CHAPTER II

HISTORICAL

1. Introduction of Flavonoid Compounds

The flavonoids are plant pigments based on the $C_6-C_3-C_6$ carbon skeleton. The major flavonoids of plants are anthocyanins, flavones and flavonols, three very numerous and widely distributed classes in plants. Accompanying these flavonoids in certain plant groups are related derivatives :- chalcones, aurones, flavanones, isoflavones, biflavonyls and leucoanthocyanidins, all of these are restricted distribution, and often found in plant as glycosides. Chemically, most flavonoids are closely related to each other (Harborne, 1967).

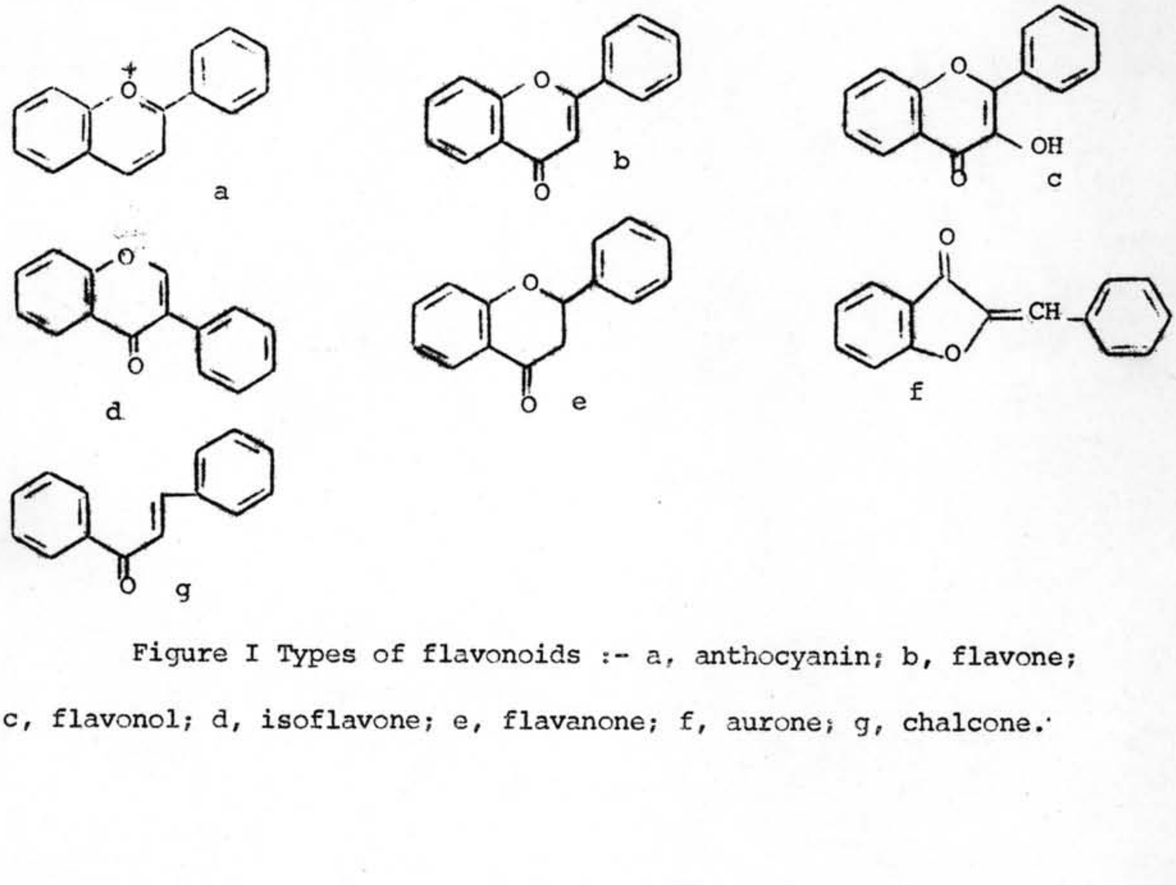
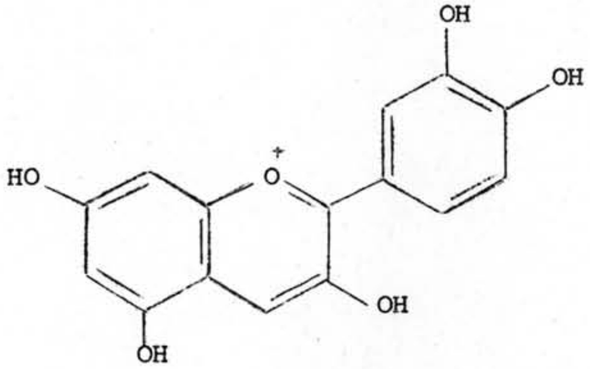


Figure I Types of flavonoids :- a, anthocyanin; b, flavone; c, flavonol; d, isoflavone; e, flavanone; f, aurone; g, chalcone.

Anthocyanins

The anthocyanins are all based chemically on a single aromatic structure-that of the 3,5,7,3',4'-pentahydroxyflavylium cation.



Naturally occurring anthocyanins are differ in substitute groups at ring B. Glycosylation, sugar attaches on C (3) position (Harborne, 1967).

Flavones and Flavonols

Of the various classes of naturally occurring compounds based on the flavonoid skeleton, flavones and flavonols are collectively the most abundant group. The structure of these two compounds being shown in Ib and Ic. Flavonols are simply a class of flavone in which the 3-position is substituted by a hydroxyl group and are known as aglycones and glycosides. Flavones occur in plants as C-glycosyl derivatives and as dimers, the biflavonyls. Flavones and flavonols contribute either as yellow pigments in their own right or else as co-pigments to anthocyanins (Harborne, 1967).

Isoflavones

Isoflavone structure is shown in Id. It is isomeric with the flavone and differ only in the position of the attachment of the aryl B-ring to the central pyran nucleus. Common isoflavones have the usual $5,7,4'$, or $5,7,3',4'$-hydroxylation patterns but there are many rarer isoflavones which have no known counterpart in the flavones series. Isoflavones are found characteristically in family Papilionaceae (Harborne, 1967).

Flavanones

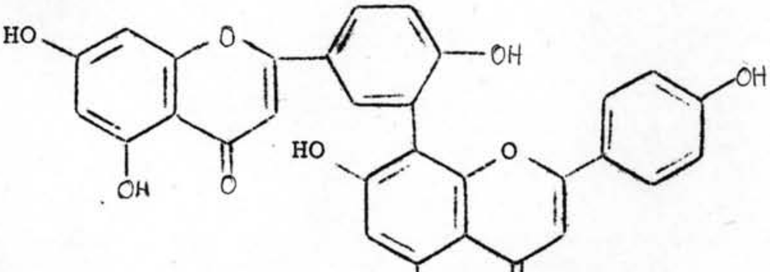
Flavanones are colourless compounds, occur mostly in Rutaceae as in the peel and juice of *Citrus* fruit and make it taste bitter (Harborne, 1967). Flavanone structure is shown in Ie. If there is a hydroxyl group attaches on C(3) position, it is flavonol-related flavanones and is called dihydroflavonol. Flavanones and dihydroflavonols are interesting compounds, since they are obligate intermediates in flavanoid biosynthesis. Flavanones can be dehydrogenated to yield flavones or can undergo hydroxylation at 3-position to yield dihydroflavonols. Dihydroflavonol, in turn, can yield several other flavanoid types: dehydrogenation yields flavonols, reduction of the carbonyl function affords flavans 3,4-diols and enolisation and oxidation yields anthocyanidins (Bohm, 1975).

Aurones

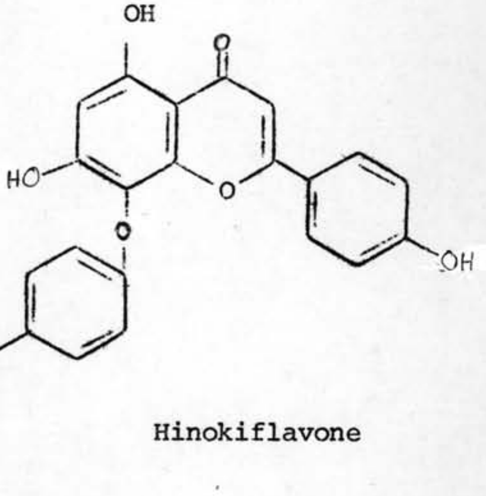
The aurones are essentially golden yellow flewer pigments. The distribution is also limited in Compositae, Leguminosae and Scrophulariaceae. Aurone structure is shown in If. (Harborne, 1967)

Biflavonyls

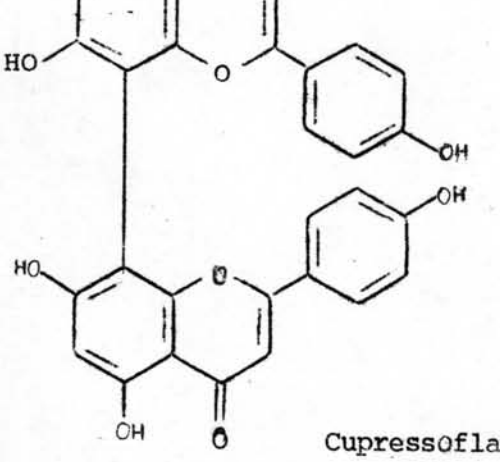
Biflavonyl structure consists of two molecules of flavones link together with carbon-carbon bond between the C (8) and C (3), amentoflavone, or C (8) and C (8), cupressoflavone, or carbon-oxygen bond between C (3) and C (4), hinokiflavone. Biflavonyls occur mostly in Gymnosperm (Harborne, 1967).



Amentoflavone



Hinokiflavone



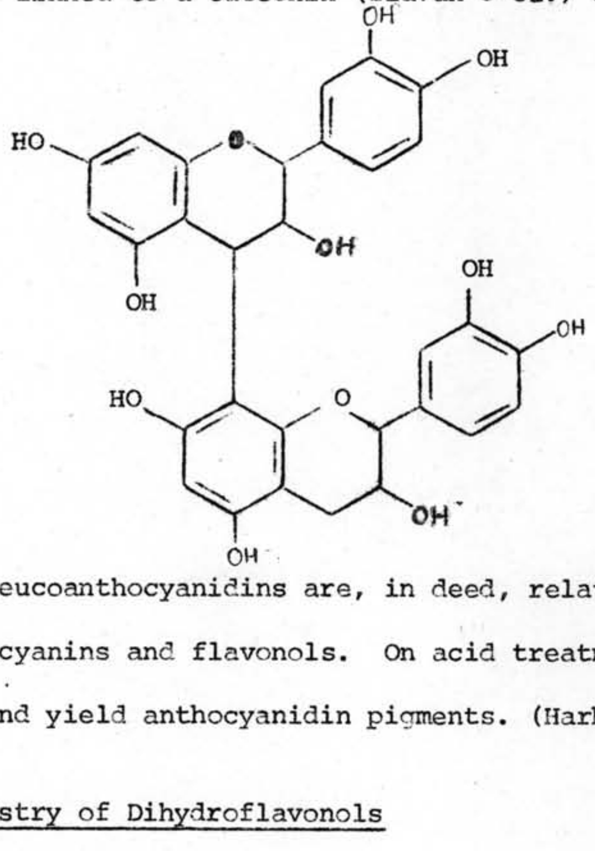
Cupressoflavone

Chalcones

Chalcones are often found as intermediate product in flavonoid biosynthetic pathway. Its structure is shown in Ig. Chalcone pigments have a very limited distribution in nature, occurring mainly as petal pigment in Compositae (Harborne, 1967).

Leucoanthocyanidins

Leucoanthocyanidins are dimers derived from one unit of flavan 3,4-diols linked to a catechin (flavan 3-ol.) as shown below :-

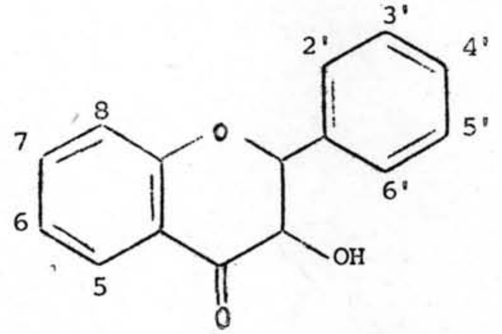


Leucoanthocyanidins are, in deed, related biosynthetically to the anthocyanins and flavonols. On acid treatment, they can condense to tannins and yield anthocyanidin pigments. (Harborne, 1967).

2. Chemistry of Dihydroflavonols

2.1 Basic Structure of Dihydroflavonols

Dihydroflavonols are 2-phenyl 3-hydroxybenzopyran 4-ones and are often called 3-hydroxyflavanones or flavanonols. Its numbering system is the same as other flavonoid series as follow :-



2.2 Stereochemistry of Dihydroflavonols

Dihydroflavonols have two asymmetric carbons at C(2) and C(3). The majority of dihydroflavonols possess (2R:3R) stereochemistry, compounds with (2S:3S) stereochemistry are little known. For example, (2R:3R) (+) fustin is shown comparing with (2S:3S) (-) fustin as follows (Bohm, 1975) :-

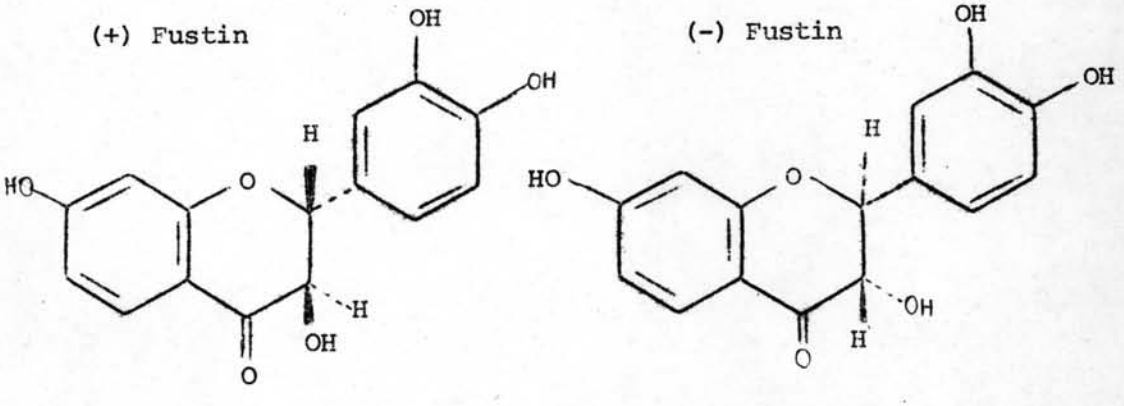
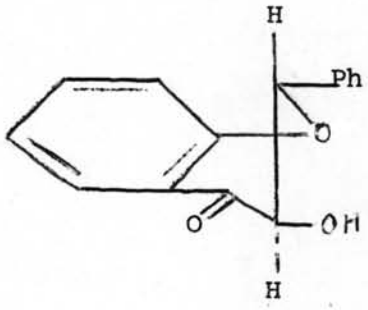


Figure II

About optical rotation, with the exception of (-) fustin the optically active dihydroflavonols isolated from natural sources are dextrorotatory in most solvents. Although the rotation is highly dependent upon the nature of the solvent it is almost certain that all except (-) fustin belong to the same stereochemical series and therefore have the absolute configuration of (+) fustin as shown in figure II (Geissman, 1962).

Configuration of Dihydroflavonols

Dihydroflavonols, having substituents at C(2) and C(3) can exist in *cis* and *trans* forms. Naturally occurring dihydroflavonols have C(2) *equatorial* phenyl and C(3) *equatorial* hydroxyl group as shown below (Geissman, 1962):

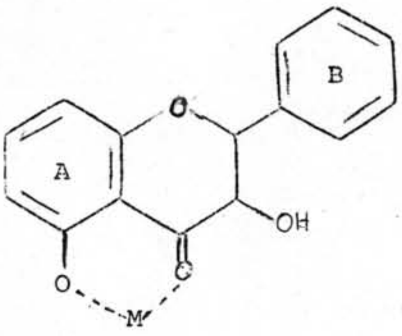


The C(3) hydroxyl group forms hydrogen bond with the C(4) carbonyl rather than hetero-oxygen atom. This also requires the C(3) hydroxyl group to be *equatorial*, resulting in *trans* form. The dihydroflavonols with 2(*axial*) H:3(*axial*) H *trans* structure are not stable when compare with *equatorial* form. So they can be easily removed by various mild oxidative process to flavonols. For example, dihydrokaempferol is oxidised to kaempferol with iodine-sodium acetate; taxifolin yielded quercetin when boiled with dilute sulphuric acid in air. *Trans*-isomers are likely to be formed in preference to the *cis*-isomers (Geissman, 1962).

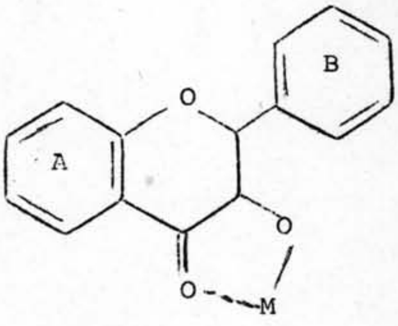
2.3 Chemical Nature of Dihydroflavonols

Dihydroflavonol is related to flavanone and flavonol groups, so chemical reaction is nearly similar.

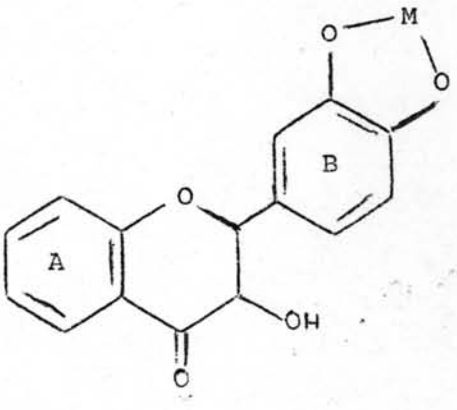
The formation of metal complex is a characteristic property of these flavonoid compounds which possess a carbonyl group and phenolic hydroxyl group. In dihydroflavonols, metal chelates with functional groups such as 5-hydroxy-4-keto-(I), 3-hydroxy-4-keto-(II) and *o*-dihydroxyl systems or an adjacent pair of phenolic hydroxyl group (III). The reaction caused bathochromic shifts of one or both bands in the ultraviolet absorption spectrum (Markham and Mabry, 1975).



(I)

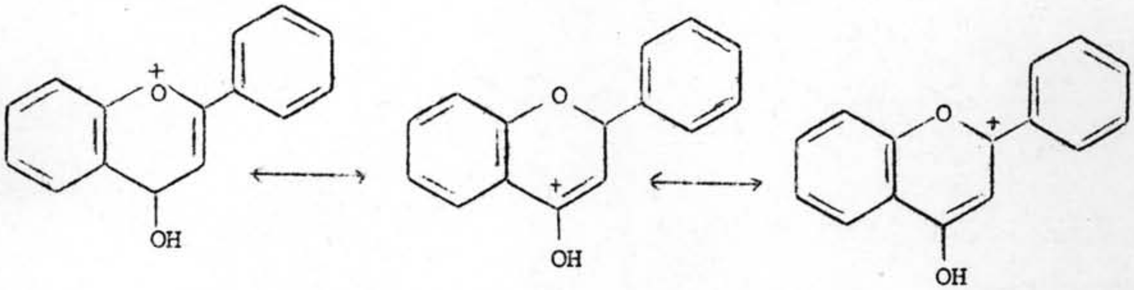


(II)



(III)

Flavones and flavonols dissolve in sulphuric acid to give intensely yellow solutions which probably contain the oxonium (flavylium) salts of the following general structure.



Colour reaction with mineral acid is useful for testing flavonoids. Reaction with boric acid, in the presence of organic acid or mineral acid, flavonols which contain a free 5-hydroxyl group produce bright yellow colour and show yellow green fluorescence under ultraviolet light.

