Phytochemistry, 1975. Vol. 14, pp. 2105–2112. Pergamon Press. Printed in England.

REVIEW

GROWTH REGULATING SUBSTANCES OF PLANT ORIGIN*

DIETER GROSS

Institute of Plant Biochemistry, Academy of Sciences, 401 Halle (Saale), Weinbergweg,
German Democratic Republic

(*Received* 6 *December* 1974)

Key Word Index— Higher plants; plant growth regulatory constituents; review; occurrence; chemical structure; biological activity.

INTRODUCTION

Extensive screening, using much improved bioassay techniques, has recently uncovered many naturally occurring plant constituents which possess plant growth regulating properties. Many other new growth regulating substances have been found by testing purely synthetic organic compounds. In some cases, the results obtained in bioassays with synthetic analogues of active substances have been used as a basis for proposing relationships between chemical structure and biological activity. This paper surveys the growth regulating substances which have been isolated from higher plants.† Details of the methods and techniques used for isolation, chemical characterization and bioassays are not included.

The first group of plant products showing growth regulating properties are the well known plant hormones. These are distributed widely and in fact are probably present in all higher plants. They have high activity, specific action and function in the regulation of growth and differentiation of plants. They include the auxins [1], cytokinins [2], gibberellins [3,4], abscisic acid and its derivatives [5,6] and ethylene [7,7a]. Since this group has been the subject of numerous recent reviews, it seems to be unnecessary to deal with them further here.

WIDELY DISTRIBUTED REGULATORS

The second group of natural plant regulators is represented by compounds which are also widely distributed in higher plants. These compounds are certainly involved in growth regulation, although they apparently do not show specific effects. In the following two sections, various chemical groups are reviewed with respect to their structure and biological activity.

Aliphatic compounds

Certain saturated fatty acids [8] and their lower alkyl esters, many known to be natural products, have been shown to possess growth inhibiting activity [9–11]. They kill or inhibit terminal meristems, but have no effect on axillary meristems. Fatty acids and their methyl esters with 8, 10 and 12 carbon atoms, respectively, show the greatest inhibition as evidenced by the fact that capric acid has been shown to be a growth inhibiting substance in dormant bulbs of *Iris hollandica* cv. Wedgewood [12,13]. Small amounts of lauric and myristic acids, which have the same inhibitory activity as capric acid on the growth of *Avena* coleoptiles, were also detected. It has also been reported that certain synthetic aliphatic hydroxycarboxylic acids show promoting activities on the root growth of lettuce seedlings [14], whereas fatty alcohols with chain length of C_9, C_{10}, and C_{11} are very active in inhibiting axillary and terminal bud growth [11,15]. Acidic growth inhibitors, isolated from dwarf pea seedlings, were identified as fumaric, palmitic and oleic acids and

---

* Dedicated to Prof. Dr. Dr. h. c. mult. K. Mothes on the 75th anniversary of his birthday.

† Revised version of a paper presented at the International Symposium "Chemistry and Biochemistry of Plant Growth Regulators". Cottbus. GDR, 24–26 September 1974.

the monomethyl and ethyl esters of succinic acid [16]. The neutral inhibitor, α-stearyl glycerol, isolated from dwarf peas, produced considerable inhibition when applied to terminal buds [17]. Furthermore, it has been reported that neutral plant lipids can double the auxin- or gibberellin-induced growth of pea stem sections. They show optimum activity at molecular length of 20–30 Å [18]. In 1971 it was shown that the light petroleum extract from avocado mesocarp extract contained a new endogenous inhibitor which was identified as 1-acetoxy-2,4-dihydroxy-*n*-heptadeca-16-ene (**1**) [19]. It inhibits elongation of wheat coleoptiles and growth of soyabean callus in the presence of cytokinin, This inhibitor was also detected in other plant tissues such as tobacco leaf, mango seed and *Annona* fruit and thus appears to be of wide occurrence. The two hydroxyl groups and the terminal acetoxy group are all important for biological activity, as revealed by the inactivity of the triacetate and the deacetylated derivative.

Phenolic compounds and coumarins

A number of natural phenolic compounds, such as salicylic acid, *p*-hydroxybenzoic acid and gallic acid as well as *p*-coumaric acid, caffeic acid and ferulic acid have been found to be active inhibitors of some growth processes [see 20–23]. The mechanism of the endogenous regulation of flowering in plants is an unsolved problem in plant biochemistry. The existence of promoting and inhibiting flowering substances has been postulated for over 30 yr. Recently it was shown that the leaves of vegetative *Kalanchoe blossfeldiana* contain a specific flowering-inhibitory substance which was isolated and identified as gallic acid [24]. It is also present in flowering *Kalanchoe* plants in an inactive form.

The widely distributed tannins appear to act as gibberellin antagonists. Chemically defined tannins were found to inhibit the gibberellin-induced growth of light-grown dwarf pea seedlings [25,26] and several authors have noted inhibitory or stimulatory effects of tannins on plant growth and development (see refs in [26]).

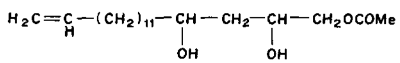
In different higher plants, phenylacetic acid [27,28] and its 4-hydroxy derivative [29] have been detected as native plant growth regulators. Both compounds have recently also been isolated as auxin-like substances from the alga *Undaria pinnatifidia* [30].

