

## CHAPTER II

### HISTORICAL

#### The Family Periplocaceae

##### 1. Introduction to Periplocaceae

Periplocaceae is a family of about 40-50 genera and almost 200 species in the tropics and the warm temperate regions of the old world, especially tropical Africa (Shaw, 1988). Plants in this family are incorporated in Asclepiadaceae by most authors. This, however, is considered unjustified by some as these two families although are closely related to each other, they still have some distinguished differences. According to Hutchinson's classification, Periplocaceae was separated as a family in order Apocynales, other families of which include Plocospermaceae, Apocynaceae, and Asclepiadaceae (Hutchinson, 1960).

The description of plants in the Periplocaceae is as below (Shaw, 1988; Dassanayake, 1983; Hutchinson, 1960):-

Perennial laticiferous herbs or shrubs with wiry or softly woody stems, erect, scrambling or twining; rootstock sometimes tuber-like, fleshy or woody. Leaves opposite, simple, entire, linear to obovate, pinnately nerved; stipule absent, but sometimes a nodal stipular annulus, which may become enlarged, indurated and variously dissected. Flowers bisexual, but sometimes functionally unisexual and then dioecious, actinomorphic, 5-merous, usually small, rarely

large and showy . Inflorescences terminal or lateral cymes ; bracts and bracteoles minute . Calyx 5 , tube short or obsolescent, valvate or imbricate, but opening very early. Corolla sympetalous, 5-lobed or-fid, tube short or sometimes as long as or longer than lobes; lobes usually contorted, rarely .valvate or imbricate, overlapping in bud to the right. Corona of five free lobes of various form arising from base of stamen filaments, sometimes of linear or fili-form scales, rarely absent or reduced to minute tubercles. Stamens 5 , alternating with the corolla lobes and inserted at or near the base of the tube, filaments free at the apex or from the base ; anthers 2-locular , introse , basifixed , connivent at the apex above the expanded style-head , longi-tudinally dehiscent along their inner side; pollen granular, the grains united in tetrads, discharged on the five spoon-shaped pollen-carriers alternating with the anthers, derived from and attached to the style-head; disk absent. Carpels 2 , free from each other but united through the expanded style-head; stigmatic surfaces concealed by the pollen-carriers; ovules numerous, multiseriate on a single adaxial placenta. Fruits of two follicles, these parallel or divergent, sometimes only one by abortion, sessile, elongated to ovoid or ellipsoidal, smooth, warted or winged, dehiscing lengthwise on the adaxial side; seeds compressed and often margined, mostly crowned with a coma or long silky hairs; endosperm present; embryo straight, nearly as long as the seed; cotyledons flat.

Periplocaceae is distinguished from Asclepiadaceae by characters of the stamen and pollen. The former have stamens of free filaments and granular pollen whereas the latter have those of connate ones and waxy pollen-masses called pollinia. The pollination mechanism of the two families is unique. This deals with a device to ensure cross-pollination by insects, which although highly specialised in both, still fundamentally differs in structure. In the Periplocaceae, the pollen is discharged on to the spoon-shaped carriers and removed by visiting insects to whose heads the glandular base of the carrier adheres (Shaw, 1988). As for the Asclepiadaceae, the pollen-masses are attached by caudicles of varied form to sutured corpuscles derived from style-apex. The proboscis or legs of an insect are grasped by these pollen-translators and the pollen-masses are then removed (Henderson, 1974).

According to "The Families of Flowering Plants" (Hutchinson, 1960), 50 names of genera in the Periplocaceae had been mentioned. They are listed as the following together with their distribution (Shaw, 1988).

*Aechmolepis* Decne. (Tropical and South Africa)

*Atherandra* Decne. (South East Asia , Malay Peninsula , Sumatra, Java)

*Atherolepis* Hook. f. (Burma, Siam)

*Atherostemon* Blume. (Burma, Malaya)

*Baroniella* Constantin & Gallaud. (Madagascar)

- Baseonema* Schlechter & Rendle (Tropical East Africa)
- Batesanthus* N.E.Br. (West Africa)
- Brachylepis* Hook.& Arn. (South America)
- Camptocarpus* Decne. (Madagascar, Mauritius)
- Chlorocodon* Hook.f. (Tropical Africa)
- Chlorocyathus* Oliv. (Tropical East Africa)
- Cochlanthus* Balf.f. (Socotra)
- Cryptolepis* R.Br. (Paleotropics)
- Cryptostegia* R.Br. (Madagascar)
- Decalepis* Wight & Arn. (Peninsula of India)
- Ectadiopsis* Benth. (Tropical and South Africa)
- Ectadium* E.Mey. (South Africa)
- Finlaysonia* Wall. (Indomalaya)
- Gongylosperma* King & Gamble. (Malay Peninsula)
- Gonocrypta* Baillon. (Madagascar)
- Gymnanthera* R.Br. (Malaysia)
- Gymnolaema* Benth. (Tropical East Africa)
- Harpanema* Decne. (Madagascar)
- Hemidesmus* R.Br. (South India, South East Asia, Malaysia)
- Ischnolepis* Jumelle & Perrier. (Madagascar)
- Macropelma*
- Mafekingia* Bail. (Tropical and South Africa)
- Menabaea* Bail. (Madagascar)
- Mitolepis* Balf.f. (Socotra)
- Myriopterion* Griff. (Assam to Malay Peninsula)
- Omphalogonus* Bail. (West Equatorial Africa)

- Parquetina* Bail. (West Equatorial Africa)
- Pentanura* Blume. (Burma, Sumatra)
- Pentopetiopsis* Constantin & Gallaud. (Madagascar)
- Pentopetia* Decne (Madagascar)
- Periploca* L. (North and Tropical Africa, Orient, East Asia)
- Phyllanthera* Blume. (Malay Peninsula, Java)
- Raphionacme* Harv. (Tropical and South Africa)
- Schlechterella* K.Schum. (East Africa)
- Stelmatocrypton*
- Stomatostemma* N.E.Br. (South East Tropical Africa, South Africa)
- Streptocaulon* Wight. & Arn. (Indomalaya)
- Streptomanes* K.Schum. (New Guinea)
- Symphytonema* Schlechter. (Madagascar)
- Tacazzea* Decne. (Tropical and South Africa)
- Tanulepis* Balf.f. (Madagascar)
- Telectadium* Bail. (Indochina)
- Utleria* Bedd.ex Benth. (South India)
- Zaczatea*
- Zygostelma* Benth. (Siam)

## 2. Periplocaceous Plants in Thailand

The occurrence of Periplocaceous plants in Thailand had been reported by A.Kerr (he incorporated them in Asclepiadaceae) in the *Florae Siamensis Enumeratio* (1951) and by Tem Smitinand in the *Thai Plant Names* (1980). Those plants

include various species as shown below :-

*Atherandra* Decne.

*A. acutifolia* Decne.

*Atherolepis* Hook.f.

*A. pierrei* Cost.

*A. pierrei* Cost.var. *glabra* Kerr

Local names: Op choei thao ออบเซยเถา (Central); Op choei paa ออบเซยป่า (Bangkok); Chueak thao เชือกเถา (Nakhon Sawan); Kam yaan กำหยาน , Kuu din กู้ดิน , Khruao khao mai เครือเขาใหม่ (Northern).

*Cryptolepis* R.Br.

*C. buchanani* Roem. & Schult.

Local names: Thao en on เถาเอ็นอ่อน , Muei เมื่อย (Central); Mon teenpet หมอนดินเบ็ด (Surat thani); Yaa lilan หล้าลิเลน (Pattani); Khruoa thao en เครือเถาเอ็น (Chiang Mai); Kuan กวน (Shan-Mae Hong Son); No-o-mee นออหมี่ (Karen-Mae Hong Son); Teenpet khruoa ดินเบ็ดเครือ (Northern).

*C. elegans* Wall. ex G.Don

Local names: Yaan kheepueng ย่านซี่ฝิ่ง (Satun); Seekoh ซีโคะ (Nakhon Ratchasima).

*Cryptostegia* R.Br.

*C. glandiflora* R.Br.

Local names: Daao pradup ดาวประดับ , Baanburee muang บานบุรีม่วง (Bangkok); Rubber vine.

*Finlaysonia* Wall.

*F. maritima* (Blume.) Back. = *F. obovata* Wall.

Local names: Kra phoh plaa กระเพาะปลา (Chanthaburi).

*Gongylosperma* King & Gamble.

*G. curtisii* King & Gamble.

*G. lanuginosum* Rindl.

*Gymnanthera* R.Br.

*G. nitida* R.Br.

*Myriopteron* Griff.

*M. extensum* (Wight) K.Schum. = *M. paniculatum* Griff.

Local names: Cha em ชะเอม , Khrua khao khom luang  
เครือเขาขมหลวง; Khaao saan ข้าวสาร (Central); Khom lueang  
ขมเหลือง (Chiang Mai); Paang mai ป้างไม้ (Lumpang); Oi saam  
suan อ้อยสามสวน , Oi saen suan อ้อยแสนสวน (Northern), Kon  
กอน (Shan-Mae Hong Son).

*Periploca* Linn.

*P. purpurea* Kerr

*Streptocaulon* Wight & Arn.

*S. juvenas* (Lour.) Merr.

Local names: Thao prasong เถาประสงค์ (Prachin Buri);  
Chukkarohinee จุกโรหิณี , Nuai nang นวยนึ่ง , Noi nang  
นอยนึ่ง (Chumphon); Tamyah haak hom ต้ายานฮากหอม (Nakhon  
Sawan); Yang samut noi หยั่งสมุทรน้อย (Chiang Mai).

*S. kleinii* Wight & Arn.

Local names: Chukkarohinee จุกโรหิณี (Chai Nat); Khee

duean ชี้เดือน (Surat Thani); Chai song ไชสง (Chaiyaphum).

*S. wallichii* Wight

Local names: Duei dip เดื่อยดิบ (Phatthalung).

*S. tomentosum* Wight var. *latifolium* Cost.

*Telectadium* Bail.

*T. edule* Bail.

*Zygostelma* Benth.

*Z. benthamii* Bail.