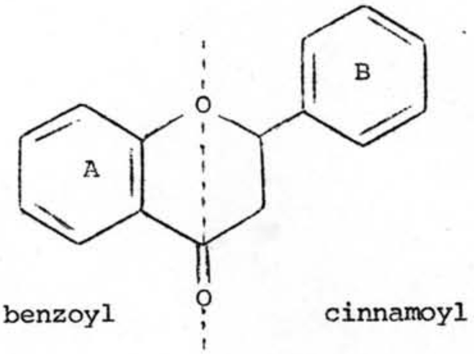
Magnesium-hydrochloric acid reaction is one of the most useful qualitative tests in the study of flavonoid compounds and is called "Shinoda test". To an alcoholic solution of the compound is added a small piece of magnesium ribbon, followed by the dropwise addition of concentrated hydrochloric acid. Characteristic colour develops with in a minute or two, ranging from orange to red (flavones), red to crimson (flavonols), crimson to magenta (flavanones). Colour intensity depends on the concentration of flavonoid presents (Farnsworth, 1966).

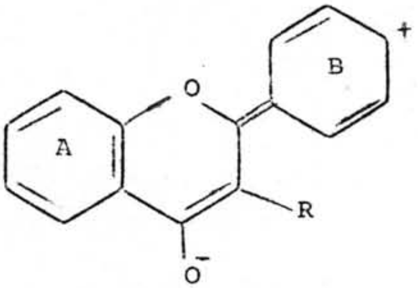
2.4 Ultraviolet Absorption Spectroscopy of Dihydroflavonols

The ultraviolet absorption spectra of most flavonoids consist of two major absorption maxima. One of which occurs in the range 240-285 nm (band II) and the other in the range 300-400 nm (band I).

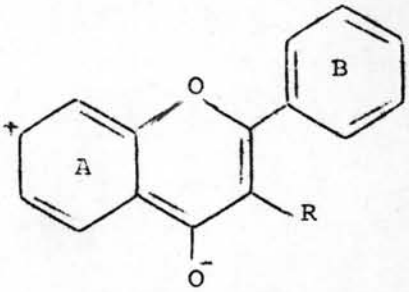
(Figure III, p.15). In general term the band II absorption may be considered as having originated from the A-ring benzoyl system and band I from the B-ring cinnamoyl system (Harborne, 1967).

The position of the λ_{max} and intensity of each of these bands varies with the relative resonance contributions of the cinnamoyl (I) (conjugation of the CO-group with the B-ring), benzoyl (II) (conjugation of the CO-group with the A-ring), and pyrone ring (III) (conjugation of the CO-group with O in pyrone nucleus) groupings to the total resonance of the flavonoid molecule.

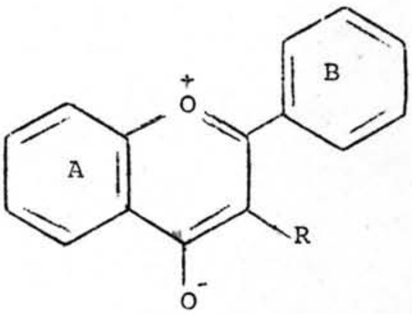




(I) cinnamoyl



(II) benzoyl



(III)

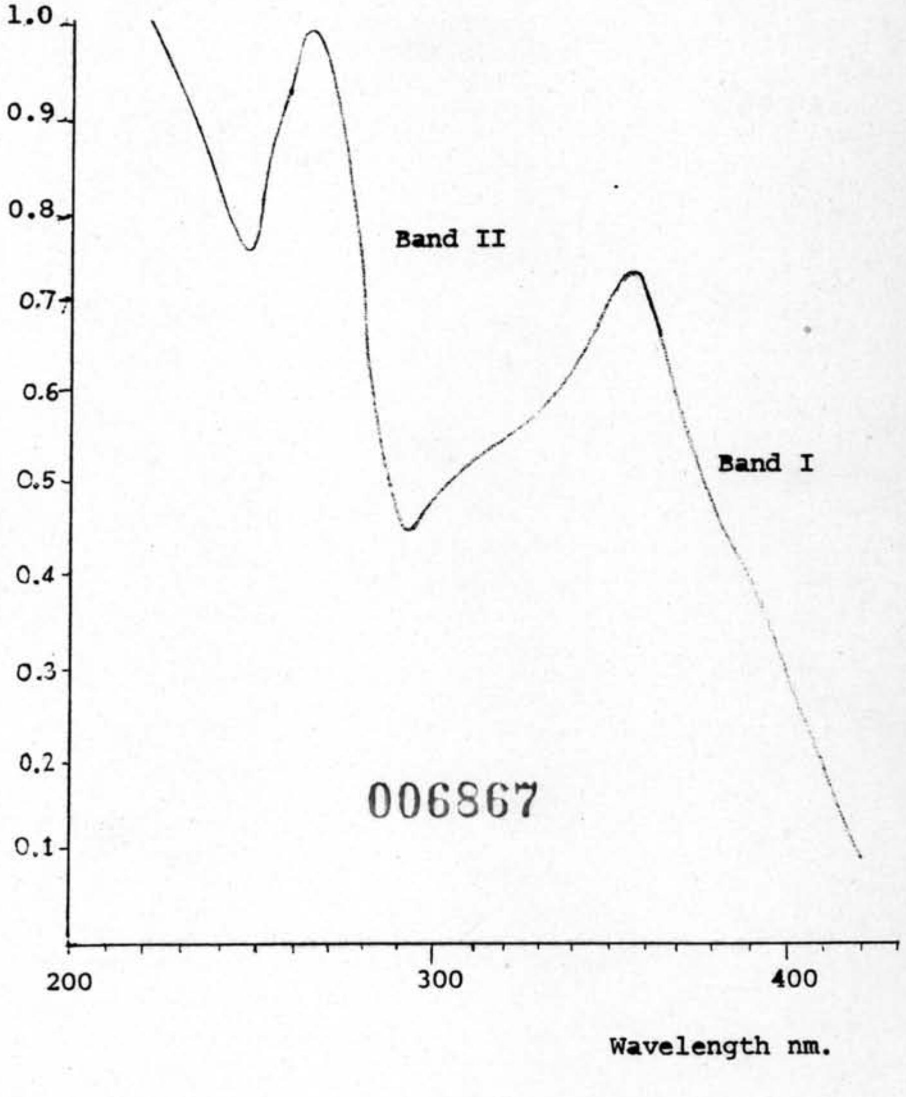


Figure III Ultraviolet absorption spectrum of flavonol (rutin) in MeOH.

The interpretation depends on the effect on absorption of substitution of the A-and B-rings. The introduction of electron donating groups such as hydroxyl into the B-ring increases its relative resonance contribution and consequently produce considerable bathochromic shifts of band I. Introduction of hydroxyl or methoxyl group into the A-ring, on the other hand primarily increases the resonance contribution of this ring and tends to increase the wavelength and intensity of maximum absorption of band II (Ribéreau-Cayon, 1972).

For dihydroflavonol, lacking conjugation between the A- and B-rings, exhibits a low intensity band I absorption which often appears as a shoulder to the band II peak. The spectrum is largely unaffected by changes in the oxygenation and substitution pattern in the B-ring. Dihydroflavonols exhibit their absorption maxima (band II) in the 270-295 nm region and the lack of a free 5-hydroxyl group causes a 10-15 nm shift of these maxima to shorter wavelengths (Markham and Mabry, 1975).

Structural information gained from ultraviolet absorption spectrum is considerably enhanced by the use of specific reagents which react with one or more functional groups on the flavonoid nmcleus. The addition of each of these reagents seperately to an alcoholic solution of the flavonoid induces structurally significant shifts in the ultraviolet absorption spectrum. Shifts of this type are commonly induced by the addition of sodium methoxide ($NaOCH_3$), sodium acetate (NaOAc), sodium acetate/boric acid ($NaOAc/H_3BO_3$), aluminium chloride ($AICI_3$) and aluminium chloride/hydrochloric acid ($AICI_3/HCI$) (Markham and Mabry, 1975).

2.4.1 The Structural Significance of Sodium Methoxide Induced Shift.

Dihydroflavonols with 5,7-dihydroxyl system exhibit a consistent 35-40 nm bathochromic shift of band II in NaOCH$_3$, accompanied by an increase in peak intensity. When the 5-hydroxyl group is absent a shift of about 60 nm is observed. All hydroxyl groups are ionised by the strong base, sodium methoxide, hence both bands of hydroxylated flavonoid shifts to longer wavelength (Markham and Mabry, 1975).

2.4.2 The Structural Significance of Sodium Acetate Induced Shift.

Sodium acetate is a weaker base than sodium methoxide and tends to ionise significantly only the more acidic phenolic hydroxyl groups. 5,7-dihydroxydihydroflavonol and 5-deoxydihydroflavonol have band II shift of 35 nm and 60 nm respectively (Markham and Mabry, 1975).

2.4.3 The Structural Significance of Borate Induced Shift.

A mixture of sodium acetate and boric acid is used for the addition of *o*-dihydroxyl groups in all flavonoids. For dihydroflavonol shift of 10-15 nm (band I) is observed but for 5,6—dihydroxyl grouping there is no shift (Markham and Mabry, 1975).

2.4.4 The Structural Significance of Aluminium Chloride Induced Shift.

In the presence of small amounts of aqueous acid, the complexes formed with *o*-dihydroxyl groups and 3-hydroxy 4-keto system in dihydroflavonol decompose (Figure IV, p.18).

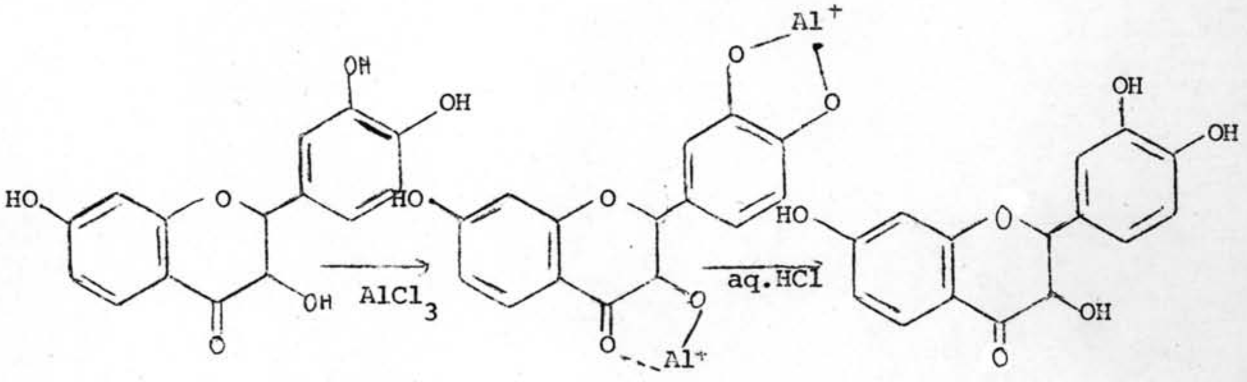


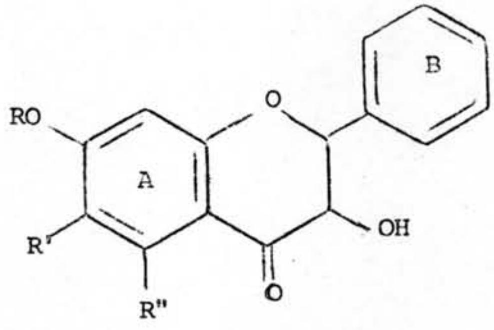
Figure IV

When an o-dihydroxy group is present together with a 5- or 3-hydroxyl, a double complex is formed (Figure IV). When both 3- and 5-hydroxyl groups are present in dihydroflavonol, formation of the 3-hydroxy-4-keto group is favoured. Traces of water in solvent prevent the formation of Al-o-dihydroxyl complexes (Markham and Mabry, 1975).

The presence of a 5-hydroxyl group in dihydroflavonol is revealed by a 20-26 nm band II bathochromic shift. The o-dihydroxyl groups are detectable only when present in the A ring at (6),(7) or (7),(8), the spectrum shows a band II bathochromic shift of 11-30 nm in $AlCl_3$/HCi. A 3-hydroxyl group in dihydroflavonol lacking a free 5-hydroxyl group gives rise to a band II bathochromic shift of 30-38 nm in $AlCl_3$ (Markham and Mabry, 1975).

2.5 Structure of Naturally Occurring Dihydroflavonols

2.5.1 Dihydroflavonols Lacking B-Ring Hydroxyls



R = R' = R" = H 7-Hydroxydihydroflavonol

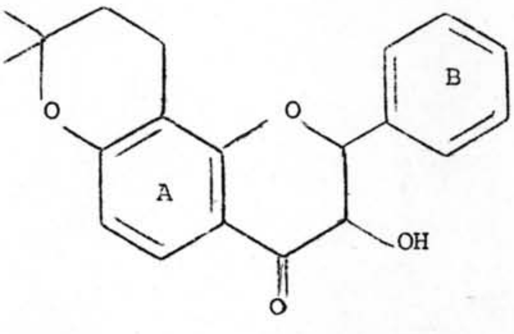
R = H, R' = OCH_3, R" = H 6-Methoxy-7-hydroxy dihydroflavonol

R = R' = H, R" = OH Pinobanksin

R = H, R' = CH_3, R" = OH Strobobanksin

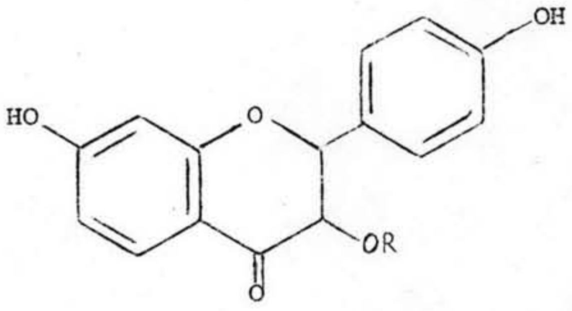
R = CH_3, R' = H, R" = OH Alipone

R = H, R' = OCH_3, R" = OH 5,7-Dihydroxy-6-methoxy dihydroflavonol

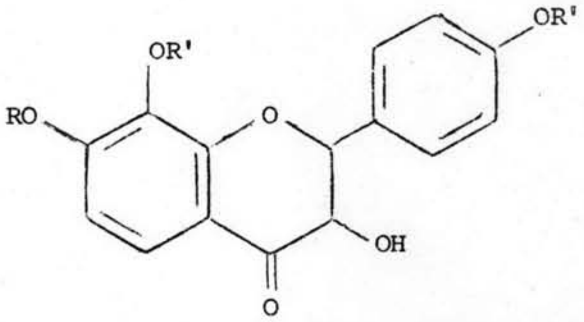


3-Hydroxy isoloncocarpin

2.5.2 Dihydroflavonols Having One B-Ring Hydroxyl

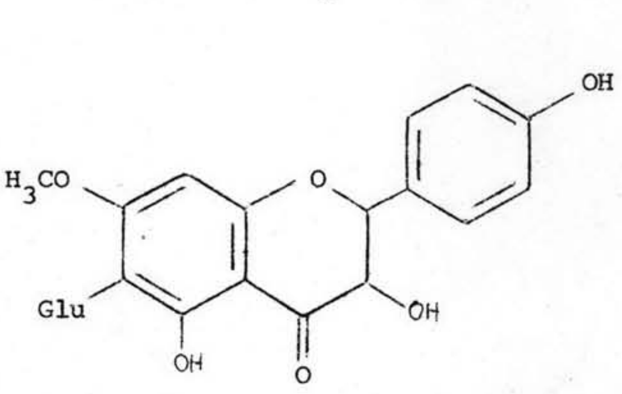


R = H Garbanzol (7,4'-Dihydroxy dihydroflavonol)

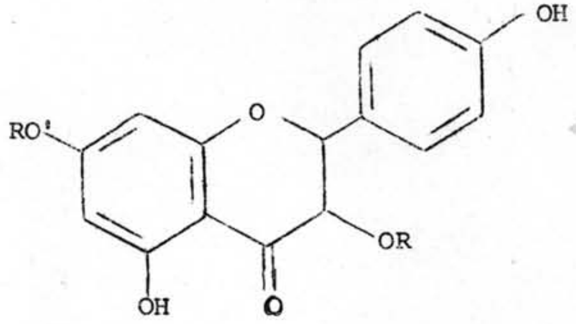


R = R' = H   7,8,4'-Trihydroxy dihydroflavonol

R = Glucose, R' = CH_3 Dihydroprunomenin



5,4'-Dihydroxy-7-methoxy-6-C-glucosyl dihydroflavonol

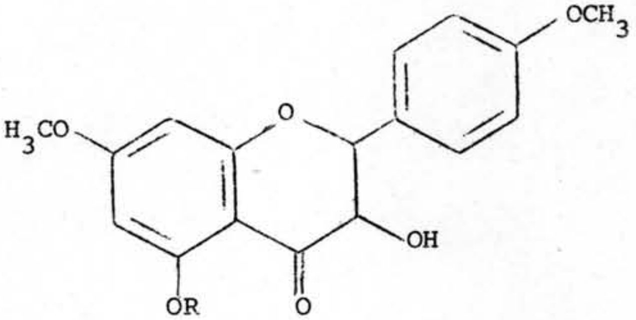


R = R' = H Dihydrokaempferol

R = Rhamnose, R' = H 3-O-Rhamnoside engelitin

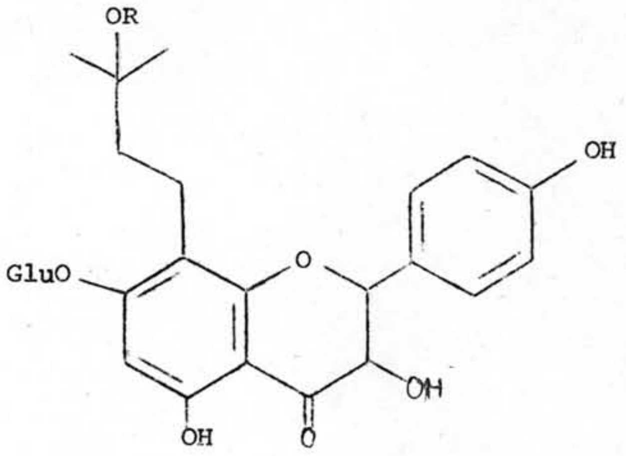
R = H, R' = Glucose 7-O-Glucoside sinensin

R = H, R' = CH_3 7-O-Methyl dihydrokaempferol

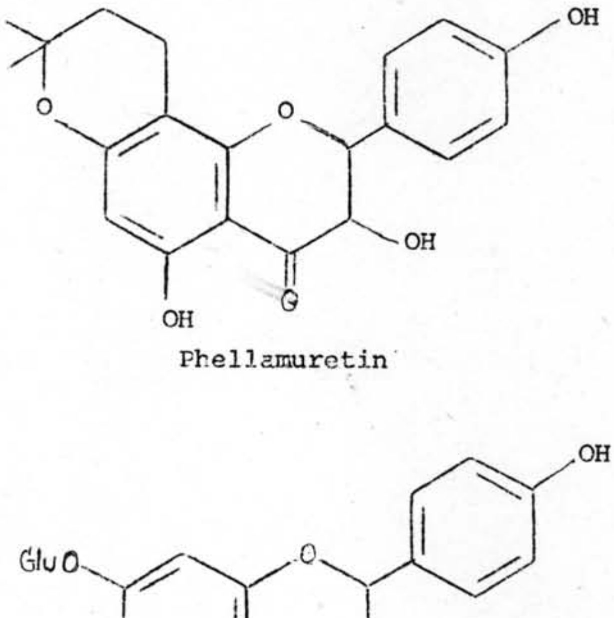


R = H Dihydrokaempforol 7,4'-dimethyl ether

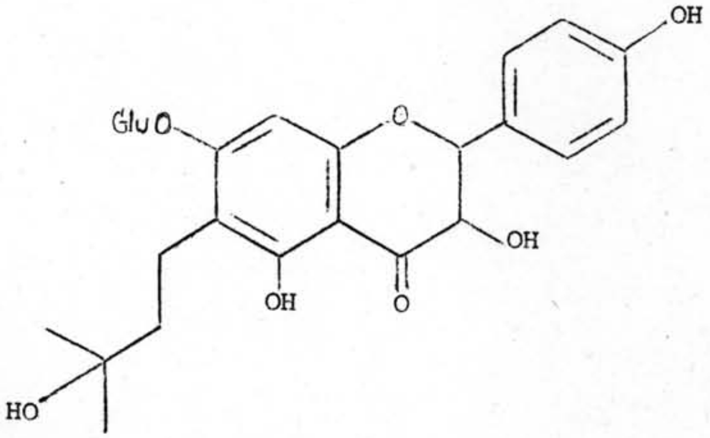
R = Glucose Dihydrokaempferol 7,4'-dimethyl ether 5-O-glucoside



Dihydrophelloside (Phellamurin-7-0-glucoside)

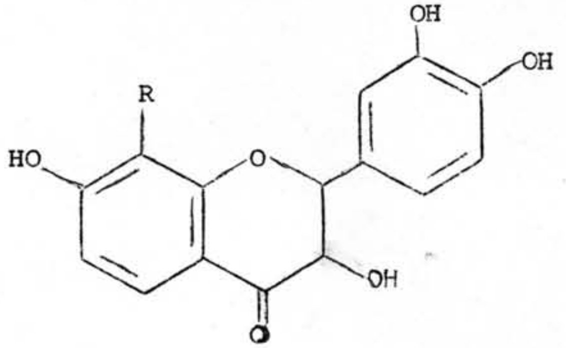


Phellamuretin



Phellavin

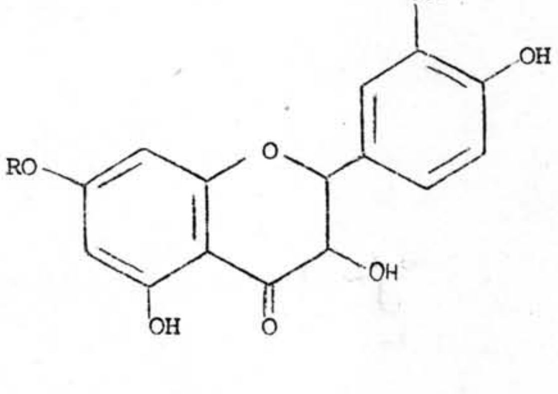
2.5.3 Dihydroflavonols Having Two B-Ring Hydroxyls



R = H Fustin

R = OH 7,8,3', 4'-Tetrahydroxy dihydroflavonol

The most common dihydroflavonol is dihydroquercetin or taxifolin which ocurrs free or as 3-O-rhamnoside (astilbin), a glucoside of undetermined structure (glycodistylin), the 7-O-glucoside, the 3'-O-glucoside, the 4'-O-glucoside and as the 3-O-xyloside.

