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Review

# Correlation of oxidative transformations of hydrolyzable tannins and plant evolution

Takuo Okuda *, Takashi Yoshida, Tsutomu Hatano

*Faculty of Pharmaceutical Sciences, Okayama University, Tsushima, Okayama, 700-8530, Japan*

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In honour of Professor Otto R. Gottlieb's 80th birthday

**Abstract**

The progressive oxidative transformations in the biogenesis of hydrolyzable tannins, gallotannin (I) → ellagitannin (II) → dehydro ellagitannin (III) → transformed dehydroellagitannin (IV), conform in several aspects to the evolutionary routes in the subclasses of Dicotyledonae, particularly in the Rosidae. 

*Keywords:* Dicotyledonae; Subclass; Oxidation; Biosynthetic pathway; Evolution; Tannin; Hydrolyzable Tannin; Gallotannin; Ellagitannin; Dehydroellagitannin

**Contents**



## 1. Introduction

Correlation of ellagitannins with angiosperm taxonomy was proposed in the past based on the ellagic acid produced by hydrolysis of ellagitannins (Bate-Smith, 1973). After isolation and structural determination of various hydrolyzable tannins widely occurring in plants (Okuda et al., 1995), the proposal was reviewed along with the tannins of related structures, based on the structure and structure type of each hydrolyzable tannin (Haslam, 1989; Hegnauer, 1990; Okuda et al., 1993, 1995). A hypothesis for the biogenesis of hexahydroxydiphenoyl (HHDP) and chebuloyl groups from a galloyl structure has been proposed (Schmidt and Mayer, 1956). Biogenetic transformation of hydrolyzable tannins is considered to occur along the following route, starting from gallotannins: galloyl group in gallotannin (I) → HHDP group in ellagitannin (II) → dehydrohexahydroxydiphenoyl (DHHDP) group in dehydroellagitannin (III) → transformed DHHDP groups in transformed dehydroellagitannins (IV) (Fig. 1)

* Corresponding author. Fax: +81-86-223-2502.
*E-mail address:* cxq05047@nifty.ne.jp (T. Okuda).

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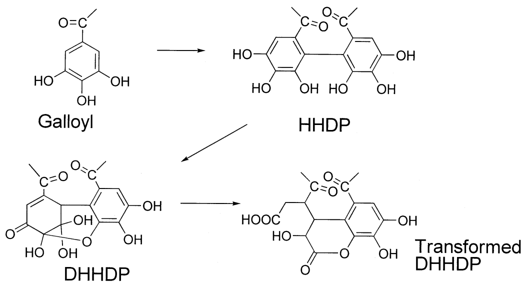



Fig. 1. Biogenetic transformations of polyphenolic functional groups, Galloyl → HHDP → DHHDP → transformed DHHDP.

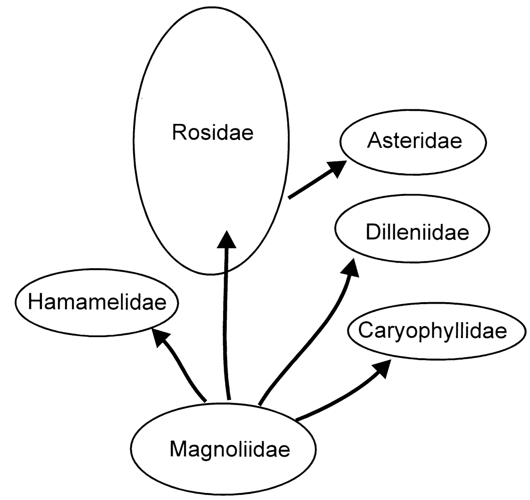



Fig. 2. Cronquist's evolution system of Dicotyledonae.

(Okuda et al., 1995). If, as suggested by Gottlieb "in plant groups of high hierarchic rank, morphological evolution is accompanied by progressive oxidation of secondary metabolites belonging to a particular biosynthetic class" (Gottlieb, 1989), this series of oxidative transformations of hydrolyzable tannins may be useful for correlating progressive oxidation with morphological evolution. As hydrolyzable tannins are generally potent antioxidants whose potency depends on their oxidation stage (Hatano et al., 1989b), their correlation with plant evolution may be more clear than with other types of plant metabolites. The evidence summarized in this review also strengthens the basis for the suggestion made by Gardner (1977), concerning the evolutionary rationale for the biosynthetic sequence of tannins.

Examples of the tannins of each type are as follows:

- Type I: Gallotannins (1,2,3,4,6-penta-*O*-galloyl-β-D-glucose) (Haddock et al., 1982a).
- Type II: Ellagitannins (pedunculagin) (Seikel and Hillis, 1970).
- Type III: Dehydroellagitannins (geraniin) (Okuda et al., 1982b).
- Type IV: Transformed dehydroellagitannins (chebulagic acid ) (Yoshida et al., 1982a).

## 2. Oxidative transformations in hydrolyzable tannins

The steps I → II → III → IV used here to describe the structural transformations of polyphenols, in contrast to the A, B and C classification used previously (Haddock et al., 1982b), can be used without applying a quantitative correlation (Gottlieb, 1989), because of their successive occurrence at a particular part of a hydrolyzable tannin molecule (Okuda et al., 1995). Using Cronquist's system of plant evolution (Cronquist, 1988), referred to in a previous review which classified the binding units between the monomers in the oligomers (Okuda et al., 1993), we have correlated the orders, families and genera in this system with the oxidative structural transformations of plant polyphenols. Among the four steps shown above, type I tannins include gallates of monosaccharides other than glucose, as well as glycitols; type IV tannins cover various structures formed from type III tannins.

Besides the structural transformations outlined above as I → II → III → IV, various additional transformations in hydrolyzable tannin monomers in plants, leading to other derivatives, have been found. These derivatives are classified as follows, with an example of each compound type:

- Type I+: *C*-Glycosidic gallotannins (Gcg) (3,4,11-tri-*O*-galloylbergenin (Saijo et al., 1990).
- Type II+: *C*-glucosidic ellagitannins (Ecg) [casuarinin (Okuda et al., 1983)], complex tannins (Ec) [camelliatannin A (Hatano et al., 1991)] and ellagitannin bound with a polyphenol through an ether linkage (Ee) [coriariin B (Hatano et al., 1986)], and the gluconic acid version of ellagitannin (ECOOH) [shephagenin A (Yoshida et al., 1996a)].
- Type III+: Dehydroellagitannin derivatives bound to a polyphenol through an ether bond (De) [mallotusinic acid (Okuda and Seno, 1978)].
- Type IV+: Transformed dehydroellagitannin bound to a polyphenol through a C–C bond (Tc) [camelliatannin F (Han et al., 1994)].

The oligomerization of monomers is analogous to the production of the monomer derivatives illustrated above, as regards the formation of the C–C or ether bond. Any oligomer composed of more than one type of monomer is represented here as the monomer of a higher transformation level. Most of the oligomers, from dimers to tetramers, are composed of monomers bound to each other through an ether linkage.

- Ed: Ellagitannin dimer [agrimoniin (Okuda et al., 1982a)].

- Et: Ellagitannin trimers [rugosin G (Hatano et al., 1990c)].
- Ete: Ellagitannin tetramers [trapanin B (Hatano et al., 1990b)].
- Ecgd: *C*-glucosidic ellagitannin dimer [alienanin B (Nonaka et al., 1991)].
- Dd: Dehydroellagitannin dimers [euphorbin A (Yoshida et al., 1988)].
- Emd: Macrocyclic ellagitannin dimers [oenothein B (Hatano et al., 1990d)].
- Emt: Macrocyclic ellagitannin trimers [oenothein A (Yoshida et al., 1991b)].
- Dmd: Macrocyclic dehydroellagitannin dimers [eugenoflorin $D_2$ (Lee et al., 1997)].

