Table III. Losses of Adsorbed Nitrapyrin from Starch–Urea Matrix at Ambient Conditions[a]

starch, %	urea, %	nitrapyrin added, %	cumulative nitrapyrin lost, %					
			initial	30 min	60 min	90 min	120 min	18 h
57.40	40	0.60	35	39	43	62	70	97
47.25	50	0.75	25	41	56	63	67	97
37.10	60	0.90	26	34	39	52	62	97

[a] Starch–urea matrix prepared by the borate method.

Surprisingly, there was no major difference during leaching studies between those samples with KOH and the other extruded products.

Formulation and Release Rate of Nitrapyrin (Table II). Nitrapyrin was evaluated with these starch–urea systems because it helps stabilize nitrogen for more efficient plant use and because it evaporates quickly when applied to soil. We incorporated 1.5% nitrapyrin (based on urea) into all the formulations listed in Table II.

Some data reported in Table II list more nitrapyrin after aging than initially, and some products show erratic release rates. These inconsistencies are attributed to the lack of uniform dispersion of nitrapyrin within the matrix. Hence, we could not determine accurate release rates over the 4-day wet and dry aging, because different samples were needed for each analysis. However, the data were sufficiently consistent to allow some general conclusions on recovery and release characteristics of the nitrapyrin.

Slightly more nitrapyrin was lost (24–38%) during formulating and drying by the extrusion method than was lost (10–26%) by the borate method. We believe that techniques could be devised for improving the retention of nitrapyrin. Once the products were dry, there was little if any further loss of nitrapyrin when the products stood in an open dish for 4 days. Nitrapyrin release was accelerated with moisture, with about half of the formulated amount evaporating after four 24-h cycles of wetting and ambient drying. These simulated tests suggest that nitrapyrin would be readily available to stabilize released urea during several rain leachings.

In contrast, data in Table III reveal much faster rates of nitrapyrin evaporation when it is coated or absorbed onto the surface of particles and exposed to moisture-drying cycles. Essentially all of the nitrapyrin evaporated within 18 h from the dry products, even without exposure to the moisture-drying cycles.

This study has shown that the dissolution rate of urea can be reduced by formulating with starch and other materials. Only through field testing can the viability of these systems as controlled-release fertilizer be determined because of the differing soil moisture levels and the effects of microorganisms on starch. Field testing of some formulations described in this paper has been initiated at other locations.

Any useful economic considerations of these systems would also require results of field testing. During the past few years, starch has sold for about 10¢/lb, which approximates the material cost per pound of sulfur coating including sulfur, sealant, and conditioner. Apparently, about 20.5% coating weight is sufficient for the sulfur method whereas 40% or more starch might be required.

ACKNOWLEDGMENT

We thank Sara Walz-Salvador of this laboratory for assisting with the analyses.

Registry No. Starch, 9005-25-8; nitrapyrin, 1929-82-4; boric acid, 10043-35-3.

LITERATURE CITED

Dalal, R. C.; Prasad, M. *J. Agric. Sci.* **1975**, *85*, 427.
Elbe, W.; Haeckert, H.; Jasche, K.; Joedicke, R.; Oertel, M.; Thieme, H. East Ger. Pat. 138935, Dec 5, 1979; *Chem. Abstr.* **1980**, *93*, 25264.
Potts, T. J. *J. Assoc. Off. Agric. Chem.* **1963**, *46*, 303.
Reddy, R. N. S.; Prasad, R. *J. Soil Sci.* **1975**, *26* (3), 304.
Shasha, B. S.; Trimnell, D.; Otey, F. H. *J. Appl. Polym. Sci.* **1984**, *29*, 67.
Trimnell, D.; Shasha, B. S.; Wing, R. E.; Otey, F. H. *J. Appl. Polym. Sci.* **1982**, *27*, 3919.