Local names: Op choei thao อบเซยเถา (Chai Nat) ;  
Khruea khao luak เครือเขาลวก , Tamyaa tua phuu  
ตำยานตัวผู้ (Nakhon Sawan).

### 3. Medicinal Plants in Periplocaceae

Some plants in the family Periplocaceae have been used as folk medicines by the natives in various countries. Those are listed here as follows:-

*Chlorocodon* sp.

In Uganda, the plant is known by the native name of "Murundo". The root of the plant has a pleasant adour intermediate between those of vanillin and piperonal, and is said to be chewed by the natives for sweetening the breath (Goulding and Pelly, 1970).

*Cryptolepis buchmanii* Roem. & Schult.

In India , the santals make a preparation from the plant which they give to children to cure them of rickets. They also combined it with *Euphorbia microphylla* (Euphorbia-



ceae) in the formation of a medicine to be given to women when the supply of milk is deficient or fails (Kirtikar and Basu, 1981). Decoction of its stems are used by some rural people as a cure for paralysis (Dutta et al, 1978).

*Decalepsis hamiltonii* Wight & Arn.

The root of this plant has a strong aromatic odour and a sweet sarsaparilla-like taste accompanied by a tingling sensation on the tongue. In India, it is considered to be an appetiser and blood purifier (Council of Scientific & Industrial Research, 1969).

*Hemidesmus indicus* R.Br.

This plant is known in the common name of "Indian Sarsaparilla". The roots of the plant are medicinal and constitute the Hemidesmus or Anatomul which is official in Indian Pharmacopoeia; they were one time official also in B.P. The drug has a characteristic fragrance and aromatic sweetish taste. It has long enjoyed a reputation as tonic, alternative, demulcent, diaphoretic, diuretic and blood purifier. It is employed in nutritional disorders, syphilis, chronic rheumatism, gravel and other urinary diseases and skin infections. It is administered in the form of powder, infusion or decoction as syrup. It is used as a substitute for Sarsaparilla (from *Smilax* spp.) and employed as a vehicle for potassium iodide and for purposes for which Sarsaparilla is used. A syrup made from the root is used as a flavouring agent and the preparation of a sherbet which is

reported to have cooling property (Council of Scientific & Industrial Research, 1969). The root in combination with other drugs is prescribed in snake-bite and scorpion-sting but it is not an antidote to either snake-venom or scorpion-venom (Kirtikar and Basu,1981).

In addition to the root other parts of the plant are also useful. The leaves are good for vomiting, colds, wounds, and leucoderma. The stems are diaphoretic, diuretic, laxative; good for disease of the brain, the liver, the kidney; useful in syphilis, uterine complaints, leucoderma, paralysis, cough, asthma; gargle, good for toothache. The milky juice is used for relieving inflammation in the eye (Kirtikar and Basu, 1981).

*Myriopteron extensum* (Wight) K.Schum.

In Thailand, the root of the plant is used as an expectorant, an antitussive and for treatments of a throat disease. The powdered root mixed with water is also claimed to be taken internally for eye-sore (Sangium Pongboonrod, 1950).

*Periploca aphylla* Decne.

In India, the milky juice is used as an external application to tumours and swelling. The flowers are eaten, and a decoction of the bark serves as a purgative medicine. The plant is considered as a fodder for camels and a cure for pains in the stomach (Kirtikar and Basu, 1981).

#### 4. Chemical constituents of Periplocaceae

Plants in the Periplocaceae are found to contain a wide range of chemical constituents: triterpenoids, steroids, flavonoids, alkaloids and miscellaneous compounds. The interesting group is a member of steroids, the cardenolide which is characteristic to the closely-related Asclepiadaceae.

Listes of compounds found in various species of the family Periplocaceae are shown in Table 2.1.

(Compounds with the asterisk are obtained as hydrolysed products.)

Table 2.1 Chemical constituents of Periplocaceae

Botanical origin	Plant part	Chemical substance	Category	References
<b>1. Chlorocodon</b>				
<i>C. sp.</i>	roots	p-methoxysalicylaldehyde	Miscellaneous	Mascre & Paris, 1947
	roots & seeds	unidentified alkaloids	Alkaloid	Mascre & Paris, 1947
<i>C. whiteii</i>	roots	p-methoxysalicylaldehyde	Miscellaneous	Gailly, 1947
<b>2. Cryptolepis</b>				
<i>C. buchanani</i>	leaves	cryptosin	Cardenolide	Venkateswara et al, 1989
		cryptanoside A	"	Purushothaman et al, 1988
		cryptanoside B	"	" "
	roots	cryptanoside C	"	" "
		cryptanoside D	"	" "
		germanicol docosonate	Miscellaneous	" "
		buchananin	Cardenolide	Khare & Shah, 1983
stems	sarmentogenin	"	Shah & Khare, 1981	
	sarmentocymarin	"	" "	
	buchananine	Alkaloid	Dutta et al, 1978	
	1,3,6-O-trinicotinoyl-a-D-glucopyranose	Alkaloid (glycoside)	" " 1980	
<i>C. sanguinolenta</i>	roots	cryptolepine quinoline	Alkaloid "	Gellert et al, 1951 Dwuma-Badu et al, 1978
	unclassified part	cryptosine	Alkaloid	Raymond-Hamet, 1937
<b>3. Cryptostegia</b>				
<i>C. grandiflora</i>	leaves & stems	cryptograndoside A	Cardenolide	Aebi & Reichstein, 1950
		cryptograndoside B	"	"
	leaves	cryptograndoside C	"	"
		16-desacetylanhydro cryptograndoside A	"	"
	16-desacetylanhydro cryptograndoside B	"	"	

<i>C. madagascariensis</i>	leaves & stems	oleandrigenin	Cardenolide	Doskotch et al, 1972
		propionylgitoxigenin	"	"
		16-anhydrogitoxigenin	"	"
		gitoxigenin	"	"
		oleandrigenin 3-rhannoside	"	"
<i>C. madagascariensis</i>	leaves & stems	oleandrigenin	Cardenolide	Sanduja et al, 1984
		16-anhydrogitoxigenin	"	"
		digitoxigenin	"	"
		16-anhydrogitoxigenin-3-rhannoside	"	"
		16-propionylgitoxigenin-3-rhannoside	"	"
		14,16-dianhydrogitoxigenin-3-rhannoside	"	"
		$\beta$ -sitosterol	Sterol	Douis et al, 1985
		lup-20(29)-en-3 $\beta$ -ol	Triterpenoid	"
		lup-20(29)-en-3-one	"	"
		3 $\beta$ -hydroxyurs-12-en-28-oic acid	"	"
4. <i>Decalepis</i>				
<i>D. hamiltonii</i>	roots	4-methoxyresorcyaldehyde	Miscellaneous	Rao and Iyengar, 1923
		$\alpha$ -amyrin	Triterpenoid	Murti & Seshadri, 1941c
		$\beta$ -amyrin	"	"
		$\beta$ -amyrin acetate	"	"
		lupeol	"	"
		inositol	"	Murti & Seshadri, 1941a
		2,4-HO (MeO) C <sub>6</sub> H <sub>3</sub> CHO	"	Murti & Seshadri, 1941b
5. <i>Finlaysonia</i>				
<i>F. obovata</i>	leaves	$\alpha$ -amyrin acetate	Triterpenoid	Pradhan & Mukhopadhyay, 1985
		$\beta$ -amyrin acetate	"	"
		stigmasterol	Sterol	"
	bark	lupeol acetate	Triterpenoid	"
	leaves & bark	$\beta$ -sitosterol	Sterol	"
	ursolic acid	Triterpenoid	"	
6. <i>Henidesmus</i>				
<i>H. indicus</i>	twigs	desinine	Steroid (glycoside)	Oberai et al, 1985
	roots	2-hydroxy-4-methoxy-benzaldehyde	Miscellaneous	Dutta et al, 1938
		henidesmol	Sterol	"
		henidosterol	Sterol	"

		hemidosterol	Sterol	"
		$\alpha$ -anyrin	Triterpenoid	Padhy et al, 1973
		$\beta$ -anyrin	"	"
		$\beta$ -anyrin acetate	"	"
		lupeol	"	"
		lupeol acetate	"	Padhy et al, 1973
		lupeol octacosanoate	"	"
		hexatriacontane	"	"
		$\beta$ -sitosterol	Sterol	Chatterjee & Bhattacharyya, 1955
	roots, leaves, stems	cholesterol	Sterol	Heble & Chadha, 1978
		campesterol	"	"
		16-dehydropregnenolone	Steroid	"
	leaves	rutin	Flavonoid (glycoside)	Subramanian & Nair, 1968
7. <i>Menabea</i>				
<i>M. venenata</i>	roots	menabein	Cardenolide	Raymond-Hamet, 1936
		menabegenin	"	Frerejacque, 1959
8. <i>Pentopetia</i>				
<i>P. androsaemifolia</i>	bark	periplocymarin	Cardenolide	Golab et al, 1959
		digitoxigenin	"	"
		cymarin	"	"
		periplogenin	"	"
9. <i>Periploca</i>				
<i>P. aphylla</i>		$C_{25}H_{42}O_3$	Resin alcohol	Chopra et al, 1937
	above ground part	lupeol	Triterpenoid	Mitsuhashi & Tomimoto, 1971
		oleanoic acid	"	"
		maslinic acid	"	"
		$\beta$ -sitosterol $\beta$ -D-gluco-pyranoside	Sterol (glycosides)	"
<i>P. calophylla</i>	twigs	calocin	Steroid (glycoside)	Srivastava et al, 1982
		calocinin	"	Sethi et al, 1988
		plocin	"	Deepak et al, 1985a
		plocigenin	Steroid	"
		plocinine	Steroid (glycoside)	Deepak et al, 1985b
		locin	"	Deepak et al, 1986
		nonhydroxyolean-12-ene-28-carboxylic acid	Triterpenoid	Srivastava et al, 1983
		dihydroxyolean-12-ene-28-carboxylic acid	"	"
		2,3,23-trihydroxyolean-12-ene-28-carboxylic acid	"	"

