Sulfur Burn in Citrus

radioactive sulfur used in studies to distinguish between fruit-contained and applied sulfur

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Radioactive sulfur tracers and a Geiger counter were used at the Riverside Experiment Station in investigations made to learn how sulfur burns citrus fruits—so sulfur could be safened.

Sulfur dust and lime-sulfur sprays—because of their low cost—probably will be used to a greater extent in pest control programs as citrus prices decline, even though sulfur burns the fruit during periods of hot weather.

Sulfur-resistant pests seldom develop—as houseflies resistant to DDT have developed—which may be due to the fact that sulfur affects several enzyme systems. An enzyme is a substance in a living cell that aids in the change of one substance to another but which is not itself changed in the process.

The multiple action—affecting several enzyme systems—of sulfur on pests is perhaps its chief drawback when used on plants.

It is believed that sulfuric acid is the end product of the chemical action of citrus fruit peel on sulfur. High air temperatures along with the sulfuric acid are thought to cause sulfur-burn.

When oranges or lemons are dusted with ground sulfur and subjected to temperatures of 90° F to 140° F, hydrogen sulfide—the rotten-egg gas—is given off by the fruit; a small amount of sulfur dioxide gas is produced; and the sulfate content of the peel and the acidity of the peel sap are increased. These products indicate that sulfuric acid is made from the sulfur dusted on citrus fruits.

When kept in hydrogen sulfide gas at temperatures of 105° F to 120° F, citrus fruits give off sulfur dioxide gas. When fruits are kept in either hydrogen sulfide gas or sulfur dioxide gas, the sulfate content of the peel and the acidity of the sap in the peel are increased. Thus, when supplied with hydrogen sulfide or sulfur dioxide gas, citrus fruit peel of fresh intact fruit will produce sulfuric acid.

Radioactive Sulfur

Radioactive sulfur tracers can be measured in amounts much smaller than similar substances that are not radioactive. A few hundred thousand radioactive atoms—too small to see with a microscope—will make themselves known because of the radio-like signal which each atom sends out. By using a Geiger counter, the signals the radioactive sulfur atoms send out can be heard. The ordinary sulfur atoms in the plant do not send out such signals.

By dusting lemons with radioactive sulfur and keeping them at 105° F, it was found that 100% of the hydrogen sulfide was radioactive; about 14% of the sulfur dioxide gas was radioactive; and 77% of the sulfate in the peel was radioactive.

Lemons kept at 105° F give off water with sugars, pentosans, oil, iron, calcium, magnesium, sodium, potassium, ammonia, chlorides, phosphates, sulfates, and oxalates in it. The radioactive sulfate in the water given off from lemons dusted with radioactive sulfur amounted to about 83% of the sulfate in the water.

The above experiments clearly show that sulfur dust somehow gets into the fruit peel; some of it is changed to hydrogen sulfide; and some of it is changed to sulfate. It appears that when there are not enough metals present in the peel sap to tie up the sulfate formed from the sulfur dust, the sulfate becomes sulfuric acid.

The hydrogen for the hydrogen sulfide may come from glutathione, a substance thought to be in all living cells which makes it possible for them to breathe. Sulfur is thought to be the important part of glutathione.

Not much is known about how sulfur is used in a plant but it is thought that radioactive sulfur must go into the protein of the fruit peel before it can be made into radioactive sulfate.

A radioautograph of a peel section of a radioactive sulfur-dusted lemon could be obtained for the studies because radioactive sulfur acts like light on a photographic film. The substances in the peel that dissolve in water and in alcohol were taken out before the slice of peel was put on the photographic film. Only the cell walls and protein in the slice of peel were left. Since sulfur is not found in the cell wall, the radioactive sulfur must have been in the protein.

Sulfur dust changes slowly to a sulfur gas much more rapidly at high than at low temperatures.

