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POSTHARVEST PRESERVATIVES

Magnitude and Stability of Captan Residues in Fresh and Preserved Plant Products

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The behavior of captan residues on several plant commodities dip-treated after harvest in a captan suspension was studied; the residues were determined colorimetrically. Dipping as an application method was tested with respect to the uniformity of residues and the effect of dip concentration, dipping time, and size of fruit on the amount of initial deposits. On stored strawberries, gooseberries, string beans, tomatoes, plums, and apples, captan had a long residual life. Losses of captan residues were also studied during various preservation processes. If the process included a heating phase, the losses were usually over 90%. Losses in freezing without blanching were much lower (10 to 50%), and the residues on frozen products were stable for several months of storage. Washing plant products in running water just after dipping or after 1 week of storage resulted in 17 to 85% losses.

CAPTAN, *N*-(trichloromethylthio)-4-cyclohexene - 1,2 - dicarboximide, has proved to be a superior fungicide and is extensively used against many diseases of fruits and vegetables. It is also an effective seed disinfectant. In addition to being a preharvest pesticide, captan also has a wide use as a postharvest chemical (*18*). Numerous studies have shown that either pre- or postharvest treatment with captan improves the keeping quality of fruits in storage—e.g., apples (*5, 6, 13, 14, 28*), pears (*20*), peaches (*9, 24, 25*), strawberries (*1, 16, 17, 21, 29, 31*), and grapes (*2, 8*). Because of the low toxicity of this chemical, its FDA tolerance limit in the United States is as high as 100 p.p.m. (*18*).

There are only a few reports in the literature on the magnitudes of captan residues and their disappearance. The investigations published (*7, 15, 26*) indicate that the residues are persistent but are readily destroyed during heating (*3, 15, 22*).

The aim of the present study was to determine the magnitude and stability of captan residues on plant commodities treated after harvest by dipping and to measure the captan losses occurring during food processing.

Materials

Captan was used in the form of Orthocide 83 wettable powder (California Chemical S. A., France). For constructing the standard calibration curve, however, purified (99%) captan (California Chemical Co., Richmond, Calif.) was used.

The following raw plant commodities were tested: strawberries (vars. Ydun and Senga Sengana), gooseberries (var. Houghton), tomatoes (vars. Selantia and Grower's Pride), plums (var. Victoria), apples (vars. Wealthy and Åkerö), and string beans (var. Hinrichs Kaenpe). In the residue stability experiments, the fruits were not completely ripe at the beginning of the trials, whereas in the preservation and washing trials they were harvest-ripe at the time of captan treatment. The stipes of the fruits (and the perianth remnants of the gooseberries) were not removed.

Analytical Methods

Captan residues were extracted from the unmacerated samples with benzene alone or, for avoiding emulsions, from the macerated samples with ethanol as a cosolvent. The extraction and cleanup procedures with activated charcoal were those employed for malathion residues (*11*). Captan was determined colorimetrically by the method of Kittleson (*10*) as applied by Taylor and Klayder (*30*); a yellow color is developed by fusion of the captan with resorcinol at 135° C. and by dissolving the mixture in glacial acetic acid.

Table I. Variation of Initial Deposits of Captan on Strawberries and Tomatoes Dipped in Captan Suspensions

Ten portions in each series

	Captan in Suspension		Initial Deposit[a] Mean,	Range,[c]	Standard deviation, s	
Fruit	%[b]	P.p.m.	p.p.m.	p.p.m.	P.p.m.	%
Strawberries	0.05	415	13.0	2.6	0.9	7.0
	0.20	1660	49.3	12.5	3.2	6.5
Tomatoes	0.05	415	1.5	0.5	0.2	9.9
	0.50	4150	9.5	2.8	0.9	9.0

[a] From each dip portion two 500-gram samples were analyzed by duplicate determinations.
[b] 83% wettable powder.
[c] Difference of highest and lowest value.