<i>P. graeca</i>	wood, bark leaves, seed	periplocin	Cardenolide	Stoll & Renz, 1939 Komissarenko & Bagirov, 1969	
	bark	periplocymarin	"	Solaculu & Herrman, 1934	
	leaves, stems	rutin	Flavonoid	Melin, 1963, 1964	
	leaves	isoquercitin astragalin esculentin glycoside	" " "	Komissarenko & Bagirov, 1969 " Melin, 1964	
	twining parts	quercetin glycoside	"	Tronchet & Melin, 1962	
	stems	cyanidin peonidin	" "	Melin, 1975 "	
	bark	scopoletin unidentified coumarin 4-methoxysalicylaldehyde	Coumarin " Miscellaneous	Komissarenko & Bagirov, 1969 " Solaculu et al, 1935	
	leaves, stems leaves	chlorogenic acids isochlorogenic acid neochlorogenic acid	" " "	Melin, 1963, 1964 Melin, 1964 "	
	stems	ursolic acid	Triterpenoid	Zorina et al, 1966	
	<i>P. laevigata</i>	stems, roots	$\beta$ -sitosterol lupeol $\alpha$ -amyrin	Sterol Triterpenoid "	Askri et al, 1982 " "
		stems	$\beta$ -amyrin	"	"
		roots	$\beta$ -amyrin acetate periplocadiol	" Sesquiterpene	" Askri et al, 1989
		<i>P. nigrescens</i>	roots	strophanthidin strophanthidin glycoside cynarin	Cardenolide " "
wood	strophanthidol		"	Schenker et al, 1954	
wood	16 $\beta$ -hydroxystrophanthidin* convallotoxin*		" "	Berthold et al, 1965a "	
	16-acetoxystrophanthidin* 16-dehydrostrophanthidin		" "	Berthold et al, 1965b "	
	3-O-digitoxosyl-16-dehydro- strophanthidin*		"	"	
	3-O-rhamnosyl-16-acetoxy- strophanthidin*		"	"	
	$\beta$ -sitosterol- $\beta$ -D-glucoside $\alpha$ -amyrin $\beta$ -amyrin		Steroid Triterpenoid "	Marks et al, 1975 " "	

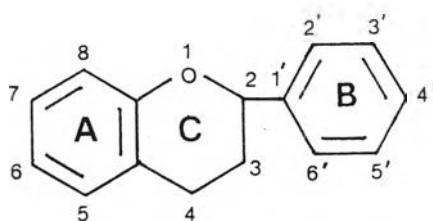
<i>P. sepium</i>	leaves	isorhoifolin apigenin ursolic acid	Flavonoid " Triterpenoid	Ogundaini & Okafor, 1987 " "
	root bark	3-O-[2-O-acetyl- $\beta$ -D-digit- alo-pyranosyl(1-4)- $\beta$ -D- cymaropyranoside] 20-O-[ $\beta$ - D-glucopyranosyl(1-6)- $\beta$ -D- glucopyranosyl (1-2) $\beta$ -D- digitalopyranoside] of preg-5-ene-3 $\beta$ ,16 $\alpha$ ,20(S)- triol and preg-5-ene-3 $\beta$ , 20 (S)-diol	Steroid (glycoside)	Itokawa et al, 1988a
		preg-5-ene-3 $\beta$ ,16 $\beta$ ,20(R)- triol 20-O- $\beta$ -D glucopyra- nosyl (1-6)- $\beta$ -D-glucopyr- anosyl (1-2)- $\beta$ -D-digital- opyranoside	"	"
		preg-5-ene-3 $\beta$ ,20(S)-diol 3-O-[ $\beta$ -D-digitalopyranosyl (1-4) $\beta$ -D-cymaropyranoside] 20-O-[ $\beta$ -D-glucopyranosyl (1-6)- $\beta$ -D-glucopyranosyl (1-2) $\beta$ -D- digitalopyrano- side]	"	"
	cortex	preg-5-ene-3 $\beta$ -20 $\alpha$ -diol 20-O- $\beta$ -D-glucopyranosyl (1-6)- $\beta$ -D-glucopyranosyl (1-2)- $\beta$ -D-digitalopyrano- side	"	Sakuma et al, 1969
	antitumor fraction	periplocosides A,B and C periplocosides M,D,E,L,N periplocosides J,K,F,O	" " "	Itokawa et al, 1988b " 1988c " 1988d
cortex and young seedlings	periplocin scopoletin 4-methoxysalicylaldehyde $\beta$ -sitosterol $\beta$ -sitosterol $\beta$ -D-glucoside	Cardenolide Coumarin Miscellaneous Sterol Steroid	Konissarenko et al, 1983 " Shoji et al, 1967 " "	



## The Flavonoids

### 1. Introduction to Flavonoids

Flavonoids represent one of the most numerous and widespread group of natural constituents. They are phenolic derivatives containing fifteen carbon atoms in their basic nucleus. Such carbons are arranged in a C<sub>6</sub>-C<sub>3</sub>-C<sub>6</sub> configuration that is two aromatic rings linked by a three carbon unit which may or may not form a third ring. For convenience the rings are labelled A, B and C and the individual carbon atoms are referred to by a numbering system which utilizes ordinary numerals for the A- and C-rings and "primed" numerals for the B-ring. The common structures of flavonoids are based on the nucleus of flavan or 2-phenyl benzopyran (1) which contains a pyran ring as the C-ring.



(1) flavan

Naturally, flavonoids occur more commonly in the form of glycoside than of free aglycone and O-glycosides are found more frequently than C-glycosides. These compounds can be found in all parts of the higher plants: root, stem, leaf, flower, pollen, fruit, seed, wood and bark. According to their natural occurrence, flavonoids can be

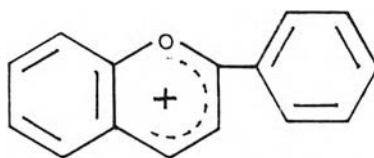
regarded into two groups as the major flavonoids and the minor ones. The former which occupied the majority of natural flavonoids include flavone, flavonols, and anthocyanidins together with their glycosides termed anthocyanins. The latter are the others such as flavanone, dihydroflavonols, chalcones, aurones, etc. The classification of these compounds into the individual groups was described in the later section.

## 2. Classification of Flavonoids

Flavonoids are classified according to the oxidation level of the C<sub>3</sub> unit in their molecule as the following:-

### 2.1 Anthocyanidins

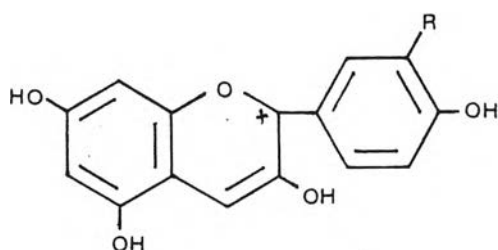
The constitution common to all anthocyanidins is the 2-phenylbenzopyrylium or flavylum structure (2) :



(2) flavylum cation

The hydroxylation patterns in natural anthocyanidins may be classified into the three basic pigment groups of pelargonidin (3), cyanidin (4) and delphinidin (5), all of which are hydroxylated in 3-, 5-, and 7-position in common, differ only in the number of B-ring hydroxyls. Because of their ionic character, both the intensity and shade of

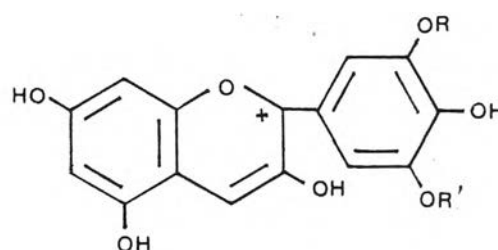
colour of anthocyanidins vary with changes in pH. The number of hydroxyl groups in the B-ring is also correlated with colour properties. In acid solution (methanol-HCl), pelargonidin with one B-ring hydroxyls, is orange-red, cyanidin with two is magenta and delphinidin with three is mauve. These three anthocyanidins together with three methylated derivatives, peonidin (6), petunidin (7), and malvidin (8), are very widespread in nature; of these, cyanidin is the most common (Ribereau-Gayon, 1972).



(3) pelargonidin; R = H

(4) cyanidin; R = OH

(5) peonidin; R = OCH<sub>3</sub>



(6) delphinidin; R = R' = H

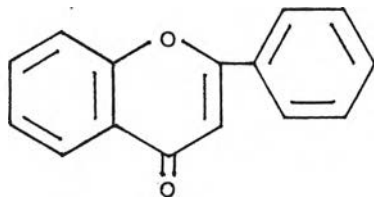
(7) petunidin; R = CH<sub>3</sub>, R' = H

(8) malvidin; R = R' = CH<sub>3</sub>

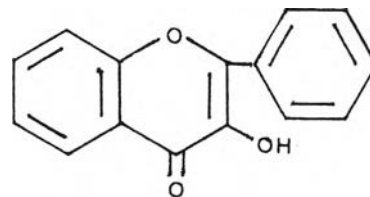
Glycosylation of anthocyanidins produces anthocyanins, the majority of which occur in the dissolved state in the cell sap of flowers, fruits, and other plant organs. The sugar components which have been frequently found in natural anthocyanins are glucose, rhamnose, galactose and gentiobiose. The attachment of sugars is found in a majority of cases to be at position 3 and less frequently at position 5. (Geissman, 1962).

## 2.2 Flavones and Flavonols

The flavone nucleus is 2-phenylbenzopyrone (9) and that of the flavonol is 3-hydroxyflavone (10).



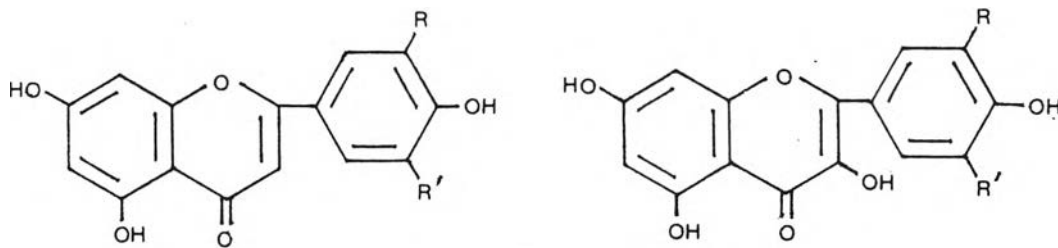
(9)



(10)

The flavones widely distributed in the angiosperms, for examples, are apigenin (11) and luteolin (12). Tricin (13), on the contrary, is common only in grasses. Flavone itself, which has no substituent in either benzene rings and which occur in *Primula*, is one of the less common member of this class and so is chrysin (5,7-dihydroxyflavone), a constituent of the heartwood of species of *Pinus*.

