

## Mini-Review

### Occurrence of Fusicoccanes in Plants and Fungi

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**Abstract.** The literature on substances structurally related to fusicoccin shows that its molecular design is not unique. Compounds of this type with a dicyclopenta[*a,d*]cyclooctane skeleton (the 5→8→5 ring system) are often encountered in nature. The compounds, systematically reviewed, comprise a single class of fusicoccane-type terpenoids characterized by the presence of the dicyclopenta[*a,d*]cyclooctane system in the structure of these molecules. The review is arranged according to the taxonomy of the organisms producing these terpenoids; it is shown that compounds of this type, including physiologically active ones, are found in the major systematic divisions: fungi, lower and higher plants, and animals (insects). Chemical, analytical, and biogenetic data are given for each compound, as well as data on their physiological activity and the mechanism of their action on plants. Nomenclature is proposed for the fusicoccane-type compounds.

The diterpenoid glycoside fusicoccin (FC) occupies a conspicuous position among biosynthetic plant growth regulators. Discovered in 1964 by Ballio et al. as a metabolite of a phytopathogenic fungus *Fusicoccum amygdali* Del., it has attracted the attention of researchers due to its high and versatile physiological activity. Fusicoccin stimulates plant growth via the elongation mechanism, promotes the opening of leaf stomata, takes seeds out of dormancy, and accelerates their germination (especially under unfavorable ambient conditions), induces root formation, and so on. On the subcellular level, fusicoccin markedly enhances membrane permeability for ions, amino acids, and sugars and ac-

tivates the chromatin-associated RNA polymerase I. The pattern of fusicoccin activity is typical of phytohormones, which allows fusicoccin to be regarded as an imitator, a physiological analogue of phytohormones.

Muromtsev et al. (1987) has noted a remarkable resemblance of fusicoccin to gibberellin, a major phytohormone: besides having a high and versatile regulatory activity, both compounds are produced by phytopathogenic fungi and are closely related chemically, belonging to the same group of natural products—diterpenoids. Gibberellin was found in higher plants about a quarter of a century after its discovery in cultures of the phytopathogenic fungus *Gibberella fujikuroi*.

This analogy prompted a suggestion about the hormonal nature of fusicoccin, and Muromtsev et al. undertook a search for compounds of this type in higher plants, which has led to identification of fusicoccin in maize roots and cobs and in cabbage leaves (Muromtsev et al. 1987).

Taking all this into account, we have tried to systematize the data available in the literature on the distribution of fusicoccin-related compounds among various organisms. It turned out that the fusicoccin structure is not unique, and similar derivatives of dicyclopenta[*a,d*]cyclooctane (a 5→8→5 ring system) are widely found in nature. They have been described in fungi, algae, higher plants (liverworts and flowering plants), and even animals (insects). As various representatives of this group of terpenoids were detected and identified, they were given trivial names usually derived from the Latin names of the producing organisms.

This review summarizes for the first time the data on compounds that contain the dicyclopenta[*a,d*]-

cyclooctane skeleton in their molecules, and attempts to group them into one class of fusicoccane-type terpenoids.

The review is structured according to the taxonomy of the producing organisms. For each compound, data are given on its chemistry, biogenesis, and analytical techniques, and for the ones most studied, data on their physiological activity and the mechanism of action in flowering plants as well.

### Biosynthetic Pathways for Dicyclopenta[*a,d*]cyclooctanes

Terpenoids are very widespread in nature. This class of compounds is characterized, on the one hand, by great diversity in the carbon skeletons, and on the other, by an obligatory reiteration therein of the five-carbon isoprene link. According to the "isoprene biogenetic rule," terpenoids are compounds that are initially formed by combinations of isoprene fragments: geraniol, farnesol, geranylgeraniol, squalene, and other aliphatic members of this series. Further, terpenoids are formed from these aliphatic precursors by usual cyclization, and in some cases with group rearrangements. Geranyl pyrophosphate, farnesyl pyrophosphate, geranylgeranyl pyrophosphate, and geranylfarnesyl pyrophosphate give rise, respectively, to mono-, sesqui-, di-, and sesterterpenes.

The fusicoccane-type compounds considered here, which are based on a dicyclopenta[*a,d*]cyclooctane ring system, have been more than once described among di- and sesterterpenes of fungal origin (fusicoccin, ophiobolin, cotylenin). Such substances have been found in higher plants (roseatoxide, roseanolone, roseadione, cheilarinosin, fusicoplugins, anadensin, fusicogigantones, fusicogigantepoxide, and fusicoccin), algae (epoxydictymene), and insects (ceroplastanes).

The presence of a complex 5→8→5 tricyclic system with various substituents and multiple asymmetric centers, as well as the biological activity of a number of such compounds, has made them a subject of ever-increasing interest.

The first such structure described was a sesterterpene ophiobolin produced by a fungus *Helmintosporium oryzae* (Orsenigo, 1957). Ophiobolin biosynthesis, which is typical of isoprenoids, has been studied in detail by Canonica et al. (1966a,c). The ophiobolin molecule is formed from five isoprene units bound head-to-tail. Cyclization of *trans*-geranylfarnesyl pyrophosphate proceeds in two steps: first there appears a system of two (five- and 11-membered) rings, and subsequent rearrangement gives rise to a tricyclic 5→8→5 system.

