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HERBICIDAL ACTIVITY AND STRUCTURE

Preliminary Evaluation of Some Quaternary Ammonium Salts as Phytotoxic Agents

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Some 60 quaternary ammonium salts $RR_1R_2R_3N$-X were prepared by standard chemical methods. Many of these quaternary salts exhibit considerable phytotoxicity in seed germination tests. In a series of 1-substituted pyridinium bromides, maximum phytotoxicity was noticed when R was C_{12} to C_{14}. Other active types of similar compounds are also mentioned. Lack of selectivity towards mono- or dicotyledenous species is evident from these examples.

QUATERNARY ammonium salts in general exhibit considerable activity in many biological applications. The bactericidal-germicidal applications are very numerous and are well known. Attempts to correlate the mode of activity of various quaternary ammonium salts as bacteriostatic agents with their colloidal and detergency activity have been presented (*3, 6, 7*).

However, prior to the disclosure of the potentialities of a few certain select quaternary salts as herbicides (*5*), little has been reported concerning this phase of their biological activity.

The laurylpyridinium salts of 2,4-D and 2,4,5-T are phytotoxic, but this type of salt combines a quaternary compound with known herbicides (*1*).

Decyldimethyl-2-methoxyethylammonium chloride is strongly "phytohormonal" (*2*).

Therefore, it became of interest to prepare a broad series of quaternary ammonium salts and attempt to correlate structure with phytotoxic activity, if any was present.

The quaternary ammonium salts were obtained by the standard reaction of the appropriate amine and organic halide in an anhydrous solvent, usually in ethyl alcohol.

$$R_1R_2R_3N + R{-}X \longrightarrow RR_1R_2R_3N^+X^- \quad (I)$$

The salts (I) were examined for phytotoxicity by a slight modification of the method of Thompson, Swanson, and Norman (*9*). Cucumber and wheat seeds (representing di- and monocotyledenous species) were germinated in Petri dishes in the presence of aqueous solutions of the test chemical. The results (Table I) are expressed as per-

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Table I. Phytotoxicity of Quaternary Ammonium Salts to Germinating Cucumber and Wheat Seeds

	Percentage Root Growth			
	100 p.p.m.	10 p.p.m.	100 p.p.m.	10 p.p.m.
	Cucumber		Wheat	
Pyridinium Bromide				
1-Methyl[a]	40	81		
1-Methyl[b]	10	86		
1-Ethyl	65	94		
1-Propyl	64	93		
1-(*iso*-butyl)	74	86		
1-(*n*-Hexyl)	34	72		
1-(*n*-Heptyl)	10	63		
1-(2-Ethylhexyl)	20	72		
1-(*n*-Octyl)	5	37	13	65
1-(3,5,5-Trimethylhexyl)	14	42		
1-(*n*-Decyl)	2	23		
1-(*n*-Dodecyl)	2	25		
1-(*n*-Tetradecyl)	4	43		
1-Propargyl	48	99		
1-Cyanomethyl[c]	73	97		
1-(2-Chloroethyl)	68	92		
1-(β-Ethoxyethyl)	83	101		
1-(β-Butoxyethyl)	68	93		
1-β-(β-Butoxyethoxy)ethyl	74	99		
1-(β-Phenylethyl)	67	102		
1-Benzyl[c]	36	59		
1-(2,4-Dichlorobenzyl)[c]	26	69		
1-(γ-Phenylpropyl)	50	98		
1-Phenacyl	82	89		
1-(6-Cyanohexyl)	54	80		
1-Carbobutoxymethyl[c]	90	99		
1-Methoxymethyl[c]	61	89		
1-(*m*-Xylyl)	32	52	22	84
1-(*p*-Ethylbenzyl)[c]	23	65	16	58
1-(2,4-Diethylbenzyl)[c]	5	53	4	38
1-(*p*-Isopropylbenzyl)[c]	7	48	9	70
1-(2,4-Diisopropylbenzyl)[c]	3	26	5	30
1-(*p-sec*-Amylbenzyl)[c]	4	25	3	22
1-(2-Cyclohexylethyl)	32	66	34	78
1-(1-Naphthylmethyl)[c]	13	57		
1-(2-Hydroxyethyl)[c]	60	82		
1-(2,4-Dinitrophenyl)[c]	44	86		
1-(3,5,5-Trimethylhexyl)-4-methyl	14	37	8	46
1-(3,5,5-Trimethylhexyl)-2-methyl-5-ethyl	92	97	94	105
1-(3,5,5-Trimethylhexyl)-2-chloro	41	81	64	98
1-(*p-sec*-Amylbenzyl)-2-methyl-5-ethyl[c]	4	27	7	36
Ammonium Bromide				
Triethyl-(3,5,5-trimethylhexyl)	15	52	23	81
Tri-(*n*-butyl)-3,5,5-trimethylhexyl	4	30	10	61
Tri-(*n*-Amyl)-3,5,5-trimethylhexyl	2	22	4	47
Trimethyl-*p-sec*-butylbenzyl[c]	36	84	34	103
3,5,5-Trimethylhexyldimethylphenyl	10	46	15	63

