

Some Factors Influencing Activity of 12 Phenoxy Acids on Mesquite Root Inhibition^{1, 2}

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The biological activity of phenoxy acids is considered greatest with 4-chloro, 2,4-dichloro, 2,4,5-trichloro, and 2-methyl-4-chloro ring substitutions (14, 26). Phenoxy acids with an even number of carbon atoms in the side chain attached directly to the oxygen are generally more active than those with an odd number due to degradation of the side chain by beta oxidation (11, 20, 26). Lowering pH of the solution in which they are applied increases the biological activity of given concentrations of phenoxy acids. This effect has been attributed to an increased concentration of undissociated molecules in the external medium (2, 5, 7, 10), a change in intracellular pH (2, 5), an effect on membrane permeability (6, 22), or a competition between phenoxy and buffer molecules (28).

Objectives of this study were A, to compare the relative activity of 12 phenoxy acids as indicated by growth inhibition of the roots of mesquite seedlings following applications to the root-bathing medium or to the cotyledons, and B, to examine some relations of structure, solubility, dissociation and pH to the inhibitory activity of these compounds.

Materials & Methods

The methods used were the same as those described in a previous paper (4). Following germination in petri dishes, mesquite [*Prosopis juliflora* (Swartz) var. *glandulosa* (Torr.) Cockr.] seedlings were suspended in 250-ml jars containing a tap water root-bathing medium and exposed to incandescent light at 1,000 to 1,500 ft-c for 16 to 24 hours before treatment.

When solution treatments were used, the length of individual roots was determined just prior to placement in tap water containing 0.00, 0.12, 0.50, or 2.00 ppm of the test compounds. Buffering with 0.0065 M phosphate aided in maintaining the solutions at pH 6, 7 or 8. The bathing solutions were replaced by equivalent solutions after 24 hours to minimize pH drift. Root lengths were remeasured after 48 hours. Growth in length, expressed as percentage of growth

of check, was used as an indication of inhibitory activity. Three replicates of 12 seedlings each were used in a completely randomized design.

When cotyledonary applications were used, the procedure was much the same. After the initial root-length measurement, the test compound was applied to one cotyledon of each seedling at rates of 0.00, 0.10, 0.41, or 1.65 μg in a 2.05- μl drop of 75% ethanol. In a single test, 0.00, 0.08, or 0.33 μg were applied in a 60% acetone-40% nontoxic oil (Sovaspray 100, a saturated, straight-chain, paraffin oil, supplied by the Socony-Vacuum Oil Co.) carrier. The second root-length measurement was made after 24 hours. The root growth, expressed as percentage of growth of check, was used as a measure of inhibitory activity. Six replicates of 12 seedlings each were included when cotyledonary applications were used.

Ring substitutions, 4-chloro, 2,4-dichloro, 2,4,5-trichloro, and 2-methyl-4-chloro, were studied because many phenoxy compounds with these substitutions are known to be highly active growth regulators. Phenoxy acids with acetic, 2-propionic and 4-butyric acid side chains were studied for the same reason. All 12 combinations of ring substitutions and side chains were included in the experiments⁴. Compounds except 2,4,5-T were obtained from the manufacturer in chemically pure form; 2,4,5-T was

