Kirk-Othmer Encyclopedia of Chemical Technology.

GROWTH REGULATORS, PLANT

1. Introduction

The availability of new plant growth regulators has not grown appreciably in the past 20 years. In part, this has been due to the high costs associated with the discovery and application of new agrochemicals which, from inception to market, are presently estimated to be in the order of US $25–35 million and ~8 years for a synthetic, and US $2–4 million, and ~2–4 years, for a natural product. Into that equation is thrown the cost of registration and the environmental impact, the latter requiring tests across many plant and zoological species. During the past decade, two other factors have entered the picture. The first is the matter of intellectual property and its protection, which translates to the fact that many researchers withhold disclosure of work to their colleagues in either verbal or written form. This was not the case 30 years ago when they often, but not always, disseminated their findings. The second, closely related to the first, are those times when the structure and activity of the new, potentially blockbuster plant growth regulator is presented by an enthusiastic researcher without benefit of patent protection. Subsequently, no chemical company will underwrite the development of a bioactive compound without patent coverage since both national and international patents, plus maintenance fees, have to be paid. Simply stated, unprotected disclosure only impedes the flow of utilitarian materials to the market place.

One further point of interest is that plant growth regulators are, by definition, bioactive compounds. This implies that their homologues and analogues may possess pharmaceutical properties. And, by way of a hypothetical example, if 50 g of a bioactive compound, used to treat 1 hm^2 at an on farm cost of US $100, the same compound used at 10 mg/dose as a medicinal at, say, US $5/tablet, will yield income of US $25,000. Little wonder that the agrochemical–plant growth regulator market has remained torpid with, perhaps, the exception of natural products where more entries have come to fruition.

2. Natural Products

The most acceptable plant growth regulators are those that perform well and, when their task has been accomplished, are degraded to nonharmful environmental products. A small number of novel natural product and their derivatives have made their way to the marketplace in the past ten years. Because of their relative ease of registration it is anticipated that this will become an expanding enterprise. Additionally, a number of microorganisms that produce profitable plant growth regulators have also been introduced, especially by the Japanese. This topic is not addressed here and only the "pure" active materials are included in Table 1.

2.1. AVG

(*E*)-L-2-[2-(2-Aminoethoxy)vinyl] glycine; (2*S*, 3*E*)-2-amino-4-(2-aminoethoxy)-3-butenoic acid [49669-74-1] is a natural product initially obtained by fermentation of a soil borne *Streptomyces* sp. X-11085, found in Arlington, California. Later the organism was accessed by the USDA as NRRL No. 5331. It was first described in Ref. 2, as a new antimicrobial and antihelmintic. Later, it was experimentally shown to have plant growth regulatory properties, but the material took a number of years to reach the market because of its initial high costs.

Its mode of action is inhibition of the key enzyme 1-aminocyclopropane-1-carboxylate (ACC) synthase, which converts *S*-adenosylmethionine to ACC; the latter governs ethylene production (see ethylene), which is necessary for maturation and fruit ripening. AVG has been used to control fruit drop in apples and is superior in activity to naphthalene acetic acid. It has also been used on horticultural plants that undergo stress during shipment to market and it markedly delays the aging process, bud abscission and flowering (3). In pears, it maintains fruit firmness. The United States EPA report issued November 2001 indicates that the material is nontoxic to freshwater fish and invertebrates, but may be moderately toxic to some avian species.

Table 1. Natural Plant Growth Regulators[a]

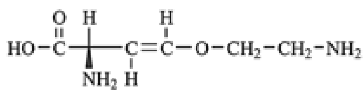
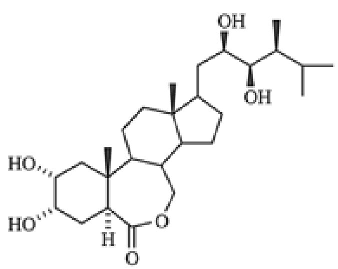
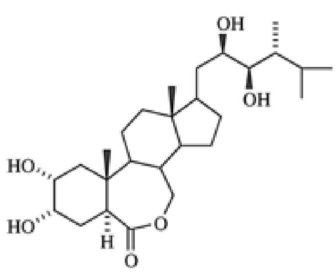
Product	Structure	Trade name	LD_{50}, g/kg
	Available Natural Product		
AVG	 1	AVG, Retain, Prestiage	no toxicity
Brassinolide	 2		mouse, 1.31[b]
24-epibrassinolide	 3		rat[b], 2 mouse, 1

Table 1. ***Continued***

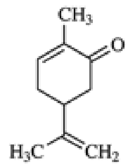
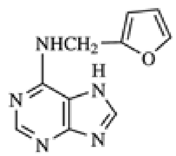
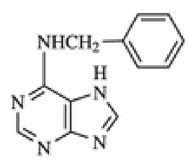
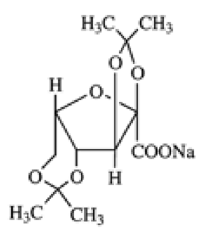
Product	Structure	Trade name	LD_{50}, g/kg
Carvone	 **4**	Carvone, Talent	rat, 1.64
Cytokinins		Trigger, Burst, Yield Booster, Jump	rat, 5
Kinetin[c]	 **5**		
6-benzyladenine	 **6**		
n-Decanol	$H_3C-(CH_2)_8-CH_2OH$ **7**	Off-Shhot-T, Antak, Sucker Pluker Contac	rat, 12.8
Dikegulac	 **8**	Dikegulac, Atrimmec, Atrimol	mouse, 19.5: rat, 3**t**
Ethylene	$H_2C{=}CH_2$ **9**		mouse, 950/L in air

Table 1. ***Continued***

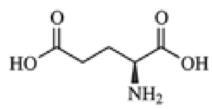
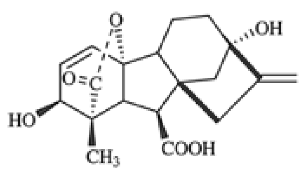
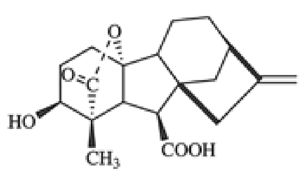
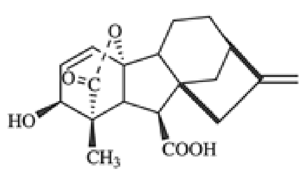
Product	Structure	Trade name	LD_{50}, g/kg
Gamma aminobutyric			
Acid (GABA) and	 10	Auxigro, GABA	rat, 5/kg
Glutamic acid	 11		
Gibberellins			
GA3	 12	G.A., Pro-Gibb, Berelex	mouse, 15
GA4 and GA7	 13  14	Provide, Regulex, Novagib	no toxicity

Table 1. ***Continued***

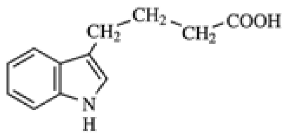
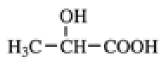
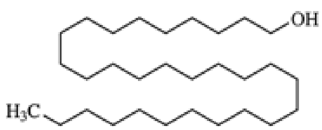
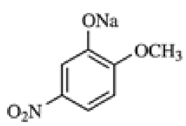
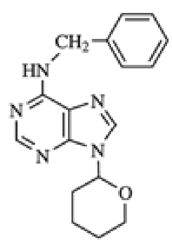
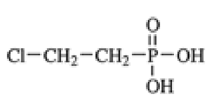
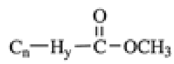
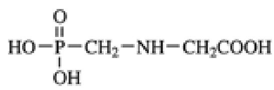
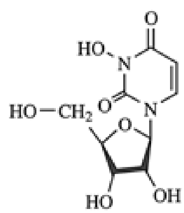
Product	Structure	Trade name	LD_{50}, g/kg
Indole-3 butyric acid	 **15**	IBA, Hormodin, Rhizopin, Jiffy Grow	mouse, 100
L-Lactic acid	 **16**	L-lactic acid, Propel	
Triacontanol	 **17**	Triacontanol	no toxicity
	Available Natural Product Derivatives		
Atonik	 **18**	Atonik	rat, 10
N–(Phenylmethyl)-1,*H*-purine-6-amine	 **19**	Accel	rat, 5
Ethephon; 2-chloro-ethylphosphonic acid	 **20**	Ethephon, Ethrel, Prep.	mouse, 3.03

Table 1. *Continued*

Product	Structure	Trade name	LD_{50}, g/kg
Fatty Acid Methyl Ester	 **21** where $n = 8$–12	Off-Shoot-O	rat, 20.5
N-(Phosphonomethyl)-glycine	 **22**	Round up, Glyphosate, Polado	rat, 3.9
	Miscellaneous		
3-Hydroxyuridine	 **23**	none	

[a]Ref. 1.
[b]Oral.
[c]Kinetin; 6-(4-hydroxy-1,3-dimethylbut-*trans*-2-enylamino)-9-β-D-ribofuranosylpurine. Sodium chloride: LD_{50} rat, oral, 3.75 g/kg.

2.2. Brassinosteroids

The brassinosteroids, especially brassinolide [72962-43-7] and 24-epibrassinolide, are an exceptionally interesting class of natural products that mediate a number of physiological and biochemical events in plants. The unique chemical characteristic of an eight-membered lactone ring is found in the aforementioned compounds and in 2-deoxybrassinolide, dolicholide, ξ-epi-23-dehydrobrassinolide, ξ-epi-28-homobrassinolide, ξ-epi-28-homodolicholide, and possibly three other brassinosteroids.

Brassinolide was originally isolated from the evergreen tree, *Distylium racemosum* Sieb et Aucc (common name, Isunoki) by Japanese scientists who extracted 430 kg of fresh leaves to yield 751 mg of *Distylium* factor A, 50 μg of factor A_2 and 236 μg of factor B. All demonstrated biological activity, but later, factor B was shown to contain a mixture of brassinolide and 2-norbrassinolide. Factor A had some brassinone and castasterone [80736-41-0] (9). Importantly, none of these structures were known in 1968 (5) and, obviously, the yields of factor A_2 and B were too little for separation and identification if one takes into account the separatory and spectroscopic capabilities available at that time. From 1963–1979, the USDA, Agricultural Research Service, mounted a program to isolate the bioactive natural product from rape pollen (*Brassica napus* L.). In a cleverly designed experiment, honey bees were used to collect pollen in flowering rape, or canola, the pollen being removed from the bees by traps placed in the hive entrance (6). The harvest was 38 kg of pollen: This harvest yielded ~4 mg of pure brassinolide upon extraction, and the structure was eventually elucidated. This eventually led to a spate of physiological, biochemical and molecular genetic studies.

24-Epibrassinolide can be obtained in relatively large quantities starting with brassinolide, present in the sterol fraction of canola oil from 10–20%. The epibrassinolide has been used fairly extensively to treat barley (*Hordeum vulgare*), lucerne (*Medicago sativa*), and some horticultural crops in Russia. Barley yields increased up to 25% using applications of 50 or 100 mg/nm^2 in 500 L of water; lucerne seed yields increased 26% (7). In China, during a 6-year period, the compound was tested on 3333 hm^2 of wheat (*Triticum aestivum*) using concentrations of 0.1–0.001 ppm (8). Yields consistently increased to 15%. During 1990–1991 real use was increased to a total of 4000 hm^2 with yield increase of 8–15%. While total land mass use was expected to increase to >23,000 hm^2 during 1992–1994 with an estimated use of 100 g of 24-epibrassinolide, those figures have not been made available. Corn, cucumber, tobacco, and watermelon have also been treated in China with, purportedly, substantially increased yields, although sesame yields have increased 17% (9). Increase fruit set brought about by spraying at the time of flowering in eggplants, grape, orange, canola, and strawberry, has also increased yields.

