Chemistry of Plant Hormones

Editor

Nobutaka Takahashi, Ph.D.

Chemistry of Plant Hormones

Editor

Nobutaka Takahashi, Ph.D.
Professor
Department of Agricultural Chemistry
Faculty of Agriculture
The University of Tokyo
Bunkyo-ku, Tokyo, Japan

Library of Congress Cataloging-in-Publication Data
Main entry under title:

Chemistry of plant hormones.

Bibliography: p.
Includes index.
1. Plant hormones. I. Takahashi, Nobutaka,
1930-
QK731·C516 1986 581.19'27 85-17475
ISBN 0-8493-5470-6

Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431.

International Standard Book Number 0-8493-5470-6

Library of Congress Card Number 85-17475
Printed in the United States

PREFACE

Plants have the photosynthetic ability to produce sugars from carbon dioxide and water by use of sunshine energy, while most living organisms other than plants have no such ability. Thus, their lives in nature really depend upon this unique ability of plants.

It is one of the most important research subjects in biology, biochemistry, and chemistry to clarify the mechanism regulating the life cycles of higher plants. It is an attractive and challenging target not only in an academic sense, but also from the viewpoint of application. This kind of research has been contributing to the development of new techniques for increasing the supply of foods for humankind and feed for animals.

About 50 years have passed since indole-3-acetic acid, which was later recognized as real auxin, was isolated as a heteroauxin from human urine; and 46 years since the isolation of gibberellin as the metabolite of a plant pathogen, *Gibberella fujikuroi*. In these years the number of the principal plant hormone groups has increased to five, namely, auxins, gibberellins, cytokinins, abscisic acid, and ethylene; and many plant growth regulators other than plant hormones have been isolated and characterized. Information on their physiological activity and chemistry should make a tremendous contribution to the understanding of the regulatory mechanism of higher plant life cycles and to the development of new technology in the cultivation of higher plants.

Many excellent books have been published which cover the physiology of plant growth regulators, but rather few on their chemistry. Thus, this book deals mainly with the chemistry of the principal plant hormones and not so much with their physiology. Further, due to limited space, plant growth regulators other than the principal plant hormones are described briefly only in the Introduction.

N. T.

THE EDITOR

Nobutaka Takahashi, Ph.D., is Professor of Pesticide Chemistry in the Faculty of Agriculture at The University of Tokyo. He graduated from The University of Tokyo in 1952 and obtained a Ph.D. He assumed his present position after serving as Assistant Professor from 1964 to 1969. In addition to his university post, Professor Takahashi has since 1977, held the position of Director of Pesticide Chemistry Laboratory III in Japan's prestigious Institute of Physical and Chemical Research.

Dr. Takahashi is Vice President of the Japanese Society of Plant Growth Regulation, a council member of the International Plant Growth Substances Association, the Agricultural Chemical Society of Japan, the Pesticide Science Society of Japan, and the Japanese Society of Plant Physiologists. He is also a member of the Chemical Society of America, Japan and London, and the American Society of Plant Physiologists.

Dr. Takahashi is the author of more than 200 papers and review articles and 7 books. He is noted for his research into the chemistry and physiology of biologically active natural products, including insect sex pheromones, naturally occurring insecticides, and plant growth regulators such as gibberellins, cytokinins, abscisic acid, and brassinosteroids.

CONTRIBUTORS

Nobuhiro Hirai, Ph.D.
Research Associate
Department of Food Science and Technology
Faculty of Agriculture
Kyoto University
Kyoto, Japan

Hidemasa Imaseki, Ph.D.
Professor
Research Institute for Biochemical Regulation
Faculty of Agriculture
Nagoya University
Chikusa, Nagoya, Japan

Hajime Iwamura, Ph.D.
Associate Professor
Department of Agricultural Chemistry
Faculty of Agriculture
Kyoto University
Kyoto, Japan

Koichi Koshimizu, Ph.D.
Professor
Department of Food Science and Technology
Faculty of Agriculture
Kyoto University
Kyoto, Japan

Shingo Marumo, Ph.D.
Professor
Department of Agricultural Chemistry
Faculty of Agriculture
Nagoya University
Chikusa, Nagoya, Japan