As to the flavonols, the most widespread of all, also of all flavonoids, is quercetin (14), especially being one of the principal phenolic constituents of plants. Kaempferol (15) and myricetin (16) are also widely distributed. Methylation of the OH groups also occur; the best known O-methylated derivative is isorhamnetin (17), which is present in the pollen of some plants (Riberean-Gayon, 1972).



- |                                      |  |
|--------------------------------------|--|
| (11) apigenin; R=R'=H                | (14) quercetin; R=OH, R'=H                   |
| (12) luteolin; R=OH, R'=H            | (15) kaempferol; R=R'=H                      |
| (13) tricetin; R=R'=OCH <sub>3</sub> | (16) myricetin; R=R'=OH                      |
|                                      | (17) isorhamnetin; R=OCH <sub>3</sub> , R'=H |

Common flavones and flavonols, although widespread in flower petals, do not contribute to their colour. However, flavonols make some contribution if they are methylated or have unusual glycosidic patterns. It must be emphasized that although flavones do not contribute directly to flower colour, they can act as co-pigments intensifying the colour of yellow flavonols, chalcones and aurones. Colourless flavones and flavonols appear to provide "body" to white, cream and ivory-coloured flowers. The major contributors to this phenomenon are kaempferol and quercetin (Goodwin and Mercer, 1983). In general flavones and flavonols make no contribution to fruit colours although they are widely distributed in fruit. Flavonols also occur with great frequency in leaves.

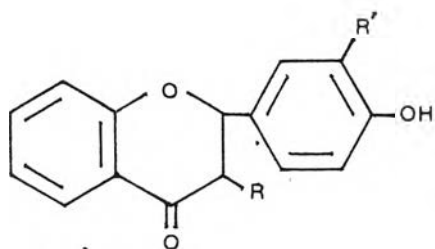
Glycosylation of flavones and flavonols may occur through either O- or C-glycosidic linkages but O-glycosides is more frequently encountered. Six monosaccharides commonly

found in O-glycosidic combination are glucose, galactose, glucuronic acid, xylose, rhamnose, and arabinose; sophorose is the most common for disaccharides (Harborne et al, 1975). Usually the sugar residue in flavonol glycosides is attached at position 3, a second sugar residue if present, being frequently in position 7. Unlike what is so usual in the anthocyanins, glycosylation at position 5 is extremely rare. In case of flavones, which lack of OH group at position 3, the principal known glycosides have a sugar residue at position 7, but a number of 5-glucosides are known (Riberean-Gayon, 1972).

### 2.3 Flavanones and Dihydroflavonols

The flavanones are derived from the flavones by elimination of the double bond in the central heterocycle. Naringenin (18) and eriodictyol (19), related respectively to apigenin and luteolin, are the best known. The flavanones are fairly widely distributed, especially in higher plants such as Rosaceae, Rutaceae, Gluminosae, Compositae, Hydrophyllaceae and Pinaceae, and in the Fern family, Polypodiaceae (Geissman, 1962).

Dihydroflavonols, also known as flavanonols, are 3-hydroxyflavanones. Taxifolin (20) or dihydroquercetin, for example, is a well known heartwood constituent of many trees, particularly gymnosperms, and has more recently been found in flowers e.g. *Petunia* and leaves e.g. *Rhododendron*, in glycosidic form.



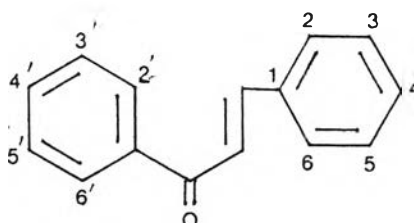
(18) naringenin;  $R=R'=H$

(19) eriodictyol;  $R=H$ ,  $R'=OH$

(20) taxifolin;  $R=R'=OH$

#### 2.4 Chalcones

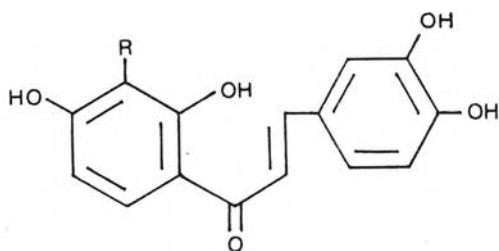
Chalcones are characterized by their possession of a three carbon,  $\alpha$ ,  $\beta$ -unsaturated carbonyl system which joins the two aromatic rings together. The numbering of positions in chalcone is reversed from the system used for other flavonoids which possess heterocyclic ring. The positions in the A-ring are numbered by the primed numerals while the unprimed ones are for that in the B-ring.



(21) chalcone

Chalcones and flavanones are interconvertible by acid or alkali catalysed ring-chain tautomerism. Both of them are generally considered to be the immediate precursors of common flavonoids. Chalcones are of relatively infrequent occurrence in the plant kingdom. They are yellow pigments, the presence of which can easily be demonstrated in petals by exposing them to ammonia vapour when the colour changes

dramatically from yellow to red. Naturally occurring chalcone are all hydroxylated to a greater or lesser extent; the parent compound chalcone (21) itself is not known as a natural product. The A-ring substitution pattern is usually based on the phloroglucinol system (2',4',6'-trihydroxy). The B-ring most commonly exhibits a 4-mono,3,4-di-, or 3,4,5-trihydroxylation pattern (Harborne et al, 1975). Examples of this class are butein (22) and okanin (23), both of them naturally occur in either free state or glycosides.

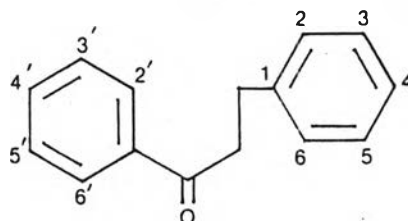


(22) butein; R=H

(23) okanin; R=OH

### 2.5 Dihydrochalcones

Dihydrochalcones (24) relate directly to the chalcones and can be derived therefrom by reduction of the chalcone  $\alpha, \beta$ -double bond. The A-ring of natural dihydrochalcone is commonly substituted in the phloroglucinol hydroxylation pattern and the B-ring usually shows the 4-mono or 3,4-dihydroxylation pattern. The numbering system of this class follows that used for chalcone (Harborne et al, 1975).

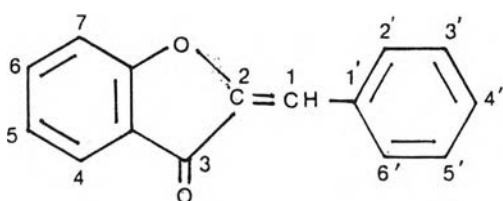


(24) dihydrochalcone

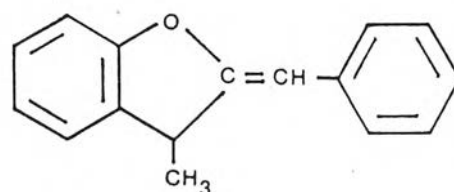


## 2.6 Aurones

Aurones (25), like chalcone, is different from the common flavonoids in the three carbon unit which links the two benzene rings. But instead of a linear chain in case of chalcone, such unit is in the form of a pentacyclic ring. The normal numbering system applies to this group of compound: positions on the A-ring are identified by unprimed numbers and those of the B-ring by primed numbers. Note that in aurones position 4 corresponds biosynthetically to position 5 of other heterocyclic flavonoids. Included in this class are "auronol" (26) derivatives distinguished by the presence of a methoxy group in place of the carbonyl group.

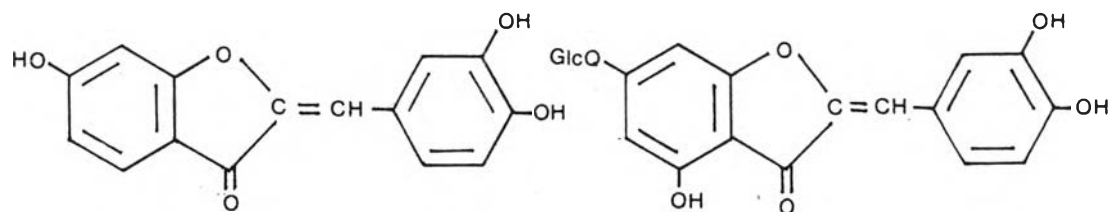


(25) aurone



(26) auronol

Aurones, the conspicuously coloured compounds, have been found in a variety of yellow flowered species; the presence of them can be detected by some method as used for chalcones. However, the aurones are not restricted to floral tissue but have been obtained from bark, wood and leaves as well (Harborne et al, 1975). Examples for this class are sulphuretin (27) which occur in yellow flower of *Cosmos sulphureus* Cav. and aureusin (28) in yellow *Antirrhinum majalis* Linn.

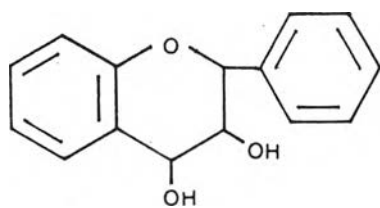


(27) sulphuretin

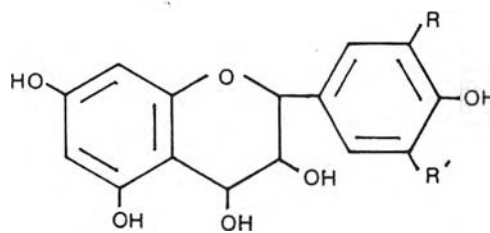
(28) aureusin

### 2.7 Leucoanthocyanidins

Compounds which are converted into anthocyanidins by being boiled with aqueous or alcoholic hydrochloric acid are termed leucoanthocyanidins, the structure of which based on the flavan-3,4-diol (29). These compounds are monomer of proanthocyanidins, the colourless substances isolated from plants when heated with acid form anthocyanidins. Examples of this class are leucopelargonidin (30), leucocyanidin (31) and leucodelphinidin (32).



