feces at the second day were analyzed. Thin-layer chromatographic analysis of the extracts of these samples indicated the presence of three major components, as shown in Figure 1. Component A, B, and C had a mobility similar to the authentic compounds: arsenic acid, DSMA, and DMAA respectively. The component A in the urine was identified as arsenate by comparing its absorption spectrum of AgDDC method with that of an authentic sample. By their comparative GC–MS spectra (Figure 2) the components B and C in the blood and urine were distinctly identified as methanearsonate and dimethylarsinate. The other component X which was observed in the blood could not be identified. These results indicated that a major portion of arsenic in feces was methanearsonate, and as a minor portion there was dimethylarsinate, the metabolite of MAF. According to the undetectability of arsenic in the bile, this metabolite might be due to the methylation slightly occurred in the intestinal tract by bacterial flora. On the other hand, the presence of dimethylarsinate as the predominant component in the blood indicates that the methylation largely occurred in the rat body. The major urinary elimination form was identified as methanearsonate, and dimethylarsinate and arsenate were minor. These results indicate that methylation occurs with organoarsenic compound such as methanearsonate. In addition, the fact that the presence of dimethylarsinate was detected predominantly in the blood of the control rats fed the control feed which contained arsenate but no dimethylarsinate as a normal component indicates that methylation also occurs with inorganic arsenic compound.

The arsenic metabolites in mammals were recently reported by Lakso and Peoples (1975) and Crecelius (1975). Lakso and Peoples analyzed the urine for inorganic arsenic (IA) and methylated arsenic (MA) in the cows (rumen) and the dogs (animal body) treated orally with arsenate and arsenite. The AgDDC colorimetric analysis revealed MA as the metabolite, and they suggested that methylation of arsenic occurred not only in rumen by the microorganisms but also in animal body. Crecelius detected DMAA, MAA, arsenate, and arsenite in human urine after drinking arsenite-rich wine, using the analytical procedures based on $NaBH_4$ reduction of the arsenic to the separating gaseous arsine by controlled pH method and the detection of the arsenic by emission spectrometry.

In these two reports, the urine of the mammals which had been treated with the inorganic form of arsenic was analyzed, and MA in cows and dogs and DMAA and MAA in human were detected as the metabolite of inorganic arsenic. However, these metabolites were not identified in detail. In our studies, the analysis was performed on the urine, the feces, and the blood of the rats which were treated before with MAF (monomethyl organic form of arsenic), and the dimethylated form of arsenic was identified as the metabolite by combining TLC and GC–MS. It was confirmed that methylation of monomethyl arsenic compound to dimethylated arsenic compound could occur in the rat. Therefore, it is conceivable that the biological methylation of arsenic in mammals occurs with inorganic arsenic and monomethyl organoarsenic compound, and dimethylated arsenic compound may be the final methylated form of arsenic in mammals.

ACKNOWLEDGMENT

The authors are grateful to Y. Shirasu, Division of Toxicology, Institute of Environmental Toxicology, for his help, advice, and encouragement, and to Y. Kabasawa for technical assistance during this investigation. The ferric methanearsonate and disodium methanearsonate used in the investigation were provided by Kumiai Chemical Co. The authors express appreciation for this support.

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Received for review May 16, 1977. Accepted September 23, 1977.

# Effect of Grain Moisture Content on the Degradation Rate of Methyl Phoxim in Corn, Sorghum, and Wheat

Residue data were obtained at five intervals over a 30-day period from wheat, corn, and sorghum containing eight levels of moisture, following 10 ppm applications of methyl phoxim emulsion spray. High-moisture content reduces the effectiveness and persistence of methyl phoxim in stored grain. Degradations differed significantly ($P$ 0.05) at each moisture level. After 30 days of storage, 10, 3, and 22.9% of the initial residue deposit remained on the 20% moisture sorghum, wheat, and corn respectively. The highest residue deposits remained in the 6% grain moisture levels. After 30 days of storage, 71, 63, and 68% of the initial residue deposit remained on sorghum, wheat, and corn, respectively.