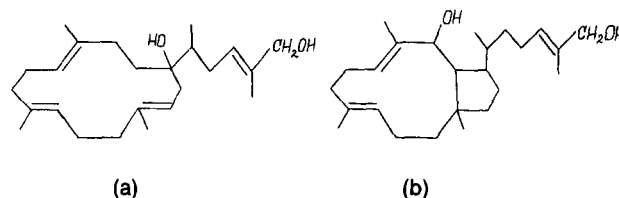


Fig. 1. Structures of albocerol (a) and albolineol (b).

A similar dicyclopenta[*a,d*]cyclooctane system is formed by a two-step cyclization of geranylgeranyl pyrophosphate: further glucosidation of this tricyclic system and alkylation of the glucose moiety in the fungus *Fusicoccum amygdali* Del. gives rise to fusicoccin (Banerji et al. 1976, Randazzo et al. 1978, 1979, Evidente et al. 1980). In the same way, the fungus *Cladosporium* makes cotylenins (Sassa 1970). The aglycon (tricyclic 5→8→5) moieties of the fusicoccin and the cotylenin molecules are stereochemically identical (Ballio et al. 1982).

To date, we have only fragmentary data on the pathways of biosynthesis of fusicoccane compounds in organisms other than fungi, and one can only speculate about the mechanisms used by plants and insects from the presence of related compounds isolated concurrently with fusicoccanes.

For example, the aphid *Ceroplastes albolineatus*, besides the fusicoccane-like compounds—ceroplastanes—has been found to contain an alicyclic C<sub>25</sub> isoprenoid alcohol geranylfarnesol, a macrocyclic alcohol albocerol (Fig. 1a), and a bicyclic alcohol albolineol (Fig. 1b), which testifies to the similarity of the biosynthetic pathways leading to ceroplastanes and ophiobolins through geranylfarnesyl pyrophosphate (Rios and Perez 1969, Veloz et al. 1975).

Formation of albocerol can be regarded as a new type of cyclization of geranylfarnesyl pyrophosphate, and that of albolineol—a bicyclic (five- and 11-membered) sesterterpenoid—as the first step of internal cyclization of a macrocyclic sesterterpene (Veloz et al. 1975) which further undergoes an intracyclic rearrangement giving rise to a tricyclic 5→8→5 system and various ceroplastan derivatives (Rios et al. 1974). Formation of such compounds is in line with the hypothesis of ophiobolin synthesis put forward by Canonica et al. (1967).

The wide occurrence of dicyclopenta[*a,d*]cyclooctanes in the plant kingdom is not incidental. A large number of macrocyclic structures are known that can be precursors to the 5→8→5 tricyclic systems. For example, cembranoid macrocyclic diterpenes are found in both plants (tobacco, fir, etc.) (Hanson 1987) and marine fauna (corals) (Hanson 1984). The 14-membered macrocyclic skeleton of

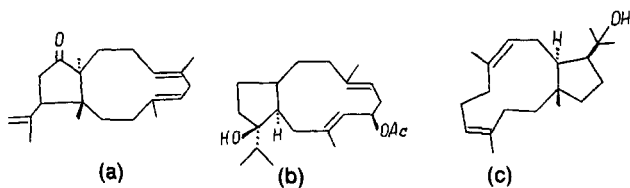


Fig. 2. Structures of dolabellanes.

these diterpenes is a unique structure which by intramolecular cyclization can give rise to various systems including the 5→8→5 tricyclic ones (Dauben et al. 1975).

Among higher plants and algae, the same sources yielded both the fusicoccane 5→8→5 systems and the diterpene dicyclic five- and 11-membered systems—dolabellanes, which are probably the precursors of the tricyclic systems.

Thus a 5→8→5 tricyclic epoxydictymene and a dolabellane (Fig. 2a) have been isolated from a brown alga *Dictyota dichotoma* (Enoki et al. 1983). A liverwort *Odontoschisma denudatum* yielded a dolabellane diterpenoid (Fig. 2b), whereas another liverwort *Plagiochila acanthophylla* yielded a 5→8→5 tricyclic diterpenoid fusicoplugin and several more oxidized analogues (Hashimoto et al. 1985).

Recently, Japanese researchers have isolated from a liverwort *Pleurozia gigantea* a new dolabellane (Fig. 2c) and diterpenoids of the fusicoccane type: fusicogigantones A and B, and fusicogigantepoxide. The position of the double bonds and the absolute configuration of the dolabellane indicate that it has common biogenetic pathways with the fusicoccane diterpenes (Asakawa et al. 1990). Thus, such structures appear to be quite widespread in nature.

The dicyclopenta[*a,d*]cyclooctane terpenoids considered in this review differ in the stereochemical orientation of the rings in their molecules, which is probably due to the differences in the cyclization mechanisms.

### Fusicoccane Compounds of Fungal Origin

#### *Fusicoccins* of *Fusicoccum amygdali* Del.

Fusicoccin is a plant growth regulator produced by the phytopathogenic fungus *Fusicoccum amygdali* Del., the causative agent of drupe canker. It was isolated in 1964 from the producer culture filtrate by a group of Italian researchers lead by Ballio (Ballio et al. 1964). Its chemical structure was established by Italian and British researchers (Ballio et al.

