PATTERN OF DISTRIBUTION

Relation of Silicon in Wheat to Disease and Pest Resistance

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The silica content of the various parts of 11 varieties of wheat was determined both in the fall and in the spring when the growth was at least 6 inches tall. It varied from an average of 1.11% in the stem to 5.61% in the sheath. Silica content of leaves in the spring was nearly twice that in the fall. By means of spodograms, the actual patterns of silica deposits in the various parts of the wheat plants were determined. Index of refraction studies showed the silica to be opal. The results show no direct relationship between total silica content and resistance to Hessian fly or to diseases.

EARLY investigators were interested in the relationship between SiO_2 deposits in wheat (*Triticum*) and resistance of the plants to insects and disease but did not make complete studies of silica in various parts of the wheat plant. McColloch and Salmon (*5*) in 1923 showed that several very susceptible varieties of wheat markedly resisted attack by the Hessian fly [*Mayietola destructor* (Say.)] when grown in Pfeffer's solution containing a small amount of sodium silicate and that the degree of resistance varied with the amount of silica. Painter (*7*) in 1951 considered that the amount of silica is related to resistance because silica strengthens the cell walls of the plant.

Refai, Jones, and Miller (*10*) determined silica in the 1.5-inch portion of the wheat stem above the root system. They studied several varieties but could show no relationship between silica content and resistance to Hessian fly.

Lanning, Ponnaiya, and Crumpton (*4*) determined the depositional pattern of silica and the silica content of the leaf sheath of Concho wheat. By means of x-rays and petrographic microscope the silica was shown to be opal.

Miller *et al.* (*6*) studied silica depositional patterns in the second leaf sheath of several varieties of wheat. Sheaths of plants resistant to Hessian fly appeared to have much more complete and even distribution of silica deposits.

Palladin (*8*) recorded that wheat and rye grown in nutrient solutions low in silicic acid suffered severely from rusts, and that *Lithospermum arvense* grown without silica was badly attacked by plant lice.

Volk, Kahn, and Weintraub (*11*) reported that silicon content of the rice plant influences its resistance to infection by blast fungus. Infestation by insects occurred only in young plants whose tissue was soft and contained less silica. Japanese scientists (*1*, *2*, *12*) have shown that silicon deficiency in rice increases susceptibility to fungus diseases and insects.

This work was initiated to make a more complete study of silica deposition in various parts of wheat plants and to relate the silica to insect and disease resistance.

Materials and Methods

The wheat plants (*Triticum aestivum* L. em. Thell.) studied were grown in experimental plots on the Agronomy Farm of Kansas State University. Available silica content of the soil was high, approximately 20 mg. per 100 grams of soil (*3*). The pH of the soil was 5.2 at 1 to 1 dilution. The 11 varieties studied and their resistances to diseases and insects are given in Table I. The first samples were collected November 5, 1964; the second, from the same plots April 13, 1965, when the spring growth was at least 6 inches. The plants were separated into roots, stems, leaves, and sheath. All 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 being weighed, the ash was treated repeatedly with 6N hydrochloric acid to remove other mineral impurities. The silica was filtered out and ignited. Silicon dioxide content was determined as difference of weights before and after hydrofluoric acid treatment. All determinations were made in duplicate.

The depositional pattern of silica was studied by the spodogram technique described by Ponnaiya (*9*) and used by Lanning, Ponnaiya, and Crumpton (*4*).

Samples used in petrographic microscope studies were obtained by completely ashing the dried plant material at 600° C. The ash was treated repeatedly with hydrochloric acid to remove mineral impurities and the silica dried at 110° C.

Results and Discussion

Petrographic microscope studies of silica from ash of wheat plants studied showed it to be clear, colorless, and isotropic with an index of refraction of 1.45, properties typical of the mineral opal, as was shown with Concho wheat (*4*).