⁴ Abbreviations and sources of compounds used: 2-methyl-4-chlorophenoxyacetic acid. MCPA (Source: Mathieson Chemical Corp., Baltimore, Md.). 2-(2-methyl-4-chlorophenoxy)propionic acid. 2-(MCP) (Source: Dow Chemical Co., Midland, Mich.). 4-(2-methyl-4-chlorophenoxy)butyric acid. 4-(MCPB) (Source: May & Baker Ltd., Daggenham, England). 4-chlorophenoxyacetic acid. 4-CPA (Source: Eastman Organic Chemicals, Rochester 3, N.Y.). 2-(4-chlorophenoxy)propionic acid. 2-(4-CP) (Source: Dow Chemical Co., Midland, Mich.). 4-(4-chlorophenoxy)butyric acid. 4-(4-CPB) (Source: May & Baker Ltd., Daggenham, England). 2,4-dichlorophenoxyacetic acid. 2,4-D (Source: Eastman Organic Chemicals, Rochester 3, N.Y.). 2-(2,4-dichlorophenoxy)propionic acid. 2-(2,4-DP) (Source: Dow Chemical Co., Midland, Mich.). 4-(2,4-dichlorophenoxy)butyric acid. 4-(2,4-DB) (Source: May & Baker Ltd., Daggenham, England). 2,4,5-trichlorophenoxyacetic acid. 2,4,5-T (Source: Dow Chemical Co., Midland, Mich.). 2-(2,4,5-trichlorophenoxy)propionic acid. 2-(2,4,5-TP) (Source: Dow Chemical Co., Midland, Mich.). 4-(2,4,5-trichlorophenoxy)butyric acid. 4-(2,4,5-TB) (Source: May & Baker Ltd., Daggenham, England).

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purified by recrystallization of the technical grade product from 30 % ethanol.

Dissociation constants (pK's) of the 12 phenoxy acids were determined at concentrations of 500 ppm in water at 60 C. This temperature was necessary to achieve a 500 ppm concentration of the less soluble compounds. A Beckman, model H-2, pH meter was used to make the necessary pH measurements. It was standardized with 0.05-molar potassium phthalate buffer taken as pH 4.10 at 60 C. The pH value of the buffer at this temperature was calculated according to the procedures outlined by Dole (9).

Water solubilities of the 12 phenoxy acids were determined by adding an excess to distilled water and holding at 50 C for 24 hours. Then, after standing for 48 hours at 25 C the undissolved residue was removed by filtration. The amount of a compound remaining in solution was determined by titration to a phenolphthalein end point with sodium hydroxide.

Results & Discussion

Compounds with the 2-methyl-4-chloro ring substitution were most effective in reducing root elongation when added to the root-bathing medium followed in order of decreasing activity by the 4-chloro-, 2,4-dichloro- and 2,4,5-trichlorophenoxy acids (table I). Deviations from this pattern were noted in the

approximately equal activity of the 4-chloro- and 2,4-dichloro substitutions in the acetic acid series and the low activity of 2-(2,4-DP).

If the side chain effect on inhibitory activity is considered, compounds with the 2-propionic side chain were the least active when added to the root-bathing medium. This might be expected since the 2-phenoxypropionic acids are stereoisomers and available information (1, 19, 21, 27) indicates that only one isomer has high biological activity. The active isomers of 2-(2,4,5-TP) and 2-(2,4-DP) have approximately twice the biological activity of the racemic compounds (3, 21). By analogy it is assumed that a similar relationship exists for the remaining 2-propionic acids, 2-(MCP) and 2-(4-CPP). If this is true, the 2-phenoxypropionic acids, considering the active isomer concentration only, would have approximately twice the activity listed in table I and the phenoxyacetic acids must be considered less active than the active isomers of the 2-phenoxypropionic acids.

Compounds with the 4-butyric acid side chain except 4-(2,4,5-TB) induced the highest levels of root growth inhibition (table I). The concentration of the active 4-phenoxybutyric acids in the root-bathing medium necessary to induce 70 % growth inhibition averaged less than 0.23 ppm versus 0.70 ppm for the

Table I
Effect of pH on Concentrations of 12 Phenoxy Acids Necessary to Induce 70 % Inhibition of Mesquite Root Growth When Added to the Root-Bathing Medium

Ring substitution	pH	Acid Side Chain			Ring substitution mean ppm
		Acetic ppm	2-Propionic ppm	4-Butyric ppm	
2-Methyl-4-chloro	6	0.23	0.30	<0.12	
	7	0.35	0.50	0.12	
	8	0.40	0.55	0.30	
Mean		0.33	0.45	<0.18	<0.32
4-Chloro	6	0.43	0.45	<0.12	
	7	0.53	0.75	0.20	
	8	0.55	1.25	0.35	
Mean		0.50	0.82	<0.22	<0.51
2,4-Dichloro	6	0.49	>2.00	0.17	
	7	0.45	>2.00	0.30	
	8	0.43	>2.00	0.40	
Mean		0.46	>2.00	0.29	>0.91
2,4,5-Trichloro	6	0.47	0.50	>2.00	
	7	1.72	1.64	>2.00	
	8	2.30	1.93	>2.00	
Mean		1.50	1.36	>2.00	>1.62
Side chain mean		0.70	>1.15 >0.58*	0.67 (approx.) <0.23**	

* Approximate mean based on an estimated active isomer concentration of 50 %.