The precision of the method was tested on gooseberries, New Zealand spinach, string beans, strawberries, plums, and tomatoes by fortifying the extraction benzene before tumbling to contain 0.6, 1.2, 3.0, 6.0, 12.0, and 60.0 p.p.m. of captan. Errors of single determinations, regardless of whether the benzene extract was concentrated or not, were less than ±10%. The average yield of all the recovery tests was 101.9% and the standard deviation of the errors ±3.7%. Macerating the plant material prior to extraction or the use of a cosolvent did not increase the recoveries from fruits having captan residues resulting from dip treatments. No noteworthy interferences in the colorimetric method produced by the plant materials were observed.

Dipping as Application Method

Dipping in a water suspension of captan prepared from 83% wettable powder formulation was considered the most suitable application method. This method was tested with respect to the uniformity of the initial deposits as well as the effect of dip concentration, dipping time, and size of fruit on the amount of initial deposits. These experiments were similar to those previously made with malathion (*11*).

Uniformity of Initial Deposit. Trials were made with strawberries and tomatoes having average weights of about 10 and 65 grams, respectively. Ten 2-kg. portions of each material in a wire basket were dipped successively in the same 10-liter dip solution of specified captan concentration for 30 seconds. The solution (temperature about 20° C.) was agitated during the course of each dip series. After dipping, the samples were air-dried, and then, without any delay, analyzed for captan.

The mean and the range values of initial deposits are presented in Table I. The standard deviations for strawberries (7.0 and 6.5%) were slightly smaller than those for tomatoes (9.9 and 9.0%). The range of deviation was relatively wider with small than with large initial deposits. In the strawberry series dipped in 0.05% suspension, a statistically significant regression of initial deposits occurred ($P < 0.05$) with the sequence number of the dip portions. When this was taken into account, a value of 0.71 instead of 0.91 was obtained for the standard deviation, which corresponds to 5.5%. The error due to dipping was actually smaller, since the analytical method itself gave errors with a standard deviation of 3.7%; thus the dipping process increased this figure by about 2% for strawberries and 6% for tomatoes.

Dip Concentration. The effect of dip concentration of captan on the amounts of initial deposits was studied with six kinds of fruits: strawberries (average weight about 10 grams), gooseberries (1.5 grams), plums (28 grams), tomatoes (60 grams), and apples (95 grams). Duplicate 1-kg. portions of the fruits were dipped for 30 seconds in a 10-liter dip solution of each concentration. One 500-gram random sample from each of the duplicate portions was analyzed for captan.

Figure 1 shows that the correlation between dip concentration and initial deposit was virtually linear within the concentration range used; the only exception was apples at the highest concentrations. With a 20-fold increase in concentration (from 0.05 to 1.0%) the initial deposits on strawberries, gooseberries, and tomatoes increased 15- to 17-fold and those on plums and apples eight- to ninefold.

The magnitude of the initial deposits of captan depended not only on the concentration of the dip solution but also on the kind of plant material. The lowest amounts of captan per unit of surface area were found on plums and tomatoes—e.g., at 0.5% about 11 μg. per sq. cm. On gooseberries the residues were about double this amount, on strawberries three to four times higher, and on apples about nine times higher at lower concentrations and six times at the highest concentration.

Dipping Time. Strawberries, tomatoes, and plums were dipped for different periods of time in solutions

