

perspective of food-chain transfer, is the acceptability of the starch-xanthate capsules as food by nontarget animals such as birds and small mammals.

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LITERATURE CITED

- American Association of Textile Chemists and Colorists "AATCC Technical Manual"; AATCC: Research Triangle Park, NC, 1979; p 168.
- Coutts, H. H. In "Field Worker Exposure During Pesticide Application"; Tordoir, W. F.; van Heemstra-Lequin, E. A. H., Eds.; Elsevier: New York, 1980; p 39.
- Dedek, W. In "Field Worker Exposure During Pesticide Application"; Tordoir, W. F.; van Heemstra-Lequin, E. A. H.,

- Eds.; Elsevier: New York, 1980; p 47.
- Getz, M. E. *Adv. Chem. Ser.* 1971, No. 104, 119.
- Hedin, P. A. *J. Agric. Food Chem.* 1982, 30, 201.
- Luna, L. G. In "Manual of Histologic Staining Methods of the Armed Forces Institute of Pathology"; Luna, L. G., Ed.; McGraw-Hill: New York, 1968; p 158.
- Otey, F. H., USDA, Peoria, IL, personal communication, 1981.
- Scheuplein, R. J.; Blank, I. H. *J. Invest. Dermatol.* 1973, 60, 286.
- Shasha, B. S. In "Controlled Release Technologies: Methods, Theory, and Applications"; Kydonius, A., Ed.; CRC Press: Boca Raton, FL, 1980; p 207.
- Shasha, B. S.; Trimmel, D.; Otey, F. H. *J. Polym. Sci., Polym. Chem. Ed.* 1981, 19, 1891.
- Speight, B. In "Field Worker Exposure During Pesticide Application"; Tordoir, W. F.; van Heemstra-Lequin, E. A. H., Eds.; Elsevier: New York, 1980; p 29.
- Tordoir, W. F. In "Field Worker Exposure During Pesticide Application"; Tordoir, W. F.; van Heemstra-Lequin, E. A. H., Eds.; Elsevier: New York, 1980; p 183.

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Effects of Selected Insecticides and Herbicides on Free Sugar Contents of Carrots

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Early carrots were grown in soils treated or not with the insecticide Birlane; the carrots were covered or not covered with a plastic film; summer carrots were grown in soils treated or not with one of the insecticides Nexion, Birlane, or Dyfonate and with one of the herbicides Afalon Spezial or Dosanex. Several harvests were made; the main free sugars of the carrots, i.e., fructose, α - and β -glucoses, sucrose, and their total, were analyzed in the root of the carrot. Soil treatment with each of the three insecticides generally increased (relatively to the untreated soil) the concentrations of each of the free sugars and of their total in the root, the effect being the largest with Birlane and Nexion. The herbicide Afalon S generally had no effect on the sugar concentrations. The herbicide Dosanex generally decreased the concentrations of each of the free sugars and of their total.

Sweeney and Marsh (1971) reported the effects of two herbicides, the urea Afalon and the carbamate CIPC, on the carotene content of carrots grown in soil treated by one of these pesticides; the active matter of Afalon is linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea], and that of CIPC is chlorpropham (isopropyl 3-chlorophenyl-carbamate). Rouchaud et al. (1982a,b) reported the effects, on the total carotene content of carrots, of the organophosphorus insecticides Nexion, Birlane, and Dyfonate and of the urea herbicides Afalon Spezial and Dosanex; the active matter of Nexion is bromophos [*O*-(4-bromo-2,5-dichlorophenyl) *O,O*-dimethyl phosphorothioate]; that of Birlane is chlorfenvinphos [2-chloro-1-(2,4-dichlorophenyl)vinyl diethyl phosphate]; that of Dyfonate is fonofos [(\pm)-*O*-ethyl *S*-phenyl ethylphosphonodithioate]; that of Afalon Spezial is a mixture of linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] and monolinuron [3-(4-chlorophenyl)-1-methoxy-1-methylurea]; that of Dosanex is metoxuron [3-(3-chloro-4-methoxyphenyl)-1,1-dimethylurea]; the total carotene content was increased by the three insecticides, did not vary significantly with

Afalon S, and decreased with Dosanex.