Since correlation of these oligomers and the monomeric derivatives with plant evolution is less clear than the transformations among the monomers (Figs. 5–9), they are represented in the figs. and most of the text as types I+, II+, III+ or IV+. The gallates of flavonoid glucosides and other glucosides such as glochiin $C_3$ (Chen et al., 1995) were excluded from the present comparison because of differences in the structural unit.

1. Gcg → I+
2. Ecg, Ee, Ec, Ecooh, Ed, Et, Ete, Ecgd, Emd, Emt → II+
3. De, Dd, Dmd → III+
4. Tc, Te → IV+

## 3. Correlation of oxidative transformation and plant evolution

The Magnoliopsida (Dicotyledonae) in the Magnoliophyta (Angiospermae) was classified by Cronquist

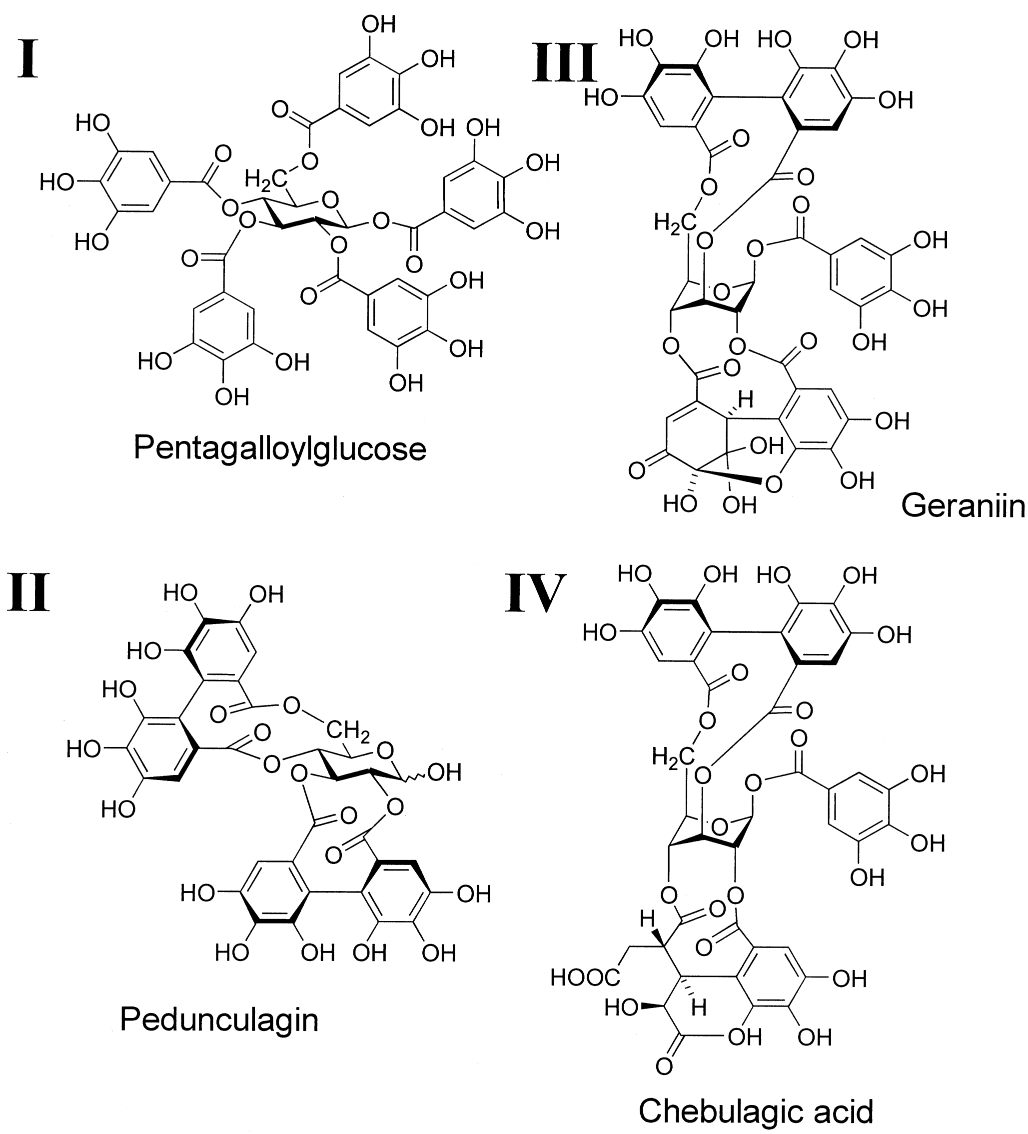
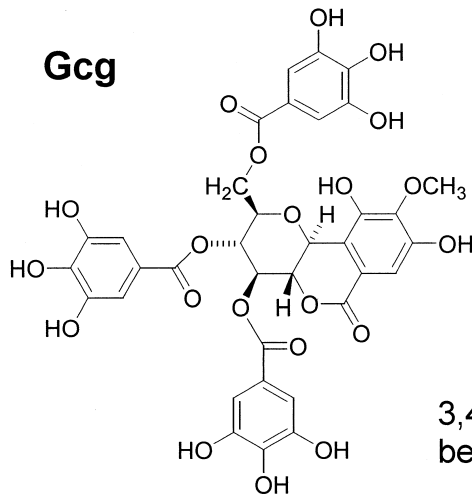



Fig. 3. Types and structural examples of monomer derivatives *(continued on next page)*.

