Levels of β-Naphthoxyacetic Acid and β-Naphthol on Field Sprayed Strawberries as Analyzed by High-Pressure Liquid Chromatography

Day-Neutral strawberry plants (berries and leaves) were investigated for levels of β-naphthoxyacetic acid and its postulated metabolite (β-naphthol) when the plants were sprayed with aqueous solutions of 50 or 100 ppm active ingredient of β-naphthoxyacetic acid (BNOA). For each concentration, one plot was sprayed and sampled for 15 days, while a second plot was resprayed after 5 days and sampled for 15 days from the initial spray application. With both spray concentrations, the BNOA on the once-sprayed berries had dissipated to <0.05 ppm in 5 to 6 days and to the same value on the resprayed berries in 10 to 11 days. After 15 days, the once-sprayed leaves had residues of 0.16 ppm for the 50 ppm spray and 0.25 ppm for the 100 ppm spray, while the resprayed leaves had 0.92 and 1.50 ppm, respectively. No β-naphthol residues were detected in any samples.

Little, if any, information is available in the literature concerning the levels and fate of β-naphthoxyacetic acid and its postulated metabolite, β-naphthol, when applied to specific crops in the field. Certain aerosol and wettable powder formulations have been used for spraying strawberry plants for increasing yields and fruit size. Usually the first application of the β-naphthoxyacetic acid is made about 14 to 16 days after full bloom, and at this time most of the flowers have opened and there should be many small fruits at about one-fourth to one-third full size on the plants from the first flowers. The blossoms and fruits should be thoroughly wetted by the spray mist during an early morning or late evening application. A second application should be made 4 or 5 days after the first application and none should be made within 14 days of harvest.

The purpose of the present investigation was to determine the levels and fate of β-naphthoxyacetic acid (BNOA) and its postulated metabolite, if any, when a wettable powder formulation of 50 or 100 ppm active ingredient BNOA in water was sprayed on strawberry plants as described above.

MATERIALS AND METHODS

Strawberry Plots. Three plots containing 35 plants each in duplicate of Day-Neutral strawberry plants (42 × 392 in for each plot) were planted in Davis, Calif., in 1976. One plot was used as a control or untreated plot, a second plot was sprayed with a water solution of 50 ppm active ingredient (AI) of BNOA, and a third plot was sprayed with a solution of 100 ppm AI of BNOA. The plant hormone was applied with a Hudson hand-sprayer in June 1976. With the exception of a few plants which had the blossoms sprayed and then sampled for residue analysis, all the blossoms on the other plants were removed before chemical treatment. This was done so that all the berries present would have been sprayed and the development of unsprayed berries was prevented.

Formulation Applied. Berry-Set, a hormone-type spray for bigger berries, Science Products Company, Inc., Chicago, Ill., EPA Reg. No. 2125-39-AA: active ingredient 2.67% as β-naphthoxyacetic acid and inert ingredients 97.33%. Two mixtures of this formulation were made: 7.1 g/gal to result in a 50 ppm solution of AI and 14.2 g/gal to result in a 100 ppm solution of AI. No β-naphthol was detected by high-pressure liquid chromatographic analysis (<0.01%) in the formulation.

Sampling of Berries and Leaves. Two sets of experimental plots were treated and sampled for each spray level, 50 and 100 ppm, as follows. One plot at each level was treated for sampling of berries and leaves from the day of application through 15 days of sampling. The strawberries were green at the date of spraying and were mature ripe at the harvest period 15 days later. A second set of plots were sprayed twice at each rate. The plots were sprayed and the berries and leaves were sampled daily for five samplings and then resprayed at each rate and sampled through 15 days after the first application. Control plots were sampled for berries and leaves concurrently with treated plots. All sampes were extracted immediately with acidified acetone and the extracts were stored at 4 °C for analysis. The residue data in Table I as shown for berries and leaves for BNOA application rates at 50 or 100 ppm are represented as composited samplings from day 1 through day 4 for the once sprayed and twice sprayed experiments.