Nobutaka Takahashi, Ph.D.
Professor
Department of Agricultural Chemistry
Faculty of Agriculture
The University of Tokyo
Bunkyo-ku, Tokyo, Japan

Isomaro Yamaguchi, Ph.D.
Department of Agricultural Chemistry
Faculty of Agriculture
The University of Tokyo
Bunkyo-ku, Tokyo, Japan

Hisakazu Yamane, Ph.D.
Department of Agricultural Chemistry
Faculty of Agriculture
The University of Tokyo
Bunkyo-ku, Tokyo, Japan

TABLE OF CONTENTS

Chapter 1

INTRODUCTION

Nobutaka Takahashi

The life cycle of higher plants is regular, though complex. Each stage, together with the shift to the next stage, is controlled by endogenous plant growth regulators. The situation is further complicated by the need for the life cycle to accomodate to environmental conditions such as light intensity, daylength, humidity, and nutritional conditions. Such responses to environmental change are believed to be due to the quantity and availability of endogenous plant hormones and other bioactive substances. In this sense the life cycle and its sensitive adjustment to outside stimuli may be due to the mediating role of such compounds, which thus fulfill a most important role.

At this stage we know of many kinds of plant growth regulators associated with a wide variety of physiological functions in higher plants. In many cases these have been isolated and chemically characterized. Among the most important of these are the so-called plant hormones (phytohormones).

The concept of plant hormones differs substantially from that of hormones in animals and insects, because the differentiation of organ tissues in plants is less extensive than in animals. Plant hormones can be broadly defined as follows: (1) they must be chemically characterized and shown to be biosynthesized in some plant organ, (2) they must be broadly distributed within the plant kingdom, (3) they must show specific biological activity in very low concentration and must be shown to play a fundamental role in regulating physiological phenomena in vivo, and (4) they are usually translocated within the plant from a biosynthesis site to an action site.

At present, five groups of plant growth regulators — auxins, gibberellins, cytokinins, abscisic acid, and ethylene — are regarded as plant hormones; however, the distinction between plant hormones and plant growth regulators other than plant hormones is not always easily seen. At this stage one new group of compounds that regulate plant growth, brassinolide and related compounds, must be considered as true plant hormones on account of their wide distribution in the plant kingdom and their unique biological activity. A less clear cut case is that of "florigen", the hypothetical flower-inducing hormone. Logical as the hypothesis may be, the evidence to support the existence of such a hormone is incomplete and it has never been isolated. Despite this, it is logical to expect that various new plant hormones will be isolated and chemically characterized in the future; the wide variety of physiological function required to maintain the complicated life cycle of the higher plants requires that a considerable complexity of chemical control should exist.

Quite apart from these compounds that might be considered plant hormones, there are many natural products that show interesting physiological activity in the higher plants. In general these compounds are of limited distribution in the plant kingdom and show a rather restricted range of activities. They have been isolated not only from plant tissues but also as metabolites of microorganisms. They can be grouped according to their origin (plant, microorganism) and physiological activity as follows:

•Plant growth regulators of plant origin

1. Plant growth promotors (Figure 1)
   - Brassinolide and related compounds: brassinolide, castasterone, dolicholide, 6-deoxocastasterone, 2-deoxocastasterone, etc.
   - Strigol (germination stimulant from witchweed)
   - Phaseolic acid

