyl glycooll (54, 57), is also interesting: Glycooll ($\text{CH}_2\text{NH}_2\text{COOH}$) is amido-acetic acid, and is one of the simpler degradation products found where decomposition is occurring. It exists in the tissue and seed of many plants. Methylglycooll ($\text{CH}_2\text{NHCH}_3\text{COOH}$) differs in its chemical structure from glycooll, not only in that it contains the methyl group, CH_3 , but also in that the amido group, NH_2 , is thereby changed to an imido group, NH . It is not a simple protein body. Glycooll is beneficial and is utilized as a source of nitrogen, while methyl glycooll is also absorbed, but causes decreased growth and a peculiar twisted lateral growth of the leaf of the plant. Among other nitrogenous compounds which have been reported as harmful are aniline (30), aspartic acid (31, 43), atropine (30), barbituric acid (25), caffeine (30), carbamic acid (25), cocaine (30), diphenylamine (30), hexamethylene tetramine (25), hippuric acid (25, 31), morphine (30), myronic acid (31), naphthylamine (30), neurine (43), piperidine (43), pyridine (43), quinine (30), skatol (43), solanine (54), tetranitromethane, (25), theobromine (31), tyrosine (43), para urezine (25, 31), and uvitonic acid (48). Quinoline and pyridine (21) have recently been found by Funchess to be very beneficial to growth in soil culture, but this beneficial action is probably due to products of decomposition of the nitrogenous compounds, and not to the compound itself.³

Among other compounds which have interesting characteristic and contrasting effects on plants are cumarin, quinone, and vanillin (52, 53). Cumarin decreases growth and causes a shorter

³ Since the preparation of this manuscript Funchess has shown that quinoline and pyridine nitrify in soils, quinoline nitrifying the more rapidly the more acid the soil. The nitrification of nitrogenous compounds was inhibited by aldehydes. (Funchess, M. J., "The Nitrification of Pyridine, Quinoline, Guanidine Carbonate, etc., in Soils," Alabama Exp. Sta., Tech. Bull. No. 3, Bull. No. 196, June, 1917.)

and broader leaf than is normal for wheat, and only the first leaves are usually unfolded, the other leaves remaining wholly or partially within the swollen sheath. The leaves that break forth are distorted, curled, and twisted. This characteristic development is not noticeable when the plants are grown in cultures containing considerable amounts of phosphates. The effect of quinone is decidedly different: it produces long, thin leaves and tall, slender plants. Potash ameliorates this effect to a large extent. Vanillin also produces thin, slender plants, but affects the roots more than the tops. It is interesting that the effects of vanillin are partially overcome by nitrate fertilizers.

In this paper the chief interest centres in the occurrence properties, and elimination of that class of soil constituents which partake of the nature of aldehydes. The results obtained in laboratory greenhouse and field with certain of these compounds will be presented, following a general discussion of the subject.

GENERAL DISCUSSION OF THE EFFECTS OF ORGANIC COMPOUNDS IN SOILS, ESPECIALLY SOIL ALDEHYDES.

Compounds, or a mixture of compounds, having the properties of aldehydes have been found in many soils, but only three—salicylic aldehyde, vanillin, and trithiobenzaldehyde—have been definitely identified, thus far, and this paper concerns itself principally with the effect of this class of compounds on plant life and their influence on soil fertility.

Salicylic aldehyde was first found in garden soils from the Mount Vernon estate, Virginia (61), and later was found in a number of other soils from widely different sections.

Materials having the odor of vanillin have been separated from a number of soils, but it was first separated in sufficient amount to identify from a Florida soil (62); it has been encountered quite frequently since in soils from other parts of the United States.

Trithiobenzaldehyde (61) was found first in a soil from California, but has not been encountered frequently.

It will be shown later that aldehydes are common in many soils, and especially in soils of low productivity. Alcohols and acids, the reduction and oxidation products of aldehydes,

Alcohols

Aldehydes

Acids

have been encountered in soils, which makes the study of the action of aldehydes on plants essential.

A review of the investigations on the action of aldehydes and other soil organic compounds on growth will be given here.

The earlier studies of the effect of soil organic compounds on growth was made in water-culture solutions. In the case of most of the compounds it was difficult to get sufficient quantities of the material to make exhaustive investigations of its effect on growth in soils. The absorptive power of some soils, together with their biological activities, affects added organic materials to such an extent that results are uncertain unless accompanied by tests to show the changes that the added substance may undergo. With water-culture experiments this difficulty is in part obviated. The experiments are made under better controlled conditions, and fewer factors enter into the results. While one should not draw definite conclusions from water-culture experiments as to what might take place under field conditions, yet it is impossible to study factors singly in the field, as must be done in scientific experimentation. The results secured in water cultures in this investigation have proved of vast importance; it would have been impossible to have shown that some of the nitrogenous compounds were used as such in plant metabolism without the use of water cultures. The field studies which are presented later are an outgrowth of the laboratory studies with water cultures.

