relatively slow compared to the effect observed in commercial practice when tomato fruit is macerated in the production of tomato juice products (*2*, *3*). However, the increased free acidity and high concentration of other constituents in tomato paste as compared to a tomato macerate strongly inhibit the activity of the pectic acid depolymerase.

Summary

It is not known that there is any standard of consistency in non-Newtonian media by which it is possible to prove conclusively the adequacy of any type of consistency measurement. Studies on consistency, therefore, must stand on inductive evidence and on the relations between objective determinations and subjective judgments. In this light, these studies are believed to indicate, so far as it is possible, that the viscometer and rotors employed as described measure consistencies in food purees and pastes with a good degree of accuracy and significance.

In the last analysis consistency, as it is related to food products, is a subjective quality. Therefore, no objective instrumental method of measuring consistency, regardless of reproducibility and accuracy, can be regarded as wholly satisfactory unless it can be shown to be correlated with subjective observations. Studies of factors affecting the consistency of tomato pastes, catsups, and purees, some of which are briefly outlined in this paper, indicate a very satisfactory correlation between the instrumental method described and subjective observations. In several cases where the authors have had the opportunity to measure the consistency of tomato paste samples which have also been judged by men long experienced in the manufacture of tomato products, they find that the instrumental determination agrees not only with the relative subjective assignments of consistencies but also with the relative orders of magnitude assigned to the differences.

Although the applications described are limited to tomato products, there is no reason to believe that consistency cannot be determined with equal satisfaction in other food purees and pastes. Preliminary studies have been made of the applicability of the instrument to such diverse materials as mashed potato, pureed baby foods, and fruit purees. The results obtained have been as promising, so far as they go, as the results obtained with tomato products. However, in the case of some products—mashed potato, for example—it is desirable to employ either a driving motor of smaller angular velocity or a smaller spiral rotor to measure the very high consistencies encountered. The range of measurable consistencies may also be extended to lower values by interchanging torque springs or by employing higher angular velocities.

Table III. Effect of Pectic Enzyme Action on Tomato Paste Consistency

Time, Min.	*Apparent Viscosity, Cps.*
Before Enzyme Addition	
0	3500
5	3400
30	3250
60	3150
75	3150
90	3150
After Enzyme Addition[a]	
0	3150
20	3250
30	3000
45	2900
60	2600
90	2355

[a] 2 ml. of concentrated preparation containing tomato pectin-methylesterase and pectic acid depolymerase.

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Literature Cited

(1) Bigelow, W. D., Smith, H. R., and Greenleaf, C. A., National Canners Association, *Bull.* 27-L rev. (1950).
(2) McColloch, R. J., and Kertesz, Z. I., *Food Technol.*, **3,** 94 (1949).
(3) McColloch, R. J., Nielsen, B. W., and Beavens, E. A., *Ibid.*, **4,** 339 (1950).
(4) Underwood, J. C., and Keller, G. J., *Fruit Products J.*, **28,** 103 (1948).

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CARBAMATE HERBICIDES

Relative Herbicidal and Growth-Modifying Activity of Several Esters of *N*-(3-Chlorophenyl)-carbamic Acid

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INVESTIGATIONS OF THE POTENTIAL UTILITY of the herbicidal and plant growth regulatory activity of derivatives of carbamic acid in the field of selective weed control during the past few years have revealed that two compounds of this class, isopropyl *N*-phenylcarbamate, IPC, and isopropyl *N*-(3-chlorophenyl)-carbamate, CIPC, show great promise as selective herbicides in a variety of crop plants. These compounds are being produced on an increasing commercial scale, especially for the control of annual weedy grasses in a variety of broad-leafed crops.

An earlier paper (*1*) reviewed the history of the development of carbamate herbicides and described the chemical properties and the preliminary results of the screening evaluations of the plant growth regulatory properties of a group of these compounds structurally related to isopropyl *N*-phenylcarbamate, the first of the commercial carbamate herbicides. The present paper describes, in a similar fashion, the chemical properties and the results of screening evaluation of a group of compounds closely related to the second commercial carbamate herbicide, iso-

As a result of growing interest in the potential herbicidal and plant growth regulatory activity of derivatives of carbamic acid, many types of substituted carbamates have been investigated. This paper describes a series of such carbamates analogous to the commercial herbicide, isopropyl N-(3-chlorophenyl)-carbamate (CIPC), in which various alterations have been made in the alkyl portion of the molecule. Chemical and physical properties, as well as results of preliminary screening evaluation of their herbicidal and plant growth regulatory activities, are reported. Relatively minor changes in this portion of the molecule can profoundly affect the biological activities of such compounds.

propyl *N*-(3-chlorophenyl)-carbamate. In the earlier publications of this series (*1*, *3*) and in the recent publications of others (*4*) both leading and specific references have been given to the discovery and initial studies of isopropyl *N*-(3 - chlorophenyl)-carbamate. Subsequent papers in this series will describe the preparation and chemical properties, as well as the results of screening evaluations of still other compounds of this general nature.