The free sugars in the carrots are important compounds for their flavor quality (Alabran and Mabrouk, 1973). To our knowledge, there is no paper describing the influence of the pesticide treatments on the free sugars concentrations in carrots. The present work reports the concentrations of each of the free sugars in the early and in the summer carrots which were grown in soil treated with one of the five pesticides and in which the total carotene content was previously analyzed (Rouchaud et al., 1982a,b).

Exploratory analysis of the free sugars according to the method of Alabran and Mabrouk (1973) realized completely indicated that fructose, α - and β -glucose, and sucrose represented about 90-95% of the total of free sugars in the carrots analyzed here; for that reason, these sugars alone were searched by the routine analysis of the samples.

EXPERIMENTAL SECTION

Culture and Treatment of the Carrots. Early and summer carrot cultures were made at the Research Station for Vegetables, St-Katelijne-Waver, Belgium.

For the early culture, 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

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emulsion contained 3% by weight of Birlane WP. Birlane WP is the commercial formulation that contains 25% by weight of chlorfenvinphos and which was obtained from Belgian Shell. 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 (Amsterdamsche Zoete Bak variety) were sown mechanically by means of pill-shaped coated seeds (Nunhems Zaden, B.V., Haelen, The Netherlands; 400 pills/m²; 12 cm of space between the rows). A part of the carrots then was immediately covered with a perforated polyethylene sheet (30 μ m thick; 500 perforations of 1 cm in diameter per m²), and the sheeting was removed at May 5, 1981.

For the summer carrots, the soil was treated with one of the following pesticides at the recommended rate: Nexion Emulsion 40 (formulation containing 370 g of bromophos/L and which was obtained from SBA, Belgium) was used at the dose of 100 mL of Nexion Emulsion 40/are; Birlane WP was used at the dose of 160 g of Birlane WP/are; Dyfonate 25 (formulation containing 25% by weight of fonofos and which was obtained from Liro-Belgium) was used at the dose of 80 g of Dyfonate 25/are; Afalon Spezial (formulation containing 23.75% by weight of linuron and 23.75% by weight of monolinuron and which was obtained from Hoechst Belgium) was used at the dose of 10 g of Afalon Spezial/are; Dosanex WP (formulation containing 80% by weight of metoxuron and which was obtained from Belgian Shell) was used at the dose of 40 g of Dosanex/are. The treatment was made according to the same technique as with the early carrots. One day after the soil treatment, the summer carrots were sown on July 1, 1981 (same carrot variety and sowing technique as with the early carrots). The summer carrots were not covered with a plastic sheet.

All experiments were arranged in a randomized block design; there were plots of control (untreated soil) and of each treatment (the early carrots being treated with Birlane either at the normal or at the exaggerated ratios and being covered or not with a plastic film; the summer carrots being treated with one of the pesticides at the normal rate). There were four plots (four replications) for each of the cultural conditions. The size of each plot was 1.3 m \times 10.0 m. At harvest, samples were collected at random from each plot. Each sample was made up of about 50 carrots which were washed in running water and dried by blotting with paper towels, and the crowns and tips were discarded. Weighing of the roots gave the mean root fresh weight for the sample; 20 roots were taken at random in the sample and diced, and the small pieces were mixed; about 15 g of the mixture was taken for dry weight measurement of the carrots from the sample; 100 g of the mixture was taken for extraction and free sugar measurement of the carrots from the sample.

At each harvest, no insect attack at all was observed on the carrots harvested from each of both the treated and the untreated soils. When harvested, the carrots were stored at 4 $^{\circ}$ C for 2–4 days before analysis.

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 m³ 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 P₂O₅; potassium, 0.8% as K₂O;

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 K₂O; water-soluble magnesium, 10% as MgO); 3 kg/are NPK 12+12+17 plus [BASF, West Germany; 12% of nitrogen (5.1% of nitric and 6.9% of ammonium nitrogen); phosphorus, 12% as P₂O₅; potassium, 17% as K₂O; sulfur, 16% as SO₃]; 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 P₂O₅; potassium, 8% as K₂O].

Analysis of the Free Sugars. For exploratory analysis, the free sugars were analysed according to the method of Alabran and Mabrouk (1973) realized completely, and including the ion-exchange liquid column chromatography for separation of free sugars and sugar phosphates. The free sugars usually found in plants (among which was maltose) were searched by gas chromatography (GC) of the silylated samples from carrots. Fructose, α - and β -glucoses, and sucrose represented 90–95% of the free sugars in the carrots analyzed here; only traces of other sugars and unknown were observed. For that reason these four sugars alone were searched by means of the simplified procedure for routine analysis which was the following.