**I+**

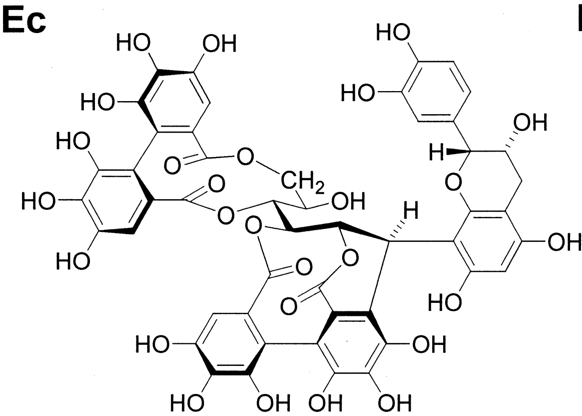
**Gcg**



3,4,11-Tri-O-galloyl-bergenin

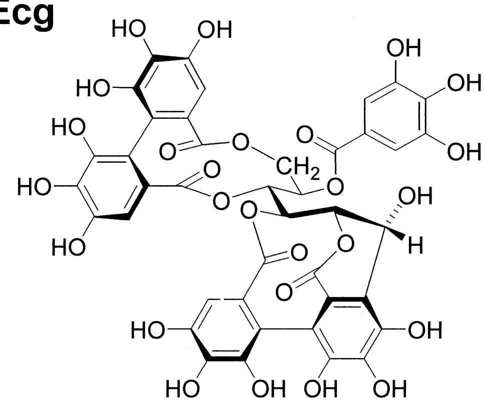
**II+**

**Ec**



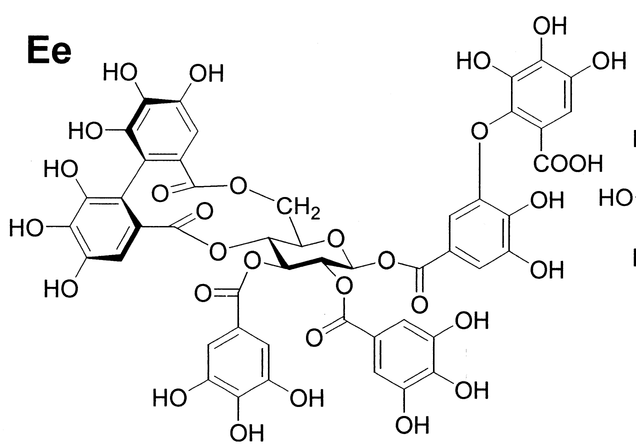
Camelliatannin A

**Ecg**



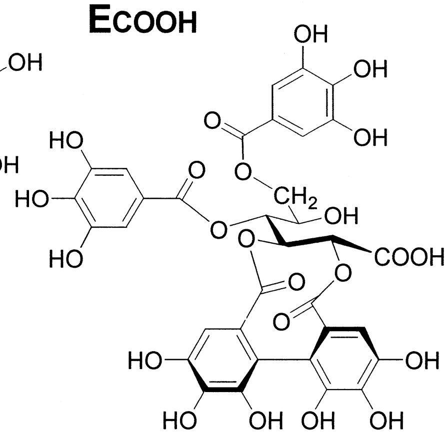
Casuarinin

**Ee**



Coriariin B

**Ecooh**

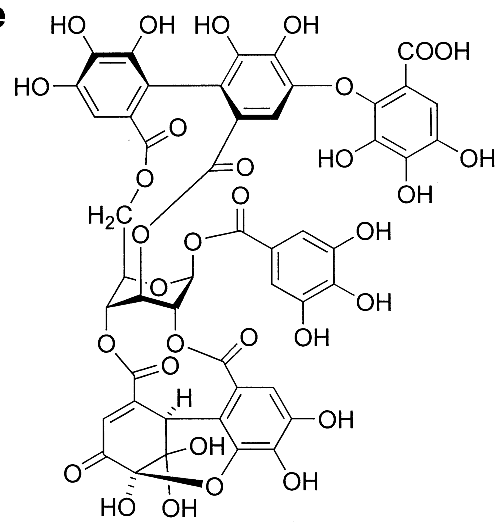


Shephagenin B

Fig. 3 (*continued*).

# III+

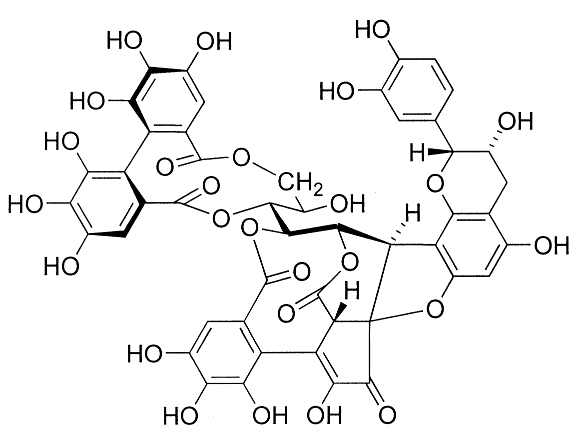
De



Mallotusinic acid

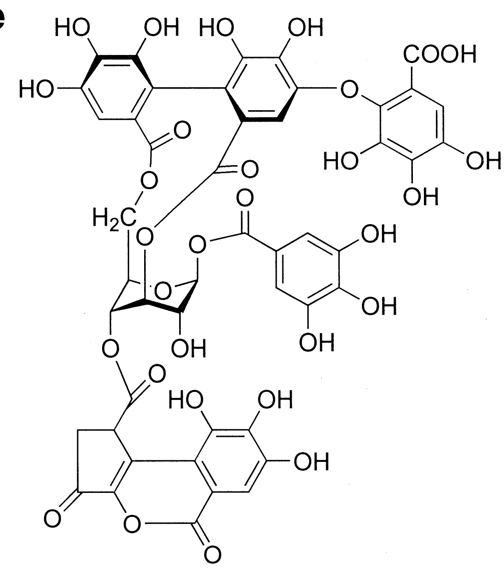
# IV+

Tc



Camelliatannin F

Te



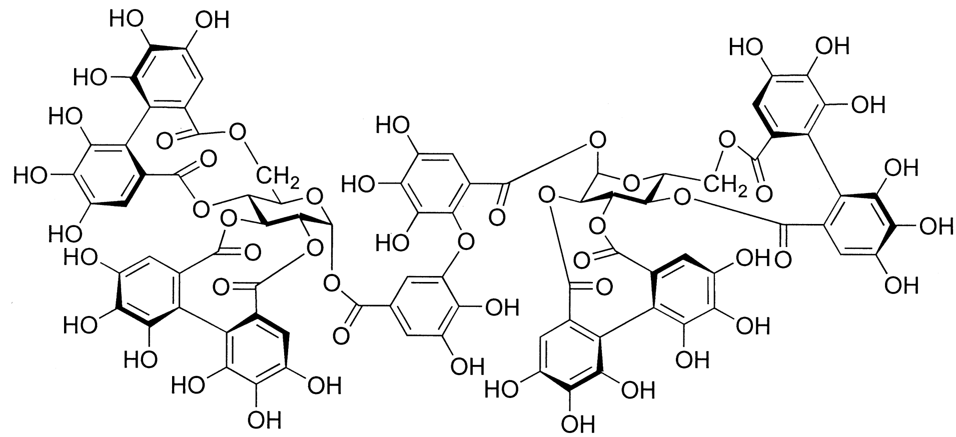
Repandusinin

Fig. 3 (*continued*).

(1988) into six subclasses: Asteridae, Rosidae, Dilleniidae, Caryophyllidae, Hamamelidae and Magnoliidae. The orders, families and genera in these subclasses producing hydrolyzable tannins, along with the tannin types, I, II, III, IV, I+, II+, III+ and IV+, are illustrated in Figs. 5–9. The following observations on each subclass shows the usefulness of outlining hydrolyzable tannins in this way.