Corn steep liquor, a by-product of the manufacture of starch from corn, is often added to the growth medium of micro-organisms. However, it was found to inhibit the germination of alfalfa seed. In 1973 an inhibitor was isolated from corn steep liquor and identified as ferulic acid [31,32] previously known as a germination inhibitor widely distributed in plants. In further experiments, it was demonstrated that the biogenetically related dihydroconiferyl alcohol is identical with the 'lettuce cotyledon factor', a synergist of the gibberellin action in inducing lettuce hypocotyl elongation [33,34]. Recently dihydroconiferyl alcohol was shown to stimulate cucumber hypocotyl elongation [35]. This phenylpropanoid was also detected in pea, cucumber, and artichoke and it has been suggested that it may be a naturally occurring plant hormone [35].

Other phenolic compounds such as the dihydrochalcone glucoside phloridzin and its aglucone phloretin from *Malus* [36,37], as well as the widely distributed ester chlorogenic acid [20,38] are known to be potent inhibitors of growth. Flavonoids like the flavanone naringenin which is found in dormant peach buds and the isocoumarin, hydrangenol (**2**) from *Hydrangea macrophylla* and *H. hortensia*, both antagonize the action of gibberellins [39,40]. 5,4′-Dihydroxy-7-methoxyflavanone and 5-hydroxy-7,4′-dimethoxyflavanone isolated from *Betula verrucosa* buds inhibit the growth of coleoptile cells of wheat [40a]. Genistein 7-glucoside, genistein *C*-monoglucoside, and 3-(5-benzodioxolyl)-5,7-dihydroxy-4H-benzpyran-4-one 7-glucoside, all present in an isoflavone preparation of *Lupinus luteus*, are characterized as endogenous growth regulators of yellow lupine [40b]. Coumarin, scopoletin and related compounds are also well known, widely occurring inhibitors of germination and growth [20,39,41,42].

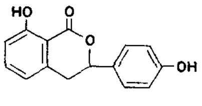
GROWTH SUBSTANCES OF RESTRICTED DISTRIBUTION

This group of compounds consists of growth regulating substances which are of limited distribution in plants. It is represented by a number of terpenoids, alkaloids and other substances possessing unusual chemical structures. Often these

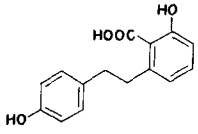


$H_2C{=}\underset{H}{C}{-}(CH_2)_{11}{-}\underset{OH}{CH}{-}CH_2{-}\underset{OH}{CH}{-}CH_2OCOMe$

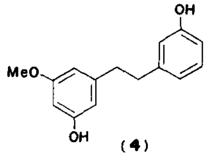
(1)



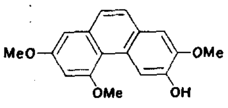
(2)



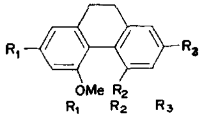
(3)



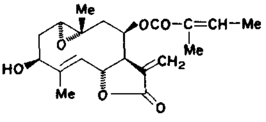
(4)



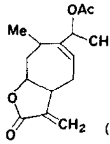
(5)



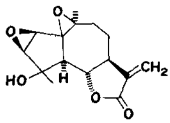
	R_1	R_2	R_3
(6)	OMe	H	OH
(6a)	OH	OH	H
(6b)	OMe	OH	H



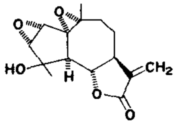
(7)



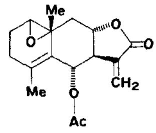
(8)



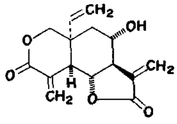
(9)



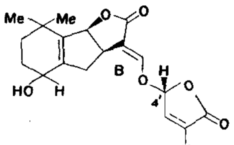
(10)



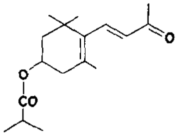
(11)



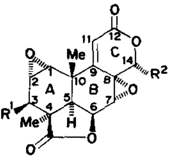
(12)



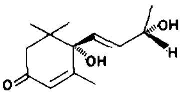
(13)



(14)



	R'	R^2
(15)	H	C(OH)CH_2OH Me
(16)	OH	C(OH)CH_2OH Me
(17)	O	C(OH)CH_2SOMe Me
(18)	OH	CH(OH)Me
(19)	OH	$CH{=}CH_2$



(14a)

compounds are designated as secondary plant substances *sensu strictu*, and most apparently do not participate in the regulation of biochemical processes during the ontogeny of specific plants. Some others, however, are known to possess regulatory activity in recognized bioassays but it is difficult to decide whether the compound is an endogenous regulator or is only effective after exogenous application.

Stilbenes and phenanthrenes

Lunularic acid (**3**), from *Lunularia cruciata* (L.) Dum., is of general occurrence in all liverworts and algae that have been examined [43–47]. These two groups of lower plants apparently lack abscisic acid, the ubiquitous growth inhibitor of mosses, ferns and higher plants. Thus, it seems possible that lunularic acid may fulfil the same growth regulating function in these lower plants as ABA does in higher plants. It is, therefore, a plant growth regulator of some chemotaxonomic and phylogenetic significance.