Table I. Levels of β-Naphthoxyacetic Acid on Day-Neutral Strawberries as Determined by High-Pressure Liquid Chromatography

	berries[a]				leaves[b]			
	sprayed on day 1		sprayed on day 1 and 5		sprayed on day 1		sprayed on day 1 and 5	
sample day	50 ppm[c]	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm	50 ppm	100 ppm
1	0.25	0.34	0.25	0.34	5.05	8.40	5.05	8.40
2	0.15	0.20	0.15	0.20	3.20	5.01	3.20	5.01
3	0.12	0.17	0.12	0.17	2.10	3.60	2.10	3.60
4	0.12	0.17	0.12	0.17	1.48	3.06	1.48	3.06
5	<0.05	0.11	0.17	0.33	1.06	2.65	5.49	9.16
6	<0.05	<0.05	0.17	0.26	0.90	2.47	5.14	7.44
7	<0.05	<0.05	0.10	0.19	0.86	2.33	4.22	6.56
8	<0.05	<0.05	0.09	0.16	0.68	1.92	3.25	5.20
9	<0.05	<0.05	0.05	0.15	0.61	1.39	2.53	3.57
10	<0.05	<0.05	<0.05	0.05	0.60	1.03	1.93	2.60
11	<0.05	<0.05	<0.05	<0.05	0.51	0.84	1.60	2.45
12	<0.05	<0.05	<0.05	<0.05	0.39	0.74	1.47	2.74
13	<0.05	<0.05	<0.05	<0.05	0.34	0.68	1.51	2.18
14	<0.05	<0.05	<0.05	<0.05	0.27	0.50	1.39	1.53
15	<0.05	<0.05	<0.05	<0.05	0.16	0.25	0.92	1.50

[a] Percent moisture in berries averaged 87.9. [b] Percent moisture in leaves averaged 66.4. [c] Method sensitivity 0.05 ppm; BNOA recoveries on berries averaged 90.4 ± 4% and on leaves averaged 90.8 ± 15%. No β-naphthol was detected in any of the samples but recoveries on berries was 93.8 ± 4.2% and on leaves 72.8 ± 7.7%.

Sample Extraction, Cleanup, and Analysis. All samples were extracted, cleaned up, and analyzed as described by Archer and Stokes (1978).

RESULTS AND DISCUSSION

The average weight of the sprayed berries from day 1 to 3 was 1.93 g; day 4 to 7 was 2.61 g; day 8 to 11 was 4.36 g; day 12 to 14 was 6.52 g; and day 15 was 10.7 g. The leaves from day 1 through 15 were approximately the same weight and averaged 0.832 g. The moisture content of the

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berries averaged 87.9% and of the leaves 66.4%.

As shown in Table I, the experimental plots that were sprayed only once at day 1 had 0.25 and 0.34 ppm BNOA residues on the berries when sprayed with 50 or 100 ppm AI, respectively. By day 5 to 6 the residues had dropped to <0.05 ppm. The experimental plots that were resprayed on day 5 showed residues of BNOA on the berries of 0.17 and 0.33 ppm and then dropped to <0.05 ppm by days 10 or 11. All mature berries at harvest (day 15) had residues <0.05 ppm.

The BNOA residues on the leaves showed similar trends of residue dissipation as on the berries except that the initial residues were much larger (5.05 and 8.40 ppm) when sprayed on day 1 with 50 or 100 ppm, respectively. On day 15 the residues had declined to 0.16 and 0.25 ppm. The residues on the resprayed leaves were proportionally higher but showed similar trends in residue dissipation as did the plots sprayed only one. No β-naphthol residues were found in either the berry or leaf samples.