(29) flavan 3,4-diol



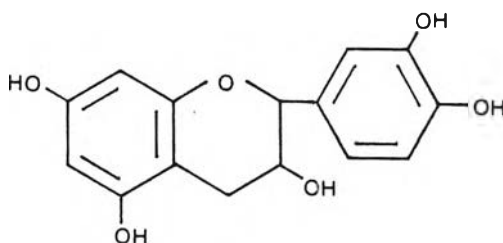
(30) leucopelargonidin; R=R'=H

(31) leucocyanidin; R=OH, R'=H

(32) leucodelphinidin; R=R'=OH

## 2.8 Catechins

Under the designation "Catechin" are grouped the polyhydroxyflavan-3-ols. The best known member is catechin (33), the chief constituent of "gambir-catechin" from *Uncaria gambir* (Hunt.) Roxb.



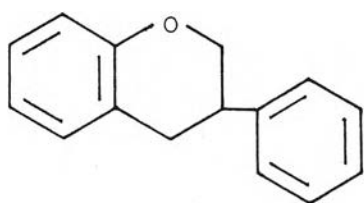
(33) catechin

Besides these 8 classes of compounds which possess relatively uniform structure of  $C_6-C_3-C_6$  configuration and are considered as normal flavonoids, there are some compounds having specialised structures which are closely related to those of the normal flavonoids and they are also included in the flavonoid grouping. These groups of such compounds are:-

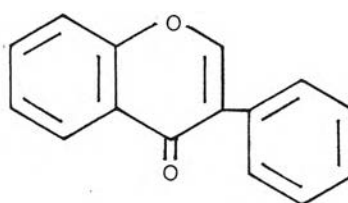
### Isoflavonoids

The structure of isoflavonoids differ from those of other flavonoid compounds in the attachment at aromatic B ring to the  $C_3$  unit. The branched  $C_6-C_3-C_6$  skeleton as a basic structural feature of these compounds is shown in (34). Isoflavonoids are included many classes of natural products. The well established members of this group are isoflavones (35), isoflavanones (36), rotenoids (37), pterocarpans (38),

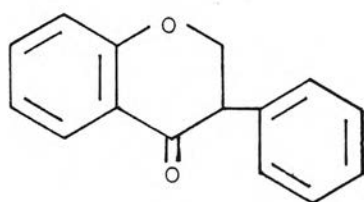
and coumestans (39). The various classes of isoflavonoid are according to their oxidation level. The structural displayed in these compounds is, in fact, greater than existing in the normal flavonoid series (Harborne et al, 1975).



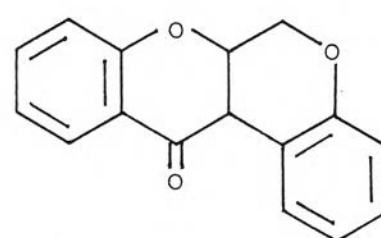
(34)



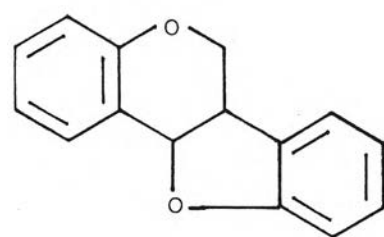
(35) isoflavone



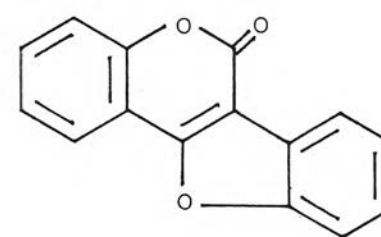
(36) isoflavanone



(37) rotenoid



(38) pterocarpan

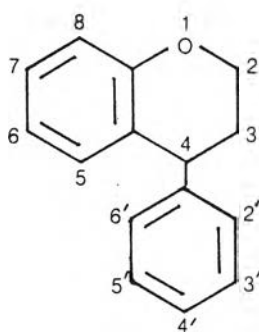


(39) coumestan

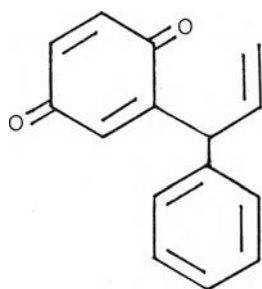
### Neoflavonoids

The term neoflavonoid was first used to describe the group of natural products with a 4-aryl chroman skeleton (40). However, the open-chain compounds, the dalbergiones (41) and the 3,3-diaryl propenes (42) have been included in the neoflavonoid class, in line with the assignment of 2'-

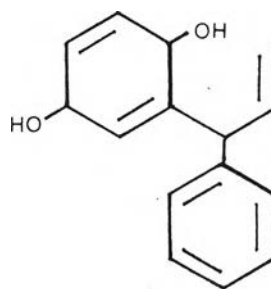
hydroxychalcone (43) and of angolensin (44) to the flavonoid and isoflavonoid classes respectively. According to their structural type, natural neoflavonoids are divided into five groups and they are: 4-arylcoumarins, neoflavenes, dalbergiquinolins, 4-arylchromones and coumaric acids (Harborne et al, 1975).



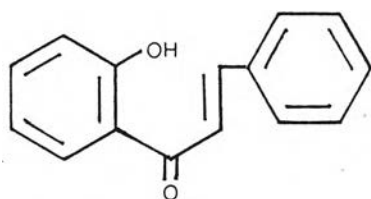
(40) 4-aryl chroman skeleton



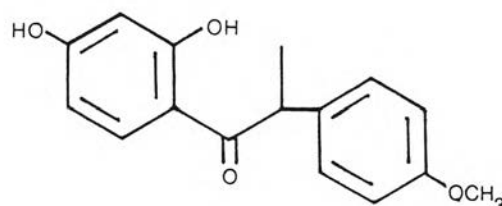
(41) dalbergiones



(42) 3,3 diaryl propenes



(43) 2'-hydroxyxhalcone



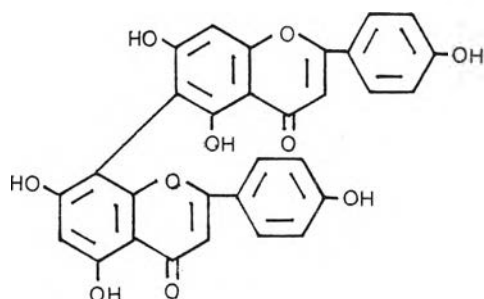
(44) angolensin

### Biflavonoids

The compounds in this group contain two units of flavonoid molecule linked together through either a carbon-carbon bond or a carbon-oxygen bond. Types of flavonoid moieties may be biflavones, flavanonyl-flavones, biflavanonones, and others. Most of known biflavonoids are dimer of apigenin and their derivatives, which can be divided into 7 groups according to types of interflavonyl linkage (Harborne et al, 1975).

Table 2.2 Types of major biflavonoids

Type	Interflavonyl linkage
The agathisflavone group	C6-C8''
The cupressoflavone group	C8-C8''
The amentoflavone group	C3'-C8''
The robustaflavone group	C3'-C6''
The hinokiflavone group	C4'-O-C6''
The ochnaflavone group	C3'-O-C3'''
The garcinia biflavonoids	C3-C8''



(45) agathisflavone

### 3. Biosynthesis of flavonoids

The establishment of flavonoid biosynthesis is based on earlier results from radioactive tracer studies *in vivo*, confirmed with more recent data obtained at the enzymic level *in vitro*. It becomes demonstrated that all classes of flavonoids are biosynthetically closely related, deriving their two component aromatic rings from different pathways. The phenylpropane residue, which includes the B-ring and C<sub>3</sub> unit, arises from *p*-coumaric acid, itself formed via the shikimate pathway. The A-ring, on the other hand, is basically derived from acetate unit through acetate-malonate pathway (Goodwin et al, 1983).

The first common intermediate in the pathway is a chalcone, the formation of which catalyzed by enzyme chalcone synthase. A chalcone convert to an isomeric flavanone by the function of enzyme chalcone isomerase. The chalcone/flavanone isomers display the significance role in the synthesis since they are central intermediates from which other flavonoids originate. The biosynthetic relationships of the flavonoids are illustrated in figure 2.1 (Harborne et al, 1982).

Further modification may occur at various stages resulting in : additional (or reduced) hydroxylation; methylation of hydroxyl groups or of the flavonoid nucleus; isoprenylation of hydroxyl groups or of the flavonoid nucleus; dimerization (to produce biflavonoids); bisulfate

formation; and most importantly glycosylation of hydroxyl groups (to produce flavonoid O-glycosides) or of the flavonoid nucleus (to produce flavonoid C-glycosides).