** Approximate mean with the inactive 2,4,5-trichloro substitution excluded.

phenoxyacetic acid group and 0.58 ppm of the active isomer for the 2-phenoxypropionic acids. Greater inherent activity of the 4-phenoxybutyric acid compounds on an equimolar basis is not a tenable hypothesis since the reduction of their side chain to acetic acid has been demonstrated as a necessary prerequisite of activity (11, 20, 26). If equimolar concentrations of the 4-phenoxybutyric acids cannot be more active than the homologous phenoxyacetic acids, their apparent higher activity is likely due to a greater uptake which results in enhanced accumulation of the active homolog (following beta oxidation) at the site of action. This possibility will be discussed further below.

The relatively low inhibitory activity of 4-(2,4,5-TB), 50% reduction in mesquite root growth at 3.0 ppm versus 50% inhibition with 4-(MCPB) and 4-(2,4-DB) at .06 ppm, was to be expected since Synerholm and Zimmerman (20) found 4-(2,4,5-TB) to be inactive in tomato epinasty tests. Also, Wain and Wightman (26) showed that the phenoxy series with the 2,4,5-trichloro ring substitution except 2,4,5-T was inactive in tomato-epinasty and pea-curvature tests but active in a wheat cylinder elongation test. They attributed the low activity of 4-(2,4,5-TB) and the higher homologs with an even number of carbon atoms in the side chain to the failure of pea and tomato stem beta-oxidation enzymes to function in the presence of the 2,4,5-trichlorophenyl ring. The low activity of 4-(2,4,5-TB) in the mesquite root inhibition tests is due, most likely, to the same causal factor.

The relationship of the dissociation constants and inhibitory activity was examined by using calculated pK' values for the 12 phenoxy acids listed in table II. It should be emphasized that the pH values used in the calculation of pK' were determined at 60°C because of the limited water solubility of some of the test compounds at room temperature. However, this should not invalidate comparisons of calculated pK' values on a relative basis. For reference, the range of pK' values obtained by other workers are included in table II.

Table II
Dissociation Constants, pK' , of 12 Phenoxy Acids

Compounds	Dissociation Found	Constants
	(pK' at 60°C)	Literature
MCPA	3.22	3.28(13)3.49(6)
2-(MCPB)	3.38	3.2(15)
4-(MCPB)	4.86	
4-CPA	3.47	2.36(16)
2-(4-CPP)	3.43	
4-(4-CPB)	4.87	
2,4-D	3.22	2.64-3.31(10,12,13,16,23,27,29)
2-(2,4-DP)	3.28	3.0(15)
4-(2,4-DB)	4.58	
2,4,5-T	3.46	3.14(16)
2-(2,4,5-TP)	3.31	
4-(2,4,5-TB)	4.78	

There is no apparent relationship between the degrees of dissociation of the 12 phenoxy acids and their ring substitutions. However, a relationship between the degree of dissociation and the side chain is evident. The pK' values of phenoxy acids with the 4-butyric acid side chain, pK' 4.58 to 4.87, differed markedly from those of compounds with acetic acid and 2-propionic acid side chains, pK' 3.22 to 3.47 (table II). Compounds with the 4-butyric acid side chain, as previously mentioned, were the most active in the root-growth inhibition tests. This suggests an inverse relationship between inhibitory activity and dissociation among these compounds.