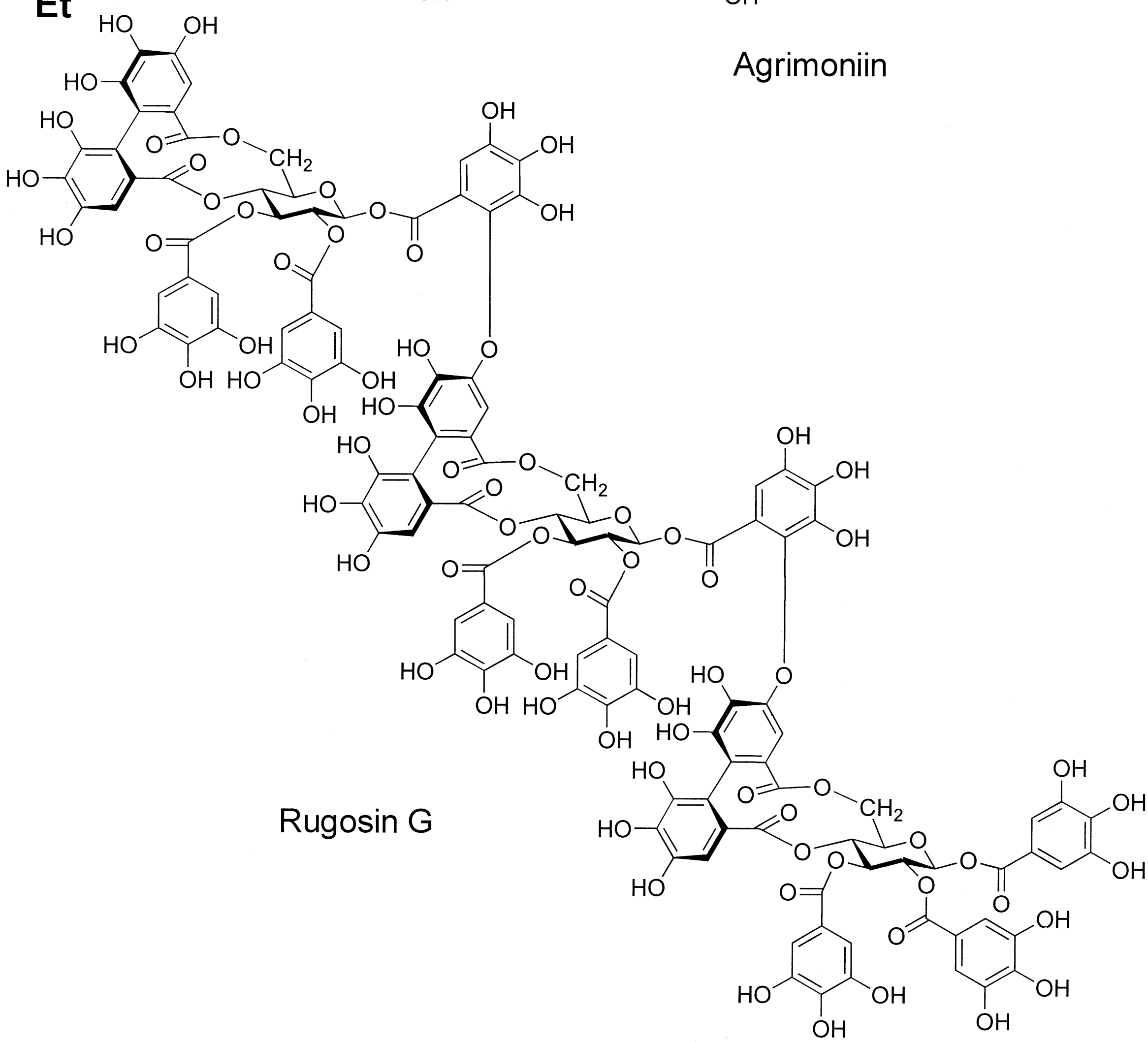
The highly oxidized tannins of types III and/or IV are found in many species of the Rosidae. Type III tannins not accompanied by type IV tannins are observed in some species of Dilleniidae and Hamamelidae. Tannins

**Ed**



Agrimoniin

**Et**



Rugosin G

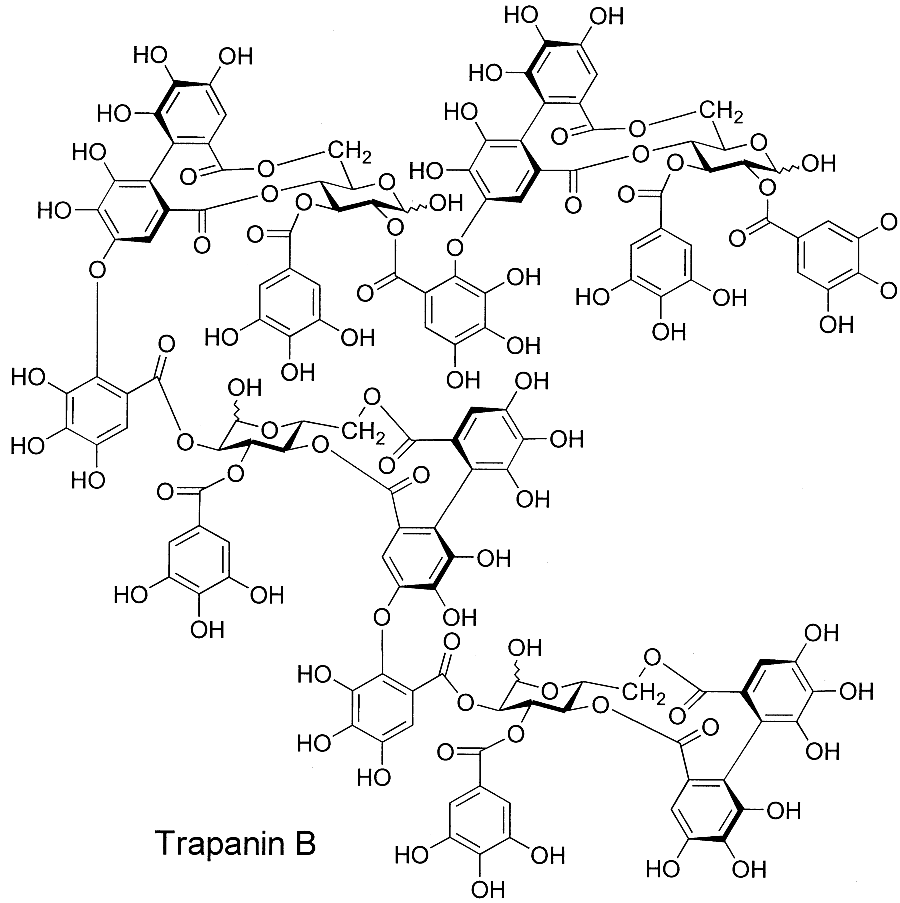
Fig. 4. Types and structural examples of the oligomers and their derivatives *(continued on next page)*.

of both type III and IV are not found in the Caryophyllales, and in the Magnoliidae, which is the earliest subgroup in the Magnoliopsida, and also in the Asteridae. The tannin types in each subclass are reviewed as follows.

### *3.1. Rosidae*

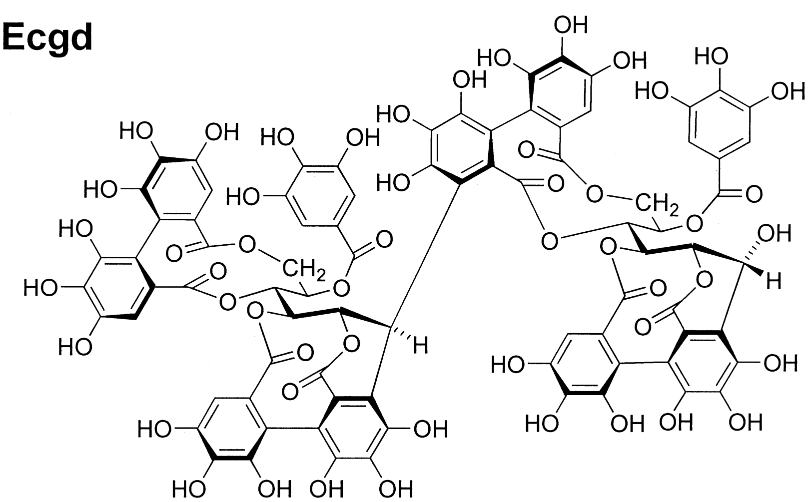
As shown in Fig. 5, the structural transformation (I, II) → II → III → IV, often accompanied by the production of derivatives and oligomers from each basic

**Ete**



Trapanin B

**Ecgd**



Alienanin B

Fig. 4 (*continued*).