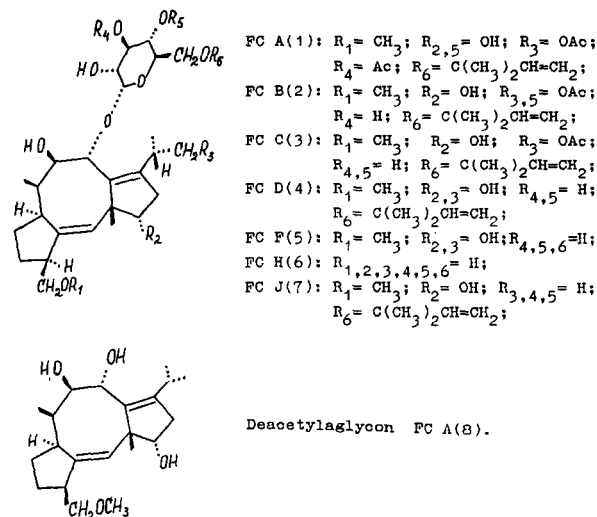


Fig. 3. Structures of fusicoccins.

1968a, 1970, Barrow et al. 1968, 1971a,b, 1973, 1975). Fusicoccin is a glycoside of a carbocyclic diterpene of mol. wt. 680 and an overall formula  $\text{C}_{36}\text{H}_{56}\text{O}_{12}$ . Besides the main compound, FC A, the fungus produces quite a number (over 15) of closely related substances differing from it in the extent of acetylation, position of the acetyl groups, or a lower extent of oxidation of the aglycon moiety (Fig. 3).

The chemistry, microbial synthesis, isolation, and analytical techniques, as well as various aspects of the physiological activity and practical use of fusicoccin have been reviewed (Ballio 1978, Marré 1977, 1979, 1980, Muromtsev et al. 1984, 1989b).

Fusicoccins are obtained by submerged cultivation of the producing fungus in liquid nutrient medium, with subsequent isolation and purification. The cultivation conditions for *F. amygdali* have been described in detail by Ballio et al. (1968b) and Krasnopolskaya et al. (Muromtsev et al. 1989a, Krasnopolskaya et al. 1984, Priede et al. 1989). FC is extracted from the culture filtrate with chloroform, ethyl acetate, or butyl acetate (Ballio et al. 1964, Kobrina and Voblikova 1980) or by adsorption on charcoal (Ballio et al. 1968b). After purification, the compound is crystallized from ethyl acetate (Sadovskaya et al. 1990). At present, FC is available from Montedison, Milan, Italy, and from the Institute of Agricultural Biotechnology, Moscow, Russia.

Fusicoccin displays versatile physiological activity of the hormonal type, its optimal doses being substantially lower and their effects often exceeding those of phytohormones. It stimulates the growth of isolated parts and organs of phanerogamous plants,

mimicking in a number of biotests the action of cytokinins (extension of cotyledons) and auxins (elongation of segments of internodes, coleoptiles, hypocotyls, roots). FC has been found to enhance the plastic extensibility of the cell envelope, by inducing a pH drop in the cell wall and activating the polysaccharide-cleaving enzymes, which results in "loosening" of the cell wall and its stretching (Marré 1979).

Another pronounced effect of FC is the marked enhancement of transpiration caused by its ability to open the stomata of mono- and dicots regardless of the illumination conditions.

An important property of FC is its ability to induce and speed up seed germination. It is especially important that its action is more pronounced under unfavorable conditions (elevated or low temperature, high water content or high salinity), which allows it to be regarded as a growth regulator with antistress activity. For this reason, FC is now used in the Commonwealth of Independent States (CIS) in the plant industry, both for presowing seed treatment and for spraying the vegetating plants (Muromtsev et al. 1989b). Another field of application of FC is to induce root formation in some shrubs and ornamental crops (Sultonov and Muromtsev 1985).

The molecular mechanism of FC action is most often reduced to stimulation of the ion-transporting system of the plasmalemma (Marré 1979, Aducci et al. 1988) which has been found to contain proteins binding FC with high affinity (De Michelis et al. 1989, Aducci et al. 1989). In 1979 Marré put forward a hypothesis that FC stimulates the plasmalemmal proton pump which excretes hydrogen ions into the milieu. The loosening of the cell wall combined with rising osmotic pressure promotes cell expansion (Abramycheva et al. 1991). Recently there have been reports on the influence of FC on the passive ion transport through the plasmalemma (Blatt and Clint 1989, Vorob'ev et al. 1987). Another aspect discussed is the stimulation by FC of the active import of potassium which is not coupled with proton extrusion (Mengel and Schubert 1985).

On the other hand, more and more evidence is accumulating for the influence of FC on the genetic apparatus and the protein synthesizing system. In particular, FC has been shown to activate RNA and protein synthesis in plant cells (Selivankina et al. 1988) and enhance the activity of chromatin-bound RNA polymerase I. The molecular target for FC is not the RNA polymerase I as such but the associated protein kinase (Selivankina et al. 1990).

A number of works (Ballio 1978, Ballio et al. 1981a,b) have been concerned with the dependence of the physiological activity of FCs on their molec-

ular structure. It has been shown that the phytotoxicity typical of FC A is fully retained only in dihydroFC. Other structural modifications markedly attenuate toxicity (Ballio et al. 1971, 1973, Bottalico et al. 1978). The stomata-opening activity is inversely correlated with the polarity of the molecule (Ballio 1978, Bottalico et al. 1978).