Perhaps the most telling report on the status of the brassinolides comes from the Huangjia Biochemicals Co. Ltd., China. To quote, in part, "Hungjia natural brassins, directly extracted from plants, is natural, effective, nontoxic and wide spectrum and its main composition is brassins (*sic*) lactone. Chemical formula $C_{28}H_{48}O_6$ . . ." "Its application tests in 80 varieties of plants in China's 800-odd counties showed it can enhance seed vitality and root's (*sic*) development and growth, increase its absorption of moisture and fertilizer, and increase chlorophyll content and photosynthesis, thus ensuring high and stable output for its function in promoting plant growth, increasing their resistance to disease and pesticide, improving winter hardiness, drought hardiness, alkaline resistance and water-logging tolerance. It is widely welcome due to its low price and easy application and is known as the "Golden Key" for increase of agricultural output in the twenty-first Century." Essentially, that sums up the practical state of the art, although two reference works are mandatory reading for the serious researcher (10,11). The aforementioned effects observed with brassinosteroid application are more eloquently elaborated, with substantial scientific foundation.

While >60 brassinosteroids have been found in plants, the relatively small amounts obtained preclude major field trials. But synthetic analogues are promising candidates and include the cyclobutane substituted brassinolide, at C25, and the homologous cyclopropane substitution, also at C25 (12). Each of these is about five to seven times more active than the parent brassinolide. Most importantly, their synthesis allows for large scale production, protection of intellectual property by patent and subsequent development by a chemical company. In the same vein, a patent (U.S. Patent No. 4,604,240, "Homobrassinolide, and its preparation and use.") was issued to Sumitomo Chemical Company (13).

3. Carvone

2-Methyl-5-(1-methylethenyl)-2-cyclohexane-1-one; 1-methyl-4-isopropyl-Δ^6-cyclohexen-2-one; carvol [99-49-0] is a natural flavoring compound used in the manufacture of perfumes and soaps (14). It is also used to flavor liqueurs, although the source material is generally used to impart a specific organoleptic flavor to ethanol, wherein it is used as a carminative. *d*-Carvone comes from caraway seed, dill seed, and mandarin orange peel oil. The isomer, *l*-carvone, occurs in spearmint and kuromoji oils, while the *dl*-mixture is found in gingergrass oil. Because of its natural occurrence in food and condiments, it is an appealing candidate for employment as an agrochemical. A primary use is on stored Irish potatoes to control tuber shoot growth. The mode of action is plasmolysis of the tender sprouts, but the action is temporary. On one hand, reapplication is necessary for continual protection. But on the other, the potatoes can be removed from storage and used directly. Many essential oils have antimicrobial properties and carvone is no exception, so that it has the dual effect of being both a plant growth regulator and microbial antibiotic. Since the material used in post harvest treatment is obtained from caraway seed oil, it is presumed to be the *d*-isomer. Unfortunately, the compound is not yet approved for use in the United States (15).

4. Cytokinins

Kinetin, N^6-furfuryladenine; *N*-(2-furanylmethyl)-1*H*-purin-6-amine, [525-79-1] was the first cytokinin discovered, by serendipity, in a stale sample of herring sperm (16) while examining random laboratory materials to enhance plant tissue cultures. Later, it was isolated from the vascular system of tobacco stems and leaves (17). Because the purines and pyrimidines form the backbone structure of both DNA and RNA, discovery of their analogs in both the animal and plant kingdom comes as no surprise. Kinetin plays an instrumental role in increasing cell division in tobacco wound callus tissue cultured on White's agar medium supplemented with 2 mg/L of indole-3-acetic acid (IAA): The IAA is a mandatory inclusion for cell division induction in the presence of kinetin.

Microorganisms have also been the source of certain cytokinins: *trans*-zeatin [1637-39-4], *trans*-zeatin riboside, and 6-(4-hydroxy-1,3-dimethylbut-*trans*-2-enylamino)-9-β-D-ribofuranosylpurine, specifically from the bacterial phytopathogen *Pseudomonas syringae* pv. *savastanoi*, which causes olive knot and galls on stems of ash, jasmine, oleander, and privet.

6-Benzyladenine, an analog of kinetin, is used to thin apples postblossom in a controlled way, and results in bigger fruit.

Earlier, certain commercial products claimed to contain zeatin [1637-39-4], dihydroxyzeatin [23599-75-1], and isopentyladenine [97856-37-6], either as free bases, or riboside derivatives, as their active ingredient (18). Critical chemical analyses, which have vastly improved, now show that certain seaweed products, such as those obtained from *Ascophyllum nodosum*, contain kinetin, solely, as the active plant growth regulator. Proprietary products include soluble seaweed extract from Acadian AgriTech, probably the largest supplier of *A. nodosum* extract. Another product is soil Trigger, a mixture of cytokinins obtained from seaweed (19,20) and other plant hormones of the auxin (indole-3-acetic acid) family. Rates that range from 3.65–43.9 mL of the mixture (5–6 oz/A) have been shown to improve root growth, control and alter flowering time and rate, increase fruit and seed set, and yield crops with uniformity and quality. Crops treated with satisfactory results include alfalfa, corn, cotton, jojoba, lupine, peanuts, rice, sorghum, sugar beets, triticale, wheat, and certain fruits, and vegetables. It is also used on turf, trees, and ornamentals, and can be tank mixed with pesticides. All the cytokinins are regarded as being environmentally benign.

The overriding fact is that the commercial preparations appear to be seaweed and fermentation products. As such, it needs to be clearly understood that there are many other natural products contained in the mixtures. While the bioactive effects are attributed to either kinetin, or benzyladenine, or mixed cytokinins, the presence of other highly potent plant growth regulators cannot be discounted. Obviously, one can only detect and report those structures that are already known, unless a massive and expensive research effort is undertaken to characterize novel compounds.

It is also of interest to note that of the cytokinins reported, they are all purine derivatives. As earlier stated, the purines form the structural skeletal backbone of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). What then of the naturally occurring pyrimidines and their bioactivity? Briefly, this has been a relatively disappointing area of research, but one example, which has not been developed commercially, is 3-hydroxyuridine obtained from the tree *Baillonella toxisperma*, found in the tropical rain forests of Cameroon.

This tree is a large species that grows to 50 m, with a trunk diameter of 1.9 m ~1.5 m from the ground. The foliar umbrella is ~30 m, and saplings growing in that shade only reach a terminal height of 1.6 m. While this may be falsely attributed to a lack of photosynthesis, the real reason is the production of a hydrophilic growth inhibitor in the leaves, stems, and roots. Methanol extraction of these organs yields the resinous 3-hydroxyuridine (21). 40 μM inhibited cucumber hypocotyls and roots 50% (I_{50}). When the compound was sprayed on rice, there were no effects. Simply, initial experiments indicated that 3-hydroxyuridine was selectively toxic to dicotyledonous plants, but not monocotyledons.

As to why 3-hydroxyuridine was not commercially developed can only be a matter for conjecture. Possibly, the intellectual property had been compromised by earlier disclosure.

Two synthetic pyrimidines have met with success. Ancymidol is an internode inhibitor on nursery stock (see ANCYMIDOL): Fluprimidol is used on turf grass and trees to reduce growth (see FLUPRIMIDOL).

5. *n*-Decanol

n-Decanol [112-30-1] may be synthetically prepared by a number of routes; it also occurs naturally in vegetable oils. While it is classified as a plant growth regulator and is used to control axillary shoot growth in mature tobacco plants as a contact spray, it is not a phytohormone. It acts by plasmolysis of the tender shoots. The substance is applied to tobacco plants when the flowers are in the button stage, as compact, immature racemes, before the corollas have burst through the calyx, or just after the inflorescences have been mechanically removed. The length of the axillary shoot is important if the *n*-decanol is to be effective for if they are >2.5 cm long they must be removed manually. The substance is applied at rates of 2.45–12.78 kg/m^2, a rather heavy application, but it is nontoxic. It has an unpleasant, acrid fatty acid odor; hence it is carefully handled by applicators (18).

6. Dikegulac

2,3:4,6-Bis-*o*-(methylethylidene)-α-L-xylo-2-hexulofuranosonic acid [18467-77-1] is a monosaccharide derivative obtained as an intermediate in the commercial synthesis of L-ascorbic acid. It possesses potent plant growth regulator properties, occurs naturally as the free acid, but is applied as the water soluble sodium salt as dikegulac. In initial experiments, plants treated with 6 g/L (6000 ppm) included barley, perennial ryegrass (*Lolium perenne*), crabgrass, apple, grape, privet, bean, tomato, gerbera (*Gerbera jasmesonii*), and rhododendron. The compound inhibited growth of the first five species, but gave variable response in the others. Bean petioles abscissed, tomato fruit were parthenocarpic, axillary shoots were increased in gerbera giving rise to more flowers, and rhododendrons were pinched so that axillary shoots broke dormancy giving bushy plants (22). It is presently used as a chemical pruning agent for woody plants, such as azaleas and other landscape shrubs, and as a growth inhibiting agent for ground covers (18). It also inhibits flowering and subsequent fruit set in glossy privet, Japanese holly, and ornamental olive.

7. Ethylene

Ethylene [74-85-1], the structurally simplest of all the plant growth regulators, occurs naturally and is of major importance. It is unique in that its natural state is gaseous and, therefore, lends itself to a number of post-harvest practical applications in gas tight enclosures. It must, however, be handled with care because of its extremely explosive nature and exposure to sparks, or naked flames can prove hazardous. This volatile characteristic always posed a problem on banana boats where ethylene produced by the ripening fruit collected below-deck in the hold. There, smoking has been expressly forbidden because of the cataclysmic combination that can result. The gas has been shown to be generated by a large number of fungi (23) and it is produced by many fruits during maturation and ripening, bananas being a prime example.

The effects of ethylene on plant growth were first reported during the last quarter of the nineteenth century. Practically, as early as 1935, ethylene gas was used in Germany to ripen, or color to a pleasing yellow, tobacco during the curing process, specifically at the coloring stage (24). During World War II, it was used in Italy for the same purpose (25): historically, tobacco is an important commodity during wartime both to sooth the nerves and as a bartering instrument. Ethylene also has been used to induce senescence and defoliation in cotton and other select plants (26).

Obviously, the use of gaseous ethylene as a practical field chemical posed a dilemma. How would it be possible to effectively use the material? Two events solved the riddle. A practical form arrived in the market ~1970 when the experimental compound Ethrel (ethephon, 2-cholorethylphosphonic acid [16672-87-0]) was distributed for field and greenhouse trials. The connecting link was 2-chloroethanol, available in tank-car quantities, which had been used as a sprout promoter in Irish potatoes (*Solanum tuberosum*). It had been extensively employed in the preparation of seed potatoes in the 1940s. The process, where seed potatoes were wrapped in cheesecloth and dunked in solutions of 2-chloroethanol, was clumsy, the chemical tended to volatilize in the heat of the sun, workers were not protected with suitable clothing as they are today, the material translocated through the epidermis, and the fumes were toxic. In 1945, the synthesis of 2-chlorethylphosphonic acid was reported by two Russian scientists (27). Bear in mind that Russia had been devastated by the Nazis in World War II and the idea of synthesizing that type of compound seems preposterous. But, there was a reason, Russia had seen the effects of the atomic bomb and was aware of the damage caused by radiation. Because of the vision of the Cold War, Russian scientist began intensive investigations with anti-radiation compounds, a major field of endeavor being phosphates and their derivatives. Subsequently, in 1965, the compound was rediscovered, lending to release for trials in 1970: The West had finally caught up with Russian literature. 2-Chlorotheylphosphonic acid, a water soluble compound, has proven to be a highly utilitarian agrochemical for use as a ripening agent in many crops. Under physiological conditions it is readily translocated and breaks down to release ethylene, chloride ions, and phosphate. The release of ethylene is pH mediated with 3.5 being the threshold. It is used to promote fruit maturity and loosening of fruit in apples, blackberries, black currants, cherries, coffee, pepper, and tomatoes. Other unique uses include increasing flower bud development in apples, uniform flower bud initiation in pineapples, stimulating latex flow in rubber trees inhibiting arrowing (flowering) in sugarcane, increasing sucrose content in sugarcane barrels, and yellowing flue-cured tobacco to reduce curing time. The cost savings in tobacco production, during the heyday of the crop, was staggering and it has been estimated in the United States that there was an annual savings of 68.9 million L of LPG, 257 million L of fuel oil, and 110 million Kwh of electricity. Altogether, this represented a huge savings in energy. Worldwide figures are not available, but presumably with reduced production of tobacco in the United States other countries, like Brazil, Venezuela, and Central America will rise to the occasion. The lure of tax income will be hard to resist.