The present paper is concerned with 16 alkyl or substituted-alkyl esters of *N*-(3-chlorophenyl)-carbamic acid.

Chemical and Physical Properties

Even though some of the compounds discussed in this paper have not been described before in the chemical literature, the classical methods for carbamic acid derivatives have been used for their preparation, and for that reason only brief notes concerning these methods are included below. The major items of new chemical information concerning these compounds are physical property data, and these properties, along with product analyses and identifications of the methods of preparation, are tabulated in Table I.

Raw materials of the best quality readily available were used in these preparations and, although the primary emphasis was placed upon the isolation of pure products, the yields of reactions were normally satisfactory. Previous experience with these preparative methods has shown that by selection of appropriate reaction conditions excellent yields of the desired products can be obtained almost invariably.

With the exception of the two sodium salts, which are very soluble in water, slightly soluble in lower aliphatic alcohols, and insoluble in other common organic solvents, these compounds are soluble in aromatic hydrocarbons, lower aliphatic alcohols, ketones, ethers, and chlorinated hydrocarbons, only slightly soluble in aliphatic hydrocarbons, and insoluble in water. The crystalline compounds can usually be purified easily by recrystallization from aqueous alcohol, aqueous acetone, or benzene–petroleum ether solvent mixtures. Most of the liquid compounds, with the exceptions noted, may be purified by short-path high vacuum distillations. In such distillations it has been found desirable to complete the distillation as rapidly as possible at the lowest practical temperature and at the best vacuum obtainable, in order to minimize thermal decomposition.

Test Methods

The test method employed for the preliminary screening evaluation of the plant growth regulatory properties of chemicals of this type has been described (*1*, *3*). Although the same method has been used to obtain the results given in this paper, it is outlined below.

Briefly, the method consists of applying various chemicals at known rates of application as pre- or postemergence treatments to planted seeds or growing plants of various species, and at intervals thereafter examining these plants for differences in growth and development, as well as for any evidences of abnormal behavior. Attempts were made to select plant species which showed as wide a range of carbamate susceptibility as was possible, since it was considered as important to show species tolerances as to show species susceptibilities. The plants for a given test, usually eight in number, were selected from the species peas, cotton, soybeans, corn, rye grass, crabgrass, barley, wheat, and pigweed, and in most cases were the first eight of these.

Sand was used as a planting medium both to eliminate soil effects and to ensure conditions of maximum effectiveness for the chemicals being tested. Treatments were applied to the sand surface of individual planted pots of the various species on the day of planting, 3 days after planting, and 7 days after planting, at rates of 10 and 20 pounds per acre. Ethyl alcohol solutions of the carbamates were normally used for the spray treatments; the exceptions were compounds that were insoluble in ethyl alcohol but soluble in water, in which case water was used as a solvent.

Symptoms resulting from treatments were noted throughout a 2-week period and the chemical's effect was finally evaluated at the end of this time. This evaluation, by comparison to untreated control plants, was made numerically on a scale of 0 to 10, corresponding approximately to the following:

0	No effect
1 to 3	Slight effect (0 to 35% reduction in height)
4 to 6	Moderate effect (35 to 65% reduction in height)
7 to 9	Severe effect (65 to 95% reduction in height)
10	Very severe effect (failure to emerge or failure to grow)

These evaluations had to be modified in some cases—e.g., where height reduction was not particularly pronounced but malformation, chlorosis, or some other departure from normal growth habit was apparent. In such cases evaluations were based more upon these effects than upon height reduction.