Some recent investigators have objected to the use of water cultures in work of this kind, and have made experiments which should and do show that organic compounds having harmful properties do not exert as harmful an effect in soil cultures as in water cultures. They decry the use of such methods in soil and plant physiological investigations. It would be just as proper for the chemist to decry the use of C.P. reagents or the bacteriologist to disavow pure cultures as for the plant physiologist to decry the use of water cultures.

The first soil organic compound isolated, picoline carboxylic acid, did not prove to be harmful to plants except in high concentration (47, 48). Below 100 parts per million in distilled water it was slightly stimulating to wheat seedlings. Dihydroxystearic acid (46, 48), which has been found in soils, was very harmful to wheat in distilled water: in as low a concentration as 20 parts per million growth was materially reduced, and with 200 parts

per million the seedlings were severely injured. In nutrient solutions (50), composed of calcium acid phosphate, sodium nitrate, and potassium sulphate, the dihydroxystearic acid in concentrations of 50 parts per million also proved to be harmful. It was less harmful in the solutions composed principally of nitrate, showing that nitrate had an influence in changing its physiological effects.

Schreiner and Skinner have shown that a group of nitrogenous soil organic compounds are beneficial to growth and are absorbed and utilized by the plant as a source of nitrogen. Among these are creatinine and creatine (64, 65), nucleic acid (54, 56), hypoxanthine and xanthine (54, 56), guanine (54, 10), histidine and arginine (54, 56), and choline (54).

An extensive study of the soil aldehydes has been made and reported by Schreiner and Skinner. Salicylic aldehyde and vanillin (58, 67, 68) were first shown to be harmful to a number of plants in distilled water, in nutrient solutions, in some soils in pots, and in the field. Salicylic aldehyde affected growth much more than did vanillin. In the investigation with soils in pots it was found that the aldehydes were harmful in some soils and not in others. The soils in which these compounds showed no detrimental effect on plant development are good productive soils, with strong oxidation powers, and have good bacterial activity. The salicylic aldehyde was applied usually in amounts of 150 pounds per acre, and the vanillin 300 pounds per acre. It was further indicated that the aldehydes were not so harmful in limed soils, and that fertilizers had an action in ameliorating their harmfulness.

Experiments were made on three different soils in the field (70), each soil differing chemically, biologically, and physically, differing as to their crop-producing powers, and differing in that each was of a different origin and different geographical location. The salicylic aldehyde and vanillin were harmful in two of these soils, and had practically no effect in the third. On the Susquehanna silty clay loam, an unproductive soil on the Arlington Experimental Farm, Virginia, both aldehydes reduced the production of cow peas, garden peas, and string beans (58, 68). These soils were analyzed to determine whether or not the aldehydes remained in the soil as such throughout the growing period. The compounds were found in this soil six months after their application; that is, at the end of the crop season. It was further shown

that lime overcame the harmful effects of both aldehyde compounds, and that on this soil fertilized with phosphate the bad effects of salicylic aldehyde were greatly reduced, and on soil fertilized with sodium nitrate the effects of vanillin were lessened. The aldehydes did not persist in the fertilized soil. That aldehydes are harmful in some soils and not in others is probably accounted for by their inability to persist in soils having strong oxidizing powers and good biological activities. This is further demonstrated by the field experiments of Skinner and Noll (70) on the strong productive Hagerstown loam. On this soil the aldehydes were not harmful, and by chemical methods it was shown that the added substances were changed or destroyed in the soil.

Fraps (20) made some pot experiments with several soil organic compounds. He studied the effects of dihydroxystearic acid in soils. He states the material he used was impure dihydroxystearic acid. In an experiment growing corn (soil No. 1600) untreated pots produced 9.3 grammes and 10.1 grammes dry weight, while the pots to which dihydroxystearic acid in amounts of 500 parts per million were added produced 8.8 grammes dry matter, a reduction of 10 per cent. When calcium carbonate was added with the dihydroxystearic acid growth was reduced 42 per cent. The two untreated pots growing sorghum were very uniform. One produced 20.9 grammes dry matter and the other only 13.5 grammes, which makes a comparison of the treated pots rather uncertain. The dihydroxystearic acid treated pot produced 19.0 grammes dry matter, and the dihydroxystearic acid plus lime 19.9 grammes. It is rather unfortunate that a culture with lime alone was not included in this test; as it is, no comparison can be made.

In another soil (No. 1956) which had been fertilized with phosphate, nitrate, and potash, dihydroxystearic acid at the rate of 500 parts per million reduced the growth of corn from 18.0 grammes to 15.1 grammes of dry material, a reduction of 16 per cent. Dihydroxystearic acid with lime was still more harmful. In the experiment growing sorghum the average dry weight of two pots of the fertilized soil was 12.7 grammes, and that of the two pots with dihydroxystearic acid 10.5 grammes, a reduction of 18 per cent. Again, the dihydroxystearic acid with calcium

carbonate was more harmful, but no checks are included with the soil untreated or with lime alone.

