Phytotoxicity of Organic and Inorganic Iodides to *Avena fatua*
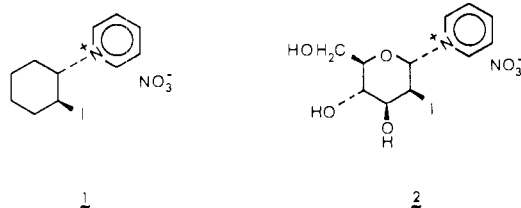
A series of α-iodoalkylpyridinium nitrates shows herbicidal activity to *Avena fatua* in the water culture, but fava bean, flax, and wheat are unaffected. The degree of activity increases with decreasing redox potential of the iodo compound. The herbicidal action is ascribed to release of iodide from the molecule in the plant system. Soil application of various inorganic and organic iodides at a moderately high rate shows similar activity to *A. fatua*. Iodoform exhibits potent herbicidal activity at a low rate but selectivity is markedly reduced. With high dosages, tested species which are resistant to iodide show better drought tolerance than untreated plants.

Research programs to evaluate possible chemical treatment to reduce seed shedding of wild oat (*Avena fatua*) prior to the harvest of infested grain crops have been undertaken during the past few years in this laboratory. A number of known synthetic plant growth hormones and regulators were applied to wild oat plants to evaluate the effects on the delay of seed drop and other aspects of plant growth. The seeds of wild oats ripen earlier than those of cultivated crops. Thus, regulation of the plant growth or delay in ripening of seed would, in effect, reduce seed shedding before crop harvest. During the course of this study a series of α-iodoalkylpyridinium nitrates and various ferrocenylmethyltrimethylammonium halides, resembling many known growth regulators in having a quaternary ammonium moiety, were screened for their effects on the growth of *A. fatua*. In the biological tests on plants grown in water culture, it became apparent that certain α-iodoalkylpyridinium nitrates showed plant retardant properties. Certain other α-iodoalkylpyridinium nitrates and ferrocenylmethyltrimethylammonium iodide exhibit phytotoxicity to *A. fatua*. However, ferrocenylmethyltrimethylammonium chloride and bromide were completely inert in the growth of *A. fatua*.

The selective herbicide ioxynil, 3,5,-diiodo-4-hydroxybenzonitrile, has been reported (Wain, 1964) as forming radicals with iodine when exposed to UV light. Breakdown in soil also leads to release of iodine among the degradation products. The main toxic effects of the compound were found to be due to inhibition of the Hill reaction and phosphorylation reactions in the biological system (Wain, 1964). It is likely that liberation of iodine from ioxynil is partially responsible for the toxic action since sodium iodide was also shown to be toxic to a variety of plants (Wain et al., 1966). This suggests that the presence of iodide in the molecule may be responsible for the phytotoxicity of a series of α-iodoalkylpyridinium nitrates. It was therefore of interest to determine the nature of herbicidal activity and mechanism of action of iodopyridinium moiety in the adduct of type 1. In conjunction with this study, a systematic investigation of the selective herbicidal activities of various organic and inorganic iodides on *A. fatua* was undertaken.

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In investigating the activities of α-iodoalkylpyridinium nitrates, fava beans, flax, barley, wheat, and oats, grown in water culture, were treated with α-iodocyclohexylpyridinium nitrate (1) and eight analogous compounds.

Certain of the tested compounds, notably 1, showed selective toxicity toward both cultivated oats (*A. sativa*) and the wild species (*A. fatua*) at a concentration of 0.1 mM in culture medium. Other compounds, such as glucal adduct of pyridinium iodide (2), were inert in the growth of oats, even at a tenfold increase in concentration. None of the other species of plants tested were affected by rates as high as 1.0 mM in the culture medium. At 2.0 mM concentration, glucal adduct significantly retarded plant growth in all tested species, but showed no obvious toxic effect. Further evaluation of 2 as a plant growth retardant was not pursued because of the obvious phytotoxicity of its analogue to certain species.

The possibility of different herbicidal effects on two species due to structural variations of the organic iodides was investigated during the early stages of screening the phytotoxicity of the α-iodopyridinium nitrates to *Avena*. No distinctive difference, however, in response to a variety of tested organic compounds, was observed. Compounds which affected oats (*A. sativa* and *A. fatua*) resulted in retardation of growth, tip burn followed by leaf scorch, and ended in death. The relative toxicity of α-iodoalkylpyridinium nitrate to *A. fatua* in water culture is shown in Table I.