Results

The numerical designations assigned to indicate the effects of the chemicals described in this paper, and tabulated in Table II, are broken down to show the consequences of each of two rates of application at three separate stages of growth for each species. Inspection of these results reveals that the effects of these chemicals vary significantly in only two respects: the general order of activity and the order of selectivity. Considerable differences in activity might have been anticipated for different times of treatment, as these compounds are normally used as preemergence herbicides and the 7-day treatment is in actuality a postemergence treatment, and especially as for many germinating seeds there is a very specific stage of development at which maximum susceptibility to carbamates occurs (*2*). Indications of such differences are obtained, although with the most active compounds they are not appreciable. At reduced dosages it is suspected that greater variations in

Table I. Preparation and Properties of Esters of *N*-(3-Chlorophenyl)-carbamic Acid

Compound[a]	Preparative Method[b]	M.P., ° C.[c]	B.P., ° C.[c]	n_D^{25}	d_{25}	Analysis			
						Theory		Found	
Methyl	B	84–5.5	...	...	...	C	51.76	C	51.74
						H	4.32	H	4.49
Ethyl	A	...	122–3/0.1 mm.	1.5490	1.234	N	7.02	N	7.14
n-Propyl	A	...	137–9/0.1 mm.	1.5410	...	N	6.56	N	6.64
Isopropyl	A	40–1	148–9/5 mm.	1.5368[d]	1.1858[d]	N	6.56	N	6.57
n-Butyl	A	...	140–2/0.1 mm.	1.5346	1.162	N	6.15	N	6.08
ec-Butyl	A	...	153–4/3 mm.	1.5319	1.156	C	58.02	C	58.11
						H	6.20	H	6.35
Amyl	A	...	150–2/0.5 mm.	1.5306	1.140	N	5.80	N	5.85
Hexyl	A	...	154–5/0.1 mm.	1.5258	1.116	N	5.48	N	5.45
2-Ethylhexyl	A	...	168–9/0.1 mm.	...	...	C	63.48	C	63.35
						H	7.82	H	7.84
Lauryl	A	53–4	...	...	...	C	67.13	C	67.06
						H	8.90	H	9.21
Allyl	A	...	135–6/0.1 mm.	1.5561	1.225	N	6.56	N	6.57
2-Chloroethyl	B	46–7	...	...	...	C	46.18	C	46.41
						H	3.87	H	4.37
2-(1-Chloropropyl)	A	...	160–2/1 mm.	1.5516	1.301	N	5.65	N	5.73
α-Carboxyethyl	C	124–5	...	...	...	NE[e]	243.7	NE[e]	243.8
α-Carboxyethyl, sodium salt	D	210 (dec.)	...	...	...	N	5.29	N	5.32
α-Carboxymethyl, sodium salt	E	185 (dec.)	...	...	...	N	5.58	N	5.60

[a] Indicated ester of *N*-(3-chlorophenyl)-carbamic acid.

[b] A. Reaction of 3-chloroaniline with the corresponding alkyl chloroformate in the presence of aqueous sodium hydroxide. B. Reaction of 3-chlorophenyl isocyanate with corresponding alcohol. C. Reaction of 3-chlorophenyl isocyanate with methyl lactate followed by mild saponification and acidification. D. Reaction of methyl lactyl chloroformate with 3-chloroaniline followed by mild saponification. E. Reaction of 3-chlorophenyl isocyanate with glycolic acid followed by neutralization.

[c] Uncorrected.

[d] Determined on supercooled liquid.

[e] Neutral equivalent.

activity as a function of time of treatment would be observed.

A useful numerical indication of the general order of activity observed in the screening evaluation of these chemicals is the "per cent general activity." This may be calculated readily, because each individual treatment which is totally effective herbicidally is given a score of 10, and if all treatments using a given chemical at all rates of application and on all dates of treatment are 100% effective, an eight-species, three-date-of-application, two-rate test has a maximum possible score of 480 points. The percentage of the total possible score actually obtained for any given chemical is referred to as its per cent general activity. Corrections have been made in the determination of the total possible score, for failure of seeds to germinate or of plants to grow, when these could be attributed to effects other than the chemical treatment.

An index of selectivity can be obtained in a somewhat similar manner. In a given test there is always a total possible effect against monocotyledons as well as against dicotyledons. Using these figures it is possible to calculate a per cent monocotyledonous activity and a per cent dicotyledonous activity. For convenience, the ratio of per cent monocotyledonous activity to per cent dicotyledonous activity has been designated as the selectivity quotient. On the most active compounds at least this quotient affords an indication of the chemical's selectivity. Selectivities are usually not considered to be meaningful when general activities fall below about 20%. There can be exceptions to this rule, however, where chemicals control particularly susceptible species, such as rye grass and buckwheat, at rates of application in no way harmful to other species. Such cases represent examples of selectivity, even though the compound's resulting general activity may be low.

