Metal-Containing Polymer Structures for Enhanced Seed Germination and Plant Growth

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ABSTRACT

A number of metal-containing polymers containing plant growth hormones, PGHs, from three of the major PGH categories were synthesized. These categories were auxins, gibberellins, and cytokinetins. These polymers generally showed equal or greater ability to perform plant-growth regulatory functions with respect to seed germination and seedling development in comparison to the controls and PGHs alone. The seeds included food producing damaged and aged seeds that themselves generally exhibited low germination rates. Increases in germination rates were at times over two fold. These polymers can be easily and quickly made employing an industrially accepted technique and commercially available reactants. Thus, production of gram to ton quantities can occur rapidly. It is believed the enhanced effects may be due to the controlled release of the PGHs.

Key words: Kinetin, kinetin-containing polymers; gibberellic acid; gibberellic acid-containing polymers; seed crop germination; Group IVB polymers; organotin polymers, plant growth hormones, auxins, gibberellins, cytokinetins, indole butyric acid, indole acetic acid, cancer, interfacial polymerization

Introduction

We have been investigating the use of polymers containing plant growth hormones, PGHs, for about two decades. Other terms such as phytohormones, plant growth regulators and plant growth substances are also employed to describe PGHs. Our efforts are aimed at increasing the germination of seeds and enhancing the growth of plants including woody plants. Incorporation of plant growth hormones in polymers allows a control release of the PGH over time. Here we review some of these efforts.

There are two general types of polymers, addition and condensation polymers [1,2]. Addition or vinyl polymers generally have a backbone that contains only carbon atoms. Examples include polyethylene, polypropylene, polystyrene, and poly(vinyl chloride). A representative unit is given below,(1).

\[-(-\text{CH}_2-\text{CHX}-)\]  \hspace{1cm} (1)

where X = H for polyethylene, CH$_3$ for polypropylene, phenylene for polystyrene, and Cl for poly(vinyl chloride).

Condensation polymers generally contain a non-carbon in their backbone with examples including polyesters, nylons, and polyurethanes. Below, (2), is a representative unit for nylon-66 with the non-carbon atom being nitrogen.

\[-(-\text{NH-CH}_2-\text{CH}_2- \text{CH}_2- \text{CH}_2- \text{CH}_2-\text{NH-C=O-CH}_2- \text{CH}_2- \text{CH}_2-\text{C=O-})\]  \hspace{1cm} (2)
We selected incorporation into condensation polymers for several reasons. The major reason was that condensation polymers offered a better possibility that release would occur at a reasonable, but not too slow or too rapid, rate. Because of the polarity of the bonds connecting the various components of the polymer backbone, the chain is susceptible to hydrolysis allowing release of the PGH.

Metal-containing polymers offer several possible advantages over other similar polymers. First, the bond connecting the metal-containing moiety and the plant growth hormone is more polar than a common carbon-based connection so it is more susceptible to natural hydrolysis releasing the PGH in a more rapid manner. Second, the metal-containing moiety may itself offer some advantage. For instance manganese is involved in the electron transfer from water to chlorophyll during the light reaction of photosynthesis [3]. It is also believed involved in the redox of the PGH indole-3-acetic acid, IAA [4]. Manganese is found in soil for plant uptake. Organotin compounds are known to add to compounds containing them the ability to inhibit bacterial growth thus extending shelf life of susceptible materials including seeds [5]. Third, certain organometallic halides act as acid chlorides but are more resistant to hydrolysis allowing the successful condensation and polymer formation through functional groups, such as carboxylic acid groups, that are present in some PGHs allowing their incorporation into polymers that would not be possible with simple organic acid chlorides [6].

The synthetic approach taken by us is easily converted to large scale production. It employs commercially available reactants, techniques that are already known industrially, and occurs rapidly. All of the reactants are available commercially. The synthetic technique, the interfacial technique, was popularized by Morgan and Carrarhe in the 1960s and 1970 and is today employed to synthesize aramid and polycarbonate polymers [7-10]. Synthesis generally occurs within less than a minute. In truth, a little goes a long ways with plant growth hormones. Thus, a gram of material can treat millions of seeds.