Methyl phoxim (phenylglyoxylonitrile oxime (*O*)-*O*,*O*-dimethyl phosphorothioate) (Bay SRA 7660) is a promising grain protectant. At 5 ppm, it was effective for 9 months against the rice weevils, *Sitophilus oryzae* (L.); for 2 months against red flour beetles, *Tribolium castaneum* (Herbst) and confused flour beetles, *T. confusum* (Jacquelin duVal); and for 6 months against lesser grain borers, *Rhyzopertha dominica* (F.) (Alnaji et al., 1977). It pro-

0021-8561/78/1426-0507$01.00/0 

Table I. Bay SRA 7660 Residues Recovered from Corn at Different Moistures, Applied at 10 ppm Emulsion Spray[a]

| % moisture content | Intervals after application, days | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 1 | 7 | 14 | 21 | 30 |
| 6 | 10.3 a | 9.9 a | 8.9 a | 8.0 a | 7.2 a | 7.0 a |
| 8 | 9.9 a | 9.8 a | 8.8 a | 7.7 b | 7.0 a | 6.5 b |
| 10 | 10.0 a | 9.0 b | 8.4 b | 7.0 c | 6.1 b | 6.4 b |
| 12 | 10.0 a | 8.8 bc | 8.0 c | 6.2 d | 6.0 bc | 5.9 c |
| 14 | 10.0 a | 8.6 cd | 8.0 c | 5.9 e | 5.8 c | 5.4 d |
| 16 | 10.0 a | 8.4 d | 7.6 d | 5.4 f | 4.9 d | 4.0 e |
| 18 | 9.9 a | 8.1 e | 7.3 e | 4.1 g | 3.0 e | 2.6 f |
| 20 | 10.9 b | 8.1 e | 6.6 f | 3.5 h | 3.3 f | 2.5 f |

[a] Each number is an average of four replicates. Numbers followed by the same letter in the same column are not significantly different at the 5% level using Duncan's Multiple Range Test.

Table II. Bay SRA 7660 Residues Recovered from Sorghum at Different Moistures, Applied at 10 ppm Emulsion Spray[a]

| % moisture content | Intervals after application, days | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 1 | 7 | 14 | 21 | 30 |
| 6 | 10.0 a | 9.7 a | 8.8 a | 8.2 a | 7.9 a | 7.1 a |
| 8 | 9.9 a | 9.2 b | 8.6 a | 8.0 b | 7.5 b | 6.9 b |
| 10 | 9.9 a | 9.0 bc | 7.5 b | 5.8 c | 5.5 c | 4.9 c |
| 12 | 10.0 a | 8.9 bc | 6.8 c | 5.7 c | 5.9 d | 4.3 d |
| 14 | 10.0 a | 8.7 c | 6.3 d | 4.9 d | 4.7 e | 3.6 e |
| 16 | 10.0 a | 8.3 d | 6.0 de | 4.7 e | 3.7 f | 3.5 e |
| 18 | 10.0 a | 8.1 d | 6.0 de | 3.9 f | 3.0 g | 2.1 f |
| 20 | 10.0 a | 7.4 e | 5.9 e | 3.8 f | 1.4 h | 1.0 g |

[a] Each number is an average of four replicates. Numbers followed by the same letter in the same column are not significantly different at the 5% level using Duncan's Multiple Range Test.

Table III. Bay SRA 7660 Residues Recovered from Wheat at Different Moistures, Applied at 10 ppm Emulsion Spray[a]

| % moisture content | Intervals after application, days | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 1 | 7 | 14 | 21 | 30 |
| 6 | 10.0 a | 9.9 a | 8.5 a | 7.3 a | 6.9 a | 6.3 a |
| 8 | 10.0 a | 9.7 ab | 8.2 b | 7.0 b | 6.1 b | 6.0 b |
| 10 | 10.0 a | 9.5 b | 8.0 c | 6.2 c | 5.9 c | 5.3 c |
| 12 | 10.0 a | 8.5 c | 7.5 d | 5.5 d | 5.3 d | 4.0 d |
| 14 | 9.7 a | 5.9 d | 4.9 e | 3.9 e | 2.9 e | 2.0 e |
| 16 | 9.8 a | 5.7 d | 4.3 f | 3.5 f | 2.4 f | 2.0 f |
| 18 | 10.1 a | 5.4 e | 3.5 g | 2.0 g | 1.6 g | 0.6 g |
| 20 | 10.1 a | 5.2 e | 2.6 h | 1.4 h | 0.7 h | 0.3 h |

