Anthocyanins and Other Flavonoids

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Reviewing the literature published between January 1992 and December 1994

1 Introduction

The chemistry of anthocyanins, the intensely coloured red to blue pigments of the flowering plants, continues to receive considerable attention. More and more polyacyl glycosides of anthocyanidins, with aliphatic, aromatic, and sugar substituents, have been described in the last three years. A landmark in the structural elucidation of natural blue pigments was announced in 1992. This was the confirmation by *X*-ray crystallography of the structure of the metal-complexed anthocyanin commelinin from *Commelina communis*.[1] This 'supermolecule' is composed of six molecules of the delphinidin-based malonylawobanin, six molecules of the flavone copigment flavocommelinin, and one atom each of iron and magnesium. The pigments of other blue-flowered plant species have also been actively investigated from *Aconitum* and *Campanula* to *Pharbitis* and *Salvia*, as described below.

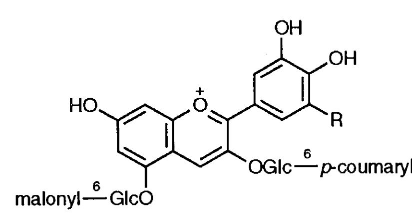
Anthocyanins are accompanied in plant cell vacuoles by many other flavonoid constituents. Some are yellow in colour (*e.g.* the chalcones) but the majority are colourless, their occurrence in green tissues being hidden behind the ubiquitous chlorophylls. These colourless flavonoids, typified by the flavonol quercetin and its glycosides, occur in small amounts in nearly all our common fruits and vegetables. They have been in the news because of their possible beneficial effects as dietary components in the prevention of human cancer. In a recent ACS publication devoted to food phytochemicals, the antioxidant and antitumour properties of flavonoids were highlighted in several chapters.[2] Quercetin itself is currently under clinical trial as an anticancer agent.[3] The possible beneficial effects of the flavonoids of red wine in inhibiting the oxidation of low density lipid in the blood are also under active investigation.[4] New antiinflammatory flavones and flavonols have been uncovered. For example, tanetin (6-hydroxykaempferol 3,7,4′-trimethyl ether), a major flavonoid of feverfew,[5] has been shown to inhibit eicosanoid generation in rat peritoneal leucocytes.[6]

The purpose of this review is to report on the flavonoid literature published since the last Flavonoids volume[7] appeared and to describe results obtained up to December 1994. It is restricted to the anthocyanins, flavones and flavonols, and the minor flavonoids. The isoflavonoids have recently been reviewed in this series[8] and the catechins and condensed tannins will be reviewed separately.

2 Anthocyanins

A correlation between anthocyanin types, pollinator, and flower colour, originally established by the general surveys of Robinson and Robinson[9] has been confirmed by more recent studies in the family Polemoniaceae.[10] An examination of anthocyanins in 49 species or cultivars of the Labiatae has shown that flower colour and pollination biology are directly correlated in this family too. Thus, all six species with long tubular scarlet flowers had pelargonidin, 17 species with red-purple flowers had cyanidin and peonidin, while 26 species with purple-violet, violet or blue flowers had delphinidin, sometimes accompanied by malvidin.[11] These anthocyanidins occur with both aromatic and aliphatic acylation and the two most common pigments in the family are cyanidin (1) and delphinidin 3-(6″-*p*-coumarylglucoside)-5-(6″-malonylglucoside) (2). Among new glycosides discovered during this survey are the 6″-monomalonate ester of peonidin 3,5-diglucoside (3) and the 4″,6″-dimalonyl esters of delphinidin (4) and malvidin 3-(6″-*p*-coumarylglucoside)-5-glucoside (5).[11]

Blue flower colour, attractive to bee pollinators, is generally based on delphinidin or its two methyl ethers, petunidin and malvidin. However, exceptions do occur. One well-known blue pigment, based on cyanidin instead of delphinidin, is protocyanin from the blue cornflower *Centaurea cyanus*, which is copigmented *in vivo* with flavone and also is reported to contain magnesium and iron.[13] Another exceptional case is the plant *Pharbitis nil* where the blue flower colour is peonidin-based. The shift to blue is achieved by intramolecular aromatic acylation, as shown in the structure of the major pigment,



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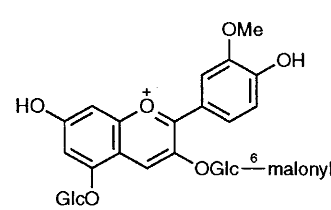
(2) R = OH



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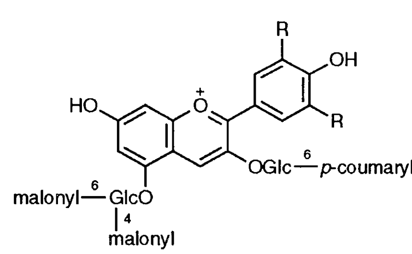
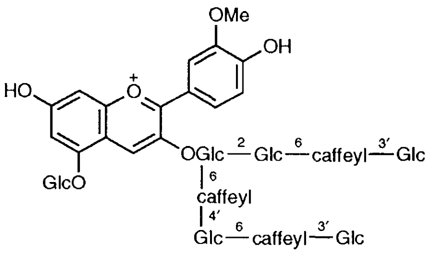


(4) R = OH
(5) R = OMe



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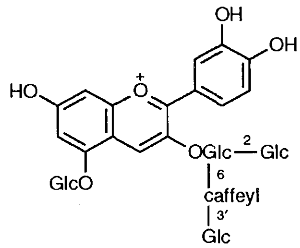

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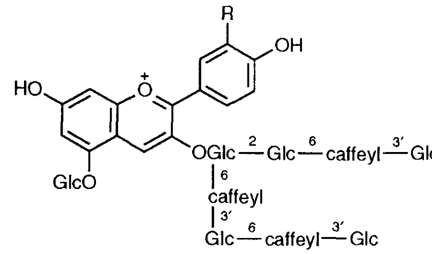
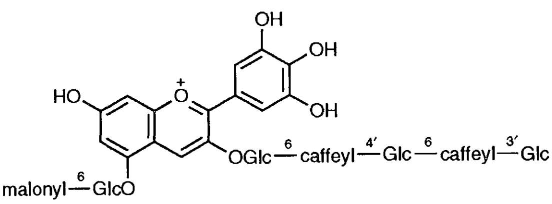