Dormant bulbils of yam (*Dioscorea batatas* Decne.) contain 3 phenolic growth inhibiting compounds which seem to be new dormancy-inducing substances not identical with previously known inhibitors [48–50]. They were named batatasin I, II, and III. Recently batatasin III was identified as another dihydrostilbene (**4**) [51], and batatasin I as 6-hydroxy-2,4,7-trimethoxyphenanthrene (**5**) [52]. This phenanthrene derivative is structurally related to the 9,10-dihydrophenanthrene antifungal derivatives orchinol (**6**) [53,54], hircinol (**6a**) and loroglossol (**6b**) [55]. These three phytoalexins are produced in infected corms of *Orchis militaris* and *Loroglossum hircinum*, respectively.

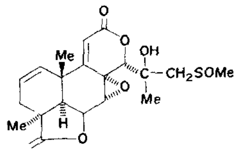
It is apparent that compounds (**3**–**6b**) represent new types of inhibitors which are biogenetically related to the stilbenes. This assumption is supported by the occurrence of a number of hydroxylated and methoxylated bibenzyl, 9,10-dihydrophenanthrene and phenanthrene derivatives in other higher plants; for instance in *Tamus communis* L. [56,56a], *Combretum apiculatum*, *C. molle* and *C. psidioides* [57,58] and *Papaver somniferum* [58a]. Moreover, in liverworts the following bibenzyl derivatives have been found: 2,3,4'-trihydroxybibenzyl in *Pellia endiviifolia* (Dicks.) Dum. [59], 2-hydroxy-3,4'-dimethoxybibenzyl in *Pellia meesiana* (Gott.) Limpr. [60] and 3-methoxybibenzyl in *Radula complanata* (L.) Dum. [61]. At present there is no information about the growth regulating activity of these last named plant products.

Sesquiterpenes and diterpenes

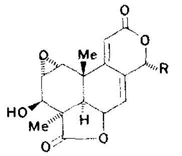
Much new and interesting work has been reported on the activity of plant growth regulators containing a terpenoid skeleton and a lactone group as their salient structural features; for example, the sesquiterpene heliangine (**7**) isolated from *Helianthus tuberosus* L. [62–68]. Heliangine inhibits the elongation of *Avena* coleoptile sections and promotes adventitious root formation of *Phaseolus* cuttings. Promotion is almost completely reduced by supplying cysteine which reacts *via* the SH-groups with the exomethylene group of heliangine suggesting that the exomethylene group conjugated to the lactonic carbonyl may therefore be responsible for the growth inhibiting activity. Several other sesquiterpenoid α-methylene-γ-butyrolactones have been isolated from higher plants, some of which possess growth regulating activity; e.g. xanthinin (**8**) found in *Xanthium pennsylvanicum* [69–72], the two guaianolides chrysartemin A (**9**) and B (**10**) from *Chrysanthemum parthenium*, *C. mexicana*, *C. klotzchiana* and *C. morifolium* [73,74] and pyrethrosin (**11**) detected in other *Chrysanthemum* species [75–77]. It is of interest that a number of related sesquiterpene lactones have been isolated during the course of a continuing search for antitumour agents from plant sources which show significant cytotoxic activity (see [78] and references therein). For instance, vernolepin (**12**) from *Vernonia hymenolepis* A. Rich. shows significant inhibitory activity against carcinoma-sarcoma in rats and it is noteworthy that it inhibits growth of wheat coleoptiles [79,80]. Further work on the synthesis of biological active α-methylene-γ-butyrolactones as well as related six-membered-ring lactones has been based on modification and simplification of the molecule [81–85] but these have not been examined as plant growth regulators.

Strigol (**13**) is of relevance here because of its structural relationship to the above lactones. It is a highly potent seed germination stimulant for the root parasite *Striga lutea* Lour. [86]. The structure and relative configuration of the biological active enantiomer have been derived from spectroscopic X-ray crystallographic data [87]. Recently the chromatographic investigation of the *Striga* seed stimulant [88], and the synthesis of DL-strigol [89,90] have been described. Active concentrations giving 50% germination of *Striga* seeds are 10^{-16} M for (**13**) and 10^{-12} M for the enantiomer at C-4′. Many biological interesting compounds can be found among carotenoids and related compounds [91]. In addition to growth regulating compounds structurally related to the plant hormone abscisic acid, there are other substances such as quiesone (**14**), isolated from infected tobacco leaves [92,93]. This has been shown to be a potent inhibitor of the germination of *Perenospora tabacina* conidia. Vomifoliol (**14a**), a compound related to abscisic acid but lacking the 2,4-pentadiene sidechain, has been found in several plants. It causes as much stomatal closure in epidermal cells of *Eichhornia crassips* (Mart.) Solms as abscisic acid at identical concentrations [93a].