Most of the FC derivatives prove to be highly active in various growth tests and seed germination tests. Of great interest is the high growth-promoting activity of deacetyl fusicoccin A (FC C) which is found in appreciable amounts in the culture medium and is much less toxic than FC A (Ballio et al. 1977).

On the whole, the physiological activity of FC and its derivatives is determined in the first place by the conformation of the eight-membered ring (Ballio et al. 1991); the glycosyl moiety is of secondary importance. In the aglycon moiety, features essential for activity include the ( $\alpha$ ) configuration at C8 and C9, and an unsubstituted hydroxyl at C8.

#### *Cotylenins of Cladosporium sp.*

Cotylenins were first described in 1970 by Japanese researchers (Sassa et al. 1970) who detected substances with cytokinin activity (Sassa 1970) in the culture filtrate of a then unidentified fungus that was subsequently classed with the genus *Cladosporium*.

The molecules of cotylenins and fusicoccins are rather similar. The main metabolite of the producing fungus is cotylenin A (Fig. 4). The culture medium also yielded cotylenins B, C, D, E, F, G, H, and I (Sassa 1971) differing from the main metabolite in the structure of the glycosyl moiety, and cotylenol (Fig. 4) which is the aglycon moiety of all cotylenins (Sassa et al. 1975a,b, Sassa and Togashi 1973, Sassa and Takahama 1975, Takahama et al. 1979).

The fungus is grown in submerged culture (Sassa et al. 1972), and cotylenins are isolated from the culture filtrate by extraction with ethyl acetate followed by chromatography on a silica gel column in a mixture of chloroform and increasing concentrations of ethanol (Sassa et al. 1972, 1975a,b, Sassa and Togashi 1973).

The major metabolites of *Cladosporium*—cotylenins A, C, E, F, and G—display the same activity on cucumber cotyledons, indicating the low specificity of this biotest (Sassa and Takahama 1975).

The high semblance between cotylenins and fusicoccins is of interest in the studies of the physiological activity of these compounds. The activity of cotylenins in a number of biotests has been assayed

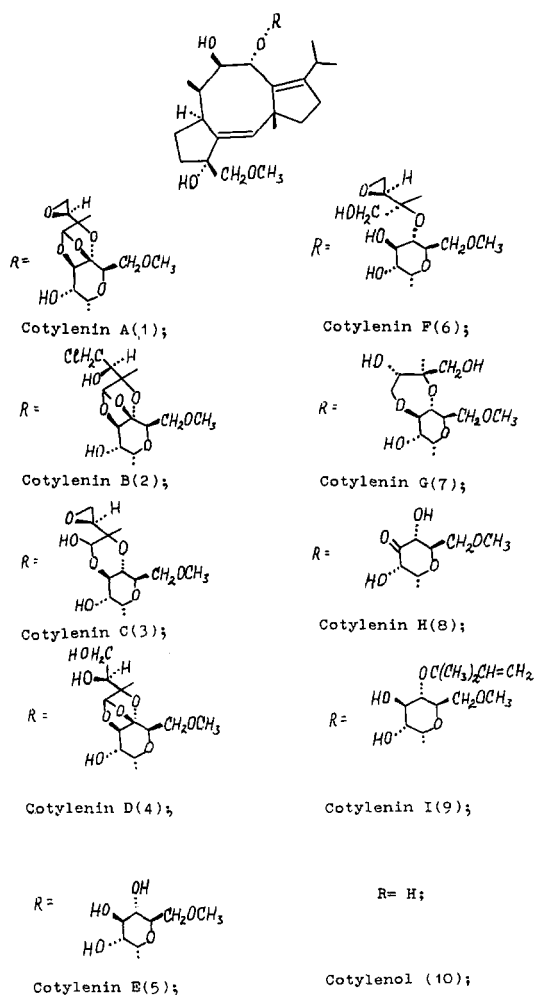


Fig. 4. Structures of cotylenins.

by Bottalico et al. (1978). In an FC-specific bio-test—wilting of tomato cuttings—cotylenin A turned out to be 2.6 times less active than FC. Cotylenins F, C, G, and E proved respectively 7, 21, 29, and 38 times less active than cotylenin A, and cotylenol activity was extremely low.

The opening of stomata, which is typical of FC, is also induced by cotylenins; cotylenol and cotylenins A, C, G, F, and E are reliably more active than FC (Bottalico et al. 1978). All cotylenins are more active than FC A in a radish cotyledon elongation assay.

#### *Ophiobolins of Drechslera oryzae and Other Fungi*

Fusicocane compounds also include a group of sesterterpenoid fungal metabolites called *ophiobolins*. About 15 such compounds are known to date.