(8) R = OMe
(9) R = H



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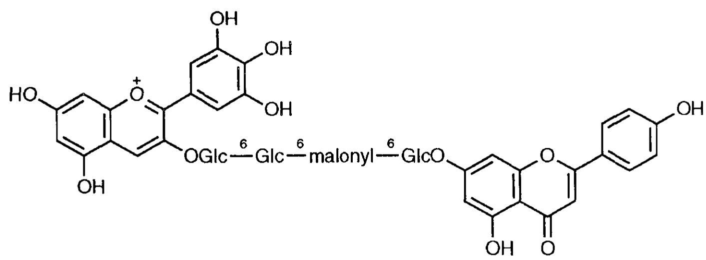

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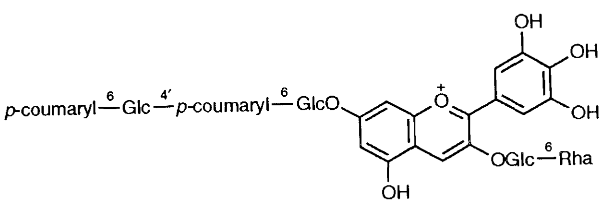

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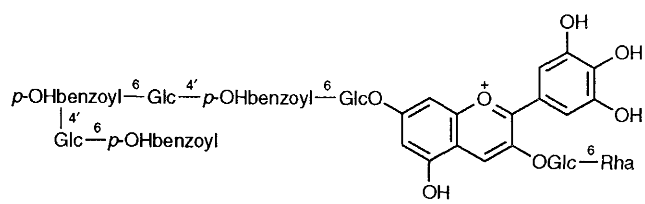


(13)

Heavenly blue anthocyanin (6).[13] A related cyanidin derivative (7) has been identified recently in violet blue flowers of the same plant.[14] A different acylated peonidin glycoside (8), isomeric with Heavenly blue anthocyanin, has been obtained from violet-blue flowers of *Pharbitis nil*,[15] while the related pelargonidin derivative (9) has been extracted from red-purple flowers.[16] Studies of (9) and related co-occurring pelargonidin glycosides in solution have confirmed that the caffeyl groups have a key role in stabilizing these pigments *in vivo*, at the same time shifting visible colour towards the blue region.[17]

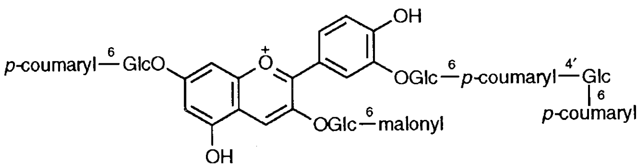
In other species of Convolvulaceae, the family to which *Pharbitis* belongs, there is a good correlation between scarlet flower colour, bird pollination, and the occurrence of pelargonidin. It is only in mauve and blue flowered species that colour is exceptionally based on cyanidin (or peonidin) rather than delphinidin. Nevertheless, one blue flowered species with the more expectable delphinidin chromophore has been discovered in the family, in *Evolvulus pilosus*. The pigment in this plant has been identified as (10).[18] It provides a stable blue colour at neutral pHs, the stability being maintained by intramolecular stacking of the caffeyl moieties between the flavylium chromophores.[18]

As already mentioned in the introduction, the blue flower pigment which has been studied in most detail over the course of many years is commelinin, from *Commelina communis*. Its three dimensional structure as a magnesium–iron chelated complex of pigment and copigment has been confirmed by *X*-ray crystallography.[1] A second metal complexed blue pigment to have been investigated more recently is protodelphin from the flowers of *Salvia patens*.[19] The delphinidin glycoside present is the same as that in *Commelina*, namely malonylawobanin, but the copigment, apigenin 7,4′-diglucoside, is different and there is only one metal component, magnesium. These authors were able to resynthesize the natural blue pigment *in vitro* by adding the three components together. Other divalent metal cations (*e.g.* Co^{2+}, Zn^{2+}) could substitute for Mg^{2+} *in vitro*.

A third blue pigment containing the metal, iron, has been reinvestigated recently from the garden ornamental *Lupinus*.[20] The chromophore has been identified as delphinidin 3-(6″-malonylglucoside) and the flavone copigment as apigenin 7-(6″-malonylglucoside) but the nature of the natural complex has yet to be determined. Since both chromophore and copigment are malonylated, it is possible that they might be linked covalently *in vivo* through the common malonic acid residue. Such a linked anthocyanin–flavone complex has in fact been reported for the first time from the purple blue flowers of the water weed *Eichhornia crassipes*.[21] This is (delphinidin 3-gentiobiosyl) (apigenin 7-glucosyl) malonate (11); the linkage between anthocyanin and flavone copigment is through the terminal glucose units to the malonyl moiety. A three dimensional structure, with the delphinidin and apigenin occupying a folding conformation as a binary complex, is suggested from the observation of a negative Cotton effect at λ_{max} 535 nm.[21]

Finally, two other blue-flowered species have been shown to have pigments with polyacyl substitution at the 7-hydroxyl of delphinidin, which are stabilized by intramolecular stacking. The simplest of the two is (12) from purple blue flowers of *Aconitum chinense* (Ranunculaceae), which is substituted by two *p*-coumarylglucose residues.[22] The more complex is campanin (13) which has three *p*-hydroxybenzoylglucose residues. It occurs in blue flowered *Campanula*, accompanied by three simpler derivatives, including monodeacylcampanin, in which the terminal *p*-hydroxybenzoyl residue of (13) is missing.[23]

An extensive electrophoretic survey of anthocyanins in 1986 showed that over 30% of the flowering plant species studied contained dibasic organic acids, such as malonic acid, linked through sugars.[24] Not surprisingly therefore, a number of new sources of malonylated anthocyanins have been found in the period under review. Thus, cyanidin 3-glucoside and 3-laminariboside and their malonyl conjugates have been reported from the red onion *Allium cepa*.[25] Likewise, a 3-malonyl-



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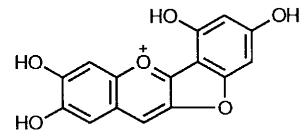


(15)

glucoside of cyanidin, with three *p*-coumarylglucose substituents (14), has been found in red purple flowers of the orchid × *Laeliocattleya* cultivar Minipurple.[26] A related pigment, with caffeyl instead of *p*-coumaryl substitution, has been identified in flowers of cineraria *Senecio cruentus* (Compositae), namely cyanidin 3-(6″-malonylglucoside)-3′-6″-(caffeylglucoside).[27] Again, malonyl conjugates of cyanidin 3-glucoside and cyanidin 3-xyloside have been found in purple seeds of the sunflower *Helianthus annuus* (Compositae).[28] Yet again malonylmalvin and malvidin 3-(6″-malonylglucoside) were found in *Lavatera maritima*, which belongs to the Malvaceae, a family already known like the Compositae (above) to produce malonated pigments on a regular basis.[29] Finally, malonylated malvidin glycosides have been reported from the Iridaceae, namely *Babiana stricta*, where such pigments are certainly uncommon.[30] Three malvidin-based anthocyanins were identified: the 3-glucoside-5-(6″-malonylglucoside), the 3-glucoside-5-(3″-sulfatoglucoside), and the 3-glucoside-(2″-sulfato-6″-malonylglucoside).[31] A unique feature of two of these pigments is the additional conjugation with sulfate, a fairly common feature in the flavone and flavonol series, but not so far recorded among anthocyanins.