Received for review September 2, 1983. Revised manuscript received January 23, 1984. Accepted May 11, 1984. The mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

Effects of Low-Dose γ-Irradiation on Grapefruit Products

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Products obtained from Florida grapefruit irradiated with low-dosage γ-rays as a possible treatment for infestation by larvae of the Caribbean fruit fly were evaluated to determine effects on flavor and composition. Seven tests were run in which twenty-two lots of fruit were exposed to 7.5, 15, 30, 60, or 90 krd of γ-irradiation covering the 1981–1982 and early 1982–1983 harvesting season. There were few significant adverse flavor effects on products from irradiated fruit with the exception of the first test run on early-season fruit. In some cases, particularly at the lower doses of radiation, there was a significant improvement of flavor in grapefruit sections. There were no marked differences in vitamin C, sugar, or acid levels in juice nor on essential peel oil composition of volatile constituents from irradiated fruit when compared with those from untreated fruit.

Grapefruit, *Citrus paradisi* Macf., grown in Florida are susceptible to infestation with larvae of the Caribbean fruit fly, *Anastreeha suspensa* (Loew). Currently, ethylene dibromide (EDB) fumigation and cold treatment are the only accepted postharvest treatments for preventing the spread of this fly to citrus-growing areas where these fruit are shipped. These treatments are particularly important for meeting the quarantine set by the Japanese on the 100

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Table I. Flavor Effects of γ Irradiation on Marsh and Ruby Red Florida Grapefruit

test no. and date	irradiation treatment,[a] krd	section flavor					fresh juice flavor		pasteurized juice flavor	
		Marsh mix	Marsh A	Marsh B	Marsh C	Ruby Red	Marsh mix	Ruby Red	Marsh mix	Ruby Red
1, 10/19/81	30	x[b]				–	x	x	–	–
	60	x				x	x	x	x	x
	90	–[d]				x	x	x	x	x
2, 12/07/81	15		–	0[c]	0	–	–	–	–	–
	30		–	–	–	–	–	–	x	–
	60		–	–	x	–	x	–	–	–
	90		–	x	–	–	x	–	–	–
3, 02/24/82	15		–	–	–	0	–	x	–	–
	30		–	–	–	–	–	x	–	–
	60		–	–	–	–	–	x	–	–
	90		–	–	–	–	x	–	–	x
4, 04/13/82	15		0	0	0	–	–	–	–	–
	30		–	–		–	x	–	–	–
	60		–	–	0	–	–	x	–	–
	90		–	–	–	–	x	x	–	x
5, 05/17/82	15		–	–	–	–	–	–	–	
	30		–	–	0	–	–	–	–	
	60		–	–	0	–	–	x	–	
	90		–	x	–	x	–	x	–	
6, 09/27/82	7.5	–				–	0	–		
	15	x				–	–	–		
	30	–				x	–	–		
	60	–				–	–	x		
7, 10/25/82	7.5	–				–	–	–		
	15	–				–	–	–		
	30	–				–	–	–		
	60	–				–	–	–		

[a] Time of fruit exposure was between 164.8 and 31.7 in./min. [b] Significant adverse flavor effects at the 95% confidence level or above. [c] Significant improved flavor effects at the 95% confidence level or above. [d] No significant flavor effects.

million dollars worth of Florida grapefruit exported annually to Japan.

Research studies involving γ-irradiation of citrus fruit as an alternative treatment to EDB were recently motivated by a proposal by the U.S. Environmental Protection Agency to restrict or eliminate the use of EDB as a quarantine treatment for citrus fruit because of possible carcinogenic effects. γ-Irradiation was proposed by Balock et al. (1956) as a treatment for fruit susceptible to fruit fly infestation. Balock et al. (1963) exposed immature stages of three species of fruit flies to low doses of γ-radiation and found that 6.5 krd destroyed 95% of eggs, larvae, and up to 3-day-old pupae. A number of studies on several species of fruit flies treated with γ-radiation under different experimental conditions have since been made (Balock et al., 1966, Benschoter and Telich, 1964 MacFarland, 1966; Cavalloro and Delrio, 1974; Seo et al., 1973; Thomas and Rahalkar, 1975). Burditt et al. (1981) determined survival rate of the Caribbean fruit fly larvae from infested grapefruit after low doses of γ-radiation. They showed adult flies did not emerge from eggs or larvae treated at 10 krd or above. Effects of gamma irradiation on the mortality of the Caribbean fruit fly in grapefruit were reported by vonWindeguth (1982), and phytotoxic response of Florida grapefruit to low-dose γ-irradiation was reported by Hatton et al. (1984).