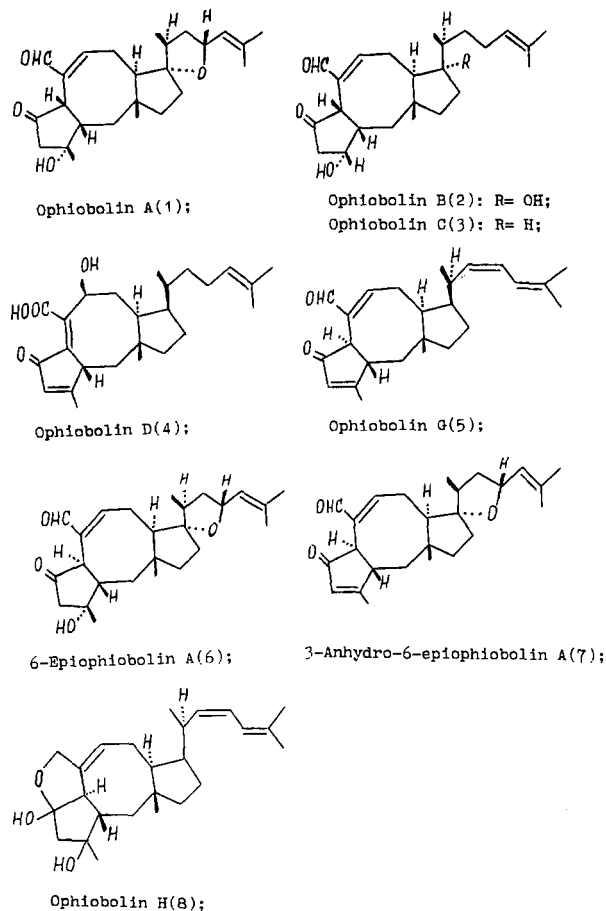


Fig. 5. Structures of ophiobolins.

The structures and overall formulae of some of them are given in Fig. 5. Among ophiobolin producers there are phytopathogenic fungi *Drechslera oryzae* (syn. *Helminthosporium oryzae*, perfect stage *Cochliobolus miyabeanus*, syn. *Ophiobolus miyabeanus*), *D. maydis*, *D. sorghicola*, *H. zizaniae*, *C. heterostrophus*, *Aspergillus ustus* (Nakamura and Ishibashi 1958, Nozoe et al. 1965, Ohkawa and Tamura 1966, Canonica et al. 1966b,c, Kim et al. 1984, Cutler et al. 1984, Sugawara et al. 1987, 1988, Yun et al. 1988).

The commonly accepted term for this group of compounds is *ophiobolins*; however, other names are also found in the literature (Table 1), which is due to the same substances having been isolated from different fungi. Ophiobolins are distinguished by letter indices; some ophiobolins are not included into the general notation system.

Ophiobolins have been isolated from the culture media of the producing fungi; the first one was ophiobolin A (Orsenigo 1957), the main metabolite of *D. oryzae*. The structure and the absolute configuration of ophiobolin A have been elucidated by

**Table 1.** Alternative Names for Ophiobolins

Ophiobolin A	Ophiobolin, cochliobolin, cochliobolin A, zizanin
Ophiobolin B	Ophiobolosin A, zizanin B, cochliobolin B
Ophiobolin C	Zizanin A
Ophiobolin D	Cephalonic acid

Source: Hanson 1986.

Japanese (Nozoe et al. 1966) and Italian (Canonica et al. 1966b) researchers.

Isolation of ophiobolins includes extraction with chloroform or ethyl acetate and subsequent purification. Ophiobolins are assayed qualitatively and quantitatively using high-performance liquid chromatography (HPLC). The structures of these compounds have been established by chemical degradation and X-ray analysis.

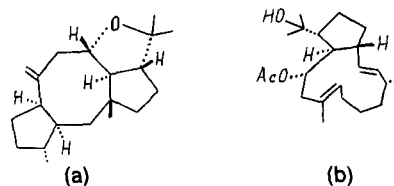
The usual tricyclic (5→8→5) ring system of ophiobolins is similar to that of fusicocin and cotylenin aglycons. The stereochemistry of the coupling between the A and B rings (C2–C6) has been clearly elucidated. Some ophiobolins—A, B, and C—have *cis* coupling, whereas others (e.g., 6-epi-ophiobolin A, ophiobolin G and H) have *trans* coupling. It is intriguing that two *trans*-coupled ophiobolins are produced by *A. ustus* (Cutler et al. 1984).

Ophiobolins take a part in the pathogenic process caused by their producers (Canales and Gray 1988). These substances inhibit root growth, retard seed germination, alter the membrane permeability, lower the photosynthetic fixation of CO<sub>2</sub>, and suppress amino acid and protein synthesis (Orsenigo 1957, Hesseltine et al. 1971, Chattopadhyay and Samadhar 1976, 1980, Nejjidat 1987). The mechanism of ophiobolin action is associated with their ability to inhibit calmodulin-mediated signaling and alter membrane permeability (Leung et al. 1984, 1985).

### Fusicoccane Compounds from Algae

#### *Epoxydictymene of the Brown Alga Dictyota dichotoma*

A group of Japanese researchers have isolated a tricyclic diterpene of the fusicoccane type, epoxydictymene (Fig. 6a), from the methanolic extract of the brown alga *Dictyota dichotoma* (Enoki et al. 1983). Its structure has been established by X-ray and spectral analysis as well as study of its chemical derivatives. The authors have suggested that epoxydictymene arises biosynthetically from a bicyclic dollabelladiene (Fig. 6b) which is also present in this alga.



**Fig. 6.** Structures of epoxydictymene (a) and dollabelladiene (b).

### Fusicoccane Compounds from Liverworts

#### *Fusicoplugins of Plagiochila acanthophylla*

In 1985 Japanese researchers reported isolation of new fusicoccane diterpenoids from the liverwort *Plagiochila acanthophylla* subsp. *japonica*. The four new compounds were termed *fusicoplugin A* (Fig. 7a), *B* (Fig. 7b), *C* (Fig. 7c), and *D* (Fig. 7d) (Hashimoto et al. 1985). Their structures were established on the basis of spectral data, X-ray analysis, and chemical derivation and analysis.