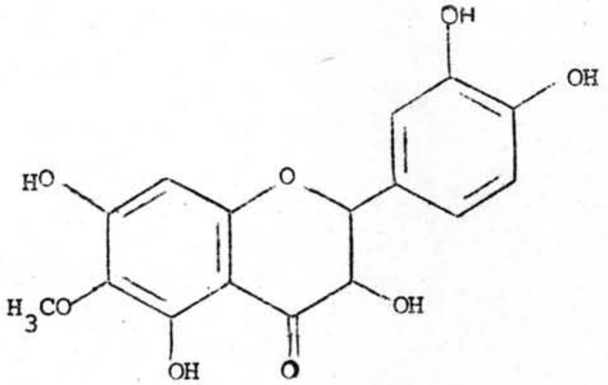


R = R' = R" = H Dihydroquercetin

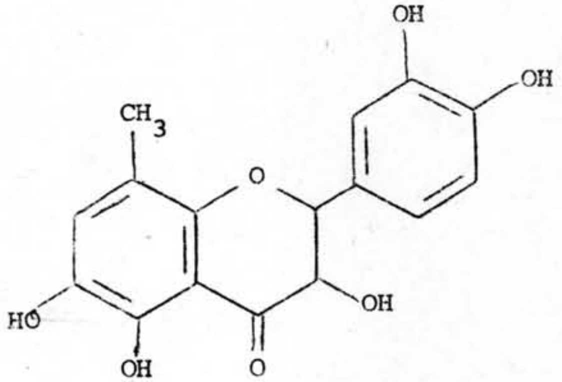
R = R" = H, R' - CH_3 Padmatin 7-methyl ether

R = Glucose, R' = CH_3, R" = H Padmatin 3-O-glucoside

R = H, R' = R" = CH_3 Dihydroquercetin 7,3'-dimethyl ether



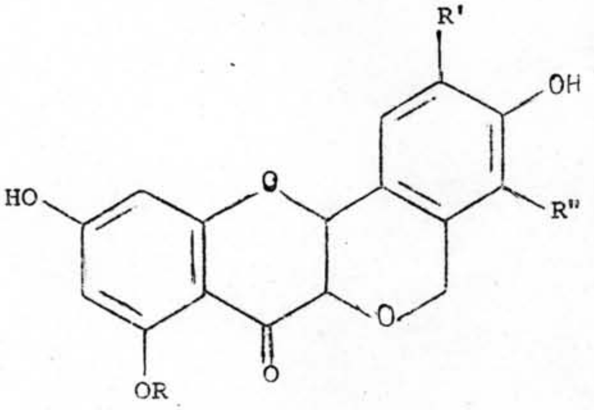
6-C-Methyldihydroquercetin



C-Methyldihydroflavonol

5,6,3',4'-Tetrahydroxy-8-methyldihydroflavonol

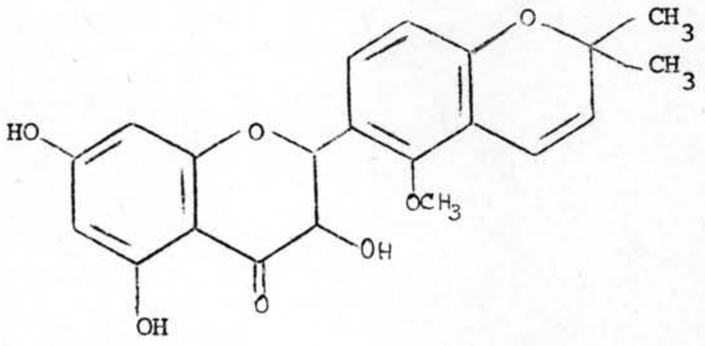
Structures of dihydroflavonols of the peltonoid type which differ only in the placement of the B-ring hydroxyls and the presence or absence of the 5-O-methyl group are as follow:-



$R = R'' = H, R' = OH$

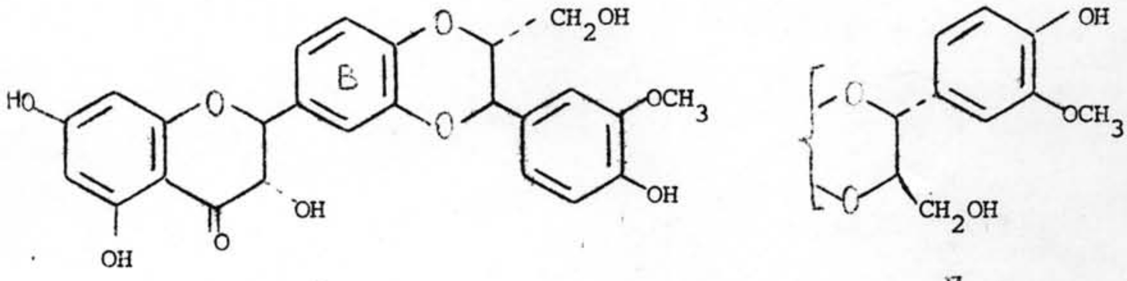
$R = CH_3, R'' = OH, R' = H$

$R = CH_3, R' = H, R' = OH$



Sophoronol

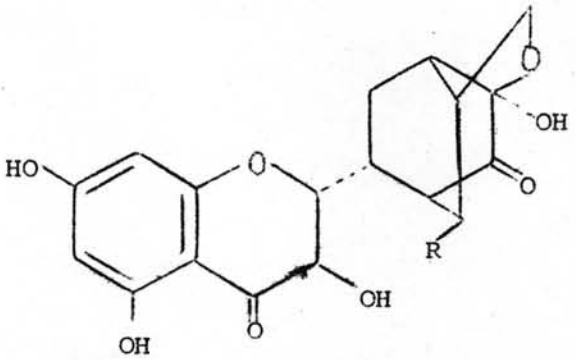
Other modified dihydroflavonols, silymarin or silybin (I or II), silydianin and silychristin, are based on dihydroquercetin.



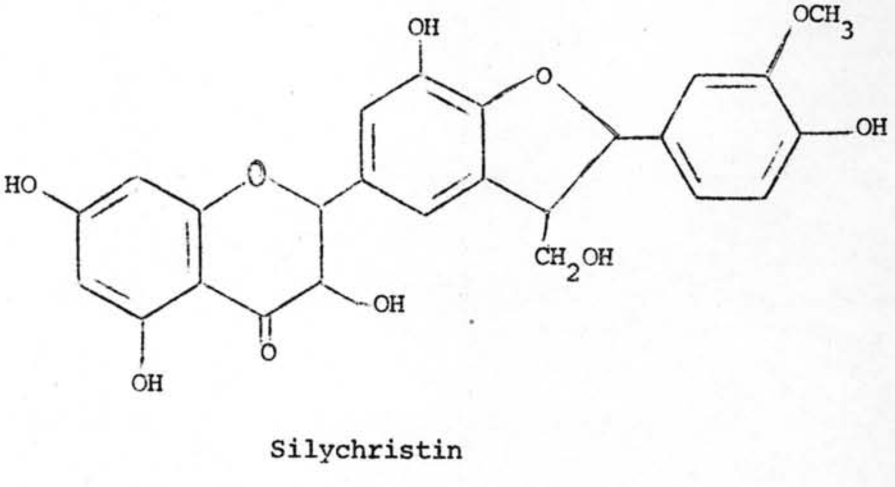
I

II

Silymarin



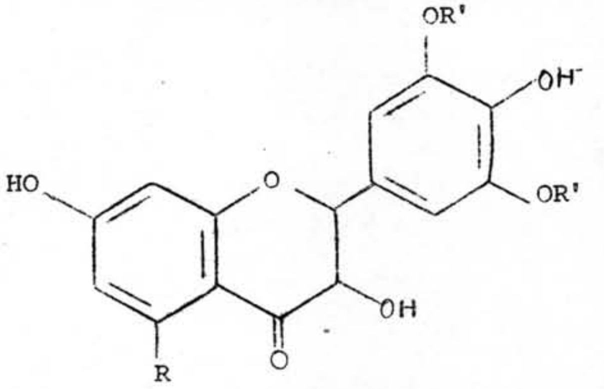
R = vanillyl; Silydianin



Silychristin

These three compounds appeared to be derived biosynthetically by the condensation of an activated dihydroquercetin molecule with coniferyl alcohol.

2.5.4 Dihydroflavonols Having Three B-Ring Hydroxyls



R = R' = H Dihydrorobinetin (7,3',4',5'-tetrahydroxy dihydroflavonol)

R = OH, R' = H Dihydromyricetin

R = OH, R' = CH_3 Dihydrosyringetin (Bohm, 1975).

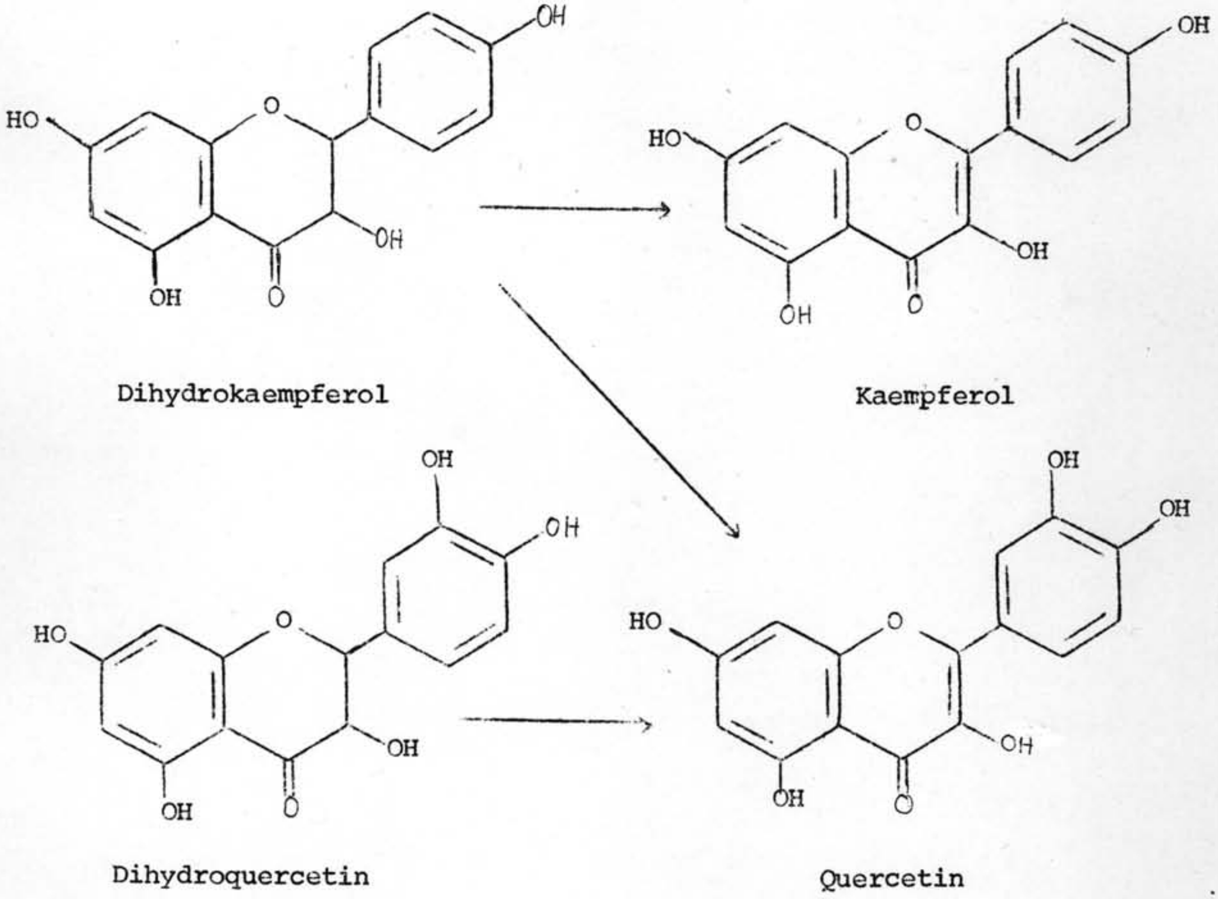
2.6 Conversion of Dihydroflavonols

As being mentioned before, dihydroflavonol, in turn, can yield several other flavonoid types:- flavonol, flavan-3,4-diol, anthocyanin, catechin and isoflavone.

2.6.1 Conversion of Dihydroflavonols into Flavonols

In vivo

By tracer studies, Patschke *et al.* (1966) showed that dihydrokaempferol is incorporated into both kaempferol and quercetin in buckwheat (*Fagopyrum sagittatum* Micheli, Polygonaceae) seedlings, and in pea plants (Hahlbrock and Grisebach, 1975). Patschke and Grisebach showed that dihydroquercetin is incorporated only to quercetin when fed to pea plant (Patschke and Grisebach, 1968).



Bate-Smith and Harborne (1971) found the difference in flavonoid content between fresh and herbarium leaf tissue of *Dillenia indica* L. Fresh tissue showed the presence of dihydrokaempferide glycoside, but in herbarium tissue showed only the presence of the related flavonol methyl ether, kaempferide. This showed that storage causes oxidation of the dihydroflavonol to flavonol. They also found that the rate of oxidation being enhanced by the presence of a methoxyl or hydroxyl group in the 4'-position (Bate-Smith and Harborne, 1971).

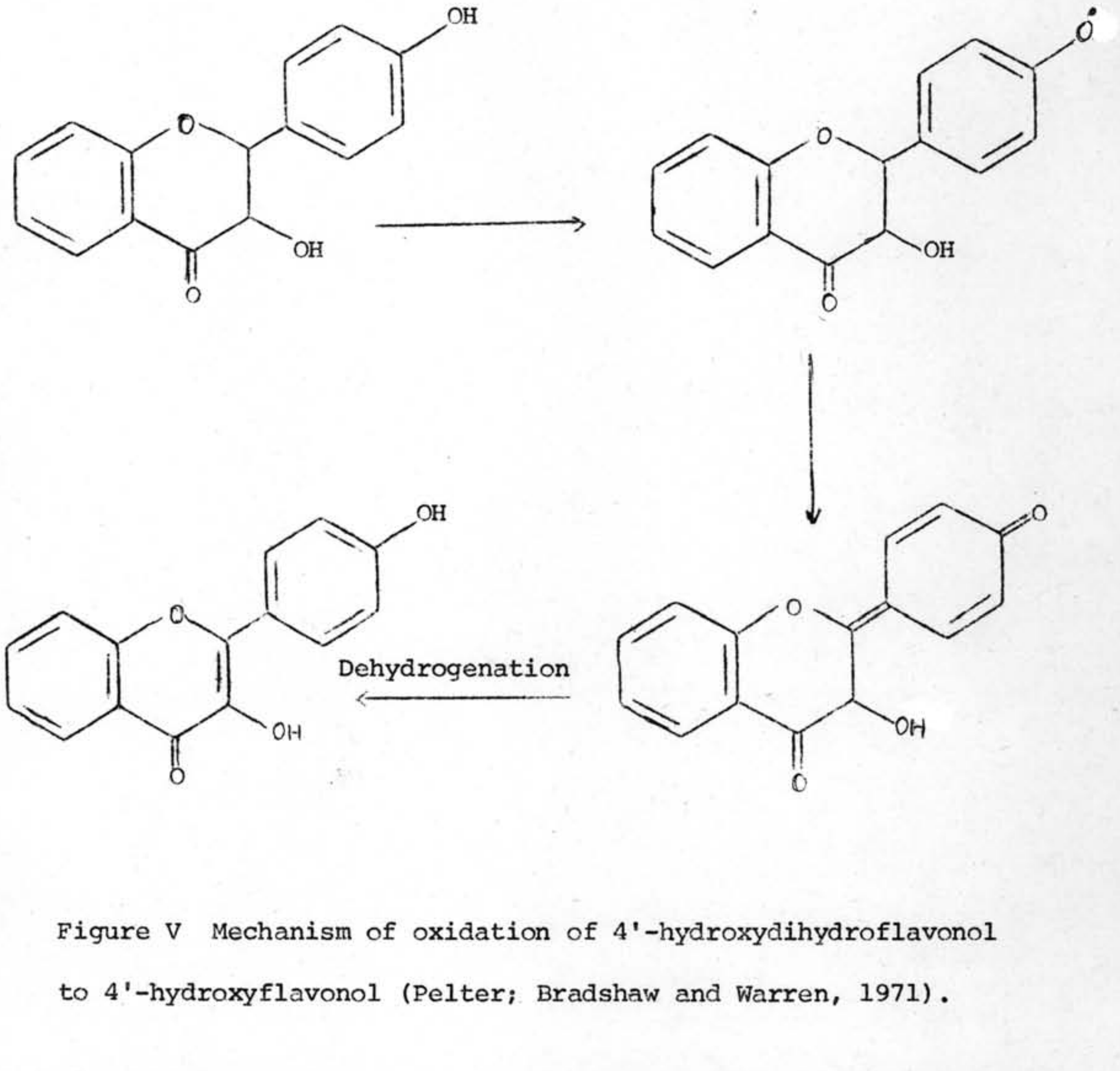
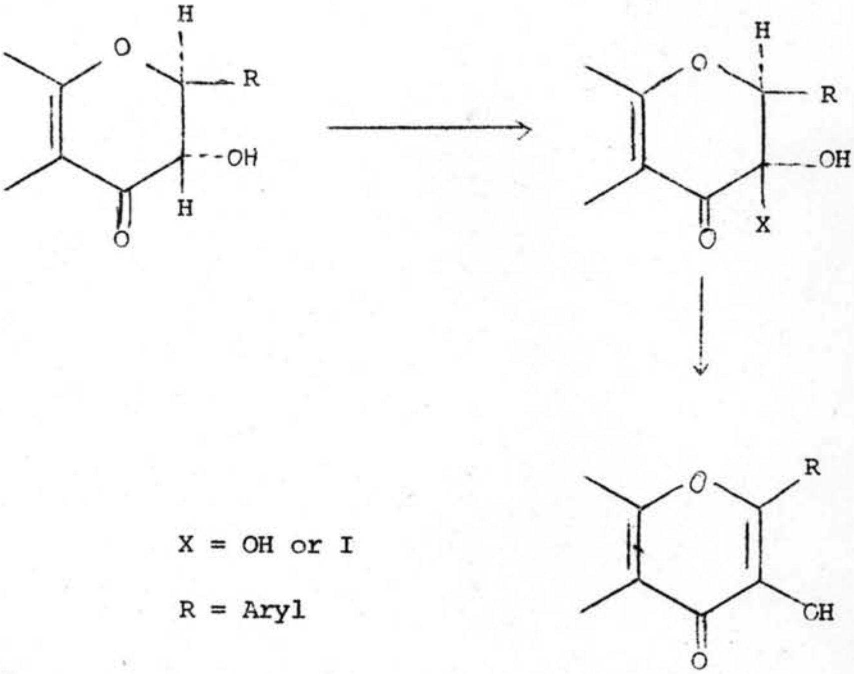


Figure V Mechanism of oxidation of 4'-hydroxydihydroflavonol to 4'-hydroxyflavonol (Pelter; Bradshaw and Warren, 1971).