The topic of metallocene-containing polymers has been recently reviewed [11] as has the topic of organotin-containing polymers [5].

**General**

Increased plant and food production has been an aim since humankind began raising their own food [12-15]. This has been accomplished in many ways throughout history. Plant antagonists are also a problem. Recent research has focused on the genetic modification of plant seeds towards the production of plants that give fruit of increased yield in some selected manner and that are able to withstand the onslaught of certain antagonists. Some of the results, while giving plants with the desired outcome, also produced plants that had other, unforeseen, affects to an extent that much of this research is being rethought. Another major recent effort has been aimed at the production of selected chemical agents, insecticides and others, that combat these unwanted plant enemies. This approach has often been successful but again sometimes with unwanted side results to the extent that even here a rethinking is underway.

The worm has in some sense turned to that there is a revival in the idea that we should be investigating ways to assist nature itself in combating antagonists and enhancing plant and food production. Our research with plant growth hormones is aimed at accomplishing this goal.

A living green plant is a stunning result of a whole series of events with chemical agents, referred to as plant growth hormones, PGHs, acting to regulate germination, seedling and plant development, flowering and fruiting, and finally death. Plant growth hormones, PGHs, generally are effective at very low concentrations over the life of the plant in many and varied ways that are plant specific [12-15]. Thus, our research is based on offering plants various materials and then observing the outcome. This “offering” is done by presenting the PGH either itself or as part of a more complex molecule, here as an integral part of a polymer. As part of a polymer, the introduction of the PGH occurs via a sustained manner.

PGHs effects are often plant specific. Specific factors that are often measured to determine the effect and extent of effect include rooting time and incidence, flowering, greening, rate of maturing, growth rate, fruit retention and maturing.

Plants have need of many metals including a number of so-called trace elements [3,4]. Currently, the list of trace metals includes iron, boron, copper, nickel, cobalt, potassium, magnesium, calcium, manganese, zinc, and molybdenum.

While some metals are essential for good plant health, other metals such as cadmium, lead, chromium, mercury, silver, and gold are not essential for plant functioning and are toxic at low concentrations. Even too high concentrations of essential metals can be toxic to plants. It appears that the toxic role of metals is varied but in cases involves the chelation of certain sites in essential materials in the plant. Thus, it is important that the metal chosen to be included is carefully chosen as to not act in an unwanted manner. Also, of consideration is the low concentrations of PGHs needed to affect desired behavior and the corresponding low concentrations of associated metals.
employed is so low as to not act as a threat to plants or to us even when cumulated ten fold.

Currently, we have included tin, manganese, titanium, zirconium, and hafnium along with specific PGHs into polymers. This group includes one metal, tin, that can act to deter unwanted fungi and bacterial growth; includes one essential metal, manganese, that may assist in the plant growth and development; and three members that are generally believed to be benign with respect to plant activity and human response at the levels employed.

Our efforts have focused on several aspects of PGH activity including seed germination, seedling development and rooting of plant parts. Because results are plant species specific, results from studying one plant are at best indicative of the behavior towards another plant and where application is desired, the specific plant species should be studied.

The PGHs employed by us are naturally occurring or in the case of auxins, a close form of the naturally occurring indole acetic acid, IAA. This is intentional since their presence offers nothing “new” to the plant kingdom except maybe the particular metal-containing moiety that can be tailored to plan an active role in the ongoing enterprise or to be benign.

In general polymers containing PGHs can act as control release agent where these formulations can offer

*greater shelf life
*sustained release
*greater retention of the active agent due to lowered solubility of the polymer and
*(in some cases) the “co-reactant” can offer additional properties such as antifungal activity.

There are a number of PGHs. The three major groupings tested by us are the auxins, gibberellins, and cytokinetins.