#### *Anadensin of Anastrepta orcadensis*

In 1983, another representative of fusicoccane diterpenoids, anadensin (Fig. 7e) was isolated from the liverwort *Anastrepta orcadensis* by German and British researchers (Huneck et al. 1983). Its structure was determined by spectral and X-ray analysis.

#### *Fusicogigantones A, B, and fusicogigantepoxide from Pleurozia gigantea*

In 1990 Japanese researchers reported three new fusicoccane diterpenoids obtained from the ether extract of the liverwort *Pleurozia gigantea*: fusicogigantone A (Fig. 7f), fusicogigantone B (Fig. 7g), and fusicogigantepoxide (Fig. 7h). The three compounds are isomeric epoxides, whose structure was elucidated by spectral analysis and chemical derivation (Asakawa et al. 1990).

### Fusicoccane Compounds from Ferns

#### *Cheilarinosin of Cheilanthes farinosa*

In 1972 Indian researchers isolated a new sesterterpenoid cheilarinosin (Fig. 8a) (Iyer et al. 1972) by extracting the plant material of *C. farinosa* with petroleum ether and subsequent purification by thin-layer chromatography. The structure of this substance was determined on the basis of its physicochemical characteristics and analysis of its derivatives, and proved to be similar to that of ophiobolins.

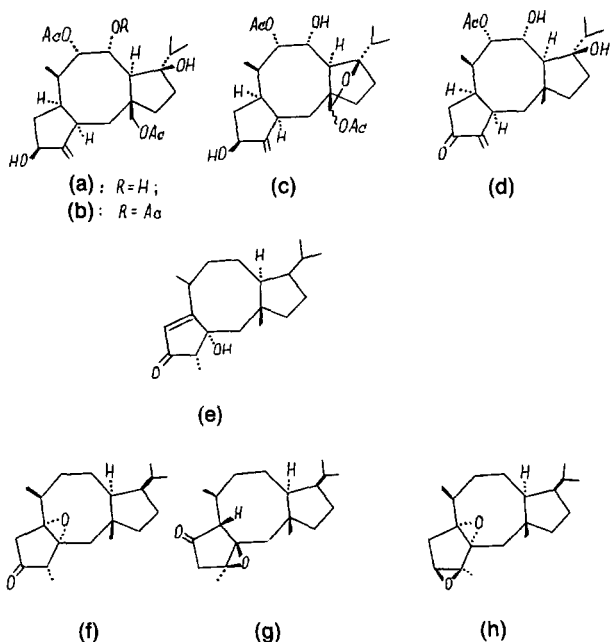


Fig. 7. Structures of fusicoplagins (a–d), anadensin (e), fusicogantones (f, g), and fusicogigantepoxide (h).

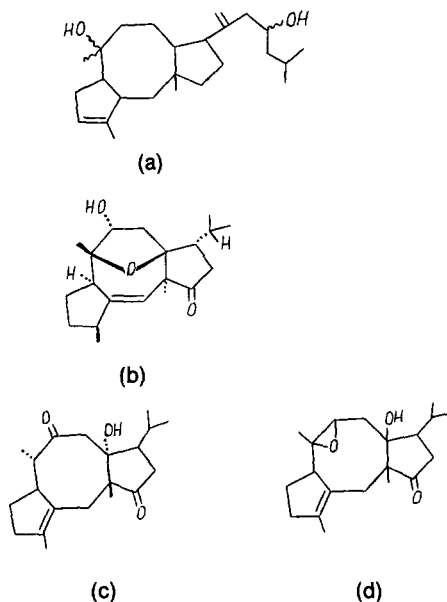


Fig. 8. Structures of cheilarinosin (a), roseanolone (b), roseadione (c), and roseatoxide (d).

### Fusicocane Compounds from Phanerogamous Plants

#### *Roseatoxide, Roseanolone, and Roseadione of an African Shrub Hypoestes rosea.*

The first report on the presence of a fusicocane-like compound in flowering plants was made by researchers from Nigeria and Germany in 1982 (Okogun et al. 1982).

Silica gel chromatography of a hexane extract from an African shrub *Hypoestes rosea* yielded several compounds, one of which was identified and called roseanolone (Fig. 8b). Its structure was determined by X-ray analysis and proved to be similar to the aglycon of fusicoccin; nevertheless, these two compounds have quite different stereochemistry, which in the authors' opinion testifies to their different biogenetic pathways.

Further work on this source led to isolation of roseadione (Fig. 8c) (Adesomoju et al. 1983) and roseatoxide (Fig. 8d) (Adesomoju and Okogun 1984). These three fusicocane diterpenoids of the higher plant *H. rosea* are isomers differing in the position of the OH group and the epoxide bridge. No data are available on their physiological activity.

#### *Fusicocins of Maize Zea mays L. and Headed Cabbage Brassica oleracea L.*

Fusicocin A was detected in 1986 by us in acetone extracts from maize roots and cobs and from cabbage leaves (Muromtsev et al. 1987). The extracts were resolved by HPLC, and fractions with the retention time corresponding to authentic FC were analyzed by gas chromatography/mass spectrometry. The identity of mass-fragmentograms and partial mass spectra of the reference FC A and of the fractions studied testified to the presence of FC A in maize and cabbage extracts. Fractions were also isolated that corresponded to FC C in the retention time on the HPLC column.