The polarographic determination of halfwave redox potentials of a series of the nitrates are included in Table I. Examination of these redox potentials reveals that they can be correlated with the equilibrium constants of the complex formation of silver cation with olefins from which adducts of type 1 were derived (Table I). The lower the polarographic reduction potential of the adduct, the more easily iodine can be liberated, with a concomitant formation of the corresponding olefin. It has become rather apparent that liberation of iodide from α-iodoalkylpyridinium may be the cause of the observed phytotoxicity in oats. Taking into consideration that structural differences in cationic moieties could possibly affect the plant uptake, biological transformation, or translocation of molecule, the degree of the phytotoxicity shows partial agreement with the trend in the ease of reduction of the series of adducts (Table I).

Although the toxicity of potassium iodide and various iodates to cultivated oats has been known for many decades (Sharrer and Shropp, 1931), exploration of the possible use of iodides as a selective wild oats herbicide has not yet been reported. Growing out of the above studies on α-iodoalkylpyridinium nitrates, the systematic evaluation of the selective herbicidal activities of various ionic and covalent iodides to *A. fatua* was undertaken. The acutely toxic effect of potassium iodide to *A. fatua* in water culture has been confirmed using a test procedure similar to that reported for cultivated oat (Borst Pauwels, 1962). Cultivated oat was shown to be very sensitive to an overdose of iodide; a pronounced inhibition of the growth of roots was observed at a very low concentration.

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Table I. Relative Toxicity (graded from 0 to +4) of 0.3 mM Various Olefin-iodopyridinium Adduct Nitrates to Wild Oat in Water Culture[a]

Olefin	Relative toxicity	Polarographic halfwave potential $(-E_{1/2})$ of adduct, V vs. SCE[d]	Equilibrium constant (K) of complex formation with silver cation[b]
2,3-Dimethylbutadiene	++++	0.50	
2-Methyl-2-propenol	+	0.77	
2-Butene-1,4-diol	+	0.46	
Glaucal	0	0.69	
trans-Hexene	+++	0.44	1.0
2-Methyl-2-butene	++	0.52	0.8
cis-Hexene	++++	0.56	3.9
Cyclohexene	+++	0.77	3.6
Norbornadiene	++	1.15	33.7[c]
(Iodoform)	+++++	0.45[e]	

[a] Hoagland solution. [b] Muhs and Weiss (1962). [c] The exceptional stability of the complex is due to endo complexation of the silver ion to the homoconjugated diene. [d] In sulfolane containing 0.1 M tetrabutylammonium perchlorate. [e] In 75% dioxane containing 0.05 M tetramethylammonium bromate, after Heyrovsky and Kuta (1966).

Table II. Percent Injury to Wild Oat with Preemergence Soil Application of Iodides (Greenhouse Test)

Iodide (% iodine)	Dosage, kg/ha					
	150	100	50	25	12.5	6
Potassium iodide (76.44)		100	88	0		
Benzyltrimethyl-ammonium iodide (45.79)		83	54	0		
(Ferrocenylmethyl)tri-methylammonium iodide (32.98)	85	67	50	0		
Ethylenetrithiocarbonate-methyl iodide complex (45.61)	100	83	60	0		
Iodoform (96.68)			100	87	66	41

It was also meticulously demonstrated that chloride ion gave a surprising synergistic effect to the iodide toxicity. In the absence of chloride, the iodide toxicity was reduced by one half (Borst Pauwels, 1962). We were able to confirm these findings for both the cultivated and the wild species. Iodoform is even more toxic to *Avena* than potassium iodide. The latter has been reported to have toxic effect at a concentration of 0.5 ppm in a hydroponic study. The minimum effective concentration of iodoform, however, was not determined because of its poor solubility in water. Incorporation of iodides into soil at a high dosage was also effective (Table II), but little toxic action was observed with foliar application.