The general activities of the compounds described in this paper are represented graphically in Figure 1, and the selectivities, as selectivity quotients, are shown in Figure 2 for application at 10 pounds per acre. In each figure an isopropyl *N*-(3-chlorophenyl)-carbamate zone is indicated which shows approximately the variability of results obtained with isopropyl *N*-(3-chlorophenyl)-carbamate in apparently normal tests, and an isopropyl *N*-(3-chlorophenyl)-carbamate. value is given which is the average value of these tests calculated from a large number of independent experiments over a period of several years. The reproducibility of plant growth regulatory effects with isopropyl *N*-(3-chlorophenyl)-carbamate have been surprisingly good, very much superior to those obtained over a similar period with isopropyl *N*-phenylcarbamate (*1*). The moisture and temperature requirements for isopropyl *N*-(3-chlorophenyl)-carbamate activity have been found to be much less stringent than those for isopropyl *N*-phenylcarbamate. In part, these discrepancies are due to relative volatilities, as isopropyl *N*-phenylcarbamate is much more readily volatilized than isopropyl *N*-(3-chlorophenyl)-carbamate, and, in part, they result from the ease with which isopropyl *N*-phenylcarbamate is decomposed by microbial action, although this factor is much less important in these tests, which used sand as a supporting medium, than in tests in which plants were grown in soil.

Shortcomings of Test Method

It may be desirable to summarize some of the recognized shortcomings and inadequacies of the test method described, the results obtained, and the mathematical treatment of those results. These tests were comparative preliminary screening tests and were not intended to provide precise quantitative data. They were conducted in a manner which has been adequately described (*1*, *3*) and which is similar to tests used by a number of other investigators in similar herbicide screening programs. The results of these treatments were observed visually and translated to a number signifying a given effect, usually a degree of height reduction. In all stages of the experiment certain degrees of variability were possible, even though every attempt consistent with the method was made to control variables. For example, in spite of considerable effort to ensure that equal amounts of all chemicals were deposited at a given rate, some variation was observed. Calibrations were made for each spraying operation, in which the amount of chemical deposited on a plate of known area was accurately weighed. The exact rate of application—i.e., the exact amount of the chemical actually applied to the sand surface by the spray operation—was thus determined, but, although these rates closely approximated 10 and 20 pounds per acre, they were not necessarily exactly these rates. Nevertheless, these approximations were so close that differ-

Table II. Herbicide Screening Evaluations of Esters of *N*-(3-Chlorophenyl)-carbamic Acid

(Application figures in pounds per acre)