Setting

Today, most commercial seeds have high rates of germination [3,4,12-15]. Yet, in developing countries where seeds have become damaged through time (age), insect infestation, excessive heat/cold/water/etc., crop production may be severely limited by the lack of high germination because of these and other factors. One of the major focuses of our studies is the evaluation of the ability of polymers containing PGHs to increase the germination rate of these older and damaged seeds in an attempt to assist situations where these are the only seeds available to the general population.

Gibberellins are cyclic diterenes with the ability to induce a number of plant responses including cell elongation and cell division [3,4,12-15]. Widespread in nature, the major commercially employed gibberellin is call gibberellic acid, GA3 (3). While widespread in nature, most are not biologically active. The formation of inactive species from active species may represent a mechanism by which excess biologically active gibberellins are removed.

Gibberellins act primarily by inducing the expression of the gene for a-amylase. The transcription of information from DNA to RNA which in turn translates into making the protein a-amylase is believed to be mediated by DNA-binding proteins similar to regulatory proteins in operons of prokaryotic cells. Using this model of an operon in a prokaryotic cell, it is believed that active gibberellins increase the level of protein that switches on the production of a-amylase mRNA by binding to an upstream regulatory sequence of the a-amylase gene. While this is a proposed model, it is not known how active gibberellins actually increase the level of this protein.

The most active of the naturally occurring gibberellins is GA3 and it is GA3 that is the most widely utilized in research and commercially to increase plant and food production. GA3, 2,4,7-trihydroxy-1,8-methylene gibb-3-ene-1,10-carboxylic acid-1-4 lactone, is sold under a number of names including Gib-tabs, Ceku-Gib, Gibrel, Brellin, Gib-Sol, Pro-Gibb, Berfelex, Activol, Grocel, Cekugib, Regulex, and floraltone. It has a LD50 of 6300 mg/kg so is relatively non-toxic. It is registered in the USA for use on grapes, cotton, spinach, turf, artichokes, hops, rye, peas, oats, soybeans, beans, rhubarb, citrus, cherries, ornaments, potatoes, sugar cane, celery, blueberries, strawberries, etc. Uses are varied but include increase in fruit size, fruit loosening, increased fruit set, prevents color change, helps against cold stress and light frost, helps break dormancy, stimulates sprouting, increases fruit yield, etc. Application rates are generally on the order of 1 ppm.
GA3 has three functional groups, two alcohols and one acid functional group, that can react in a condensation reaction \[5,11\]. The resulting products are crosslinked and consequently insoluble \[1,2\]. Thus, any release of the GA3 occurs through the break down or degradation of the polymer chain releasing the GA3. This probably occurs through physical hydrolysis as the polymer comes into contact with the water \[5,11\]. Following is a brief description of some of our efforts with GA3 \[16-23\]. In our research, a number of food-producing seeds were studied including soybeans, purple top turnips, Little Marvel peas, Jagger wheat, Florida Broad Leaf mustard, Calabrese broccoli and seeds that contained mold and which were exposed to animals and insects \[18,19,21\]. Germination decreases with the age of the seed often decreasing by over 50% for each year after the initial year. The seeds were about four years old so three years past the indicated time for planting.

Following are generally results for the seeds. Table 1 contains the results for GA3 and four of the seeds.