On the basis of the pK' values (table II), the concentrations of un-dissociated molecules in root-bathing solutions containing the 4-phenoxybutyric acids at pH 6 to 8 are 10 to 50-fold greater than in equimolar solutions of the phenoxyacetic and 2-phenoxypropionic acids. If it is assumed that un-dissociated molecules are absorbed with greater ease than dissociated ones (2,7), the higher concentration of the undissociated molecules in the root-bathing solutions containing the 4-phenoxybutyric acids would result in greater accumulation within the roots of compounds with this side chain than of compounds with the 2-propionic or acetic side chains. As mentioned previously, this might account for their greater activity in the root-inhibition tests.

For all compounds tested except 2,4-D a given concentration in the root-bathing solution was most effective in inducing root-growth inhibition at pH 6 and least effective at pH 8 (table I). The greatest pH response was exhibited by 2,4,5-T. A 0.47-ppm concentration of 2,4,5-T was required to cause a 70% reduction in root growth at pH 6 whereas a 2.30-ppm concentration was necessary at pH 8, approximately a fivefold difference. There was no apparent association of a particular ring substitution or side chain with the magnitude of the pH effect.

Audus (2), Wedding et al. (29), Blackman and Robertson-Cunningham (5) and Erickson, et al. (10) are among those reporting that the biological activity of 2,4-D is affected by external pH. In the present experiments, 2,4-D was the only compound that did not induce a different degree of root inhibition when the pH of the root-bathing medium was changed. When the test was repeated, the lack of response of 2,4-D to changes in pH was demonstrated again. No obvious reason for the failure of pH to influence 2,4-D activity was evident. A possible explanation might be based on the suggestion of Simon and Beevers (18) that the pH effect on biological activity may differ with the specific test and the organism.

An increase in the hydrogen-ion concentration of the phenoxy solutions from pH 8 to 6 increased the concentration of undissociated growth regulator molecules in the root solution almost 100-fold and resulted in greater inhibitory activity (table I). Yet, equivalent increases in root growth inhibition could be achieved with, at most, a fivefold increase

in the total concentration of growth regulator. If it takes 20 times as great a change in concentration of undissociated molecules to equal the response brought about by a variation in the total concentration of a compound, some effect of pH other than on the degree of dissociation of the phenoxy acids would appear to be the major determinant of the degree of root absorption.

The beta oxidation of 4-phenoxybutyric acids to the corresponding phenoxyacetic acids is necessary for biological activity. Keeping this in mind, a comparison of the undissociated molecular concentrations in equi-effective solutions of a 4-phenoxybutyric acid and its active homolog, phenoxyacetic acid, might provide further evidence on the importance of the concentration of undissociated molecules in inducing root-growth inhibition. Equi-effective concentrations of undissociated 4-(2,4-DB) and 2,4-D required for 70 % root-growth inhibition, averaged for the 3 pH levels, were 4.41×10^{-9} and 2.71×10^{-10} , respectively. The undissociated concentration of 4-(2,4-DB) was 20 times as great as that of 2,4-D, indicating a considerably lower effectiveness on the basis of undissociated 4-(2,4-DB). This difference again suggests the limited importance of the concentration of undissociated molecules as a determinant of root-growth inhibition. On the other hand, there is a possibility that this difference could be due to low efficiency of mesquite roots, about 5%, in the betaoxidation of 4-(2,4-DB) to 2,4-D.

There was no evident relation between the ring substitutions of the 12 phenoxy compounds and the degree of root inhibition that developed after cotyledonary applications (table III). The high activity of 2-(4-CPP) was striking. A 0.103- μ g application induced root-growth inhibition equal to or greater than that induced by the other compounds at 4 to 16 times this application rate.