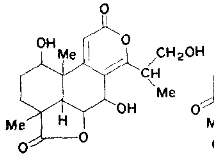
Furthermore, some novel nor- and bisnor-diterpene lactones have been isolated from *Podocarpus* species [94–104]. They are designated as podolactones (podolactone A (**15**), B (**16**), C (**17**), D(**20**), and E(**21**), inumakilactones [inumakilactone A (**18**) and its 15-β-glucoside, B (**19**), and E(**23**)], ponalactone A (**22**), momilactone A (**24**), and nagilactones [nagilactone A (**25**), B (**26**), C (**27**), and D (**28**)]. Some of these show strong inhibitory activity, in particular podolactone E (**21**). Detailed



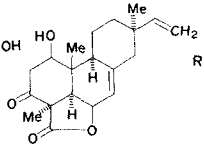
(**20**)



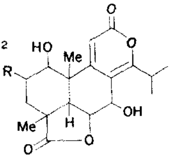
(**21**) R = CH=CH₂
(**22**) R = CHMe₂



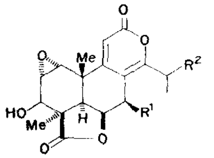
(**23**)



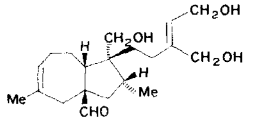
(**24**)



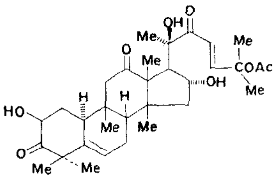
(**25**) R = H
(**26**) R = OH



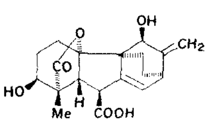
(**27**) R¹ = OH R² = Me
(**28**) R¹ = H R² = H



(**29**)



(**30**)



(**31**)

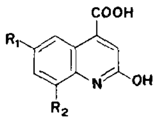
studies have established the relationship between chemical structure and biological activity of these *Podocarpus* lactones [105]. Moreover, a neutral substance has been obtained from the leaves of *Portulaca grandiflora* Hook, which inhibits the elongation of *Avena* coleoptiles induced by indoleacetic acid. This substance, portulal (**29**), has been identified as a new type of bicyclic terpene containing a perhydroazulene nucleus [106–108].

The cucurbitacins, a group of some 25 or more compounds, have been found in plants of the Cucurbitaceae. They are designated as cucurbitacin A, B, C etc. and differ mainly in the pattern of hydroxylation and other substituents as well as the type of glycosidation [108a]. It has been reported that the cucurbitacins B (**30**), E, I, J, and K possess gibberellin antagonistic activity [109].

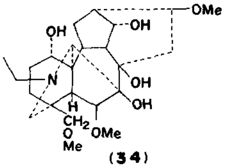
The last type of compound to be mentioned here induces antheridia formation in many, if not all, species of the fern family Polypodiaceae. Antheridium-inducing substances have been termed antheridiogens. The chemical structure of the antheridiogen (**31**) isolated from *Anemia phyllitidis* and *A. hirsuta* has been determined [110–112].

Nitrogen containing compounds

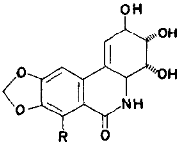
Among the class of *N*-heterocyclic natural products, 2 hydroxylated cinchoninic acids show promoting activities. The first was isolated from corn steep liquor and named zeanic acid (**32**) [31,32]; the second was found in rice bran 50 yr ago and identified as the isomeric 2,6-dihydroxycinchoninic acid (**33**) [113]. In 1974 *N,N*-dimethyltryptophan was found in *Abrus precatorius* L. seeds as a plant growth inhibitor [114]. Furthermore, it has been reported that some alkaloids possess plant growth regulating activity, for example, delcosine (**34**) found in *Delphinium ajacis* [115]. This diterpenoid alkaloid of the lycoctine type interacted with gibberellins and was growth inhibitory on phloem and xylem tissue. The similarity in structure between delcosin and gibberellic acid suggested to the authors that delcosine may compete with gibberellic acid for enzyme-active sites and thereby change their catalytic function. The methanol extract of the bulbs of *Lycoris radiata* Herb. has high growth inhibiting activity in the *Avena* straight growth test and rice assay. It was shown that lycoricidine (**35**) (identical with narciclasine from *Narcissus* bulbs [116,117]) and lycoricidinol (**36**) are responsible for this marked inhibitory action [118].



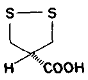
(**32**) $R_1 = H$ $R_2 = OH$
(**33**) $R_2 = OH$ $R_1 = H$



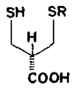
(**34**)



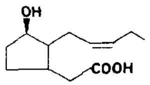
(**35**) R = H
(**36**) R = OH



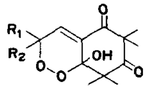
(**37**)



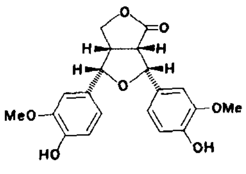
(**38**) R = H
(**39**) R = Ac



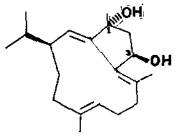
(**40**)



	R_1	R_2
(**41**)	Et	Me
(**42**)	Me	Me
(**43**)	Me	Et



(**44**)



(**45**)

Sulphur containing compounds

Three *S*-containing inhibitors with high activity have been isolated from *Asparagus officinalis* L. and identified as asparagusic acid (**37**), dihydroasparagusic acid (**38**), and *S*-acetyldihydroasparagusic acid (**39**) [119–123]. Their growth inhibiting activities are very similar to that of abscisic acid. They completely inhibit the growth of roots and hypocotyls of lettuce seedlings at $6{\cdot}7 \times 10^{-4}$ M to $6{\cdot}7 \times 10^{-7}$ M respectively.