Ester	Day of Ap-plic.	Peas		Cotton		Soy Beans		Corn		Rye Grass		Crab Grass		Barley		Wheat		Pigweed		Activity, % Monocot.		Activity, % Dicot.		Selectivity Quotient	
		10	20	10	20	10	20	10	20	10	20	10	20	10	20	10	20	10	20	10	20	10	20	10	20
Methyl	1	0	4	0	3	2	9	7	9	10	10	9	10	9	10	9	10	..	..						
	3	3	7	0	9	6	9	8	9	9	10	6	10	9	9	7	9	..	..						
	7	4	9	1	10	8	9	4	9	0	9	10	10	0	8	0	9	..	..	65	94	27	77	2.4	1.2
Ethyl	1	8	9	7	8	9	9	9	10	10	10	10	10	10	10	10	10	..	..						
	3	9	10	5	8	8	9	10	10	10	10	10	10	10	10	8	9	..	..						
	7	8	8	8	9	8	10	10	10	10	10	10	10	10	10	9	10	..	..	96	99	78	89	1.2	1.1
n-Propyl	1	7	9	4	4	7	8	7	10	10	10	10	10	7	10	9	8	..	..						
	3	7	9	0	5	7	9	8	9	9	9	10	10	7	8	5	7	..	..						
	7	7	7	6	10	7	8	7	10	3	8	10	10	3	5	1	3	..	..	71	85	58	77	1.2	1.1
Isopropyl	1	9	9	3	4	7	7	9	10	10	10	10	10	..	..	10	10	10	10						
	3	9	9	2	3	7	8	9	9	10	10	10	10	..	..	5	7	10	10						
	7	7	9	3	5	7	7	7	9	10	10	10	10	..	..	2	9	10	10	85	95	70	76	1.2	1.3
n-Butyl	1	0	0	0	0	1	4	2	3	10	10	0	5	4	5	4	4	..	..						
	3	0	3	0	0	4	6	4	5	8	9	5	6	2	5	4	5	..	..						
	7	0	1	0	0	1	6	5	7	9	9	7	9	5	7	6	7	..	..	50	64	7	22	7.1	2.9
sec-Butyl	1	10	9	3	3	6	6	8	8	10	10	8	9	..	..	9	9	9	10						
	3	6	9	0	1	7	6	9	7	9	9	7	9	..	..	5	5	10	10						
	7	6	7	0	3	3	5	7	7	0	3	6	8	..	..	0	4	10	10	65	73	58	66	1.1	1.1
Amyl	1	4	4	0	2	2	1	6	8	..	..	2	3	..	..	6	9	1	4						
	3	3	3	0	1	1	5	6	3	..	..	3	3	..	..	0	1	4	7						
	7	0	3	3	4	4	7	4	8	..	..	8	9	..	..	4	4	1	10	33	40	19	42	1.7	0.9
Hexyl	1	0	0	0	0	0	1	0	0	6	6	0	0	..	..	5	4	8	10						
	3	0	3	0	0	0	1	0	3	3	8	0	0	..	..	0	0	10	5						
	7	0	0	0	0	1	2	2	3	4	6	5	8	..	..	4	7	9	7	24	37	23	24	1.0	1.5
2-Ethylhexyl	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	..	..						
	3	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	..	..						
	7	0	0	0	0	0	0	0	2	0	0	0	8	0	3	0	3	..	..	0	11	0	0	...	...
Lauryl	1	0	0	..	..	1	2	0	0	0	0	0	0	0	0	0	0	..	..						
	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	..	..						
	7	0	0	0	0	0	0	0	0	0	0	0	0	3	1	0	0	..	..	3	1	1	2	...	...
Allyl	1	9	9	7	7	8	8	9	10	10	10	9	10	9	10	10	10	..	..						
	3	8	9	2	1	5	7	9	10	8	10	10	10	5	8	8	8	..	..						
	7	7	9	8	9	8	8	9	10	9	10	10	10	10	10	7	10	..	..	88	97	69	74	1.3	1.3
2-Chloroethyl	1	7	9	1	3	5	6	7	8	10	10	9	9	7	8	4	6	..	..						
	3	1	1	3	3	6	7	7	7	8	9	10	10	5	6	4	5	..	..						
	7	7	7	10	10	9	10	8	9	5	4	10	10	7	7	4	7	..	..	70	77	54	62	1.3	1.2
2-(1-Chloropropyl)	1	9	9	8	8	9	..	8	9	10	9	10	10	9	8	8	9	..	..						
	3	7	9	4	4	7	9	8	9	9	8	10	10	9	8	9	8	..	..						
	7	7	8	5	9	5	8	7	9	3	9	10	10	7	9	8	8	..	..	83	89	68	71	1.2	1.3
α-Carboxyethyl	1	2	5	9	8	6	9	9	9	10	10	0	8	9	9	9	10	..	..						
	3	1	4	9	9	6	6	8	8	9	9	7	8	8	9	7	8	..	..						
	7	0	7	7	8	3	7	7	8	4	6	8	7	7	8	1	5	..	..	69	81	48	71	1.4	1.1
α-Carboxyethyl, sodium salt	1	0	4	4	5	6	5	8	9	10	9	9	7	9	9	9	9	..	..						
	3	0	0	5	6	3	4	7	9	8	9	1	7	8	8	7	8	..	..						
	7	0	0	3	3	4	7	3	4	2	2	2	3	3	3	0	0	..	..	57	64	28	38	2.0	1.7
α-Carboxymethyl, sodium salt	1	0	0	0	0	0	1	0	0	10	10	0	3	6	4	4	5	..	..						
	3	0	0	0	0	3	5	0	1	2	4	3	3	1	3	3	3	..	..						
	7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	..	..	19	24	3	7	...	...

entiation of biological effects would have been impossible and, therefore, the nominal use of 10 and 20 pounds per acre is indicated for convenience.

Admittedly, the sums of the components of variability in the over-all experiments were potentially large. As evidence that they were reasonably controlled it can be stated that the comparative effects of the chemicals were reproducible not only in the authors' greenhouse and field tests but also in the greenhouse and field tests of others.