The pot experiments with the aldehyde vanillin are also interesting and valuable in that he studied the persistence of the aldehyde in the different soils used in the experiment. In the experiments, adding vanillin in amount of 100 parts per million before planting, it was harmful in two soils out of nine used. When used at the rate of 200 parts per million it was harmful in each case. In other experiments the vanillin was supplied in fractional parts to the soil during the growth of the plant. In virtually all cases the growth of the plant was injured, except in the lower concentrations of 100 parts per million. Periodical application of this concentration injured the plants but did not kill them in the case of these Texas soils, in which vanillin disappeared rapidly. An examination of the results shows that the more rapid and complete the loss of vanillin in the soil the less is the injury observed in the growing plant. Thus his soil No. 3346 with vanillin showed a decrease in plant growth of 27 per cent. and a loss in vanillin in two weeks' time of only 24 per cent.; soil No. 4747 with vanillin showed a decrease in plant growth of about 14 per cent. and a loss of vanillin in two weeks' time of 60 per cent.; soil No. 4605 with vanillin showed a decrease of only 6 per cent. in growth but a loss of 71 per cent. in vanillin in two weeks' time.

Fraps's experiment with the effect of vanillin on three soils (Nos. 5101, 5649, and 1579) which had been fertilized with acid phosphate plus ammonium nitrate showed that the vanillin was extremely harmful to sorghum in each of these soils with the fertilizers applied. One hundred parts per million was injurious in two of these soils. Where 200 parts per million were added it killed the plants in one case and severely injured growth in the other two cases. Where 1000 parts per million were applied with the fertilizers, the plants were killed in every case. In another experiment in which he used seven soils, vanillin at the rate of 200 parts per million without and with acid phosphate and ammonium nitrate produced very injurious effects on the plants grown. In the experimental work of the present investigation, as will be shown later in this paper, acid phosphate did not overcome the bad effects of vanillin. No additional injurious action has been observed, however, when applied with this fertilizer. In the field experiments and with the soil in pots the

harmfulness of vanillin was lessened by sodium nitrate; nitrogen in the form of ammonium nitrate or in other forms was not used. Fraps's work seems to show that ammonium nitrate makes the vanillin even more harmful, indicating that some biological action takes place which produces conditions very bad for plant growth.

Fraps points out the well-known fact that these organic compounds are not as harmful in soils as in water culture, but seems to lose sight of the important results which his work so well demonstrates; that is, that these compounds act differently in different soils and under different conditions, and that they act differently because when formed or added they will remain in some soils and under some conditions, while they are destroyed in other soils.

Upson and Powell (76), working with a black silt loam of excellent texture and rich in organic matter, found that vanillin in amounts varying from 250 to 1000 parts per million had no effect on the growth of wheat plants in pots, but with another soil of equally good texture but less productive vanillin depressed growth slightly. Salicylic aldehyde in the same soil was somewhat more harmful, but it did not depress growth below 15 per cent. in any case. They conclude that aeration and absorption are important factors in overcoming the effects of the aldehydes, but give no experimental evidence. They made no attempt to ascertain whether vanillin or salicylic aldehyde existed in their soil for any length of time or whether it was destroyed.

Davidson (16) made some experiments with the effect of vanillin on wheat in pots in Dunkirk clay loam. He obtained practically no effect with added amounts of vanillin less than 1000 parts per million. With vanillin used in amounts of 1000 parts per million without fertilizers a depression of 10 per cent. in growth resulted, and the effect with the soil limed was about the same; with fertilizers the results were irregular. No attempt was made to determine if the added vanillin remained in the soil or whether it was changed or destroyed. These results do not agree with those of field experiments made on the Dunkirk silty loam reported in this paper, in which vanillin and salicylic aldehyde proved harmful to cow peas, even when fertilized.

Funchess (21) studied the effect of several organic compounds, among them the aldehyde vanillin, on crops grown in pots, in several soils. He presents no data showing the fate of

the compounds after their addition to the soil. Vanillin, in a Norfolk sandy loam, was quite harmful to oats in amounts of 500 and 1000 parts per million, but had only an indifferent effect in small concentrations. With a second crop grown after the harvesting of the first there was no residual harmful effect observed, indicating that the vanillin had been oxidized before the second crop was planted. A second application of vanillin before planting the third crop again caused considerable reduction in growth.