Table I. Varieties of Hard Red Winter Wheat Used for Silicon Determinations and Response to Certain Diseases and Hessian Fly

Variety	*Type of Resistance*
Ponca CI 12128	Hessian fly, some races of leaf rust
Ottawa CI 12804	Hessian fly, some races of leaf and stem rust
Gage CI 13532	Hessian fly, some races of leaf and stem rust and soil-borne mosaic
Pawnee CI 11669	Hessian fly, some races of leaf rust and loose smut
Wichita CI 11952	None
Turkey CI 1558	None
Triumph CI 12132	Loose smut
Bison CI 12518	Bunt, tolerance to wheat streak mosaic virus
Comanche CI 11673	Bunt
CI 13285	Hessian fly, some races of leaf rust
Kaw CI 12871	Some races of leaf and stem rust and bunt

Results of silica and ash analyses are given in Table II. On the average, silica content of wheat leaves in spring was nearly double that in the fall. The increase in Gage was slightly over three times. Silica was greater in the sheath in spring than in the fall. Averages of the sheath plus stem were considerably higher in the spring.

On the average, there was slightly less silica in the roots in the spring than in the fall. However, Bison roots had twice as much in the spring and three other varieties had somewhat more than in the fall.

Silica percentage was highest in the

Table II. Silica and Ash in Wheat Plants

(% dry matter)

	Collected Nov. 5, 1964						Collected April 13, 1965							
	Roots		Sheath and Stems		Leaves		Roots		Sheath		Stems		Leaves	
Variety	Ash	Silica	Ash	Silica	Ash	Silica	Ash	Silica	Ash	Silica	Ash	Silica	Ash	Silica
Ponca CI 12128	12.10	7.05	16.13	4.55	14.47	2.46	8.15	4.30	16.50	8.32	7.55	1.95	12.65	3.46
Ottawa CI 12804	9.54	4.07	13.62	2.22	15.22	2.24	9.65	3.68	11.80	4.55	11.60	0.58	13.42	4.10
Gage CI 13532	9.56	3.44	14.04	2.22	14.90	1.31	7.75	2.18	10.70	3.24	11.80	0.72	14.50	4.10
Pawnee CI 11669	8.90	3.00	12.90	1.30	12.40	2.32	10.25	3.04	12.50	4.75	11.75	0.80	11.75	3.96
Wichita CI 11952	9.90	3.80	12.07	1.38	14.57	1.95	11.40	2.95	12.40	6.10	13.60	0.51	15.20	3.74
Turkey CI 1558	12.90	5.87	12.01	1.28	14.90	2.45	10.90	4.50	12.20	8.25	16.80	0.92	11.60	3.38
Triumph CI 12132	12.04	5.31	13.62	2.12	15.41	2.41	13.80	5.10	12.30	5.30	12.00	0.79	13.60	3.20
Bison CI 12518	8.79	2.18	13.22	1.94	14.85	2.28	10.60	4.30	12.50	5.90	12.70	1.43	16.10	5.53
Comanche CI 11673	10.22	3.82	11.84	1.27	15.80	2.43	7.53	2.98	9.64	4.68	13.11	1.48	12.20	4.21
CI 13285	9.50	3.81	13.12	2.54	14.55	2.83	12.50	4.90	13.90	5.20	5.20	0.91	16.80	4.20
Kaw CI 12871	10.82	3.88	14.30	1.66	14.55	2.11	12.99	4.45	12.50	5.45	14.50	1.01	17.50	4.54
Av.	10.39	4.20	14.17	2.04	14.69	2.25	10.50	3.85	12.45	5.61	11.87	1.11	14.12	4.09

sheath and lowest in the stems. That of leaves and roots was about the same in the spring and averaged about 1.7% less silica than in the sheath. In the fall leaves had only about half as much silica as roots did.

Although silica contents of the plants studied varied considerably, none were low in silica, probably because of the high available silica content of the soil.

Ash content was highest in leaves, next highest in the sheath, and lowest in roots. Variation in ash content among plants was somewhat less than variation in silica content. Percentage of silica in the ash was highest in the sheath, (averaging 45.0%) and low in the stems (averaging 9.35%).

