PLANT CONSTITUENTS

Silicon in Rice

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The silica content of the various parts of the rice plant has been determined at the inflorescence emerging stage. This varied from 2.63% in the inflorescence to 13.13% in the leaf sheath. By means of a spodogram, the actual pattern of silica deposition in the rice leaf sheath was determined. Index of refraction and x-ray studies of silica from rice, silica gel, and opal showed them all to be a similar type of amorphous silica. Absorption and specific gravity studies indicate that silica from the rice sheath had very little adsorptive capacity and was not very porous. Silica in rice can properly be classified as biogenetic opal.

SINCE 1934, Japanese scientists have observed that silicon is beneficial in the normal growth of rice (5, 11). Lack of available silicon greatly lowers the yield of rice. Yoshida, Ohnishi, and Kitagishi (17) showed that a low available supply of silicon increases susceptibility of rice to diseases and insects. Field tests have indicated that application of suitable silicon compounds to the soil greatly diminished the appearance of blast and brown spot and has increased the yield (6).

Lanning and co-workers (7-9), by means of indices of refraction, determined the chemical nature of silica in several varieties of plants. Only opal was observed in some plants, and both opal and α-quartz were observed in lantana, strawberries, and black raspberries. X-ray diffraction studies gave strong supporting evidence to these observations. Workers in the field, such as Beavers (1) and Smithson (13), commonly refer to amorphous plant silica as opal.

Recently Yoshida, Ohnishi, and Kitagishi (17), by means of infrared absorption studies and solubility, concluded that silicon occurs in the rice plant as silica gel and not as opal. Actually, their infrared spectra showed almost insignificant differences between rice silica and their opal sample. They did not report index of refraction which is used by mineralogists to distinguish between opal (1.41–1.46) and other forms of silica.

Swineford and Franks (14) have used x-rays to distinguish between biogenetic opal and low-cristobalite–tridymite types. Biogenetic opal is the type produced (directly or indirectly) by the growth processes of certain plants and diatoms.

Liu (10) made some preliminary solubility studies on silicon in rice hull. Some evidence was obtained that some of the silica might be tied up with organic groups. He misquoted the paper by Lanning et al. (9) by stating that SiO2 occurred only in the ash and not in plant tissue.

Engel (3) extracted a silico-galactose compound from oat straw, and Weiss (16) has synthesized a class of stable organosilicon compounds in an aqueous solution.

The present study was made in order to evaluate these somewhat conflicting reports in the literature and to study the silica deposition in the various parts of the rice plant.

Materials and Methods

The rice plants (Oryza sativa) studied, were collected at the inflorescence emerging stage at Davis, California, in July 1961. The plants were separated into roots,st ems, sheath, leaves, and inflorescence. All plant parts were thoroughly washed and then dried at 110° C.

Silica and ash contents of plant materials were determined by classical gravimetric techniques. The material was ashed at about 600° C. After weighing, the ash was treated repeatedly with 6.\mathcal{N} hydrochloric acid to remove other mineral impurities. The silica was filtered out and ignited. The silicon dioxide content was determined as difference of weights before and after treatment with hydrofluoric acid.

The depositional pattern of silica was studied by the spodogram technique described by Ponnaiya (12) and used by Lanning, Ponnaiya, and Crumpton (9).

Samples used in x-ray and petrographic microscope studies were obtained by completely ashing the dried plant material at 700° C. The ash was treated repeatedly with hydrochloric acid to remove mineral impurities and the silica dried at 110° C. Dry, powdered leaf sheath was also used in an x-ray study. The x-ray diffraction patterns were made on the same equipment and in the same manner described by Lanning et al. (9).

Silica gel used in x-ray and petrographic microscope studies was prepared from water glass and sulfuric acid by the method described by Walton (15). The final product was free of acid.

The adsorptive capacities of silica from rice sheath and silica gel were compared in two ways. Adsorption of water vapor was determined by exposing samples, dried in an oven at 600° C., to moist air (relative humidity 50%) for both 1-hour and 24-hour periods. A second method was to study the adsorption of methyl orange from a neutral water solution containing $1/1000$ of a gram of solute per liter.

The specific gravities of the rice silica and silica gel were determined by displacement of water at 20° C. The bottle was agitated to remove air bubbles.

Results and Discussion

Results of silica analysis made on the various parts of the rice plant are given in Table I. The highest percentage of silica was in the leaf sheath, and the lowest was in the inflorescence. The latter was newly formed tissue, and even though low in silica content, there was enough present to indicate that silica deposition took place rapidly.