In another experiment, vanillin materially reduced the oats crop grown in this soil when used alone and with potash and phosphate and a complete fertilizer. Vanillin without fertilizers reduced green weight 66 per cent. with applications of 1000 parts per million and 42 per cent. with applications of 500 parts per million. Where the vanillin was used in pots with phosphates and potash the vanillin in amounts of 1000 parts per million reduced growth 69 per cent., and with 500 parts per million 50 per cent. Vanillin in pots with a complete fertilizer containing acid phosphate, sodium nitrate, and kainit, when added in concentrations of 1000 parts per million, reduced growth 40 per cent., and in 500 parts per million 32 per cent. While it appears from this experiment that the vanillin is slightly more harmful with phosphate and potash than in unfertilized soil, it is much less harmful in the soil fertilized with the complete fertilizer containing sodium nitrate. Funchess's results in the Alabama soil are in harmony with the results obtained by the writer on the action of this aldehyde in soils fertilized with sodium nitrate, previously reported. In the experiment with the Alabama soil the pots were planted to another crop, corn and cow peas, without any further addition of vanillin, but a second application of fertilizers was made. There was only a slight reduction in growth. This may be accounted for by oxidation or destruction of the vanillin, as four to five months intervened between the application of the aldehyde and the planting of the second crop. The alternate drying and wetting of the small volume of soil held by the pots, which in all probability occurred, would induce oxidation processes and thus change or destroy the vanillin. Again, in this work it is unfortunate that the absence or presence of the added substance was not determined from time to time during the experiments.

Other organic compounds were tested in the soil by Funchess, among them cumarin, which behaved somewhat as did vanillin, and dihydroxystearic acid, but they are not of interest in this paper dealing with the effects of aldehydes and therefore are not reviewed here.

Robbins (38) conducted some bacteriological experiments on the Alabama soils and secured results which seem to indicate that the disappearance of the added compounds vanillin, cumarin, pyridine, and quinoline was chiefly due to biological causes. The number of microorganisms increased greatly in the treated pots, following a depression in number which is analogous to that found in partial sterilization. The compounds added to sterile soils remained harmful to growth after a period of time, while the sterile soil which was inoculated with an infusion from normal soil showed no toxicity, the growth of the plants showing that the toxic properties of the compounds had largely disappeared. It is suggested by Robbins that the persistence of a compound—vanillin, for example—in some soils and not in others may be due to the fact that the vanillin-destroying organism is absent or to the fact that conditions are not suitable for its development or for the use of vanillin as a source of energy.⁴

Truog and Sykora (75) found vanillin, when added at the rate of 500 pounds per acre, in a sandy soil low in fertility and strongly acid in reaction, to be harmful to wheat grown in pots. Its harmfulness was overcome when the soil was limed, or when a complete nutrient solution was added. Vanillin added to a fertile silt loam produced no decreased growth. They also found guanidine to be very harmful. The effect of this strong basic compound was ameliorated by the addition of an acid kaolin to the sand culture. They concluded that chemical reactions are

⁴ Since the preparation of this manuscript Floyd reports the results of some work with vanillin on citrus seedlings, in connection with investigations of the dieback of citrus fruits. In concentrations of from 39 to 1250 parts per million vanillin caused a shorter growth in stems and roots of grape-fruit seedlings; in the higher concentrations there was much surface injury of the roots. In amounts higher than 1250 parts per million there was much injury. The roots in all concentrations were discolored from a purplish brown to brown color. No gum was formed on the seedlings by the toxic action of vanillin (Floyd, B. F., "Toxic Effect of Organic Chemicals on Citrus," report of Florida Agricultural Experiment Station for 1916, p. 30 R.).

probably important factors in lessening the effects of harmful organic compounds in soils.

Thus, from the results of various investigations cited, it is seen that the effects of the soil aldehydes studied vary, depending upon the soil used and the method of study. However, it is shown that the aldehydes, salicylic aldehyde and vanillin, are harmful in soils in which they were not destroyed or changed by biological agencies. Before proceeding to give the detailed data showing the effects of the aldehydes studied, the results of a chemical examination to determine the occurrence and distribution of aldehydes in field soils will be presented.

OCURRENCE OF ALDEHYDES IN GARDEN AND FIELD SOILS.

The discovery of salicylic aldehyde in the Mount Vernon gardens and the harmful properties of the aldehyde toward plants led to a study of the extent to which material of this type is likely to be encountered in soil investigations. In extending this study to many soils it was not feasible to examine large quantities of such soil, so that it was not possible to demonstrate clearly the identity of the aldehyde obtained, but it was possible so to treat a sample of soil as to obtain the compounds of an aldehyde nature contained therein, separated from compounds having non-aldehyde properties. This aldehyde material was tested as far as the quantity permitted for such reactions as are given by salicylic aldehyde; namely, coloration with ferric chloride, and the general aldehyde reaction with fuchsins reagent. In all cases the aldehyde material was subjected to the physiological test as to its effect on plant growth, using wheat seedlings in the well-known manner. The procedure employed in extracting the aldehyde material from the soil and the manner of testing it was as follows:

Twelve to sixteen pounds of soil were used in the examination for aldehyde. The soils were extracted with eight litres of a three per cent. solution of sodium hydroxide. The mixture was stirred for six to eight hours and, after settling over night, the liquid was poured off. The alkaline extract was acidified with sulphuric acid and filtered from the so-called humus precipitate. The acid filtrate was shaken out with several portions of ether, the ether extract combined and shaken with a concentrated aqueous solution of sodium bisulphite, which will remove aldehydes from the ether solution if present, by forming a water-soluble combina-

tion with the sodium bisulphite. The bisulphite solution was separated from the ether, strongly acidified with sulphuric acid, and air was blown through to remove the sulphur dioxide liberated. This acidified solution, in which the aldehyde is now liberated from its combination with the bisulphite, was then shaken with several portions of fresh ether, the ether extracts combined, and the ether removed by evaporation. There remained a small quantity of material, often resinous or oily in appearance.

This material was further purified by again taking up in water, extracting with ether, and the ether solution, after filtering, allowed to evaporate. Sometimes this operation was repeated. The purified residue contains the aldehyde material.

This aldehyde material was treated with a small quantity of water. The aqueous solution is frequently colored, and on evaporation a yellow oil is often noticeable, as would be the case if salicylic aldehyde were present. The odor of the latter is also sometimes observed, although in other cases other odors are perceptible, suggesting other aldehydes.

The fuchsine reagent was added to a portion of the solution, and to another portion a small amount of ferric chloride was added. Salicylic aldehyde, as mentioned, gives a violet color with ferric chloride and a pink color with the fuchsine reagent. Where both these reactions were observed the soil was considered as containing aldehyde. While the nature of the material is not thereby definitely shown to be salicylic aldehyde, yet the manner of isolation with ether and extraction therefrom with sodium bisulphite, together with the reaction shown with the fuchsine reagent, show the material to be an aldehyde, and the physical character of fluidity and the reaction with ferric chloride make it quite probable that in most of these cases salicylic aldehyde was under consideration. The amount obtained did not permit of further identification than is here given, especially as the main object was to determine the physiological property of the extracted material.

The main portion of the material remaining after making the above tests was dissolved or mixed with 250 c.c. of pure distilled water and the resulting liquid used as a culture for wheat seedlings in order to test the physiological effect of the extracted material from the soil. This was done with every soil examined, whether the above chemical tests were negative or positive.

In order to study the presence of aldehydes a number of soils were tested. Included in this test were a number of soils sent to this bureau from time to time by gardeners and greenhouse men. The soils submitted were garden and greenhouse soils, on which the owners had experienced some difficulty in producing vegetables or flowers. Often the soils had grown good crops, were intensively cultivated and heavily manured, and later failed. In this respect the conditions were similar to those on the Mount Vernon soil. This soil had been used for growing flowers and garden plants for a long time, had failed to show further response to manure, had been declining in productivity, and had been shown to contain salicylic aldehyde in the investigations reported. It seemed profitable, therefore, to include soils in this examination which in some degree had a similar history. The results of the examination of these soils, 14 in number, are given in Table I.

In addition to this adventitious examination of garden soils, a similar survey was made with soils collected in the open field by soil experts under instructions furnished them. Accordingly, samples of field soils were collected from various parts of the United States. A productive sample and an unproductive sample of the same soil type, either from the same field or at least in the same vicinity, were sent in for investigation. The history of the soils as to crops grown, fertilization, drainage, etc., was secured so far as available.

The result of this examination for the occurrence of aldehyde compounds in soils includes good and poor samples from many parts of the United States, comprising acid, neutral, and alkaline soils, soils of different cropping, different texture, drainage conditions, climatic conditions, etc. The results of the examination of these soils are given in Table II.

A total of 74 soils is described in the two tables. Of these, 14 are garden and greenhouse soils which had failed to grow good crops, and 60 are field soils under general farming conditions. Of these 60, 30 were productive soils and 30 unproductive. In this connection, attention should again be called to the fact that the field samples were collected in pairs, one good and the other poor, of the same soil type and from the same field or locality, so that statements concerning productivity pertain to the relation existing between the samples of the same type.

TABLE I.
Results of Examination of Unproductive Garden Soil for Aldehydes.