The dehydrogenation of naturally occurring dihydroflavonols to flavonols has been explained by Mahesh and Seshadri as due to their *trans*-structure. This will aid the elemination of the hydrogen atoms under oxidising conditions. An alternative mechanism would be the initial replacement of hydrogen atom in the 3-position with a hydroxyl or iodine and its subsequent elimination *(trans)*. Favourable conformation *(axial)* also helps this elimination (Geissman, 1962).



X = OH or I

R = Aryl

In vitro

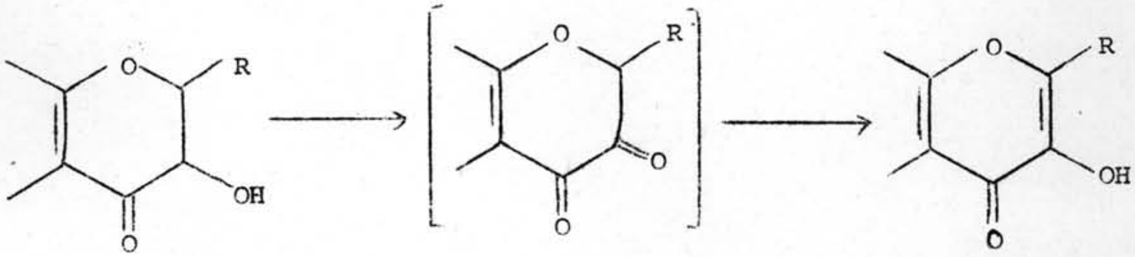
A number of methods have been employed for this dehydrogenation:

i) Kotake and Kubota heated ampleopsin with cinnamic acid in the presence of palladized charcoal at 170° C and obtained myricetin. Later Lindstedt used this method for the dehydrogenation of pinobanksin.

ii) Murakami and Irie first showed that dihydroflavonols underwent dehydrogenation to flavonols with alkaline hydrogen peroxide. By similar oxidation in alkali in the presence of air, fustin yields fisetin. Even under mild basic condition this change takes place, e.g. by boiling an anhydrous acetone solution in the presence of potassium carbonate. For this reason methylation of dihydroflavonols frequently yields the methyl ether of flavonols as product. A similar change is brought about even in boiling dilute sulphuric acid solution in the presence of air.

iii) The most convenient method is to use iodine and potassium acetate in boiling acetic acid medium; this brings about smooth dehydrogenation.

iv) Guider *et al.* have used bismuth acetate. This reagent is specific for the oxidation of -CHOH- to -CO- and is considered to function here in this manner. Mahesh and Seshadri converted taxifolin and 3-hydroxy-naringenin into quercetin and kaempferol respectively by this method.



R = Aryl

2.6.2 Conversion of Dihydroflavonols into Catechins

In vivo

Zaprometov and Grisebach (1973) found by tracer studies that dihydrokaempferol was incorporated into catechins in young tea shoots with about the same efficiency as ^{14}C-shikimic acid or $\underline{1}$ ^{14}C-phenylalanine (Hahlbrock and Grisebach, 1975). Wong and Brich (1975) showed that aromadendrin was incorporated into procyanidin and epicatechin in rasberry stem (*Rubus idaeus* L.) and flavan-3, 4-diols were intermediates in this transformation (Wong and Brich, 1975).

Figure VI shows the suggested pathways of the conversion of dihydroflavonol to flavan-3-ols (catechin and epicatechin) and, also, anthocyanidin which are the two principle groups of flavonoids which lack an oxygen atom at 4-position on the heterocyclic ring. The flavan 3-ene-3-ol is a key intermediate on this pathway; reduction would give the flavan 3-ol and oxidation the anthocyanidin.

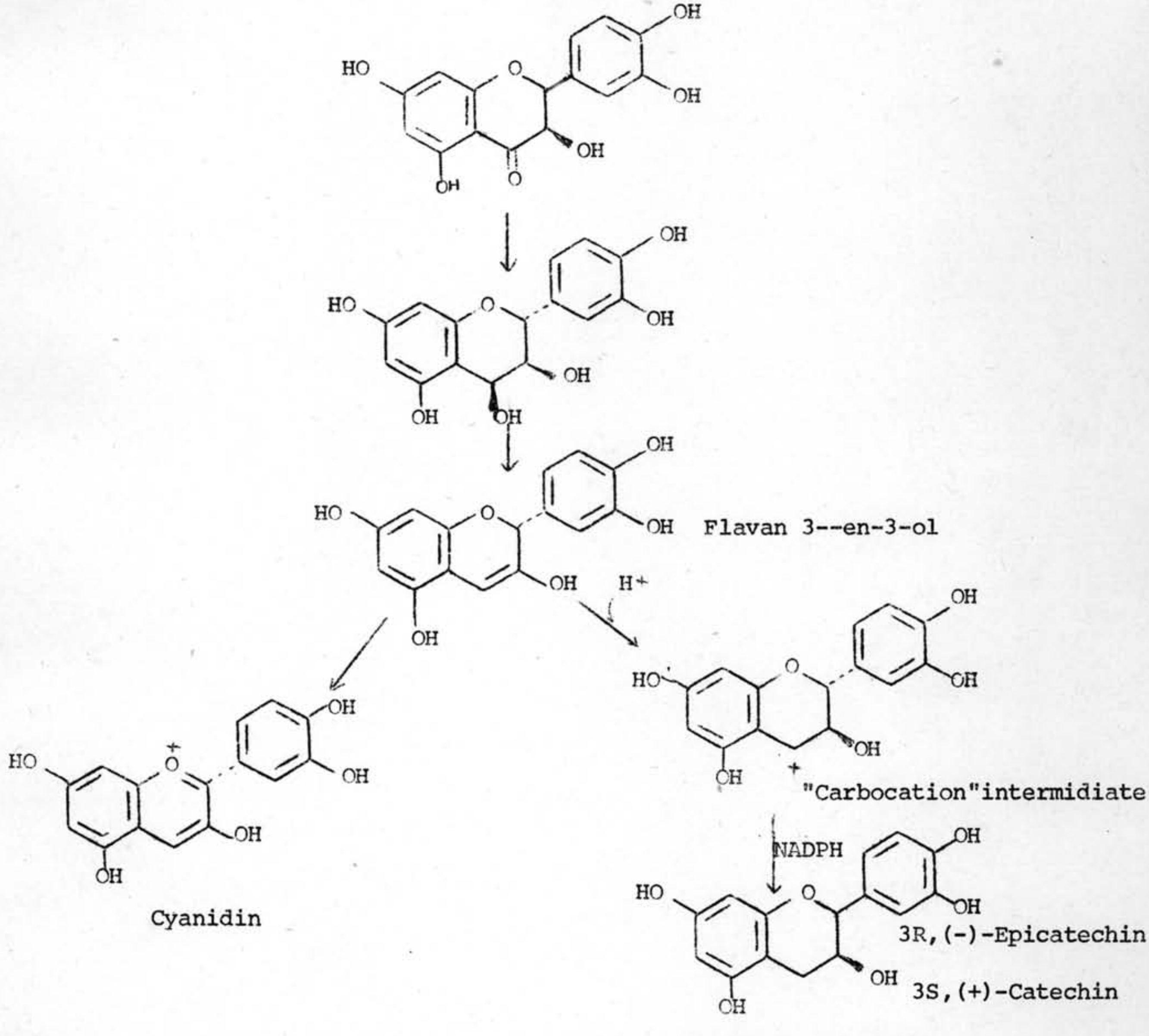


Figure VI Suggested pathways of biosynthesis of cyanidin, catechin and epicatechin from dihydroflavonol.

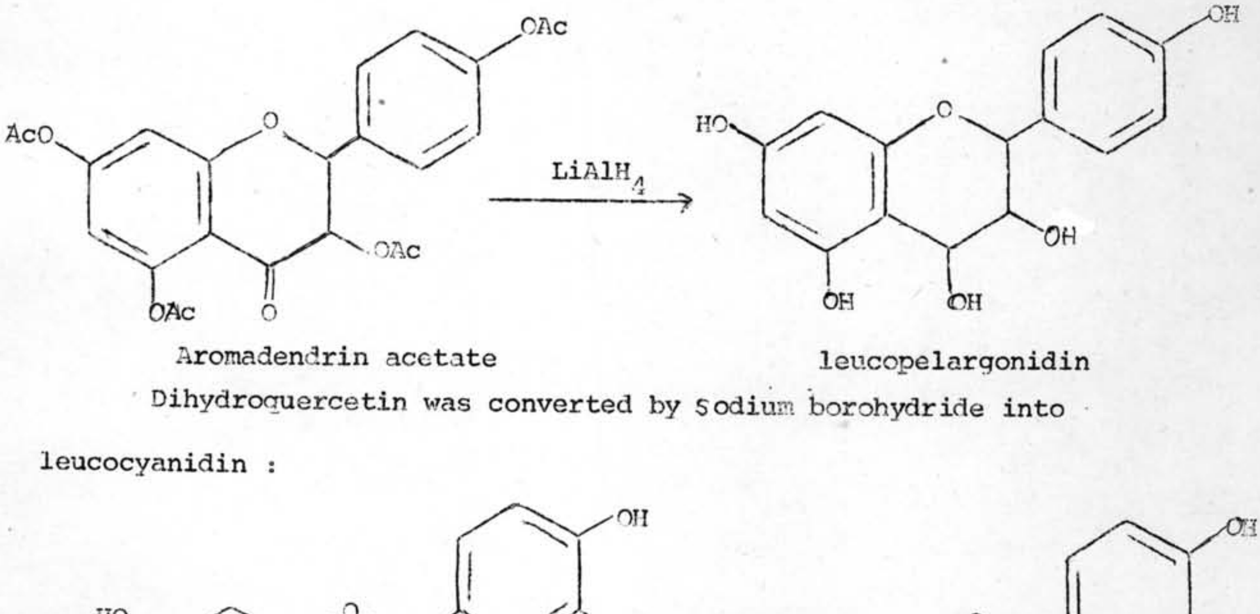
In vitro

Synthesis of catechin depends upon the reducibility, first of dihydroflavonols to diols, then of the diols to catechins. Corresponding to *in vivo experiment*, dihydrorobinetin can be hydrogenated to the corresponding diol (3',4',5',7-tetrahydroxyflavan-3,4-diol), which occurs along with dihydrorobinetin in the wood of *Robinia pseudocacia* L.

i) Reduction of dihydroflavonols into flavan 3,4-diols

a) Reduction with complex metal hydrides

Reduction of a dihydroflavonol to flavan-3,4-diol was first recorded by Bauer *et al.* Aromadendrin tetraacetate was reduced to leucopelargonidin by lithium aluminium hydride:



Aromadendrin acetate

leucopelargonidin

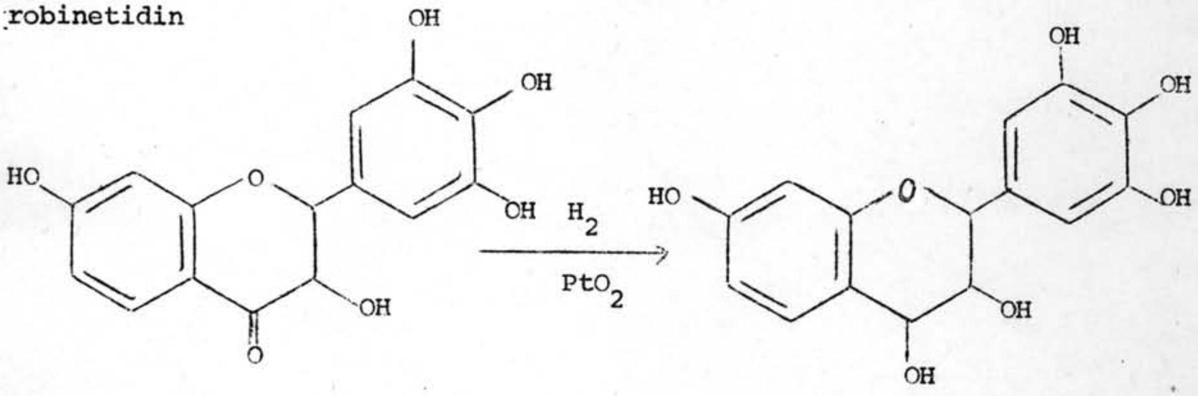
Dihydroquercetin was converted by sodium borohydride into leucocyanidin :

Dihydroquercetin

leucocyanidin

b) Catalytic hydrogenation of dihydroflavonol

Freudenberg and Roux converted dihydrorobinetin from *Robinia pseudocacia* L, via hydrogenation over Adams catalyst giving leucorobinetidin



ii) Reduction of flavan 3,4-diols to flavan 3-ol

Natural or synthetic flavan 3,4-diols can be reduced with suitable catalyst to flavan 3-ols i.e. catechins.

2.6.3 <u>Conversion of Dihydroflavonols into Anthocyanins</u>

Many experiments were studied concerning to conversion of dihydroflavonols to anthocyanins in plant by feeding experiment. Stickland and Harrison observed that white flower of *Antirrhinum majus* L., *Streptocarpus hybridus* Hort. ex Kaven, *Anemone coronaria* L. and *Primula obconica* Hance produced anthocyanins when the flower stems were placed in aqueous solutions of the flavonone and dihydroflavonol precursors (Kho, 1978). Patschke *et al.* (1966) reported on the incorporation of dihydrokaempferol into cyanidin in buckwheat seedlings (Hahlbrock and Grisebach, 1975) and confirmed experiments by cell suspension culture of *Haplopappus gracilis* A. Gray, (*Aplopappus gracilis* A. Gray (Hooker and Jackson, 1885)) (Fritsch and Grisebach, 1975). It has been concluded that substituted dihydroflavonols may be expected to act as precursors only of these anthocyanins with an analogous substituted B-ring.

In *Petunia hybrida* Hort. ex Vilm. the experiment was set by feeding differently substituted natural and synthetic dihydroflavonols to corolla of white flowering plant. Dihydroflavonol is not a precursor of pelargonidin in *Petunia* and only compounds with the 3',4'-dihydroxy or the 3',4'5'-trihydroxy substituted B-ring, substitution pattern can be converted into the corresponding anthocyanin.

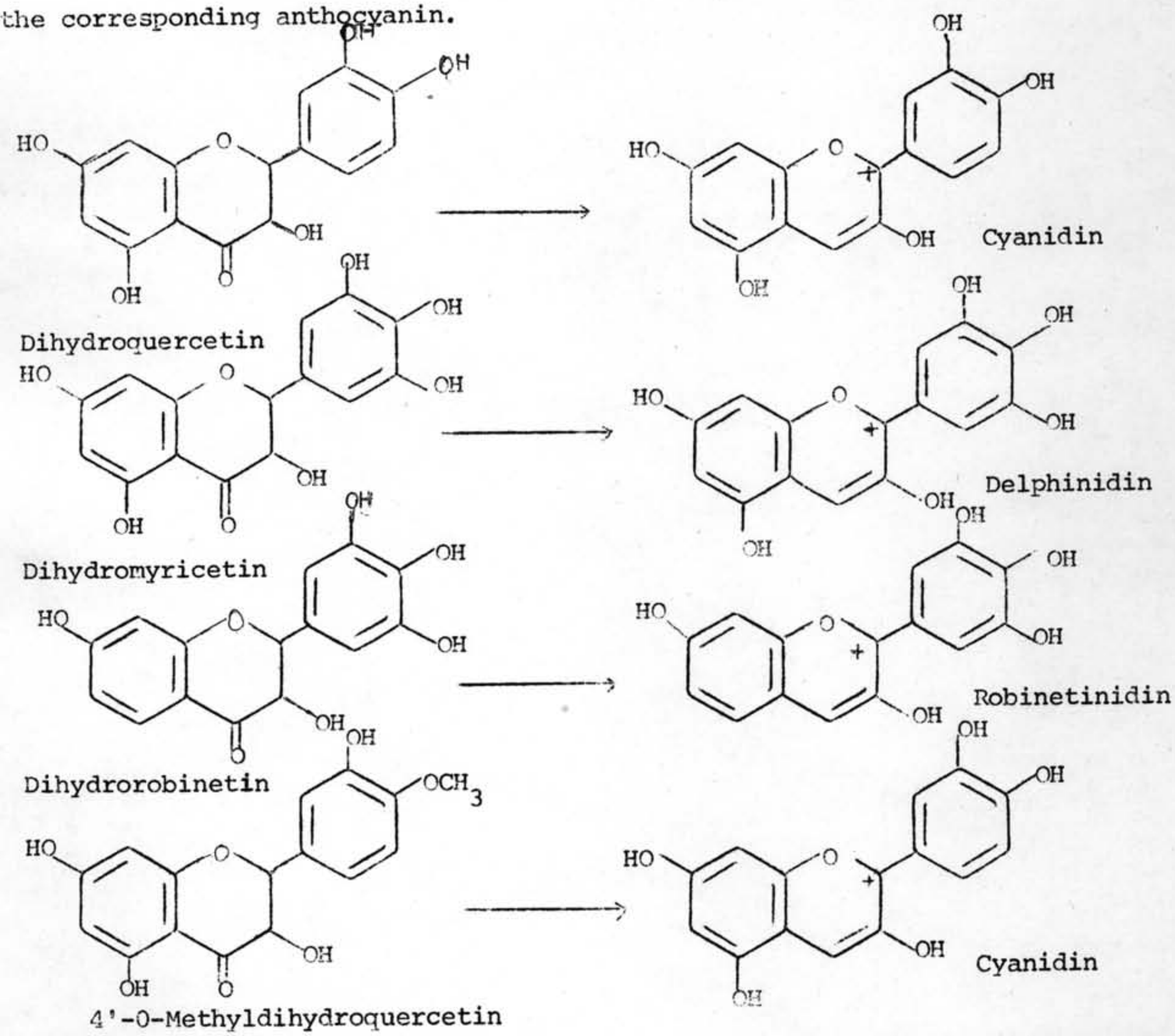


Figure VII Conversion of dihydroflavonols into anthocyanidins in *Petunia hybrida* Hort. ex Vilm.

I16699099

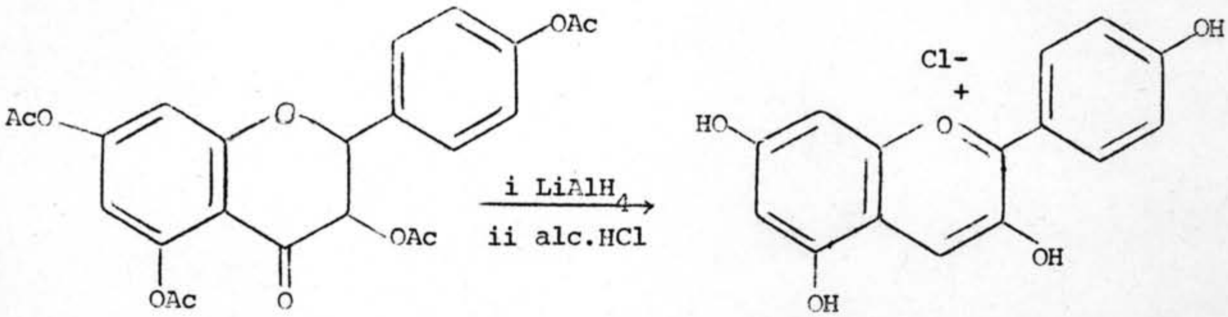
The conversion of dihydromyricetin into delphinidin and its O-methyl derivatives petunidin and malvidin suggest that this dihydroflavonol is a ready precursor of delphinidin. This implies that B-ring hydroxylations occur prior to the conversion of dihydroflavonol into anthocyanin.