### Fusicocane Compounds from Insects

#### *Ceroplastanes of the Aphid*

##### *Ceroplastes albolineatus*

Ceroplastanes belong to the ophiobolane type of tricyclic dicyclopenta[*a,d*]cyclooctane skeletons of sesterterpenoids with a side chain of the steroid type. The 5→8→5 ring coupling in the tricyclic skeleton of ceroplastanes differs from that in ophiobolanes, the stereochemical orientation at C6/C2/C11/C10 being *trans-anti-trans*. However, the absolute configuration at C6, C10, and C11 is the same as in ophiobolins A, B, and C.

Ceroplastanes are represented by a number of derivatives isolated from the scale wax of the aphid *Ceroplastes albolineatus*, and are the first example of sesterterpenoids in insects.

Ceroplastol I (Fig. 9a) and ceroplastol II (Fig. 9e) were isolated from a fraction of aphid wax; both alcohols have the same mol. wt. (356) and molecular formula  $C_{25}H_{40}O$ , and differ in the position of

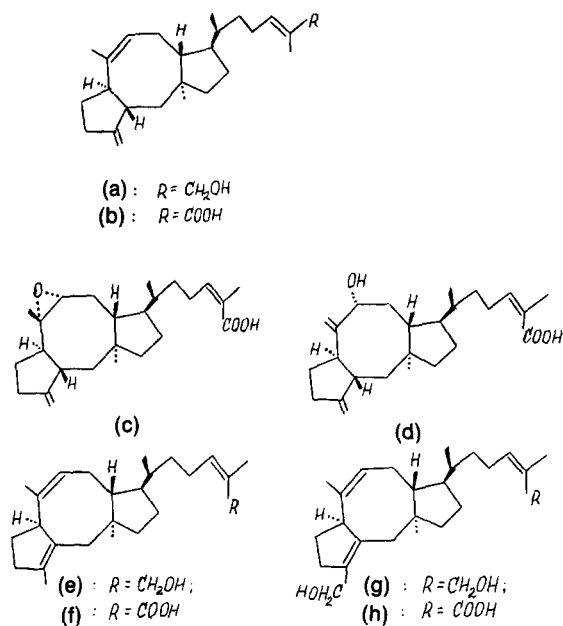


Fig. 9. Structures of ceroplastanes.

the double bond. Ceroplastol I was isolated as the 3,5-dinitrobenzoate, and after saponification obtained as the alcohol. The absolute configuration of ceroplastols was determined by X-ray crystallographic analysis of ceroplastol I (Rios and Colunga 1965).

The acidic fraction of scale wax yielded several acids of close structure but different degrees of oxidation. Ceroplastic acid (Fig. 9b) was isolated by counterflow distribution chromatography in aqueous methanol/hexane; it has an overall formula C<sub>25</sub>H<sub>38</sub>O<sub>2</sub>, optical rotation  $[\alpha]_D = +87^\circ$ , and its structure was confirmed by reduction to ceroplastol I (Iitaka et al. 1968).

Ceralbic acid I (Fig. 9c) and ceralbic acid II (Fig. 9d) have the same overall formula C<sub>25</sub>H<sub>38</sub>O<sub>3</sub>; one contains a closed epoxide ring and the other its open form. The structure of these acids was proved by their infrared, NMR and mass spectra (Calderon et al. 1978).

Another structurally similar pair from the scale wax are the already mentioned ceroplastol II (Fig. 9e) (melting temp. 116–118°C,  $[\alpha]_D = +80^\circ$  (Rios and Quijano 1969) and albolic acid (Fig. 9f) with  $[\alpha]_D = +139^\circ$  isolated from the acidic fraction (Rios and Gomez 1969).

Later oxidized compounds of the same structure were isolated from both the acidic and the neutral fractions of aphid wax (Quijano et al. 1979). These were ceroplastolic acid (Fig. 9h) of the overall formula C<sub>25</sub>H<sub>38</sub>O<sub>3</sub> whose structure was proved by infrared, UV, NMR, and mass spectroscopy and by

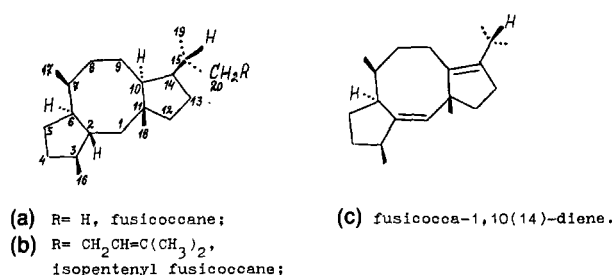


Fig. 10. Structures of fusicoccane (a), isopentenyl fusicoccane (b), and fusicocca-1,10(14)-diene (c).

conversion to albolic acid; and ceroplastodiol II (Fig. 9g) whose structure was proved in the same way. Ceroplastodiol II has an overall formula C<sub>25</sub>H<sub>40</sub>O<sub>2</sub>, mol. wt. 372, melting temp. 120°C, and  $[\alpha]_D = +143.7^\circ$  (Quijano et al. 1981).