The compound is also used to loosen walnuts, and the flower industry to shorten stems in daffodil bulbs that have been forced and to stimulate and increase branching in geraniums, greenhouse roses (*Rosa* sp.) may also be treated to increase basal budding. Application rates vary, depending on the crop being treated. Of paramount importance is the fact that the compound is nonflammable yet possesses many of the useful properties exhibited by gaseous ethylene.

8. Gamma Aminobutyric Acid

4-Aminobutyric acid [56-12-2]; 4-amino-*n*-butyric acid, *dl*-4-aminobuytyric acid; GABA, is a naturally occurring amino acid. The commercial product, Auxigro®, is sold as a mixture of GABA with glutamic acid (50:50), the latter being a well-known cooking ingredient as monosodium glutamate (28). The proprietary mixture is applied at 4 oz/A and has the advantage of compatibility with fertilizers and pesticides. Crop yields and quality, which may include increased sugars and earlier maturity, have been reported for almonds, broccoli, and cauliflower, celery, cucumber, edible dry beans, grapes, grass (for seed production), onions, peppers, head and leaf lettuce, peanuts, Irish potatoes, snapbeans, stone fruits, strawberries, sugar beets, tomatoes, and watermelons. When applied at the proper time there is enhanced flowering, increased fruit size and great yields of 10–30%. An additional bonus in using the product is the control of powdery mildew (*Uncinula necator*), gray mould (*Botrytis cinerea*) and suppression of gummy stem blight of watermelon (*Didymella bryoniae*).

9. Gibberellins

Of the 116 gibberellins discovered, 10 are from fungi alone, 14 are found in fungi and plants, and 92 occur in only plants (29). Despite this relatively large number, only three have found their way into commercial applications: GA_3 [77-06-5], GA_4 [561-56-8] and GA_7 [510-75-8]. For the most part, they are responsible for cell elongation in plants and their initial discovery, reported in 1926, was the result of observing hyperelongation in diseased rice plants infected with Bakanae, or "crazy disease", namely, *Gibberella fujikuroi* (30). Subsequently, culture filtrates of *G. fujikuroi* induced seedling elongation not only in rice, but also in grass. In 1938, 12-years later, the isolation of gibberellin A and B were reported from the same fungus, but the findings were largely ignored because they were in Japanese, and World War II was imminent in Europe, with the United States following close behind. At the end of hostilities, reconstruction began in Japan in late 1945. Japanese scientific literature was methodically examined and the gibberellins came sharply into focus because of a unique feature: their ability to increase plant yields. This was important not only for Japan, but also for Europe and the Far East. Oddly, by coincidence, 12 years after the end of World War II, the USDA Agricultural Research Service issued a compilation of 632 scientific articles dealing with the gibberellins, in 1957. Obviously, since that time the discovery of new gibberellins has gone through exponential growth but, ironically, it is still those that were first discovered that form the backbone of gibberellin commerce. While GA_3 is often used exclusively alone, both GA_4 and GA_7 are generally for field applications in combination with 6-benzylaminopurine; however, there are limited exceptions where they are used without 6-benzylaminopurine.

GA_3 is, 1-α, 2β, 4aβ, 10β-2,4a-trihydroxy-1-methyl-8-methylenegibb-3-ene-1, 10-dicarboxylic acid, 1,4a lactone; GA_4 is, 1-α, 2β, 4$a\alpha$, 4$a\beta$, 10β-2,4a-dihydroxy-1-methyl-8-methylenegibbane-1, 10-dicarboxylic acid, 1,4a lactone; GA_7 is, 1-α, 2β, 4aα, 4$a\beta$,-2,4a-dihydroxy-1-methyl-8-methylenegibb-3-ene-1, 10-dicarboxylic acid, 1,4a lactone. These three gibberellins are produced by fermentation.

When GA_4 and GA_7 are used together at rates of $\sim$50 ppm/hm^2 in aqueous solution, they induce development of male flowers on gynoecious cucumber plants, thereby increasing the chances of fertilization and fruit set. This is done every five days for a total of three applications. Another use is in apples to suppress the development of physiological fruit russeting, to obtain quality fruit. Generally 2–4 applications are necessary when the apples are developing, at rates of 15–20 ppm, depending on rainfall and other weather conditions. The same mixture is applied at 24–50 ppm to control preharvest fruit cracking exclusively in "Stayman" apples, but it must be applied before cracking occurs, not after. Meticulous records of the history of each orchard must be kept because the chemicals have to be applied 2–3 weeks prior to the time that fruit cracking is likely to be observed. Another caveat is that "Stayman" apples that have received prior treatment with GA_4 and GA_7 to suppress russeting may not be treated for cracking suppression during the same growing season.

Depending on the concentrations used, mixtures of N-(phenylmethyl)-1H-purine-6-amine and GA_4 GA_7 are used for fruit thinning, or to induce other horticultural traits. For example, mixtures of 1.8% N-(phenylmethyl)-1H-purine-6-amine and 0.18%GA_4 GA_7 will thin fruit, resulting in harvest of increased fruit size. Mixtures of 1.8% and 1.8% of both ingredients are used on apples, nonbearing pear trees and nonbearing cherries. The shape of "Red Delicious" apples is changed in length and in the production of accentuated calyx lobes, which are characteristic of the variety. Increased fruit size and weight are brought about in most apple varieties and there is improvement in branch architecture. Branching and lateral bud break are also enhanced.

The chemical congener GA_3 exhibits a vast range of growth regulating responses on a variety of crops. Its application amounts range from 10 ppm for hops (*Humulus lupulus*) to 30 ppm/hm^2 for sugarcane. The material is used on blueberries (*Vaccinium* sp.) to increase fruit set when pollination by honey bees is insufficient. In cherries, depending on the variety, GA_3 acts as an antagonist to the effects of cherry yellows virus; in sweet cherries, application of the chemical improves fruit size, texture, color, and prolongs harvest time. The compound is applied to both tart and sweet cherries to reduce flowering and, consequently, fruiting.

Prior to the advent of GA_3 it was common practice to girdle grape vines to increase yields. An unfortunate result, although rare, was that the girdling knife cut through the vascular cambium thereby destroying productive, well established vines. The technique could only be carried out by highly skilled workers, but in the early 1950s their jobs became redundant; GA_3 replaced the girdler's knife. Most applications to grapes are made either at berry shatter or normal girdling time. The results are increased berry size and, in the case of raisin grapes, maturity is hastened with a concomitant rise in quality.

The citrus industry also uses GA_3 to improve crop quality. In lemons (*Citrus* sp.), application delays yellowing and fruit size is increased. Treated lemons also have increased shelf life. Both Navel and Valencia oranges have delayed ripening when treated with GA_3 and the skins of both varieties are considerable improved. Whereas the same holds true for tangerines, one of the main uses in that crop is to improve fruit set, especially in those varieties in which pollen production is insufficient, eg, Minneola, Orlando, and Robinson. If grapefruit are treated with GA_3, the fruit is retained longer on the tree and there are fewer losses due to early fruit drops; the skin remains firmer and takes on a less mature look. GA_3 has been used to control the attack of the Caribbean fruitfly (*Anastrepha suspensa*) by keeping the skin of the grapefruit firmer and in less mature state: the reduction of chemical attractants in the peel or the color of the skin, or both, makes the fruit less attractive to the insect (31,32). In the Pome family, the only member that responds favorably to GA3 treatment is the pear (*Pyrus communis*); the compound is generally used to increase fruit set especially in those varieties where pollination is poor. Apart from the cherries, which have been discussed, the other stonefruit routinely treated with GA_3 is the Italian prune. Spraying with GA_3 increases yields and inhibits internal browning. Other horticultural crops also improved with standard GA_3 treatments include rhubarb (*Rheum* sp.), artichokes (*Cymara scolymus*), asparagus (*Asparagus officionalis*), bean (*Phaseolus vulgaris*), celery (*Apium graveolens*), cucumber (*Cucumis sativus*), lettuce seed production (*Lactuca sativa*), parsley (*Petroselinum crispum*), peas (*Pisum sativum*), seed-potato (*Solanum tuberosum*) to break dormancy, barley (*Hordeum vulgare*) in the malting process to control malt production and, thereby, increase the relative concentration of neutral grain spirit in the manufacture of gin and vodka, oats (*Avena sativa*), cotton (*Gossypium hirsutum*), rye (*Secale cereale*), soybeans (*Glycine max*), strawberries (*Frageria* sp.) and wheat (*Triticum aestivum*). The material also has application on golf courses where Bermuda grass (*Cynodon dactylon*) may be induced to start growth, or growth may be maintained throughout the season. Aesthetically, GA_3 may be used to keep the grass during times of stress, or when light frosts occur.

The effects of GA_3 are also responsible for its use in sugarcane where ground or aerial application just prior to harvest increases sucrose yields, with solutions containing 30 ppm of active ingredient. However, these effects were only seen in Hawaii where sugar was a 2-year crop when harvested and the rootstock was mechanically destroyed. Since sugarcane is no longer grown in Hawaii as a commercial crop, the matter is a moot point, but it does not preclude the use of GA_3 in other sugarcane growing areas. There are exceptions to the possible use of GA_3 in sugarcane and that is the West Indies, where sugarcane is harvested annually and each rootstock is viable for about seven years. That is, crops are cut from the same rootstock. There, GA_3 has no effect on sucrose content. But one important feature does come from the applications carried out in Hawaii. First, there appears to be a direct correlation between altitude, temperature, and response. Sugarcane grown in the lowlands of Hawaii experienced some stress as the result of reduced seasonal temperatures with concomitant slowing of growth and it is those varieties that respond well to GA_3 treatments (33). To better understand the matter, it should be pointed out that a company may grow several different varieties of sugarcane, depending upon the specific environment.

Gibberellic acid is also used successfully in rice culture to promote seed germination and the growth of semidwarf varieties. The treated seed can be planted deeper than normal. In addition, the sprouting seedlings are much taller than the untreated ones and they compete well against weeds.

Ornamentals are treated with GA_3 for a variety of purposes including more profuse flowering, increasing flower numbers and, in some circumstances, flower size. It is common practice in the southeastern United States to "gib" camellias prior to flowering. A small amount of the potassium salt of GA_3 at 100 ppm is dropped into the floral bud at a very early stage of development to produce large flowers. Horticultural scientists have fine tuned the use of GA_3 to an exquisite degree. It can be used to inhibit flower bud formation during the vegetative growth of azaleas and can also be used to break dormancy in the same species. The acceleration of flowering and the increase in flower size can also be enhanced with the material in calla lilies, geranium and statice.

Even specific niche markets such as increase in stem length of Queen Anne's lace and longer petal production in pompom chrysanthemums are part of the panoply of GA_3 uses. To say that GA_3 has been a highly profitable, environmentally safe, and multipurpose agrochemical is an understatement.