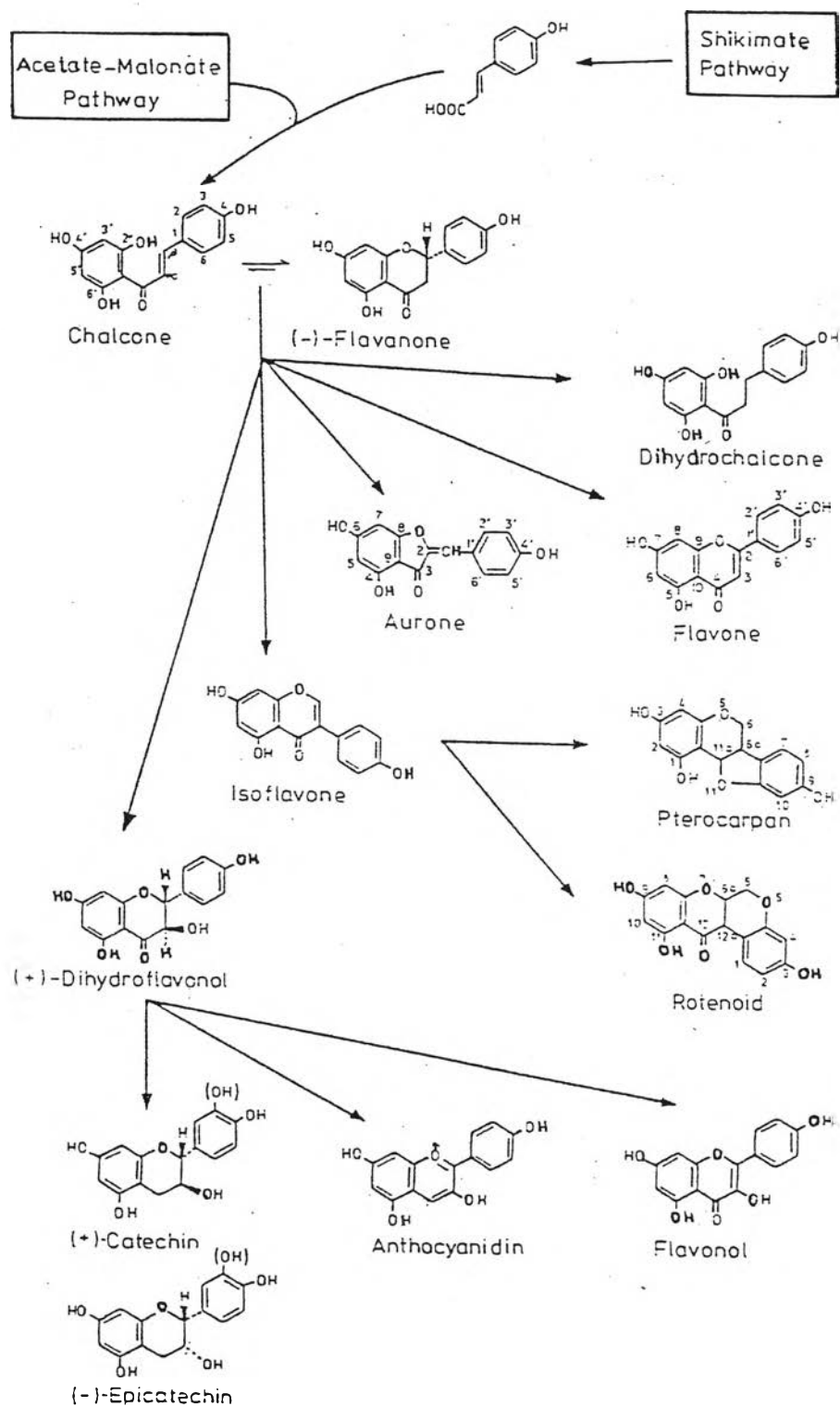
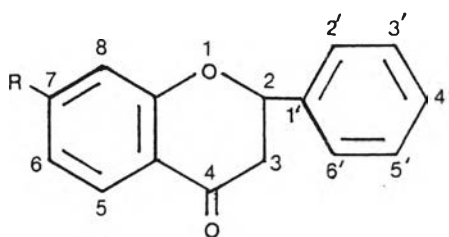


Figure 3.1 Biosynthetic interrelationship of flavonoids

## The Flavanones

### 1. Introduction to Flavanones

Flavanones are regarded to be a member of minor flavonoids according to their natural occurrence. These compounds are based upon the structure of 2-phenyl benzopyran-4-one (46), which is flavanone itself. The parent compound, a colourless substance, is not known to be naturally occurring; the simplest plant flavanone has a hydroxy group at position 7 (47). Flavanones are isomeric with chalcones from which they can be obtained synthetically and from which they arise biosynthetically. Since carbon-2 of the flavonoid molecule is a centre of asymmetry, two isomeric forms of each structure are possible. Most of natural occurring flavanones are laevorotatory and thus they belong to the same (2S) configurational series. (Harborne et al, 1975).



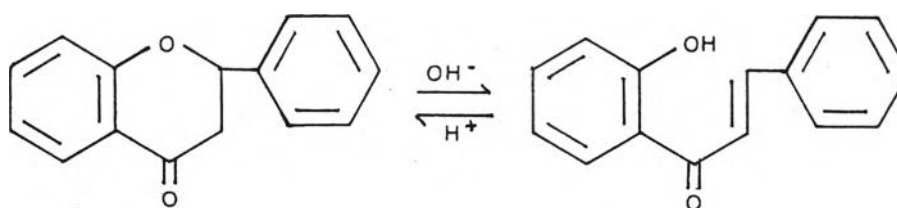
(46)    R = H

(47)    R = OH

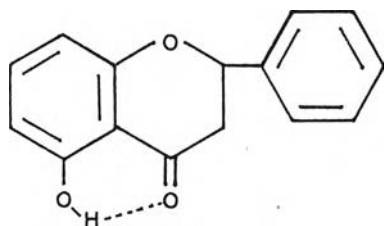
## 2. Chemistry of Flavanones

Chemically flavanone differs from flavone in being saturated between carbon 2 and 3 and thus lacking the conjugation of a double bond between the carbonyl group, conjugated with the A ring, and the 2-phenyl group (B ring). Consequently, in case of UV absorption flavanones absorb at comparative short wavelengths and hydroxylation in the 2-phenyl group has very little influence on the positions of maximum absorption of flavanones.

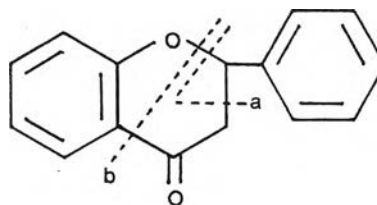
The dihydropyrone ring of flavanones is far more unstable than the pyrone ring of flavones or flavanols and is apt to open between O (position 1) and CH (position 2), giving a chalcone compound. Flavanones in an alkaline solution are readily converted to chalcones by ring-fission. On the contrary chalcones in an acid medium are converted to flavanones.



There had been experiments pointed out that when the 5-hydroxyl group is present in the flavanone, the chalcone-flavanone tautomerism is strongly on the side of the flavanone (Geissman, 1962). This is owing to the resulting hydrogen bonding stabilization of the ring (48).



(48)



(49)

The 4-carbonyl group of the flavanone shows typical carbonyl reactions, giving an oxime, and the 3-methylene group is active.

The behaviour of flavanones toward alkali is different from that of flavones, giving *O*-hydroxyacetophenone and benzaldehyde derivatives (49a) when the concentration of alkali is relative low, and corresponding derivatives of phenol and cinnamic acid when stronger alkali is used for the decomposition (49b). Flavanones decompose, however, into benzaldehyde, acetic acid and phenol when a strongly alkaline reaction mixture is heated drastically (49a + 49b). The first step of the decomposition reaction can be regarded to be ring-opening giving a chalcone derivative.

Among colour reactions used for the qualitative tests for flavonoids, the most useful reaction is that of Shinoda in which a compound or a suitably prepared plant extract is treated with magnesium and concentrated hydrochloric acid, usually in ethanolic solution. The positive test is indicat-

ed by the quick developing of characteristic colours, and the subsequent addition of more acid or magnesium often causes modification of the colour in a manner characteristic of the compound being examined. The test is generally strongly positive for flavonols, flavanones, and flavanols, producing pink, cherry-red, crimson or occasionally ink-blue colours. Shinoda found that some xanthone derivatives also react positively. Flavones which lack the 3-hydroxy substituent respond with the production of much less striking colours. The characteristic yellow-orange to red-orange shades given by this class of compounds make it possible to distinguish them from flavonol and flavanone derivatives, the colour of which are deeper and more intense (Geissman, 1962).

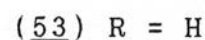
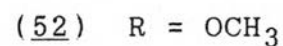
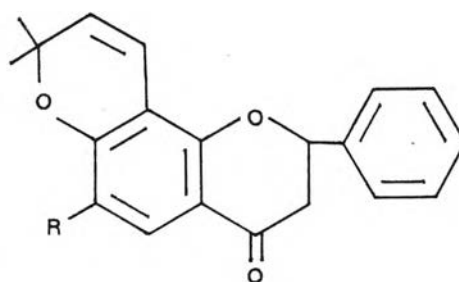
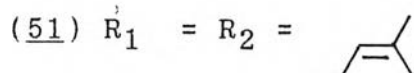
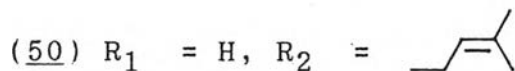
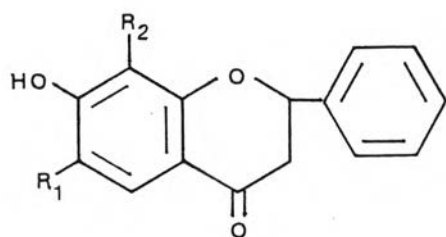
### 3. Structures of naturally occurring flavanones

The naturally occurring flavanones will be treated according to their B-ring hydroxylation pattern as follows (Harborne et al, 1975;1982):-

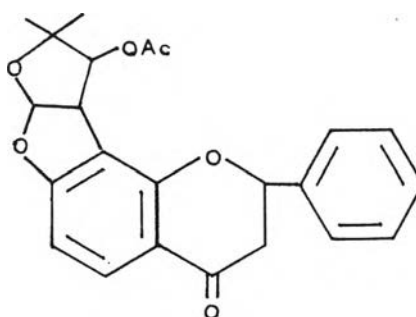
#### 3.1 Flavanones lacking B-ring hydroxyls

The simplest member of the group, also of the natural flavanones, is 7-hydroxy flavanone (47) which was isolated from two species of Leguminosae and one of Compositae. Other members may be considered as the derivatives of this compound by hydroxylation, methoxylation, methylation, prenylation, combination with sugar molecule(s) and others. An interesting case is the

prenylation of the parent compound on the A-ring which is characteristic of the Leguminosae. Prenylation of position 8 affords flavanone (50) while prenylation at both positions 6 and 8 gives (51). Ovalichromene (52) and isolonchocarpin (53), the dimethyl chromenoflavanones, are the products of cyclization of the prenylated flavanone.



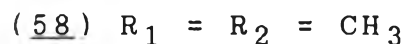
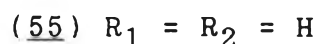
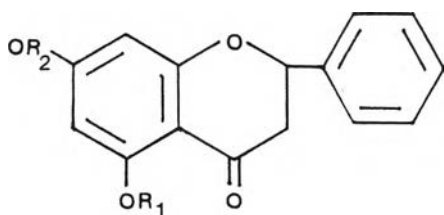
In addition to the prenylated ones the highly unusual alkylated flavanone was also found in a member of Leguminosae. This compound is purpurin(54) from *Tephrosia purpurea*.