A correlation of side-chain structure and inhibitory activity was apparent when cotyledonary applications were used. The 2-phenoxypropionic acids in-

Table III

Root Growth as % of Check Following Cotyledonary Applications of 12 Phenoxy Acids Applied in 75 % Ethanol

Compound	Quantity applied to cotyledon (μ g)			
	0.103	0.412	1.648	Mean
2,4,5-T	92	71	59	74
2-(2,4,5-TP)	90	69	55	71
4-(2,4,5-TB)	107	100	98	102
2,4-D	92	85	74	84
2-(2,4-DP)	103	84	52	80
4-(2,4-DB)	109	89	83	94
4-CPA	84	83	75	81
2-(4-CPP)	59	52	39	50
4-(4-CPB)	96	98	93	96
MCPA	93	75	57	75
2-(MCPB)	92	79	75	82
4-(MCPB)	90	80	66	79

Table IV

Water Solubility of 12 Phenoxy Acids & Relative Inhibitory Activity Rank* in Cotyledonary & Root Solution Applications

Compound	Water solubility (ppm at 25 C)	Relative Inhibitory activity rank	
		Root solution application	Cotyledonary application
2-(4-CPP)	1475	8	1
MCPA	1174	4	4
2-(MCPB)	895	6	8
4-CPA	848	7	7
2-(2,4-DP)	829	11	6
2,4-D	682	5	9
2,4,5-T	281	10	3
4-(4-CPB)	110	2	11
2-(2,4,5-TP)	71	9	2
4-(2,4-DB)	67	3	10
4-(MCPB)	48	1	5
2-(2,4,5-TB)	42	12	12

* Compounds ranked 1 to 12 with 1 being most active and 12 being least active.

duced considerably more root-growth inhibition than the phenoxyacetic acids if only the active stereo isomer of the 2-phenoxypropionic acids is considered. Compounds with the 4-butyric acid side chain except 4-(MCPB) were least active.

It is apparent from the activity rankings in table IV that the site of application had an important influence on the relative inhibitory activity of the 12 compounds. While 4-(MCPB), 4-(4-CPB) and 4-(2,4-DB) ranked 1, 2 and 3, respectively, in root solution applications, they ranked 5, 10 and 11, respectively, when cotyledonary applications were used. Numerous other changes in activity ranking were evident.

The addition of test compounds to the root solution places them adjacent to the elongation region of the root which is in all probability the area of response. Reaching the area of response requires only absorption and diffusion through a few layers of cells, a distance of a few millimeters at the most. On the other hand, cotyledonary applications place the compounds 60 to 80 mm from the responsive area of the root. In addition, the cuticle is a barrier to cotyledonary uptake. After penetration of the cuticle, the compound must move through the cotyledon to the phloem. Translocation through the phloem to the root is followed by diffusion throughout the root. In the previously described pathways, differences in cuticular absorption and phloem translocation or phloem translocation alone, could account for the observed variations in activity arising from the method of application.

The influence of the cuticle on absorption of the phenoxy compounds was indicated in the following experiment. The 2,4,5-trichloro-substituted series of phenoxy acids was applied to the cotyledons of mesquite seedlings in an acetone-nontoxic oil carrier known to induce greater absorption than 70 % ethanol

Table V

Mesquite Root Growth as % of Check After Cotyledonary Applications of 2,4,5-T, 2-(2,4,5-TP), & 4-(2,4,5-TB) Applied With Acetone-Nontoxic Oil or 70 % Ethanol as Carrier

Compound	Micrograms of compound applied					
	Acetone-nontoxic oil			70 % Ethanol		
	0.02	0.08	0.32	0.10	0.40	1.60
2,4,5-T	50	31	10	92	71	59
2-(2,4,5-TP)	60	33	16	90	69	55
4-(2,4,5-TB)	80	49	40	107	100	98

(4). Eightyfold increases in inhibitory activity were obtained when this carrier was used (table V). Nevertheless this group of compounds retained the same relative activity ranking as when the ethanol carrier was used. Apparently, the factors giving rise to the differences in inhibitory activity of these compounds were not influenced by the greater degree of absorption induced by the acetone-nontoxic oil carrier.