Spodograms of the silica deposition in various parts of the wheat plant (Figure 1) were some of the better ones photographically and were chosen as representative of the plants studied. The silica particles in the sheath (Figure 1, *B* and *D*) are oblong and have crenate edges. Miller *et al.* (*6*) did not report the crenate edges that were evident in their spodograms. Silica particles are arranged in parallel double or triple rows that alternate and are about equidistant. The rows were somewhat closer in Ottawa than in the Gage sheath. No marked differences were observed between Hessian fly–resistant and nonresistant varieties.

Silica in the leaves was more uniformly distributed and oblong silica particles were much less evident. The Turkey leaf spodogram, *A*, was more typical for wheat than the Ottawa leaf one, *C*, in which oblong particles were more evident. In a few leaves like Turkey and Ponca silicified trichomes were present.

Ponca stems had the highest silica content of any variety studied. Large numbers of oblong crenate silica particles are shown in spodogram *E*. Other stems showed less development of particles.

The roots, like the leaves, did not show many oblong particles but some were evident in Pawnee roots, *F*. Silica in roots seemed to occur primarily in very small particles.

The results show no direct relationship between silica content and resistance to Hessian fly or to diseases. Both resistant and nonresistant varieties had high silica contents. There may be a relationship between early deposition and type of deposition of silica to such resistances, as was indicated by Miller *et al.* (*6*).

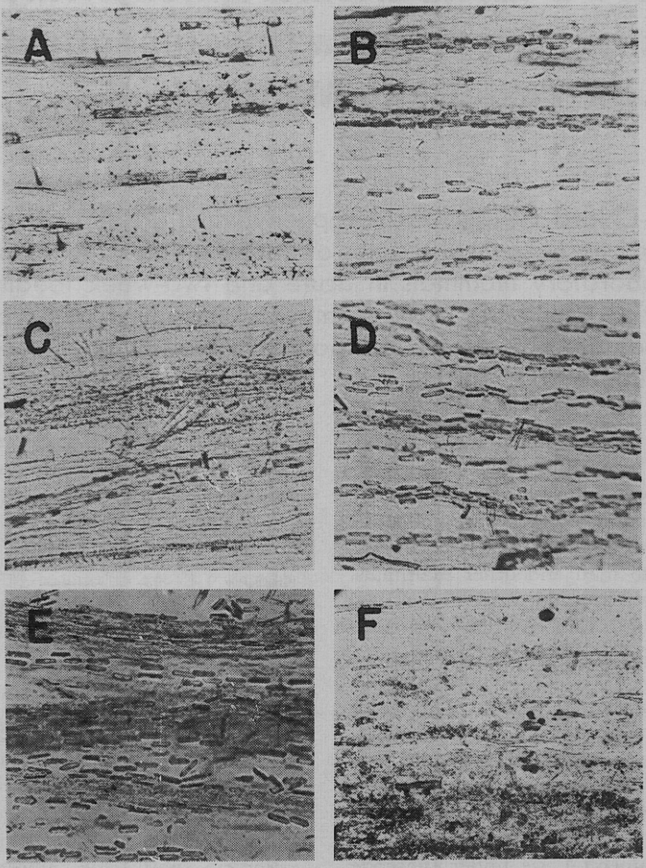

Figure 1. Spodograms of parts of wheat plants at 80×

- A. Turkey leaf. Note rather uniform deposition of silica and absence of rectangular silica particles. Some silicified trichomes present
- B. Gage sheath. Note oblong crenate edged silica particles arranged in parallel double or triple rows that alternate and are equidistant
- C. Ottawa leaf. Differs from Turkey leaf in having some oblong silica particles
- D. Ottawa sheath. Rows of oblong silica particles closer together than in Gage sheath
- E. Ponca stem. Oblong silica particles arranged in rows
- F. Pawnee root. Most of silica in small particles. A few oblong particles