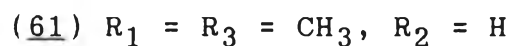
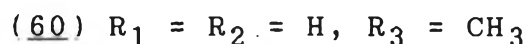
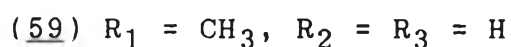
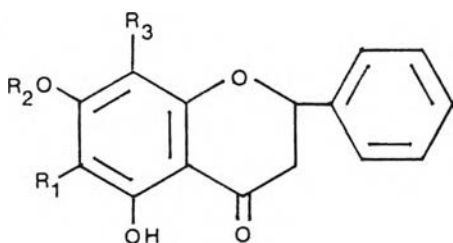
(54)

The simplest flavanone that bears the phloroglucinol hydroxylation pattern on the A ring is pinocembrin (55) which has been reported from several plant families such as Pinaceae, Rosaceae, Leguminosae, and Compositae. Its natural

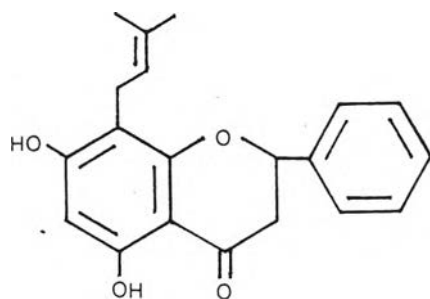
derivatives occur in various forms : the 7-rhamnoside, the 7-neohesperidoside, 5-and 7-methyl ethers of pinocembrin named alpinetin (56) and pinostrobin (57) respectively, and 5,7 dimethylpinocembrin (58).



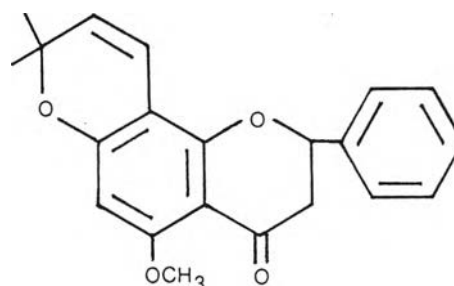
Several C-methyl derivatives of pinocembrin have been reported from nature. Examples of such compounds are strobopin (59) from Filicinae and Pinaceae, cryptostrobin (60) from Pinaceae and Myrtaceae, and desmethoxymatteucinol (61) from Filicinae, Myrtaceae, Anonaceae, and Leguminosae.



In case of prenylation, most of pinocembrin derivatives have been found in members of Leguminosae and Compositae. Examples are 6-prenylpinocembrin and glabranin (62). In addition to the prenylated pinocembrin its cyclization product, the dimethylchromenoflavanone (63), has also been reported from nature.



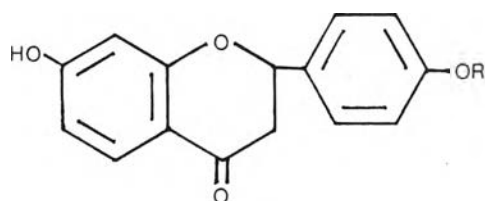
(62)



(63)

### 3.2 Flavanones having one B-ring hydroxyl

The simplest member of this group is liquiritigenin or 7,4'-dihydroxy flavanone which has been reported from several legumes (64). Its naturally occurring glycosides include the 4'-O-glucoside named liquiritin (65), the 7-O-glucoside and the 7-O-diglucoside.



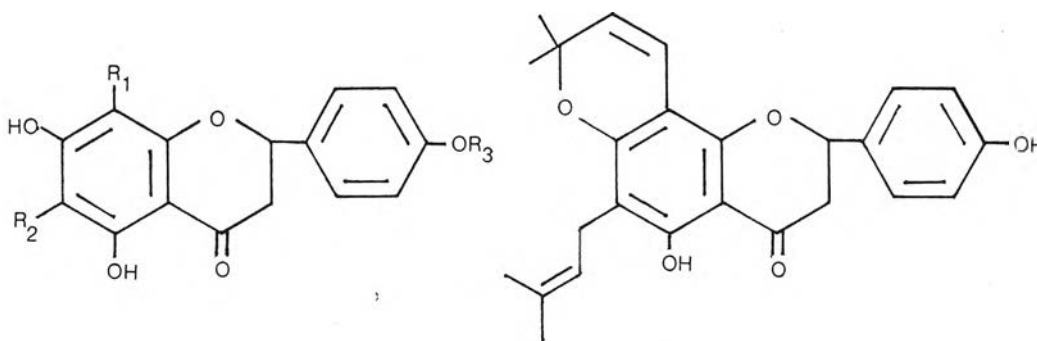
(64) R = H

(65) R = Glc

Prenylated derivatives of liquiritigenin which are 5-deoxyflavanone have been reported to be found in nature; they are bavachinin (66), bavachin (67), isobavachin (68), sophoranone (69) and sophoranochromene (70). All of these compounds occur in members of Leguminosae.



C-Alkylation of the naringenin occurs in several plants to provide various derivatives such as 6-C-B-D-glucopyranosyl derivative from Liliaceae; farrerol (72) from Ericaceae, Myrtaceae and Filicinae; matteucinol (73) from Filicinae and Ericaceae ; 8-C-prenylnaringenin from Compositae ; and cajaflavanone (74) from Leguminosae.

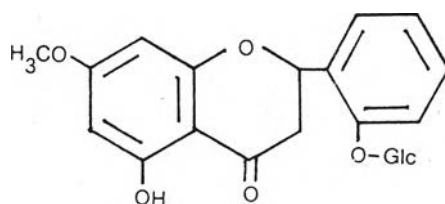


(72) R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = H

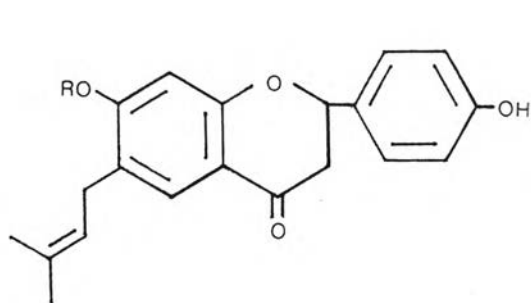
(74)

(73) R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = CH<sub>3</sub>

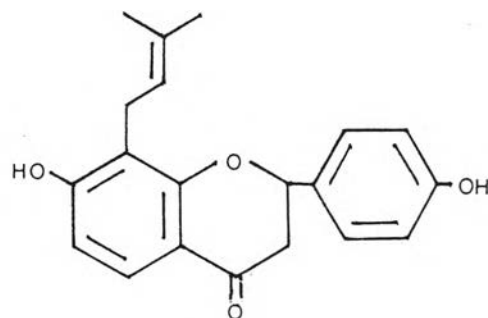
In addition to the compounds mentioned above there is a flavanone which is a new member of the rare flavonoid group having only 2'-hydroxylation on the B ring. This member is known as haplanthin (75), isolated from a variety of *Haplanthus tentaculatus* (Acanthaceae).



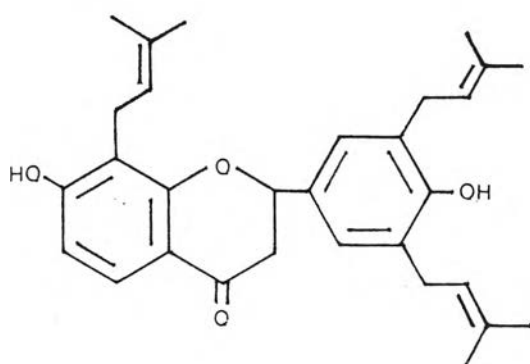
(75)

(66) R = CH<sub>3</sub>

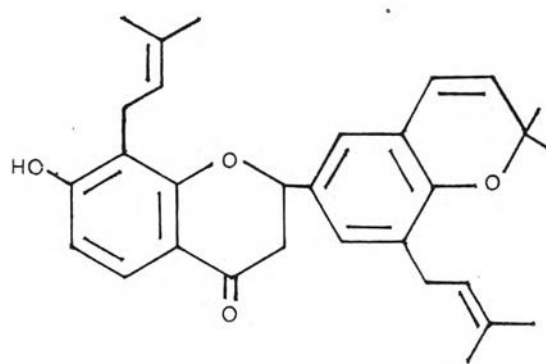
(67) R = H



(68)

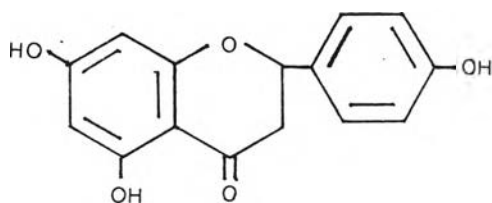


(69)



(70)

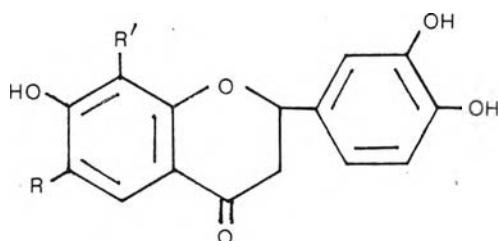
The most widely occurring of all flavanones is naringenin (71). Its three mono-O-methyl and two di-O-methyl derivatives are known to occur naturally. The former are the 7-methyl ether named sakuranetin, the 4' methyl ether named isosakuranetin and 5-O methyl naringenin. The latter include naringenin-5,7-dimethyl ether and naringenin-7-4' dimethyl ether.



(71)

### 3.3 Flavanones having two B-ring hydroxyls

The simplest flavanone of this series is butin or 7,3',4'-trihydroxyflavanone (76) which has been reported from Leguminosae and Anacardiaceae. Its glycosidic forms include isocoreopsin (the 7-O-glucoside), isomonospermoside (the 3'-O-glucoside) and butrin (the 7,3'-di-O-glucoside). Other related 5-deoxyflavanones are plathymenin (77), 8-methoxybutrin, and isookanin (78).