In evaluating low-dose radiation used to control the fruit fly larvae in grapefruit, it is important to determine whether products from these fruit have in any way been adversely affected. Hatton et al. (1982) reported on the phytotoxicity of γ-irradiation on Florida grapefruit. The effects of X-ray and γ-irradiation on grapefruit products within a week after irradiation were reported by Moshonas and Shaw (1982). The current investigation assesses the effects of low-level γ-irradiation on flavor and composition of grapefruit products compared to similar products from untreated fruit throughout the harvesting season.

EXPERIMENTAL SECTION

Irradiation. "Marsh seedless white" and "Ruby Red" grapefruit from Florida were irradiated in five tests conducted throughout the 1981–1982 harvesting season. Two additional tests were run on early-season fruit of the 1982–1983 season. A "lot" of fruit consisted of 10 boxes of one variety of grapefruit harvested from a particular grove. Each lot was divided into the number of samples needed for each test and each sample exposed to one level of radiation. In the first, sixth, and seventh tests there was one lot of Marsh and one lot of Ruby Red grapefruit. In the remaining four tests there were three lots each of Marsh and one lot of Ruby Red grapefruit. Lots were labeled Marsh A, Marsh B, Marsh C, or Ruby Red. Lots of Marsh grapefruit for tests 3 and 4 were obtained from groves that were fully exposed to cold weather and from groves less susceptible to cold weather (protected). This precaution was taken to make sure that there were no weather-related effects entering into the analysis. Evaluation of the harvested and irradiated fruit showed that all fruit was of equally good quality and unaffected by weather. The grapefruit were packed in fiberboard boxes by commercial packinghouses in the Indian River region and taken to the USDA laboratory in Orlando. The fruit was then placed on a refrigerated truck at ideal temperature (15.6 °C for early-season fruit and 10.0 °C for mid- and late-season fruit) recommended for grapefruit storage by Lutz and Hardenburg (1968) and transported to the U.S. Department of Energy's Sandia National Laboratories at Albuquerque, NM.

Grapefruit were placed in single layers in buckets and passed by a cesium-137 source to be irradiated at dosages of 15, 30, 60, and 90 krd during the 1981–1982 harvesting season and at 7.5, 15, 30, and 60 krd for the two tests on early-season fruit in the 1982–1983 season. The dose rate

Table II. Analysis of Pasteurized Juice from γ-Irradiated Marsh and Ruby Red Grapefruit