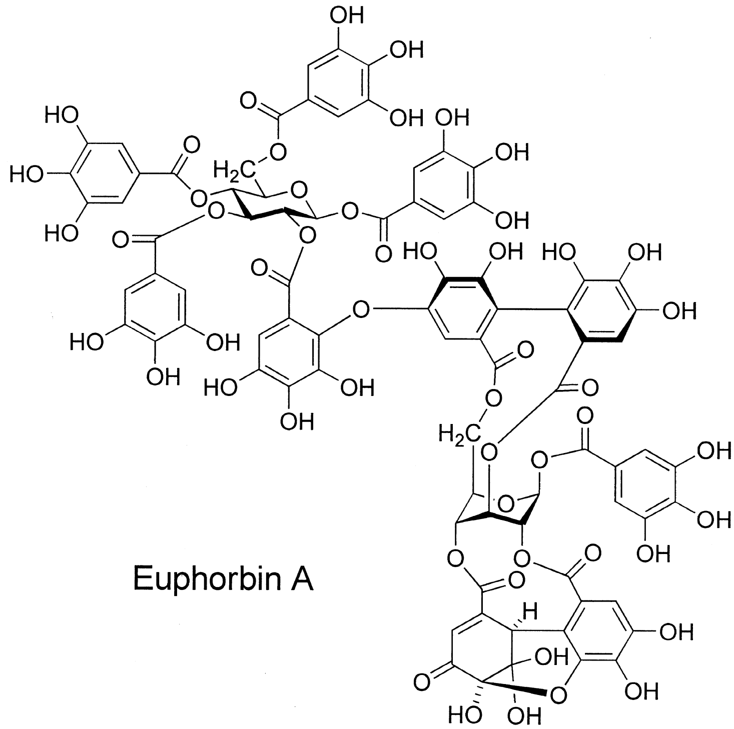
monomer, occurs along the plant evolution routes in the Rosidae as follows:

[Rosales]

Saxifragaceae: *Bergenia*, I (Chen et al., 1987); *Tellima*, II (Wilkins and Bohm, 1976).

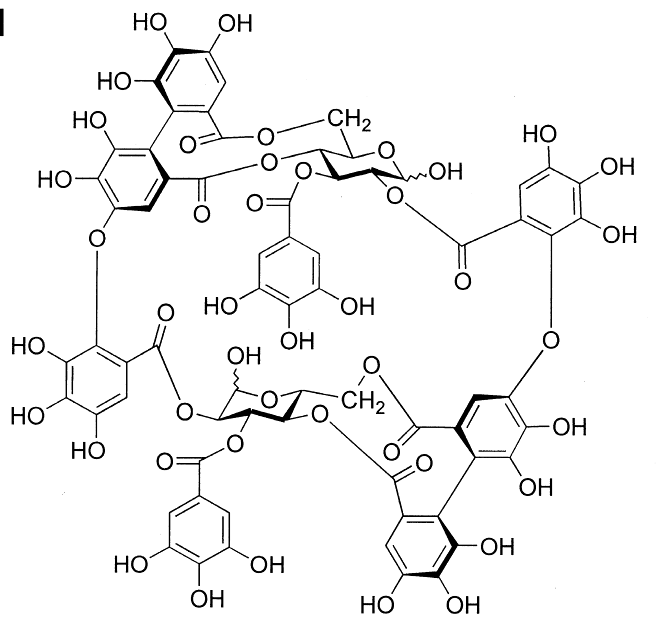
Rosaceae: *Agrimonia*, II, II+ (Ed) (Okuda et al., 1992); *Duchesnea*, II, II+ (Ed) (Okuda et al., 1992); *Filipendula*, II, II+ (Ed) (Okuda et al., 1992); *Fragaria*, II, II+ (Ed) (Okuda et al., 1992); *Geum*, II, II+ (Ed), III (Gupta et al., 1982; Okuda et al., 1992); *Rosa*, I, II, II+ (Ecg, Ee, Ed,

**Dd**



Euphorbin A

**Emd**



Oenothein B

Fig. 4 (*continued*).

Et) (Hatano et al., 1990c; Okuda et al., 1992); *Rubus*, I, II, II+ (Ecg, Ed, Ete) (Gupta, et al., 1982; Okuda et al., 1992); *Potentilla*, II, II+ (Ed) (Okuda et al., 1992); *Sanguisorba*, II, II+ (Ee, Ed, Ete) (Okuda et al., 1992); *Sieversia*, II, II+ (Ecg) (Okuda et al., 1992).

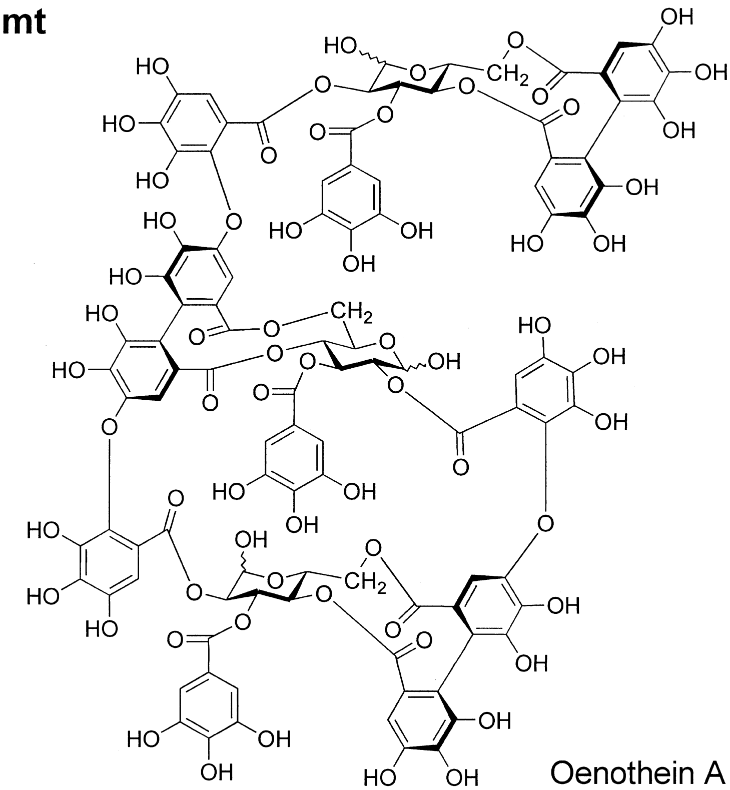
Leguminosae: *Caesalpinia*, I, III, III+ (Jochims et al., 1968); *Haematoxylon*, I (Kandil et al., 1996).

[Sapindales]

Aceraceae: *Acer*, I, II, III (Hatano et al., 1990a).

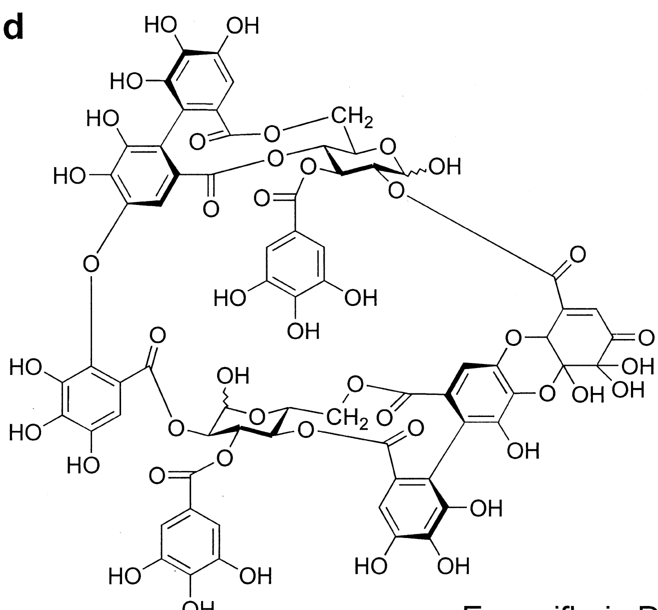
Anacardiaceae: *Cotinus*, I (Haddock et al.,

**Emt**



Oenothein A

**Dmd**



Eugeniflorin $D_2$

Fig. 4 (*continued*).

1982a); *Mangifera*, I (Tanaka et al., 1984); *Rhus*: I, II (Haddock et al., 1982b).