The strawberry blossoms that were sprayed, sampled, and analyzed had residues of 4.7 and 7.6 ppm when sprayed with 50 or 100 ppm AI BNOA, respectively. Due to the limited number of plants available, no berries were sampled from sprayed blossoms. However, since the directly sprayed berries only gave residues of 0.25 and 0.34 ppm when sprayed with 50 or 100 ppm AI BNOA, respectively, it is probably reasonable to assume that by harvest time 15 days later, the residues would have been <0.05 ppm due to dissipation and dilution of the plant residues by growth and environmental factors.

β-Naphthoxyacetic acid residues dissipated very rapidly on berries and leaves of strawberry plants that were sprayed in the field. Apparently BNOA does not degrade in the field to its postulated mebabolite, β-naphthol, since it was not detected by high-pressure liquid chromatographic analysis at 0.05 ppm or higher.

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LITERATURE CITED

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Effect of Maturity, Cultivar, Field History, and the Operations of Peeling and Coring on the Geosmin Content of *Beta vulgaris*

The purpose of this study was to obtain information about the origin and distribution of geosmin (*trans*-1,10-dimethyl-*trans*-(9)-decalol), the earthy odor component in beets. The geosmin content of *Beta vulgaris* L. cv. Ruby Queen was monitored throughout growth and storage. The data indicate that geosmin content is directly related to the surface area of the beet. In addition the geosmin content of eight different cultivars of *B. vulgaris* showed little variation except for two cultivars which had a large number of secondary roots (i.e., more surface area). An analysis of the distribution of geosmin in the root of Ruby Queen beets showed that the peels of the beets had the highest concentration. The high concentration of geosmin in the surface of the beet implies that the geosmin may be derived from the soil in which it is grown. However, the geosmin content of beets grown in two fields with different histories of cultivation was the same.

Geosmin (*trans*-1,10-dimethyl-*trans*-(9)-decalol) has been identified as an odorous metabolite of many soil microorganisms of the family Streptomyces (Gerber and Lechevalier, 1965; Collins et al., 1970; Kikuchi et al., 1972), and as a metabolite of several species of blue-green algae (Safferman et al., 1967; Medsker et al., 1968; Kikuchi et al., 1973). The strong earthy odor of this compound led scientists to the suspicion that it was responsible for musty off-odors sometimes present in water supplies and in fish (Gerber and Lechevalier, 1965; Safferman et al., 1967; Lovell, 1972). Geosmin was subsequently identified as an earthy odor contaminant of water, catfish, rainbow trout, and dry beans (Rosen et al., 1970; Lovell, 1972; Yurkowski and Tabachek, 1974; Buttery et al., 1976). In each case, earthiness was recognized as an abnormal odor produced by microorganisms. In contrast, geosmin, isolated from red table beets, was perceived as part of the characteristic aroma of beets (Murray et al., 1975; Acree et al., 1976).

It is not known whether the geosmin in table beets is an endogenous metabolite of the beet itself or a contaminant produced by microorganisms. In an attempt to answer this question, the changes in the geosmin content of one cultivar of *Beta vulgaris* (Ruby Queen) during 5 months of growth and 2 months of storage were measured by gas chromatography. In addition, the differences in the geosmin content of Ruby Queen beets grown in two different fields and the variations in the geosmin content of eight cultivars of *Beta vulgaris* were determined. Since the origin of geosmin may be reflected in its distribution within the root, differences in the geosmin content of various parts of Ruby Queen beets are presented in this paper.

EXPERIMENTAL SECTION

Beet Samples. An experimental field of lima silt loam soil at the New York State Agricultural Experiment Station was fertilized with 250 kg/acre of 10-20-20 fertilizer on May 2, 1977. The following day the field was treated with 2 kg/acre of Ro-Neet herbicide (Stauffer Chemical Co., Westport, Conn.). On May 4, 1977 eight cultivars of *Beta vulgaris* seed were planted about 0.75 in. deep at a rate of about 9 kg/acre with a mechanical planter. This field was fertilized again on June 22, 1977 with 25 kg/acre of ammonium nitrate. A commercial field of the same soil type was fertilized on May 2, 1977 with about 360 kg/acre of 10-20-20 fertilizer. The same herbicide was used on the

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