Effects of Soil Treatment with the Insecticide Chlorfenvinphos and of Covering of the Culture with Plastic Film on the Provitamin A Content of Early Carrots

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Early carrots were grown in soils treated or not treated with the insecticide chlorfenvinphos; the carrots were covered or not covered with a plastic film, and several harvests were made. For the carrots grown covered with a plastic film, at each harvest the concentrations of total carotene were on an average 34% higher when the soil had been insecticide treated than when it was untreated; for the carrots grown uncovered, at the first harvests the concentrations of total carotene were similar for the carrots from the treated and untreated soils, and at the following harvests they were about 22% higher in the carrots from the treated soils. None of the used cultural conditions modified the ratio of *all-trans*-α-carotene to *all-trans*-β-carotene and the ratio of cis isomers to all-trans isomers.

Interest in possible effects of pesticides on nutritional value and quality of foods has made desirable investigations in this field. The insecticides aldrin and dieldrin had no effect on ascorbic acid or sugar content of carrots (Schuphan, 1960). An increased carotene content has been reported for carrots grown in soil treated with the fumigants and nematicides 1,3-dichloropropene (Telone) or 1,2-dibromo-3-chloropropane (Nemagon) (Emerson et al., 1970; Wu et al., 1970) or with the herbicides linuron or chlorpropham (CIPC) (Sweeney and Marsh, 1971). The soil insecticide chlorfenvinphos (Birlane) is widely used to control the root flies and the root worms of the carrot. In the present work, we studied the effect of chlorfenvinphos on the provitamin A content of the carrot.

Direct covering with a perforated plastic film on early carrots greatly enhances yields (Benoit and Ceustermans, 1977, 1978a,b, 1979); for that reason, we studied the effect of chlorfenvinphos on the provitamin A content of early carrots grown directly covered or not covered with a plastic film.

EXPERIMENTAL SECTION

The carrot cultures were made at the Research Station for Vegetables, St-Katelijne-Waver, Belgium. When treated, the soil was sprayed on Feb 2, 1981, with an aqueous emulsion of Birlane WP at the normal rate of 160 g of Birlane WP/are or at the exaggerated rate of 1600 g of Birlane WP/are. The emulsion contained 3% by weight of Birlane WP. Birlane WP is the commercial formulation that contains 25% by weight of chlorfenvinphos. The treatment was made by an overall surface spray on the finely granulated soil; the soil then was raked so that the pesticide was incorporated at a depth of about 6 cm.

One day after the pesticide treatment, the early carrots (Amsterdamse Zoete Bak variety) were sown mechanically by means of pill-shaped coated seeds (Nunhems Zaden, B.V., Haelen, the Netherlands; 400 pills/m^2; 12 cm of space between the rows). A part of the carrots then was immediately covered with a perforated polyethylene sheet (30 μm thick; 500 perforations of 1 cm in diameter per square meter), and the sheeting was removed at May 5, 1981. All experiments were arranged in a randomized block design; there were plots of control (untreated soil), of each treatment (normal or exaggerated rate), and with or without covering with a plastic film; there were four plots (four replications) for each of the cultural conditions. The size of each plot was 1.3 m × 10.0 m. At harvest, samples were collected at random from each plot. At each harvest, no insect attack at all was observed on the carrots harvested from each of both the treated and the untreated soils.

The plots here called treated and untreated all were of the same soil that, in the past, had received the following common treatments made at equal rates: on Sept 19, 1980, treatment by 9 kg/are of the insecticide methyl bromide; on Oct 10, 1980, treatment with an organic fertilizer (1 m^3 of fertilizer/are) for mushroom (Timac, Belgium; dry matter, 38%, organic matter, 20%; calcium, 2.5% as CaO; total salt, 3%; chlorine, 0.3%; nitrogen 0.6%; phosphorus, 0.5% as P_2O_5; potassium, 0.8% as K_2O; magnesium, 0.3% as MgO); on Jan 26, 1981, treatment with a mixture of mixed mineral fertilizers—5 kg/are marl (Timac, Belgium; calcium carbonate, 80%; magnesium carbonate, 10%; MgO, 4%; neutralizing value, 45%); 6 kg of Patentkali/are (Belgopotasse, Belgium; potassium, 8% as K_2O; water-soluble magnesium, 10% as MgO); 3 kg/are NPK 12+12+17 plus [BASF, Germany; 12% of nitrogen (5.1% of nitric and 6.9% of ammonium nitrogen); phosphorus, 12% as P_2O_5; potassium, 17% as K_2O; sulfur, 16% as SO_3]; 6 kg/are NPK 6+7+8 [SBA, Belgium; 6% of nitrogen (1% of ammonium, 2% of urea, and 3% of organic nitrogen); water-soluble phosphorus, 7% as P_2O_5; potassium, 8% as K_2O].