[Geraniales]
Geraniaceae: *Geranium*, I, III, IV (Okuda et al., 1982b; 1986a).

[Rafflesiales]
Rafflesiaceae: *Cytinus*, III (Schildknecht et al., 1985).

[Cornales]
Cornaceae: *Cornus*, I, II, II+ (Ee, Ed, Et), III (Hatano et al., 1989a).

Nyssaceae: *Camptotheca*, II, II+ (Ed) (Hatano et al., 1988)

[Rhamnales]
Vitaceae: *Vitis*, II, III (Karl et al., 1983).

[Euphorbiales]
Euphorbiaceae: *Alchornea*: III, III+ (De) (Okuda et al., 1980); *Aleurites*: I+ (Gcg), III, III+ (De), IV (Nonaka et al., 1990); *Antidesma*: III, III+ (Dt) (Yoshida et al., 1992b); *Euhorbia*: I, II, II+ (Ee, Ed), III, III+ (Dd), IV (Yoshida et al., 1988; 1990a); *Excoecaria*: I, II, II+ (Ed), III, III+ (Dd) (Lin et al., 1990); *Macaranga*: I,II, III, IV (Lee et al., 1990); *Mallotus*: I, I+ (Gcg), II+ (Ed), III, III+ (De), IV (Okuda and Seno, 1978; Saijo et al., 1989); *Phyllanthus*: III, IV (Yoshida et al., 1992a; Foo, 1995)

[Myrtales]
Combretaceae: *Anogeissus*, I, II+ (Ecg, Ecgd ) (Lin et al., 1991) ; *Terminalia,* I, II, II+ (Ec, Ed, Et), III, IV (Tanaka et al., 1991); *Quiscalis*, II, II+ (Ed) (Haddock et al., 1982b).
Lythraceae: *Cuphea*, I, II, II+ (Emd) (Chen et al., 1999); *Lagerstroemia*, II, II+ (Ee, Ed, Et, $E_{COOH}$) (Tanaka et al., 1992b), III, IV (Xu et al., 1991); *Woodfordia*, I, II, II+ (Ee, Ed, Emd, Emt) (Yoshida et al., 1990b).
Melastomataceae: *Bredia*, II, II+ (Ecg, Ed, Et) (Yoshida et al., 1994); *Heterocentron*, II, II+ (Ecg, Ed, Et, Ete, Ecgd) (Yoshida et al., 1995); *Medinilla*, II, II+ (Ee, Ed) (Yoshida et al., 1986); *Melastoma*, I, II, II+ (Ed, Et, Ecgd) (Yoshida et al., 1992c); *Tibouchina*, I, II, II+ (Ecg, Ee, Ed, Et) (Yoshida et al., 1991c)
Myrtaceae: *Eucalyptus*, II, II+ (Ecg, Ed, Emd) (Yoshida et al., 1992d); *Eugenia*, II+(Emd), III+(Dmd) (Lee et al., 1997); *Feijoa*, II, II+ (Ecg) (Okuda et al., 1982c); *Melaleuca*, I, II, II+ (Ecg, Emd) (Yoshida et al., 1996b), *Psidium*, II, II+(Ecg) (Okuda et al., 1982c; Tanaka et al., 1992a); *Syzygium*, II, II+ (Ecg) (Okuda et al., 1982c).
Punicaceae: *Punica*, I, II, II+(Ecg), III (Okuda et al., 1981).
Onagraceae: *Epilobium*, I, II+(Emd, Emt) (Ducrey et al., 1997); *Oenothera*, I, II, II+(Emd, Emt) (Hatano et al., 1990d; Yoshida et al., 1991b).
Trapaceae: *Trapa*, II, II+(Ee, Ecg, Ed, Et, Ete) (Hatano et al., 1990b)

While tannins of types I and/or II are the main tannins in the Rosales, which is the earliest order in the Rosidae, type III and IV tannins and their derivatives are often found in the orders evolved from the Rosidae. Among the plants in these orders, *Geranium* species in Geraniaceae in Geraniales are rich in geraniin, a type III tannin (Okuda et al., 1980), accompanied by type IV tannins (Ito et al., 1999); these species lack oligomers. In the Sapindales, which is between Rosales and Geraniales, monomers of types I and II (Anacardiaceae), or I and III (Aceraceae), which are not accompanied by oligomers, are the main tannins.

Type III tannins, accompanied by various oligomers often having geraniin as a monomer (or are even fully composed of geraniin), are also the main components in many euphorbiaceous plants separately evolved from Rosales. The vitaceous plants in Rhamnales, which evolved via a route branching off that leading from Rosales to Euphorbiales, are rich in type II and III tannins.

The plants of Combretaceae, Lythraceae, Melastomataceae, Myrtaceae, Punicaceae, Onagraceae and Trapaceae in the Myrtales produce type II tannins, sometimes accompanied by tannins of type I, III and/or IV. Elaeagnaceous plants in Proteales, which evolved from the Myrtales, give tannins of types I and II, and also Ecg and/or $E_{COOH}$ tannins.

Oligomerization from monomer $\rightarrow$ dimer $\rightarrow$ trimer $\rightarrow$ tetramer, particularly up to the dimer or trimer, frequently occurs in many species in the Myrtales. Dimers and trimers are abundant in Cornales, and dimers are common in the Euphorbiales and Rosales.

### 3.2. Dilleniidae

Type I tannins are in the Paeoniaceous plants in Dilleniales, the earliest order in Dilleniidae, and type II and II+ tannins (along with type I tannins) are in the Theales, which evolved from Dilleniales (which yields type I tannins). Exceptionally, a *Camellia* species in the Theales also produces type IV tannins (Han et al., 1994). Type II and II+ tannins are in the Violales and Lecythidales, and a type III tannin was found in Malvales, all of which evolved via the Theales. The tannins found in Ericales are of types I and II. The types of tannins in this subclass are as follows:

[Dilleniales]
Paeoniaceae: *Paeonia*, I (Yoshikawa et al., 1992).

[Theales]
Theaceae: *Camellia*, I, II, II+ (Ecg, Ed, Emd ) (Hatano et al., 1991); IV (Han et al., 1994); *Gordonia*, I, II+ (Ed, Emd) (Chang et al., 1994); *Schima*, I, II, II+ (Ee, Ed, Emd) (Yoshida et al., 1991d); *Thea*, I (Nonaka et al., 1984b).
Stachyuraceae: *Stachyurus*, I, II, II+ (Ee, Ecg) (Okuda et al., 1982c; Han et al., 1995).

[Ericales]
Ericaceae: *Arctostaphylos*, I, II (Britton and Haslam, 1965)
Pyrolaceae: *Pyrola*, I (Yazaki et al., 1989).