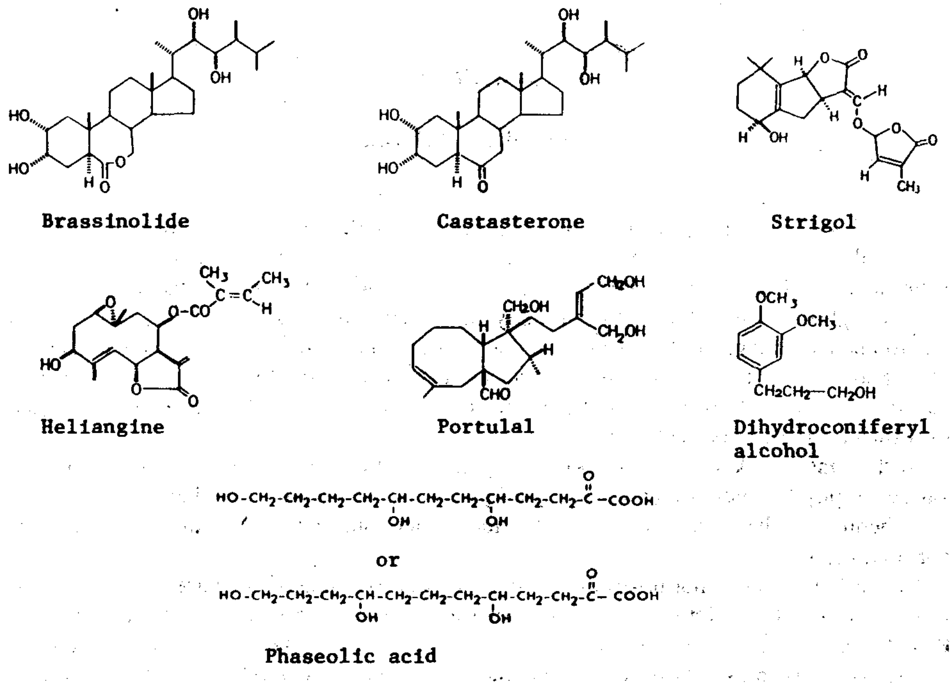


FIGURE 1. Structures of plant growth regulators of plant origin.

Dihydroconiferyl alcohol (synergist of gibberellin)

2. Plant growth inhibitors (Figure 2)
   - Benzoic acid and related compounds
   - Cinnamic acid and related compounds
   - Phenolic compounds including flavonoids
   - Unsaturated lactones: scoporetin, parasorbic acid, psoraen, seselin, etc.
   - Growth inhibitors isolated from *Podocarpus*: podolactones A—E, inumakilactones A—D, ponalactone A and its glucoside, hallactones A, B, sellowins A—C, nagilactones A—G, podolide, etc.
   - Momilactone and related compounds: momilactones A, B, annonalide
   - Jasmonic acid and related compounds: jasmonic acid and its methyl ester, cucurbic acid and its glucoside
   - Asparagusic acid and related compounds: asparagusic acid and its sulfoxide, dihydroasparagusic acid, S-acetyldihydroasparagusic acid, etc.
   - Poly-yne-ene compounds: matricariaester, 2-(*Z*)-dehydromatricariaester, methyl 2-(*Z*)-decene-4,6-diynoate, etc.
   - Batatacins: batatacins I, II, III
   - Rooting inhibitors from *Eucalyptus*: G-regulators, G1, G2, G3, grandinol
   - Growth inhibitors in liverwort and algae: lunularic acid and related compounds
   - Growth inhibitors from bulbs of *Lycoris radiata*: lycoricidinol and lycoricidine
   - Others: harrintonolide, methyl pheoborides, juglone, 3-acetyl-6-methylbenzaldehyde, lignans with germination inhibitory activity, 4,8,13-duvatriene-1,3-diol

Plant Growth Regulators of Microbial Origin

1. Plant growth promotors (Figure 3)
   - Helminthosporol and related compounds from *Helminthosporium sativum*: helmintho-