test no.	irradiation date	irradiation treatment	vitamin C, mg/100 mL		°Brix (corrected)		% acid		Brix/acid ratio	
			Marsh	Ruby Red	Marsh	Ruby Red	Marsh	Ruby Red	Marsh	Ruby Red
1	10/19/81	0 (control)	33.7	33.3	9.0	8.9	1.26	0.94	7.2	9.4
		30	33.9	32.2	9.0	9.1	1.15	0.93	7.7	9.7
		60	32.3	32.3	8.3	8.8	1.13	0.96	7.3	9.1
		90	33.7	31.6	8.8	8.6	1.12	0.94	7.8	9.1
2	12/07/81	0 (control)	40.6	35.3	10.1	9.3	1.22	1.03	8.3	9.0
		15	36.8	38.4	9.9	9.2	1.26	1.05	7.8	8.8
		30	38.7	36.9	10.1	9.6	1.19	1.01	8.5	9.4
		60	36.0	35.2	9.7	9.1	1.26	0.97	7.7	9.4
		90	35.1	33.9	9.7	9.3	1.17	0.95	8.3	9.7
3	02/28/82	0 (control)	32.1	30.0	9.5	9.5	1.15	0.91	10.3	10.9
		15	31.2	29.2	9.5	9.5	1.05	0.92	10.0	10.4
		30	30.0	28.5	9.4	9.4	1.11	0.99	10.0	9.5
		60	28.6	28.9	9.5	9.5	0.94	0.87	9.7	11.0
		90	28.6	26.7	9.2	9.2	1.02	0.96	10.6	9.6
	02/28/82[a]	0 (control)	32.2		9.7		0.81		8.5	
		15	32.1		9.8		0.72		9.9	
		30	32.5		9.7		0.69		8.7	
		60	31.9		9.7		0.77		10.0	
		90	31.6		9.7		0.65		9.7	
4	04/13/82	0 (control)	26.0	29.4	8.5	8.4	0.85	0.92	10.0	9.1
		15	27.2	27.3	8.7	9.7	0.85	0.74	10.3	13.2
		30	24.2	28.4	8.7	8.8	0.71	0.87	12.2	10.1
		60	25.2	25.7	8.4	8.5	0.82	0.84	10.2	10.2
		90	25.3	25.5	8.7	9.2	0.74	0.81	11.7	11.4
	04/13/82[a]	0 (control)	23.6		7.9		0.82		9.5	
		15	30.0		9.6		0.95		10.1	
		30	24.0		9.1		0.81		11.3	
		60	25.1		9.0		0.76		11.8	
		90	28.0		8.9		0.76		11.7	
5	05/17/82	0 (control)	30.0	23.9	8.6	9.5	0.89	0.93	9.6	10.2
		15	26.5	23.4	8.4	10.0	0.83	0.84	10.1	11.9
		30	25.8	21.2	9.6	9.4	0.94	0.81	10.2	11.6
		60	27.2	25.4	9.8	10.7	1.06	0.98	9.3	10.9
		90	25.9	23.5	9.5	10.4	1.02	0.94	9.3	11.1
6	09/27/82	0 (control)	48.7	45.6	8.7	8.0	1.39	1.26	6.3	6.4
		7.5	45.6	38.7	9.0	8.1	1.34	1.22	6.7	6.7
		15	49.8	40.3	8.5	8.0	1.19	1.24	7.2	6.5
		30	48.1	37.3	9.0	7.8	1.26	1.23	7.1	6.4
		60	48.1	35.6	8.9	8.1	1.43	1.13	6.2	7.2
7	10/25/82	0 (control)	32.2	32.4	8.5	8.0	1.00	0.88	8.5	9.0
		7.5	33.6	35.6	8.6	9.0	1.03	0.85	8.4	10.5
		15	32.8	33.4	8.4	8.9	1.00	0.84	8.4	10.5
		30	30.7	32.4	8.2	8.8	0.99	0.81	8.3	10.9
		60	29.4	32.1	8.1	8.1	0.97	0.86	8.1	9.4

[a] Marsh grapefruit from grove protected from cold weather.

was controlled by the exposure time of each bucket to the source. Each lot of fruit contained thermoluminescent detector dosimetry chips so that the dosage could be verified. The irradiated and untreated control fruit were returned by refrigerated truck to the USDA laboratory in Orlando and placed in storage at 10.0 or 15.6 °C until a 28-day period simulating shipping time to Japan was completed. This period began when the fruit was placed on the reefrigerated truck after it had been irradiated. Upon completion of the refrigerated storage period and before product analyses began, the fruit was placed at 21.1 °C for 14 days to further simulate marketing conditions that the grapefruit undergo in Japan.

Juice Samples. Experimental and control grapefruit samples were prepared identically. Grapefruit were thoroughly washed and processed with a commercial FMC in-line extractor. The juice was then passed through a pressure screen finisher with 0.033 in. diameter holes to remove seeds and excess pulp. A portion of the fresh juice was immediately evaluated for flavor quality by an expert taste panel, and the remaining juice was pasteurized, sealed in 46-oz cans, and stored at −18 °C until used. Vitamin C levels were determined in pasteurized juice by the AOAC (1965) method. °Brix/acid ratios were determined according to Praschan (1976). Duplicate analyses were run on each sample.