10. Indole 3-Butyric Acid

Some 500 compounds were evaluated for plant growth regulating properties from the late 1920s–1950, a period often described as the Golden Age for bioactive compounds. Of these, a homologue of indole-3-acetic acid [133-32-4], the naturally occurring chemical also known as auxin, was synthetically produced (34). It was indole-3-butyric acid and structurally differed by the addition of two extra carbons in the side chain. What made it a highly utilitarian marketable product was the ease by which it could be inexpensively obtained in large quantities, its stability both in storage and aqueous conditions, especially in sterile solution, and the small amounts needed to produce effects. The LD_{50} is 100 mg/kg in mice administered ip.

Originally sold in 1936, it was considered a non-natural product, but in the early 1990s it was found in *Arabidopsis*; tobacco leaves; maize kernels, leaves and roots; and in pea epicotyls, roots and shoots. It is now considered to be a storage form of indole-3-acetic acid (35).

The material has generally been sold as a talc impregnated product containing 0.1–1.5% of the active compound, higher concentrations being used on woody, or more difficult plants to root.

11. Lactic Acid

L-Lactic acid [79-33-4]; 2-hydroxypropanoic acid (*d*-isomer [50-21-5], *dl*-isomer [598-82-3]), is a ubiquitous natural product throughout the animal and plant kingdoms. It is the result of glucose metabolism in the Embden-Meyerhof pathway wherein glucose is split to yielded phosphoglyceraldehyde by a series of steps. In turn, this is acted upon by the enzyme phosphoglyceraldehyde dehydrogenase to produce phosphoglyceric acid. The latter comes under the influence of lactic dehydrogenase and L-lactic acid is formed. Applied at the rate of 4.39 mL/hm^2, using a stock 80% solution, it has been used to increase fruit set, ripening, and promote shoot formation in members of the *Cruciferae*, stonefruit, *Solanaceae*, citrus, corn, grapes, pineapples, strawberries, sugarcane, and walnuts. Most recently, its major applications are on apples to enhance ripening, when applied 30–45 days before harvest; to enhance ripening, increase sugar, and promote fruit weight; to increase bulb diameter in onions; and to increase size and yields by a minimum of 5–10% in Irish potatoes (15,36).

While the mode of action of the material is not known, it appears to be most efficacious when plants undergo physiological stress. This indicates, possibly, that the material feeds into the Embden-Meyerhof pathway and, subsequently, into the Kreb's cycle. Because lactic acid is a terminal metabolic product these are few clues as to its ultimate fate in plants.

12. Triacontanol

This 30 carbon, straight chained, hydrophobic alcohol [593-50-0], has been found as an ester of palmitic acid; it occurs in the free form in the cuticular waxes of plants. In conjunction with other waxes and alcohols, it serves to protect plants from invasion by insects and phytopathogens, and as a water antitranspirant, especially in xerophytes and tropical plants. Its discovery in alfalfa, *Medicago sativa*, and subsequent experimental application on barley, *Hordeum vulgare* and maize, *Zea mays*, led to its use as a plant growth regulator (37). A major difficulty in applying triacontanol to crops has been its water insolubility, which poses a formulation problem, combined with penetration through leaf and stem surfaces, giving rise to sporadic responses. It has been prepared as a colloidal solution in an attempt to solve the problem (38). Nanomolar concentrations increase rice seedling growth and its mode of action is attributed to the elicitation of L (+) adenosine, a second messenger in the cycle of plant growth (39). Crops that have benefited from triacontanol application are: barley, bean, beet, carrot, cucumber, cauliflower, flowers, lettuce, maize, peanuts, potatoes, rice, sugarcane, tomato, and vegetables. In all cases, increased yields have been reported. The compound is not toxic to plants or animals and, therefore, it is considered to be environmentally benign.

Reference 40, eloquently outlined the invention. In 20 claims, it is stated that triacontanol can be applied as a foliar spray, a soil drench, a side dressing, or in conjunction with a fertilizer and insecticide application. Furthermore, the compound acts as a stimulant on a wide range of plants to increase dry weight gains, water uptake, water efficiency use and effectively promote protein synthesis in treated plants.

13. Natural Product Derivatives

During the past decade, there has been a marked move to the introduction of natural products, and their immediate derivatives, as agrochemicals. This has been predicated on the increased ease and relatively lower cost that are expanded in registration and development. Many of the newer products are mixtures of older natural product plant growth regulators and, while interesting, are not exceptionally innovative and are not discussed here in any detail.

13.1. Atonik

5-Nitroguaiacol sodium salt [61233-85-6]; Atonik, was introduced by Asahi Chemical Manufacturing Co. Ltd in 1990 for worldwide distribution, and is registered in the United States as a “biochemical”. It speeds up cytoplasmic streaming in plant cells and caused significant increase in mineral uptake and translocation of assimilates. This results in higher yields and better quality. Another function is that it induces recovery in plants that have been damaged by herbicides, pests, drought, frost, and other forms of stress.

It may be applied as a mixture with other treatments generally 1–3 times per season at specific stages of organogenesis, such as rooting, budding, flowering, fruit set, and vegetative growth. It has been evaluated on apples, black currants, coffee, cotton, cucumber, mango, lichi, oil-seed rape, pepper, sugarbeets, sunflower, tomato, tea, tobacco, to name but a few. It has the property of being relatively nontoxic with and LD_{50} of 10 g/kg: sodium chloride has an LD_{50} of 3.75 g/kg (41).

13.2. *N*-(Phenylmethyl)-9-(tetrahydro-2*H*-pyran-2-yl)-9*H*-purin-6-amine

N-(Phenylmethyl)-9-(tetrahydro-2*H*-pyran-2-yl)-9*H*-purin-6-amine once had the trademark ACCEL, which should not be confused with the material registered as Accel. The former is the purine plant growth regulator (42), while the latter is a lactic acid starter consisting of *Pediococcus cerevesia* for the fermentation of summer sausage. Except for older literature, the name ACCEL has been replaced by Proshear. The only use for Proshear is as a plant growth regulator in white pine where it is applied two weeks before or after shearing to shape the trees (36). To add to the apparent nomenclature and marketing confusion, Abbott Labs withdrew Proshear from the market on 7 July 1995. This action was not due to the active ingredient but, rather, to an inert ingredient which may have had deleterious environmental impact. Abbott planned to reformulate and reregister the "new" product. In the meantime, Abbott sold most of its agricultural acquisitions. From the most recent listings, the compound is available from Sumitomo Chemical Co. Formerly, Proshear was used to enhance the number of lateral buds in carnations, chrysanthemums, and roses (18). It is considered to be a synthetic cytokinin that stimulates dormant lateral buds. Presently, it is sold as a mixture consisting of 1.8% of the compound, plus 0.18% gibberellins A4 and A7, to thin apples, thereby increasing fruit size and quality. Note that 6-benzyladenine [1214-39-7] has an identical structure, but lacks the pyran ring (43,44,45,46). It is sold under various trade names as BA, Beanin, and Paturyl (13).

13.3. Fatty Acid Methyl Esters

A mixture of C6–C12 fatty acid methyl esters [67762-39-4] are related to the long-chain fatty alcohols, eg, *n*-decanol, in that they are acids of their alcoholic chemical cousin which have, in addition, been methylated. As such, their mode of action mirrors that of *n*-decanol in that they plasmolyze young tissue and are used as pinching agents on azaleas. The material may be used on container, or field grown plants. Tips of treated plants darken within 1 h of treatment and after 24 h turn deep brown to black, indicating tissue necrosis. The loss of apical dominance forces the axillary shoots to break dormancy, thereby increasing branching and foliar density. Sold as Off-Shoot-O, the mixture has also been used on privets, juniper (*Juniperus* sp.), yew (*Taxus* sp.), rhamnus, and cotoneaster (36).

13.4. *N*-(Phosphonomethyl) Glycine

Glyphosate [1071-83-6]; Round-up; Polado is a prime example of a lucrative agrochemical that is a natural product derivative. L-Glycine is ubiquitous in nature, both in plants and animals and this compound is the phosphorylated material. Oddly, it is the only active simple amino acid insofar as plant growth regulation is concerned, although the entire series has been tested. First prepared and synthesized in Switzerland in 1950 (47), its potential herbicide and other useful properties were not discovered until 1970 by Monsanto Chemical Co.

Roundup is a broad-spectrum postemergence herbicide that exhibits unique action. Depending on the temperature it may take up to 5, or more, days before any effects are seen on sprayed plants, which can be deceptive if immediate results are needed. Certain crop plants have been genetically engineered to be Round-up resistant, eg, cotton and other major crops. It is active against most annual and perennial herbaceous plants and it has the added feature of being environmentally compatible and is safe to use around mammals, fish, birds, insects, and many bacteria. Therefore, it does not enter the food chain. It is bound to soil where it rapidly undergoes microbial degradation to glycine and phosphate. In spraying near woody plants, it is necessary to avoid contact with actively growing vegetative parts since these will be necrotized. It is extremely useful in orchards to control grasses and broadleaved weeds and it is easy for homeowners to handle in vegetable gardens, provided the crops are screened from the chemical, and may be used as an edging agent to control borders of lawns. For the avid gardener, Round-up, when judiciously applied to crabgrass, makes light of a time consuming chore. The material also effectively controls honeysuckle (*Lonicera japonica*), poison ivy (*Rhus toxicodendson*), and kudzu vine (*Pueraria thunbergiana*).

The mode of action of Round-up is by inhibition of 5-enolpyruvyl-shikimate-3-phosphate synthase. It shuts down the production of the aromatic amino acids phenylalanine, tyrosine, and tryptophane (48). Whereas all these are essential to the growth and development of the plant, tryptophane is of paramount importance because it is the progenitor for indole-3-acetic acid, or auxin, which plays a major role in cell extension and organogenesis.

The isopropylamine salt of *N*-phosphonomethylglycine, Polado L, has been used to accelerate ripening in sugarcane, and brings about an increase in the sucrose levels in the barrels (internodes). Most often, it is used on green sugarcane that has been slow to ripen because of climatic conditions. But, application timing is critical and it must be applied at 4–10 weeks prior to harvest (15). An added bonus is that the green leaves are desiccated and when fields are fired to remove debris, trash, scorpions, rats, and snakes, it is necessary to have dried leaves to fuel the flames. The compound also has herbicidal properties, like its parent, and has been used to inhibit seed head development in certain turf species (15). It is environmentally benign and does not affect wildlife, but one caveat is that the compound should not be used on sugarcane that is to be used for propagation.

14. Synthetic Compounds

There are more synthetic plant growth regulators than naturally occurring agents. Historically, with the ability of the organic chemist to synthesize novel agents, which were previously impossible to make, it became common practice to generate a number of synthetics and test them in various biological systems. With a better understanding of organic synthetic pathways, if a particular structure demonstrated interesting biological effects, it was used as a "lead" compound in the synthetic exploitation of more active agents. This classic structure–activity relationship led to the development of some of the most interesting agents used in agrochemistry. Much of the information concerning the development of synthetic plant growth regulators remains proprietary expect in very successful cases. Table 2 offers added information on commercially available synthetic plant growth regulators.