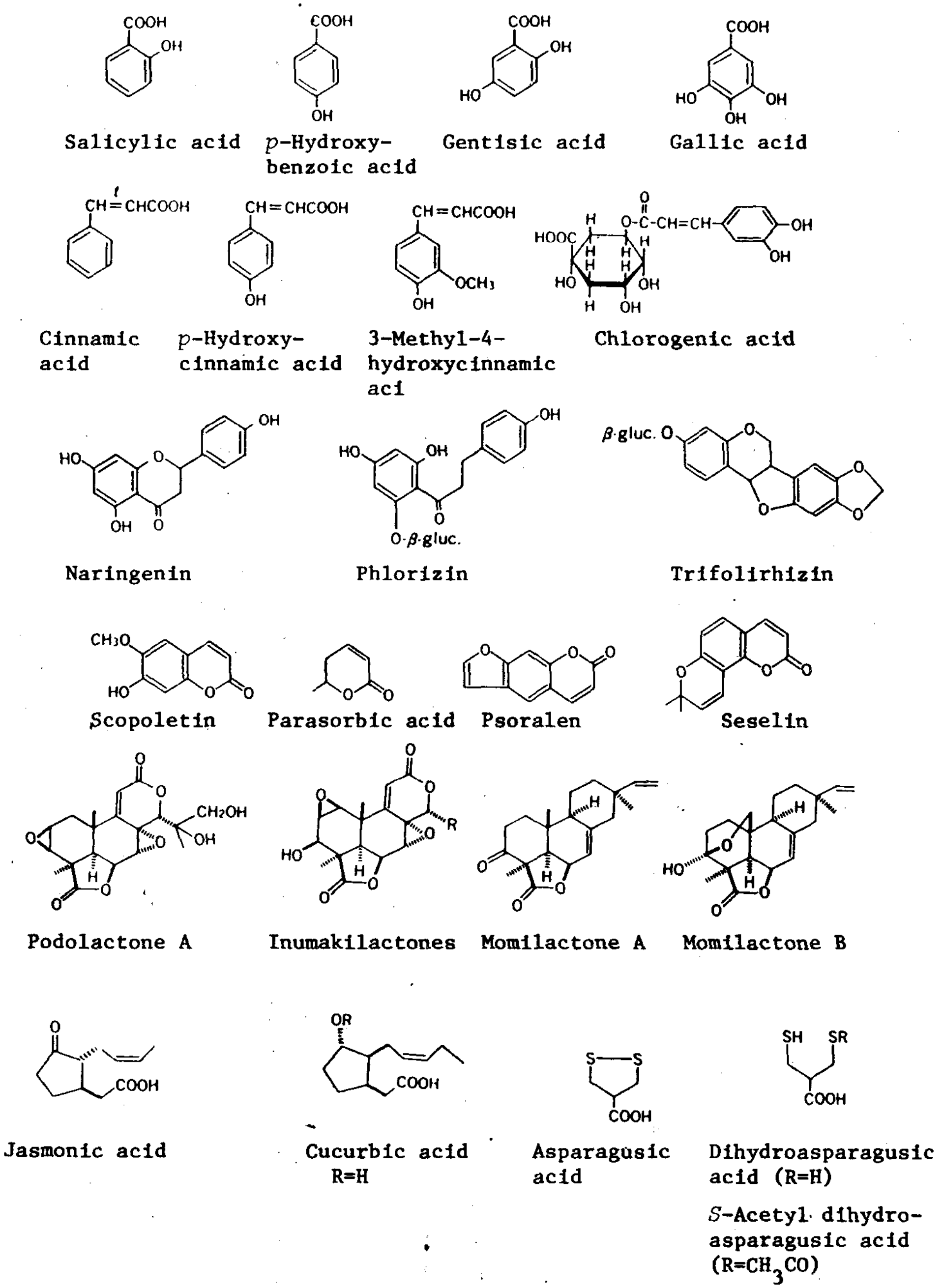


FIGURE 2. Structures of plant growth inhibitors.

sporol and *cis*-sativendiol, etc.

Sclerin and related compounds from *Sclerotinia* spp.: sclerin, sclerotinins A, B

Malformins from *Aspergillus* spp. (malformation inducing substances): malformins A_1, A_2, B_1, B_2, C

Cotylenol and related compounds from *Clodosporium* sp.: cotylenol, cotylenins A—F