Solubility of a compound may greatly influence the degree of cuticular absorption (8, 22, 25). Van Overbeek et al. (24) associated the activity of a group of maleimides directly with water solubility. They explained this relationship on the basis of greater water solubility being associated with low lipid solubility and maintained that the maleimides with high water solubility did not readily penetrate the lipid phases in the plant and were, therefore, inactive. The possibility of a similar relation for the 12 phenoxy acids was examined. The compounds used are listed in order of decreasing water solubility in table IV. They are ranked also on the basis of their relative inhibitory activity in cotyledonary and root solution applications. A correlation of water solubility and the inhibitory activity of the 12 phenoxy acids is not evident for either application method.

Table VI

Root Growth as % of Check Following Cotyledonary Applications of 2,4,5-T & 2-(4-CPP) Using 3 pH Levels for the Root-Bathing Medium

Compound	Amount applied (μ g)	pH of root bathing medium		
		6	7	8
2,4,5-T	0.103	85	70	89
	0.412	73	59	72
	1.648	53	51	58
	Mean*	70	57	73
2-(4-CPP)	0.103	86	75	77
	0.412	58	50	54
	0.648	35	32	39
	Mean**	60	52	57

* LSD for pH means at P .01 = 13.

** LSD for pH means at P .01 = 14.

The influence of the hydrogen-ion concentration of the root-bathing medium on the relative inhibition of root growth induced by phenoxy compounds applied to the cotyledons of mesquite seedlings was examined. By this technique the possible effect of external pH on the inhibitory activity of phenoxy compounds within the root could be examined without root absorption being a factor. Two test compounds, 2,4,5-T and 2-(4-CPP), were selected because they induced significant increases in inhibitory activity of root-bathing solutions as pH was lowered. The data in table VI show that the pH of the root-bathing medium in most instances was not correlated with root-growth inhibition when cotyledonary applications were used. The one exception, 2,4,5-T combined with pH 7 of the root-bathing solution, induced significantly greater root-growth inhibition than pH 6 or pH 8. While this effect is of interest, it is unlike the response to pH obtained when 2,4,5-T was added to the root-bathing medium (table I). In that case, root-growth inhibition was inversely correlated with pH, a trend that is not evident in this test.

The fact that the influence of pH on inhibitory activity cannot be wholly attributed to dissociation of the compound in the external medium or to an effect within the cells of the root draws attention to the cell membrane as a likely site of the response to pH. The most probable effect of pH on the cell membrane would be on its permeability as suggested by Brian and Rideal (6) and van Overbeek (22).

Summary

The activity of 12 chlorinated phenoxy acids was determined in root-growth inhibition tests by applying the compounds to the roots or to the cotyledons of mesquite [*Prosopis juliflora* (Swartz) var. glandulosa (Torr.) Cockr.] seedlings. In the root applications the 2-methyl-4-chloro ring substitution induced the greatest inhibition followed by the 4-chloro, 2,4-dichloro and 2,4,5-trichloro substitutions in order of decreasing activity. Relative inhibitory activity did not appear to be correlated with the ring substitution when cotyledonary applications were used. The 4-butyric acid side chain except 4-(2,4,5-TB) imparted the greatest inhibitory activity in root solution applications followed by the active stereoisomers of the 2-propionic acids and the acetic acids in order of decreasing activity. The greater inhibitory activity of the 4-phenoxybutyric acids was associated with less dissociation. However, inhibitory activity was not proportional to the concentration of undissociated molecules in the root-bathing solution. In the cotyledonary applications, the active stereoisomers of the 2-propionic acids induced the greatest degree of root-growth inhibition followed by compounds with acetic acid and 4-butyric acid side chains in order of decreasing activity. The use of another carrier, acetone-nontoxic oil, greatly increased the inhibition induced by cotyledonary applications of 4-butyric acids indicating that absorption rather than

translocation may limit the action of these compounds.

In root solution applications, root inhibition was usually increased by decreasing pH. However, the increase in inhibition was not proportional to the increase in concentration of undissociated phenoxy acid molecules. This strongly suggests that pH has a more important role than its effect on phenoxy acid dissociation. The pH of the root-bathing solution did not influence the degree of root inhibition induced by cotyledonary applications which nullifies the possibility of intracellular influences of external pH.

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