While substitution of anthocyanins with aromatic hydroxycinnamic acids is common, the occurrence of anthocyanins with hydroxybenzoic acids as in the *Campanula* pigment (13) is relatively rare. The discovery of gallic (3,4,5-trihydroxybenzoic) acid substituted anthocyanins in *Acer* leaves is therefore noteworthy. Two new pigments, cyanidin 3-(2″-galloylglucoside) and 3-(2″-galloylrutinoside), were encountered.[32] The first pigment is almost universal in its occurrence in maple leaves, since it was present in almost all of 111 species surveyed.[33] The related cyanidin 3-(2″-galloylgalactoside) together with the delphinidin analogue have been found in leaves of the enormous waterlilies *Victoria amazonica* and *V. cruziana* (Nympheaceae).[34] The leaf colour in these lilies is hidden, since it is confined to the undersurface of these giant water plants. These two sources of galloylated anthocyanins, in *Acer* and *Victoria*, could not be further apart in taxonomic terms!

While the anthocyanins of floral tissues, leaves, and fruits in the flowering plants receive most attention, there are continuing studies of these pigments in these and other parts of angiosperm shrubs, gymnosperms and bryophytes. Thus the heartwood of the shrub *Acacia auriculata* has yielded a new naturally occurring glycoside of pelargonidin, the 5-galactoside.[35] Very rarely do anthocyanins occur without a sugar in the 3-position, and the fact that this new pigment lacks such a sugar may be related to its occurrence in heartwood tissue. In gymnosperms, anthocyanin pigmentation is confined to the primitive flowers and the cones. Andersen[36] has found that the three *O*-methylated anthocyanins, peonidin, petunidin, and malvidin 3-glucosides, accompany the more common cyanidin and delphinidin 3-glucosides in *Pinus*, *Picea*, and *Larix* species. This is the first record of methoxylated pigments in gymnosperms. In bryophytes, anthocyanin pigments are located in the cell wall and are usually based on 3-desoxyanthocyanin structures. This is true of riccionidin A (15), which has been obtained from the cell wall of the liverwort *Ricciocarpos natans*.[37] It could be derived from 6,7,2′,4′,6′-pentahydroxyflavylium, having undergone ring closure of the 6′-hydroxyl at the 3-position. The visible spectrum of (15) in methanolic HCl is at 494 nm, close to that of the 3-desoxyanthocyanidin luteolinidin (λ_{max} 493 nm). This novel structure is accompanied by a dimer, riccionidin B, which is probably based on two molecules of (15) linked *via* the 3′- or 5′-position. Both pigments also occur in *Marchantia polymorpha* and two other liverworts.[37]

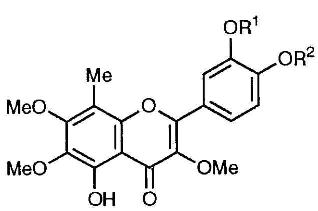
One of the main purposes of studying anthocyanins in plant cell culture is to obtain new data on biosynthesis, but relatively little new has emerged over the last three years. A major study of the anthocyanins produced by purple cell cultures of *Daucus carota* has been published.[38] It should be pointed out that although the ordinary red carrot is pigmented by carotenoids, there is a purple variety with high concentrations of anthocyanins. The cell culture pigments, which are aromatic acyl esters of cyanidin 3-(2″-xylosyl-6″-glucosylgalactoside), are essentially similar to those produced by the intact plant. The same is true in plants of the Araliaceae, where a major pigment is cyanidin 3-lathyroside. This has *inter alia* been identified in ripe red berries of *Fatsia japonica*[39] and in the cultured cells of the closely related *Aralia cordata*, where it is accompanied by peonidin 3-lathyroside.[40]

The isolation of the enzymes flavonoid 3′-hydroxylase and flavonoid 3′,5′-hydroxylase, involved in anthocyanin synthesis, from floral tissues or cell cultures is difficult because of their low abundance and instability. This difficulty has now been overcome in the case of *Petunia* flowers by the cloning and expression of the cytochrome P-450 genes which code for these two enzymes.[41] Malonyl- and acetyltransferases involved in the final stages of pigment synthesis can be obtained more readily from flower buds. A malonyltransferase from *Dendranthema morifolium* was shown to be specific for cyanidin and pelargonidin 3-glucosides, the corresponding malonates being the main pigments of these flowers. Two other anthocyanins, cyanidin 3,5-diglucoside and cyanidin 3-rutinoside, expectably failed to serve as substrates.[42] An acetyltransferase in flowers of *Zinnia elegans*, however, failed to acetylate cyanidin and pelargonidin 3,5-diglucosides, although the products of this reaction are the main floral pigments. Instead, the acetyltransferase was active with the two 3-glucosides, indicating that 5-*O*-glucosylation must be the terminal step in the biosynthesis of these anthocyanins.[43]

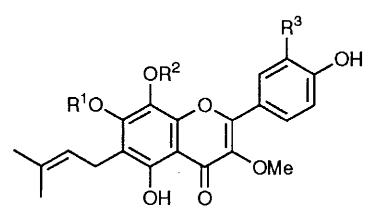
Improved methods of analysing anthocyanins and studying their conformations and *in vivo* associations have been developed in the period under review. Plasma desorption mass spectrometry (PD-MS) has been applied successfully to anthocyanins for determining the molecular weights.[44] Sensitivities to nanogram levels have been achieved; pigments should be extracted with methanolic HCl and the use of acetic acid must be avoided.[45] The stereochemistry of some grape anthocyanins has been established by homonuclear Hartmann-Hahn (HOHAHA) spectroscopy and LC-MS.[46] Confirmation of intermolecular aromatic acid association in the anthocyanin petanin has been obtained by 2D-NOE NMR experiments and Distance Geometry calculations.[47] The self-association of flavylium cations of anthocyanidin 3,5-diglucosides have been studied by circular dichroism and ^{1}H NMR and estimates have been provided for the self-association constants of the six common 3,5-diglucosides.[48] Resonance Raman Spectroscopy has been applied to anthocyanidins and their glycosides in aqueous solutions.[49] An anthocyanin anti-copigment effect has been observed in aqueous solution at pH2 between pelargonidin 3-glucoside and β-cyclodextrin, which leads to almost complete discolouration.[50] The synthetic 7-hydroxy-3,4′-dimethoxyflavylium chloride will associate with copigments in mimicry with natural anthocyanins. It has advantages over the latter for