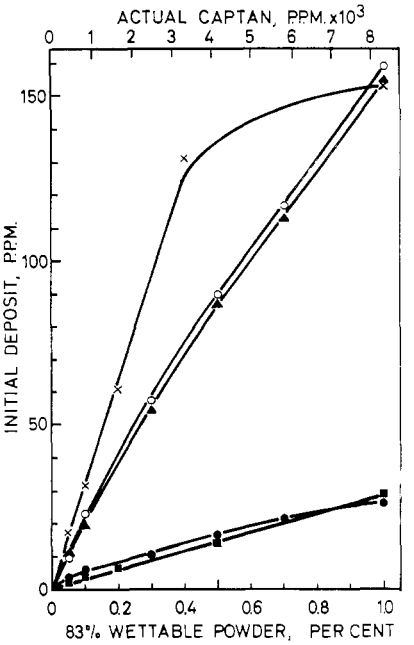
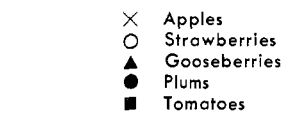


Figure 1. Effect of concentration of dip suspension on initial deposits of captan



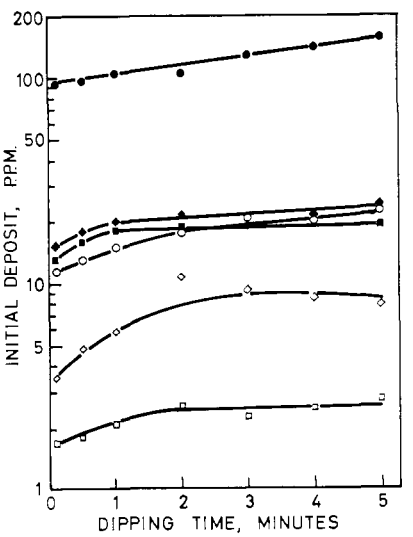
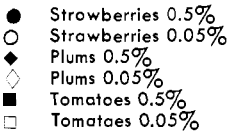


Figure 2. Effect of dipping time on amount of captan initial deposits from suspensions of two concentrations



of two concentrations (0.5 and 0.05%). The dipping was performed as described above.

The results (Figure 2) show that dipping time had apparently no great effect on the initial deposits of captan. A 60-fold increase in dipping time from 5 seconds to 5 minutes caused only a two-

fold (or even less) increase in initial deposits.

Size of Fruit. The effect of fruit size on the initial deposits of captan was studied with tomatoes of two different size groups. The average weight of the "large" tomatoes was 100 grams and that of the "small" 21 grams. Three 1-kg. portions from each group were immersed for 30 seconds in a 0.5% captan suspension, and two random samples from each portion were subsequently analyzed for captan.

The results (Table II) show that both the large and small tomatoes absorbed equal amounts of captan per unit of surface area. When expressed in terms of parts per million, however, the amounts varied inversely to the weight of the fruit.

Table II. Effect of Size of Tomatoes on Initial Deposits of Captan

Av. Weight, Grams	Av. Surface Area,[a] Sq. Cm.	Initial Deposit	
		P.p.m.	μg./sq. cm.
100	104.2	17.4	16.7
21	36.9	29.3	16.7

[a] In calculations, tomatoes assumed to be spherical and to have specific gravity of 1.0.

Storage Experiments

The disappearance of captan postharvest residues from fresh plant commodities was studied with strawberries, gooseberries, string beans, tomatoes, plums, and apples. The fruits were treated after harvest by dipping in a captan suspension of a specified concentration and were then stored at different temperatures. The initial concentration on the fruits was adjusted to be less than 100 p.p.m. The residues and loss percentages were determined by analyzing at certain intervals two or more samples from each batch of material.

The results (Table III) show that at 4° C. insignificant amounts of captan had disappeared from strawberries in 2 days and from gooseberries and beans in 1 week, but at 20° C. losses of about 20 to 30% occurred. On tomatoes, plums, and apples stored for longer periods, residue losses occurred at both temperatures and were somewhat higher at 20° C. than at 4° C. The figures clearly indicate that the residue levels, reached during the first 1 to 2 weeks of long-term storage, were very stable, and therefore the residual life of captan on stored fresh commodities seems to be very long.