Soil-applied herbicidal activity was carried out with a series of iodides, including potassium iodide, benzyltrimethylammonium iodide, (ferrocenylmethyl)trimethylammonium iodide, ethylenetrithiocarbonate–methyl iodide complex, and iodoform (Table II). The ethylenetrithiocarbonate–methyl iodide complex was included because the complex releases iodine slowly and is a flotation agent or surfactant. The iodides also form a series of increasing covalent character of iodine linkage. Although α-iodoalkylpyridinium nitrates and certain water-soluble aromatic iodides such as p-iodoaniline hydrochloride showed potent phytotoxicity to wild oat in water culture, incorporation of the compounds into soil drastically reduced their activities. 2,3,4,5-Tetraiodopyrrole (iodol) was extremely toxic to *A. fatua*. However, a thorough test of this compound was not attempted because of difficulty in synthesis.

Except iodoform, the degree of toxicity of the iodides listed in Table II clearly increases with increasing iodine content of the molecule. At rates higher than 50 kg/ha, all chemicals showed selective herbicidal activity to wild

oats. But at a lower rate weed control became uncertain.

The remarkable phytotoxicity of iodoform cannot be explained by its higher iodine content alone. Unfortunately, selectivity of iodoform is markedly reduced as compared to other iodides; at dosages of 25 kg/ha, both wheat and flax become susceptible to it. Notwithstanding, iodoform exhibits enough selective herbicidal activity to suggest that further study might make its use on the field scale economically feasible.

It may be relevant to mention here that iodides have been noted as a micronutrient; growth of a number of crops responds favorably to minute applications of iodides and iodates (Borst Pauwels, 1961). We have observed heretofore unreported favorable effects of iodide on the growth of wheat, barley, fava bean, and flax, in that these crops exhibit better drought tolerance with a high dosage of potassium iodide (150 mg/6-in. pot). In a typical experiment, both control and iodide-treated plants grown in a growth chamber were withdrawn from watering for a week, 4 weeks after seeding. Under the tested drought conditions, the KI-treated plants were still fairly turgid and healthy. In contrast, the control showed extensive drooping of the leaves. A similar phenomenon could be observed at later stages of the plant growth, although it was less obvious than that observed at the less mature stage.

EXPERIMENTAL SECTION

Synthesis of Compounds. α-Iodoalkylpyridinium nitrates were synthesized from the appropriate olefins by the procedure previously reported from this laboratory (Diner and Lown, 1971). Ethylenetricarbonate–methyliodide complex, mp 90–91 °C, was prepared by mixing ethylenetrithiocarbonate and 2–3 equiv of methyl iodide in the presence of nitromethane.

Biological Testing. Evaluation of the phytotoxicity of various α-iodoalkylpyridinium nitrates to wild oat (*A. fatua*) was carried out in reagent tubes using the overhead watering vermiculite culture. Wild oat seeds were germinated on filter papers moistened with 20 ppm of gibberellin aqueous solution in a petri dish. After germination, three seedlings were transplanted to the tube filled with 6 g of vermiculite and 25 mL of Hoagland solution 2 (Hoagland and Arnon, 1950) containing 0.3 mM α-iodopyridinium nitrate. The plants were grown in a growth chamber under 16 000 lx for a 16-h photoperiod at about 25 °C during the day and 12 °C at night and a 60% humidity control.

In a separate investigation, the selective herbicidal activity of α-iodocyclohexenylpyridinium nitrate was tested

on both monocots and dicots in the same vermiculite culture but using subirrigation in a woodbox.

Testing of the soil-applied activity of various iodides was undertaken using routine greenhouse procedures. The chemical was mixed thoroughly in the top 7 cm of soil in pots. Seeds were planted in pots about 2 cm below the surface of the soil composed of 0.5 silt top soil, 0.25 sand, and 0.25 peat, and fertilized with urea, 11-55-0, and potash in a rate of 60, 20, and 60 kg/ha for N, P_2O_5, and K_2O, respectively. Herbicidal dosages are expressed in terms of kg/ha. The treatments were evaluated 4 weeks after seeding and were at least duplicated.

LITERATURE CITED

Borst Pauwels, G. W. F. H., *Plant Soil* 14, 377 (1961).
Borst Pauwels, G. W. F. H., *Plant Soil* 16, 284 (1962).
Diner, U. E., Lown, J. W., *Can. J. Chem.* 49, 403 (1971).
Heyrovsky, J., Kuta, J., "Principles of Polarography", Academic Press, New York, N.Y., 1966, p 550.
Hoagland, D. R., Arnon, D. I., "The Water-Culture Method for Growing Plants without Soil", California Agricultural Experiment Station, Circular 347, 1950.
Muhs, M. A., Weiss, F. T., *J. Am. Chem. Soc.* 84, 4697 (1962).
Scharrer, K., Schropp, W., *Biochem. Z.* 239, 74 (1931).
Wain, R. L., *Proc. Brit. Weed Control Conf.* 7, 306 (1964).
Wain, R. L., Balayannis, P. G., Taylor, H. F., Zake, M. A., *Nature (London)* 209, 98 (1966).

