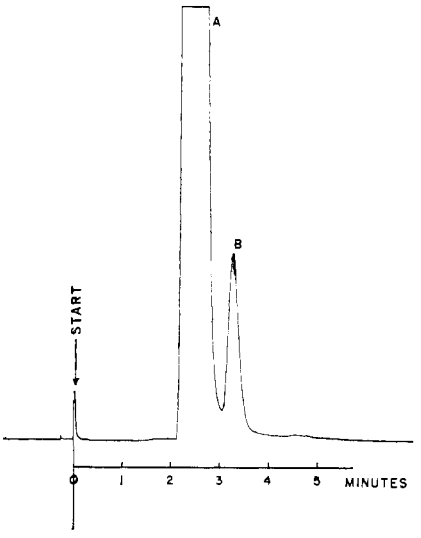

Figure 1. Chromatogram of phosphine, 1.5 mg. per liter in air, using thermistor detector at 1-mv. sensitivity
Sample size: 0.25 ml.; peaks: A, air and carbon dioxide; B, phosphine

injected into the instrument. The sample size was 0.05 ml. for about 10 mg. of PH_3 per liter of air, 0.25 ml. for about 2 mg. per liter of air, and 1 ml. for below 0.5 mg. per liter of air.

The amount of phosphine represented by the area under the curve obtained by gas chromatography was determined as follows. Gas samples were drawn into special evacuated flasks (*1*) of 230 ml. volume. The flasks were then connected to the fumigation chamber through two gas-washing bottles, one filled with 20% H_2SO_4 solution and the other with 20% NaOH solution. In this way, the ammonia and carbon dioxide produced with phosphine from Phostoxin tablets was eliminated. Each

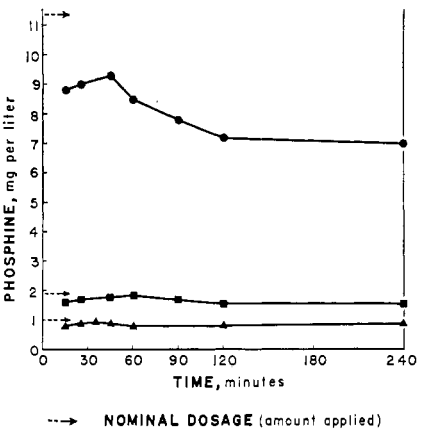

Figure 2. Phosphine concentration during fumigation

flask had an outlet with a rubber septum so that a small gas sample could be withdrawn for the analysis by gas chromatography. The remaining gas in the flask was analyzed by the White and Bushey method (*5*), which was considered satisfactory as a standard for comparative purposes at the concentration of 10 mg. of PH_3 per liter of air. In this method, phosphine was reacted with mercuric chloride, and the resulting HCl was titrated by standard NaOH solution.

Results and Discussion

When the sample was introduced into the gas chromatograph, the retention time for phosphine was 3 minutes and 21 seconds, for carbon dioxide 2 minutes and 42 seconds, and for air 2 minutes and 28 seconds. For very low concentrations of phosphine in air, the carbon dioxide peak does not separate from the air peak. Figure 1 shows a gas chromatogram of a 0.25-ml. gas sample of 1.5 mg. of PH_3 per liter of air. In this experiment, the standard deviation for seven consecutive determinations was 0.05. This shows that this method is very accurate even at low concentrations of fumigant.

The concentrations of phosphine determined during a 2-hour fumigation experiment at nominal dosage (initial amount applied) of 11.4, 1.9, and 1 mg. of PH_3 per liter of air, assuming 1 gram phosphine per tablet of Phostoxin, are shown in Figure 2.

These results indicate that analysis of phosphine by gas chromatography gives good separation of this compound from air in the presence of other contaminants such as ammonia and carbon dioxide, which might be encountered in fumigation practice.

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INSECT ATTRACTANTS

tert-Butyl and *tert*-Pentyl Esters of 6-Methyl-3-cyclohexene-1-carboxylic Acid as Attractants for the Mediterranean Fruit Fly

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GERTLER *et al.* (*3*) reported on the synthesis of 31 esters of 6-methyl-3-cyclohexene-1-carboxylic acid that were tested as attractants for the Mediterranean fruit fly [*Ceratitis capitata* (Weidemann)]. The *sec*-butyl ester, known as siglure, played an important role in the eradication of an infestation of the insect from the state of Florida in 1957.