The reasons for the residue losses were not studied. It is certain that they were partially due to the mechanical displacement of captan from the plant surfaces during handling of the products. The increase in losses with storage temperature, as well as the negligible losses in some of the trials, suggests that there were also other mechanisms responsible for the disappearance of the residues. Studies on the reactions of captan with thiols (*19*) and its behavior in fungal conidia (*23*) indicate the possibility that this compound can be decomposed in biological material. In contrast, migration of captan—at least in an intact form—in plant tissue is apparently poor (*23, 27*). The spontaneous hydrolysis of captan in aqueous matrix (*22*) is furthermore a possible degrading factor to be considered.

Preservation Experiments

Gooseberries, strawberries tomatoes, string beans, plums, and apples were treated after harvest by dipping in a captan suspension and were, after air-drying, preserved by different processes. Captan was determined just before preservation by analyzing four representative 500-gram samples. After processing, when the material had reached

Table III. Captan Residues[a] (P.P.M.) on Fresh Plant Products and Loss Percentages during Storage

Time after Dipping, Days	Strawberries				Gooseberries				String Beans				Tomatoes			
	4° C.		20° C.		4° C.		20° C.		4° C.		20° C.		4° C.		20° C.	
	P.p.m.	%	P.p.m.	%	P.p.m.	%	P.p.m.	%	P.p.m.	%	P.p.m.	%	P.p.m.	%	P.p.m.	%
0	59.0	0	59.0	0	40.1	0	40.1	0	89.3	0	89.3	0	16.7	0	16.7	0
1	55.4	4	53.8	9	...	...	...	...	...	...	...	...	...	...	...	...
2	55.8	5	47.2	20	39.3	2	38.0	5	84.7	5	73.9	17	...	...	...	...
3	...	...	...	...	...	...	...	...	...	...	...	...	...	...	10.8	35
4	...	...	...	...	36.8	8	32.5	19	87.2	2	72.7	19	...	...	...	...
Weeks																
1	...	...	...	...	38.3	4	28.0	30	84.7	5	75.3	16	9.5	43	8.9	47
2	...	...	...	...	...	...	...	...	...	...	...	...	8.1	51	7.9	53
3	...	...	...	...	...	...	...	...	...	...	...	...	7.9	53	7.2	57
4	...	...	...	...	...	...	...	...	...	...	...	...	7.7	54	6.5	61
5	...	...	...	...	...	...	...	...	...	...	...	...	7.6	54	...	...
8	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
12	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
20	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...

Time after Dipping, Days	Plums				Apples							
					Wealthy				Åkerö			
	4° C.		20° C.		4° C.		20° C.		0° C.		10° C.	
	P.p.m.	%	P.p.m.	%	P.p.m.	%	P.p.m.	%	P.p.m.	%	P.p.m.	%
0	23.7	0	23.7	0	41.1	0	41.1	0	15.1	0	15.1	0
1	...	...	...	...	...	...	...	...	...	...	...	...
2	...	...	...	...	...	...	...	...	...	...	...	...
3	18.3	23	17.6	26	...	...	...	...	...	...	...	...
4	...	...	...	...	...	...	...	...	...	...	...	...
Weeks												
1	17.2	27	15.9	33	32.7	10	25.1	39	...	...	...	...
2	...	...	...	...	27.9	32	...	...	...	...	...	...
3	18.2	23	...	...	...	...	...	...	...	...	...	...
4	16.5	30	...	...	30.3	26	...	...	8.7	42	4.7	69
5	...	...	...	...	...	...	...	...	...	...	...	...
8	...	...	...	...	29.9	27	...	...	10.0	34	...	...
12	...	...	...	...	...	...	...	...	...	...	3.9	74
20	...	...	...	...	...	...	...	...	6.7	56	...	...

[a] Dip concentrations: strawberries 0.2%, gooseberries 0.25%, stringbeans 0.35%, tomatoes 0.5%, plums 0.5%, apples 0.2%.

room temperature, two samples from each product were similarly analyzed. On certain processed materials, the use of ethanol as a cosolvent was convenient to prevent emulsion formation during extraction. The loss of captan was calculated as the percentage of its initial amount in the raw material. These trials were similar to those on malathion-treated materials (*12*).