Table 2. Authorized Synthetic Plant Growth Regulators[a]

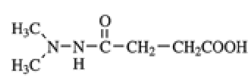
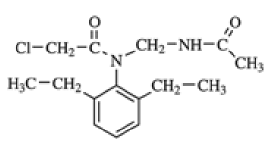
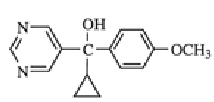
Product	Structure	Trade name	LD_{50}, g/kg
Alar[b]	 24	Alar, B-Nine, Daminozide Dazide	rat, 8.4
Amidochlor	 25	Amidochlor, Limit	rat, 3.1
Ancymidol	 26	Ancymidol, A-Rest, Reducymol, Slectone	mouse, 5 rat, 4.5

Table 2. ***Continued***

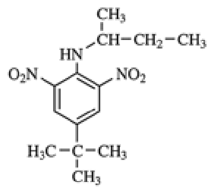
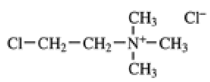
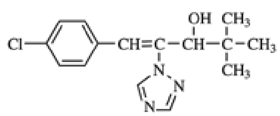
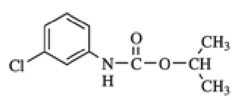
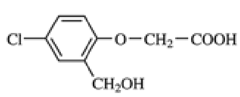
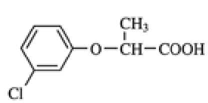
Product	Structure	Trade name	LD_{50}, g/kg
Butralin	 **27**	Butralin, Tamex	rat, 1.26
Chlormequat chloride	 **28**	CCC, Cycogan, Hormocel, Chlomequat chloride, Cycocel, Arotex 5C	rat (male), 31 rat (female), 18
4-Chlorophenyl-4,4-dimethyl-triazol pentenol	 **29**	Uniconazole, Sumagic	rat, 1.79
Chlorpropham	 **30**	Chlorpropham, CIPC, Sprout Nip, Bud-Nip, ChloroIPC, Taterpix	rat, 1.2
Cloxyfonac[b]	 **31**	Cloxyfonac, Tomatlane, CHPA	rat, 5.0
Copper hydroxide	$Cu(OH)_2$ **32**	Copper hydroxide, Spinout	
3-CPA	 **33**	Fruitone CPA, 3-CP, Cloprop	rat, 10

Table 2. ***Continued***

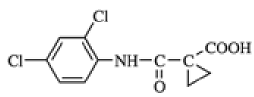
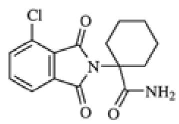
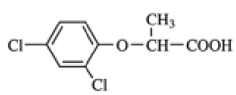
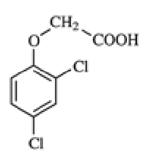
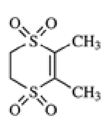
Product	Structure	Trade name	LD_{50}, g/kg
4-CPA	 **34**	PCPA, Tomato Fix, Sure-Set	rat, 0.85
Cyclanilide	 **35**	Cyclanilide, Finish	rat, 0.21
Cyclohexane-carboxamide	 **36**	Cyclohexanecarboxamide, AC 94377	rat, 5.0
Dichloroprop[b]	 **37**	Dichloroprop, 2,4-DP, Dormone	rat, 0.5
2,4-Dichlorophenxoy-acetic acid	 **38**	2,4-D, Citrus Fix, Hivol-44	mouse, 0.368 rat, 0.375
Dimethipin	 **39**	Dimethipin “N252,” Harvade, Dimethipin “UBI-N252”	rat, 1.18
Dormex	$H_2N-C\equiv N$ **40**	Dormex, Alzodel	rat, 1.25

Table 2. ***Continued***

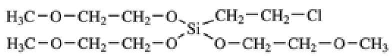
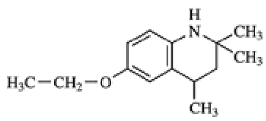
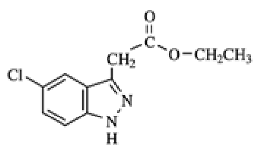
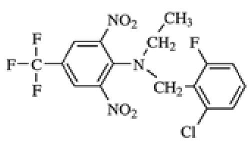
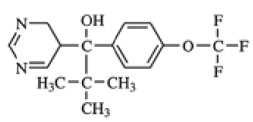
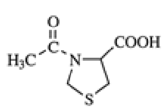
Product	Structure	Trade name	LD_{50}, g/kg
Etacelasil[b]	 **41**	Etacelasil, Alsol, CGA 13586	rat, 2.06
Ethoxyquin	 **42**	Stop Scald, Nix-Scald, Santoquin	rat, 1.92 mouse, 1.73
Ethylchloroindazolyl-acetate[b]	 **43**	Ethylchlozate, Figaron	rat, 4.8
Flumetralin	 **44**	Primet, CGA 41065	rat, 3.1
Flurprimidol	 **45**	Cutless, Cutless-TP	rat, 0.914 (male)
Folcysteine[b]			rat, 0.71
	 **46**	Ergostim	(female) rat, 4.5

Table 2. ***Continued***

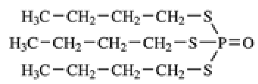
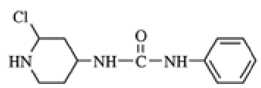
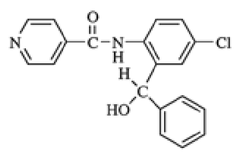
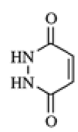
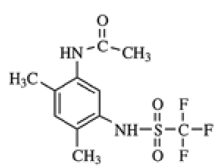
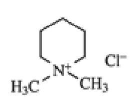
Product	Structure	Trade name	LD_{50}, g/kg
Folex	 **47**	Folex, Tribufos, Merphos	rat, 0.234
Forchlorfenuron[b]	 **48**	Forchlorfenuron, CPPU, Sitofex	rat, 4.92
Inabenfide[b]	 **49**	Seritard, CGR 811	rat, 15
Maleic hydrazide	 **50**	Maleic hyrdazide, Sucker-Stuff MH-30, Retard, Fair-plus, Royal MH-30	rat, 4
Mefluidide	 **51**	Embark 2-S	mouse, 1.92 rat, 4.0
Mepiquat chloride[b],[c]	 **52**	PIX, Bas 08300, Ponnax, Terpal (with Ethephon)[c]	rat, 1.42 (Terpal) rat, 1.5
Morphactin[b]			

Table 2. ***Continued***

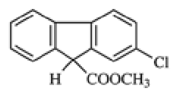
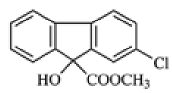
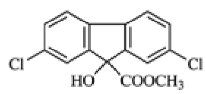
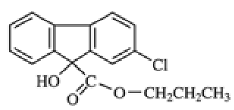
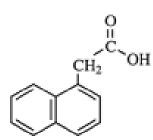
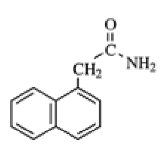
Product	Structure	Trade name	LD_{50}, g/kg
Chlorfluren-Me	 **53**		
Chlorfurenol-Me	 **54**	Morphactin, Maintain-CF125, Curbiset	rat, 4.0
Dichloroflurenol-Me	 **55**		
Flurenolbutyl	 **56**		
Naphthaleneacetic acid	 **57**	NAA-800, NAA	rat, 1.0
Naphthaleneacetamide	 **58**	Fruitone-N	rat, 6.4

Table 2. ***Continued***

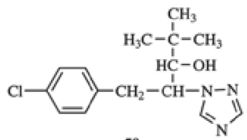
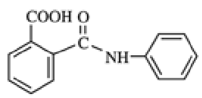
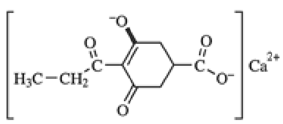
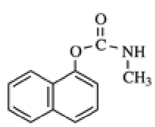
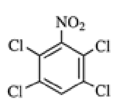
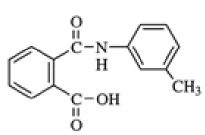
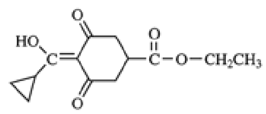
Product	Structure	Trade name	LD_{50}, g/kg
Paclobutrazol	 **59**	Bonzi, Clipper, PP333, Proturf Bounty, Parlay	rat, 1.356
N-Phenylthalamic acid[b]	 **60**	Nevirol	rat, 9.0
Prohexadione-calcium	 **61**	Apogee, Viviful, Medex, Baseline	rat, 2.0
Sevin	 **62**	Sevin, Carbaryl	rat, 0.56
Tetrachloronitrobenzene	 **63**	Technazene, Fusarex, Chipman 3	rat, 2.047
Tomaset[b]	 **64**	Tomaset, N-M-T	rat, 5.0

Table 2. ***Continued***

Product	Structure	Trade name	LD_{50}, g/kg
Trinexapac-ethyl[d]	 65	Omega, Vision, Primo, Nomow	rat, 4.46

[a]Ref. 1.
[b]Not available in theUnited States.
[c]Terpal product available only outside the United States.
[d]May only be used on noncrop plants in the United States.
[e]Used on turf, but only outside the United States.

14.1. Alar

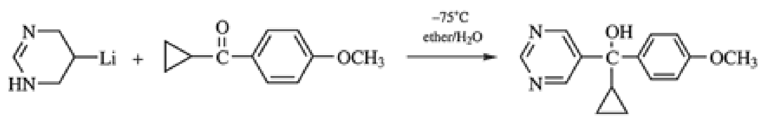
Butanedioic acid mono-(2,2-dimethylhydrazide) [1596-84-5]; Diaminozide; B-nine; Diazide is water soluble, readily translocated in plants and is not persistent in soil. In experimental trials, 50% of the compound could not be found in a variety of treated soils after 1 week and in greenhouse tests up to 90% could not be found after 2 weeks. Furthermore, it is readily degraded microbially and has low toxicity to wildlife and fish. For example, the LD_{50} for mallard duck is 4.64 g/kg in 8-day trials, whereas the acute LD_{50} for rats is 8.4 g/kg. Even 2-year feeding studies with rats and dogs showed that 3 g/kg/day produced no adverse effects. In the late 1980s, residues of Alar began to appear in apples where it was used to develop and accentuate the lobes, a characteristic of the “Delicious” variety. Because many of the apples were used for juice production, which later translated into use by infants and children as a part of their diet, it was insinuated that the plant growth regulator was hazardous to health. The two operative words, growth regulator, taken out of context, led to high drama in political hearings and the compound was removed from sale in the US agricultural market by the manufacturer. The voluntary ban not only applied to its use in apples, but also cherries, grapes, peanuts, and many other crops. Alar still has many uses in the United States on ornamental plants where it is used to control vegetative growth, reduce plant height, and add to the general vigor of plants by stimulating resistance to stress conditions. Many store bought plants are treated with the material, including azaleas, chrysanthemums, hydrangeas, and poinsettias, to give them a dwarf, compact shape(36). It also stimulates flower production, strengthens stems, and stimulates root growth. Certain metals are incompatible with Alar, especially copper, presumably because there exists the possibility of forming a chelate with the two carbonyl groups, thereby inactivating the compound. Its mode of action is by inhibition of gibberellin transport, as opposed to gibberellin biosynthesis, and this accounts for the internode inhibition observed in treated ornamentals (49,50). In this regard, it is unique among plant growth regulators.

14.2. Amidochlor

N-[(Acetylamino)methyl]-2-chloro-*N*-(2,6-diethylphenyl) acetamide [40164-67-8]; Limit; has been registered by the Environmental Protection Agency (EPA) for nonresidential turf use only. It is not phytotoxic if used according to label instructions and only inhibits the height of grasses, thereby reducing vegetative growth, for ∼6 weeks following treatment. The material is absorbed through the roots so that it first has to reach the soil to be effective, and from there it is translocated to the shoot apex. The mode of action appears to be suppression of mitosis and may include inhibition of cellular differentiation in the meristematic zone (51). It does not inhibit either gibberellin biosynthesis, or transport. It does not inhibit the growth of all grass varieties and it is active only on cool-season turf, including Kentucky bluegrass, tall and fine fescues, and perennial ryegrass; in these species vegetative growth may be cut by 50%. Unfortunately, it does not inhibit the pest grasses crabgrass and quackgrass: neither can it be used to control growth in zoysia, Bermuda, or St. Augustine, or broadleaved weeds. There, the antimitotic and antidifferentiation properties are quite selective. The anomalies, in which some grasses are controlled, whereas others are not, are a fertile area for research, bearing in mind that mitosis is common to all.