Miscellaneous structures

Cucurbic acid (**40**), its glucoside and its methyl ester isolated from *Cucurbita pepo* L. are effective inhibitors when assessed in the *Avena* coleoptile and rice seedling tests [124]. Cucurbic acid is structurally related to the prostaglandins, although these compounds have not yet been detected with certainty in higher plants. In *Eucalyptus grandis* seedlings, three endogenous inhibitors (**41**–**43**) of root formation, all bicyclic compounds with a peroxide linkage, have been found [25–127].

The chemical structure and the activity of an inhibitor (**44**) isolated from *Aegilops ovata* have been described [128]. A characteristic feature of this molecule is the five-membered ring lactone. It may be that this inhibitor is synthesized from two C_9-C_3-units. It is very interesting that this inhibitor is effective in light while it is inactive in the dark. This is the first instance to be reported of a compound having such a property, since all the germination inhibitors already described inhibit more effectively in dark than in light. Recently a new type of plant growth inhibitor has been extracted from immature tobacco leaves and identified as 4,8,13-duvatriene-1,3-diol (**45**) [129].

CONCLUSION

The following general observations may be made. In addition to the well known plant hormones, a number of plant growth regulating substances have been isolated from higher plants. These belong to different groups of natural products. Thus, aliphatic and aromatic carboxylic acids, phenolic and neutral compounds, *S*- and *N*-heterocyclic compounds, alkaloids and terpenes are all represented. Examination of the formulae of the growth regulating substances described reveals the absence of any common structural feature. Only a few functional groups such as phenolic hydroxy groups and α-methylene-γ-butyro-lactones are found to recur. This diversity indicates that in all probability these active substances are involved in different regulating processes of plant growth and differentiation.

These biological active compounds can be used as models which may be modified and simplified without loss of activity. For this the essential functional groups must be retained. Such chemical work is only possible if sufficient knowledge of the relationship between chemical structure and biological activity is available. Since different authors use different methods for the quantitative assessment of the inhibitory or promoting activity, the correlation of results is very difficult and can only be made with considerable reservations. Thus, present methods used for estimation of biological activities are inadequate and it is desirable to develop new internationally accepted standards for bioassays.

REFERENCES

1. Schneider, E. A. and Wightman, F. (1974) *Ann. Rev. Plant Physiol.* **25**, 487.
2. Hall, R. H. (1973) *Ann. Rev. Plant Physiol.* **24**, 415.
3. Jones, R. L. (1973) *Ann. Rev. Plant Physiol.* **24**, 571.
4. MacMillan, J. and Pryce, R. J. (1973) *Phytochemistry* (Miller, L. P., ed.), Vol. **3**, p. 283, van Nostrand, New York; MacMillan, J. (1974) *Recent Adv. in Phytochemistry* **7**, 1.
5. Gross, D. (1972) *Pharmazie* **27**, 619.
6. Milborrow, B. V. (1974) *Ann. Rev. Plant Physiol.* **25**, 259; (1974) *Recent Adv. in Phytochemistry* **7**, 57.
7. Abeles, F. B. (1973) *Ethylene in Plant Biology*, Academic Press.

7a. Yang, S. F. (1974) *Recent Adv. in Phytochemistry* **7**, 131.