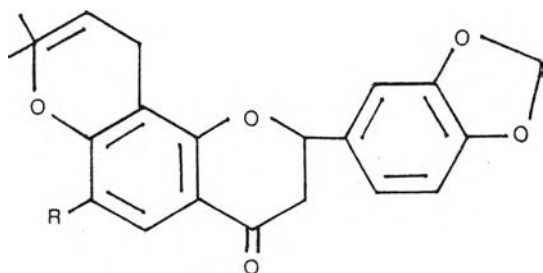


(76) R = R' = H

(77) R = OH, R' = H

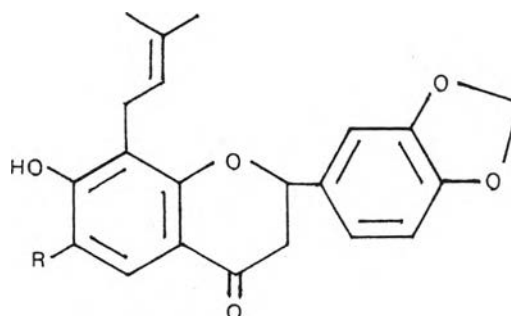
(78) R = H, R' = OH

A complex series of C-alkylated flavanones, all possessing the 3',4'-methyl-enedioxy function, has been studied. The compounds are from *Milettia ovalifolia* and are ovalichromene-A (79), ovalichromene-B (80), ovaliflavanone-C (81) and ovaliflavanone-D (82).



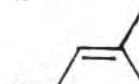
(79) R = OCH<sub>3</sub>

(80) R = H



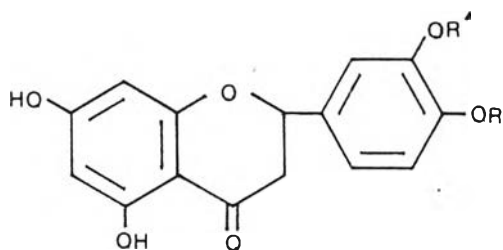
(81) R = H

(82) R =



Eriodictyol (83), which occurs widely in flowering plants, is the parent compound of several natural flavanones. Among its known glycosides are eriodictin ( the 7-O-rhamnoside) eriocitin ( the 7-O-rutinoside ) and neoeriocitrin ( the 7-O-neohesperidoside ) along with an unusual glycoside, the 5,3'-di-O-glucoside.

The monomethyl ethers of eriodictyol reported from nature are homoeriodictyol (84) and hesperitin (85). The latter is a well known constituent of *Citrus* where it occurs as the 7-O-rutinoside (hesperidin) and/or as the 7-O-neohesperidoside (neohesperidin).



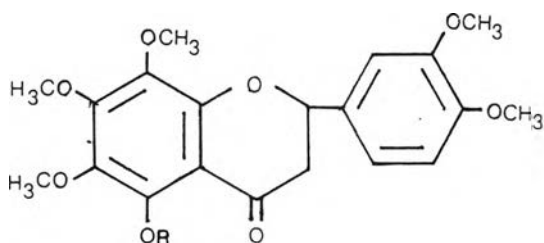
(83) R = R' = H

(84) R = CH<sub>3</sub>, R' = H

(85) R = H, R' = CH<sub>3</sub>

The known dimethyl ethers of eriodictyol include persicogenin, (the 7,4' dimethyl ether) with its 5-O-glucoside named persiconin, the 7,3'-dimethyl ether and the 7,3' dimethyl-4'-Y,Y-dimethyl ether.

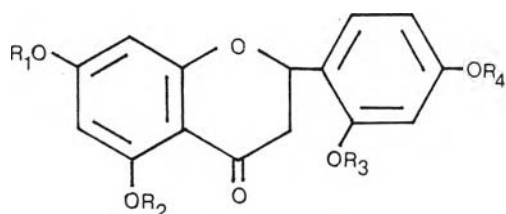
Citromitin(86), one of the most highly methoxylated flavonoids known, is 5,6,7,8,3',4' - hexamethoxyflavanone and was found along with the 5-demethyl derivative(87) in the peel of *Citrus*.

(86) R = CH<sub>3</sub>

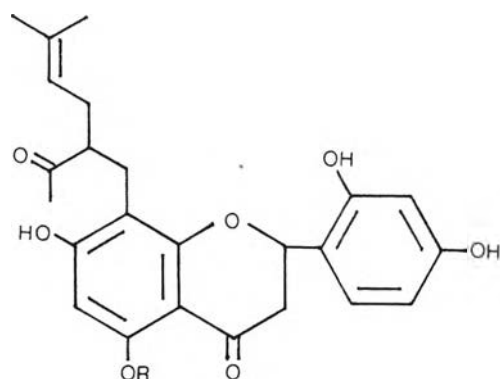
(87) R = H

Two C-methyl derivatives of eriodictyol are known: cyrtominetin, the 6,8-di-C-methyl derivative which occur as a glucoside in ferns; and the 6-C-methyl derivative which was isolated as the 7-O-glucoside. The prenyl derivative of eriodictyol was also reported from nature, and it is 7-methoxy-8-prenyl eriodictyol.

The last group of flavanones having two B-ring hydroxyls exhibit either the 2',5'- or the 2',4'- pattern. Only one member of the former type has been found and it is 5,7,2',5' - tetrahydroxyflavanone which occurs in *Inula cappa*. As for the latter type the members include artocarpanone (88), steppogenin (89), stepposide (the 7-O-galactoside of steppogenin), 7-hydroxyl - 5,2',4' - trimethoxyflavanone (90) and arjunone (91).

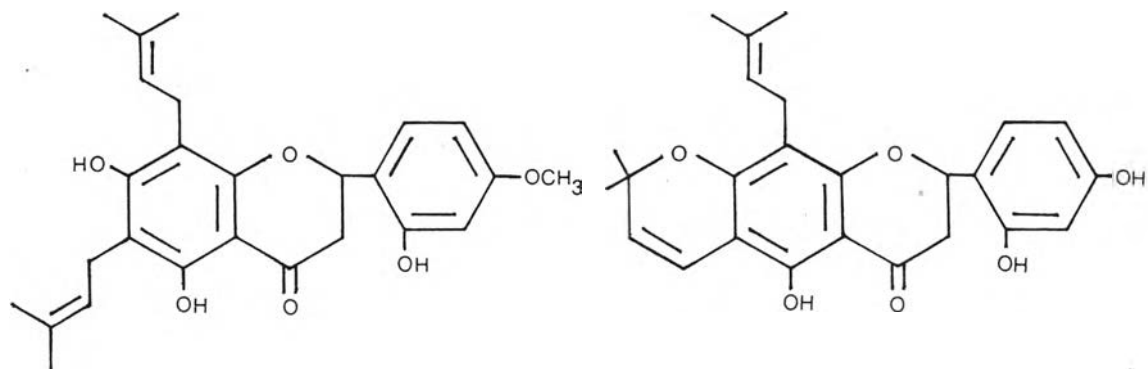
(88) R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H(89) R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H(90) R<sub>1</sub> = OH, R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = CH<sub>3</sub>(91) R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = CH<sub>3</sub>

Seven compounds are also known as the additional members of this type. All of them have been isolated from members of the Leguminosae; two from *Sophora* and five from *Flemingia*. The constituents of *Sophora* are kurarinone (92) and nor-kurarinone (93). Those of *Flemingia* include flemi-flavanone-A (94), flemichin-D (95), flemichin-E (96), flemichin-A (97) and flemiflavanone-C which is concluded to be an enantiomer of flemichin-D on the basis of its optical rotation.



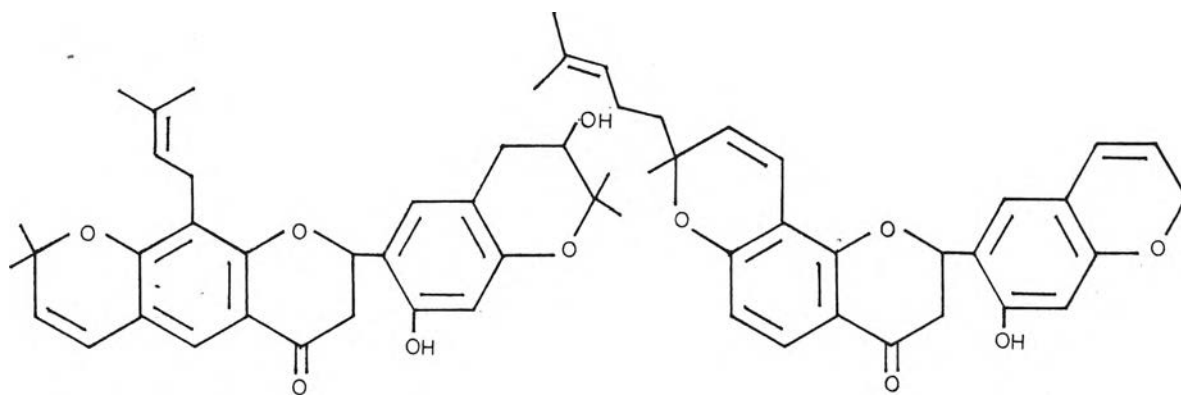
(92) R = H

(93) R = CH<sub>3</sub>



(94)

(95)

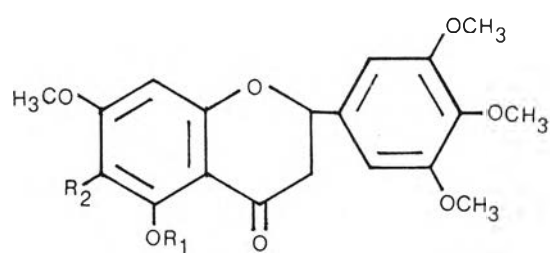


(96)

(97)

### 3.4 Flavanones having three B-ring hydroxyl

Only two such compounds are known. Compound (98) occurs in the fern while compound (99) was found in a Legume.



(98)  $R_1 = R_2 = H$

(99)  $R_1 = \text{Rhamnose}, R_2 = OCH_3$