In contrast, B-ring methylated dihydroflavonols were not converted into methylated anthocyanins. The production of some cyanidin from 4'-O-methyldihydroquercetin could have been the result of demethylation prior to anthocyanin formation. Demethylation activity in flowers of *Petunia hybrida* Hort. ex Vilm. has been reported by Steiner (1970). So the B-ring methylation is the ultimate step in anthocyanin biosynthesis (Kho, 1978).

Biosynthesis of anthocyanidin from dihydroflavonol is shown in figure VI, p. 32 Oxidation of flavan-3-ene-3ol yields anthocyanidin.

In vivo

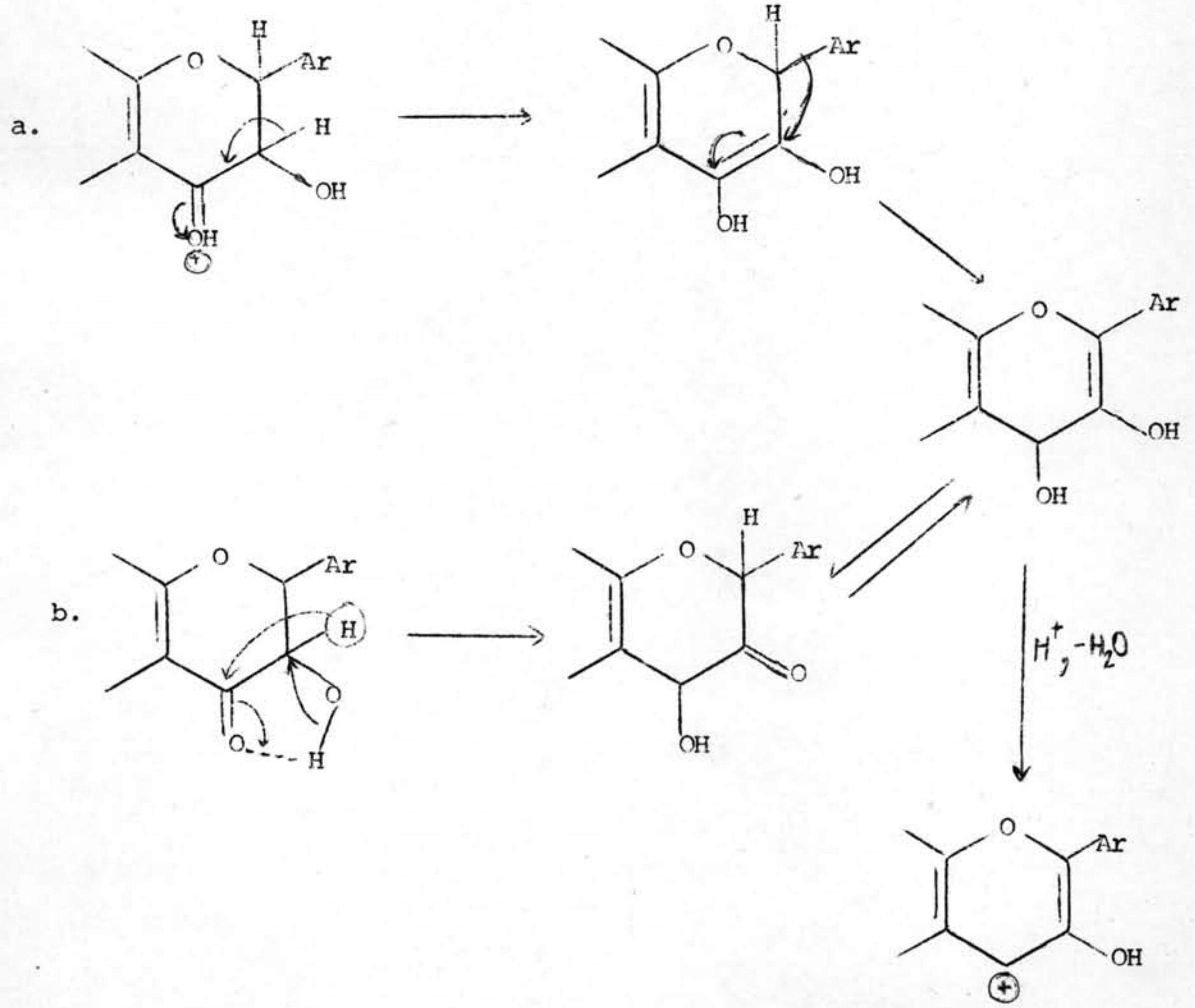
As mentioned above, dihydroflavonols could be converted to flavan-3,4-diols, leucoanthocyanins. All these flavan diols when isolated with alcoholic hydrochloric acid undergo conversion into the corresponding anthocyanidins (Geissmann, 1962).



A reasonable mechanism for this rearrangement might involve in two ways :-

Process a, an acid catalyzed enolisation, allylic arrangement of flav 3-ene-3, 4-diol to flav-2-ene-3, 4-diol involving a hydride shift from C(2) to C(4)

Process b, cyclic process in which a hydride ion from C(3) of dihydroflavonol shifts to C(4) to form the anthocyanin pseudo-base.



Under alcoholic mineral acid condition, the presence of free 5-hydroxyl group inhibit the dihydroflavonol flavylium salt conversion. This inhibitory effect suggests that hydrogen bonding of the 5-hydroxyl with the 4-carbonyl group prevents protonation of the 4-carbonyl group (by acid or through hydrogen bonding with the 3-hydroxyl) (Jurd, 1969).

2.6.4 Conversion of Dihydroflavonols into Isoflavones

In vitro

By tracer studies, garbanzol, 4',7-dihydroxy dihydroflavonol, was fed either through the cut end of the stems or roots of chana (*Cicer arietinum)* seedlings, and isoflavone, formononetin, was obtained. Imaseki *et al.* (1965) suggested that this was the direct conversion of the dihydroflavonol to the corresponding isoflavone, therefore, the phenyl group rearranges after the pyrone ring formation (Imaseki, Wheeler and Geissmann, 1965).

In vivo

Dihydroflavonol, fustin (I) can be enolised to a flav-3-ene-3,4-diols by photolysis or by chemical reaction as mentioned before. Then, the flav-3-ene-3, 4-diols intermediate (II) undergo inversion at C(3) to give 2, 3-*cis*-fustin and also oxidative rearrangement via a spirodienone (III) to the isoflavone (IV) (Fourie, Ferreira and Roux, 1977). Grisebach showed that isoflavones could be formed by rearrangement of derivatives of dihydroflavonol (Grisebach, 1971).

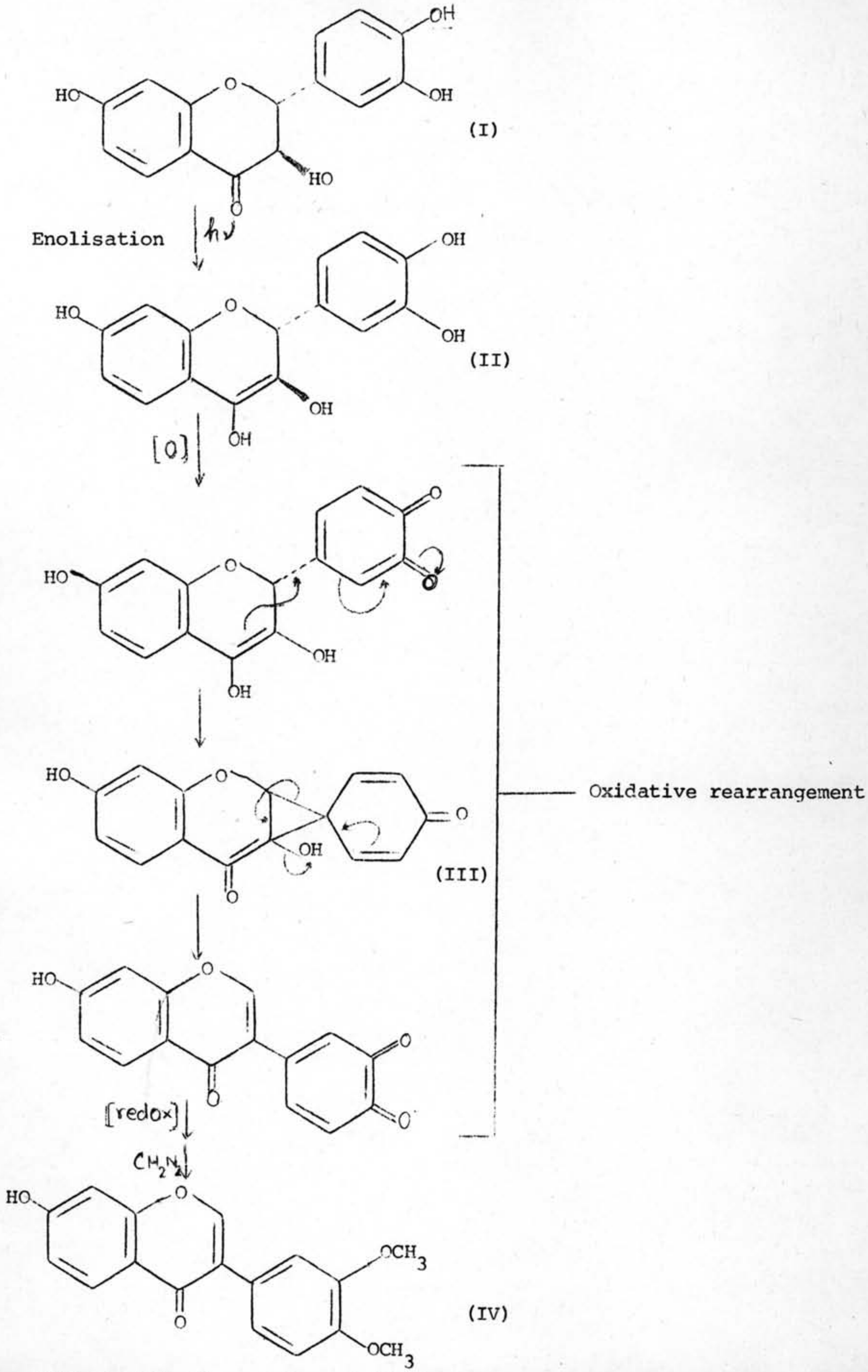


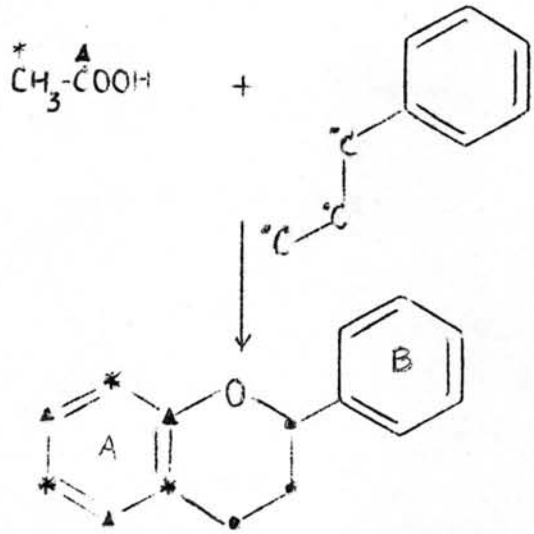
Figure VIII Conversion of dihydroflavonol into isoflavone

3. Biosynthesis of Flavonoids

3.1 Origin of Flavonoids from Primary Metabolism

It has now been established by the use of radioactive tracer and enzymic studies that flavonoids oringnate from "acetate units" and a phenylpropanoid intermediate derived from the shikimic acid pathway.

Basically, ring A (the C 6-unit) is formed by head-to-tail condensation of three "acetate units" while ring B (C 6-unit) as well as C-atom 2,3 and 4 (C 3-unit) arise from a phenylpropanoid precursor (Hahlbrock and Grisebach, 1975).



The phenylpropanoid precursor may be cinnamic acid, *l*-phenylalanine, shikimic acid, *p*-coumaric acid etc. corresponding to each specific flavonoid. For example, shikimic acid and phenylalanine are the best precursors of ring B of quercetin; cinnamic acid is a best precursor of pelargonidin and cyanidin (Ribereau-Gayon, 1972).

The phenylpropanoid metabolism involved the conversion of phenylalanine and/or tyrosine to activated cinnamic acids. By enzymic studies, each enzyme involved in the following reaction step was isolated from many plants to support figure IX (Hahlbrock and Grisebach, 1975).

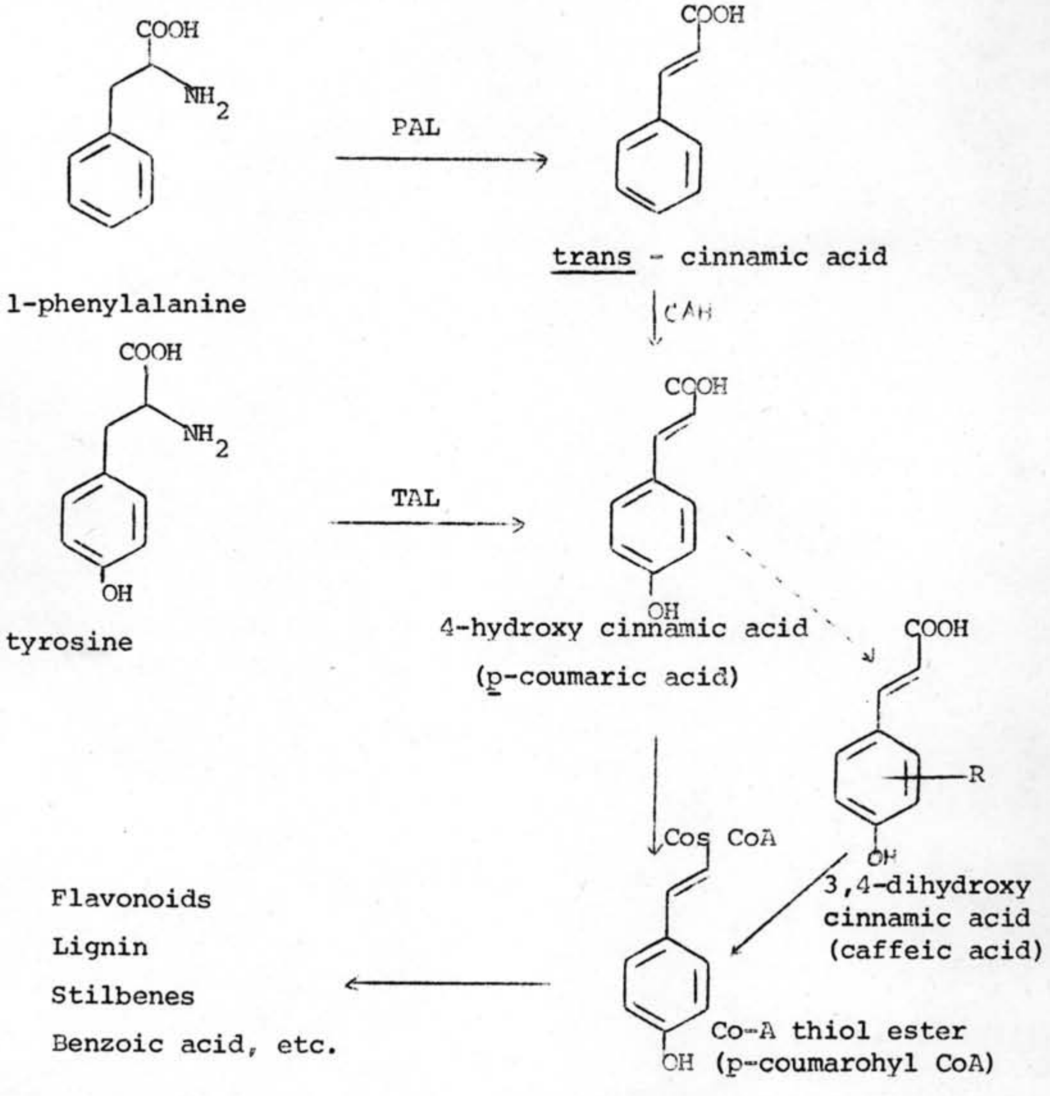


Figure IX Reaction catalysed by the enzymes of general phenylpropanoid metabolism

PAL = Phenylalanine ammonia-lyase ; TAL - Tyrosine ammonia-lyase ; CAH = Cinnamic acid 4-hydroxylase ; R = Hydroxyl and/or methoxyl groups in various positions.

3.2 Intermediate and End Products of Flavonoid Biosynthesis

3.2.1 The Chalcone/Flavanone Intermediate

The first specific reaction in flavonoid biosynthesis is the condensation of an activated cinnamic acid with three molecules of malonyl Co A to give a chalcone or flavanone (Hahlbrock and Grisebach, 1975).

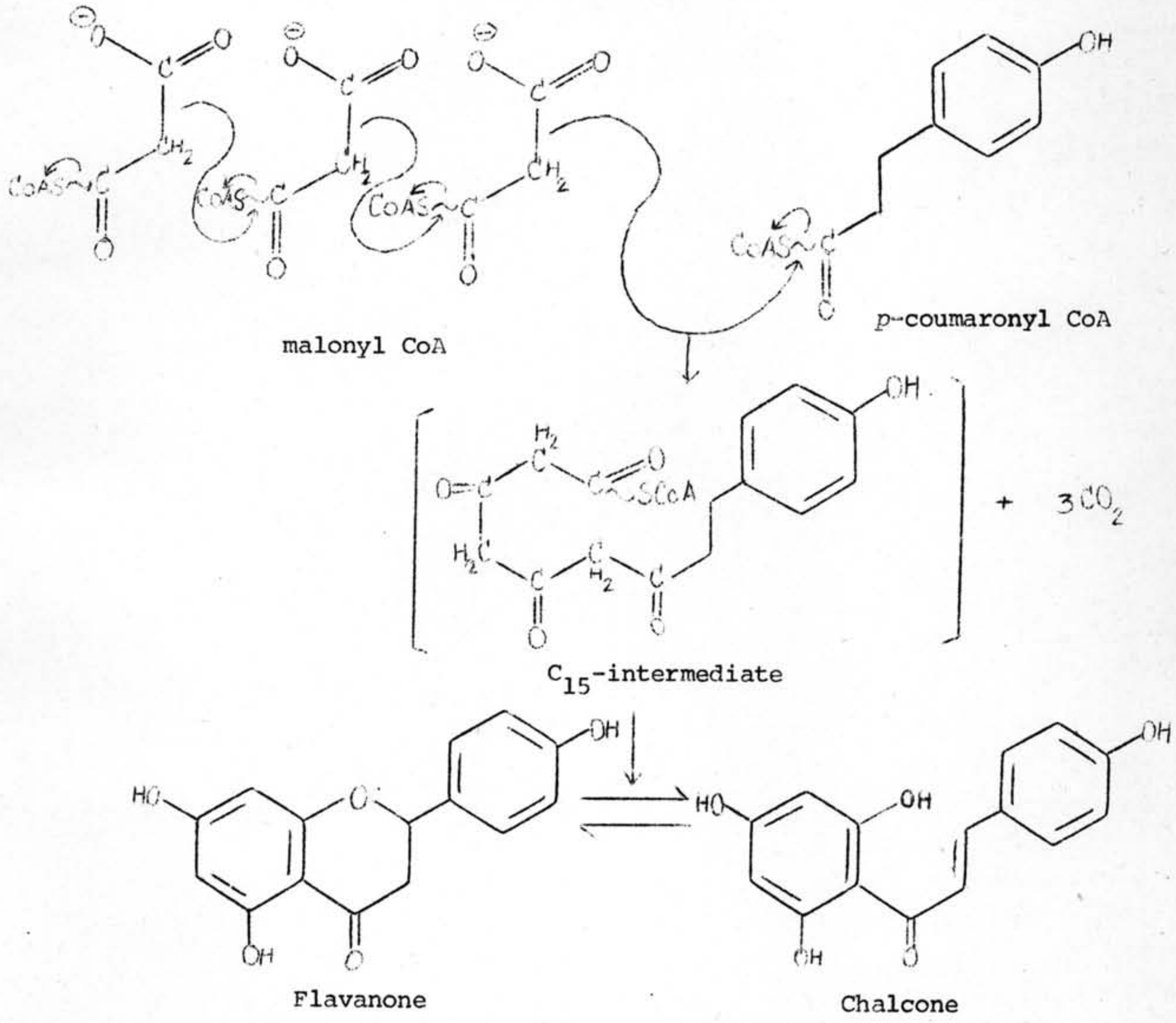


Figure X Proposed mechanism for the formation of chalcone/ flavanone from Co A thio ester of malonic acid and *p*-coumaric acid.