For Jagger wheat the largest percentages germinations were for GA3, 10 ppm itself (the concentration amounts are the amount of test material in talc), dimethyltin/GA3, 1000 ppm, and dibutyltin/GA3, 10 ppm. These also represents most of the highest percentage germinations (control 9% verses 43% for GA3, 10 ppm; 27% for dimethyltin/GA3, 1000 ppm \[4\]; and 23% dibutyltin/GA3, 10 ppm). For the peas the increases were larger with the control giving only a 3% germination whereas this was significantly larger for most of the polymer-containing mixtures with the hafnocene/GA3 10 ppm gave the largest germination of 24%; titanocene/GA3 1000 ppm giving a germination of 23% and zirconocene/GA3 1000 ppm and dibutyltin/GA3 1000 ppm both giving 20% germination. For the turnip, the control was 23% with some of the polymers acting to increase this germination to about 30% and greater (dibutyltin/GA3 1000 and 10 ppm; dimethyltin/GA3 10 ppm; diethyltin/GA3 10 ppm and hafnocene/GA3 1000 and 10 ppm). For the Jagger wheat the control was 9% germination whereas all of the polymers giving germination rates equal to and greater than this. Many of the polymers gave germination rates double this with the largest being number of the polymers (hafnocene/GA3 10 ppm; dimethyltin/10 and 1000 ppm; diethyltin/GA3 10 and 1000 ppm).

In all cases, seedling development appeared to be independent of the particular seed treatment.

It must be remembered that GA3 itself must be refrigerated to maintain viability, the polymers have been stored in the open and in the Florida sunlight for over two years without any change in their infrared spectra consistent with them being stable. Thus, incorporation into polymers appears to lock in the GA3 moiety structure giving it an increased thermal and hydrolytic stability over GA3 itself.

We found with common pole beans (Phaseolus vulgaris L.; Kentucky Wonder, rust resistant pole; Ferry-Morse) that use of 1000 ppm of GA3 alone caused too rapid growth so that the pole beans outgrew bean stalk strength and after two weeks they were so thin and wiry in appearance that they could no longer support their own weight and died \[20,21\]. But with the use of titanocene, \(5\), and manganese-GA3 containing polymers that growth, while greatly accelerated, was controllable so that the resulting plants were robust enough to be considered viable food producing plants. Similar results were found for Red Kidney pole beans \[20,21\].

Of interest, is the intermediate results for the polymer-containing systems so that the magnitude of growth rate was 1000 ppm GA3 > 1000 ppm GA3-Polymer > 100 ppm GA3 > 100 ppm GA3-Polymer > 10 ppm GA3 > 10 ppm GA3-Polymer > Untreated. This trend is consistent with the polymer acting as a controlled release agent. These results are also consistent with the polymer degrading to give the active GA3 since other, even very similar gibberellin structures, are inactive.
Another study involved the rooting and flowering of Hibiscus rosa-sinensis, variety Albo Lacinatus (Anderson’s Crepe Pink) [20,21]. Here addition of GA3 or GA3-containing polymer inhibited the normal rooting of the hibiscus stocks. Of interest was the large number of stocks that formed roots along the stem, above the treated portion at sites where small branches had been removed. Thus, the hibiscus “wanted” to root but the presence of the GA3 discouraged this activity.

As an extension to this study, the rate and extent of flowering of hibiscus bushes that formed from treated stock generally decreased as the concentration of GA3 or GA3-containing polymer increased [20,21]. The rate of flowering is most rapid for bushes formed from stocks treated with low levels of GA3 or GA3-containing polymer.

Related to the seed germination studies employing food seeds was an effort to increase the seed germination of sawgrass seeds [16,17,22]. The single most prominent aspect of the Florida everglades and many wet lands around the world is the presence of sawgrass. Sawgrass is not a grass but rather a sedge. It is responsible to trapping sediments in the presence of sawgrass seeds [16,17,22]. The seed germination of sawgrass while increasing sawgrass germination. Thus, it appears that in some cases the polymeric materials bias towards germination of the sawgrass while inhibiting cattail germination. This observation might be used when seeding areas that currently contain invading cattail.

Auxins

Auxin is a generic name for compounds with the ability to induce elongation in shoot cells [3,4,12-15]. The most rapidly growing parts of plants typically contain the highest concentrations of indole-3-acetic acid, IAA (6), in the tip of the coleoptile, in buds, and in the tips of leaves and roots. The concentration of auxin drops from the tip of the coleoptile to the base. The amount of auxin in the shoot tip, however, is usually much greater than in the tip of the root. In fact, the auxin concentration that promotes cellular elongation in the shoot appears to be too great for the root, and somehow results in actual inhibition of cell elongation in the root. While the application of relatively high concentrations of IAA retard elongation, there may be a considerable increase in the development of branch roots and root hairs due to this high concentration of auxin.