No.	Soil	Location	Crop on soil when sample was taken	Reaction of soil	Presence (+) or absence (-) of aldehyde	Effect of extracted substance on growth of wheat	
1	Garden soil, loam	Mount Vernon, Va.	Flowers	Acid	+	Very harmful	Rich loam, well manured for over a century.
2	Garden soil, silt loam	Mechanicsburg, Pa.	Vegetable	Very acid	+	Very harmful	Poultry manure and commercial fertilizer used for 10 years.
3	Garden soil, loam	Washington, D. C.	Flowers	Acid	-	No effect	Heavily manured.
4	Garden soil, loam	Pittsburgh, Pa.	Flowers	Acid	-	-	Manured, responds to lime.
5	Garden soil, gray sandy loam	Philadelphia, Pa.	Garden crops	Acid	-	Harmful	
6	Garden soil, loam	Phoenixville, Pa.	Garden crops	Alkaline	-	No effect	Well manured, salt content high
7	Garden soil, red loam	Orange, N. J.	Vegetables	Acid	+	Slightly harmful	Rich loam, declining, manure ineffective.
8	Truck soil	Chester Co., Pa.	Truck crops	Alkaline	+	Very harmful	Commercial fertilizer and rotation, trucked for 20 years, crops now failing. Soil contains excess of salts (0.15 %); sub line also contains aldehydes.
9	Greenhouse soil, loam	Arlington, Va.	Flowers	Neutral	+	Very harmful	Heavily manured.
10	Greenhouse soil, loam	Arlington, Va.	Flowers	Neutral	-	No effect	Soil weathered for months since it had been used for floriculture.
11	Greenhouse soil, raw loam	Arlington, Va.		Acid	-	No effect	Raw soil used in making soils Nos. 9 and 10.
12	Garden soil, gray	Philadelphia, Pa.	Garden crops	Alkaline	-	No effect	Drainage poor.
13	Garden soil, waxy black	Green Co., Ind.	Garden crops	Acid	-	No effect	Responds to lime and potash fertilizer.
14	Dark gray	Sanford, Fla.	Citrus	Alkaline	-	No effect	Calcareous soil.

TABLE II.
Results of Examination Productive and Unproductive Field Soils for Aldehydes.

No.	Soil type	Location	Productive			Unproductive				
			Crop on soil when sample was taken	Reaction of soil	Presence (+) or absence (-) of aldehyde	Effect of extracted substance on growth of wheat	Crop on soil when sample was taken	Reaction of soil	Presence (+) or absence (-) of aldehyde	Effect of extracted substance on growth of wheat
1	Tifton sandy loam	Covington Co., Ala.	Corn	Slightly acid	-	Harmful	Corn	Slightly acid	-	Harmful
2	Huntington fine sandy loam	Pope Co., Ark.	Corn	Slightly acid	-	Slightly beneficial	Corn	Slightly acid	-	Slightly beneficial
3	Decatur clay loam	Chattooga Co., Ga.	Cotton	Acid	-	Not tested	Cotton	Acid	-	Not tested
4	Noesloe silt loam	Cherokee Co., Kan.	Wheat	Slightly acid	-	Beneficial	Corn	Slightly acid	-	Beneficial
5	Colby silt loam	Jewell Co., Kans.	Corn	Neutral	-	Beneficial	Wheat	Neutral	-	Beneficial
6	Osage loam	Greenwood Co., Kans.	Grass	Alkaline	-	Beneficial	Corn	Alkaline	-	Beneficial
7	De Kalb silt loam	Christian Co., Ky.	Clover	Neutral	-	No effect	Tobacco	Neutral	-	Slightly harmful
8	Miami loam	Groesbeck Co., Mich.	Grass	Slightly acid	-	Harmful	Wheat	Slightly acid	-	Harmful
9	Carrington silt loam	Goodhue Co., Minn.	Barley	Slightly acid	-	Beneficial	Grass	Slightly acid	-	Beneficial
10	Memphis silt loam	Lafayette Co., Miss.	Corn	Not tested	-	No effect	Grass	Acid	+	Very harmful
11	Summit silt loam	Cass Co., Mo.	Oats	Neutral	-	Beneficial	Wheat	Not tested	-	No effect
12	Aurora silt loam	Miller Co., Mo.	Corn	Slightly acid	+	Harmful	Millet	Slightly acid	-	No effect
13	Freehold loam	Monmouth Co., N. J.	Grass	Slightly acid	-	Beneficial	Corn	Slightly acid	-	Slightly harmful
14	Dutchess silt loam	Orange Co., N. Y.	Millet	Neutral	-	Slightly harmful	Grass	Neutral	-	Harmful
15	Norfolk very fine sandy loam	Pender Co., N. C.	Cotton	Acid	+	Harmful	Cotton	Acid	+	Very harmful
16	Charolain loam	Ashe Co., N. C.	Corn	Neutral	-	No test	Corn	Neutral	-	No test
17	Tortway fine sand	Ashe Co., N. C.	Grass	Slightly acid	-	Harmful	Grass	Slightly acid	-	Harmful
18	Pertmouth silt loam	Perquimans Co., N. C.	Cotton	Slightly acid	-	Slightly harmful	Corn	Slightly acid	+	Harmful
19	Miami stony loam	Oneida Co., N. Y.	Corn	Acid	-	Slightly harmful	Meadow	Acid	+	Harmful
20	Ontario loam	Oneida Co., N. Y.	Oats	Neutral	-	Slightly harmful	Corn	Neutral	+	Harmful
21	Muskogee silt loam	Muskogee Co., Okla.	Peanuts	Acid	-	Beneficial	Cotton	Acid	+	Harmful
22	Berks shale loam	Lehigh Co., Pa.	Grass	Slightly acid	-	No effect	Grass	Slightly acid	+	No effect
23	Norfolk fine sandy loam	Georgetown Co., S. C.	Wheat	Slightly acid	-	No effect	Corn	Acid	+	Harmful
24	Clarksville silt loam	Robertson Co., Tenn.	Wheat	Acid	-	No effect	Clover	Acid	+	No effect
25	Jordan loam	Cache Co., Utah	Oats	Alkaline	-	Beneficial	Oats	Alkaline	-	Beneficial
26	Salt Lake clay	Cache Co., Utah	Wheat	Alkaline	-	Slightly harmful	Wheat	Alkaline	+	Harmful
27	DeKalb silty clay loam	Preston Co., W. Va.	Grass	Slightly acid	+	Harmful	Fallow	Slightly acid	+	Harmful
28	Carrington silt loam	Dane Co., Wis.	Tobacco	Neutral	-	Harmful	Oats	Acid	-	Harmful
29	Sioux fine sandy loam	Buffalo Co., Wis.	Corn	Slightly acid	-	No effect	Rye	Slightly acid	-	No effect
30	Miami silt loam	Jefferson Co., Wis.	Corn	Neutral	-	Harmful	Alfalfa	Neutral	-	Harmful