The C_{15}-intermediate is an unidentified substance which is so rapidly turned over to chalcone and flavanone (Harborne, 1967). Chalcones are the common intermediates in the synthesis of all the different types of flavonoids (Wong, 1968).

3.2.2 Variation of the Structure of the Central C_3 Moiety of the Flavonoids

Cyclisation of the chalcone can be easily effected by isomerisation to the flavanone which is stabilised by the formation of a hydrogen bond between the CO and OH groups in position 5 (Ribéreau-Gayon, 1972).

Several facts have been discovered to support figure XI :-

a) An enzyme capable of isomerising chalcones into flavanones has been isolated (Wong and Moustafa, 1966) and its activity has been studied (Moustafa and Wong, 1967).

b) The formation of dihydroflavonols by oxidation of the corresponding chalcones has been proposed (Pelter; Bradshaw and Warren, 1971), and the hydroxylation of flavanones into dihydroflavonols has been carried out (Mahesh and Seshadri, 1955).

c) The oxidation of dihydroflavonols into flavonols presents no difficulty; the 2 and 3 carbons have a *trans* configuration and consequently dehydrogenation is easier than dehydration. (Ribéreau-Gayon, 1972).

d) Different flavonol glycosides has been chemically synthesised from the corresponding chalcones and transformation of dihydroflavonol into flavonol, *in vivo*, has also been shown (Wong,Mortiner and Geissmann, 1965).

e) Synthesising anthocyanidins from dihydroflavonols has been investigated *in vitro* (Kho, 1978) and *in vivo* (Jurd, 1969).

f) The oxidation of chalcone to aurone has been studied (Pelter; Bradshaw and Warren, 1971).

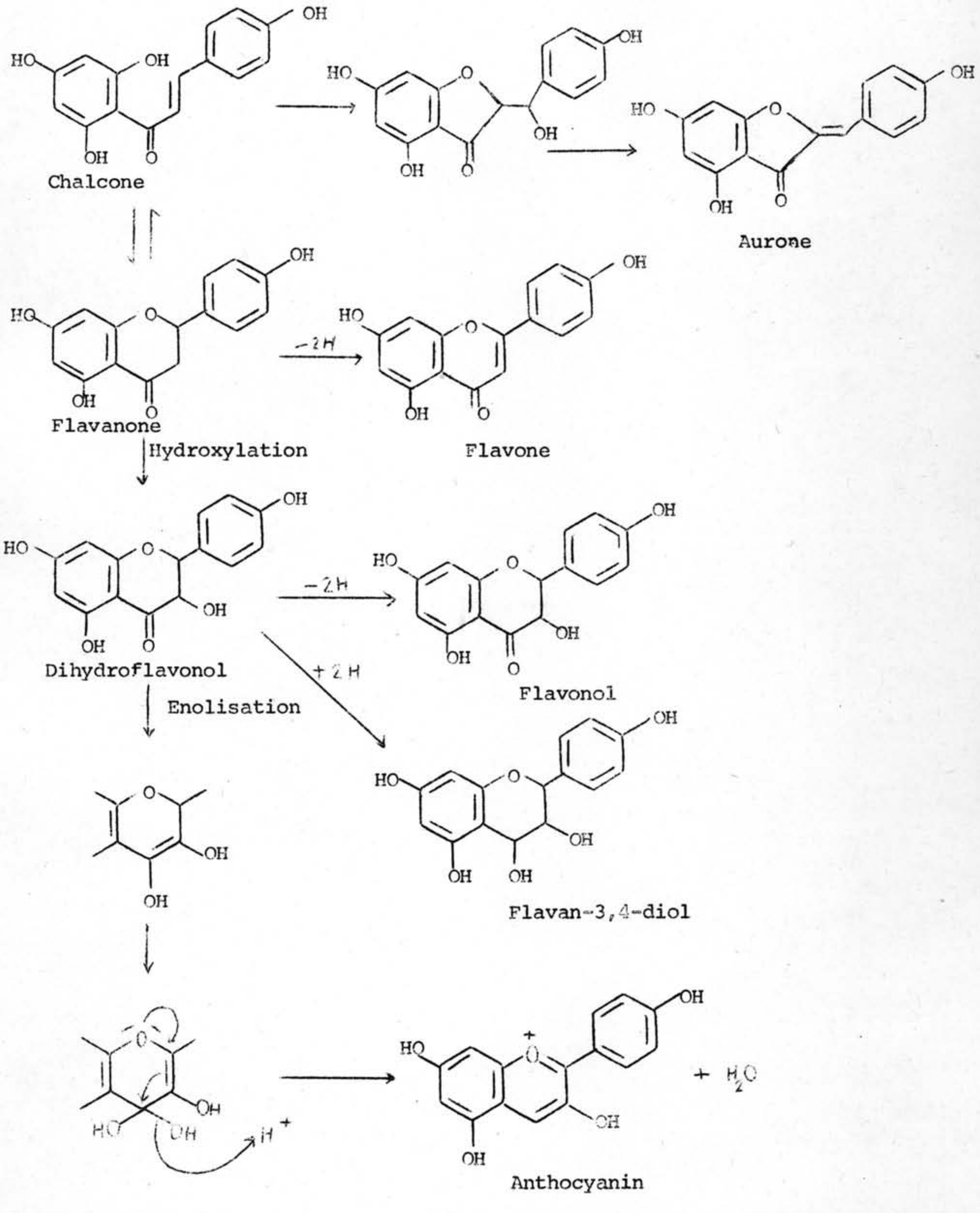


Figure XI Reactions leading to the formation of the principal types of flavonoids from chalcone (Ribéreau-Gayon, 1972).

3.3 Hydroxylation of the Flavonoid System

Studies of the structure variation of flavonoids show that the main differences lie in the number of hydroxyl groups attached to the flavonoids.

Ring A. Grisebach (1965), using specific labelled chalcones as precusors, showed that various other flavonoids formed in plants all had identical substituted to that of the precusor in ring A, but differed in ring B. It thus seems that the hydroxyl groups of ring A must be introduced before cyclisation and that thereafter, the gain or loss of an OH is difficult. If so, chalcones with a phloroglucinol-type ring-A are exclusively incorporated into 5,7-dihydroxyflavonoids, which chalcones with a resorcinol-type ring-A are selectively converted to 7-hydroxyflavonoids (Ribéreau-Gayon, 1972).

Ring B. Concerning ring B, the first OH (4') is introduced before the chalcone formation. (Ribereau-Gayon, 1972; Raymond and Maier, 1977). The second OH (3') achieved by hydroxylation of monohydroxylated (B-ring) chalcone (Tabak; Meyer and Bennink, 1978), and after chalcone formation (Wallace, 1975). Patschke and Grisebach (1968) showed that in biosynthesis of kaempferol and quercetin, the introduction of the second OH (3') occurs at the dihydroflavonol stage. So, *p*-coumaric acid (1 OH) is a better precursor of quercetin (*p* OH) than is caffeic acid (2 OH) (Patschke and Grisebach, 1968). The trihydroxylated B-ring can be formed by addition of an extra OH to an existing diphenol or by its direct formation from shikimic acid, analogous to that of gallic acid (Ribéreau-Gayon, 1972).

Introduction of 3-hydroxyl group into the C_{15}-skeleton.

Genetic studies have been taken to indicate the introduction of a 3-hydroxyl group of a flavonol at a relatively early stage of the biosynthesis. Numerous studied have shown that production of 3-hydroxylated flavonoids is subject to specific gene control (Harborne, 1967). Figure XII suggests the mechanism for the introduction of a 3-hydroxyl group into the C_{15}-flavonoid skeleton by attack by water or hydroxyl radical on the radical (I) or its cyclised form (Pelter; Bradshaw and Warren, 1971).

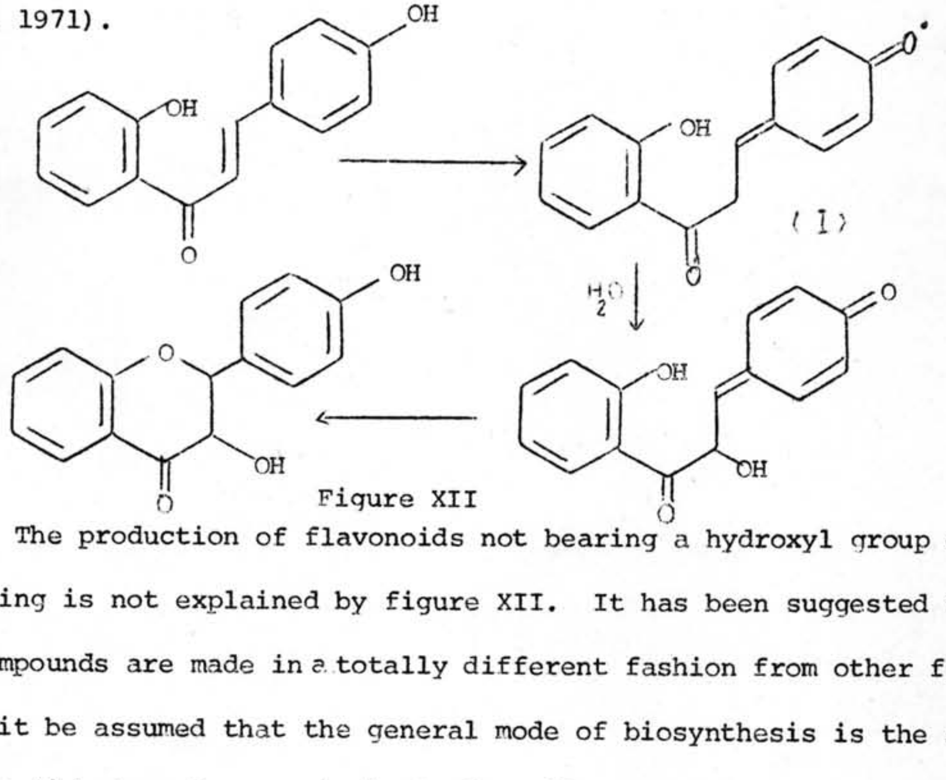


Figure XII

The production of flavonoids not bearing a hydroxyl group on the B-ring is not explained by figure XII. It has been suggested that such compounds are made in a totally different fashion from other flavonoids, but if it be assumed that the general mode of biosynthesis is the same, either a 4'-hydroxyl group is lost after flavone formation or it may be that these compounds arise directly from chalcones by a modification of the Birch proposal, as in figure XIII. Cyclisation of the 2'-hydroxychalcone is initiated by a metal ion to yield the metal enolate (I) directly (Pelter; Bradshaw and Warren, 1971).

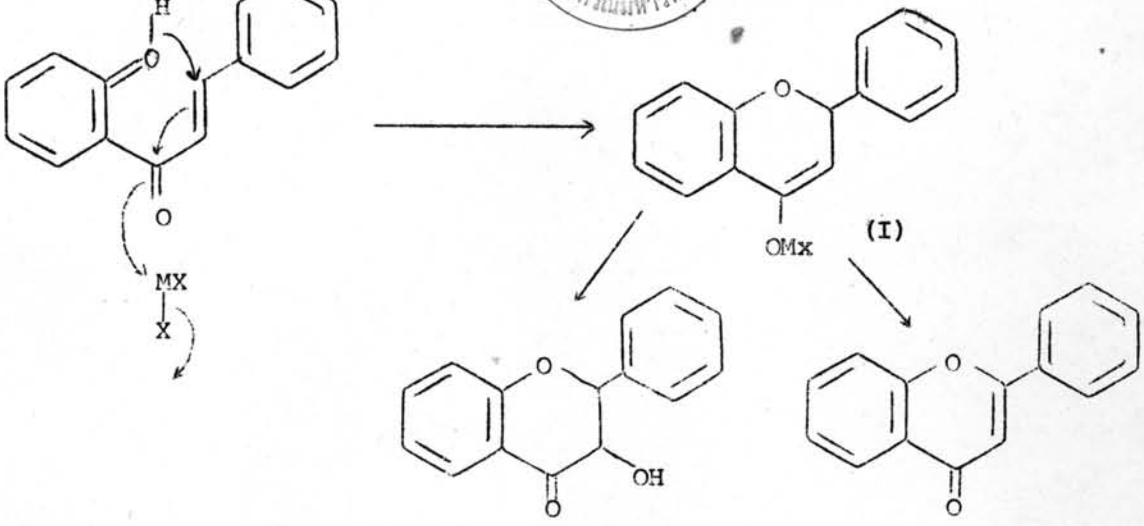
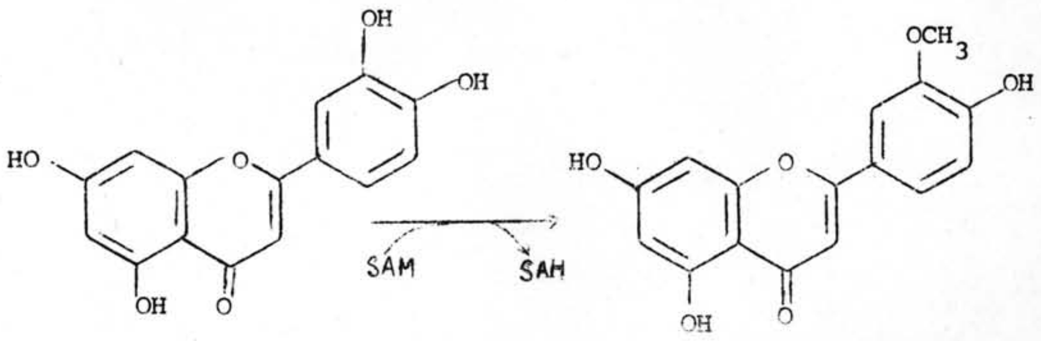


Figure XIII

Common flavonoids have hydroxy substituents at the 5-, 7-and 4'-positions. Flower colouration are flavonols having an extra hydroxyl in the 6-(quercetagetin) or 8-position (gossypetin), which are much yellower in colour than the common flavonols. The introduction of extra hydroxyl groups into flavonols is often accompanied by O-methylation, and many different O-methyl ethers of quercetagetin and gossypetin have been found (Harborne, 1973).

3.4 Methylation of Flavonolids

It is not yet certain whether O-methyl groups are introduced into flavonoids at the phenylpropanoid stage or at a latter stage during flavonoid biosynthesis, or both . The O-methyl groups may be occur by methylation of hydroxyl groups with methionine acting as the CH_3group donor. The enzyme methyltransferase has been isolated from illuminated cell suspension cultures of parsley is specifically involved in the methylation of flavonoids (Hahlbrock and Grisebach, 1975).



Luteolin

Chrysoeriol

SAM = S-adenosylmethionine

SAH = S-adenosylhomocysteine

At present, many evidences has been shown to support that methylation occurs after C_{15}-skeleton in *Petunia hybrida* Hort. ex Vilm. (Kho, 1978), and after cyclisation of chalcones to flavanones in grapefruit (Raymond and Maier, 1977) and, also, in many plants (Ebel; Hahlbrock and Grisebach, 1972). Heursel (1975), by genetic studies, found gene which control methylation of flavonol to methoxyflavonol in Azalea flowers (Heursel, 1976). In the case of quercetin, O-methylation may take place at any of the hydroxyls, and all the five possible isomeric monoethyl ethers have been found (Harborne, 1973).

However, it is also possible that O-methyl groups are fromed by direct methoxylation of the benzene ring without intermediate formation of the corresponding phenol (Ribéreau-Gayon, 1972).

3.5 Glycosylation of Flavonoids

Flavonoid may be found in glycosylated form as well as aglycone. O-glycosylation occurs at (3),(5),(6),(7),(3')and(4') while C-glycosylation occurs at C(6). The enzymes which glycosylate aglycone and sugar moiety to corresponding flavonol glycosides have been isolated from many plants (Hahlbrock and Grisebach, 1975). Raymond and Maier (1977) suggested that in grapefruit, glycosylated flavonoids occurred during chalcones formation. They found that the chalcone aglycones were much less stable than their respective glycosides and, so, would probably cyclise spontaneously before glycosylation could occur (Raymond and Maier, 1977).

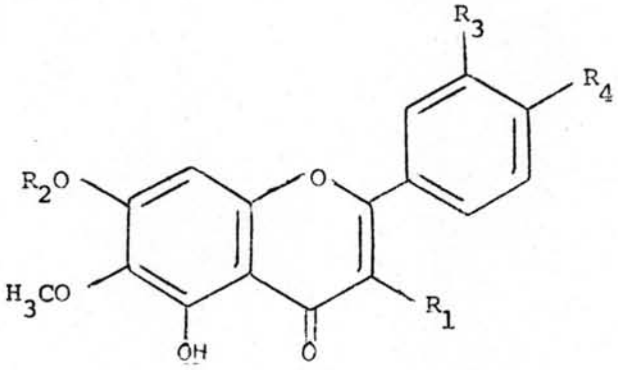
4. Flavonoids in Compositae

From present data available, it is clear that the Compositae is significantly heterogeneous in flavonoid patterns. A considerable range of flavonoid types and of glycosidic or other combinations have been encountered in different tribes and subtribes of the family. There is no special flavonoid structure that one can associate immediately with the family. For example, the flavolignans, such as silybin, occur in the fruit of *Silybum mariamun* Gaertn. are not entirely restricted to the family, since related structure do occur elsewhere (Heywood, Harborne and Turner, 1977).

In Compositae the common flavonols, kaempferol and quercetin and the common flavones apigenin and luteolin are widely distributed; they are represented by several of their glycosides. The flavonol myricetin with a trihydroxylated B-ring is absent. At the flavone level, however, trihydroxylation of the B-ring occurs. Some rare flavonoids also occur in many Compositae and account for a somewhat distinctive flavonnoid chemistry for the family. These features are: (Heywood, Harborne and Turner, 1977)

a) Frequent occurrence of 6-hydroxylated compounds such as quercetagetin (6-hydroxyquercetin), scutellarein (6-hydroxy apigenin) and 6-hydroxyluteolin.

b) Methylation of flavonoids occur free or as glycosides. Several of these compounds have cytotoxic properties (Kupchan *et al.*, 1969; Dobberstein *et al.*, 1974).



$R_1 = R_3 = R_4 = OCH_3$, $R_2 = CH_3$ Artemitin

$R_1 = R_4 = OCH_3$, $R_2 = H$, $R_3 = OH$ Jaceidin

$R_1 = R_3 = OCH_3$, $R_2 = H$, $R_4 = OH$ Centaureidin

$R_1 = R_2 = H$, $R_3 = R_4 = OCH_3$ Eupatilin

$R_1 - H$, $R_2 = CH_3$ $R_3 = OH$, $R_4 = OCH_3$ Eupatorin

$R_1 = R_2 = H$, $R_3 = R_4 = OH$ Eupafolin

Some methylated flavonoids of Compositae

c) Chalcone glycosids occur as flower pigments and are often accompanied by the corresponding aurones or flavanones. Dihydroflavonols are rare but not totally absent (Heywood, Harborne and Turner, 1977).