![Auxin molecule](image)

The known biological effects of auxin are numerous [3,4,12-15]. In addition to cellular elongation, apical dominance and root initiation, the more important effects include callus formation, parthenocarpy, phototropism, and geotropism. While auxins play an important role in cell elongation, they also are active in cell division.

The various PGHs interact with one another. For instance IAA interacts with kinetin such that a low ratio of cytokinin to auxin gives a mass of loosely arranged, undifferentiated cells or callus, but a high cytokinin to auxin ratio results in the growth of cultured plantlets with stems and leaves [12-15].

The major commercially employed auxin is indole-3-butyric acid, IBA (7). It is sold under a number of tradenames such as Indole Butyric, Hormodin, Jiffy Grow, Hormex Rooting Powder, Seradix, Rhizopon AA, Chryzopon, Chryzosan, and Chryzotek. It is present in almost all commercial rooting mixtures. It has an LD50 of about 100 mg/kg in mice. Formulations generally contain on the order of 100 ppm IBA. Commercially it is mainly employed to promote and accelerate the rooting of plant cuttings.

Much of the effort with IBA concerned the ability of IBA and IBA-containing polymers to promote the rooting and development of woody plants [20,21,24-26]. Studies were carried out employing dipyr dine manganese (8) and titanocene.
derivatives of IBA. In these studies the effect of the polymers containing IBA was studied using as the woody plant *Hibiscus rosa-sinensis*, variety *Albo Lacinatus* (Anderson’s crepe pink). Unlike seeds where there is a great variation between species, the effect on one woody plant should more closely follow the effect on other woods plants.

As in the case with GA3 and GA3-containing polymers, in general, the polymer treatments produced greater and more rapid rooting in comparison to IBA alone and both were better than the control. Further, the average number of roots were greater for the polymers, both the Mn and Ti (9), in comparison to IBA itself which in turn was greater than no treatment with the least rooting activity found for the monomers titanocene dichloride and dipyridine manganese dichloride. The number of roots for the polymers at concentrations of 0.02% to 1% were almost double that for IBA and three times that of the control and the two metal-containing monomers. Thus, for this study, incorporation of the IBA into a polymer structure had an overall favorable affect on rooting and production of side roots.

The polymers also created a greater number of leaves in comparison to the IBA and control with almost three times the leaves at day ten for the polymers in comparison to IBA and the control. The general results held for the test period of a month.

Cytokinetins

Cytokinetins are most influential on bud and shoot initiation from leaf cuttings and in tissue culture systems [3,4,12-15]. Natural and synthetic cytokinins include zeatin, thidiazuron, benzyladenine, zeatin riboside, and kinetin. They are commercially available under a number of tradenames including Burst, Yield Booster, Jump, Arise, and Cytogen for use on fruits and vegetables, cotton, corn, rice, sorghum, soybeans, and wheat to increase plant vigor and yield. While they are sold for promoting bud initiation and development, they are said to also interact with the plant hormonal system affecting cell division and reproductive activity, promoting female vigor, promoting root initiation and development, and increasing tolerance to stress.

Our work involves the cytokinin kinetin (6-furfurylaminopurine) itself (10). It is the most widely studied cytokinin and is naturally found in plants. Past work emphasized the use of organotin-kinetin containing polymers and their effect on the germination and seedling development of sawgrass and cattail as an extension of our Everglades restoration work noted above.

In general, treatment with kinetin and polymers containing kinetin resulted in an increase in the germination rate of both sawgrass and cattail. In this study there was no real advantage to using the polymer-containing kinetin in comparison to kinetin itself.