### Propositions for the Nomenclature of Fusicoccane-Related Compounds

In conclusion, analysis of the literature has made it possible to describe a very specific group of terpenoids encountered in a wide variety of organisms. Many of these compounds display high physiological activity. It should be noted that structurally similar substances have been isolated from taxonomically very remote sources and have been assigned different names. Such substances are ophiobolins from a lower fungus *Drechslera oryzae* and cheilari-nosin from a fern *Cheilanthes farinosa*; the aglycons are similar to fusicoccin and cotylenin isolated respectively from the fungus *Fusicoccum amygdali* and *Cladosporium* sp. belonging to different families; fusicoccin compounds are found both in the fungus *F. amygdali* and in flowering plants.

We dare make some propositions for the nomenclature of fusicoccane-type compounds. A unified semisystematic chemical nomenclature may be expediently based on a hypothetical *trans-syn-trans* C<sub>20</sub> hydrocarbon which we propose to call *fusicocane* (Fig. 10a). The name, numeration, and stereochemistry of the substituents at C6, C7, C11, and C15 are taken by analogy with fusicoccin, the best studied representative of this group.

Accordingly, this class of terpenoids would be called *fusicoccane compounds*, being treated as structural derivatives of fusicoccane (Fig. 10a) regardless of their biological origin and properties; this is the term used in this review.

The proposed chemical names of various fusicoccane compounds are given in Table 2; unsaturation, substitution, and stereochemical details are denoted



**Table 2.** Fusicoccane Nomenclature

Trivial names	Proposed chemical names
Fusicoccin A (Fig. 3.1) (Ballio et al. 1968a, 1970, Barrow et al. 1968, 1971a, 1971b, 1973, 1975)	9 $\alpha$ -(3'-O-acetyl-6'-O-isopentenyl- $\alpha$ -D-glucopyranosyloxy)-8 $\beta$ ,12 $\alpha$ -dihydroxy-16-methoxy-20-acetoxymuscocca-1,10(14)-diene
Cotylenin E (Fig. 4, 5) (Sassa 1971, Sassa et al. 1975b)	9 $\alpha$ -(6'-O-methyl- $\alpha$ -D-glucopyranosyloxy)-8 $\beta$ , 3 $\alpha$ -dihydroxy-16-methoxymuscocca-1,10(14)-diene
Ophiobolin B (Fig. 5.2) (Canonica et al. 1966a,c, 1967, Nozoe 1966)	3 $\alpha$ ,14 $\alpha$ -dihydroxy-7-formyl-20-isopentenyl-6 $\beta$ -muscoc-7-en-5-one
Ophiobolin H (Fig. 5.8) (Cutler et al. 1984)	3,5-dihydroxy-5,17-oxy-20-isopentenylmuscocca-7,20-diene
Epoxydictymene (Fig. 6.1) (Enoki et al. 1983)	9 $\alpha$ ,15-oxy-2 $\alpha$ ,3 $\alpha$ ,14 $\alpha$ -muscoc-7(17)-ene
Fusicoplugin A (Fig. 7.1) (Hashimoto et al. 1985)	4 $\beta$ ,9 $\alpha$ ,14 $\beta$ -trihydroxy-8 $\alpha$ ,18-diacetoxy-2 $\alpha$ -muscoc-3(16)-ene
Anadensin (Fig. 7.5) (Huneck et al. 1983)	2 $\alpha$ -hydroxy-3 $\alpha$ -muscoc-5-en-4-one
Fusicogigantone B (Fig. 7.7) (Asakawa et al. 1990)	2 $\beta$ ,3 $\beta$ -oxy-6 $\beta$ ,16 $\alpha$ -muscocan-5-one
Roseanolone (Fig. 8.2) (Okogun et al. 1982)	8 $\alpha$ -hydroxy-7 $\beta$ ,10 $\beta$ -oxy-11 $\alpha$ ,14 $\alpha$ -muscoc-1-en-12-one
Roseadilone (Fig. 8.3) (Adesomoju et al. 1983)	10 $\alpha$ -hydroxy-7 $\alpha$ -muscoc-2-en-8,12-dione
Ceroplastol I (Fig. 9.1) (Rios and Colunga 1965)	20-(4'-hydroxy-3'-methylbut-2'-enyl)-10 $\beta$ ,11 $\alpha$ -muscocca-3(16),7-diene

in the usual way according to the IUPAC rules for organic compounds (Cahn and Dermer 1979).

In Table 2 we have tried to present the trivial and the proposed chemical names for the most typical and simple representatives, without attempting to cover all the diversity of fusicoccane-related compounds.

The proposed system does not exclude the existence of some subclasses having such half-systematic, half-trivial names as, for example, those in steroid chemistry.

The nomenclature of subclasses may be based on ancestral structures differing from fusicoccane (Fig. 10a) in the extent of unsaturation, characteristic substituents, or stereochemistry. For instance, ophiobolins and ceroplastanes can be united into one subclass based on the hydrocarbon isopentenyl fusicoccane (Fig. 10b) differing from (Fig. 10a) in the size of the substituent at C15; thereby the terpenoids of this type can be classed as C<sub>25</sub> terpenoids. On the other hand, cotylenins and fusicoccins can also be united into one subclass in view of the fact that the aglycons of numerous fusicoccin and cotylenin diterpenoids are based on the same hydrocarbon muscocca-1,10(14)-diene (Fig. 10c) (Ballio et al. 1982) and differ only in the glycosyl moieties.

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