Table 1 New flavones reported in the period 1992–1994

Flavone	Source	Ref.
*Tri-*O*-substituted Flavones*		
6,7-Dihydroxy-5-methoxyflavone (isolated as 7-Glc)	*Cephalocereus senilis*, chitin-treated cell suspension cultures (Cactaceae)	52
5,8-Dihydroxy-7-methoxyflavone (Pediflavone)	*Didymocarpus pedicellata* immature leaves (Gesneriaceae)	53
*Tetra-*O*-substituted flavones*		
7-Hydroxy-6,3′,5′-trimethoxyflavone (Grantionin)	*Inula grantioides* aerial parts (Compositae)	54
7,2′,4′,5′-Tetramethoxyflavone	*Calliandra californica* root (Leguminosae)	55
*Penta-*O*-substituted flavones*		
5,7,2′-Trihydroxy-6,4′-dimethoxyflavone (Tamaridone)	*Tamarix dioica* aerial parts (Tamaricaceae)	56
5,4′,5′-Trihydroxy-6,2′-dimethoxyflavone	*Teucrium quadrifarium* (Labiatae)	57
2′,4′,5′-Trihydroxy-5,7-dimethoxyflavone (Isoetin 5,7-dimethyl ether)	*Pedalium murex* fruits (Pedaliaceae)	58
5-Hydroxy-7,2′,4′,5′-tetramethoxyflavone (Isoetin 7,2′,4′,5′-tetramethyl ether)	*Calliandra californica* root (Leguminosae)	55
8,5′-Dihydroxy-7,3′,4′-trimethoxyflavone	*Muntingia calabura* roots (Elaeocarpaceae)	59
5′-Hydroxy-7,8,3′,4′-tetramethoxyflavone		
7,8,3′,4′,5′-Pentamethoxyflavone		
*Hexa-*O*-substituted flavones*		
5,2′,4′-Trihydroxy-6,7,8-trimethoxyflavone (Tamadone)	*Tamarix dioica* aerial parts (Tamaricaceae)	56
5,7,3′-Trihydroxy-2′,4′,5′-trimethoxyflavone	*Psiadia arabica* aerial parts (Compositae)	60
5,6,7,3′,4′,5′-Hexamethoxyflavone	*Ageratum conyzoides* (Compositae)	61
5,7,4′,5′-Tetrahydroxy-6,8,3′-trimethoxyflavone	*Tetraneuris linearifolia* var. *arenicola* aerial parts (Compositae)	62
5-Hydroxy-6,7,2′,3′,4′,5′-hexamethoxyflavone (Agecorynin F)	*Ageratum corymbosum* aerial parts (Compositae)	63
3′-Hydroxy-5,6,7,2′,4′,5′-hexamethoxyflavone (Agecorynin G)		
C-Methylflavones		
5,7-Dimethoxy-6-*C*-methylflavone	*Leptospermum scoparium* aerial parts (Myrtaceae)	64
5-Hydroxy-7-methoxy-6,8-di-*C*-methylflavone	*Desmos cochinchinensis* (Annonaceae)	65
5-Hydroxy-7-keto-6-*C*-methyl-8,8-*C*-dimethyl-7,8-dihydroflavone (Dasytrichone)	*Dasymaschalon trichophorum* stems and leaves (Annonaceae)	66
Prenylated Flavones		
7,4′-Dihydroxy-6,3′-diprenylflavone (Licoflavone B)	*Glycyrrhiza inflata* roots (Leguminosae)	67
5,7,4′-Trihydroxy-6-prenylflavone		
5,7,4′-Trihydroxy-8-prenylflavone (Licoflavone C)		
5,7,4′-Trihydroxy-6-prenylflavone	*Maclura pomifera* fruit (Moraceae)	68



(16) $R^1 = Me$; $R^2 = H$
(17) $R^1 = H$; $R^2 = Me$



(18) $R^1 = R^2 = Me$; $R^3 = H$
(19) $R^1 = R^2 = H$; $R^3 = OH$
(20) $R^1 = Me$; $R^2 = H$; $R^3 = OH$

copigmentation studies in being strongly fluorescent and its complexation can be observed by ^1H NMR spectroscopy.[51]

3 Lipophilic Flavones and Flavonols

Some 50 new flavone aglycones and 62 new flavonols have been recorded in the years 1992–94 of which 24 flavones[52–68] and 61 flavonols[69–95] are listed in Tables 1 and 2. The remaining more complex structures will be described in the text. Although the majority of flavonoids occur naturally in glycosidic combination (see Section 4), an increasing number of 'free' aglycones that are essentially lipophilic in nature are now being discovered on the leaf surface, in bud exudates, and in bark. The lipophilic properties are due to the presence in the flavonoids of *O*-methyl and *C*-methyl substitution and isoprenylation of various kinds. It is only since about 1980 that surface flavonoids have been detected at all regularly and it is possible that highly methylated and prenylated compounds previously reported from leaves or aerial parts may in fact be present at the surface, rather than within the leaf. If they are in fact located in the leaf, they are more likely to be present in the cytoplasm rather than the cell vacuole, because of their solubility properties.

Many of the compounds listed in Tables 1 and 2 are new methyl ethers of well-known flavones or flavonols and thus require little further comment. For example, isoetin (5,7,2′,4′,5′-pentahydroxyflavone) was first reported from *Isoetis durinei* (Isoetaceae) in 1975. Two new methyl ethers are listed in Table 1: the 5,7-dimethyl ether from *Pedalium murex* (Pedaliaceae);[58] and the 7,2′,4′,5′-tetramethyl ether from *Calliandra californica* (Leguminosae).[55]

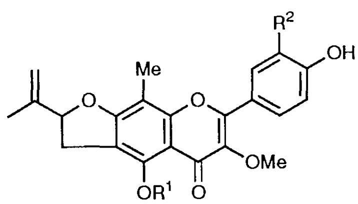
Some other new flavonoid structures are more noteworthy, especially when a number of related compounds are described from the same genus or family. Thus, 23 new lipophilic flavonols have been encountered variously in ten *Vellozia* species (Velloziaceae) (see Table 2). These include nine *C*-methylflavonols [*e.g.* 8-*C*-methylquercetagetin 3,6,7,3′- and 3,6,7,4′-tetramethyl ethers, (16) and (17)], three prenylated flavonols, (18)–(20), and eleven unusual dihydrofuranoflav-