Small Amount

To show that a small amount of sulfur gas will go into lemons, the following experiment was tried:

A dish of radioactive ground sulfur was placed at the bottom of a glass bottle, and lemons piled above it in such a way that they could not touch the sulfur. The bottle was then heated to 106° F for several hours. At the end of that time about 5.7% radioactive hydrogen sulfide, 1% radioactive sulfur dioxide, and 2% radioactive sulfate were obtained from anal-

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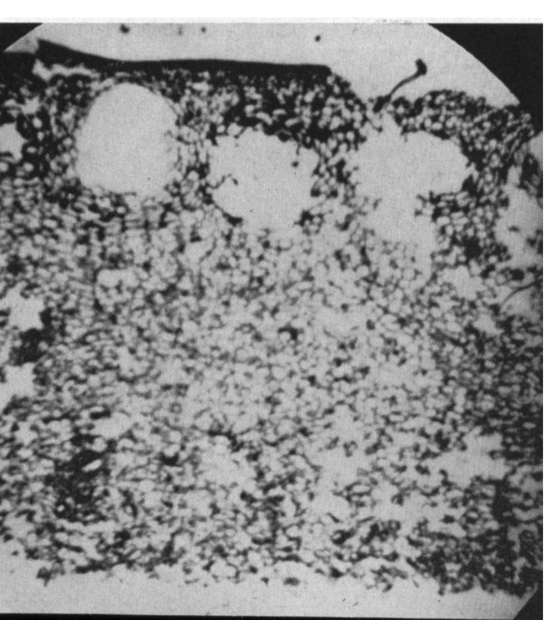

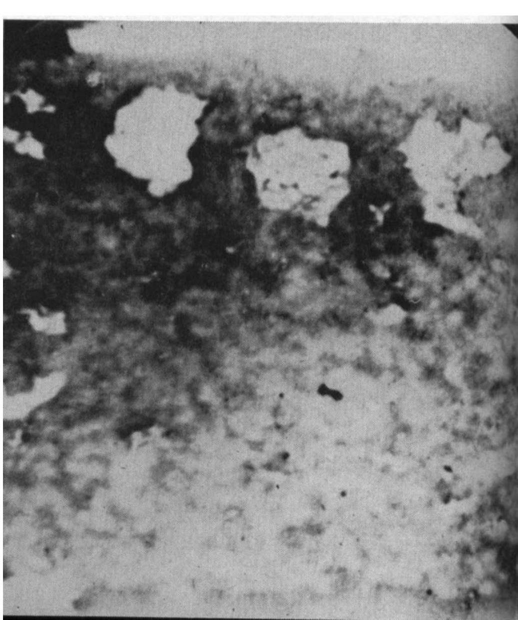

Left. **A photomicrograph of a radial section through the peel of a lemon dusted with radioactive sulfur and kept at 106°F.**

Right. **The image made on dental x-ray film—a radioautograph—made by the radioactive sulfur contained in the radial section shown in the illustration on the left.**

STORAGE

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to storage the grapefruit were washed with ½% soap solution, then treated with 1¼% of Exchange Wax No. 22.

Compared to nonsprayed fruit, those sprayed with either eight or 16 ppm 2,4-D had a reduced amount of surface decay, aging and black buttons throughout the storage. There was also a decrease in internal Alternaria decay as shown by cutting the black button fruit after storage.

After 15 weeks of storage, the fruit from trees sprayed with 16 ppm 2,4-D was rated the best with regard to firmness, color and general appearance. The eight ppm 2,4-D fruit rated next best, and the nonsprayed fruit was the poorest of the three lots.

2,4-D Treatment After Harvest

On May 17, 1948, after washing and waxing, both light green and green lemons from non-2,4-D-sprayed trees were dipped for two minutes in a lanolin emulsion containing either 500 or 1,000 ppm acid equivalent of the butyl ester of 2,4-D.

Another sample of green lemons was exposed for 69 hours to the vapor of the isopropyl ester of 2,4-D. After exposure, the treated lemons were placed in the storage chamber with the nontreated fruit.

Inspection showed that after 115 days of storage at 58° F to 60° F and 88% relative humidity, the nondipped light green lemons had 1.88% surface decay and 51.3% black buttons.