Gooseberries. Gooseberries were dipped in a 0.25% captan suspension; residue was 40.1 p.p.m.

CANNING. Berries (500-gram portions) were placed in glass jars and 200 ml. of 40% sugar solution was added. The jars were autoclaved at 120° C. for 30 minutes. Separate determinations of captan were made on the berries and the juice.

MASHES. Three slightly different methods were used to prepare mashes.

No. 1. Berries were crushed with a wooden masher. Sodium benzoate was added as a preservative (500 mg. per kg.).

No. 2. Berries and water (1 kg. per 100 ml.) were boiled for 10 minutes, during which time the berries were crushed; 400 grams of sugar was added and the mixture was boiled for 30 minutes.

No. 3. Berries and water (1 kg. per 65 ml.) were boiled for 10 minutes and the mixture pressed through a strainer (2-mm. mesh). Sugar (400 grams per kg.) was added and the mash was boiled for 25 minutes.

JAM. Sirup (containing 250 ml. of water and 600 grams of sugar) was added to 1 kg. of berries. The mixture was boiled for 15 minutes with occasional stirring.

STEAM JUICE. Berries in 3.5-kg. portions were steamed for 1 hour and the juice was bottled.

DRYING. A thin layer of berries was heated at 50° C. for 3 days and then at 75° C. for 7 days. Six kilograms of fresh berries yielded 0.92 kg. of dried berries.

FREEZING. Berries (500-gram portions) were placed in plastic bags, frozen, and stored at about −18° C. They were analyzed for captan after storage periods of 1, 2, 4, and 8 months.

The results (Table IV) show that captan residues on gooseberries disappeared almost completely in processes including boiling, steaming, or autoclaving. Drying resulted in an increase in the relative concentration of captan residues despite the large absolute losses (about 70%). In the frozen gooseberries practically no captan disappeared during the 8 months of storage.

Strawberries. Strawberries were dipped in a 0.2% captan suspension; residue was 48.5 p.p.m.

CANNING. Berries (500 grams) and sugar (100 grams) were placed in glass jars and autoclaved at 120° C. for 20 minutes.

JAM 1. Berries and sugar (1 kg. per 600 grams) were placed in layers in a kettle and boiled for 20 minutes.

Table IV. Losses of Captan[a] in Processing Gooseberries and Strawberries

Process	Captan in Preserved Product, P.P.M.	Total Loss, %
Gooseberries		
Canning		
Berries	<0.1	98
Sirup	1.0	
Mashes		
1	32.4	19
2	<0.1	>99
3	<0.1	>99
Jam	<0.1	>99
Steam juice	0.2	>99
Drying	80.9	69
Freezing, stored		
1 month	35.7	11
2 months	38.1	5
3 months	38.4	4
8 months	37.2	7
Strawberries		
Canning	0.2	99
Jam 1	0.1	99
Jam 2		
Before boiling	27.1	10
After boiling	1.1	98
Freezing	21.6[b]	56

[a] Residue on raw material: gooseberries 40.1 p.p.m., and strawberries 4.1 p.p.m. [b] Analyzed after 1 month of storage.

JAM 2. Same as above, but before boiling the mixture was allowed to stand overnight at +4° C. Analyses were made both before and after boiling.

FREEZING. Berries (500-gram portions) were placed in sealed plastic bags, frozen, and stored at about −18° C. Samples were analyzed after one month.

Table IV shows that practically all the captan disappeared from the strawberries during boiling and autoclaving. In freezing the losses after 1 month were 56%, which is much more than in the case of frozen gooseberries.

Tomatoes. Green tomatoes were dipped in a 0.5% captan suspension; residue was 14.4 p.p.m.