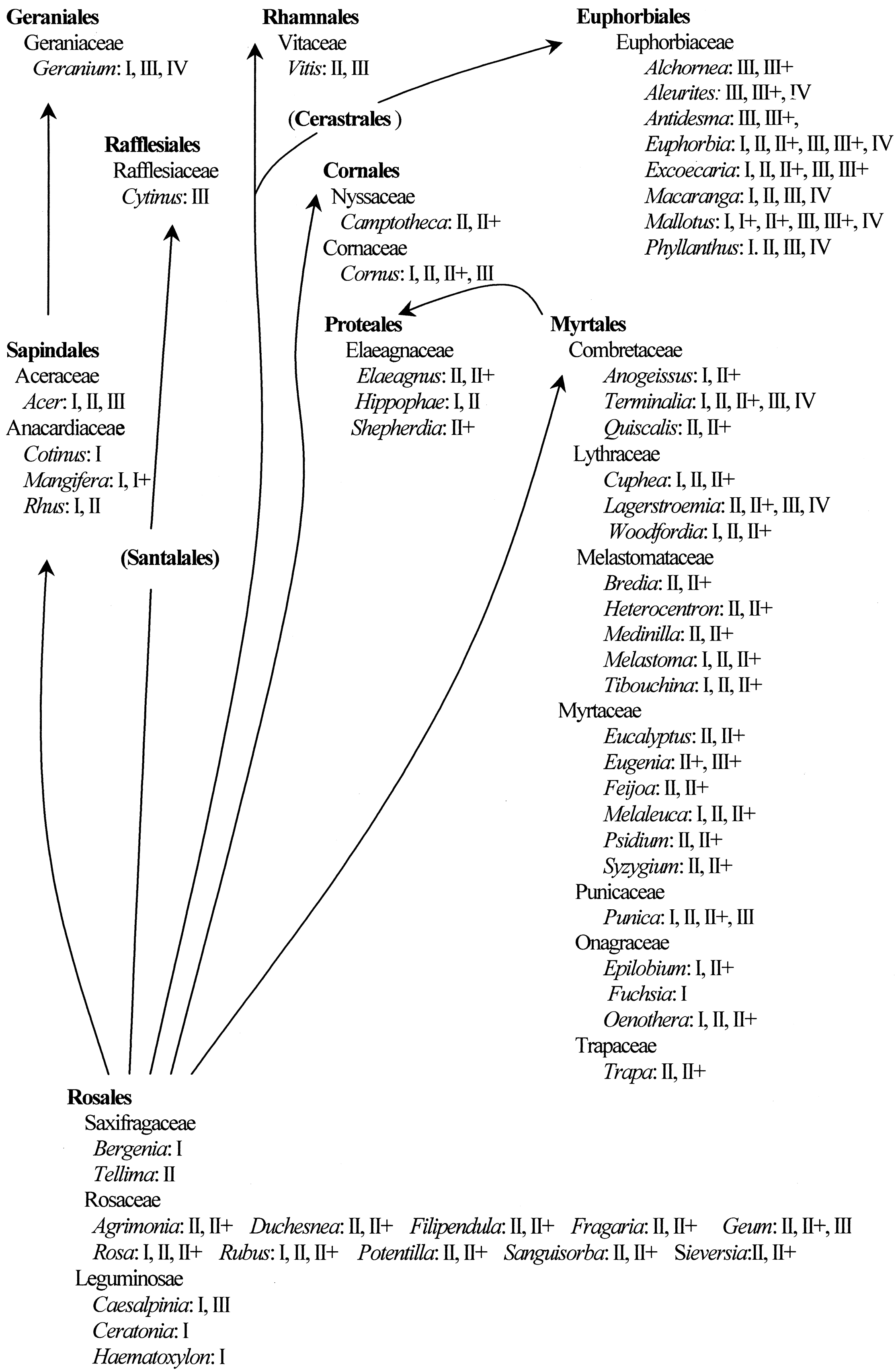



Fig. 5. Types of hydrolyzable tannins in the Rosidae.

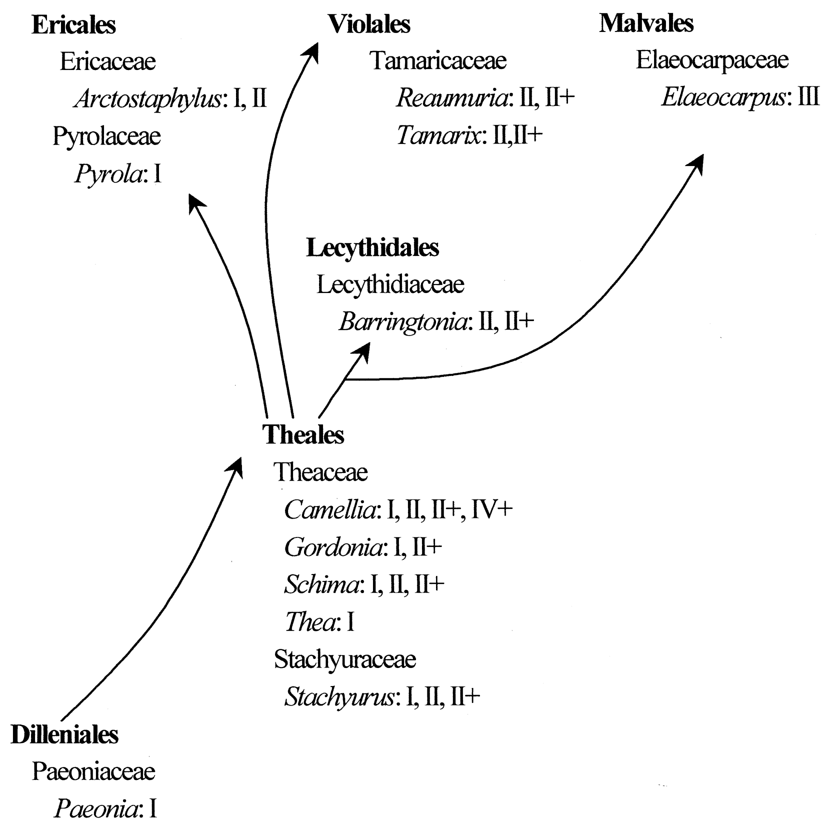



Fig. 6. Types of hydrolyzable tannins in the Dilleniidae.

[Violales]
Tamaricaceae: *Reaumuria*, II, II+ (Ee) (Ahmed et al., 1994); *Tamarix*, II, II+ (Ee) (Yoshida et al., 1993a).

[Lecythidales]
Lecythidiaceae: *Barringtoni*a, II, II+ (Ee) (Kobayashi et al., 1992).

[Malvales]
Elaeocarpaceae: *Elaeocarpus*, III (Tanaka et al., 1986).

### 3.3. Hamamelidae

Hamamelidaceous plants in the Hamamelidales, which is the earliest order in the Hamamelidae, produce type I and II tannins, and a *Cercidiphyllum* species in Cercidiphyllaceae yields tannins of types I, II and III. The plants of Juglandales give type II or II+ tannins, and plants of Casuarinales and Fagales hitherto analyzed produce tannins of types I, II and II+. A *Carpinus* species and a *Corylus* species (Betulaceae) in this order additionally yield type III and IV tannins, respectively (Nonaka et al., 1992). The correlation of the level of oxidation with plant evolution, based on available data concerning the structural transformation I → II → III → IV, is not clear in this subclass. However, the production of Ecg-type tannins by the plants of Fagales, Casualinales and Hamamelidales in this subclass, along with the production of the Ecg type tannins in Theales (Dilleniidae), is of note. The similarity of hydrolyzable tannin structures in the Casuarinaceae with those in the Stachyuraceae (Dilleniidae) and the Myrtaceae (Rosidae) (Okuda et al., 1982c) shows structural transformations occurring parallel to the evolution routes in each subclass.

[Hamamelidales]
Cercidiphyllaceae: *Cercidiphyllum*, I, II, III (Haddock et al., 1982b; Nonaka et al., 1989).
Hamamelidaceae: *Hamamelis*, I (Mayer et al., 1965) ; *Liquidambar*, I, II, II+ (Ee, Ecg, Ed) (Yoshida et al., 1991e); *Loropetalum*, II, II+ (Ee, Ed, Et, Emd, Emt) (Yoshida et al., 1993b).