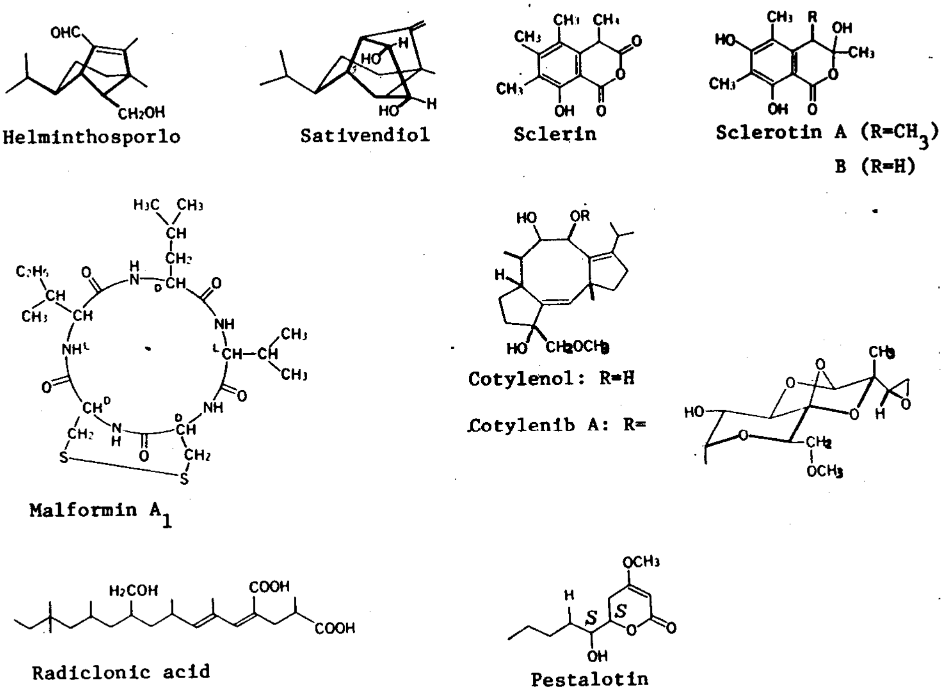


FIGURE 3. Structures of plant growth promotors of microbial origin.

Radiclonic acid from *penicillium* sp.

Synergist to gibberellins from *Pestalotia crytmeraecola* and other unidentified fungi: pestalotin and related compounds

2. Plant growth inhibitors and phytotoxins

Host-specific toxins (Figure 4) have been isolated mainly from *Helminthosporium* and *Alternaria* spp. and have been shown to be used for host recognition by plant pathogens: AM-toxins I—III (*Alternaria mali*), AK-toxin (*A. kikuchiana*), HMT-toxins (*Helminthosporium madys* race T), HC-toxin (*H. carbonum*), toxin from *A. alternata* F. sp. *cycopersici*.

Nonspecific toxins (Figure 5) involve compounds with a wide variety of structures and cause very divergent symptoms on host plants. Some examples follow.

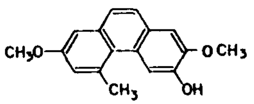
a. Terpenoids: diacetoxysciprenol (*Fusarium equiseti*), aphidicolin (*Harziella entomophilla*), ophiobolins (*Ophiobolus* and *Helminthosporium* spp.), Fusicoccins (*Fusicoccum amygdali*).
b. Other carbocyclic compounds: phyllosinol (epoxidon) and related compounds (*Phyllosticta* sp.).
c. Aromatic and heteroaromatic compounds: piryculol (*Pyricularia oryzae*), fusaric acid (*Gibberella fujikuroi*, *Fusarium*, and *Nectria* spp.), α-picolic acid (*Pyricularia oryzae*), tenuazoic acid (*P. oryzae*, *Alternaria longipes*).
d. Amino acids and peptides: rhizobitoxine and dihydro derivative (*Rhizobium japonicum*), coronatine (*Pseudomonas coronafaciens*), lycomarasmins (*Aspergillus flavus* and *oryzae*), tentoxin (*Alternaria* spp.), phaseotoxin (*Pseudomonas phaseolicola*), tabtoxin (*Pseudomonas tabaci*).