One sample was made up of 20 roots of carrots which were diced, the small pieces were mixed, and 100 g of the mixture were taken for extraction in a Sorvall omnimixer (5 min, 8000 rpm) with about 380 mL of cooled 95% ethanol to obtain an 80% ethanol solution by volume. One gram of calcium carbonate then was added to the mixture to neutralize organic acids, thus minimizing sugar hydrolysis; the mixture was boiled for 30 min to inactivate the enzymes and filtered, and 95% ethanol was added to restore the initial volume. The solid residue was extracted overnight with 350 mL of 80% ethanol in a Soxhlet apparatus. The ethanol extracts were combined and concentrated to about 110 mL under vacuum at 40 $^{\circ}$ C in a rotavapor.

To an aliquot of 0.2 mL of this concentrate were added 4 mL of benzene and 2 mL of absolute ethanol; the mixture was evaporated to dryness at 40 $^{\circ}$ C under a flow of nitrogen. To the dry residue were successively added 1 mL of dry pyridine (dried on potassium hydroxide), 1 mL of hexamethyldisilazane (HMDS), and 0.1 mL of trifluoroacetic acid. The mixture was shaken by hand and heated at 60 $^{\circ}$ C for 3 min to obtain complete dissolution, and an aliquot of 5 μ L was injected in the Varian 2700 gas chromatograph (flame ionization detector; 3.2 m \times 2 mm i.d. glass column containing 3% SE-52 on 80–100-mesh Gas-Chrom Q; 60 mL/min of nitrogen as the carrier gas; column oven programmed from 150 to 250 $^{\circ}$ C at 2 $^{\circ}$ C/min; injector temperature, 225 $^{\circ}$ C; detector temperature, 240 $^{\circ}$ C). Retention times were as follows (minutes): fructose, 13.8; α -glucose, 17.6; β -glucose, 21.0; internal standard (mioinositol), 26.0; sucrose, 47.4.

Calibration curves for GC were made by silylation of aliquots from standard solutions of the pure separate sugars and of the mixed pure sugars.

For recovery studies, one sample of diced carrot sample was divided into several parts before extraction; to each part, an increasing amount of pure sugar was added, the amounts being chosen in order to cover the amounts observed in the routine analyses of the carrot samples. Then complete analysis of each part gave the recovery for each sugar: fructose, 91–102%; α -glucose, 85–101%; β -glucose, 80–96%; sucrose, 88–105%.