(continued on page 34)

centages of the normal growth of the primary root in a water control. The phytotoxic activity of 1-alkylpyridinium bromides rises to a maximum around an alkyl chain length of 12 to 14. Lo Cicero *et al.* (*4*) found that the fungitoxicity of a related series of alkylpyridinium chlorides rose to a similar maximum at C_{14}. Examination of Table I indicates that branching of the alkyl chain does not have much effect on phytotoxicity. When the substituent on the pyridine nitrogen atom becomes an alkylbenzyl group, activity is still retained. For example, 1-(2,4-diisopropylbenzyl)-pyridinium chloride (C_{18}) has the same order of activity as 1-dodecylpyridinium bromide (C_{12}). Substituting alkyl groups for hydrogen around the heterocyclic ring does not seem to affect activity appreciably. Pyridine or alkylpyridines are not necessary for activity as shown by the phytotoxicity exhibited—e.g., by tri-(*n*-amyl)-3,5,5-trimethylhexylammonium bromide and similar quaternary salts.

The quaternary salts are nonselective in their phytotoxic action towards cucumber and wheat seeds, as evidenced by the data of Table I.

Table I (Continued)

	Percentage Root Growth			
	100 p.p.m.	10 p.p.m.	100 p.p.m.	10 p.p.m.
	Cucumber		Wheat	
Ammonium Bromide				
Phenyldimethyl-*p*-*sec*-amylbenzyl[c]	7	32	10	46
Tris-(β-hydroxyethyl)-*p*-*sec*-amylbenzyl[c]	27	78	41	77
Tris-(β-hydroxypropyl)-*p*-*sec*-amylbenzyl[c]	54	100	71	92
Dimethyl-β-hydroxyethyl-4,5,5-trimethylhexyl	21	79	12	79
Trimethyl-*p*-isopropylbenzyl-	50	84	32	58
Trimethyl-*p*-*sec*-amylbenzyl-	14	40	5	23
Others				
1-(3,5,5-Trimethylhexyl)-quinolinium bromide	7	48	4	51
2-(3,5,5-Trimethylhexyl)-isoquinolinium bromide	8	45	6	43
3-(3,5,5-Trimethylhexyl)-benzothiazolium bromide	58	86	47	102
1-(*p*-*sec*-Amylbenzyl)-quinolinium chloride	4	43	12	61

[a] *p*-Toluenesulfonate instead of bromide. [b] Iodide instead of bromide. [c] Chloride instead of bromide.

Experimental

Procedure for Herbicidal Assay. The method is substantially that described by Thompson *et al.* (*9*) with the modifications noted by Schlesinger and Mowry (*8*). Where compounds were tested with wheat, the procedure was the same except for substitution of wheat seeds for cucumber seeds in the Petri dishes. The data obtained are listed in Table I.

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MEASUREMENT OF PLANT PECTIC SUBSTANCES

Reaction of Hydroxylamine with Pectinic Acids. Chemical Studies and Histochemical Estimation of the Degree of Esterification of Pectic Substances in Fruit

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The reaction of the carbomethoxyls of pectinic acids with hydroxylamine in aqueous-alcoholic solutions was studied. The rate and extent of formation of pectin hydroxamic acid were followed by developing the colored spots of the ferric-pectin hydroxamic complex on filter paper strips and measuring the reflection densities. These series of reactions were applied to measure the degree of esterification of pectic substances in fruit tissue sections. This procedure introduces a new direct method for following the esterification of pectic substances in fruits at different stages of their development.

THE REACTION of the carbomethoxy groups of pectin with alkaline hydroxylamine produces pectin hydroxamic acids which react with ferric ion to form insoluble red complexes and has been used as the basis for a qualitiative histochemical test for pectic substances in tissue sections (*12*). When the reactions were conducted in an aqueous-alcoholic suspension they appeared to offer a quantitative means of determining directly the degree of esterification of pectic substances in tissue sections. The experiments reported here show some of the variables involved in the course of the reactions to produce pectin hydroxamic acids and the validity of reflection density measurements for the determination of the degree of esterification of pectic substances.

The degree of esterification is considered important in determining the solubility properties of pectins and, consequently, in understanding their probable role in fruit texture. Pectic substances extracted from fruits are known to have from 60 to 80% of their carboxyl groups esterified with methanol. The per cent esterification found in extracted pectins, however, depends