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LOW TOXICITY PHOSPHATES

2-Chloro-1-(2,4,5-trichlorophenyl)vinyl Dimethyl Phosphate, a New Insecticide with Low Toxicity to Mammals

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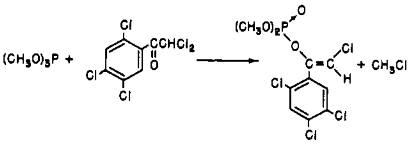
2-Chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate (SD 8447) has shown excellent toxicity to several species of insects in laboratory and field tests but is remarkably safe to laboratory mammals in acute and two-week feeding tests. The poor solubility or partition properties of the compound may limit penetration and translocation in mammals so that amounts of the compound in blood and tissues are low enough to be metabolized without toxic effect.

A MAJOR GOAL of insecticide research, even before the recent public concern over pesticide residues, has been to find compounds which are effective against insects but which are less hazardous to man and other mammals. With this goal in mind, work in the Shell Development Laboratories on insecticidal vinyl phosphates has led to 2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate (I) (*9*). This compound is highly toxic to several insect species in both laboratory and field tests but is relatively nontoxic to laboratory test mammals in acute and subacute tests. Compound I is now under development toward commercial use under the code number SD 8447. The present paper presents chemical and biological data for this compound in comparison with data for several of its analogs. An explanation for the outstanding selective toxicity of (I) is suggested from exploratory experiments.

Methods and Results

Preparation and Properties of Compounds. Data on chemical and physical properties of (I) and of four analogs are given in Table I. Compound I was prepared by the reaction given below; the four analogs were obtained in the same way. With chlorine in the 2 and 4 positions of the benzene ring of the ketone intermediate, the reaction is highly selective for the β-isomer (I, II, III), presumably for steric reasons. The β-isomer is arbitrarily designated as the one in which the phosphate group and the largest group on the second vinylic carbon are cis. Only 10% or less of the α-isomer, with the phosphate and chlorine atoms trans on the double bond, were formed and were removed from (I) and (II) by crystallization. By contrast, the α-isomer predominated when the benzene ring was not chlorinated (IV) or with dichloroacetaldehyde as the carbonyl reactant (V); preferential formation of the α-isomer is "normal" in this reaction (*5*). Configurations of the individual isomers and the isomeric content of the five compounds of Table I were assigned from NMR and infrared-absorption spectra following methods used earlier for Phosdrin insecticide (*13*). Both (I) and its ethyl analog (II) are crystalline solids of moderately high melting point which are only very slightly soluble in water. Compound I is also only moderately soluble in hydrocarbons and other common organic solvents; the ethyl analog is more soluble.



I (β-isomer), SD 8447

Compound I and its analogs are, like other organophosphate insecticides, good inhibitors of acetylcholinesterases, although enzyme inhibition studies with (I) and (II) are complicated by the low water solubility of the compounds. Presumably, this inhibition is the principal mechanism of their biological action. Fukuto and Metcalf (*3*) have shown that rates of hydrolysis of substituted phenyl phosphates correlate well with acetylcholinesterase inhibition. However, the data in Table I for the four ethyl esters (II), (III), (IV), and (V) indicate that the reactivity of this group of compounds with cholinesterases does not parallel hydrolysis data at pH 9.1. Secondary interactions between the chlorinated phenyl ring of (II) and (III) with the enzymes increase the inhibition.

Insect and mammalian toxicity data for the same five compounds are given in Table II with similar data for malathion.

Syntheses. The intermediate acetophenones were prepared using the Friedel-Crafts ketone synthesis. Dichloroacetyl chloride (Kay-Fries Co., 99% pure, 88 grams, 0.60 mole) was added in 10 minutes to a stirred slurry of 88 grams, 0.66 mole, of anhydrous, purified, powdered aluminum chloride (Matheson Coleman & Bell) in 109 grams, 0.60 mole of 1,2,4-trichlorobenzene (Matheson Coleman & Bell,

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