The mathematical treatment of the data obtained is arbitrary and was included only to provide derived data to allow generalized comparisons of the effects of the chemicals. It is recognized that the first paper of this series (*3*), in which three other carbamates were compared to isopropyl *N*-(3-chlorophenyl)-carbamate and where the system of probits was employed, gave a much more exact comparison of the relative effects of the chemicals. To use this system, however, requires much more involved testing than can be justified in a simple screening evaluation, and, in the present program, has been reserved for chemicals that have shown outstanding promise in preliminary and secondary screening tests.

Discussion

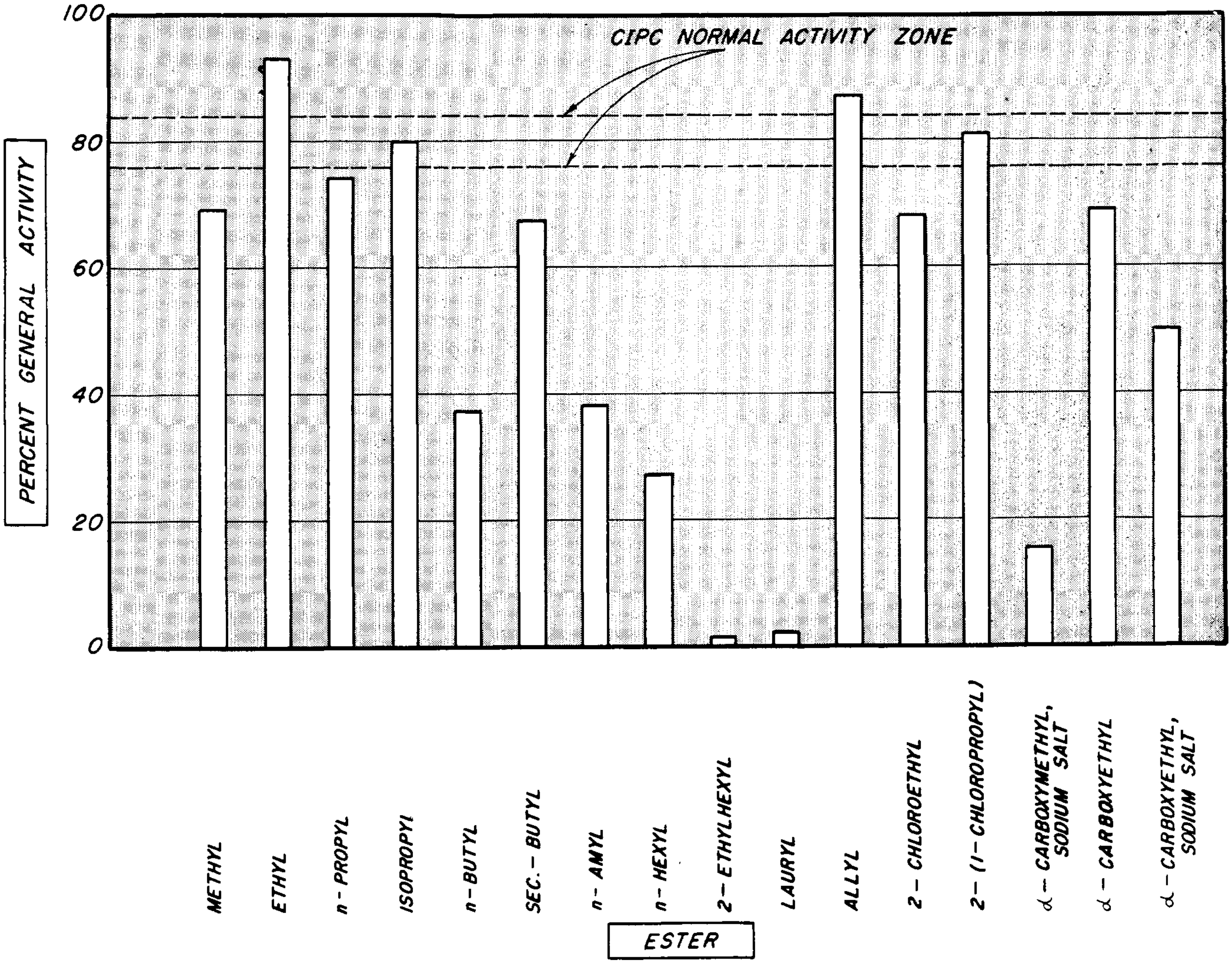
Thorough comparisons of the activities of these chemicals are somewhat difficult, because all compounds were not tested against exactly the same plant species. This condition arose because of efforts to obtain the maximum amount of information from these tests by changing test species, in order to obtain as many degrees of species susceptibility to the carbamates as was possible—i.e., from very susceptible to resistant.