The tomatoes were pickled by boiling for 20 minutes in a solution (750 ml. per kg. of tomatoes) containing vinegar (3.3%) and sugar (600 grams per liter) The loss in this process was 100%, and not even traces of captan were detected.

String Beans. Beans were dipped in a 0.35% captan suspension; residue was 89.3 p.p.m.

CANNING. Two-kilogram portions of beans were blanched by immersing in 1.5% NaCl solution (80° to 90° C.) for 2 minutes, removed, and allowed to cool. One-kilogram portions were put into glass jars, and 700 ml. of 1.5% NaCl solution was added. The jars were autoclaved for 30 minutes at 120 °C. Separate analyses of the beans and the juice were made just after blanching and then after canning.

FREEZING. Beans were blanched as above. One-kilogram portions were put into plastic bags, frozen, and stored at at −18° C. The beans were analyzed immediately after blanching and then after 1, 2, 4, and 8 months.

SALTING. Fresh beans were cut into pieces and packed in layers with salt (300 grams of NaCl per kg. of beans) in glass jars and stored at +4° C. They were analyzed just after preservation and then after 1, 2, 4, and 8 months.

The analysis results showed that after the canning process the juice in the jars contained 0.7 p.p.m. of captan but the beans contained no detectable amounts. The total loss of captan from the beans was more than 99%, and nearly 90% had disappeared during blanching.

The captan losses from the frozen and salted beans are shown in Table V. During freezing the losses were about 90%; these large losses can be attributed to the blanching before freezing, even though the heating lasted only 2 minutes. During the subsequent 8 months of storage, however, there were no further losses. In the salted beans, whose preparation did not include heating, 30% of the captan had disappeared during the course of the processing and 88% after 8 months of storage at +4° C.

Plums. Plums were dipped in a 0.5% captan suspension; residue was 23.7 p.p.m.

CANNING. Plums (500 grams) and 25% sugar solution (200 ml.) were put in glass jars and autoclaved at 120° C. for 30 minutes.

JAM. Plums, sugar, and water (1 kg. per 600 grams per 100 ml.) were boiled for 15 minutes.

DRYING. A thin layer of plums were dried at 75° C. for 2 days in an oven with a rotating damper.

FREEZING. Plums were frozen and stored in the same way as strawberries.

The losses of captan in the preserving of plums were almost complete during canning, boiling, and drying (Table VI). In freezing, about 30% disappeared.

Table V. Losses of Captan[a] from String Beans in Freezing[b] and Salting

Storage Time, Months	Captan in Preserved Product, P.P.M.	Total Loss, %
	Freezing	
0	9.7	89
1	10.7	88
2	10.7	88
4	12.5	86
8	9.0	90
	Salting	
0	48.6	30
1	39.4	43
2	22.0	68
4	17.5	75
8	8.6	88

[a] Residue on raw material 89.3 p.p.m. [b] With blanching.

Table VI. Losses of Captan[a] in Processing Plums and Apples

Process	Captan in Preserved Product, P.P.M.	Total Loss, %
	Plums	
Canning	<0.1	>99
Jam	0.4	98
Drying	0.5	98
Freezing	16.5[b]	30
	Apples	
Canning	<0.1	>99
Mash	0.2	>99
Steam juice	0.2	>99
Pressed juice	7.5	88
Pressed juice, pasteurized	0.1	>99
Freezing	32.0[b]	22

[a] Residue on raw material: plums 4.1 p.p.m. and apples 41.1 p.p.m.
[b] Analyzed after 1 month of storage.

Table VII. Effect of Washing on Captan Residues

Plant Commodity	Washed Immediately after Treatment: Residue, P.P.M. Before washing	After washing	Loss, %	Washed 7 Days after Treatment: Residue, P.P.M. Before washing	After washing	Loss, %
Gooseberries	40.1	11.3	72	38.3	14.7	62
Plums	23.7	7.6	68	18.3	8.2	55
Tomatoes	16.7	2.5	85	9.5	2.3	76
Apples	41.1	34.0	17	32.7	23.8	27
String beans	89.3	48.2	46	...	...	...