Table I. Silica in Rice at the Inflorescence Emerging State

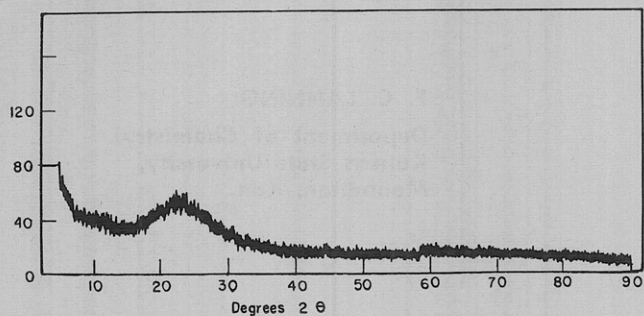| Part of Plant	Ash, Dry Matter, %	SiO2, Dry Matter, %
Roots	11.50	5.82
Stems	10.82	5.10
Sheath	17.50	13.13
Leaves	14.70	10.13
Inflorescence	7.46	2.63

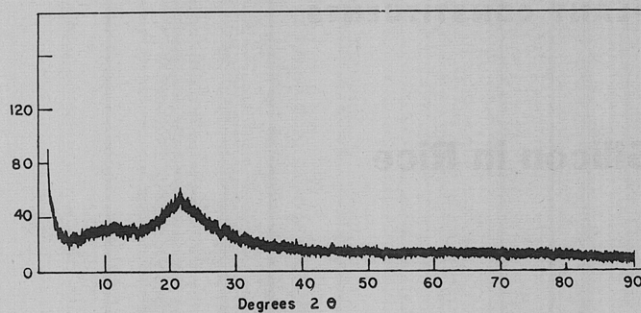**Figure 1.** X-ray diffraction pattern of silica gel

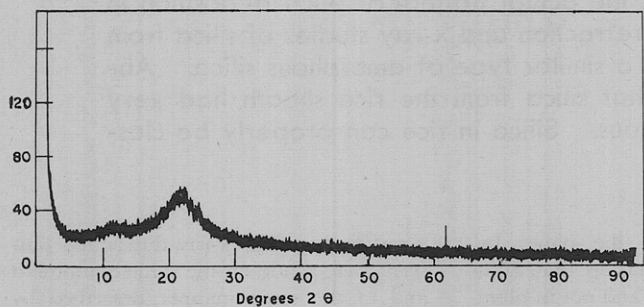**Figure 2.** X-ray diffraction pattern of silica from rice leaf sheath

Figure 3. X-ray diffraction pattern of silica from rice inflorescence
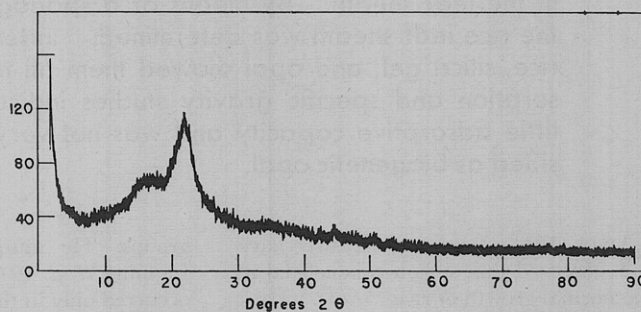

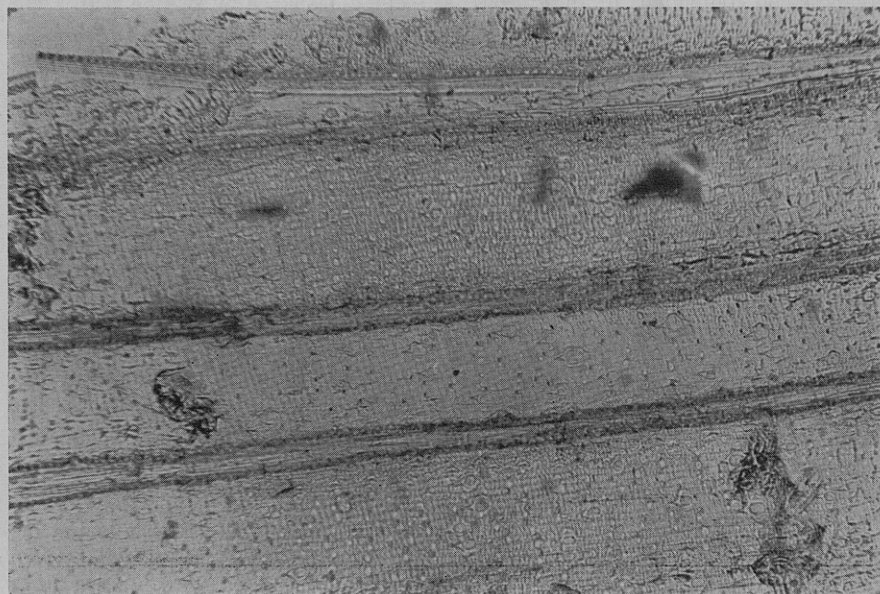**Figure 4.** X-ray diffraction pattern of dry powdered rice leaf sheath

Figure 5. Spodogram of rice leaf sheath

Petrographic microscope studies of silica from the ash, silica gel, and mineral opal showed them all to be clear, colorless, and isotropic. The indices of refraction are tabulated as follows:

Variety of Silica	Index of Refraction at 25° C.
Rice sheath	1.451
Inflorescence	1.456
Silica gel	1.456
Opal (Scott Co., Kan.)	1.446 (4)

These values were obtained with white light and the accuracy is ±0.002. The results indicate that all silica samples were mineralogically the same and could be classified as opal.