The strong tendency in Compositae to methylate flavonoids is shared by many sympetalous families and by the Rutaceae. Such a combination of flavonoids in Compositae is not found in any families near to

Compositae in taxonomic systems, e.g. the Capprifoliaceae, Rubiaceae or Campanulaceae. Indeed, the only other plant family where many of the same features are found together is the Leguminosae. The association between two families in terms of flavonoid chemistry has been remarked upon more than one occassion. The occurrence of isoflavonoids, which are found abundantly in the plant kingdom only in the subfamily Lotoideae of the Leguminosae and, in three Compositae genera (*Balduina, Eclipta, Wedelia)*, provides a further link between these two families (Heywood, Harborne and Turner, 1977).

In tribe Inuleae, the most characteristic feature of flavonoids is the presence of flavonols lacking B-ring hydroxylation. 6-and/or 8-hydroxyflavonols and their methyl ethers occur regularly in this tribe (Heywood, Harborne and Turner, 1977).

5. Dihydroflavonols in Compositae

5-Deoxy dihydroflavonol 3,7-glucoside

- *Georgia pellucida* (L.) Raah.

(Vandekerkhove, 1977)

Aromadendrin

- *Psiadia altissima* Benth. et Hook.

(Canonica et al., 1967)

7-Methyl aromadendrin

- *Eupatorium capillifolium* (Lam.) Small
- *E. foeniculaceum* Willd.

(Bohm, 1975)

- *E. padale* DC.

(Callegari, 1979)

7-Methyl aromadendrin

- *Psiadia altissima* Benth. et Hook.

(Canonica *et al.*, 1967)

5,7-Dimethyl aromadendrin

- *Eupatorium capillifolium* (Lam.) Small

(Bohm, 1975)

Dihydroquercetin

- *Silybum marianum* Gaertn.

(Becker and Schrall, 1977)

Dihydroquercetin 3-acetate

- *Tessaria dodoneifolia* (Hook et Arn.) Cabr.

(Karka *et al.*, 1977)

Dihydroquercetin 3', 7-dimethyl ether

- *Artemisia pygmaea* A. Gray
- *Eupatorium* (hybrid)

  (Bohm, 1975)

- *Jasiania tuberosa* DC.

  (Gonzale *et al.*, 1977)

Dihydroquercetin 7-methyl ether

- *Pulicaria undulata*(L.) Kostel

  (Khafagy *et al.*, 1976)

Silybum

- *Silybum marianum* Gaertn.

  (Becker and Schrall, 1977)

Silydianin

- *Silybum marianum* Gaertn.

  (Becker and Schrall, 1977)

6. Dihydroflavonols in other Plant Sources

7-Hydroxy dihydroflavonol

- *Platymiscium praecox* Mart. ex Benth., Papilionaceae

  (de Oliveira *et al.*, 1972)

7-Hydroxy 6-methoxy dihydroflavonol

- *Dalbergia ecastophyllum* Taub., Papilionaceae

  (*D. hecastophyllum-brownei* Pres. (Hooker and Jackson, 1886-1895))

  (Bohm, 1975)

Pinobanksin (5,7-Dihydroxy dihydroflavonol)

- *Cedrus libani* Barrel, Pinaceae
- *Eremophila alternifolia* R.Br., Myoporaceae
- *Morus mesozygia* Stapf, Moraceae

  (Bohm, 1975)
- *Pinus contorta* Dougl., Pinaceae

  (Hergert, 1956)

  P. formosana Hayata

  P. parviflora Sieb. & Zucc.

  (Wang *et al.*, 1970)
- *Platanus vulgaris* Spach, Platanaceae

    (*P. oriontalis* L. (Hooker and Jackson, 18856 b))

  (Bohm, 1975)
- *Prunus avium* L., Rosaceae

  P. vulgaris Schur.

    (*P. cerasus* L. (Hooker and Jackson, 18856 b))

  (Bohm, 1975)
- *Tilia plataphylla* C.A., Tiliaceae

    (*T. rubra* DC. (Hooker and Jackson) 18856 b))

  (Bohm, 1975)

Strobobanksin (5,7-Dihydroxy 6-methyl dihydroflavonol)

- *Pinus* spp., Pinaceae

  (Bohm, 1975)

3-Hydroxy isoloncocarpin

- *Lonchocarpus eriocarinalis* Micheli, Papilionaceae

  (Delle *et al.*, 1979)

3-Hydroxy isoloncocarpin

- *Lonchocarpus eriocarinalis* Micheli,

  (Delle *et al.*, 1979)

Alpinone (5-Hydroxy 7-methoxy dihydroflavonol)

- *Alpinia japonica* Miq., Zingiberaceae

  (Bohm, 1975)

3-Acetyl alpinone

- *Alpinia japonica* Miq., Zingiberaceae

  (Bohm, 1975)

Alnustinol (5,7-Dihydroxy 6-methoxy dihydroflavonol)

- *Alnus firma* Sieb. & Zucc., Betulaceae

  (Bohm, 1975)

Garbanzol (7,4'-Dihydroxy dihydroflavonol)

- *Capsella brusa-pastoris* Medic., Cruciferae
- *Cicer arietium* L., Papilionaceae

  (Bohm, 1975)

- *Onobrychis viciaefolia* Scop., Papilionaceae

  (Ingham, 1978)

Lecontin (Garbanzol 3-glucoside)

- *Bapticia lecontii* Torr, & Gray, Papilionaceae

  (Markham and Mabry, 1968 a, b)

7,8,4'-Trihydroxy dihydroflavonol

- *Acacia auriculaeformis* A. Cunn. ex Benth., Mimosaceae

  A. maidenii F. Muell.

  A. orites Pedley

  (Drewes and Houx, 1966; Tindale and Houx, 1969)

Dihydrokaempferol, Aromadendrin (5,7,4'-Trihydroxy dihydroflavonol)

- *Abies alba* Mill., Pinaceae
  (Kowalska, 1979)
- *Aflatunia ulmifolia*, Rosaceae
  (Bohm, 1975)
- *Afzelia discolor* Hort. ex Steud., Caesalpiniaceae
  (King and Acheson, 1950)
- *Calligonum leucocladum* Bunge, Polygonaceae
  (Dubinin *et al.*, 1976)
- *Cedrus libani* Barrel, Pinaceae
- *Cercidiphyllum japonicum* Sieb. & Zucc., Cercidiphyllaceae
- *Chlorophora tinctoria* Gaudich, Moraceae
- *Citrus paradisi* Macf., Rutaceae
  (Bohm, 1975)
- *Echites hirsuta* Rich., Apocynaceae
  (Chien *et al.*, 1979)
- *Equisetum arvense* L., Equisetaceae
  (Syrchina *etal* ., 1979)
- *Eucalyptus acmenieides* Schau., Myrtaceae
  E. agglomerata Maiden
  (Hillis, 1967 a)
  E. alba Reinw. ex Blume
  (Hillis, 1967 b)

Aromadendrin (Cont.)

Ecalyptus albens Miq.

(Hillis, 1967 c)

E. amplifolia Naud.

(Hillis, 1967 b)

E. annulata Benth.

E. astringens Maiden

(Hillis, 1967 d)

E. baxteri R.Br. ex Benth.

(Hillis, 1967 a)

E. blakelyi Maiden

(Hillis, 1967 b)

E. blaxlandii Maiden & Cambage

(Hillis, 1967 a)

E. brevifolia F. Muell.

(Hillis, 1967 b)

E. burracoppinensis Maiden & Blakely

(Hillis, 1967 d)

E. caleyi Maiden

(Hillis, 1967 c)

E. caliginosa Blakely & Mckie

(Hillis, 1967 a)

E. calophylla R.Br.

(Bohm, 1975)

E. camaldulensis Dehnh.

(Hillis, 1966 a)

Aromadendrin (Cont.)

Ecalyptus camphora R.T. Baker

E. dealbata A. Cunn. ex Schau.

(Hillis, 1967 b)

E. decipiens Endl.

(Hillis, 1967 c)

E. deglupta Blume

(Hillis, 1967 a)

E. diversicolor F. Muell.

E. exserta F. Muel.

(Hillis, 1967 b)

E. flocktoniae Maiden

E. forrestiana Diels

E. gillii Maiden

(Hillis, 1967 d)

E. haemastoma Sm.

(Hillis, 1967 a)

E. hemiphloia F. Muell.

(Bohm, 1975)

E. largiflorens F. Muell.

(*E. bicolor* A. Cunn. ex Hook. (Hooker and Jackson, 1885 a))

(Hillis, 1967 c)

E. lehmanni Preiss ex Schau.

E. leptopoda Benth.

(Hillis, 1967 d)

Aromadendrin (Cont.)

Ecalyptus maideni F. Muell.

E. major(Maiden) Blakely

(Hillis, 1967 b)

E. melliodora A. Cunn. ex Schau.

(Hillis, 1967 c)

E. microcorys F. Muell

E. mitchelliana Cambage

(Hillis, 1967 a)

E. moluccana Roxb.

(Hillis, 1967 c)

E. nova-anglica Deane & Maiden

(Hillis, 1967 b)

E. nutans F. Muell.

(Hillis, 1967 d)

E. obliqua L' Herit.

E. oblonga DC.

(Hillis, 1967 a)

E. occidentalis Endl.

(Hillis, 1967 d)

E. odorata Behr.

(Hillis, 1966 a)

E. oleosa F. Muell.

(Hillis, 1967 d)

E. oreades R.T. Baker

(Hillis, 1967 a)

Aromadendrin (Cont.)

Eucalyptus paniculata Sm.

(Hillis, 1967 c)

E. paramattensis C. Hall

E. pellita F. Muell.

(Hillis, 1967 b)

E. phaeotricha Blakely & Mckie

(Hillis, 1967 a)

E. polyanthemos Schau.

E. preissiana Schau.

E. punctat DC.

E. quadrangulata Deane & Maiden

(Hillis, 1967 b)

E. radiata Sieb. & Zucc.

(*E. amygdalina* Labill (Hooker and Jackson, 18885 a))

(Hillis, 1967 a)

E. remota Blakely

(Hillis, 1967 a)

E. resinifera Sm.

(Hillis, 1967 b)

E. rossii R.T. Baker

(Hillis, 1967 a)

E. salmonophloia F. Muell.

E. salubris F. Muell.

(Hillis, 1967 d)

Aromadendrin (Cont.)

Ecalyptus scoparia Maiden

E. seeana Maiden

(Hillis, 1967 b)

E. spatholata Hook.

(Hillis, 1967 d)

E. tereticornis Sm.

(Hillis, 1967 b)

E. thozetiana F. Muell. ex R.T. Baker

(Hillis, 1967 c)

E. tindalae Blakely

(Hillis, 1967 a)

E. wandoo Blakely

(Hillis, 1967 d)

E. laevopinea R.T. Baker

(Hillis, 1967 a)

- *Larix dahurica* Turcz., Pinaceae

L. europaea DC.

L. kaempferi Fortune ex Gord.

L. laricina C. Kock

(*L. americana* Michx. (Hooker and Jackson, 1885 b))

(Bohm. 1975)

L. leptolepsis Hort. ex Endl.

L. lyallii Parl.

L. occidentalis Nutt.

L. sibirica Ledeb.

(Bohm, 1975)

Aromadendrin (Cont.)

- *Matthiola incana*, Cruciferae

  (Forkman, 1980)

- *Morus alba* L., Moraceae

  M. indica L.

  M. lacta Mildbr.

  M. rubra L.

  M. serrata Roxb.

  (Deshpande, 1975)

- *Nothofagus cliffortioides* Oerst., Fagaceae

  (*Fagus cliffortioides* Oerst. (Hooker and Jackson, 1885 b))

- *Nothofagus dombeyi* Blume, Fagaceae

  N. fusca Oerst.

  N. solanderi Oerst.

  N. truncata Cockayne

- *Platanus orientalis* L., Platanaceae

- *Podocarpus spicatus* R. Br., Podocarpaceae

  (Bohm, 1975)

- *Picea ajanensis* Fisch. ex Trautv., Pinaceae

  (Ivanova *etal.*, 1976)

  P. excelsa (Lam.) Lk.

  (Kowalska, 1979)

- *Pinus contorta* Dougl., Pinaceae

  (Hergert, 1956)

  P. palustris Mill.

  P. resinosa Ait.

Aromadendrin (Cont.)

- *Pinus taeda* L.

  (Strohl and Seikel, 1965)

- *Prunus aequinotialis* Miyoshi, Rosaceae

  P. avium L.

  (Bohm, 1975)

  P. cerasus L.

  (Nagarajan and Parmar, 1977)

  P. cornuta Wall.

  (*P. padus* L. (Hooker and Jackson, 1885 b))

  (Bohm, 1975)

  P. mahaleb L.

  P. maximowiczii Rupr.

  P. persica Stokes

  P. spinosa L.

  (Bohm, 1975)

- *Rhododendron beanianum* Cowan, Ericaceae

  R. Coelium Balf. & Farrer

  R. croceum Balf. & Smith.

  R. cuneatum W.W. Smith.

  R. decorum Franch.

  R. elliotii Watt. Lace & W.W.Smith.

  R. heliolepis Franch.

  R. megeratum Ealf. & Forr.

  R. oreotrephes W.W.Smith.

  R. pachytrichum Franch.

Aromadendrin (Cont.)

Rhododendron phaeochrysum Balf. & Smith

R. rirei Hemsl & Wils.

R. rupicola Smith.

R. schlippenbachii Maxim.

R. simiarum Hance

R. stewartianum Diels

R. thomsonii Hook.

R. wightii Hook.

(Harborne and Williams, 1971)

- *Stellera chamaejasme* L., Miliaceae

(Rezanova and Bubeeva, 1976)

- *Thuja orientalis* L., Cupressaceae

- *Tilia platyphylla* C.A., Tiliaceae

(*T. rubra* DC. (Hooker and Jackson, 1885 b))

(Bohm, 1975)

Engelitin (Aromadendrin 3-rhamnoside)

- *Engelhardtia formosana* Hayata, Juglandaceae

E. flocktoniae Maiden, Myrtaceae

E. hemiphloia F. Muell.

E. salubris F. Muell.

E. aideroxylon A. Cunn.

(*E. leucoxylon* F. Muell. (Hooker and Jackson, 1885 a))

(Bohm, 1975)

- *Nothofagus procera* Oerst., Fagaceae

(Bohm, 1975)

Aromadendrin 7-glycoside

- *Matthiola incane*, Cruciferae

  (Forkmann, 1980)

- *Primula sinensis* Sabine ex Lindl., Primulaceae

  (Bohm, 1975)

Aromadendrin 7-glycoside

- *Prunus avium* L., Rosaceae

  P. cerasus L.

  P. mahaleb L.

  (Bohm, 1975)

Aromadendrin 7-rhamnoside

- *Exocarpus cupressiformis* Hook. & Arn., Santalaceae

  (*E. gaudichaudii* A. DC., (Hooker and Jackson, 1885 a))

  (Bohm, 1975)

- *Chamaecyparis obtusa* Sieb. & Zucc., Cupressaceae

  (*Thuja obtusa* Sieb. & Zucc. (Hooker and Jackson, 1885 a))

  (Bohm, 1975)

Aromadendrin 4'-xyloside

- *Cleome viscosa* L., Capparidaceae

  (Chauhan *et al.*, 1980)

7-Methyl aromadendrin *(trans)*

- *Eucalyptus citriodora* Hook., Myrtaceae

  E. maculata Hook.

- *Populus alba* L., Salicaceae

- *Prunus avium* L., Rosaceae

  (Bohm, 1975)

7-Methyl aromadendrin *(cis)*

- *Glycyrrhiza glabra* L. var. *glandulifera* Waldstein et Kitaibel, Papilionaceae
- *G. glabra* L. var. *typica* Regel et Herder

(Bohm, 1975)

4'-Methyl aromadendrin

- *Prunus communis* Huds., Rosaceae

(*P. spinosa* L. (Hooker and Jackson, 1885 b))

(Bohm, 1975)

P. domestica L.

(Bohm, 1975)

Dihydroprunomenin (5-hydroxy,8,4'-dimethoxy dihydroflavonol) 7-0-glucoside)

- *Prunus mune* Sieb. & Zucc., Rosaceae

(Bohm, 1975)

Keyakinol (5,4'-Dihydroxy,7-methoxy 6-glucosyl dihydroflavonol)

- *Zelkova serrata* Makino, Urticaceae

(Bohm, 1975)

Phellamurin (Dihydroflavonol with monocarboxylated 5 Carbons at C(8)

- *Phellodendron amurense* Rupr., Rutaceae

P. japonicum Maxim

(Bohm, 1975)

Dihydrophelloside (Phellamurin 7-0-glucoside)

- *Phellodendron amurense* Rupr., Rutaceae

P. sachalinense Sargent

(Bohm, 1975)

Phellavin (C-6 Isomer of Phellamurin)

- *Phellodendron amurense* Rupr., Rutaceae

P. lavallei Dode

(Bohm, 1975)

7,4'-Dimethyl aromadendrin

- *Cephalanthus spathelliferus* Baker, Rubiaceae

(Bohm, 1975)

7,4'-Dimethyl aromadendrin 5-0-glucoside

- *Cephalanthus spathelliferus* Baker, Rubiaceae

(Bohm, 1975)

7,8,4'-Trihydroxy dihydroflavonol

- *Acacia auriculaeformis* A. Cunn. ex Benth., Mimosaceae

A. maidenii F. Muell.

A. orites Pedley

(Tindale & Roux, 1969)

Fustin (Dihydrofisetin; 7,3',4'-Trihydroxydihydroflavonol)

- *Acacia adunca* A. Cunn. ex G. Don., Mimosaceae

(*A. crassiuscula* Wendl. (Hooker and Jackson, 1885 a))

(Tindale & Roux, 1969)

A. baileyana F. Muell.

A. binervata DC.

A. botrycephala Desf.

(*A. discolor* Willd (Hooker and Jackson, 1885 a))

(Tindate & Roux, 1969)

A. buxifolia A. Cunn.

Fustin (Cont.)

Acacia calamifolia Sweet

A. *cardiophylla* A. Cunn. ex Benth.

A. *Clunies-rossiae* Maiden

A. *cultriformis* A. Cunn. ex G. Don.

A. *dealbata* Link.

A. *decona* Reichb.

A. *decurrens* Willd.

A. *deamii* (Britton & Rose) Standley

A. *elata* A. Cunn. ex Benth.

A. *falciformis* DC.

(*A. penninervis* Sieber ex Dc. (Hooker and Jackson, 1885 a))

A. *filicifolia* Cheel & Welch

A. *fimbrita* A. Cunn. ex G. Don.

(*A. prominens* A. Cunn. ex G. Don., (Hooker and Jackson, 1885 a))

A. *irrorata* Sieber ex Spreng.

A. *kettlewelliae* Maiden

A. *lanigera* A. Cunn.

A. *mabellae* Maiden

A. *mearnsii* De Wild.

A. *mollifolia* Maiden & Blakely

A. *neriifolia* A. Cunn. ex Benth.

A. *o'shanesii* F. Muell.

A. *parramattensis* Tindale

Fustin (Cont.)

Acacia pycnantha Benth.

A. rubida A. Cunn.

A. silvestris Tindale

A. trachyphloia Tindale

A. vestita Ker-Gawl.

(Tindale & Roux, 1969)

- *Capsella brusa-pastoris* Medic., Cruciferae
- *Mimosa pudica* L., Mimosaceae
- *Platanus vulgaris* Spach., Platanaceae

  (*P. orientalis* L. (Hooker and Jackson, 1885 b))
- *Rhus cotinus* L., Anacardiaceae

  R. glabra L.

  R. succedanea L.

  R. javanica L.

  (*R. semialata* Murr. (Hooker and Jackson , 1885 b))
- *Schinopsis balansae* Engl., Anacardiaceae

  S. lorenzii Engl.
- *Sequoia gigantea* Lindl. & Gord., Taxodiaceae
- *Tilia platyphylla* C.A., Tiliaceae

  (*T. rubra* D.C. (Hooker and Jackson, 1885 b))

(Bohm, 1975)

Fustin 3-glucoside

- *Baptisia lecontii* Torr. & Gray, Papilionaceae

  (Markham and Mabry, 1968 a,b)

7,8,3',4'-Tetrahydroxy dihydroflavonol

- *Acacia acminata* Benth., Mimosaceae

  A. aneura F.Muell.

  A. aulacocarpa A. Cunn. ex Benth.

  A. burrowii Maiden

  A. cambagei R.T.Baker

  A. cheelii Blakely

  A. cunninghamii Hook.

  A. doratoxylon A. Cunn.

  (Tindale & Roux, 1969)

  A. excelsa Benth.

  (Bohm, 1975)

  A. floribunda Willd.

  (*A. longifolia* Willd.(Hooker and Jackson, 1885 a))

  A. glaucescens F. Muell.

  A. harpophylla F. Muell.

  A. implexa Benth.

  A. melanoxylon R.Br.

  A. nigrescens Oliver

  A. obtusifolia A. Cunn.

  (*A. longifolia* Willd.,(Hooker and Jackson, 1885 a))

  A. oswaldii F. Muell.

  A. pendulata A. Cunn. ex G. Don.

  A. pubifolia Pedley

  A. pycnostachya F. Muell.

  A. rigens A. Cunn. ex G. Don.

7,8,3',4'-Tetrahydroxy dihydroflavonol (Cont.)