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Spectrophotometric Determination of Dissociation Constants of Selected Acidic Herbicides

pK_a values have been determined for ten acidic herbicides and one fungicide using a spectrophotometric method. pK_a values are reported for [(4-chloro-*o*-tolyl)oxy]acetic acid (MCPA), 3.13; ($\pm$)2-[(4-chloro-*o*-tolyl)oxy]propionic acid (mecoprop), 3.11; (2,4-dichlorophenoxy)acetic acid (2,4-D), 2.87; 2-(2,4-dichlorophenoxy)propionic acid (dichlorprop), 2.86; (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T), 2.85; 2-(2,4,5-trichlorophenoxy)propionic acid (fenoprop), 2.83; 3,6-dichloro-*o*-anisic acid (dicamba), 1.90; 2-*sec*-butyl-4,6-dinitrophenol (dinoseb), 4.62; 4,6-dinitro-*o*-cresol (DNOC), 4.46; 3,5-dibromo-4-hydroxybenzonitrile (bromoxynil), 4.20; and pentachlorophenol (PCP), 4.71. The pK_a values for (*o*-chlorophenoxy)acetic acid (2-CPA), 3.00, and (*p*-chlorophenoxy)acetic acid (4-CPA), 3.05, have been included for comparative purposes. The pK_a values for 2-CPA, 4-CPA, MCPA, 2,4-D, and 2,4,5-T from this study were in close agreement with those previously reported from potentiometric and conductimetric determinations. The pK_a values for 4-[(4-chloro-*o*-tolyl)oxy]butyric acid (MCPB), 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB), 4-amino-3,5,6-trichloropicolinic acid (picloram), 3,6-dichloropicolinic acid (M-3723), and 2,3,5-triiodobenzoic acid (TIBA) could not be determined using the spectrophotometric method.

The degree of dissociation of weakly acidic organic herbicides determines not only their entry into plants, both via leaf surfaces (Simon and Beevers, 1952) and roots (Grover, 1968), but also their adsorption, mobility, and deactivation in soil (Adams, 1973) and water (Weber, 1972). Thus, in order to gain an understanding of the fate and behavior of these biologically active compounds in the environment, accurate ionization constants or pK_a values (negative logarithm of the ionization constant) for these herbicides are necessary.

pK_a values for several of these herbicides (MCPB, 2,4-DB, mecoprop, dichlorprop, fenoprop, bromoxynil, dinoseb, dicamba, picloram) have been published in reviews (Bailey and White, 1965; Weber, 1972) with no reference to the methodology employed in their determination. However, even when the methodology has been described, there is wide disagreement in the pK_a values for many of these weakly acidic herbicides (MCPA, 2,4-D, 2,4,5-T, picloram). For example, the reported pK_a values for 2,4-D varied from 2.64–3.28 (Audus, 1949; van Overbeek et al., 1951; Ketelaar and Gersmann, 1952; Wedding et al., 1954; Matell and Lindenfors, 1957; Wershaw et al., 1967;

and Nelson and Faust, 1969).

Although most herbicide pK_a determinations have been made using either the potentiometric titration or conductimetric methods, the spectrophotometric method has been used (Weber, 1967) to determine the pK_a values for several triazine herbicides. One of the main advantages of the spectrophotometric method is that pK_a determinations can be made at solute concentrations in the range 10^{-3} to 10^{-5} M, whereas, accurate pK_a values cannot be achieved using the potentiometric titration method unless the pK_a value is greater than the negative logarithm of the molar concentration. Consequently, the potentiometric titration method is not ideal for many herbicides because of their low solubilities. The conductimetric method, although suitable at low concentrations, has to be carried out at a number of dilutions, with each conductimetric value requiring different activity corrections. The practical work is time-consuming, and the activity correction calculations are quite tedious in contrast to those required by the spectrophotometric method. All three methods have been recently described in detail by Albert and Serjeant (1971).