8. Le Poidevin, N. (1965) *Phytochemistry* **4**, 525.
9. Tso, T. (1964) *Nature* **202**, 511.
10. Tso, T., Steffens, G. and Engelhaupt, M. (1965) *J. Agr. Food Chem.* **13**, 78.
11. Cathey, H. M., Steffens, G. L., Stuart, N. W. and Zimmerman, R. H. (1966) *Science* **153**, 1382.
12. Tsukamoto, Y. and Ando, T. (1973) *Proc. Japan. Acad.* **49**, 627.
13. Ando, T. and Tsukamoto, Y. (1974) *Phytochemistry* **13**, 1031.
14. Mikami, Y., Takahara, H., Imura, H., Suzuki, A. and Tamura, S. (1970) *Agr. Biol. Chem.* **34**, 977.
15. Steffens, G. L., Tso, T. C. and Spaulding, D. W. (1967) *J. Agr. Food Chem.* **15**, 972.
16. Komoto, N., Ikegami, S. and Tamura, S. (1972) *Agr. Biol. Chem.* **36**, 2547.
17. Komoto, N., Noma, M., Ikegami, S. and Tamura, S. (1972) *Agr. Biol. Chem.* **36**, 2555.
18. Stowe, B. B. (1970) *Plant Growth Substances* (Carr, D. J., ed.) p. 30, Springer-Verlag, Berlin; (1974) *Proc. of the 8th International Conference on Plant Growth Substances*, Tokyo, p. 997, Hirokawa, Tokyo.
19. Bittner, S., Gazit, S. and Blumenfeld, A. (1971) *Phytochemistry* **10**, 1417.
20. Moreland, D. E., Egley, G. H., Worsham, A. D. and Monaco, T. J. (1966) *Adv. Chem. Ser.* **53**, 112.
21. Steward, F. C. and Krikorian, A. D. (1971) *Plants, Chemicals and Growth*, Academic Press, New York.
22. Wang, T. S. C., Yang, T. K. and Chuang, T. T. (1967) *Soil Sci.* **103**, 239.
23. Kefeli, V. I. and Kadyrov, C. S. (1971) *Ann. Rev. Plant Physiol.* **22**, 185.
24. Price, R. J. (1972) *Phytochemistry* **11**, 1911.
25. Corcoran, M. R. (1971) *Plant Physiol.* (*Suppl*) **47**, 34.
26. Corcoran, M. R., Geissman, T. A. and Phinney, B. O. (1972) *Plant Physiol.* **49**, 323.
27. Wightman, F. and Rauthan, B. S. (1974) *Proc. of the 8th International Conference on Plant Growth Substances*, Tokyo, 26.8.–1.9.1973, p. 15, Hirokawa, Tokyo.
28. Okamoto, T., Isogai, Y. and Koizumi, T. (1967) *Chem. Pharm. Bull.* **15**, 159.
29. Isogai, Y., Nomoto, S., Noma, T. and Okamoto, T. (1974) *Proc. of the 8th International Conference on Plant Growth Substances, Tokyo*, 26.8.–1.9.1973, p. 9, Hirokawa, Tokyo.

30. Abe, H., Uchiyama, M. and Sato, R. (1974) *Agr. Biol. Chem.* **38**, 897.
31. Matsushima, H., Fukumi, H. and Arima, K. (1973) *Agr. Biol. Chem.* **37**, 1865.
32. Matsushima, H. and Arima, K. (1973) *Agr. Biol. Chem.* **37**, 1873.
33. Kamisaka, S. (1973) *Plant Cell Physiol.* **14**, 747.
34. Shibata, K., Kubota, T. and Kamisaka, S. (1974) *Plant Cell Physiol.* **15**, 191.
35. Sikurai, N., Shibata, K. and Kamisaka, S. (1974) *Plant Cell Physiol.* **15**, 709.
36. Hutchinson, A., Taper, C. D. and Tower, G. H. N. (1959) *Can. J. Biochem. Physiol.* **37**, 901.
37. Kefeli, V. L., Kof, E. M., Knipl, J. S., Bukhanova, L. V. and Yarviste, E. L. (1969) *Biochimia (Moskau-Leningrad)* **34**, 891.
38. Sondheimer, E. (1964) *Bot. Rev.* **30**, 667.
39. Phillips, I. D. J. (1962) *J. Exp. Botany* **13**, 213.
40. Asen, S., Cathey, H. M. and Stuart, N. W. (1960) *Plant Physiol.* **35**, 815.

40a. Popravko, S. A., Kononenko, G. P. and Vul'fson, N. S. (1974) *Jzv. Akad. Nauk SSSR Ser. Khim.* 2389.

40b. Laman, N. A. (1974) *Fiziol. Rast.* **21**, 301.

41. Berrie, A. M. M., Parker, W., Knights, B. A. and Hendrie, M. R. (1968) *Phytochemistry* **7**, 567.
42. Garb, S. (1961) *Bot. Rev.* **27**, 422.
43. Valio, I. F. M., Burdon, R. S. and Schwabe, W. W. (1969) *Nature* **223**, 1176.
44. Valio, I. F. M. and Schwabe, W. W. (1970) *J. Exp. Botany* **21**, 112, 138.
45. Pryce, R. J. (1972) *Phytochemistry* **11**, 872, 1355, 1759.
46. Pryce, R. J. (1971) *Planta* **97**, 354.
47. Pryce, R. J. and Linton, L. (1974) *Phytochemistry* **13**, 2497.
48. Hashimoto, T., Hasegawa, K. and Kawarada, A. (1972) *Planta* **108**, 369.
49. Hasegawa, K. and Hashimoto, T. (1973) *Plant Cell Physiol.* **14**, 369.
50. Hasegawa, K. and Hashimoto, T. (1974) *Plant Cell Physiol.* **15**, 1.
51. Hashimoto, T., Hasegawa, K., Yamaguchi, H., Saito, M. and Ishimoto, S. (1974) *Phytochemistry* **13**, 2849.
52. Letcher, R. M. (1973) *Phytochemistry* **12**, 2789.
53. Hardegger, E., Biland, H. R. and Corrodi, H. (1963) *Helv. Chim. Acta* **46**, 1354.
54. Steiner, K., Egli, C., Rigassi, N., Helali, S. E. and Hardegger, E. (1974) *Helv. Chim. Acta* **57**, 1137.
55. Fisch, M. H., Flick, B. H. and Arditti, J. (1973) *Phytochemistry* **12**, 437.
56. Reisch, J., Bathory, M., Szendrei, K., Minker, E. and Novak, I. (1969) *Tetrahedron Letters* 67; (1973) *Phytochemistry* **12**, 228.