Table I. Concentration of Free Sugars in Early Carrots

harvest date (year 1981)	g of sugar in 100 g of fresh carrot ^b for soil treatment					
	carrots covered with plastic film			uncovered carrots		
	control (untreated soil)	treated soil, g of Birlane WP/are		control (untreated soil)	treated soil, g of Birlane WP/are	
		160 (normal dose) ^a	1600 (exaggerated dose) ^a		160 (normal dose) ^a	1600 (exaggerated dose) ^a
Fructose						
5-25	1.10 ± 0.05	1.24 ± 0.04	1.08 ± 0.04			
6-3	1.09 ± 0.04	1.08 ± 0.05	1.12 ± 0.05	1.03 ± 0.05	1.09 ± 0.05	1.04 ± 0.04
6-10	0.96 ± 0.05	1.11 ± 0.05	1.00 ± 0.03	0.89 ± 0.05	1.11 ± 0.05	0.93 ± 0.05
6-17	0.90 ± 0.03	0.96 ± 0.05	0.96 ± 0.05	0.92 ± 0.05	0.96 ± 0.04	0.97 ± 0.04
6-24	0.93 ± 0.04	0.97 ± 0.05	1.03 ± 0.05	0.75 ± 0.03	0.95 ± 0.04	0.87 ± 0.04
7-1	0.80 ± 0.05	0.90 ± 0.04	0.91 ± 0.05	0.79 ± 0.04	0.78 ± 0.03	0.88 ± 0.04
7-8	0.84 ± 0.04	0.88 ± 0.04	0.98 ± 0.05	0.68 ± 0.03	0.77 ± 0.04	0.79 ± 0.04
Sum of α- and β-Glucose						
5-25	1.81 ± 0.08	1.84 ± 0.09	1.97 ± 0.08			
5-3	1.62 ± 0.07	1.80 ± 0.07	1.81 ± 0.08	1.58 ± 0.08	1.91 ± 0.09	2.07 ± 0.09
6-10	1.62 ± 0.07	1.78 ± 0.08	1.79 ± 0.08	1.51 ± 0.07	1.84 ± 0.08	1.76 ± 0.08
6-17	1.45 ± 0.07	1.60 ± 0.07	1.72 ± 0.07	1.29 ± 0.05	1.49 ± 0.06	1.67 ± 0.07
6-24	1.43 ± 0.06	1.64 ± 0.07	1.55 ± 0.07	1.24 ± 0.06	1.41 ± 0.06	1.34 ± 0.07
7-1	1.39 ± 0.06	1.45 ± 0.06	1.50 ± 0.07	1.10 ± 0.04	1.11 ± 0.05	1.25 ± 0.06
7-8	1.25 ± 0.05	1.45 ± 0.06	1.41 ± 0.06	0.83 ± 0.04	1.05 ± 0.05	0.95 ± 0.04
Sucrose						
5-25	1.09 ± 0.05	1.20 ± 0.05	1.36 ± 0.06			
6-3	1.45 ± 0.07	1.61 ± 0.07	1.44 ± 0.06	1.71 ± 0.08	1.87 ± 0.08	1.78 ± 0.08
6-10	1.57 ± 0.08	1.70 ± 0.07	1.82 ± 0.08	2.07 ± 0.09	2.31 ± 0.10	2.24 ± 0.10
6-17	1.93 ± 0.09	2.11 ± 0.09	1.91 ± 0.09	2.15 ± 0.09	2.51 ± 0.12	2.36 ± 0.11
6-24	2.04 ± 0.09	2.23 ± 0.10	2.34 ± 0.10	2.60 ± 0.12	3.00 ± 0.15	2.82 ± 0.12
7-1	2.43 ± 0.10	2.59 ± 0.10	2.40 ± 0.11	2.65 ± 0.11	3.20 ± 0.12	2.98 ± 0.14
7-8	2.52 ± 0.11	2.74 ± 0.11	2.80 ± 0.12	3.11 ± 0.12	3.68 ± 0.15	3.45 ± 0.15
Total						
5-25	4.00 ± 0.08	4.28 ± 0.13	4.40 ± 0.14			
6-3	4.16 ± 0.12	4.49 ± 0.09	4.37 ± 0.13	4.32 ± 0.20	4.86 ± 0.07	4.89 ± 0.11
6-10	4.15 ± 0.07	4.59 ± 0.12	4.60 ± 0.09	4.47 ± 0.12	5.26 ± 0.05	4.92 ± 0.06
6-17	4.28 ± 0.15	4.67 ± 0.20	4.60 ± 0.12	4.35 ± 0.08	4.96 ± 0.14	4.99 ± 0.21
6-24	4.40 ± 0.12	4.83 ± 0.17	4.91 ± 0.09	4.58 ± 0.14	5.36 ± 0.18	5.03 ± 0.06
7-1	4.62 ± 0.12	4.95 ± 0.22	4.81 ± 0.15	4.54 ± 0.11	5.09 ± 0.04	5.11 ± 0.20
7-8	4.61 ± 0.06	5.06 ± 0.20	5.19 ± 0.07	4.62 ± 0.08	5.50 ± 0.21	5.18 ± 0.14

^a Concentrations significantly different from that of control at the 1% level when the comparison, made for each of the sugars and their total, includes the seven harvests for the carrots grown covered and the six harvests for the carrots grown uncovered. ^b Data are the means (±SD) for four replications for each of the pesticide treatment dose and the controls.

Several silylated samples from carrots were analyzed by using the combined Varian 3700 gas chromatograph and the Varian MAT 44S mass spectrometer; the mass spectra of the gas chromatograph peaks of each of the sugars indicated that no contaminant cochromatographed with each of the silylated sugar; this was seen by comparison with the mass spectra of the corresponding GC peaks of each of the pure silylated sugars.

For the statistical analysis of the results, differences between means were tested for significance by application of the T method (method of Tukey) (Scheffé, 1959).