Table 2 New flavonols reported in the period 1992–1994

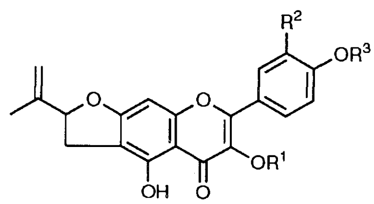
Flavonol	Source	Ref.
Tetra-O-substituted flavonols		
3,5,6,7-Tetrahydroxyflavone (6-Hydroxygalangin)	*Platanus acerifolia* buds (Platanaceae)	69
	Cassinia quinquefaria resinous exudate of aerial parts (Compositae)	70
6,7,4′-Trihydroxy-3-methoxyflavone	*Graziela mollissima* aerial parts (Compositae)	71
Penta-O-substituted flavonols		
3,5,6,7,4′-Pentahydroxyflavone (6-Hydroxykaempferol)	*Carthamus tinctorius* petals (Compositae)	72
6,4′-Dihydroxy-3,5,7-trimethoxyflavone	*Jasonia candicans* leaf (Compositae)	73
3,5,7,8-tetrahydroxy-4′-methoxyflavone (Herbacetin 4′-methyl ether)	*Pentagramma triangularis* hybrid frond exudate (Adiantaceae)	74
3,5,7,8,4′-pentamethoxyflavone	*Drummondita calida* aerial parts (Rutaceae)	75
6,7,3′,4′-Tetrahydroxy-3-methoxyflavone	*Graziela mollissima* aerial parts (Compositae)	71
3,5,7-Trihydroxy-2′,4′-dimethoxyflavone	*Machilus bombycina* leaf (Lauraceae)	76
3,5-Dihydroxy-7,2′,4′-trimethoxyflavone		
Hexa-O-substituted flavonols		
3,5,6,7,8,4′-Hexamethoxyflavone (Auranetin 5-methyl ether)	*Drummondita calida* aerial parts (Rutaceae)	75
Quercetagetin 3,5,7,4′-tetramethyl ether	*Jasonia candicans* leaf (Compositae)	73
3,5,7,3′,4′,5′-Hexamethoxyflavone	*Murraya paniculata* flower (Rutaceae)	77
Hepta-O-substituted flavonols		
3,5,3′-Trihydroxy-6,7,8,4′-tetramethoxyflavone	*Zieridium pseudobtusifolium* leaf (Rutaceae)	78
3,5-Dihydroxy-6,7,8,3′,4′-Pentamethoxyflavone	*Acronychia porteri* leaf (Rutaceae)	78
5,7,5′-Trihydroxy-3,6,2′,4′-tetramethoxyflavone	*Eupatorium buniifolium* leaf and stem (Compositae)	79
5-Hydroxy-3,7,2′,3′,4′,6′-hexamethoxyflavone	*Distemonanthus benthamianus* heartwood (Leguminosae)	80
Octa-O-substituted flavonols		
3,5,3′-Trihydroxy-6,7,8,4′,5′-pentamethoxyflavone (3-*O*-Demethyldigicitrin)	*Zieridium pseudobtusifolium* leaf (Rutaceae)	78
C-methylflavonols		
6-*C*-Methylquercetin 3-methyl ether	*Vellozia phalocarpa* leaf (Velloziaceae)	81
8-*C*-Methyl 6-hydroxykaempferol 3,6,7-trimethyl ether	*Vellozia nanuzae* leaf (Velloziaceae)	82
8-*C*-Methylquercetagetin		
3,6,7-Trimethyl ether	*V. lilacina* and *V.* aff. *epidendroides* leaf (Velloziaceae)	83
3,6,3′-Trimethyl ether	*V. nanuzae* leaf (Velloziaceae)	82
3,6,7,3′-Tetramethyl ether (16)	*V. lilacina*, *V.* aff. *epidendroides* leaf (Velloziaceae)	83
3,6,7,4′-Tetramethyl ether (17)	*V. nanuzae* and *V. phalocarpa* leaf surface (Velloziaceae)	81
Methylenedioxyflavonol		
3,5-Dihydroxy-6,7,8-trimethoxy-3′,4′-methylenedioxyflavone	*Melicope triphylla* leaf (Rutaceae)	84
Furanoflavonols		
3-Methoxyfurano[2″,3″:7, 6]flavone	*Pongamia pinnata* root bark (Leguminosae)	85
2″-Isopropenyldihydrofurano[4″,5″:6,7]kaempferol (Vellokaempferol)		
3-Methyl ether (26)	*Vellozia stipitata* and *V. streptophylla* leaf (Vellozioceae)	86
3,4′-Dimethyl ether		
3,5-Dimethyl ether	*V. stipitata* leaf (Velloziaceae)	87
Velloquercetin (24)	*V. stipitata* and *V. streptophylla* leaf (Velloziaceae)	86
4′-Methyl ether (25)		
3,3′-Dimethyl ether		
3,3′,4′-Trimethyl ether		
3-Methyl ether	*V. stipitata* leaf (Velloziaceae)	87
3,5,3′-Trimethyl ether		
C-Methylfuranoflavonols		
8-*C*-Methylvellokaempferol	*Vellozia stipitata* leaf (Velloziaceae)	87
3,5-dimethyl ether		
8-*C*-Methylvelloquercetin		
3-methyl ether		
3,5,3′-trimethyl ether		
Prenylated flavonols		
6-*C*-Prenylkaempferol	*Platanus acerifolia* buds (Platanaceae)	69
8-*C*-Prenylkaempferol		
3′-*C*-Prenylkaempferol		
6-*C*-Prenylherbacetin	*Vellozia* aff. *scoparia* leaf surface (Velloziaceae)	81
3,8-Dimethyl ether (18)		
3-Methyl-6-*C*-prenylkaempferol (Topazolin)	*Lupinus luteus* roots (Leguminosae)	88
3-Methyl-6-*C*-(3-hydroxy-3-methylbutyryl)-kaempferol (Topazolin hydrate)		
3,6,7,3′,4′-Pentahydroxy-2′-prenylflavone (Neouralenol)	*Glycyrrhiza uralensis* leaf (Leguminosae)	90
3,5,7,3′,4′-Pentahydroxy-5′-prenylflavone (Uralenol)		
5,6,3′,4′-Tetrahydroxy-3-methoxy-6′-prenylflavone (Uralene)	*Glycyrrhiza uralensis* leaf (Leguminosae)	89
5,7,3′,4′-Tetrahydroxy-3-methoxy-5′-prenylflavone (Uralenol 3-methyl ether)		
6-*C*-Prenylquercetin	*Vellozia coronata* leaf surface (Velloziaceae)	82
3-Methyl ether (19)		
3,7-Dimethyl ether (20)		
7,4′-Dimethyl ether (Isorhynchospermin)	*Paracalyx scariosa* (Leguminosae)	91