Only three compounds—the ethyl, allyl, and 2-(1-chloropropyl) esters—reported in this paper are considered to be as active as, or more active than, isopropyl *N*-(3-chlorophenyl)-carbamate; the first two of these actually showed somewhat higher activities than did isopropyl *N*-(3-chlorophenyl)-carbamate. Five other compounds—the methyl, *n*-propyl, *sec*-butyl, 2-chloroethyl, and α-carboxyethyl esters—approach the activity of isopropyl *N*-(3-chlorophenyl)-carbamate. The relative orders of activity of these esters of *N*-(3-chlorophenyl)-carbamic acid were similar to those previously reported for the *N*-phenylcarbamic acid esters (*1*). The lower alkyl esters were generally active and showed a peak activity at ethyl or isopropyl. This activity fell off rapidly above about hexyl, and esters such as 2-ethylhexyl and lauryl showed little or no activity.

The introduction of unsaturation in the alkyl side chain appeared to enhance activity in comparison to the corresponding saturated compound; this effect was also observed in the isopropyl *N*-phenylcarbamate series (*1*).

In contrast to the isopropyl *N*-phenylcarbamate series, however, introduction of a chlorine atom into the ethyl and isopropyl analogs failed to increase activity. Actually the 2-chloroethyl analog of isopropyl *N*-(3-chlorophenyl)-carbamate was considerably less active than the unsubstituted ethyl compound. The 2-(1-chloropropyl) analog of isopropyl *N*-(3-chlorophenyl)-carbamate was equivalent to isopropyl *N*-(3-chlorophenyl)-carbamate in activity, whereas in the

Figure 1. General activity of esters of N-(3-chlorophenyl)-carbamic acid



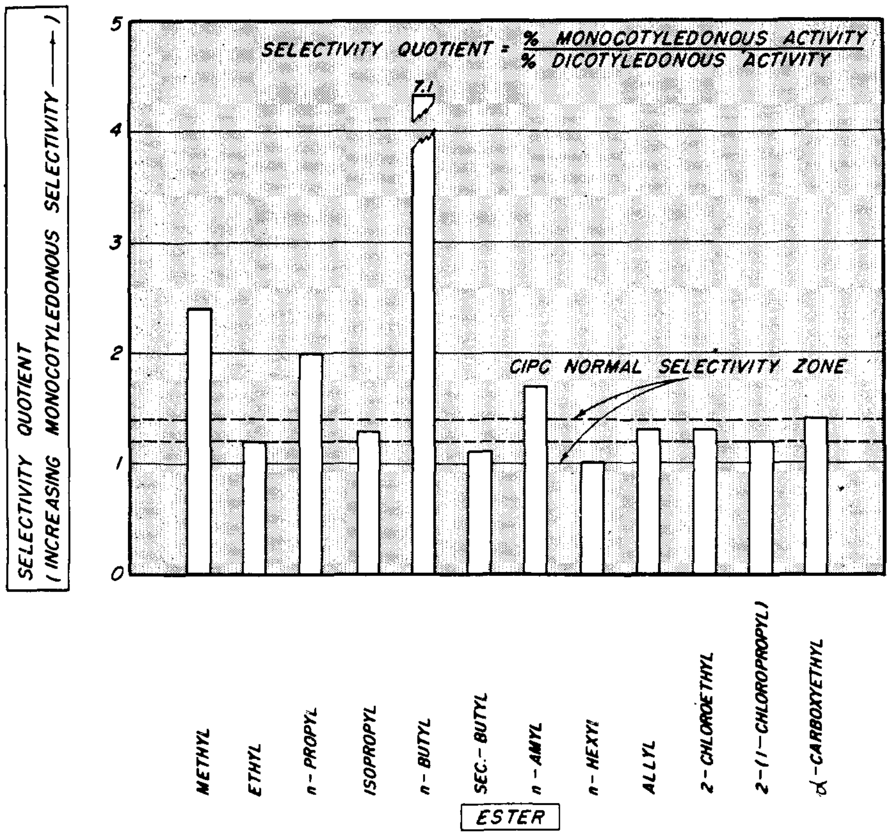


Figure 2. Selectivity of esters of N-(3-chlorophenyl)-carbamic acid applied at a rate of 10 pounds per acre

isopropyl *N*-phenylcarbamate series the corresponding chloroalkyl ester showed a marked increase in activity over isopropyl *N*-phenylcarbamate. Greater variations in activities of the α-carboxyethyl ester and its sodium salt were noted in the isopropyl *N*-(3-chlorophenyl)-carbamate series than had been found with the isopropyl *N*-phenylcarbamate relatives.