RESULTS

The unitary mean fresh weights and percentages of dry matter of the roots of the carrots did not vary according to the pesticide treatments of the early and of the summer carrot cultures.

For the early carrots grown uncovered, the mean unitary fresh weights of the roots at the harvest of 6-3, 6-10, 6-17, 6-24, 7-1, and 7-8, respectively, were 11, 14, 18, 18, 19, and 20 g; they were slightly higher for the covered culture, the corresponding weights being 14, 18, 22, 24, 25, and 27 g. For the summer carrots, the mean unitary fresh weights of the root at the harvests of 8-24, 8-31, 9-7, 9-14, 9-21, 9-28, and 10-5, respectively, were 17, 32, 51, 70, 88, 108, and 126 g.

For both the early carrots grown covered and uncovered, the percentage of dry matter of the root at the harvests

of 6-3, 6-10, and 6-17 were respectively 15, 18, and 19; these percentages were about 20 at the three latest harvests. For the summer carrots, the percentages of dry matter were about 20 at all the harvests.

For all the assays, the ratio of α-/β-glucose was approximately constant (~0.77). For that reason it is the sums of the α- and β-glucoses which are reported here.

Early Carrots. From one harvest to the other, the concentrations of fructose and glucoses (the sum of the α- and β-glucoses) decreased, and the concentrations of sucrose and of the total of the free sugars increased (Table I). Soil treatment with the insecticide Birlane increased, relatively to the control (the untreated soil), the concentrations of fructose, glucoses (the sum of the α- and β-glucoses), sucrose, and the total of the free sugars in the early carrots grown uncovered or covered.

For the early carrots grown uncovered in a soil treated by a normal dose of Birlane, the mean increases, relative to that of the control, of the concentrations of fructose, of the sum of the glucoses, of sucrose, and of the total of the free sugars, respectively, were 12, 18, 16, and 15%. For the carrots grown uncovered in a soil treated by a 10 times exaggerated dose of Birlane, these mean increases respectively were 9, 18, 9, and 12%.

For the early carrots grown covered, the normal and exaggerated doses of Birlane gave similar increases, relative to that of the control, of the concentrations of each of the free sugars and of the total of them. The mean increases