Apples. Apples were dipped in a 0.2% captan suspension; residue was 41.1 p.p.m.

CANNING. Samples of halved apples (500 grams) were placed in glass jars and 300 ml. of 4% sirup was added. The jars were autoclaved at 120° C. for 30 minutes.

MASH. Apples were cut into four segments, boiled in water (100 ml. per kg.) for 40 minutes, and pressed through a strainer (2-mm. mesh). The mash was heated to boiling, sugar (400 grams per kg.) added, and the mixture boiled for 30 minutes.

STEAM JUICE. Apples were cut into four segments and steamed in 3-kg. portions for 1 hour. The juice was bottled.

PRESSED JUICE. Apples were pressed in a hand-operated screw press. The juice was bottled and pasteurized by autoclaving at 80° C. for 10 minutes. Analyses were made before and after pasteurization.

FREEZING. Apples in 500-gram portions were frozen in plastic bags and stored at about −18° C.

Table VI shows that captan disappeared nearly completely from apples during processes including heating. The captan loss from pressed juice was as much as 88% even before pasteurization and 99% after this process. During freezing 22% disappeared.

Effect of Washing on Residues

The effect of washing on the disappearance of captan residues was studied on gooseberries, tomatoes, apples, and string beans.

Immediately after the applied suspension had dried, two 500-gram samples were taken to be washed. The rest of the material was stored at about +4° C. for 7 days, after which two similar samples were taken and washed. The samples were washed in a strainer under running tap water (about +20° C.); the washing time was 30 seconds for gooseberries and beans and 60 seconds for the other fruits. After draining, determinations of captan were made.

Table VII shows that immediately after application, the losses of captan due to washing ranged from 17% in apples to 85% in tomatoes. After a storage period of 7 days the losses were slightly less than just after dipping, except for apples. These results indicate that, during 1 week, part of the residue had absorbed into the cuticle, and thus it was not removed by washing.

Conclusions

Captan residues resulting from dip treatments of fresh plant commodities after harvest were determined by the method of Taylor and Klayder (*30*) as modified from that of Kittleson (*10*). The method proved to be very accurate and reliable, giving a standard deviation of 3.7% for errors when captan was added in the extraction solvent. When several strawberry and tomato samples were dip-treated in the same way, the standard deviations of the mean recoveries were somewhat higher, about 6 and 9%, respectively (Table I).

When the effect of dip concentration, dipping time, and size of fruit on the initial deposit was tested it was found (Figures 1 and 2 and Table II) that the magnitude of initial deposits of captan from postharvest dip treatments depends mainly on the dip concentration and the type of plant commodity.

The captan residues on strawberries, gooseberries, and string beans stored 1 week or less were not significantly reduced at 4° C., but at 20° C. the losses were 20 to 30% (Table III). At longer periods of storage (as long as 5 months for apples) appreciable residue losses from tomatoes, plums, and apples were observed, varying from 30 to 70%. Increasing the temperature resulted in somewhat greater losses. These trials indicate that captan has a long-term residual life on fresh plant commodities in storage.

Preservation experiments showed that the loss percentages of captan in various preservation processes depended chiefly on whether or not the process included a heating phase. Boiling, steaming, autoclaving, or pasteurization generally resulted in 98 to 100% losses (Tables IV to VI). Blanching of string beans for 2 minutes at 80° to 90° C. was also destructive to captan, causing a 90% loss (Table V). Canning in these experiments was done in glass jars, and thus possible reaction with metal (*4*) was eliminated.