56a. Letcher, R. W. and Nhamo, L. R. M. (1972) *Tetrahedron Letters* 4869.

57. Letcher, R. M. and Nhamo, L. R. M. (1971) *J. Chem. Soc. C* 3070; (1972) *Perkin I*, 2941.
58. Letcher, R. M., Nhamo, L. R. M. and Gumiro, I. T. (1972) *J. Chem. Soc. Perkin I*, 206.

58a. Gambos, M., Szendrei, K., Istvan, V. and Reisch, J. (1974) *Herba Hungarica* **13**, 63.

59. Huneck, S. and Schreiber, K., *J. Hattori Bot. Lab.* (in press).
60. Benesova, V. and Herout, V. (1970, 1972) *Collection Czechosl. Chem. Comm.* **35**, 1926; **37**, 1764.
61. Suire, C. (1970) *Du Botaniste* **53**, 125.
62. Shibaoka, H. (1961) *Plant Cell Physiol.* **2**, 175.
63. Morimoto, H., Sanno, Y. and Oshio, H. (1966) *Tetrahedron* **22**, 3173.
64. Nishikawa, M., Kamiya, K., Takabataka, A. and Oshio, H. (1966) *Tetrahedron* **22**, 3601.
65. Yamaki, T., Shibaoka, H., Syono, K., Morimoto, H. and Oshio, H. (1966) *Bot. Mag. Tokyo* **79**, 339.
66. Shibaoka, H. Mitsuhashi, M. and Shimokoriyama, M. (1967) *Plant Cell Physiol.* **8**, 161.
67. Shibaoka, H., Shimokoriyama, M., Iriuchijima, S. and Tamura, S. (1967) *Plant Cell Physiol.* **8**, 297.
68. Shibaoka, H., Anzai, T., Mitsuhashi, M. and Shimokoriyama, M. (1967) *Plant Cell Physiol.* **8**, 647.
69. Bonde, E. K. (1953) *Physiol. Plant.* **6**, 234.
70. Khudairi, A. K. (1954) *Physiol. Plant.* **7**, 66.
71. Geissman, T. A., Deuel, P., Bonde, E. K. and Addicott, F. A. (1954) *J. Am. Chem. Soc.* **76**, 685.
72. Deuel, P. D. and Geissman, T. A. (1957) *J. Am. Chem. Soc.* **79**, 3778.
73. Romo, J., Romo De Vivar, A., Trevino, R., Joseph-Nathan, P. and Diaz, E. (1970) *Phytochemistry* **9**, 1615.
74. Osawa, T., Suzuki, A. and Tamura, S. (1971) *Agr. Biol. Chem.* **35**, 1966.
75. Barton, D. H. R. and De Mayo, P. (1957) *J. Chem. Soc.* 150.
76. Barton, D. H. R., Böckman, O. C. and De Mayo, P. (1960) *J. Chem. Soc.* 2263.
77. Iriuchijima, S. and Tamura, S. (1970) *Agr. Biol. Chem.* **34**, 204.
78. Kupchan, S. M. (1970) *Trans. N.Y. Acad. Sci.* **32**, 85.
79. Sequeira, L., Hemingway, R. J. and Kupchan, S. M. (1968) *Science* **161**, 789.
80. Kupchan, S. M., Hemingway, R. J., Wesner, D. and Karim, A. (1968) *J. Am. Chem. Soc.* **90**, 3596.
81. Grieco, P. A. and Hirio, K. (1973) *Tetrahedron Letters* 1831.
82. Hudrlik, P. F., Rudnick, L. P. and Korzeniowski, S. H. (1973) *J. Am. Chem. Soc.* **95**, 6848.
83. Divakar, K. J., Sane, P. P. and Rao, A. S. (1974) *Tetrahedron Letters* 399.
84. Grieco, P. A. and Reap, J. J. (1974) *Tetrahedron Letters* 1097.
85. Yamada, K., Kato, M. and Hirata, Y. (1973) *Tetrahedron Letters* 2745.
86. Cook, C. E., Whichard, L. P., Turner, B., Wall, M. E. and Egley, G. H. (1966) *Science* **154**, 1189.
87. Cook, C. E., Whichard, L. P., Wall, M. E., Egley, G. H., Coggon, P., Luhan, P. A. and McPhail, A. T. (1972) *J. Am. Chem. Soc.* **94**, 6198.
88. Visser, J. H. and Botha, P. H. (1974) *Z. Pflanzenphysiol.* **72**, 352.
89. Heather, J. B., Mittal, R. S. D. and Sih, C. J. (1974) *J. Am. Chem. Soc.* **96**, 1976.
90. MacAlpine, G. A., Raphael, R. A., Shaw, A., Taylor, A. W. and Wild, H. J. (1974) *Chem. Commun.* 834.
91. Isler, O. (ed.) (1971) *Carotinoids*, Birkhäuser Verlag, Basel.
92. Leppik, R. A., Hollomon, D. W. and Bottomley, W. (1972) *Phytochemistry* **11**, 2055.
93. Mori, K. (1973) *Agr. Biol. Chem.* **37**, 2899.