Table II. Concentration of Free Sugars in Summer Carrots

harvest date (year 1981)	g of sugar in 100 g of fresh carrot ^d for soil treatment					
	control	Dyfonate	Birlane	Nexion	Afalon S	Dosanex
	Fructose					
8-24	1.48 ± 0.04	1.60 ± 0.07 ^c	1.69 ± 0.07 ^a	1.66 ± 0.07 ^a	1.37 ± 0.06 ^c	1.45 ± 0.06 ^a
8-31	1.33 ± 0.04	1.45 ± 0.07 ^c	1.51 ± 0.07 ^a	1.55 ± 0.07 ^a	1.43 ± 0.06 ^c	1.34 ± 0.06 ^a
9-7	1.29 ± 0.05	1.28 ± 0.06 ^c	1.40 ± 0.06 ^a	1.45 ± 0.06 ^a	1.29 ± 0.05 ^c	1.28 ± 0.04 ^a
9-14	1.04 ± 0.05	1.20 ± 0.05 ^c	1.14 ± 0.04 ^a	1.18 ± 0.05 ^a	1.06 ± 0.05 ^c	1.09 ± 0.04 ^a
9-21	0.99 ± 0.04	0.89 ± 0.05 ^c	1.02 ± 0.04 ^a	1.08 ± 0.05 ^a	0.94 ± 0.05 ^c	1.06 ± 0.05 ^a
9-28	0.72 ± 0.05	0.79 ± 0.03 ^c	0.72 ± 0.02 ^a	0.80 ± 0.03 ^a	0.88 ± 0.03 ^c	0.81 ± 0.04 ^a
10-5	0.64 ± 0.04	0.52 ± 0.03 ^c	0.64 ± 0.03 ^a	0.71 ± 0.04 ^a	0.67 ± 0.03 ^c	0.79 ± 0.04 ^a
	Sum of α- and β-Glucose					
8-24	2.40 ± 0.11	2.54 ± 0.09 ^a	2.88 ± 0.10 ^a	2.93 ± 0.09 ^a	2.18 ± 0.09 ^a	2.17 ± 0.10 ^b
8-31	2.20 ± 0.13	2.58 ± 0.08 ^a	2.63 ± 0.09 ^a	2.69 ± 0.09 ^a	2.33 ± 0.09 ^a	2.02 ± 0.08 ^b
9-7	2.10 ± 0.08	2.12 ± 0.07 ^a	2.46 ± 0.07 ^a	2.34 ± 0.09 ^a	1.99 ± 0.07 ^a	1.93 ± 0.09 ^b
9-14	1.69 ± 0.08	1.92 ± 0.08 ^a	2.03 ± 0.10 ^a	2.12 ± 0.09 ^a	1.88 ± 0.09 ^a	1.72 ± 0.09 ^b
9-21	1.44 ± 0.06	1.49 ± 0.07 ^a	1.81 ± 0.08 ^a	1.69 ± 0.07 ^a	1.56 ± 0.06 ^a	1.41 ± 0.05 ^b
9-28	1.32 ± 0.06	1.29 ± 0.05 ^a	1.35 ± 0.06 ^a	1.23 ± 0.05 ^a	1.50 ± 0.06 ^a	1.35 ± 0.06 ^b
10-5	0.90 ± 0.04	0.84 ± 0.04 ^a	1.16 ± 0.05 ^a	0.87 ± 0.04 ^a	1.12 ± 0.04 ^a	1.03 ± 0.05 ^b
	Sucrose					
8-24	1.43 ± 0.10	1.63 ± 0.09 ^a	1.54 ± 0.06 ^a	1.55 ± 0.08 ^a	1.36 ± 0.07 ^a	1.30 ± 0.05 ^a
8-31	1.54 ± 0.11	1.80 ± 0.06 ^a	1.83 ± 0.08 ^a	1.72 ± 0.08 ^a	1.47 ± 0.04 ^a	1.45 ± 0.07 ^a
9-7	1.82 ± 0.06	1.94 ± 0.07 ^a	1.89 ± 0.07 ^a	2.04 ± 0.09 ^a	1.72 ± 0.07 ^a	1.42 ± 0.06 ^a
9-14	1.85 ± 0.04	2.23 ± 0.10 ^a	2.21 ± 0.09 ^a	2.25 ± 0.08 ^a	1.75 ± 0.06 ^a	1.58 ± 0.05 ^a
9-21	2.08 ± 0.07	2.24 ± 0.09 ^a	2.27 ± 0.08 ^a	2.26 ± 0.07 ^a	1.96 ± 0.09 ^a	1.49 ± 0.05 ^a
9-28	2.10 ± 0.07	2.55 ± 0.07 ^a	2.58 ± 0.08 ^a	2.64 ± 0.10 ^a	1.98 ± 0.09 ^a	1.64 ± 0.06 ^a
10-5	2.34 ± 0.07	2.54 ± 0.09 ^a	2.61 ± 0.09 ^a	2.77 ± 0.09 ^a	2.24 ± 0.09 ^a	1.60 ± 0.07 ^a
	Total					
8-24	5.32 ± 0.21	5.76 ± 0.12 ^a	6.10 ± 0.19 ^a	6.14 ± 0.22 ^a	4.91 ± 0.10 ^c	4.91 ± 0.08 ^a
8-31	5.06 ± 0.21	5.83 ± 0.14 ^a	5.97 ± 0.10 ^a	5.95 ± 0.21 ^a	5.22 ± 0.13 ^c	4.81 ± 0.08 ^a
9-7	5.20 ± 0.17	5.34 ± 0.07 ^a	5.75 ± 0.08 ^a	5.83 ± 0.12 ^a	4.99 ± 0.15 ^c	4.63 ± 0.15 ^a
9-14	4.58 ± 0.12	5.35 ± 0.15 ^a	5.37 ± 0.16 ^a	5.55 ± 0.15 ^a	4.69 ± 0.07 ^c	4.38 ± 0.08 ^a
9-21	4.51 ± 0.11	4.61 ± 0.11 ^a	5.10 ± 0.19 ^a	5.04 ± 0.15 ^a	4.46 ± 0.09 ^c	3.96 ± 0.07 ^a
9-28	4.13 ± 0.12	4.63 ± 0.07 ^a	4.64 ± 0.12 ^a	4.67 ± 0.10 ^a	4.36 ± 0.09 ^c	3.79 ± 0.12 ^a
10-5	3.88 ± 0.13	3.89 ± 0.14 ^a	4.40 ± 0.10 ^a	4.35 ± 0.13 ^a	4.02 ± 0.09 ^c	3.41 ± 0.06 ^a

^a Concentrations significantly different from that of the control at the 1% level when the comparison, made for each of the sugars and their total, includes the seven harvests for the carrots grown in each of the treated soils and the control.