14.3. Ancymidol

α-Cyclopropyl-α-(*p*-methoxyphenyl)-5-pyrimidinemethanol [12771-68-5]; A-rest, is a heterocyclic nitrogenous compound, a pyrimidine, and is used to control the height of container-grown ornamental plants. These include azaleas (*Azaela* sp.), chrysanthemums (*Chrysanthemum* sp.), dahlias (*Dahlia* sp.), delphiniums (*Delphinium* sp.), lilies (*Lilium* sp.), poinsettias (*Euphorbia pulcherrima*), tulips (*Tulipa* sp.) and bedding plants (18,36). It is a plant growth inhibitor that reduces internode length: But, this inhibition may be reversed by treatments with GA_3. The specific mode of action is inhibition of the oxidative steps from *ent*-kaurenoic acid where *ent*-kaurene is metabolized to *ent*-kaurenol, then to *ent*-kaurenal and, finally, to *ent*-kaurenoic acid. The synthesis of ancymidol is relatively simple.



14.4. Butralin

N-*sec*-Butyl-4-*tert*-butyl-2,6-dinitroanaline [33629-47-9]; 4-(1,1-dimethylethyl)-*N*-(1-methylpropyl)-2,6-dinitrobenzeneamine; Tamex, is an aniline that plays a dual role as a plant growth regulator. One of its primary uses is as a contact agent to control axillary shoot growth in all types of tobacco and, in that regard to inhibit the growth of young shoots, or suckers, as effectively as maleic hydrazine, or the long chain C_8–C_{10} fatty acids and their methyl esters. In stark contrast to the fatty acids, its mode of action is mainly by apical cell inhibition, though it appears not to be translocated throughout the plant since solutions of the material must travel down the stem to each axil to obtain good inhibition of the buds. It has also been incorporated as a preplant herbicide. The principle break down product is 4-*tert*-butyl-2,6-dinitroaniline, the result of soil degradation by soil microflora, especially *Paecilomyces* sp (52).

14.5. Chlormequat Chloride

(2-Chloroethyl) trimethylammonium chloride [999-81-5], chlormequat chloride; CCC, is an onium-type plant growth regulator with multipurpose use. CCC alone is registered for use in the United States by the Environmental Protection Agency, but the mixture of CCC with choline chloride, while commonly used in Europe, has not been approved.

The early development of the compound by the American Cyanamide Co. and BASF, took place in the 1960s, when the chemical structure and details about the activity of CCC as a plant growth inhibitor were disclosed (53). The effects induced in plants were opposite to those induced by gibberellic acid, but it was concluded that CCC and gibberellins were not in competition at a common enzymatic site (54). By 1981, CCC had been used experimentally as a growth inhibitor on a number of economic crops and ornamentals (33). Outside the United States the chemical has been used for a number of treatments. In India, it has been registered for use to promote fruit bud formation and increase yields in apples and pears; it has been used in grapes to inhibit floral drop, and increase fruit set and yields (33). Another benefit in grapes is the increase in leaf disease resistance (33). India also uses the compound to ripen sugarcane and, at one time used CCC to reduce sugarcane lodging which, in turn, gave greater yields and improved tillering in ratoons. For a short period, it was used in Hawaii to ripen sugarcane, but since that industry is now defunct it remains an interesting piece of history.

On ornamental plants CCC is applied to azaleas, geraniums, and hibiscus (*Hibiscus* sp.) to form compact plants, and to poinsettias to reduce stem height and inhibit lodging. In Europe, the effect of CCC on shortening the culms of cereals is genotype dependent. It has been demonstrated that the effect is as follows: wheat > triticale > durum wheat > rye > oats > barley > corn = millet = rice (55). In barley, culms are initially inhibited, but later this is overcome (55). This has been attributed to poor assimilation, translocation, and rapid breakdown in wheat (56). Mixtures of CCC with other compounds to control lodging in cereals have been approved for use in Europe, but not in the United States. These include Terpal C, which consists of CCC plus ethephon; Terpal M, a mixture of CCC, mepiquat chloride, and ethephon, and Oyter, which is CCC plus mepiquat chloride.

The mode of action of CCC is attributed to the inhibition of the enzyme *ent*-kaurene synthetase A, the enzyme that directs the biosynthesis of geranylgeranylpyrophosphate by copalyl pyrophosphate to *ent*-kaurene.

14.6. (*E*)-(*RS*)-1-(4-Chlorophenyl)-4,4-dimethyl-2-(1*H*-1,2,4-triazol-1-yl)pent-1-en-3-ol

Uniconazole [83657-22-1]; uniconazole-P (*S*-isomer); Sumagic is used as a growth retarding agent on nursery plants. These may include, but are not limited to, azaleas, bedding plants, bulbs, Easter lilies, geraniums, grown in greenhouses, or under shade, in containers. Treatment gives rise to more desirable compact plants, suitable for market. In addition, there is greater chlorophyll content, deeper colors, increased leaf thickness, stronger stems, increased water retention and, sometimes, increase in flower size and numbers (56). Its mode of action is inhibition of gibberellin biosynthesis.

14.7. Chlorpropham

(3-Chlorophenyl) carbamic acid 1-methyl ester [101-21-3]; isopropyl *N*-(3-chlorophenyl) carbamate; CIPC; Chloro-IPC, was patented in the early 1950s and is a carbamate. In the United States, its only use is on stored Irish potatoes to inhibit bud, or "eye", development. The potatoes, which are generally stored at temperatures $>10^{\circ}$C for maximum flavor, are treated by passing a stream of air laden with chloropropham over the potatoes for 48 h after which the potatoes are purged with pure air (36).

The compound is ineffective when applied as a preharvest dormancy agent on potatoes and it should not be used until injuries to the tuber coat have healed. Neither should it be applied until some suberization has occurred, generally 2 weeks after storage at $>10^{\circ}$C. CIPC is widely used outside the United States on a number of crops as a herbicide.

14.8. Cloxyfonac

4-Chloro-2-hydroxymethylphenoxyacetic acid [32791-87-0]; Tomatlane, is a chlorinated phenoxy compound that is used outside the United States. As such, it is an auxin type compound related to 2,4-D and has to be applied at the correct time of plant development and organogenesis. It is used on eggplants and tomatoes to create uniform fruit development and size. The material must be applied by hand in tomatoes to individual flower clusters; but on processing tomatoes it is applied at full bloom stage from six to seven weeks after planting, depending on weather conditions and temperature which may affect growth (58,59).

14.9. Copper Hydroxide

Copper hydroxide [2047-59-2]; Spinout, is an inorganic, water soluble compound, used to coat the inside surfaces of pots and containers in nurseries. It acts as a root inhibitor and causes root pruning, induces fibrous root formation, and controls spiraling. This eliminates the necessity of cutting root balls when ornamental shrubs are moved from containers to landscapes (60).

14.10. 3-CPA

2-(3-Chlorophenoxy) propanoic acid [5825-87-6]; (*RS*)-2-(3-chlorophenoxy) propanoic acid; 3-CPA; Fruitone CPA, has been on the market for almost 60 years. It was primarily used in the United States to thin stonefruit, especially plums. The material also is used in pineapples to inhibit vegetative crown growth and to increase fruit size, presumably by partitioning minerals and growth factors away from the vegetative plant parts. 3-CPA is not easily translocated from the foliage and it is important to contact the fruit during application. Treatment must be made $\sim$15 weeks prior to harvest, or at dry petal fall (18).

14.11. 4-CPA

p-Chlorophenoxyacetic acid [122-88-3]; 4-CPA (15), is a close relative of 3-CPA and was one of many chlorophenoxy compounds that were being synthesized and evaluated during the late 1940s and early 1950s. It has a limited, but essential use as a plant growth regulator to improve fruit set in tomatoes, and may also replace pollination (15). The compound was reported as having unique activity in 1949 (61) when it was noted that it induced the apex of kalanchoe to develop a pseudospathe that could be excised, then rooted. It has also been used to induce slip production in pineapples that have been forced with naphthalene acetic acid (62). 4-CPA is sold as an aerosol spray in either a 2 or 0.005% solution, as the diethanolamine or sodium salt, or it may be purchased as tablets. It is sprayed only on fully opened corollas. The spray should be lightly applied and, because tomato plants flower and fruit asynchronously, care should be taken not to spray the fruit or leaves. Because it may replace pollination, 4-CPA should not be used on plants designated for seed production. Since the resulting fruit may be parthenocarpic, seed set may not occur and if it does, the F1 generation may be genetically aberrant. That is, the seed would not have the same genotype as the normally pollinated germplasm. In addition to treating tomatoes, the compound is used to treat mung bean seed, bean sprouts, prior to germination. The seed is soaked for 5–8 h in a solution so that 3 g of compound treats 450 kg (1000 lb) of seed. Following treatment, the seed is washed and sown, resulting in bean sprouts having inhibited root growth.

The 2-isopropylhydrazide derivative is iproclozide, a pharmaceutical that inhibits monoamine oxidase (63). Other close relatives include clofibric acid, wherein C2 has 2 CH_3 attached, and clofibric acid ethyl ester (clofibrate). Clofibrate, as well as other chemically related medicinal agents, is administered to control type III hyperlipoproteinemias, where triglycerides and total cholesterol are elevated (64).

14.12. Cyclanilide

1-(2,4-Dichlorophenylaminocarbonyl)-cyclopropane carboxylic acid [113136-77-9]; Cyclanilide; Finish, is structurally interesting because of the cyclopropane carboxylate feature, which prompts that it may play a role in ethylene production. Its main use is as a cotton boll opener and defoliant, and is used to prevent lodging in cereal crops. Another use is on turf to reduce the amount of mowing. With respect to cotton, application can result in earlier harvest and, as the result of small immature boll drop, increased yields may be obtained. It should not be applied until sufficient mature bolls have developed and this can generally be determined by examining the seed coats that should be light brown, plus noting the seed cavity and embryos, which should be creamy colored.

Finish 720 is favored for use as a cotton defoliant and is a mixture of cyclanilide and ethephon (Ethrel) (65).

14.13. Cyclohexanecarboxamine

The compound 1-(3-chlorophthalimide)cyclohexanecarboxamide [51971-67-6]; cyclohexanecarboxamide; originally AC94377, is a phthalamide with plant growth regulating properties. It is relatively nontoxic so that its use in floricultural crops appears to be safe, and mainly it is used to control stem length and stem numbers in hybrid tea roses. Beneficial effects have been recorded on several floricultural varieties, including gerbera daisies and snapdragons (15).

14.14. Dichloroprop

Dichloroprop [120-36-5]; 2,4-DP, is a further chlorophenoxy plant growth regulator first described in the literature in 1945 (66). It is not used in the United States, but in other countries it has a singular use in citrus to increase fruit size and fruit color intensity. The change in size is brought about by aborting the smaller fruits. The compound is presently sold in Europe under the name Citrimax, which speaks of its utility, as the 2-butoxyethyl ester. Applications times are critical with respect to rainfall and temperature. Formerly, it was use to thin apples, but better compounds are now available.

14.15. 2,4-Dichlorophenoxyacetic Acid

Two phenoxyacetic acids, namely, 2,4-dichlorophenoxyacetic acid [94-75-7]; (2,4-D) and 2,4,5-trichlorophenoxyacetic acid; (2,4,5-T) [93-76-5], are the first principal synthetic plant growth regulators used extensively as herbicides. 2,4-D is especially lethal to all broadleaved weeds but not to grasses, although it has been used to control grasses when used at very high concentration in sugarcane in the West Indies. The first report of the synthesis of 2,4-D was made in 1941 (67) from the model template, indole-3-acetic acid (68,69); 2,4-D was a substituted phenyl and IAA was a phenyl-pyrrole. For years, 2,4-D was the chemical paradigm for manufacturers of agricultural chemicals, *vide supra*.