Acacia salicina Lindl.

(Tindale & Roux, 1969)

A. saxatilis S. Moore

(Fourie *et al.*, 1975)

A. sowdenii Maiden

(Bohm, 1975)

A. trineura F. Muell.

A. verniciflua A. Cunn.

(Tindale & Roux, 1969)

Dihydroquercetin; Taxifolin; Distylin (5,7,3',4'-Tetrahydroxy dihydroflavonol)

- *Abies nephrolepis* Maxim., Pinaceae

  (*A. veitchii* Lindl., (Hooker and Jackson, 1885 a))

  (Gromova *et al.*, 1978)

- *Austrocedrus chilensis* (D.Don) Florin & Boutelje, Cupressaceae
- *Cedrus libani* Barrel, Pinaceae

  (Bohm, 1975)

- *Coleus aromaticus* Benth., Labiatae

  (Brieskorn and Riedel, 1979)

- *Cytisus laburnum* L.

  (*Laburnum vulgare* L. (Hooker and Jackson, 1885 A))

  (Bohm, 1975)

- *Distylium racemosum* Sieb. & Zucc., Hamalidaceae

  (Bohm, 1975)

- *Equisetum arvense* L., Equisetaceae

  (Syrchina *et al.*, *1976*)

Dihydroquercetin (Cont.)

- *Erica arborea* L. Ericaceae

  (Bohm, 1975)

- *Eucalyptus coronata* Tausch ex Maiden, Myrtaceae

  (Hillis, 1966 a)

  E. alba Rein W. ex Blume

  (Hillis, 1967 b)

  E. astringens Maiden

  (Hillis, 1967 d)

  E. flocktoniae Maiden

  E. forrestiana Diels

  (Hillis, 1967 c)

  E. radiata Sieber ex DC.

  (*E. amygdalina* Labill (Hooker and Jackson, 1885 a))

  (Hillis, 1967 a))

  E. salmonophloia F. Muell.

  E. salubris F. Muell.

  (Hillis, 1967 d)

- *Larix dahurica* Turica., Pinaceae

  (*L. europaea* DC. (Hooker and Jackson, 1885 a))

  L. kaempferi Fortune ex Gord., Pinaceae

  L. laricina C. Koch., Pinaceae

  (*L. americana* Michx. (Hooker and Jackson, 1885 b))

  L. lyallii Parl.

  (Bohm, 1975)

  L. leptolepsis Gord.

  (Takehara and Sasayu, 1980)

Dihydroquercetin (Cont.)

- *Larix occidentalis* Nutt.
  - *L. sibirica* Ledeb.
  - (Bohm, 1975)
- *Liquidambar styraciflua* L., Hamamelidaceae
- *Lophophytum leandri* Eichl., Balanophoraceae
- *Madhuca latifolia* J. F. Gmel., Sapotaceae
- *Machilus thunbergii* Sieb. & Zucc., Lauraceae
  - (Bohm, 1975)
- *Melanorrhea* sp., Anacardiaceae
  - (King *et al.*, 1962)
- *Mimosops elengi* L. Sapotaceae
  - *M. manilkara* G. Don.
    - (*M.kauki* L. (Hooker and Jackson, 1885 b))
- *Nothofagus cliffortioides* Oerst., Fagaceae
    - (*Fagus cliffortioides* Oerst. (Hooker and Jackson, 1885b))
  - *N. fusca* Oerst.
  - *N. solandri* Oerst.
  - *N. truncata* Cockayne
- *Ocotea usambarensis* Engl., Lauraceae
  - (Bohm, 1975)
- *Picea ajanensis* Fisch. ex Trautv., Pinaceae
  - *P. korariensis* Nakai
  - (Gromova *et al.*, 1978; Ivanova *et al.*, 1979)
  - *P. obovata* Ledeb.
  - (Shibanova *et al.*, 1977)

Dihydroquercetin (Cont.)

- *Picea sitchensis* Trautv. & Mey.

  (Bohm, 1975)

- *Pinus sibirica* Turcz., Pinaceae

  (*Abies sibirica* Ledeb. (Hooker and Jackson, 1885 b))

  (Gromova *et al*.,1978)

  P. echinata Mill

  P. resinosa Ait.

  (Strohl and Seikel, 1965)

  P. sylvestris L.

  (Gromova *et al*., 1978)

  P. taeda L.

  (Strohl and Seikel, 1965)

- *Pistacia chinensis* Bunge, Anacardiaceae
- *Platanus vulgaris* Spach, Platanaceae

  (*P. orientalis* L. (Hooker and Jackson, 1885 b))

- *Podocarpus spicatus* R. Br., Podocarpaceae
- *Poupartia axillaris* (Roxb.) King & Prain,, Anacardiaceae
- *Prunus avium* L., Rosaceae

  P. campanulata Maxim

  (Bohm, 1975)

  P. cerasus L.

  (Nagarajan and Parmar, 1977)

  P. mahaleb L.

  P. nipponica Matsum.

  P. spinosa L.

Dihydroquercetin (Cont.)

- *Prunus ssiori* F. Schmidt, Rosaceae
- *Pseudotsuga douglasii* Carr., Pinaceae
- *Rhododendron formosanum* Hemsl., Ericaceae

(Bohm, 1975)

R. ambiguum Hemsl.

R. amoenum Planch.

R. anthopogan D. Don.

R. araiophyllum Balf. & W.W.Smith

R. arizelum Balf. & Forr.

R. augustinii Hemsl

R. baileya Balf.

R. brevistylum Franch.

R. calendulaceum Torr.

R. calostrotum Balf. & Ward

R. campanulatum Don.

R. campylocarpum Hook.

R. cantabile Balf. ex Hutch

R. canadense (L.) Torr.

R. capitatum Maxim

R. carolinianum Rehder

R. cephalanthum Franch.

R. charidotes Balf. & Farrer

R. chasmanthum Diels.

R. chrysum Balf. & Ward

R. cinnabarinum Hook.

(Harborne and Williams, 1971)

Dihydroquercetin (Cont.)

- *Rhododendron complexum* Balf. & Smith , Ericaceae

  R. concatenans Hutch.

  R. coryanum Tagg. & Forr.

  R. coryphaeum Balf. & Forr.

  R. crassum Franch.

  R. croceum Balf. & Smith

  R. cuneatum W.W.Smith

  R. dasypetalum Balf. & Forr.

  R. dauricum L.

  R. desquamatum Balf. & Forr.

  R. drumonium Balf. & Ward

  R. dryophyllum Balf. & Forr.

  R. edgarianum Rehder & Wilson

  R. edgeworthii Hook.

  R. eximum Nutt.

  R. fictolacteum Balf.

  R.flavum Balf. & Smith

  R. fulgens Hook. L & S Form

  R. floribundum Franch.

  R. hemitrichotum Balf. & Forr.

  R. hippophaeoides Balf. & Smith

  R. idoneum Balf. & Smith

  R. impeditum Balf. & Smith

  R. indicum Sweet.

  R. insigne Hemsl. & Wils.

  (Harborne and Williams, 1971)

Dihydroquercetin (Cont.)

- *Rhododendron intricatum* Franch., Ericaceae
  - *R. juncundum* Balf. & Smith
  - *R. kaempferi* Planch.
  - *R. keiskai* Miq.
  - *R. keleticum* Balf. & Forr.
  - *R. kongboense* Ward ex Rothschild
  - *R. kotschyii* Simon K.
  - *R. lacteum* Franch.
  - *R. leucopis* Tagg.
  - *R. litangense* Balf.
  - *R. ludlowii* Cowan
  - *R. macabeanum* Watt. ex Balf.
  - *R. manipurense*BBalf. & Watt.
  - *R. megaratum* Balf. & Forr.
  - *R. microleucum* Hutch.
  - *R. minus* Michx.
  - *R. mucronatum* (Bl.) Don.
  - *R. mucronulatum* Turez.
  - *R. myiagrum* Balf. & Forr.
  - *R. nitens* Hutch.
  - *R. occidentale* A.Gray
  - *R. oreotrephes* W.W.Smith
  - *R. orthocladium* Balf. & Forr.
  - *R. ovatum* Maxim
  - *R. paludosum* Hutch. & Ward

(Harborne and Williams, 1971)

Dihydroquercetin (Cont.)

- *Rhododendron pemakoense* Ward, Ericaceae

R. phaeochrysum Blaf. & Smith

R. praestans Balf. & Smith

R. pseudoyanthinum Balf.

R. pumilum Hook.

R. primulaeflorum Bareau & Franch..

R. racemosum Franch.

R. ramosissimum Franch.

R. rex Levl.

R. rigidum Franch.

R. riparium Ward

R. rirei Hemsl. & Wils.

R. rubiginosum Franch.

R. rupicola Smith

R. russatum Balf. & Forr.

R. saluenense Franch.

R. schlippenbachii Maxim

R. scintillans Balf. & W.W.Smith

R. semnoides Tagg. & Forr.

R. sinogrande Balf.& W.W.Smith

R. spiciferum Franch.

R. tatsienense Franch.

R. traillianum Forr. & W.W. Smith

R. vaseyi A. Gray

R. wallichii Hook.

(Harborne and Williams, 1971)

Dihydroquercetin (Cont.)

- *Rhododendron wardii* W.W.Smith

  R. wightii Hook.

  R. williamsianum Rehd.& Wils.

  R. yedoense (Maxim) Regal

  R. yunnanense Franch.

  (Harborne and Williams, 1971)

- *Rhus javanica* L., Anacardiaceae

  (*R. semialata* Murr. (Hooker and Jackson, 1885 b))

- *Sequoia gigantia* Lindl. & Gord., Taxodiaceae

- *Tilia platyphylla* C.A., Tiliaceae

  (*T. rubra* DC. (Hooker and Jackson, 1885b))

- *Thuja orientalis* L., Cupressaceae

  T. plicata Donn

  (Bohm, 1975)

- *Urginea maritima* Baker , Liliaceae

  (*U. scilla* Steinh. (Hooker and Jackson, 1885 b))

  (Vega, 1976)

- *Zea mays* L., Graminae

  (McCormida, 1979)

Astilbin (Taxifolin 3-rhamnoside)

- *Astilbe odontophylla* Miq., Saxifagaceae

  (*A. chinensis* Franch. & Sav. (Hooker and Jackson, 1885 a))

  A. thunbergii Miq., Saxifagaceae

- *Litsea glauca* Siebold, Lauraceae

- *Lyonia ovalifolia* Hort. ex Gord., Ericaceae

- *Quintinia serrata* A. Cunn., Saxifagaceae

  (Bohm, 1975)

Taxifolin 3-xyloside

- *Chamaecyparis obtusa* Sieb. & Zucc., Cupressaceae

  (*Thuja obtusa* Sieb. & Zucc. (Hooker and Jackson, 1885 a))

Taxifolin 3-xyloside (Cont.)

- *Leucothoe keiskei* Miq., Ericaceae

  (Bohm, 1975)

Taxifolin 4'-glucoside

- *Petunia hybrida* Hort. ex Vilm., Solanaceae

  (Bohm, 1975)

- *Urginea maritima* Baker, Liliaceae

  (*U.Scilla* Steinh (Hooker and Jackson, 1885 b))

  (Vega, 1976)

Taxifolin 3-glucoside

- *Abies nepholepsis* Maxim., Pinaceae

  (*A. veitchii* Lindl. (Hooker and Jacson, 1885 a))

  (Gromova *et al.*, 1978)

- *Calluna vulgaris* Salisb., Ericaceae

  (Olechnowiez et al., 1979)

- *Chamaecyparis obtusa* Sieb. & Zucc., Cypressaceae

  (*Thuja obtusa* Sieb. & Zucc. (Hooker and Jackson, 1885 a))

- *Chamaecyparis pisifera* Sieb. & Zucc., Cypressaceae

  (*Thuja pisifera* Sieb. & Zucc. (Hooker and Jackson, 1885 a))

Taxifolin 3-glucoside (Cont.)

- *Picea ajanensis* Fisch. ex Trautv., Pinaceae

  P. korariensis Nakai

  (Bohn, 1975)

- *Pinus contorta* Dougl.

  (Hergert, 1956)

  Pinus jeffreyii A. Murr.

  P. sibirica Turez

    (*Abies sibirica* Turez., (Hooker and Jackson, 1885 b))

  P. sylvestris L., Pinaceae

  (Hergert, 1956)

- *Prunus avium* L., Rosaceae

  P. mahaleb L., Rosaceae

  (Bohm, 1975)

Taxifolin 3'-glucoside

- *Abies amabilis* Forb., Pinaceae
- *Cedrus libani* Barrel, Pinaceae
- *Larix occidentalis* Nutt., Pinaceae
- *Picea sitchensis* Trautv. & Mey., Pinaceae
- *Pseudotsuga douglasii* Carr., Pinaceae
- *Thuja plicata* Donn, Cupressaceae
- *Tsuga heterophylla* Sargent, Pinaceae

  (Bohm, 1975)

Taxifolin 3-glycoside

- *Eucryphia milliganii* Hook., Eucryphiaceae

    (*E. billardieri* Spach (Hooker and Jackson, 1885 a))

  (Bohm, 1975)

Taxifolin 3-O-galactoside

- *Rhododendron canescens* G. Don., Ericaceae

  (*R. nudiflorum* Torr. (Hooker and Jackson, 1885 a))

  (King, 1978)

Padmatin (5,3',4'-Trihydroxy 7-methoxy dihydroflavonol)

- *Prunus paddum* Roxb. ex Wall., Rosaceae

  (Bohm, 1975)

Padmatin 3-glucoside (Dihydroquercetin 7-methyl ether 3-glucoside)

- *Cassia javanica* L., Caesalpiniaceae

  (Bohm, 1975)

6-C-Methyldihydroquercetin

- *Populus alba* L., Salicaceae

  (Bohm, 1975)

Deodendrin (5.6.3',4'-Tetrahydroxy 8-methyl dihydroflavonol)

- *Cedrus deodara* Loud., Pinaceae

  (Bohm, 1975)

  (*C. libani* Barrel, (Hooker and Jackson, 1885 a))

7,8,3',4,-Tetrahydroxy dihydroflavonol

- *Acacia acuminata* Benth., Mimosaceae

  A. aulacocarpa A. Cunn. ex Benth.

  A. aneura F. Muell.

  A. burrowii Maiden

  (Tindale & Roux, 1969)

  A. cambagei R.T. Baker

  (Bohm, 1975)

7,8,3',4'-Tetrahydroxy dihydroflavonol (Cont.)

Acacia cheelii Blakely

A. cunninghamii Hook.

A. doratoxylon A. Cunn.

(Tindale & Roux, 1969)

A. excelsa Benth.

(Bohm, 1975)

A. floribunda Wild.

(*A. longifolia* Wild. (Hooker and Jackson, 1885 a))

A. glaucescens Wild.

A. harpophylla F. Muell. ex Benth.

A. implexa Benth.

A. melanoxylon R.Br.

A. nigrescens Oliver

A. obtusifolia A. Cunn.

A. oswaldii F. Muell.

A. pendula A. Cunn. ex G. Don.

A. pubifolia Pedley

A. rigens A. Cunn. ex G. Don.

(Tindale and Roux, 1969)

A. salicina Lindl.

A. sowdenii Maiden

(Bohm, 1975)

A. trineura F. Muell.

A. verniciflua A. Cunn.

(Tindale and Roux, 1969)

7,8,3',4'-Tetrahydroxy dihydroflavonol (Cont.)

Albizzia adianthifolia

(Candy *et al.*, 1979)

Dihydromorin (5,7,2',4'-Tetrahydroxy dihydroflavonol)

Artocarpus heterophyllus Lam., Moraceae

(*A. integrifolia* L.)

A. hirsuta Lam.

Chlorophora tintoria Gaudich

Maclura pomifera Miq.

Morus alba L.

M. indica L.

M. mesozygia Stapf.

M. rubra L.

M. serrata Roxb.

(Bohm, 1975)

Dihydroisorhamnetin (4',5,7-Trihydroxy 3'-methoxy dihydro flavonol)

- *Dillenia indica* L.,

(Pavanasasivam and Sultanbawa, 1975)

Benthamianin (Peltonoid type)

- *Distemonanthus benthamianus* Baillon, Caesalpiniaceae

(Malan and Roux, 1980)

Peltonoid 5-methyl ether

- *Goniorrhachis marginata* Taub., Caesalpiniaceae

(Bohm, 1975)

2,3-*trans* Pubeschin

- *Peltogyne pubescens* Benth., Caesalpiniaceae

2,3-*trans* Pubeschin

Peltogyne venosa Benth.

(Malan and Roux, 1974)

Sophoronol

- *Sophora tomentosa* L., Papilionaceae

(Delle et al., 1977)

Dihydrorobinetin (7,3',4'5'-Tetrahydroxy dihydroflavonol)

- *Adenanthera pavonina* L., Mimosaceae
- *Mimosa pudica* L. Mimosaceae
- *Robinia pseudocacia* L. Papilionaceae
- *Schinopsis* sp. Anacardiaceae
- *Wisteria sinensis* Sweet. Papilionaceae

(*W. chinensis* DC. (Hooker and Jackson, 1885 b))

(Bohm, 1975)

Ampleopsin, Dihydromyricetin (5,7,3',4',5'-Pentahydroxy dihydroflavonol)

- *Adenanthera pavonina* L. Mimosaceae
- *Ampleopsis meliaefolia*, Vitaceae
- *Cercidiphyllum japonicum* Sieb. & Zucc., Cercidiphyllaceae
- *Eugenia jambolana* Lam., Myrtaceae

(Bohm, 1975)

- *Leptarrhena pyrolifolia* Ser., Saxifragaceae

(*L. amplexifolia* R. Br. (Hooker and Jackson, 1885 b))

(Miller and Bohm, 1980)

Ampleopsin (Cont.)

- *Pinus contorta* Dougl., Pinaceae
  (Hergert, 1956)
- *P. latifolia* Engelm.
  (Hergert, 1956)
- *Rhododendron acroanthum* Balf. & Smith, Ericaceae
  R. aeruginosum Hook.
  R. capitatum Maxim
  R. chamaeunum Balf. & Forr.
  R. cinnabarinum Hook.
  R. contabile Balf. ex Hutch.
  R. dasypetalum Balf. & Forr.
  R. decorum Franch.
  R. elliotii Watt. Lace & W.W. Smith
  R. flavum Balf. & Smith
  R. impeditum Balf. & Smith
  R. lanigenum Tagg.
  R. leucaspis Tagg.
  R. nitens Hutch.
  R. niveum Cowan
  R. rex Levl.
  R. rubiginosum Franch.
  R. scintillans Balf. & W.W. Smith
  R. sinogrande Balf. & Smith
  R. sphaeranthum Balf. & W.W. Smith
  R. sylvaticum Ward

Ampleopsin (Cont.)

Rhododendron trichostomum Franch.

R. vernicosum Franch.

R. wightii Hook.

(Harborne and Williams, 1971)

- *Soymidia febrifuga* Juss., Miliaceae

(Rao *et al.*, 1979)

Dihydrosyringetin (5,7,4' Trihydroxy 3',5'-dimethoxy dihydroflavonol)

- *Soymidia febrifuga* Juss., Miliaceae

(Rao et al., 1979)