CH_3-CH=CH-C≡C-C≡C-CH=(Z)CH-$COOCH_3$

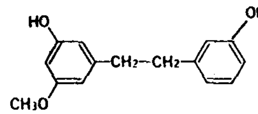
Matricaria ester; 8*Z*, 8*E*

CH_3-C≡C-C≡C-C≡C-CH=(Z)CH-$COOCH_3$

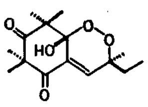
2-Z-Dehydromatricaria ester



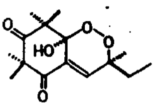
Batatasin I



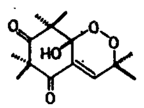
Batatasin II



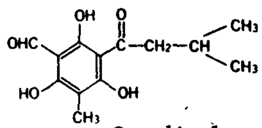
G-Regulator G-I



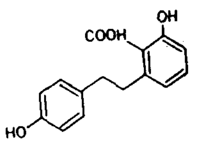
G-II



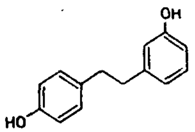
G-III



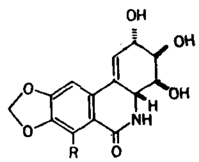
Grandinol



Lunularic acid

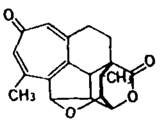


Lunularin

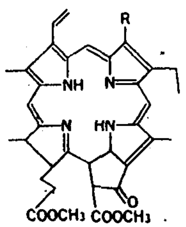


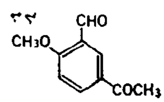
Lycoricidinol (R=OH)

Lycoricidine (R=H)



Harringtonolide

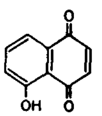




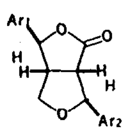
3-Acetyl-6-methoxy-benzaldehyde

Methyl pheophorbide a (R=CH_3)

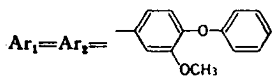
b (R=CHO)

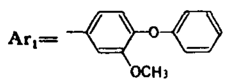


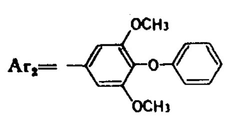
Juglone

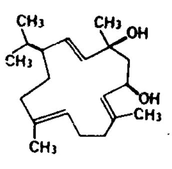


Lignans from *Aegilops ovata*





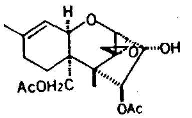




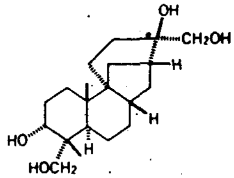
4,8,13-duvatrien-1,3-diol

FIGURE 4. Structures of host-specific phytotoxins.

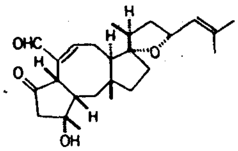
Clarification of the mechanism for the regulation of the life cycle in higher plants has been one of the most important areas of research in plant physiology. An ideal approach to such research should include all the following aspects: (1) isolation and characterization of endogenous compounds responsible for the physiological phenomenon; (2) exogenous ap-



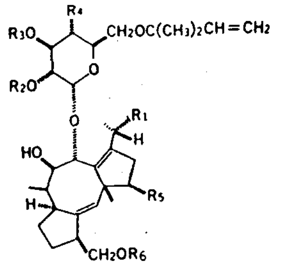
Diacetoxyscirpenol



Aphidicolin

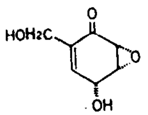


Ophiobolin A

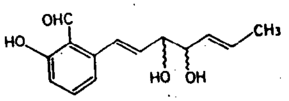


R_1=CH_2OAC, R_3=AC, R_2=R_4=H, R_5=OH, R_6=CH_3
R_1=CH_2OAC, R_2=AC, R_3=R_4=H, R_5=OH, R_6=CH_3
R_1=CH_2OAC, R_4=AC, R_2=R_3=H, R_5=OH, R_6=CH_3
R_1=CH_2OAC, R_2=R_3=R_4=H, R_5=OH, R_6=CH_3
R_1=CH_2OH, R_2=R_3=R_4=H, R_5=OH, R_6=CH_3
R_1=CH_2OH, R_2=AC, R_3=R_4=H, R_5=OH, R_6=CH_3
R_1=CH_2OH, R_3=AC, R_2=R_4=H, R_5=OH, R_6=CH_3
R_1=CH_2OH, R_4=AC, R_2=R_3=H, R_5=OH, R_6=CH_3
R_1=CH_3, R_2=R_3=R_4=R_5=H, R_6=H
R_1=CH_3, R_2=R_3=R_4=H, R_5=OH, R_6=CH_3