The commercial use of 2,4-D has decreased substantially and it now has general use for home lawns to control broadleaved weeds; it is also used to control broadleaved weeds in commercial monocotyledonous crops. 2,4-D is used on citrus when the fruit is 1/3 to 1 in. in diameter to increase fruit size and to limit fruit drop on trees >6 years old. It should not be applied to trees that are in full flush. A further use includes treatment of harvested lemons at 500 mg/L to improve storage properties and to delay yellowing (36). It is used in certain parts of the world to increase latex flow in old rubber tree plantations. The compound is the least expensive of the plant growth regulators.

2,4,5-T is a potent brush killer and when combined with 2,4-D it can defoliate dense jungles. A combination of the two formed the main components in Agent Orange, used with devastating effects in Vietnam. Unfortunately, supplies were limited and in order to produce enough of the material, the Q_{10} (reaction temperature $\rightarrow$ yield increase) was raised. At that point, an unexpected reaction took place and dioxin, a potent carcinogen, contaminated the product. The two excellent agrochemicals were under suspicion for some time.

14.16. Dimethipin

2,3-Dihydro-5,6-dimethyl-1,4-dithiin-1,1,4,4-tetraoxide [55290-64-7]; dimethipin; oxidimethiin; UBI-N252; Harvard, is used outside the United States as a cotton defoliant and has been used as an experimental desiccant in potato vines. In addition, it defoliates nursery stock, grapes, dry beans, and natural rubber and is used as a desiccant for canola seed, flax (*Linum usitatissimum*), rice, and sunflower (*Helianthus annuus*) (18). The product has been available since the mid-1970s and the experimental work was first reported in 1974 (70).

Oxidimethiin acts as a cotton defoliant by eliciting the formation of an abscission layer at the middle lamella, and examination with cotton explants indicates that cellulase activity is increased at the abscission zone.

14.17. Dormex

Dormex [156-62-7]; Alzodep; hydrogen cyanamide, should not be confused with the same nomenclature used for calcium cyanamide. Its other names include carbamide, cyanogenamide, and amidocyanogen. The compound is easily prepared by the continuous carbonation of calcium cyanamide in water.

Dormex is used as a plant growth regulator and has shown remarkable responses in grapevines, sugarcane, and kiwifruit (*Actinidia deliciosa*). On grapevines, the material is sprayed onto the buds prior to their breaking dormancy and causes swift bud break (55). In sugarcane, the setts, or short three-eyed pieces of sugarcane that are planted, may be treated with hydrogen cyanamide; this results in shoot formation approximately two weeks earlier than in controls (58). In late 1999, Dormex was approved for the Florida Department of Agriculture and Consumer Services for use on Florida blueberries. A Special Local Needs Label allowed the use following experiments in “Misty”, “Climax”, “GulfCoast”, “Star”, and “Southmoon” cultivars. Dormex induced increased leafing and earlier fruit ripening without significant flower bud thinning (71).

Dormex is highly toxic and must be handled with extreme care. Because it may produce severe dermatitis on moist skin, it is difficult to use in hot, humid climates; inhalation of the dust or spray may irritate the mucous membranes. Whereas symptoms may include a flushed face, tachycardia, headache, vertigo, and hypotension, it does not produce the typical cyanide effect (72).

14.18. Etacelasil

2-Chloroethyl-tris (2-methoxy-ethoxy)-silane [37894-46-5]; Etacelasil; Alsol, is made by the reaction of three moles of 2-methoxyethanol with one mole of Cl_3SiCH_2Cl. The name Alsol is also given to aluminum acetotartrate, and the two products should not be confused. Etacelasil is sold in Europe for use as an abscissing agent in olives and it is applied 6–10 days before harvest. It is not sold for use in the United States and has a very limited market. The compound acts by releasing ethylene which affects the abscission layer and allows for easier harvesting when the trees are either mechanically or hand shaken. The parent compound is rapidly degraded in a few hours. It is not readily absorbed by leaves and is not translocated (36).

14.19. Ethoxyquin

6-Ethoxy-1,2-dihydro-2,2,4-trimethylquinoline [91-53-2]; Ethoxyquin, is something of a curiosity insofar as plant growth regulation is concerned. The material has been available since the 1940s and the chemical structure was described in 1933 (73). The primary use is as an antioxidant in food and feed and as an antidegradation compound for rubber. As a growth regulator it has been used to control common scald in apples and “Anjou” pears (35) and is applied as a postharvest dip or wax emulsion. The material should not be used on late harvested “Winesap” apples, it should never be used in hydrocooler water, temperatures must be $<27^{\circ}C$, and produce should not remain in the dip >2–3 min. Treated fruit must be allowed to drip before being placed in cold storage, and treated fruit should be kept out of sunlight because it may polymerize. Dip water must be completely chlorine free (36).

Presently, the compound is on the European Commission list for removal and is targeted for removal under the Agricultural Pesticides Directive (91/414) and it is probable that the manufacturers will not want to spend the vast sums of money for safety tests to support their product (74). A word of caution is necessary since not all countries will be under the ban and may produce ethoxyquin for local use. Certainly, politics and a "must use" scenario will affect both this material and other suspect agrochemicals.

14.20. Ethyl-5-chloro-1*H*-3-indazolyl-3-acetate

Ethylchlozate [27512-72-7]; Figaron, is a benzimidazole presently used in Japan as a thinning agent in citrus to improve color and fruit quality (15). It is also being used experimentally to promote sugars in grapes, pineapples, and sugarcane. Additionally, it is used as a thinning agent in apples, peaches, and pears and may be used to increase maturation in apples and pears by 1 to 2 weeks. It also increases yields and promotes protein content in soybeans and wheat. The substance is extremely toxic to fish and it is not available in the United States. Examination of the structure is reminiscent of a chlorinated, ethyl ester of indole-3-acetic acid, with the exception that the B ring is a diazole in Figaron, versus a pyrrole in IAA. Figaron does have auxin like activity and its mode of action is attributed to the release of ethylene.

14.21. Flumetralin

2-Chloro-*N*-[2,6-dinitro-4-(trifluoromethyl)-phenyl]-*N*-ethyl-6-fluorbenzenenemethanamine [62924-70-3]; Flumetralin; CGA 41065; Prime +; Premier, is a dinitroaniline that has specific use as an axillary shoot inhibitor in tobacco. It was first prepared in 1977 (75) and further reports followed (76,77). Flumetralin is applied at the early elongated button stage of flowering and controls axillary shoot, or sucker growth, only if they are <1-in. long. Larger suckers must be removed by hand. When there is highly variable tobacco plant growth, it is advisable to apply contact axillary shoot inhibitors until there is uniform growth. This should be followed by Prime+, an emulsified concentrate of Flumetralin. It may also be advisable to spray Prime+ and maleic hydrazide. Flumetralin, to be effective, must contact each sucker and the young shoots are not burned as they are with contact agents, such as 1-docosanol, but they may take on a chlorotic appearance (77,78). The chemical has residual properties.

The mode of action has not been fully elucidated but the manufacturer states that it probably behaves like the herbicide triflurolin and its congeners. These materials inhibit cell division by binding to tubulin, thereby interrupting microtubule development. This, in turn, stops spindle fiber formation essential to mitosis and cell division. Experiments with ^{14}C-labeled Prime+ show that it is acutely toxic to fish with estimated LC_{50} (96 h) of <100 ppb for rainbow trout and bluegill sunfish. However, channel catfish did not exhibit any toxic response at the maximum attainable water concentration.

14.22. Flurprimidol

α-(1-Methylethyl)-α-4-(trifluoromethoxy)phenyl-5-pyrimidinemethanol [56425-91-3]; Flurprimidol; Cutless, is a pyrimidine that is mainly used to inhibit the growth of turf and ornamentals (78). With respect to the former, it is generally applied after the second mowing, which may take place in late spring or early summer, although application can be made in late summer. With respect to its use on golf courses, it should not be used on putting greens. The mode of action is by inhibiting the oxidative steps from *ent*-kaurene to *ent*-kaurenoic acid (49).

14.23. Folcysteine

3-Acetyl-4-thiazolidinecarboxylic acid [8064-47-9]; Folcysteine; Ergostim, has been used as a seed germination biostimulant, to promote plant growth, enhance fruit set, and increase yields in corn, rice, wheat, potatoes, sugar beets, grapes, strawberries, apples, and several other crops (36). It is not used in the United States. It acts by stimulating the general chemistry of the plant, and making metabolic reserves available during development and organogenesis. Thiol groups are released in the plant, which bind to specific substrates.

These groups also play an important role in DNA, RNA, and, therefore, protein synthesis, which may result in growth and development regulation. The compound is readily synthesized by treating 4-thioazolidine with acetic anhydride. Its position in the market is somewhat overshadowed by other seed germination promoters, fruit setting agents, and crop yield enhancers.

14.24. Folex

(*S*,*S*,*S*),-Tributylphosphorotrithioate [78-48-8]; Tribufos; Merphos, is a trithiophosphite and has limited use as a cotton defoliant. It may be used as a bottom defoliant, as a preconditioning defoliant, or as a complete defoliant, but the material appears not to translocate well since only treated leaves will defoliate. As a bottom defoliant, it is used as a directed bottom spray to selectively defoliate bottom leaves when the first set bottom bolls are sufficiently mature. When bottom leaves fall, there is increased air circulation among the rows and boll rot is prevented. As a preconditioning agent, the compound is sprayed onto green, rank cotton leaves. This gives some leaf drop and slows plant growth. It is not uniform in its action against all varieties of cotton and, furthermore, its effects depend on fertility level in the plant and the soil type on which the cotton plants grow. Also, it should not be used on varieties that have already been chopped-out. Application to induce total defoliation should be made when the upper bolls cannot easily be squeezed between the thumb and forefinger, while the boll content is still quite firm. The chemical acts by affecting the abscission zone at the base of the petiole, which is implied because the leaves are still green at drop. The applications must have many parameters covered, such as soil type, moisture stress in the plants, nutrient levels, insect damage, growth rate of plants, and temperature prior to application of the material for a successful outcome (15).

14.25. Forchlorfenuron

N-(2-Chloro-4-pyridinyl)-*N′*-phenylurea [68157-60-8]; 1-(2-chloro-4-pyridyl)-3-phenylurea; forchlorfenuron (KT-3), is a phenylurea plant growth regulator presently sold outside the United States. It is used to increase fruit size of grapes and kiwifruit, and to limit fruit abscission. Both fruit quality and yield increases are the result of its application (15).

14.26. Inabenfide

[4-Chloro-2-(α-hydroxybenzyl)]-isonicotonanilide) [82211-24-3]; Inabenfide, is not for use in the United States, but is used in other countries to inhibit the growth of rice plants (80). The compound is applied to the soil 40–60 days prior to the heading up of plants, where it is absorbed through the roots and translocated throughout the stem. It acts by reducing the levels of GAs, thus reducing lodging. The major drawback to using the compound is its extreme toxicity to fish.

14.27. Maleic Hydrazine

1,2-Dihydro-3,6-pyridazinedione [123-33-1]; maleic hydrazide; Royal MH-30; Super Sucker-Stuff, is one of the earliest organic plant growth regulators to be marketed. It is of approximately the same vintage as 2,4-dichlorophenoxyacetic acid and is prepared by the treatment of maleic anhydride with hydrazide hydrate in alcohol. It inhibits the growth and development of plants, although not all plants respond to treatment. It is highly effective in controlling the growth of axillary shoots, or ‘suckers’, in tobacco after the floral apices have been removed. The reason for the latter step is to alter the assimilate partitioning of energy from the flowers, whose aim is to produce seed for the next generation, to the leaves which are the saleable commodity. Applications are also made to stored potatoes and onions to stop shoot growth in storage. Another use is on grass, trees, shrubs, and ivy to inhibit runaway growth. Unfortunately, not all ivy species respond to treatment. Maleic hydrazine may be used in conjunction with other contact agents.