These soils were all subjected to the method described for obtaining aldehyde compounds from soils, and the material thus obtained tested with the reagents mentioned. Five of the garden soils and twelve of the field soils gave an appreciable amount of aldehyde compounds when thus extracted, and this material gave positive reactions with the fuchsine reagent and with the ferric chloride.

An examination of the data in Tables I and II shows that the aldehyde from certain of these soils is harmful to growth, and

FIG. 1.

Effect of salicylic aldehyde extracted from Mount Vernon garden soil on wheat seedlings: (1) Nutrient solution; (2) nutrient solution plus salicylic aldehyde; (3) distilled water; (4) distilled water plus salicylic aldehyde.

that these soils behave in this respect like the Mount Vernon soil (Table I, No. 1, Fig. 1), which has been already more fully described and in which salicylic aldehyde of poisonous properties was demonstrated.

In Fig. 2 is shown the effect of this material from soil No. 2, Table I. This has been used for gardening and trucking for the last ten years, and has been manured each year with poultry manure and commercial fertilizers. The soil in the last two years produced poor vegetables and truck crops, and corn failed en-

tirely. The soil is grayish-yellow in color, is quite acid and low in organic matter. The separated aldehyde extract was harmful to the growth of wheat seedlings, causing a decrease of 33 per cent.

In Fig. 3 is shown the effect of the aldehyde extract from soil No. 8, Table I, showing an alkaline reaction. This soil had been growing vegetables and truck crops for 20 years with frequent use of commercial fertilizers. Corn, cabbage, and cantal-

FIG. 2.

Effect of aldehyde extracted from garden soil (No. 2, Table I) from Mechanicsburg, Pa., on growth: (1) Distilled water; (2) distilled water plus aldehyde.

oupes had failed in certain sections of the field for the last two years, whereas formerly the soil grew excellent truck crops of all kinds. The soil and subsoil were quite alkaline to litmus paper, and both showed the presence of considerable aldehyde material. This aldehyde reduced growth of the test plants by 26 per cent., both tops and roots being severely injured.

The heavily manured greenhouse soil (No. 9, Table I) is particularly interesting in that considerable aldehyde was found, whereas neither the raw soil (No. 11, Table I) nor similarly

treated soil which had been used and then weathered for some time (No. 10, Table I) contained the harmful aldehyde material. This examination was made because the soil in question had been used on benches for floriculture and did not give good results. Soil No. 9, Table I, was a composite taken from two benches in the greenhouse where carnations and roses did not thrive. This contained aldehyde, which, when tested with wheat seedlings, gave reductions in growth of 35 per cent. Soil No. 10, Table I, had been previously used for greenhouse purposes and had been

FIG. 3.

Effect of aldehyde extracted from a poor garden soil (No. 8, Table I) on wheat seedlings: (1) Distilled water; (2) distilled water plus aldehyde from garden soil.

made in the same way by manuring heavily the raw soil, but without experiencing any difficulty. Since then it had been in a pile outside for several months. At the time of testing no aldehyde could be found, nor was the residue obtained harmful to the seedling wheat. Soil No. 11, Table I, was the raw soil as it was hauled from the field prior to the incorporation of manure in preparation for greenhouse use. No aldehyde could be detected in this soil, nor did such residue as was obtained show any harmful effect.

Soil No. 19, Table II, the unproductive sample of Miami stony

loam, contained aldehyde, and the depressed growth obtained is shown in Fig. 4, together with the effect of the identically extracted good field sample. The latter showed no aldehyde reactions, but, as seen from the photograph, it was, nevertheless, somewhat harmful—a fact which is recorded in the table.