^b Concentrations significantly different from that of the control at 5% level when the comparison, made for each of the sugars and their total, includes the seven harvests for the carrots grown in each of the treated soils and the control. ^c Concentrations not significantly different from that of the control when the comparison, made for each of the sugars and their total, includes the seven harvests for the carrots grown in each of the treated soils and the control. ^d Data are the means (±SD) for four replications for each of the pesticide treatment dose and the controls.

of the concentrations of fructose, of the sum of the glucoses, of sucrose, and of the total of free sugars, respectively, were 7, 9, 9, and 9%. The positive effect of the soil treatment with Birlane thus was lower when the culture was covered then when it was uncovered. The reverse was observed with the concentration of total carotene: the positive effect of the treatment with Birlane on the total concentration of carotene was higher when the culture was covered (Rouchaud et al., 1982a,b).

Summer Carrots. From one harvest to the other, the concentrations of fructose, of the sum of the glucoses, and of the total of the free sugars decreased, whereas the concentrations of sucrose increased (Table II).

The soil treatment with one of the assayed insecticides or herbicides generally changed, relative to the control (the untreated soil), the concentrations in the summer carrots of each of the free sugars and of their totals.

Soil treatment with the insecticide Dyfonate or with the herbicide Afalon S did not change, relative to the control, the concentrations of fructose. Soil treatment with one of the insecticides Birlane or Nexion or with the herbicide Dosanex increased the concentrations of fructose mainly by respectively 8, 12, and 5%.

Soil treatment with one of the insecticides Dyfonate, Birlane, or Nexion or by the herbicide Afalon S increased, relative to the control, the concentration of the sum of glucoses mainly by respectively 6, 19, 15, and 4%; soil treatment with the herbicide Dosanex decreased by con-

centrations of the sum of glucoses mainly by 3%.

Soil treatment with one of the insecticides Dyfonate, Birlane, or Nexion increased, relative to the control, the concentration of sucrose mainly by respectively 13, 13, and 16%; soil treatment with one of the herbicides Afalon S or Dosanex decreased the concentration of sucrose mainly by respectively 5 and 20%.

Soil treatment with the herbicide Afalon S had no influence, relative to the control, on the concentrations of the total of free sugars; soil treatment with one of the insecticides Dyfonate, Birlane, or Nexion increased the concentrations of the total of free sugars mainly by respectively 8, 14, and 15%; treatment with the herbicide Dosanex decreased the concentrations in the total of free sugars mainly by 9%.

DISCUSSION

The insecticides Dyfonate, Birlane, and Nexion and the herbicides Afalon S and Dosanex change, relative to the control (the carrots grown in untreated soil), in the same direction the concentrations of total carotene and of each of the free sugars in the carrot grown in soil treated with one of these pesticides (Rouchaud et al., 1982a,b). However, with the early carrots the increase, through the treatment with Birlane, of each of the sugar concentrations was higher when the culture was uncovered then when it was covered; the reverse was observed with the total carotene concentrations.

The unexpected effects of the pesticide treatments, relative to that of the control, were not uniform for each of the free sugars. When there was an increase of the concentrations of each of the sugars, that increase was higher for the glucoses and sucrose than for fructose. When the pesticide treatment decreased the sugar concentrations, it was the concentration of sucrose which was the most diminished. The pesticide treatment thus not only changed the concentration of the total of the free sugars but also changed their distribution. As each sugar has its own sweetening power and taste, the pesticide treatment thus could change the taste and thus the quality of the carrot.

Speculations only can be made about the effects observed here of the pesticides on the free sugar concentrations in the carrots. Some remarks, however, may be made.

The active matter of Dosanex is the urea herbicide metoxuron which, like many ureas, inhibits the plant photosynthesis (Corbett, 1974). This could explain the general negative effect of Dosanex on the sugar concentrations.