The mode of action was under discussion for a number of years and, in 1975, it was finally shown that the compound mimicked certain base pairs. Originally, it was believed that maleic hydrazide replaced uracil in the RNA sequence, but by measuring interatomic distances it became obvious that it could be a pyrimidine or purine analog. Therefore, base-pair formation is possible with uracil and thymine and the probability of base-pair formation with adenine. If maleic hydrazide remains as the diketo species *in vivo*, then base-pairing may take place with guanine (81). The inhibitory effects may be a attributed not only to the shut-down of mitosis, but also to the *de novo* synthesis of protein. Approximately 25 years ago, it was considered to be a health hazard because of its effect on nucleic acids and protein biosynthesis, but this was not proven from a human perspective.

14.28. Mefluidide

N-[2,4-Dimethyl-5-[[(trifluoromethyl)sulfonyl]amino]phenyl]-acetamide [53780-34-0]; Mefluidide, was the result of a synthetic program whose goal was the manufacture of *N*-aryl-1,1,1-trifluoromethanesulfonamides. The compound has been evaluated under several experimental situations to control seed head formation in grass and to improve protein, sugar, and digestibility. It has also been used to increase sucrose levels in sugarcane and is applied at the time that the cane matures (55). This is generally done in specific geographical areas, such as Brazil, where a large percentage of the Brazilian sugar crop is converted to ethanol for motor fuel (82) and pesticide residues do not pose a problem. For the most part, mefluidide is used to regulate the growth of turf in public and commercial lands. It is a growth inhibitor and should be applied to grass at the height that is aesthetically appealing to the eye. The compound may be applied 1 day after mowing or the grass may be mowed 3–7 days after application (18): it should not be applied to golf course greens, but may be used on fairways. Another use is on ornamentals, shrubs, and trees where it is applied 1–2 weeks after shaping and reduces pruning for up to 3 months. It is also used as a post–emergence herbicide in soybeans.

Mefluidide inhibits the growth of the meristems and, therefore, probably inhibits mitosis or cell elongation. It is degraded into numerous metabolites that are biologically insignificant (17). Its life in the soil is short: the half-life is 2 days. Photodecomposition proceeds rapidly on wet soil surfaces, but the element of moisture is critical for this reaction. In cow and sheep experiments, using radiolabeled mefluidide, neither milk nor meat were affected (82).

14.29. Mepiquat Chloride

1,1-Dimethylpiperidinium chloride [24307-26-4]; mepiquat chloride; Pix, first became available in 1973. This quaternary ammonium is remarkably active as a growth regulator in cotton, where it is used as the *N*,*N*-dimethylpiperidinium pentaborate. It inhibits growth, boll set, and yields (18), and leads to early maturation (55). As the genesis of the compound progresses, it is applied as multisplit treatments in opposition to a single application. There may be as many as five low rate applications, the first being at matchhead square in the absence of stress, and the rest at suitable intervals depending on vegetative vigor. The material is ideally suited to cotton cultivation and produces many desired effects. These include reduction in vegetative growth, giving rise to compact plants that have healthy, dark green leaves. Rows become easily accessible and air currents circulate unhindered so that invasion by phytopathogens is reduced. Furthermore, there is less abscission of essential plant organs. Several morphological and anatomical studies have shown that the stems and branches are shorter. There is also an increase in the spongy mesophyll with a concomitant elongation of the palisade cells. The final product, cotton fiber, is not affected by treatment (84).

In basic soils mepiquat chloride is nonpersistent and is rapidly degraded. There is a half-life of 2 years in other soil types, but 86–93% is metabolized within 30 days (18). Breakdown does not appear to be a function of microbial activity.

Mepiquat chloride is mixed with 2-chloroethylphosphonic acid to control lodging of winter barley in Europe under the name Terpal. The plants are treated after the first nodes have become visible and treatments may be applied until the flag leaf develops. Terpal is not used in the United States.

14.30. Morphactins

This class of compounds comes from four congeners: 2-chloro-9H-fluorene-9-carboxylic acid methyl ester [22909-50-8]: 2-chloro-9-hydroxy-9*H*-fluorene-9-carboxylic acid methyl ester [2536-31-4]: 2,7-dichloro-9-hydroxy-9*H*-fluorene-9-carboxyic acid methyl ester [21634-96-8]: 9-hydroxy-9*H*-fluorene-9-carboxylic acid butyl ester [2314-09-2].

All compounds were developed in Germany from 1960 to 1963 (85). Examination of the overall structures show that they are fluorine derivatives; the parent consisting of the A, B, C rings only and substituents were synthesized on to the B ring at the C-8-position. Since one of the functional groups was a carboxylic acid, it is conveniently available for ester production (86). The morphactins are novel structures that interfere with morphogenesis (87). 2-Chloro-9-hydroxyfluorene-9-carboxylic acid methyl ester, also called chlorflurenol and, more generally “morphactin”, has been mixed with other compounds as herbicides.

The same material has been used to control weed growth along roadsides when mixed with maleic hydrazide; to control tree height, shrubs, and vines (36); and to make plants bushier. Earlier use included pineapple where it improved slip propagation. It also has improved the size and yield of cucumbers (35). In early tests the morphactin induced odd effects when applied to lettuce and timothy grass (*Phleum psatense*). In both species the roots, hypocotyls, and coleoptiles, respectively, grew in all directions and exhibited negative geotropism (88). The mode of action appears to be the blocking of auxin transport (55). Chlorfurenol has been used on mango trees in Australia to enhance flowering and fruiting (89). This compound is not used in the United States: Neither are the congeners.

14.31. Naphthalene Acetic Acid and Naphthalene Acetamide

α-Naphthalene acetic acid [86-87-3] is historically one of the first plant growth regulators; its bioactivity was reported in 1939 (90). Results of its activity in crops and plants have been a subject in much of the early literature (91). Consequently, it has been used as a starting material for other successful compounds, for example Sevin®, *vide infra*. Naphthaleneacetamide [86-86-2], the water soluble version of the parent, has been used as a standard material to evaluate abscission prior to 1953 and its effect on apple drop was reported in 1953 (92). The substance is used as an internal standard in the abscission bioassay (93).

α-Naphthalene acetic acid is used to thin apple and pear blossoms and to control apple and pear preharvest drop. It also is used to induce flowering in pineapple, but conversely inhibits sprouting in potatoes, sweet potatoes, and turnips (*Brassica napa*). It also is used to promote rooting in cuttings and may substitute for, or be mixed with, indole-3-butyric acid in this purpose. It is considered to be an auxin, albeit a synthetic one. Obviously, naphthalene acetic acid and naphthalene acetamide have virtually the same properties and may be used interchangeably. The former is hydrophilic, the latter hydrophobic. Of interest in the fact that Naproxin (naprosine), the anti-inflammatory pharmaceutical, is a substituted β-naphthalene acetic acid derivative.

15. Paclobutrazol

1-(4-Chlorophenol)-4,4-dimethyl-2-(1*H*-1,2,4-triazol-1-yl)-pentan-3-ol [76738-62-0]; Paclobutrazol, is a triazole plant growth regulator that has received a good deal of attention as a synthetic inhibitor and has been evaluated in several crops (17). Whereas it may be applied at any time to trees, injection through the trunk is recommended when they are transpiring. Successful tree treatments include Norway maple, red maple, silver maple, sugar maple, Australian pine, sweet gum, laurel oak, water oak, willow oak, live oak, Chinese elm, and Siberian elm. Sugar maples should not be treated within one year of tapping for syrup; nut and fruit trees should not be harvested for fruit consumption until a year after application. The compound may be used for ornamentals including chrysanthemums, coleus freesias (*Freesia* sp.), geraniums, impatiens, marigolds, pansies, and other bedding plants (36). Outside the United States, it has been used to reduce lodging and to increase tillering and yields in rice. The main use in fruit trees is to halt vegetative growth and to promote spur growth. Its mode of action is inhibition of gibberellin biosynthesis (49). Translocation occurs in the xylem, but not the phloem. While it is sold as a granular, older formulations were made in methanol and could, therefore, not be made safe. If it is discovered, upon reading the label, that methanol is present, the material must be kept away from water and mammals.

15.1. *N*-Phenylthalamic Acid

N-Phenylthalamic acid; Nevirol, was introduced 20 years ago as a benzoic acid derivative in Hungary. It is not sold in the United States, but is available elsewhere and aids to increase pollination, resulting in greater fruit set. Application is generally made when weather conditions are unfavorable for pollination and subsequent fertilization. It is employed in both greenhouses and fields on apples, beans, cherries, grapes, lupine, peas, peppers, rice, soybeans, and sunflower. Of paramount importance is that it is not toxic to honey bees, which are highly important for crop pollination (15).

15.2. Prohexadione–Calcium

Calcium 3-oxido-5-oxo-4-propionylcyclohex-3-enecarboxylate; calcium 3,5-dioxo-4-propionylcyclohexane carboxylate [127277-53-6]; Apogee, was first used outside the United States, but was approved for United States use in ∼2000. The compound was developed jointly between Kumai Chemical Industry Co. Ltd., Japan, and the BASF Corporation (94). It is generally used to control vigorous vegetative growth in apple trees and its mode of action is by inhibiting gibberellin production. In particular, new twig growth is inhibited for one to two months following application, so that both internode length and leaf growth are controlled. The net result is greatly increased color production in red apple varieties. Another benefit is dispensing of pruning during the growing season.

Other applications have included treatments to control growth in ornamentals, peanuts, and grass. It has also been used as an antilodging agent in cereals.

15.3. Sevin

1-Naphthalenol methylcarbanate [63-25-2]; Sevin; Carbaryl, was primarily developed as an insecticide using α-naphthalene acetic acid, *vide supra*, as one of the starting materials. However, the initial proposal was to synthesize and test the product as a potential herbicide in the mid 1950s. The compound ultimately was useless as a herbicide, but in routine testing across many disciplines it was found to be an excellent insecticide. Sevin was active in the oat mesocotyl assay and demonstrated weak auxin-like activity (95). During the development of Sevin, an apple orchard in the western United States, being treated for insect control, aborted all the fruit and was initially deemed to be a disaster. As with most serendipity, the discovery led to the judicial use of the compound as an apple thinning agent to produce larger fruit. It is still used today for the same purpose.

The name Sevin is derived from the fact that the initial sample, sent to the Boyce Thompson Institute for Plant Research, was labeled "7744" as the accession number.

15.4. 1,2,4,5-Tetrachloro-3-nitrobenzene

Technazene; Fusarex; Chipman 3 [117-18-0]; 1,2,4,5-tetrachloro-3-nitorbenze, serves as a dual purpose agrochemical. First, it is a fungicide used on potato to prevent storage dry rot and second, it inhibits sprout formation in stored potatoes. While sprouts are inhibited for 4–6 months, when the potatoes are removed from storage atmosphere, the buds may break fairly quickly. This is important for seed potato production (15).

15.5. Tomaset

N-*m*-Tolylphthalamic acid [85-72-3]; Tomaset, is no longer sold in the United States, but is being produced by Makhteshim Agan, Israel, as a plant growth regulator. It is a flower and fruit setting agent. When fruit set is poor, for example, when bees or other insects fail to pollinate, Tomaset is applied. The compound also prevents abscission of flowers and young fruits and is used on tomatoes, lima beans, and other crops. Application on vegetables is at the height of the blossom production; but, on fruit trees the treatment is made when flowering is at $\sim$80% (96).

15.6. Trinexapac-Ethyl

4-Cyclopropyl(hydroxy)methylene-3,5-dioxocyclohexane carboxylic acid ethyl ester [95266-40-3]; Primo; Nomow, is used on turf to retard growth and may be used on warm season, or cool season grass. It also prevents lodging in cereal and oilseed rape. The main effect is reduction in internode length (13).

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