[Fagales]
Fagaceae: *Castanea*, I, II, II+ (Ee, Ecg) (Nonaka et al., 1984a); *Castanopsis*, I, II, II+ (Ecg) (Ageta et al., 1988); *Quercus*, I, II, II+ (Ecg, Ecgd) (Nonaka et al., 1991).
Betulaceae: *Alnus*, I, II, II+ (Ee, Ecg, Ed) (Yoshida et al., 1982b); *Carpinus*, I, II, II+ (Ee, Ec, Ecg), III (Akazawa et al., 1989); *Corylus*, I, II, II+ (Ecg, Ed) (Yoshida et al., 1991a), IV+ (Nonaka et al., 1992).

[Casuarinales]
Casuarinaceae: *Casuarina*, I, II, II+ (Ecg) (Okuda et al., 1982c, 1983).

[Juglandales]
Juglandaceae: *Juglans*, II (Jurd, 1958)
Rhoipteleaceae: *Rhoiptelea*, II+ (Ec) (Tanaka et al., 1997).

**Juglandales**
Juglandaceae
*Juglans*: II
Rhoipteleaceae
*Rhoiptelea*: II, II+

**Casuarinales**
Casuarinaceae
*Casuarina*: I, II, II+

**Fagales**
Fagaceae
*Castanea*: I, II, II+
*Castanopsis*: I, II, II+
*Quercus*: I, II, II+
Betulaceae
*Alnus*: I, II, II+
*Carpinus*: I, II, II+, III
*Corylus*: I, II, II+, IV

**Hamamelidales**
Cercidiphyllaceae
*Cercidiphyllum*: I, II, III
Hamamelidaceae:
*Hamamelis*: I
*Liquidambar*: I, II, II+
*Loropetalum*: II, II+

Fig. 7. Types of hydrolyzable tannins in the Hamamelidae.

**Nymphaeales**
Nymphaeaceae:
*Nuphar*: I, II, II+

**Ranunculales**
Coriariaceae:
*Coriaria*: I, II, II+

(**Magnoliales**)

Fig. 8. Types of hydrolyzable tannins in the Magnoliidae.

**Polygonales**
Polygonaceae:
*Rheum*: I

(**Caryophyllales**)

Fig. 9. Types of hydrolyzable tannins in the Caryophyllidae.

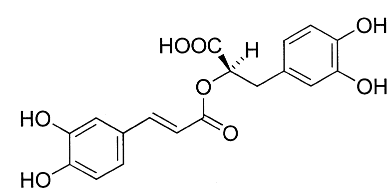
### *3.4. Caryophyllidae and Magnoliidae*

Type I, II and II+ tannins have been found in plants of Nymphaeales (Ishimatsu et al., 1989) and Ranunculales (Okuda et al., 1981) in the Magnoliidae, and small amounts of type I tannins have been found in plants of Polygonaceae (Nonaka et al., 1981; Friedrich and Hohle, 1966) (Polygonales) in the Caryophyllidae. However, because of the lack of data on the Magnoliales and Caryophyllales, which are the earliest orders in each of these subclasses, their correlation is impossible.

### *3.5. Asteridae*

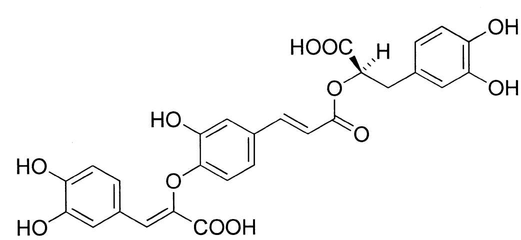
Caffeate oligomers (abbreviated as follows, with an example of each type) have been found in plants of Lamiales in Asteridae, which lack both hydrolyzable tannins and condensed tannins. The wide distribution of chlorogenic acid in Rosaceae, detected in practically all

**Cd**



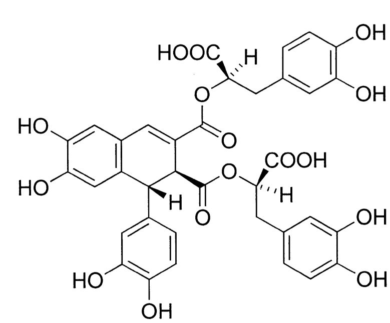
Rosmarinic acid

**Ct**



Melitric acid A

**Cte**



Rabdosiin

Fig. 10. Caffeate condensates in the Asteridae.

80 species of rosaceous plants examined (Okuda et al., 1992), may be associated with the evolutionary route from Rosidae to Asteridae, although the distribution of various caffeic acid derivatives in other plant groups (Mølgaard and Ravn, 1988) must be considered (Fig. 10).

- Cd: caffeate dimers [rosmarinic acid in Labiatae (Okuda et al., 1986b)].
- Ct: caffeate trimers [melitric acid A in Labiatae (Agata et al., 1993) and Boraginaceae (Kelley et al., 1976)].
- Cte: caffeate tetramers [rabdosiin in Labiatae (Agata et al., 1989), and in Boraginaceae (Nishizawa et al., 1990)].

The families in Asteridae which give caffeate condensates are as follows:

[Lamiales]
Labiatae: Agastache: Cd; Glechoma: Cd; Isodon: Cd, Cte; Melissa: Cd,Ct; Mentha: Cd; Ocinum: Cd; Origanum: Cd; Perilla: Cd; Prunella: Cd; Rosmarinus: Cd Salvia: Cd, Cte; Thymus: Cd.
Boraginaceae: Cd, Ct.
*Lithosperumum*: Cd, Ct; *Macrotomia*: Cte

## 4. Conclusions

The successive oxidative and subsequent transformations of the polyphenol type in hydrolyzable tannin molecules, I → II → III → IV, can be correlated in several aspects with the evolution of "plant groups of high hierarchic rank" in Cronquist's evolution system, and are in accord with "progressive oxidation of secondary metabolites belonging to a particular biosynthetic class (Gottlieb, 1989)" as follows.

1. Oxidized tannins, types III and IV, are frequently found in the Rosidae, but are found only in a small number of plants in the Dilleniidae and Hamamelidae. These oxidized tannins are not found in the Caryophyllales and Magnolidae (the earliest subclass in the Dicotyledonae).
2. Rosales, which is the earliest order in Rosidae, mostly produce type I and II tannins. Oxidative transformations to types III and IV progress according to Rosales → Sapindales → Geraniales without being accompanied by production of oligomers; these types, often accompanied by the II and III+ type tannins, occur in plants of Rhamnales, Euphorbiales, Cornales, Myrtales and Proteales.
3. The oxidative transformations in the Dilleniidae seem to progress from Dilleniales (I) to Theales (I, II and IV+), although tannins in the plants of Lecythidales, Violales, Malvales and Ericales do not allow further oxidative progress.
4. In Hamamelidae, the oxidative progression I → II → III → IV is not clear, although Ecg type tannins in many genera in Fagales is characteristic of this subclass, also being present in plants of Theales (Dilleniidae).
5. The correlation in Magnolidae and Caryophyllales is unknown because of lack of tannin data in the earliest orders of these subclasses.
6. The correlation of oligomerization with plant evolution is also unclear. In Rosidae, type II+ oligomers produced by Rosales are not produced along the route → Sapindales → Geraniales, but they are abundantly produced by plants of Euphorbiales, Cornales and Myrtales. In Dilleniidae, oligomers are not found in Dilleniales, the earliest order, but are produced by plants of Theales, Lecythidales and Violales, evolved from the Dilleniales. On the other hand, the oligomers are produced by the earliest order, Hamamelidales (Hammamelidae).
7. Caffeate oligomers are produced by plants of Lamiales and Rubiales in the Asteridae, which does not yield hydrolyzable tannins.

The evidence thus summarized here may provide a perspective for the correlation of progressive oxidation of hydrolyzable tannins with plant taxonomy and evolutionary hierarchy.

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