[a] Each number is an average of four replicates. Numbers followed by the same letter in the same column are not significantly different at the 5% level using Duncan's Multiple Range Test.

tected at 10 ppm against the lesser grain borer equally as well as malathion. New chemical protectants have low mammalian toxicity are urgently needed because some insect species have developed a resistance to present chemicals (Zettler, 1974).

Methyl phoxim has an acute oral $LD_{50}$ (rat) of >2500 mg/kg (Baychem Corporation, 1976) compared with 1375 mg/kg for malathion (Thomson, 1973). Because data were incomplete on methyl phoxim degradation from grain at different moisture levels, we determined the amounts remaining on wheat, corn, and sorghum treated at one dosage.

## MATERIALS AND METHODS

Cleaned, uninfested soft red winter wheat, corn, and sorghum were tempered to 6 ± 0.1, 8 ± 0.1, 10 ± 0.1, 12 ± 0.1, 14 ± 0.1, 16 ± 0.1, 18 ± 0.1, and 20 ± 0.1% moisture and maintained at 26.7 ± 1 °C and 60 ± 5% RH for 14 days to equilibrate moisture.

An emulsifiable concentrate containing 25% methyl phoxim (weight AI/volume) was diluted with distilled water to apply (in 1-mL amounts) a dose of 10 ppm on wheat, corn, and sorghum. A 1-mL volumetric pipet was used to apply the emulsions to the inside wall of the glass jars (above the grain level) while the jars were on a 33-rpm turntable. Immediately afterward, the jars were shaken manually for 30 s and then rotated for 15 min on a mechanical tumbler to mix the insecticide with the grain. Sufficient grain was treated for all analyses during a 30-day study. Treatments were replicated four times at each moisture level. The treated grain was stored in the jars, 2–1000 g lots/jar, at ca. 26 °C and 60% RH. After 1, 7, 14, 21, and 30 days in the sealed jars, ca. 150 g of grain were removed from each replication and residues determined. The collected samples were placed in 473-mL glass jars and stored at −20 °C until analyzed.

**Extraction and Clean-Up Procedures.** The method of analysis was adapted from Thornton (1969). Jars of the 150-g samples of grain reached room temperature and then were thoroughly shaken by hand. Subsamples of 25 g were placed in a Sorvall Omnimixer with 150 mL of acetone and blended rapidly for 2 min. The mixture was then decanted through a No. 43 Whatman filter into a stoppered graduate containing 50 mL of a precipitating reagent of 1.25 g of ammonium chloride and 2.5 mL of orthophosphoric acid diluted with distilled water to 1 L. The filtrate in the stoppered graduate was shaken vigorously by hand. Fifteen minutes later, it was decanted into a Erlenmeyer flask through a Buchner funnel (size 0) fitted with a No. 42 Whatman filter paper covered with a 6.4-mm layer of Super-Cel. The filter paper was washed with 25 mL of the precipitating reagent, and the total extract transferred to a 500-mL separatory funnel. A 50-mL chloroform rinse of the Erlenmeyer flask was added to the filtrate in the

separatory funnel, which was shaken manually for 30 s, and the phases were allowed to separate. The lower chloroform phase was drained off and retained. The extraction was repeated twice with 40-mL portions of chloroform. The combined chloroform extract was filtered through a No. 43 Whatman filter paper containing a teaspoonful of powdered anhydrous sodium sulfate ($Na_2SO_4$) into a 500-mL, round-bottom boiling flask. The combined extract was evaporated at 40 °C to ca. 10 mL. Each 10-mL sample was washed into a 25-mL volumetric flask with acetone to bring the volume to 25 mL.