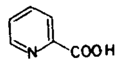
Fusicoccin homologs



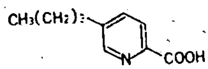
Phyllostine



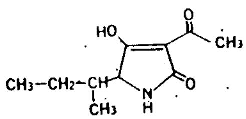
Pyriculol



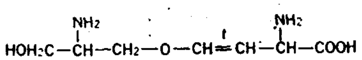
α-Picolic acid



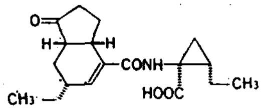
Fusaric acid



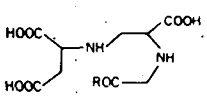
Tenuazoic acid



Phizobitoxine

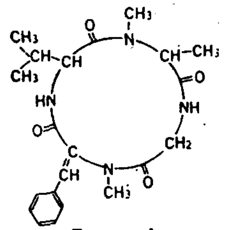


Coronatine

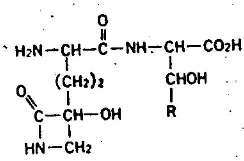


Lycomarasmine (R=H)

Lycomarasmic acid (R=OH)

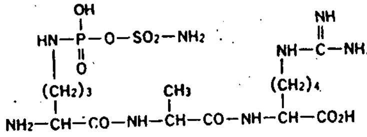


Tentoxin



Tabtoxin (R=CH_3)

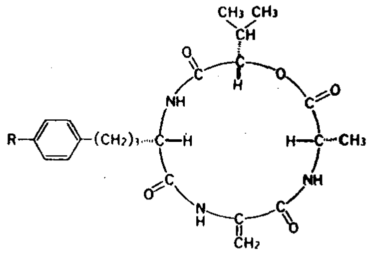
2-Seryltabtoxin (R=H)



Phaseotoxin

FIGURE 5. Structures of non-specific phytotoxins.

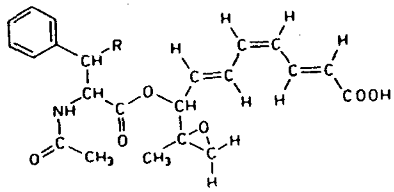
plication to other species to check for the appropriate physiological response (in this way we can hope to establish the generality of the response); (3) examination of the fluctuation in the level of the endogenous regulator in the course of the life cycle of higher plants. This permits correlation between the level of the regulator and the growth and differentiation of



AH-toxin I (R=OCH_3)

II (R=H)

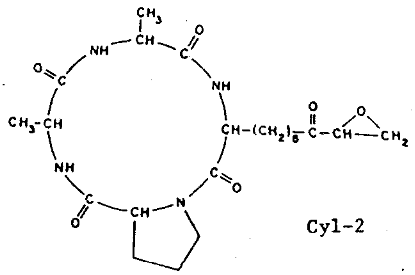
III (R=OH)



AK-toxin

HMT-toxin: Band 1 toxin (R=O)

Band 2 toxin (R=H, OH)



Cyl-2

FIGURE 5. Continued.

the plant, as well as revealing environmental responses. In the course of such studies, the biosynthetic and metabolic pathways should be clarified. An approach such as this can only be brought to fruition by the integration of biological and chemical methodology.

Due to space limitation, this book describes only the chemistry of plant hormones and the reader is referred to other excellent books[1-3] for information on growth regulators other than the recognized plant hormones.

ACKNOWLEDGMENT

The author wishes to express his thanks to Professor Crow of The Australian National University, Canberra, for critical comments.

REFERENCES

1. **Letham, D. S.,** Natural-occurring plant growth regulators other than the prinicpal hormones of higher plants, in *Phytohormones and Related Compounds — A Comprehensive Treatise*, Vol. 1, Lethan, D. S., Goodwin, P. B., and Higgins, T. J. V., Eds., Elsevier/North Holland, Amsterdam, 1978, 349.
2. **Bearder, J. R.,** Plant hormones and other growth substances — their background, structures and occurrence, in *Hormonal Regulation of Development I, Encyclopedia of Plant Physiology*, Vol. 9, MacMillan, J. Ed. Springer-Verlag, Berlin, 1980, 56.
3. **Wood, R. K. S., Ballio, A., and Graniti, A., Eds.,** *Phytotoxins in Plant Disease*, Academic Press, New York, 1972.