Essential Peel Oil Preparation and Analysis. The oil emulsion from each sample of grapefruit processed with a commercial FMC in-line extractor was passed through a screen with 0.20 in. diameter holes and then through a 30–60-mesh shaker screen for removal of residual solid materials. The emulsion was then placed in a holding tank for 4 h. The water was removed and the oil-rich emulsion centrifuged at 16000 *g* at 10 °C to break the emulsion and allow the separation of the cold-pressed peel oil. The oils were stored at −18 °C until analysis. Each whole oil from treated and untreated fruit was quantitatively and qualitatively analyzed on a Hewlett-Packard Model 5880A gas chromatograph equipped with an integrator and a 25-m fused silica capillary column coated with Carbowax 20M. The helium flow was 1.5 mL/min at 80 °C. The injection port and the flame detector temperatures were 250 °C. The capillary inlet was operated in the split mode, which split the 0.2-μL sample 100/1. The oven temperature was held at 80 °C for 4 min, raised to 190 °C at 6 °C/min, and held at 190 °C for 60 min. Quantitative data were determined by a Hewlett-Packard Model 5880A computing integrator that was coupled to the gas chromatograph to measure peak areas. Authentic compounds previously identified as constituents of grapefruit peel oil were simultaneously injected with the sample for peak identifications based on peak enrichment. The GLC curve and data of each sample from irradiated fruit were compared with those from corresponding samples from untreated fruit to determine if there were any significant compositional effects caused by the irradiation treatments.

Flavor Evaluation. Triangle and paired flavor tests described by Boggs and Hanson (1949) were used in which 12 experienced tasters were each given two presentations. For triangle tests, each presentation consisted of three samples, two of which were identical. Judges were asked to indicate which sample was different. In paired comparison tests, judges were asked to indicate which sample they preferred. Tests compared fresh juice, fresh sections, and pasteurized juice from irradiated and untreated control fruit.

RESULTS AND DISCUSSION

Twenty-two 10-box lots of Florida grapefruit were exposed to 7.5-, 15-, 30-, 60- or 90-krd γ-irradiation treatment in seven tests covering the 1981–1982 and early 1982–1983 harvesting season. After irradiation, these fruit were held at temperatures and time periods that would simulate their trip by boat to Japan and their shelf life to the market. Flavor effects of irradiation treatments of Marsh white and Ruby Red Florida grapefruit are shown in Table I.

Fruit harvested early in the season (Oct 1981) and irradiated at 30, 60, or 90 krd had rind scald and were softer than that the untreated fruit. Significant flavor changes were found in most sections, fresh juice, and pasteurized juice obtained from irradiated fruit. The severity of irradiation effects on flavor of these early grapefruit samples prompted two more tests from early fruit harvested in Sept (sample no. 6) and Oct (sample no. 7) of 1982. These fruit, which were exposed to 7.5, 15, 30, or 60 krd, had not softened and had considerably less rind scald than that noted on early fruit in the Oct 1981 test. Flavor tests of products from the very early preseason fruit (test no. 6) showed an adverse flavor change in one Marsh section sample, one Ruby Red section, and one juice sample. The flavor results of the early-season fruit irradiated in October (test no. 7) showed no adverse effects on products from irradiated fruit. The reason for flavor and physical damage that occurred in the first test of early fruit (test no. 1) has not been determined.

Adverse flavor effects found in the products from early-season irradiated Marsh and Ruby Red grapefruit decreased dramatically in fruit harvested from December through May. Significant adverse flavor effects occurred in one section sample from fruit exposed to 60 krd and one exposed to 90 krd in test no. 2 and one section sample exposed to 90 krd in test no. 5.

In some cases, particularly at lower doses of irradiation, there was a preference for the irradiated sample. Thus, the expert taste panel judged six section samples at 15 krd, one at 30 krd, and two at 60 krd to show a significant improvement in flavor when compared to the control samples. These results parallel those of Marshall and Ismail (1984) that soluble pectins not only increased with maturity but also increased at low-level irradiation (15 and 30 krd). These soluble pectin levels were not elevated at higher doses (60 and 90 krd). However, no correlation between soluble pectin content and flavor has been established. In those fresh samples where a significant adverse flavor change occurred, the exposure to γ-irradiation was at the higher levels of 60 and 90 krd. Adverse flavor changes found in juice that had been pasteurized occurred only at the 60- or 90-krd exposure level, except for one sample in test no. 2 in which a flavor change was significant at the 30-krd level.