Table 2 (*cont.*)

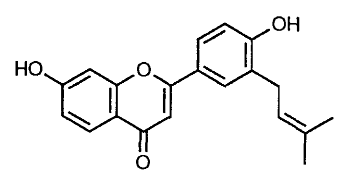
Flavonol	Source	Ref.
Prenylated flavonols (cont.)		
8-*C*-Prenylquercetin	*Paracalyx scariosa* (Leguminosae)	92
7,3′-Dimethyl ether (Scarciosin)		
5,7,3′,4′,6′-Pentahydroxy-3,8-di-*C*-prenylflavone	*Artocarpus altilis* (Moraceae)	93
Prenyloxyflavonols		
5,7-Dihydroxy-3′-methoxy-4′-diprenyloxyflavone	*Bosistoa brassii* leaf (Rutaceae)	94
5,7-Dihydroxy-8-methoxy-3,4′-diprenyloxyflavone	*Boronia coerulescens* ssp. *spicata* aerial parts (Rutaceae)	95
5,7-Dihydroxy-3,6-dimethoxy-4′-prenyloxyflavone		
3,5,7-Trihydroxy-8-methoxy-4′-prenyloxyflavone		
3,5,7-Trihydroxy-6-methoxy-4′-prenyloxyflavone		
5,4′-Dihydroxy-3,8,3′-trimethoxy-7-prenyloxyflavone		
5,4′-Dihydroxy-3,6,3′-trimethoxy-7-prenyloxyflavone		
5,7-Dihydroxy-3,8-dimethoxy-4′-prenyloxyflavone	*Boronia coerulescens* ssp. *spinescens* aerial parts (Rutaceae)	95
5,7-Dihydroxy-3,8,3′-trimethoxy-4′-prenyloxyflavone		



(21) R^1 = Me; R^2 = H
(22) R^1 = H; R^2 = OH
(23) R^1 = Me; R^2 = OMe



(24) $R^1 = R^3$ = H; R^2 = OH
(25) R^1 = H; R^2 = OH; R^3 = Me
(26) R^1 = Me; $R^2 = R^3$ = H



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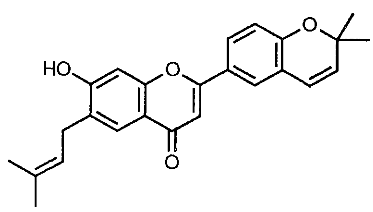

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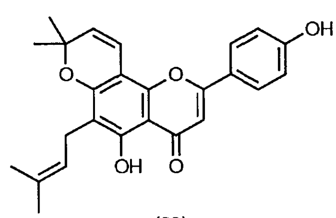

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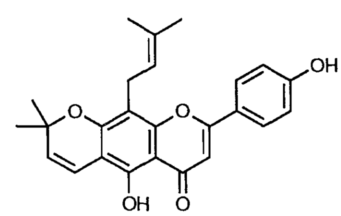


(30)

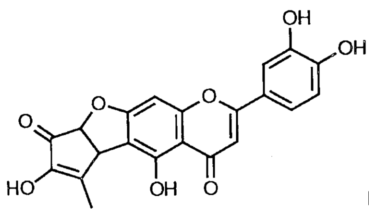
onols, three of which are also *C*-methylated, (21)–(23). 2″-Isopropenyldihydrofurano[4″,5″:6,7]quercetin, named velloquercetin (24), was first characterized from the leaf surface of *V. streptophylla*, where it co-occurs with its 4′-methyl ether (25) and vellokaempferol 3-methyl ether (26). Flavonoid analysis of other *Vellozia* species revealed the related structures velloquercetin 3-methyl ether, 3,3′-dimethyl ether, 3,5,3′- and 3,3′,4′-trimethyl ethers, and vellokaempferol 3-methyl ether and 3,5- and 3,4′-dimethyl ethers in the leaf wax of *V. stipitata*, and velloquercetin 3,3′-dimethyl ether in *V. laevis*. The prenylated flavonols were present only as surface constituents, the vello derivatives occurred mostly on the leaf surface, and the *C*-methylated flavonols predominantly in the cytoplasm within the leaf.

The structure of velloquercetin (24) was established by NMR spectroscopy and comparison with rotenone, in the isoflavonoid series, which has an identical isopropenyl-dihydrofuran substitution. The location of the isopentenyl side-chain at C-6 was serendipitously shown to be correct from an experiment designed to confirm the absence of *O*-methylation. Treatment with pyridinium chloride at 140 °C for 6 hr opened the furan ring, with reclosure on the 5-hydroxyl. The structure of the product as a 5-*O*-substituted flavonol was immediately apparent from its intense yellow fluorescence.[86]

The Velloziaceae is a completely new source of prenylated flavonols, but such compounds are well known in several dicotyledonous families, notably in the Leguminosae. A variety of new prenylated and pyranoflavonoids have been reported from four genera of this family. Thus, four prenylated flavonols, neouralenol, uralenol, uralene, and uralenol 3-methyl ether, have been characterized from leaf extracts of *Glycyrrhiza uralensis* (see Table 2) while from roots of *G. inflata* three prenylated flavones have been reported. These are 6-prenylapigenin, 8-prenylapigenin, and 6,3′-diprenyl-7,4′-dihydroxyflavone.[67] 6-Prenylapigenin has also been found contemporaneously in the fruits of *Maclura pomifera* (Moraceae).[68] 8-Prenylapigenin is a new structure, although it had previously been described from *Marshallia grandiflora* (Compositae). Reinterpretation[67] of the data for the compound from *Marshallia* showed that it was, in fact, the 6-prenyl isomer.