We did several studies involving kinetin-containing polymers related to their ability to influence plant growth. Here we describe those related to seed germination [27-32]. For kinetin-containing mixtures, the same battery of food seeds as noted before were studied. Results for three of the seeds appear in Table 2.
Table 1: Germination results for seeds treated with GA3 and GA3-containing polymers. Figures given are averages of three replicate studies and are the average germination percentages.

<table>
<thead>
<tr>
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<th>Turnip</th>
<th>Mustard</th>
<th>Pea</th>
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<td>19</td>
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where Me2Sn/GA3 represents the polymeric product from the reaction of GA3 and dimethyltin dichloride; Et2Sn/GA3 represents the product from diethyltin dichloride; Bu2Sn/GA3 represents the product from dibutyltin dichloride; Cp2Ti/GA3 the product from titanocene dichloride; Cp2Zr/GA3 the product from zirconocene dichloride; and Cp2Hf/GA3 the product from hafnocene dichloride.

Table 2: Germination results for seeds treated with kinetin and kinetin-containing polymers. Figures given are averages of three replicate studies and are the average germination percentages.

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where Me2Sn/K represents the polymeric product from the reaction of kinetin and dimethyltin dichloride; Et2Sn/K represents the product from diethyltin dichloride; Bu2Sn/K represents the product from dibutyltin dichloride; Cp2Ti/K the product from titanocene dichloride; Cp2Zr/K the product from zirconocene dichloride; and Cp2Hf/K the product from hafnocene dichloride.

For the kinetin containing treatments significant increases in germination were found for many of the treatments. The repeat unit for the dimethyltin/kinetin product is given in (10). The increases were modest for mustard with the largest germination rates found for the higher concentrations (1000 ppm) for the Group IV B containing polymers with averages being 32 % (Cp2Ti), 34 % (Cp2Zr), and 40 % (Cp2Hf) in comparison to the control value of 23 %. For Jagger Wheat, the highest yields were found for kinetin, 10 ppm itself (25 %) and Cp2Ti/K, 1000 ppm (20 %; compared to a control value of 9 %). These increases represent a doubling in the percentage germination in comparison to the control. The largest differences were found for turnip seeds where all of the treatments gave at least a doubling in the germination rate with several giving about a six to eight fold increase. The highest increases were for Me2Sn/K, 10 ppm (31 % germination) and Cp2Zr/K, 1000 ppm (27 %). There appeared to be little correlation between the concentration treatments.

(11)

In all cases seedling development appeared independent of the particular seed treatment. This is consistent with the favored use of "natural" PGHs incorporated in polymers with respect to their lack of production of negative side effects.
As an aside, the organotin kinetin-containing polymers were tested for their ability to inhibit Balb 3T3 cells as part of our overall interest in developing anticancer drugs [33-35]. It was found that the polymers has good activity against the Balb 3T3 cell with the greatest activity found for the dibutyltin derivative as found in other studies by us. It is not unexpected that kinetin-containing materials have an effect on cell growth since kinetin itself is a substituted aminopurine. Further, kinetin is known to directly interact with at least plant nucleic acids. This is based on a number of observations including the following: kinetin composition containing the adenine ring; existence in cells of active cytokinin ribonucleosides and nucleotides; cytokinin-stimulated RNA and protein synthesis; cytokinin stimulation of certain enzyme activities and product formation; binding of kinetin to oligonucleotides; and in vivo presence of kinetin in RNA.(Devin and Witham, 1983)36 The results are consistent with kinetin itself not being active but rather the combination of the organotin and kinetin are active either working in concert as individual, freed chain segments from the polymer, or in concert as members of the same chain; or some combination of the afore.

By comparison, the Group IVB metallocene derived polymers showed little or no inhibition of the Balb 3T3 cells [34,35].

Summary

The incorporation of PGHs into metal-containing condensation polymers generally as a positive effect increasing the germination of seeds, including food seeds, and on the rooting of woody plants. Increased germination rates should allow older seeds a better chance at producing food crops. Increased rooting of woody plants should likewise allow greater success at propagating such plants.

References