The data from this series of compounds throw no additional light upon the question of the mode of action or mode of entry of these compounds into the plants affected. These compounds, which are applied to the soil and not to actual plant parts, may come in contact with the seedlings mechanically as they grow up through the treated zone, they may dissolve in the soil moisture and by diffusion reach water-absorbing rootlets, or they may volatilize and the vapors come in contact with absorbent plant surfaces. Alternatively, the process may be a combination of any two or of all three of these.

Although this paper considers relatively too few compounds to support any general theories concerning modes of entry, some apparent trends may be noted. In general, the most active compounds are the most volatile; the lower alkyl esters, those which are most volatile, are most active. This order is also obvious in the series which includes the α-carboxyethyl ester, its sodium salt, and methyl ester. The latter compound, α-carbomethoxyethyl *N*-(3-chlorophenyl)-carbamate, is not included in this paper, because analytical data obtained for it were not entirely satisfactory. There was little question of its identity, however, as both the free acid and the sodium salt could be prepared from it in high yields. These compounds showed increasing activity in the order sodium salt, free acid, and methyl ester, which is also the order of increasing volatility. These results are not too surprising in view of recent reports of high vapor activity of carbamate herbicides against susceptible species (*2*).

Not even tentative conclusions concerning the relationship between water solubility and plant growth regulatory activity can be drawn from the above data. High activity in the lower alkyl esters is associated with the more water-soluble members of lower molecular weight. In the α-carboxyethyl series just discussed, highest activity is associated with the least water-soluble members. Despite these disparate indications of relationships between water solubility and general activity, it seems unreasonable to believe that activity *per se* of these compounds is independent of water solubility.

The selectivities observed with this series of esters are more regular than those found with the corresponding series related to isopropyl *N*-phenylcarbamate. Four esters—the methyl, *n*-propyl, *n*-butyl, and *n*-amyl *N*-(3-chlorophenyl)-carbamates—show better monocotyledonous selectivity than do average tests with isopropyl *N*-(3-chlorophenyl)-carbamate. The most selective of these, the *n*-butyl ester, showed activity against soybeans at the rate of 20 pounds per acre but only negligible activity against the other broad-leafed species. Two esters, the *sec*-butyl and *n*-hexyl *N*-(3-chlorophenyl)-carbamates, were slightly less selective than the average isopropyl *N*-(3-chlorophenyl)-carbamate tests. These selectivities are applicable only to the specific assortment of species actually tested. To gain an accurate general picture of the monocotyledonous selectivity of any of these chemicals would require a comprehensive test of a large number of narrow- and broad-leafed species, and the results presented here can be considered to give only a tentative and preliminary indication of relative selectivity.

The only valid conclusions which can be drawn from these data are those reached in the earlier study—i.e., that the structure of the side chain portion of the compounds such as these is an essential feature in the determination of activity and that alterations to its structure can markedly influence, or even completely change, the plant growth regulatory properties of the compound in question.

The discussion of possible relationships between structure and activity in the preceding paper (*1*), which was concerned with analogous esters of *N*-phenylcarbamic acid, is also pertinent here. However, to demonstrate accurately the subtle relationships between structure and activity would require very careful and quantitative experiments of a type well beyond the intent of this work. In the course of work with the carbamates using this test method, some observations of gross relationships between structure and activity have been noted. These observations will be reviewed and discussed in a final paper in the current series, in order to avoid admixture of speculation with factual reports of screening experimental results.

Literature Cited

(1) George, D. K., Moore, D. H., Brian, W. P., and Garman, J. A., J. Agr. Food Chem., **2**, 356–63 (1954).

(2) Linder, P. J., Shaw, W. C., and Marth, P. C., *Proc. Northeastern Weed Control Conf.*, **1954**, 11–12.

(3) Moore, D. H., George, D. K., Martin, V. O., and Garman, J. A., J. Agr. Food Chem., **1**, 1154–8 (1953).

(4) Shaw, W. C., and Swanson, C. R., *Weeds*, **2**, 43–65 (1953).

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