Two further diprenylated flavones, kanzonol D (27) and kanzonol E (28), have been identified from *Glycyrrhiza eurycarpa* roots.[96] Two more complex structures have been found which have both prenyl and pyrano side chains, laxifolin (29) and isolaxifolin (30), and these occur in *Derris laxifolia* roots.[97] Two flavones, from the aerial parts of *Cassia nomame*, are demethyltorosaflavone C (31) and demethyltorosuflavone D (32);[98] the related 3′-methyl ethers were earlier obtained from another *Cassia* species, *C. torosa*.[99] Compound (32) has a degraded isoprenyl side chain, which could either be derived from a prenylated side chain by loss of two carbons followed by oxidation or by oxidative breakdown of the co-occurring pentacyclic compound (31). Another unique pentacyclic flavone, (33), has been described from aerial parts of *Tephrosia vicioides*.[100]

The genus *Artocarpus* in the Moraceae is another rich source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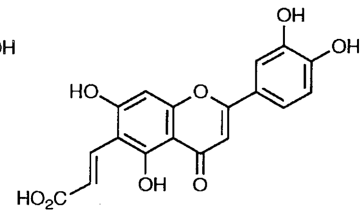
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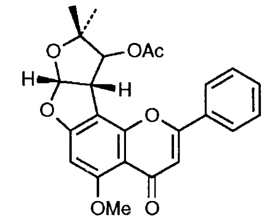
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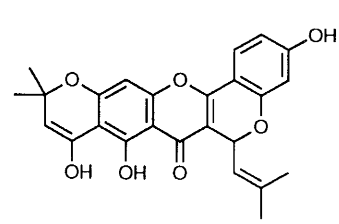
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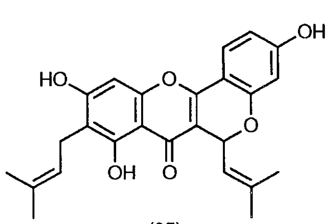
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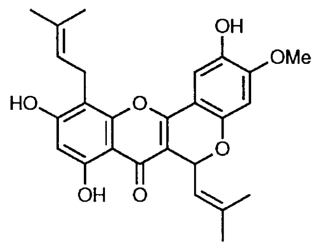
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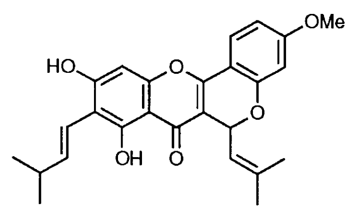
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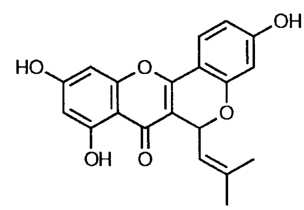
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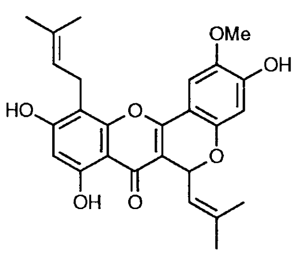
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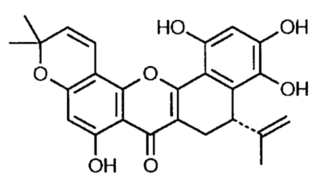
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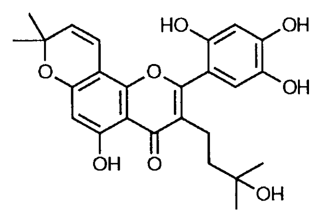
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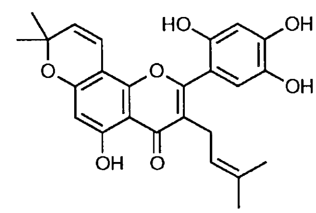
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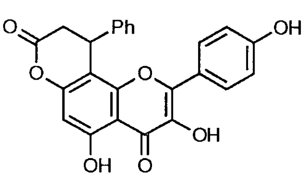
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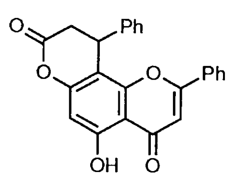
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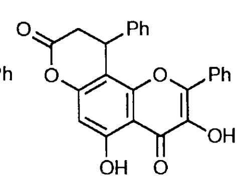
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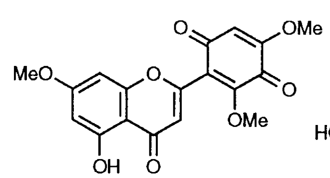
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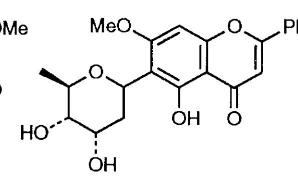
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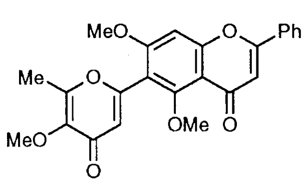
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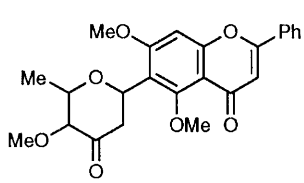
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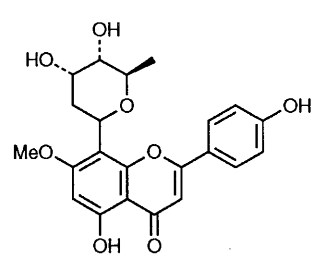
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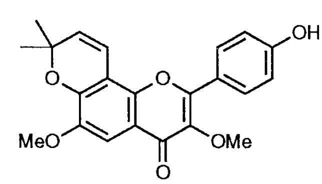

(51)

of prenylated flavones and more complexly derived structures. For example, isocyclomorusin (34), isocyclomulberrin (35), and cycloaltilisin (36) have been identified from stems of *A. altilis*[101] and cycloartocarpin A (37) from root bark of *A. heterophyllus*.[102] Five other new compounds should be mentioned; cyclocommunol (38), dihydroisocycloartocommunin (39),[103] and structures (40)–(42) have been characterized from root bark of *A. communis*.[104]

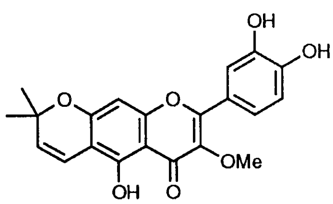
Two unique phenylpropanoid substituted flavonols, calomelanol D (43) and calomelanol F (44), have been obtained from the fern *Pityrogramma calomelanos* (Polypodiaceae).[105,106] Three similarly substituted chalcones, named calomelanols A–C, and flavanones have already been identified from the farinose extract of this plant by the same authors,[107] and the structure of another flavonol, referred to previously as 'D-2/6' (45), has been confirmed recently by NMR spectral analysis.[108] The remaining compounds described in this section come from four different plant families. They include an unusual methylated flavone (46) from *Chrysosplenium grayanum* (Compositae) with a 2″,5″-quinone grouping, which could be derived from the corresponding 2″, 5″-hydroxylated flavone.[109] In twigs of *Hoslundia opposita* (Labiatae) four further tetracyclic flavones, hoslunddiol (47), oppositin (48), 5-*O*-methylhoslundin (49), and aciculatin (50), all related to the previously determined hoslundin and hoslundal, have been reported.[110] A 5-deoxyflavonol with pyrano substitution (51) has been characterized