Drying of gooseberries at 75° C. resulted in a loss of about 70%, but nevertheless because of the great weight decrease of the berries the parts per million figure was doubled (Table IV). On plums (Table VI) the corresponding loss percentage was higher (98%) and also the parts per million figure decreased greatly. These results indicate that drying of fruits even at relatively high temperature does not guarantee reduction in captan residues, but may even cause them to increase, a fact which must be considered in regard to official tolerance limits.

In the juice mechanically pressed from apples, 88% of the captan was lost during pressing, and it was nearly completely decomposed in pasteurization (Table VI).

The loss percentages of captan in freezing varied greatly. If the materials were frozen without blanching, the losses were generally small, only 10 to 50% (Tables IV and VI). If, however, blanching preceded freezing, losses were naturally much higher—for instance, about 90% on beans (Table V).

In salted string beans, captan decreased gradually during storage (Table V), indicating a continuous decomposing reaction taking place under these circumstances.

Washing plant commodities resulted in considerable losses of captan residues, varying from 17 to 85% according to the type of plant material (Table VII). The residues were most easily removed from tomatoes, followed by gooseberries, plums, string beans, and apples. After a storage period of 1 week, the losses were generally slightly smaller than just after dipping.

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INSECTICIDE SCREENING

Insecticidal Activity of Alkylthiophenyl *N*-Methylcarbamates

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The anticholinesterase activity and toxicity to three species of insects were compared for 30 alkylthiophenyl *N*-methylcarbamates substituted in the ortho-, meta-, and para- positions. Among these compounds, most of them new, are the methyl, propyl, isopropyl, butyl, isoamyl, allyl, and propargyl phenylthioethers, and several sulfonium salts and oxidation products. Some of the thioether carbamates were highly toxic to insects, and their activities are contrasted with those previously obtained with the corresponding oxygen ethers.

The interesting biological activities of a series of alkoxyphenyl *N*-methylcarbamates (*7*) invited comparison with the related alkylthiophenyl *N*-methylcarbamates. The latter may be expected to have a somewhat different mode of action because of the ease with which the outer octet of electrons can be expanded to a decet, thus permitting the formation in vivo of stable sulfoxide and sulfone derivatives. The first descriptions of a thioether carbamate, *m*-methylthiophenyl *N*-methylcarbamate, and its methylsulfonium salt were given by Alexander and Cope (*1*). The latter compound was nearly as toxic to mice as the corresponding quaternary ammonium compound (respective subcutaneous LD_{50} values, 0.37 and 0.27 mg. per kg.). However, the *m*-methylthiophenyl *N*-methylcarbamate does not seem to have been tested biologically. Schrader (*10*) has described the insecticidal activity of 4-methylthiophenyl, 3-methyl-4-methylthiophenyl, and 3,5-dimethyl-4-methylthiophenyl *N*-methylcarbamates (Bayer 37344). Fukuto, Metcalf, and Winton (*3*) described the anticholinesterase and insecticidal properties of the three isomeric methylthiophenyl *N*-methylcarbamates and of the *d*- and *l*-isomers of 2-(*sec*-butylthio)-phenyl *N*-methyl carbamate.

The present paper reports the results of a systematic examination of the anticholinesterase and insecticidal activities of the ortho-, meta-, and para-isomers of some straight- and branched-chain alkylthiophenyl *N*-methylcarbamates and of the related allylthio- and propargylthiophenyl *N*-methylcarbamates.

Experimental

Materials and Methods. Most of the compounds investigated were new and were characterized by carbon and hydrogen determination by C. F. Geiger, Ontario, Calif., as shown in Tables I and II and by infrared spectrophotometry. The thioether phenols (Table I) were prepared by treating 2-, 3-, or 4-hydroxybenzenethiol, prepared by a minor modification of the method of Miller and Read (*9*), with a slight excess of the appropriate aliphatic bromide or iodide. The *N*-methylcarbamates were prepared from the phenols by treatment with methyl isocyanate in a pressure bottle and were recrystallized from Skellysolve B (hexane fraction) or from benzene.