93a. Stuart, K. L. and Coke, L. B. (1975) *Planta* **122**, 307.

94. Hayashi, Y., Takahashi, S., Ona, H. and Sakan, T. (1968) *Tetrahedron Letters* 2071.
95. Galbraith, M. N., Horn, D. H. S., Sasse, J. M. and Adamson, D. (1970) *Chem. Commun.* 170.

96. Ito, S., Sunagawa, M.. Kodama, M., Honma, H. and Takahashi, T. (1971) *Chem. Commun.* 91.
97. Galbraith, M. N., Horn, D. H. S. and Sasse, J. M. (1971) *Chem. Commun.* 1362.
98. Ito, S., Kodama, M. and Sunagawa, M. (1971) *Chem. Commun.* 855.
99. Hayashi, T., Kakisawa, H., Ito, S., Chen, Y. P. and Hsu. H. Y. (1972) *Tetrahedron Letters* 3385.
100. Galbraith, M. N., Horn, D. H. S. and Sasse, J. M. (1972) *Experientia* **28,** 253.
101. Russell, G. B., Fenemore, P. G. and Singh, P. (1972) *Australian J. Biol. Sci.* **25,** 1025.
102. Silva, M.. Bittner, M. and Sammes, P. G. (1973) *Phytochemistry* **12,** 883.
103. Russell, G. B., Fenemore, P. G. and Singh, P. (1973) *Chem. Commun.* 166.
104. Brown, K. S. and Sanchez, W. E. (1974) *Biochem. Systematics Ecology* **2,** 11.
105. Galbraith, M. N., Horn, D. H. S., Ito, S., Kodama, M. and Sasse, J. M. (1972) *Agr. Biol. Chem.* **36,** 2393.
106. Mitsuhashi, M. and Shibaoka, H. (1965) *Plant Cell Physiol.* **6,** 87.
107. Yamazaki, S., Tamura, S., Muramoto, F. and Saito, Y. (1969) *Tetrahedron Letters* 359.
108. Tokoroyama, T., Matsuo, K., Kanazawa, R., Kotsuki, H. and Kubota, T. (1974) *Tetrahedron Letters* 3093.
108a. Lavie, D. and Glotter, E. (1971) *Progr. Chem. Org. Natural Products* (Herz, W., Griesebach, H., Kirby, G. W., eds.), Vol. **29,** p. 307, Springer-Verlag, Wien.
109. Guha, J. and Sen, S. P. (1973) *Nature New Biology* **244,** 223.
110. Nakanishi, K., Endo, M., Näf, U. and LeRoy, F. Johanson (1971) *J. Am. Chem. Soc.* **93,** 5579.
111. Endo, M., Nakanishi, K., Näf, U., McKeon, W. and Walter, R. *Physiol. Plantarum* **26,** 183.
112. Zanno, P. R., Endo, M., Nakanishi, K., Näf, U. and Stein, C. (1972) *Naturwissenschaften* **59,** 512.
113. Sahashi, Y. (1925, 1926, 1927) *Biochem. Z.* **15,** 221; **168,** 69; **189,** 208.
114. Mandava, N., Anderson, J. D. and Dutky, S. R. (1974) *Phytochemistry* **13,** 2853.
115. Waller, G. R. and Burström, H. (1969) *Nature* **222,** 576.
116. Ceriotti, G. (1967) *Nature* **213,** 595.
117. Piozzi, F., Mondelli, R., Fuganti, C. and Ceriotti, G. (1968) *Tetrahedron* **24,** 1119.
118. Okamoto, T., Torii, Y. and Isogai, Y. (1968) *Chem. Pharm. Bull.* **16,** 1860.
119. Kitahara, Y., Yanagawa, H., Kato, T. and Takahashi, N. (1972) *Plant Cell Physiol.* **13,** 923.
120. Yanagawa, H., Kato, T., Kitahara, Y., Takahashi, N. and Kato, Y. (1972) *Tetrahedron Letters* 2549.
121. Yanagawa, H., Kato, T., Kitahara, Y. and Takahashi, N. (1973) *Plant Cell Physiol.* **14,** 791.
122. Yanagawa, H., Kato, T. and Kitahara, Y. (1973) *Plant Cell Physiol.* **14,** 1213.
123. Kuhnle, J. A., Corse, J. and Cahn, B. G. (1975) *Biochem. Physiol. Pflanzen* **167,** 188.
124. Koshimizu, K., Fukui, H., Usuda, S. and Mitsui, T. (1974) *Plant Growth Substances 1973*, p. 86, Hirokawa, Tokyo.
125. Crow, W. D., Nicholls, W. and Sterns, M. (1971) *Tetrahedron Letters* 1353.
126. Sterns, M. (1971) *J. Cryst. Mol. Structures* **1,** 373.
127. Paton, D. M. and Willing, R. R. (1974) *Plant Growth Substances 1973*, p. 126, Hirokawa, Tokyo.
128. Lavie, D., Levy, E. C., Cohen, A., Evenary, M. and Guttermann (1974) *Nature* **249,** 388.
129. Springer, J. P., Clardy, J., Cox, R. H., Cutler, H. G. and Cole, R. J. (1975) *Tetrahedron Letters* 2737.