**Gas Chromatographic Analysis.** Residues were determined with a Bendix 2110 X GLC equipped with a Bendix flame photometric detector. The GLC and detector were used with these conditions: column, 4 mm i.d. × 30.5 cm glass packed with 2% D.C. 200 and 2% QF-1 on Gas-Chrom Q 60–80 mesh, temperature, column 160 °C, injection port 190 °C, detector 160 °C; carrier gas, nitrogen 185 mL/min, hydrogen 150 mL/min, oxygen 25 mL/min, air 90 mL/min; volume injected, 4 μL of extract.

## RESULTS AND DISCUSSION

Tables I, II, and III show methyl phoxim residues during the 30-day study. The corn, sorghum, and wheat were analyzed immediately after treatment and found to contain deposits from 9.9 to 10.3, 9.9 to 10, and 9.7 to 10.1 ppm, AI, respectively. After 30 days of storage 77.1, 90, and 97% of the initial deposits disappeared from 20% moisture corn, sorghum, and wheat. Apparently higher moisture content does not accelerate residue degradation on corn compared with sorghum and wheat. Twenty-four hour methyl phoxim residues in wheat were much lower than in corn and sorghum above 10% grain moisture level. Residue loss increased in all grains with increase in moisture content. Methyl phoxim residues in corn, wheat, and sorghum decreased gradually with 22.9, 10, and 3% of the initial deposit remaining on the 20% m.c. grain, respectively, after 30 days of storage. Methyl phoxim residues were markedly reduced when the moisture content of all grains was increased to 20%. However, the residue recovered from the lowest moisture content of the grain (6%) was the highest at all intervals during the 30 days.

Cleaned grain of low moisture content retains sufficient methyl phoxim residue to resist most stored-grain insects (Alnaji et al., 1977; McDonald and Gillenwater, 1976). These results coincide with observations of Kadoum and LaHue (1969, 1975), viz., increased moisture content of grain enhances malathion degradation; however, degradation of methyl phoxim is less in corn and sorghum than in wheat. Kadoum and LaHue (1972) reported that the biological activity of live sorghum kernels enhances breakdown; hence, age of grain, moisture content and physical characteristics may influence retention of residue in the grain.

The average moisture content of the samples of corn and wheat from the western part of the state, when collected, averaged ca. 11.1 and 10.6%; that from the eastern part averaged 13.1 and 12.9% for the corn and wheat (LaHue, 1976). Rapid rate of degradation on corn up to 14 days with less rapid decrease up to 30 days was observed. On sorghum the rate of decrease in residue is rather sharp up to 14–21 days also. On wheat the degradation follows a more gradual trand. This is especially true at the higher moistures.

Hence, these data can be used effectively to establish rate of application to grain harvested and stored under adverse moisture conditions. Our study can be applied to storing and marketing treated grain, predicting the methyl phoxim level in stored sorghum, corn, and wheat so dosage can be biologically effective (Alnaji, 1977) for extended storage periods.

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Received for review September 19, 1977. Accepted November 29, 1977. Contribution no. 78-58-j, Department of Entomology, Kansas Agricultural Experiment Station, Kansas State University. This paper reports the results of research only. Mention of an insecticide or proprietary product does not constitute a recommendation or an endorsement by Kansas State University or by the USDA.

# Cucurbit Root Starches: Isolation and Some Properties of the Starch from *Apodanthera undulata* Gray

Starch has been found in the roots of the feral xerophytic gourd *Apodanthera undulata* Gray. This perennial is well adapted to marginal agricultural lands of semi-arid and arid environments. The starch can be readily isolated from the large storage roots. It has an iodine affinity value of 5.01, and the granules have an average diameter of 17 μm and resemble tapioca starch granules in appearance.

The potential of wild perennial gourds indigenous to western and southwestern United States as oilseed crops was first suggested by Curtis in 1946. Interest in xerophytic cucurbits has increased with additional studies and growing water shortages (Shahani et al., 1951; Bemis and Whitaker, 1969; Jacks et al., 1972). Three species, *Cucurbita foetidissima*, *Cucurbita digitata*, and *Apodanthera undulata*, are currently being investigated at this Univ-

0021-8561/78/1426-0509$01.00/0 