Analysis of pasteurized juice from irradiated fruit showed no marked change in vitamin C, sugar, or acid levels (Table II) when compared to those from similar juice from untreated fruit. Volatile flavor constituents separated and identifed from cold-pressed peel oil from irradiated or untreated grapefruit were similar to those previously published (Moshonas and Shaw, 1982) and showed no significant quantitative or qualitative differences at any of the radiation levels to which the fruit was exposed.

This study demonstrated that low-dose γ-irradiation of "Marsh" (the principle cultivar exported to Japan) and Ruby Red grapefruit has no detrimental effects on vitamin C, sugar, or acid levels nor on essential peel oil composition. Flavor effects of fresh grapefruit sections, fresh juice, and pasteurized juice from fruit exposed at the 7.5-, 15-, and 30-krd levels were minimal, with a few samples judged to have an improved, and a few having an adverse flavor change. The lone exception to this evaluaton occurred in test no. 1 in which irradiated fruit had incurred physical damage and most products were judged to have undergone an adverse flavor change when compared with control, untreated fruit. Adverse flavor effects increased in products from fruit exposed to γ-radiation at the 60-krd level and were most prominent at the 90-krd level.

Registry No. Vitamin C, 50-81-7.

LITERATURE CITED

AOAC "Official Method of Analysis", 10th ed.; Association of Official Analytical Chemists: Washington, D.C., 1965; p 306, 764.
Balock, J. W.; Burditt, A. K., Jr.; Christenson, L. D. *J. Econ. Entomol.* **1963**, *56*, 42.
Balock, J. W.; Burditt, A. K., Jr.; Seo, S. T.; Akamine, E. F. *J. Econ. Entomol.* **1966**, *69*, 202.
Balock, J. W.; Christenson, L. D.; Burr, G. O. *Proc. Annu. Meet. Hawaii. Acad. Sci., 31st* **1956**, 18.
Benschoter, C. A.; Telich, C., Jr. *J. Econ. Entomol.* **1964**, *57*, 690.
Boggs, M. N.; Hanson, H. L. *Adv. Food Res.* **1949**, *2*, 222.
Burditt, A. K., Jr.; Moshons, M. G.; Hatton, T. T.; Spalding, D. H.; vonWindeguth, D. L.; Shaw, P. E. *Adv. Agric. Tech. (U.S. Dep. Agric., Sci. Educ. Adm.)* **1981**, *ARR-S*-10.
Cavalloro, R.; Delrio, G. *Proc. Natl. Symp. Radioecol.*, 3rd **1971**, *2*, 1179.
Hatton, T. T.; Cubbedge, R. H.; Risse, L. A.; Hale, P. W.; Spalding, D. H.; Reeder, W. F. *Proc. Fla. State Hortic. Soc.* **1982**, *95*, 232.
Hatton, T. T.; Cubbedge, R. H.; Risse, L. A.; Hale, P. W.; Spalding, D. H.; vonWindeguth, D. L.; Chew, V. *J. Am. Soc. Hortic. Sci.* **1984**, in press.
Lutz, J. M.; Hardenburg, R. E. U.S., Dep. Agric., Agric. Handb. **1968**, *No.* 66, 1–94.
MacFarlane, J. J. *J. Econ. Entomol.* **1966**, *59*, 884.
Marshall, M., Ismail, M. A. *HortScience* **1984**, in press.
Moshonas, M. G.; Shaw, P. E. *J. Food Sci.* **1982**, *47*, 958.
Praschan, V. C. "Quality control manual for citrus processing plants"; Intercit, Inc.: Safety Harbor, FL, 1976; p 40.
Seo, S. T.; Kabayashi, R. M.; Chambers, D. L.; Dollar, A. M.; Hanaoka, M. *J. Econ. Entomol.* **1973**, *66*, 937.
Thomas, P.; Rahalkar, G. W. *Curr. Sci.* **1975**, *44*, 775.
vonWeindeguth, D. L. *Proc. Fla. State Hortic. Sci.* **1982**, *95*, 235.

Received for review December 30, 1983. Revised manuscript received April 16, 1984. Accepted June 4, 1984. Mention of a trademark or proprietary product is for identification only and does not imply a warranty or guarantee of the product by the U.S. Department of Agriculture over other products that may also be suitable.