The carotenes were analyzed according to a described procedure (Sweeney and Marsh, 1970). The leaves of the carrots were cut just at the surface of the root; the whole roots were diced and extracted. Extractions were made immediately after harvest, and the extracts transferred to petroleum ether, concentrated under reduced pressure, and stored at −20 °C. Vitamin A values, determined by Zechmeister (1962) for the various carotene stereoisomers, were used in calculating biological values. Differences between means were tested for significance by application of the *F* test (Fisher-Snedecor).

RESULTS AND DISCUSSION

Total Carotene Content. *Influence of Pesticide Treatment of the Soil.* For the carrots grown both covered and uncovered, there was no difference for the total carotene content when the Birlane dose was normal or exaggerated (Table I). The total carotene contents of the carrots harvested at the same dates were compared according to whether their soil of culture was treated or not with Birlane.

For the carrots grown covered, at each harvest the total carotene contents were on an average 34% higher in the carrots grown in Birlane-treated soils than in the controls.

For the carrots grown uncovered, at the three first harvests (June 3, 1981; June 10, 1981; June 17, 1981), the total carotene contents were not different when the carrots

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Table I. Concentration of Total Carotene in Carrots Grown in Soils Treated or Not Treated with Birlane WP

harvest date	time delay, days	total carotene, μg/100 g fresh wt[d]		
			treated soil, g of Birlane WP/are	
		untreated soil (control)	160 (normal dose)	1500 (exaggerated dose)
		Carrots Covered with Perforated Plastic Film		
5-25-81	0	2958 ± 279	4345 ± 398[a]	4200 ± 381[a]
6-3-81	9	4308 ± 467	6490 ± 531[a]	6150 ± 535[a]
6-10-81	16	6475 ± 422	8523 ± 409[a]	8720 ± 441[a]
6-17-81	23	6558 ± 545	8603 ± 478[a]	8738 ± 389[a]
6-24-81	30	8118 ± 441	10528 ± 468[a]	10133 ± 696[a]
7-1-81	37	9603 ± 903	12738 ± 522[a]	12373 ± 594[a]
7-8-81	44	9420 ± 659	11590 ± 623[a]	11460 ± 717[a]
		Uncovered Carrots		
6-3-81	9	4888 ± 270	5205 ± 451[c]	4640 ± 347[c]
6-10-81	16	5980 ± 373	6575 ± 321[c]	6813 ± 603[a]
6-17-81	23	7525 ± 515	8223 ± 436[b]	8018 ± 457[c]
6-24-81	30	7953 ± 505	9373 ± 362[a]	9715 ± 602[a]
7-1-81	37	8673 ± 375	10625 ± 413[a]	10245 ± 450[a]
7-8-81	44	7923 ± 633	9795 ± 648[a]	10025 ± 738[a]

[a] Significantly different from the control at 1% level. [b] Significantly different from the control at the 5% level. [c] Not significantly different from the control. [d] Means ± SD of four replications.

Table II. Distribution of α- and β-Carotenes in Carrots Grown in Soils Treated or Not Treated with Birlane WP[a]

harvest date	treatment	carrots covered with plastic film		uncovered carrots	
		α-carotene, %	β-carotene, %	α-carotene, %	β-carotene, %
5-25-81	control	47.1	52.9		
	normal dose	45.6	54.4		
	exaggerated dose	41.0	59.0		
6-3-81	control	40.2	59.8	40.3	59.7
	normal dose	42.4	57.6	45.7	54.3
	exaggerated dose	44.8	55.2	41.1	58.9
6-10-81	control	43.2	56.8	45.2	54.8
	normal dose	43.4	56.6	47.5	52.5
	exaggerated dose	40.7	59.3	47.7	52.3
6-17-81	control	45.1	54.9	42.8	57.2
	normal dose	47.6	52.4	40.3	59.7
	exaggerated dose	43.8	56.2	42.6	57.4
6-24-81	control	44.5	55.5	44.8	55.2
	normal dose	42.3	57.7	45.2	54.8
	exaggerated dose	41.3	58.7	39.9	60.1
7-1-81	control	40.1	59.9	46.6	53.4
	normal dose	46.0	54.0	41.4	58.6
	exaggerated dose	44.5	55.5	43.0	57.0
7-8-81	control	42.2	57.8	42.1	57.9
	normal dose	46.7	53.3	44.0	56.0
	exaggerated dose	41.9	58.1	46.4	53.6
mean	control	43.2	56.8	43.6	56.4
	normal dose	44.9	55.1	44.0	56.0
	exaggerated dose	42.6	57.4	43.5	56.5

[a] Values are means of four replications.