Table I. Physical and Chemical Data for the *tert*-Butyl and *tert*-Pentyl Esters of 6-Methyl-3-cyclohexene-1-carboxylic Acid

Ester	Boiling Point, ° C./mm. Hg	n_D^{25}	Carbon		Hydrogen		Yield, %
			Calcd.	Found	Calcd.	Found	
tert-Butyl	99/14	1.4445	73.43	73.58	10.27	10.38	65
tert-Pentyl	114–115/12	1.4503	74.24	74.17	10.54	10.38	79

Previous preparations of the titled compounds did not have the structures represented and were inactive as lures for the medfly *Ceratitis capitata* (Weidemann). The compounds now prepared have the proper structures and are very attractive to the medfly.

Table II. Number of Flies Attracted by *tert*-Butyl and *tert*-Pentyl Esters of 6-Methyl-3-cyclohexene-1-carboxylic Acid, Siglure, and Trimedlure

	Olfactometer Data (1)							
		Wick test[c]			Field Tests[a]			
Attractant	Trap test[b]	Fresh	1 Day	4 Days	7 Days	1st Wk.	2nd Wk.	3rd Wk.	Total
Siglure	1535	370	300	30	5	...	...	...	...
tert-Butyl ester	2362	480	430	5	0	3417	971	84	4472
tert-Pentyl ester	1820	425	330	150	100	2730	1472	2785	6987
Trimedlure	...	530	470	250	500	2986	2281	4462	9729

[a] Seven replicates of Steiner traps with 3 ml. of attractant on wick per trap. [b] Glass trap containing 50 ml. of 0.1% emulsion. [c] Wicks with 0.5 ml. of attractant.

The authors' attention was recently directed to a large difference between the boiling point of the *tert*-butyl ester of the series and that of the other butyl isomers (*4*). Furthermore, the refractive index of the *tert*-butyl ester appeared to be incorrect. Large differences were also noted between the physical constants of the *tert*-pentyl ester and its isomers (boiling point and refractive index). An infrared spectrum of these two preparations, which were still available, disclosed that they were not the compounds supposed. Neither of the preparations was attractive.

The compounds were synthesized by reacting the acid chloride with the appropriate alcohol in the presence of pyridine. The physical and chemical data are given in Table I.

The new constants agree with isomeric data, and the infrared spectra are consistent with the proper structures. Furthermore, the new compounds are highly attractive; they exceed the attractiveness of siglure in olfactometer trap and wick tests (*1*), the *tert*-pentyl ester being the more attractive of the two. In field tests, however, the *tert*-pentyl ester was not as attractive as trimedlure [*tert*-butyl *trans*-4(or 5)-chloro-2-methylcyclohexanecarboxylate] (*2*), the hydrochlorinated analog of the *tert*-butyl ester of the siglure series. Trimedlure is the best lure found thus far for the Mediterranean fruit fly.

The most attractive esters of the *trans*-4(or 5)-chloro-2-methylcyclohexanecarboxylic acid (trimedlure series) possess an alcohol moiety with branching in the 1 position (*2*)—i.e., isopropyl, *tert*-pentyl, *sec*-butyl, *tert*-butyl. Now that the two new esters have been shown to be attractive, this statement may be broadened to include the esters of 6-methyl-3-cyclohexene-1-carboxylic acid (siglure series).

Biological data are summarized in Table II. Field tests were run in coffee-growing areas on the southwest coast of Hawaii at an altitude of approximately 1500 feet where the temperature range was 52° to 82° F.

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DIGESTION IN INSECTS

Colorimetric Analysis of Chromic Oxide Used to Study Food Utilization by Phytophagous Insects

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THE PERCENTAGE utilization of diets by animals can be calculated from measurements of food consumed and excreta passed. This procedure has been used with insects (*8, 13*), but is too cumbersome for routine measurement of food utilization. Another method that has been used extensively with higher animals employs an indigestible index compound that is incorporated into the diet. The percentage utilization is calculated from the concentrations of the index compound in the food and the excreta. Although iron oxide, barium sulfate, and lignin have been used as index compounds with higher animals, chromic oxide (Cr_2O_3) is used most extensively (*4, 6, 7, 12*). The index method using Cr_2O_3 would be of value for measuring food utilization by insects. However, the methods for analysis of Cr_2O_3 used with laboratory and farm animals are not sensitive enough for the small quantities that would be present in either food or excreta of individual insects. Therefore, to use Cr_2O_3 as the index compound for studies of food utilization by insects it was necessary to develop a suitable method of analysis. This paper describes a procedure which was satisfactory for the determination of Cr_2O_3 in food and excreta of phytophagous insects.

Materials and Methods

The method developed consists of a wet oxidation of Cr_2O_3 to $Cr_2O_7^{-2}$ (*2*), followed by colorimetric determination of the dichromate ion with diphenylcarbazide (*15*). Other methods, with and without modification, were