Soil No. 20, Table II, the Ontario loam, unproductive, from Oneida County, New York, together with its good companion sample, presents an interesting story. In 1907 both fields were poor, unproductive soils. Both fields were manured heavily every year. One field responded to this treatment, the other did not.

FIG. 4.

Effect of substance extracted from poor and good Miami stony loam (No. 19, Table II) on wheat plants: (1) Distilled water; (2) distilled water plus material from poor soil containing aldehyde; (3) distilled water plus material from good soil showing no aldehyde reactions.

The field now good, represented by the productive sample, grew corn in 1907 and produced a poor crop. In 1908 the field was manured and planted to oats, giving a good yield. It was manured every year after this. In 1909 and 1910 hay was grown with good results, the largest crop being in 1910. In 1911 an excellent crop of corn was grown, and in 1912 oats were again grown with good yields.

The other field represented by the unproductive sample was in meadow in 1907 and gave poor yields. In 1908 the field was manured and planted to corn, which failed entirely. It was

manured every year after this without good results. In 1909 oats were planted, but made very little growth. In 1910 and 1911 grass was sown and gave poor results. In 1912 the soil was heavily manured and again planted to corn. The yield of stover was very poor, and no grain was formed.

The laboratory examination of the two soils showed them to be neutral in reaction. The good soil gave no reactions for aldehydes when extracted for this purpose, but the extracted material was slightly harmful. The poor soil, however, gave considerable amounts of aldehyde material, and this was distinctly harmful to the wheat seedlings, reducing growth 28 per cent.

The unproductive sample soil No. 26, Table II, the Salt Lake clay, is from a poor spot in an otherwise good field. The remainder of the field is represented by the productive sample of soil No. 26, Table II, and was collected about 35 feet from the poor spot. The color of the soil in the poor spot is light gray, while the good soil is gray with a pink tint. This spot is generally bare and seldom produces a crop, while the remainder of the field is very productive, yielding from 20 to 30 bushels of wheat per acre. The drainage in the poor spot is poorer than in the remainder of the field. The subsoil of both good and poor soil is a light, calcareous clay. Both soils are alkaline in reaction, and both showed the same content of water-soluble salts (0.03 per cent.). The good sample contained no aldehydes, and such residue as was obtained proved only slightly harmful to wheat seedlings, whereas the poor sample contained considerable aldehydes, which proved very harmful to wheat seedlings in the cultural tests, reducing growth 30 per cent.

Returning now to a discussion of the data as a whole, it is shown that the aldehyde extract is uniformly harmful to the test plants. This is apparent from the next to the last column of Table I and the fifth and last column of Table II.

In the tables are also given the field record of the soils as to their productivity, the data being furnished by the collector. The garden soils (Table I) were all soils with which trouble of one kind or another had been experienced. In general, the data show that the soils containing the aldehyde were also poor soils in garden and field, with some few exceptions. One notable exception is found in the Aurora silt loam, good (No. 12, Table II), from Miller County, Missouri. This soil contained aldehyde,

whereas the corresponding poor sample from another farm gave no indication of the presence of aldehyde. This observation was confirmed by procuring a new sample from the farmer on the good soil six months later. The other exceptions are the Norfolk very fine sandy loam, good (No. 15, Table II), and the Dekalb silty loam, good (No. 27, Table II), in which aldehyde was found, but it will be noticed that in both cases the poor soil contained the aldehyde also. It would appear, therefore, that both the good and poor soil samples contained some aldehyde. It might be further pointed out that in both cases the greater productivity of the sample designated as good is doubtless due to the direct fertilizing value of the applied manure, the less productive samples having no manure applied. That manure is not antagonistic to aldehyde is indicated by its presence in the exceedingly well-manured garden soils (Table I) (see notes in last column), as well as by some of the field results.

From these two tables it is at once apparent that only a relatively small number of the poor soils showed the presence of aldehydes, which means that the poorness of many of the soils must be attributed to other causes, since soil infertility may be due to a great many factors other than the presence of toxic compounds, and especially any particular toxic compound.

The material extracted in the aldehyde method, as in all these cases, was extremely small and gave no aldehyde reactions, but in some cases it proved harmful, nevertheless. What the nature of the harmful substance in these cases was it is impossible to state, as further study was excluded. If aldehyde was present, it was at least so small in amount that it escaped chemical detection; nor does the method wholly exclude the occurrence at this place of traces of other compounds. In the majority of cases the material was not harmful, occasionally even showing a slightly good or stimulating effect.

Seventy-four soils are described in the foregoing tables. Of these, 14 were garden and greenhouse soils which had failed to grow crops, and 60 were field soils, under general farming conditions. Of these 60, 30 were productive soils and 30 unproductive. These soils were all examined for aldehydes. Of the 14 garden soils, five contained aldehydes, and of the 60 field soils, 12 contained aldehydes.

(To be continued.)