Chapter 2

AUXINS

Shingo Marumo

TABLE OF CONTENTS

I. DEFINITION OF A PLANT HORMONE AND AUXIN

A Committee of the American Society of Plant Physiologists published the nomenclature of chemical plant regulators[1] in 1954, in which plant hormones and auxins are defined as follows:

"(Plant) Hormones (Synonym: Phytohormones) are regulators produced by plants, which in low concentrations regulate plant physiological processes. Hormones usually move within the plant from a site of production to a cite of action."

Auxin is a generic term for compounds characterized by their capacity to induce elongation in shoot cells. They resemble indole-3-acetic acid (IAA)(**1**) in physiological action. Auxins may, and generally do, affect other processes besides elongation, but elongation is considered critical. Auxins are generally acids with an unsaturated cyclic nucleus or their derivatives.

Auxin precursors are also defined as compounds which, in the plant, can be converted into auxins. Anti-auxins are defined as compounds which competetively inhibit the action of auxins.

As seen from this definition, the term "auxin", as a type of plant hormone, does not refer to IAA alone; rather, it represents a group of compounds with similar physiological activities, such as elongation of the *Avena* coleoptile.

As natural auxins, IAA (**1**) and 4-chloroindole-3-acetic acid (**2**) have been isolated from higher plants. 5-Hydroxyindole-3-acetic acid (**3**) was suggested to be present in tomatoes, and 1-methoxy- and 4-methoxyindole-3-acetonitrile have been isolated from the diseased clubroots of Chinese cabbage, *Brassica pekinensis*. Many other related metabolites of natural auxins have also been identified in higher plants (see Section III).

Synthetic auxins, which were found from the screening of a large number of synthetic compounds, include 1-naphthalene-acetic acid (NAA) (**4**), phenylacetic acid (**5**), *cis*-cinnamic acid (**6**), and 2,4-dichlorophenoxyacetic acid (2,4-D)(**7**). Two new synthetic auxins, α-chloro-β-(3-chloro-*o*-tolyl) pronionitrile (**8**)[2] and 1,2-benzisothiazol-3-ylacetic acid (BIA)(**9**),[3] were reported. Among them, 2,4-D (**8**), in particular, is an important synthetic auxin that is used extensively in place of IAA in plant physiology studies. Phenylacetic acid (**5**) has been isolated from the etiolated seedlings of *Phaseolus mungo*[4] and stem extracts of tomato and sunflower,[5] and now is recognized as a natural auxin. A new synthetic auxin (**8**) exerted growth-promoting activity in general auxin bioassays, such as elongation of mung bean hypocotyl and *Avena* coleoptile segments. BIA (**9**) showed obvious auxin-like activity in the split pea internode curvature test.

Anti-auxins have been discovered throughout the biological investigation of synthetic auxins and related compounds. Natural compounds with anti-auxin activity have been isolated from higher plants and fungi. Synthetic and natural anti-auxins are described in Section IV.

II. THE HISTORY OF CHEMICAL RESEARCH ON AUXINS

An auxin was the first plant hormone to be chemically identified, and auxins played important roles in early research on plant hormones because they were the sole type of hormone available for plant physiologists to use in their physiological studies until gibberellin (isolated from a fungus) was recognized as a second type of plant hormone. The early history of chemical research on auxins is recorded in *Phytohormones* (Went and Thimann, 1937).[6]

The first substantial evidence that auxin was present in plants was reported by Darwin and Darwin in 1880 in their publication, *The Power of Movement in Plants*. They illuminated seedlings of *Phalaris canariensis* horizontally and showed that the effect of this light was perceived by the tip of a seedling and that the effect was transmitted from the tip to a lower part of the seedling's coleoptile, causing the latter to bend toward the light.

This transmittance of a light stimulus downward in the phototropism of *Phalaris* was confirmed by Boysen Jensen[7] in 1913 in his experiments with *Avena sativa*. He cut off the