X-ray diffraction patterns of silica gel, silica from rice sheath, and silica from inflorescence are all alike (Figures 1, 2, and 3). These patterns were also like those obtained by Swineford and Franks (14) for biogenetic opal. This gives further support to the conclusion that the silica samples were all very much alike mineralogically. An x-ray diffraction pattern (Figure 4) of dry powdered rice

sheath is essentially an opal pattern modified by cellulose peaks. The latter has a high peak at 22.5° 2θ and a moderate one at 16° 2θ (2).

The infrared experiments of Yoshida et al. (17) also support the conclusion that silicon in rice is in the form of SiO_2. They characterized it as silica gel, for rice silica and silica gel had about the same solubility and it was higher than their mineral opal sample. The solubility differences they reported may actually have been due to a more finely divided and open structure in rice silica and silica gel.

The spodogram of rice leaf sheath (Figure 5) shows that the silica was deposited in rows of spherical particles. Furthermore, there appears to be a continuous layer of SiO_2 which tends to hold the structure together. The fact that depositional pattern is preserved after low temperature ashing supports the conclusion that Si—O—Si bonding exists, and therefore opal exists in the plant. This does not say that there is no bonding between silica tetrahedra and carbohydrates which some research indicates may be possible.

The silica gel was much more adsorptive than the silica from rice sheaths. An 0.8535-gram sample of silica gel adsorbed 0.1465 gram of water vapor in 1 hour and 0.1990 gram in 24 hours. This amounted to a 23.3% increase in weight in a day's time. The rice silica adsorbed only 0.0027 gram in 1 hour and 0.0052 gram in 24 hours—only a 0.566% increase in a day's time.

The silica gel readily adsorbed methyl

orange and turned a bright pink color. Silica from rice sheath adsorbed only enough to show a slight trace of pink color.

The adsorptive capacities of the two forms of silica were quite different and indicated that the rice silica was not porous like the silica gel.

The specific gravity of the rice sheath silica at 20° C. was 2.257. This is at the upper end of the opal range. The corresponding value for the silica gel was 2.102. This was also good evidence that the rice silica was the least porous.

These studies indicate that rice silica is not exactly the same as ordinary silica gel and that it would be better to classify it as biogenetic opal. This is in line with the common practice of classifying amorphous plant silica as opal.

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2,4-D RESIDUES

Residues in Stored Lemons Treated with Various Formulations of 2,4-D

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Analysis of lemons for 2,4-D residues showed a small amount of ester-like residue whether the fruit was treated with isopropyl ester or various salt formulations. The use of carboxyl-C^{14}-labeled 2,4-D acid indicated that part of the 2,4-D reacted with some plant constituent to produce an ester-like complex. A C^{14}-label in the isopropyl group provided evidence that all of the isopropyl ester in the cells was hydrolyzed and that any ester-like residue was synthesized in vivo.

IT was shown previously (*3*) that 2,4-D (2,4-dichlorophenoxyacetic acid) applied to citrus in the form of isopropyl ester was recovered in what appeared to be both acid and ester fractions. The acid fraction partitioned to organic solvents at a low pH and to water in a neutral solution. The fraction considered to be the ester comprised only a small part of the residue but was found to be water-insoluble in a neutral solution. Alkaline hydrolysis yielded the acid.

Although Crafts (*2*) found that hydrolysis of isopropyl 2,4-D occurred in barley leaves, the evidence did not indicate the extent of hydrolysis. Previous data from the study of citrus indicated that some of the residue might remain as the isopropyl ester.

Further investigation was undertaken to determine the amount and nature of residues left by various salt forms of 2,4-D. C^{14}-labeled 2,4-D was also used to determine the degree of hydrolysis of the isopropyl ester. Results of these investigations are presented here.

Procedure

Lemons were washed in a commercial-type washer. The wash water contained 0.5% soap and 2% soda ash; it was kept at 110° F., and the fruit remained submerged for 2 minutes. The final rinse in the washing process consisted of a wax emulsion containing 0.5% of Sunkist water-wax. The 2,4-D was added to the wax emulsion in forms described in the separate experiments. Each treatment contained more than 400 fruit known commercially as light green.

Analyses for 2,4-D residues of individual fruits taken at random were made initially and after various periods of storage by using a Dohrmann microcoulometric gas chromatograph and a method previously described (*3*). The fruit remaining at the end of the experiments was inspected for soundness and general appearance.

Additional experiments were made with C^{14}-labeled 2,4-D. The C^{14}-label was present in the carboxyl position of both isopropyl ester and acid forms of the growth regulator and also in the isopropyl group (1,3 position) of another preparation of the isopropyl ester. Fruit in these experiments was hand-washed and treated with 2,4-D over a small marked area of the fruit surface by application with a micropipet. The 2,4-D compounds were dissolved in acetone to facilitate application. The treated fruit was kept in large closed jars and aerated with humidified air. After storage, the treated portion of the peel was grated, frozen, and extracted with acetone for about 4 hours in a Bailey-Walker extractor. The acetone was evaporated and the residue dissolved in ether, filtered, and finally concentrated to about 0.5 ml. before