On the other hand, one knows that the carotenoids contribute to the plant photosynthetic procedures; in photosynthesis, the carotenoids absorb light of wavelengths not absorbed by chlorophylls and pass the energy on to chlorophyll and also protect cell against photosensitized oxidations which otherwise prove lethal to the plant. The functional relationship between sugar photosynthesis and the carotenoids could explain the same direction observed for the pesticide effects on the total carotene and free sugar concentrations (Rouchaud et al., 1982a,b).

The active matters of Dyfonate, Nexion, and Birlane, respectively, are fonofos, bromophos, and chlorfenvinphos, which all are organophosphorus insecticides working on the target insect by inhibiting the acetylcholinesterase. At our knowledge, nothing so far has been reported about the influence of these insecticides, or of their metabolites in

the plant, on the plant sugars and carotenoids syntheses. One remarks, however, that bromophos and chlorfenvinphos have halogenated benzene rings similar to the ones of compounds that interfere with plant growth, like 2,4-D (Thimann, 1951). According to the chemical structure of fonofos, one may speculate that by metabolism in plant it could, proceeding from its ethyl groups, generate ethylene which also is a plant growth regulator.

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Registry No. Birlane, 470-90-6; nexion, 2104-96-3; dyfonate, 944-22-9; afalon spezial, 8000-65-5; dosanex, 19937-59-8; fructose, 57-48-7; sucrose, 57-50-1; α -glucose, 492-62-6; β -glucose, 492-61-5.

LITERATURE CITED

- Alabran, D. M.; Mabrouk, A. F. *J. Agric. Food Chem.* 1973, 21, 205.
 Corbett, J. R. "The Biochemical Mode of Action of Pesticides"; Academic Press: New York, 1974; p 64.
 Rouchaud, J.; Moons, C.; Meyer, J. A. *J. Agric. Food Chem.* 1982a, 30, 1036.
 Rouchaud, J.; Moons, C.; Meyer, J. A. *Sci. Hortic. (Canterbury, Engl.)* 1982b, in press.
 Scheffé, H. "The Analysis of Variance"; Wiley: New York, 1959; p 73.
 Sweeney, J. P.; Marsh, A. C. *J. Agric. Food Chem.* 1971, 19, 854.
 Thimann, K. V. "Plant Growth Substances"; Skoog, F., Ed.; University of Wisconsin Press: Madison, WI, 1951; pp 21-36.

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Comparative Volatilization and Dissipation Rates of Several Pesticides from Soil

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The volatilization and soil dissipation rates of heptachlor, trifluralin, lindane, heptachlor epoxide, *cis*- and *trans*-chlordane, dieldrin, endrin, DDT, and the isooctyl and propylene glycol butyl ether esters of 2,4-D and 2,4,5-T from fallow soil in microagroecosystem chambers were compared. Volatilization rates of surface-applied pesticides depended upon the vapor pressure of the pesticide. However, changes in volatilization rates immediately after application were nearly the same (ca. 8 h to decline by half) for all pesticides. Volatilization of the higher vapor pressure pesticides (heptachlor, trifluralin, and lindane) was high initially ($>30 \text{ g ha}^{-1} \text{ day}^{-1}$) and decreased rapidly with time, while volatilization of the lower vapor pressure pesticides (dieldrin, endrin, and DDT) was lower initially ($<10 \text{ g ha}^{-1} \text{ day}^{-1}$) and decreased slowly. Both vapor pressure classes were volatilizing at nearly the same rate (ca. $5 \text{ g ha}^{-1} \text{ day}^{-1}$) on day 9, because the amount of pesticide left on the soil surface was about 10% for the volatile pesticides and $>50\%$ for the less volatile pesticides.

Volatilization is a major dissipation route for many pesticides used in agriculture (Caro and Taylor, 1971; Cliath and Spencer, 1971; Farmer et al., 1972, 1973; Gile

et al., 1980; Harper et al., 1976; Nash and Beall, 1970; Nash et al., 1977; Nash and Woolson, 1968; Spencer and Cliath, 1970, 1972, 1973, 1974, 1975, 1976; Spencer and Farmer, 1980; Spencer et al., 1969, 1973; Taylor et al., 1976, 1977; White et al., 1977; Willis et al., 1971, 1972, 1980). Volatilization seems particularly important for the low vapor pressure, persistent pesticides, such as the chlorinated hydrocarbon insecticides, primarily because small pesticide

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