In contrast, after 162 days of storage, the light green 2,4-D-dipped lemons had only 3% with black buttons and none with Alternaria decay. At this time no surface decay had developed on the dipped fruit compared to 3.85% on the nondipped.

The green lemons dipped in either 500 or 1,000 ppm 2,4-D solutions had failed to develop a single fruit with a black button or Alternaria decay after 162 days of storage. Surface decay was 0.60% for the dipped fruit compared to 12.25% for the nondipped.

The 2,4-D vapor treatment of green lemons for 69 hours at the beginning of storage also reduced black buttons and Alternaria decay as well as surface decay compared to nontreated fruit. The reduction was much less than for the dip treatment.

Wax Preparations

In addition to the dip and vapor 2,4-D treatments, 500 ppm 2,4-D as the butyl ester was added to the Exchange Water-Wax preparations. In comparison to nontreated lemons in all color groups there was a remarkable reduction in percentage of fruit with black buttons, internal Alternaria decay and surface decay.

In a single storage test of Valencia oranges dipped in 2,4-D solutions, it was found that, as with the lemons, they developed fewer black buttons than the nontreated fruit.

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The above progress report is based upon Research Project No. 1346.

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POMEGRANATES

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being sharply delimited. The lower two fruits have the blemish occasionally found on pomegranates, but not associated with the mites. The checked and dark brown discolored areas coincide and are sharply defined. There is no tendency for the blemished area to be concentrated at the stem end of the fruit.

Control

In experiments made in 1948 it was shown that all the commonly used mite treatments will control the *Brevipalpus* mite, but since sulfur dust is highly effective as well as being inexpensive, it is recommended as a control measure. Experimental and commercial control treatments made in June and July 1948 with one half pound of sulfur dust per tree, resulted in excellent control, while untreated check trees were severely infested, with a high percentage of blemished fruit.

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ALMOND

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There is a great variation in the type of hulls obtained in harvesting different varieties of almonds. Certain hulls, such as the IXL which were used in this test, are thick and meaty, while those from some other varieties are thin and papery. The nutritive value of the hulls undoubtedly varies accordingly. It is planned to do further work on almond hull feeding this fall.

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SULFUR

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yses of the lemon peel. Thus it was proved ground sulfur can enter citrus fruits as sulfur vapor or gas.

Sulfur vapor alone in a glass bottle heated to the melting point of sulfur will combine with hydrogen to produce hydrogen sulfide. Oxygen is needed for this reaction and sulfur dioxide is produced in the process.

Glass tubes having the same surface as the lemons used in the experiments were sulfur dusted and placed in a bottle which was kept at 105° F. At the end of two days time, no hydrogen sulfide nor sulfur dioxide gas had been formed. This, it is believed, shows that elemental sulfur must get into citrus fruit to make hydrogen sulfide and sulfur dioxide gases at atmospheric temperatures.

Plants need sulfur to build proteins. Sulfur, usually in the form of sulfate, is supplied to plants through the soil. The sulfate may be put on the soil as a neutral salt or as a weak solution of sulfuric acid. The roots absorb sulfate, but must be able to change the sulfate into other forms in order to build the sulfur into protein.

Enzymic Action Suggested

Another experiment was conducted to observe what would happen if citrus fruit were dipped in weak radioactive sulfuric acid and kept at about 115° F for several hours. The fruit yielded slightly radioactive sulfur dioxide and hydrogen sulfide gases, very radioactive sulfate and protein. The sap in the peel had become more acid.

It might be said in passing that the fruit resembled sulfur-burned fruit as did the fruit kept at 105° F in hydrogen sulfide or sulfur dioxide gas for a few hours.

This experiment suggests that enzymes are present in the fruit peel which can change sulfate to other forms of sulfur. But the rate of change of sulfur to sulfate is a more rapid process than the one changing sulfate back to other forms of sulfur.

Experiments are under way to determine the effect of temperature on the relative rates of changing sulfur to sulfate or vice versa.

Other experiments in which lemons are being treated with radioactive hydrogen sulfide and sulfur dioxide are being run. This and other work probably will bear out the evidence already found on how ordinary elemental sulfur is changed to sulfuric acid.

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