Table III. Distribution and Biopotency (Percent) of Carotene Isomers in Carrots[a]

treatment	neo-α-carotene B	*all-trans*-α-carotene	neo-α-carotene U	neo-β-carotene B	*all-trans*-β-carotene	neo-β-carotene U	biopotency[b]
			Carrots Covered with Perforated Plastic Film				
control	2.5	39.9	0.8	4.6	50.4	1.8	75.1
normal dose	1.4	43.1	0.4	5.1	48.6	1.4	74.9
exaggerated dose	1.8	40.1	0.7	3.2	52.6	1.6	76.6
			Uncovered Carrots				
control	1.6	41.1	0.9	3.5	51.4	1.5	76.1
normal dose	2.1	41.3	0.6	5.2	49.5	1.3	75.1
exaggerated dose	2.3	40.5	0.7	4.4	51.0	1.1	75.7

[a] Values are means of four replications for each harvest and for all the harvests. [b] Values based on biopotency values reported by Zechmeister (1962), with *all-trans*-β-carotene as 100%.

were grown in Birlane-treated or untreated soils. At the three latest harvests (June 24, 1981; July 1, 1981; July 8, 1981), the total carotene contents were on an average 22% higher in the carrots grown in Birlane-treated soils than in controls.

Influence of Covering Carrots with Plastic Film. For the carrots grown in Birlane-untreated soils, the total carotene contents were generally similar whether the carrots had been covered or not; exceptions were observed at the harvests of June 17, 1981, and July 8, 1981.

For the carrots grown in Birlane-treated soils, the total carotene contents were on an average 18% higher in the carrots grown covered than in the uncovered; exceptions were the harvests of June 17, 1981, and June 24, 1981.

Carotene Stereoisomers. None of the cultural conditions used (the pesticide treatment or the covering with perforated plastic film) appeared to have significant effects on the formation of carotene stereoisomers (Tables II and III). The *all-trans*-α-carotene is known to have a lower provitamin A value than the *all-trans*-β-carotene; the cis stereoisomers of α- and β-carotenes are known to have lower provitamin A values than do the *all-trans*-carotenes (Zechmeister, 1962); the fact that the cultural conditions did not cause significant changes in the ratio of the *all-trans*-α-carotene to the *all-trans*-β-carotene and in the ratio of cis isomers to all-trans isomers is therefore important from the standpoint of the quality of the food.

There was no insect attack on the carrots from both the treated and the untreated soils; the marked difference in carotene in the insecticide-treated plots over untreated plots thus seems to be actually due to an interaction between carrot and pesticide; this chloroorganophosphate, or some of its metabolites, thus would directly influence the metabolism of the carrots.

The effect of the pesticide on the total carotene content was not the same when the carrots were covered or not covered. Several speculations may be proposed in order to interpret these differences. The enhanced yield (weight of root per square meter), obtained here by covering with a plastic film (whether there was a pesticide treatment or not), clearly indicated that covering significantly altered the physiology and the metabolism of the carrots, among others by increasing the soil temperature (Benoit and Ceustermans, 1977, 1978a,b, 1979); moreover, the degradation of the pesticide in the soil, the evaporation of the pesticide from the soil, and thus the influence of the pesticide and of its metabolites on the metabolism of the carrots all could also be influenced by soil covering and by the effect of this last factor at least on the soil temperature; thus, it is not astonishing that the effects of the pesticide treatment were different according to the covering or not of the carrots with a plastic film.

In any of the assays made here, the soil treatment with chlorfenvinphos was beneficial to the total carotene content of the carrots, without altering the distribution of the carotene isomers and thus the biopotency of the total of the carotenes.

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Automated Gel Permeation System for Rapid Separation of Industrial Chemicals and Organophosphate and Chlorinated Pesticides from Fats

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A gel permeation chromatography (GPC) system for the rapid separation of industrial chemicals and organophosphate and chlorinated pesticides from fats has been developed. The system uses Bio-Beads SX-3 with a methylene chloride–*n*-hexane (50:50 v/v) solvent system. This gives good recoveries for a wide range of industrial chemicals and pesticides. Less than 1% fat remained in the pesticide fraction.

Gel permeation chromatography (GPC) was introduced as a cleanup technique for pesticides by Stalling et al. (1972). They found that Bio-Beads SX-2 gel with a cyclohexane solvent system removed the lipids from fish extracts and gave good recoveries of pesticides. This GPC system was automated by Tindle and Stalling (1972). The automated method was evaluated by Griffitt and Craun (1974) as a cleanup procedure for the removal of fats and oils from foods during pesticide residue analysis. The automated system was found to be more efficient and faster in the analysis of pesticide residues in fats than the acetonitrile–petroleum ether partitioning cleanup procedure. The recoveries for the pesticides through the GPC system were better than the acetonitrile–petroleum ether partitioning and Florisil cleanup method. The dump fraction removed 98% of the lipds from the pesticide fraction.

Stalling (1974) introduced a different GPC system that used Bio-Beads SX-3 and toluene–ethyl acetate (25:75 v/v) as the solvent system. This system gave quantitative recoveries of nonionic chlorinated pesticides and PCB's. This system could clean up a wider range of sample types, including green plant lipids, animal feed extracts, human adipose tissue, and beef tallow. Johnson et al. (1976)

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