Table 3 New flavone glycosides reported in the period 1992–1994

Flavone	Source	Ref.
5,6,7-Trihydroxyflavone (Baicalein)		
7-(6″-Malonylglucoside)	*Cephalocereus senilis* cell suspension cultures (Cactaceae)	113
6,7-Dihydroxy-5-methoxyflavone		
7-Glucoside	*Cephalocereus senilis* chitin-treated cell suspension cultures (Cactaceae)	114
5,7-Dihydroxy-6-methoxyflavone		
5-Rhamnoside	*Trichosanthes anguina* seed (Cucurbitaceae)	115
5,7,8-Trihydroxyflavone		
5-Glucoside	*Pyracantha coccinea* roots (Rosaceae)	116
7-Hydroxy-5,8-dimethoxyflavone		
7-Glucuronide	*Scutellaria rivularis* root (Labiatae)	117
7-Rhamnoside-4′-glucosyl-rhamnoside	*Asplenium normale* fronds (Aspleniaceae)	118
6-Hydroxyapigenin (Scutellarein)		
7-Xylosyl(1→6)galactoside	*Semecarpus kurzii* leaf (Anacardiaceae)	119
7-Glucuronosyl(1→2)-glucuronide	*Perilla ocimoides* leaf (Labiatae)	120
7-[6″-(3-Hydroxy-3-methylglutaryl)glucoside]	*Frullania muscicola* whole plant (Frullaniaceae)	121
Scutellarein 6-methyl ether (Hispidulin)		
7-Neohesperidoside	*Ipomoea purpurea* flowers (Convolvulaceae)	122
Scutellarein 4′-methyl ether 7-(2″,6″-Diacetylalloside)	*Sideritis perfoliata* (Labiatae)	123
Scutellarein 6,7-dimethyl ether		
4′-Glucuronide	*Conyza linifolia* (Compositae)	124
Scutellarein 6,4′-dimethyl ether (Pectolinarigenin)		
7-(2‴-acetylrutinoside)	*Linaria japonica* whole plant (Scrophulariaceae)	125
7-(3‴-acetylrutinoside)		
7-(4‴-acetylrutinoside)	*Linaria haelava* whole plant (Scrophulariaceae)	126
Scutellarein 7,4′-dimethyl ether		
6-Xylosyl(1→2)glucoside	*Gelonium muliflorum* seed (Euphorbiaceae)	127
6-Rhamnosyl(1→2)glucoside		
Scutellarein 6,7,4′-trimethyl ether (Salvigenin)		
5-[6‴-acetylglucosyl(1→3)-galactoside]	*Striga aspera* (Scrophulariaceae)	128
8-Hydroxyapigenin (Isoscutellarein)		
8-Sophoroside	*Gratiola officinalis* leaf (Scrophulariaceae)	129
8-(2″-Sulfatoglucuronide)	*Helicteres angustifolia* root bark (Sterculiaceae)	130
Isoscutellarein 4′-methyl ether		
7-Allosyl(1→2)glucoside	*Sideritis javalambrensis* aerial parts (Labiatae)	131
8-(2″-Sulfatoglucuronide)	*Helicteres angustifolia* root bark (Sterculiaceae)	132
Luteolin		
7-Galactosyl(1→6)-galactoside	*Anogeissus latifolia* (Combretaceae)	133
7-Galactosylglucuronide	*Andryala reguisina* aerial parts (Compositae)	134
4′-Rutinoside	*Dalbergia stipulacea* leaf (Leguminosae)	135
7-[6″-(2-Methylbutyryl)glucoside]	*Arnica chamissonis* flowers (Compositae)	136
7-[6″-(3-Hydroxy-3-methylglutaryl)glucoside]	*Frullania muscicola* whole plant (Frullaniaceae)	121
3′-(3″-Acetylglucuronide)	*Rosmarinus officinalis* leaf (Labiatae)	137
3′-(4″-Acetylglucuronide)		
Luteolin 4′-methyl ether (Diosmetin) 3′-Glucoside	*Cassia torosa* leaf (Leguminosae)	138
7-Neohesperidoside (Neodiosmin)	*Citrus aurantium* leaf (Rutaceae)	139
6-Hydroxyluteolin	*Hebe stricta* leaf (Scrophulariaceae)	140
7-Sambubioside		
7-[3″-(3-Hydroxy-3-methylglutaryl)glucoside]	*Frullania muscicola* whole plant (Frullaniaceae)	121
7-[4″-(3-Hydroxy-3-methylglutaryl)glucoside]		
7-[6″-(3-Hydroxy-3-methylglutaryl)glucoside]		
6-Methoxyluteolin (Nepetin, leupafolin)		
7-Glucuronide	*Digitalis lanata* leaf (Scrophulariaceae)	141
7-Methylglucuronide		
7-Rhamnoside-3′-xyloside	*Chenopodium ambrosioides* (Chenopodiaceae)	142
7-[6″-(2-Methylbutyryl)glucoside]	*Arnica chamissonis* flowers (Compositae)	136
6-Hydroxyluteolin 3′-methyl ether (Nodifloretin)		
7-[6″-(3-Hydroxy-3-methylglutaryl)glucoside]	*Frullania polysticta* whole plant (Frullaniaceae)	121
8-Hydroxyluteolin (Hypolaetin)		
7-Sophoroside	*Gratiola officinalis* leaf (Scrophulariaceae)	129
8-Hydroxyluteolin 3′-methyl ether		
8-Glucuronide	*Gratiola officinalis* leaf (Scrophulariaceae)	129
7-Sophoroside		
8-Hydroxyluteolin 4′-methyl ether		
7-(6‴-Acetylallosyl)(1→2)(6″-acetylglucoside)	*Sideritis syriaca* and *S. scardica* (Labiatae)	143
5,6,7,3′,4′-Pentahydroxy-8-methoxyflavone (Pleurostimin)		
7-Glucoside	*Vellozia nanuzae* leaf (Velloziaceae)	144
5,6,3′,4′-Tetrahydroxy-7,8-dimethoxyflavone (Pleurostimin 7-methyl ether)		
6-Glucoside	*Vellozia nanuzae* leaf (Velloziaceae)	144
5,7,8,2′-Tetrahydroxyflavone		
7-Glucuronide	*Scutellaria rivularis* root (Labiatae)	117
5,2′,6′-Trihydroxy-7,8-dimethoxyflavone		
2′-Glucuronide	*Scutellaria rivularis* root (Labiatae)	117
5,2′-Dihydroxy-7,8,6′-trimethoxyflavone		
2′-Glucuronide	*Scutellaria rivularis* root (Labiatae)	117
5,7,3′,4′,5′-Pentahydroxyflavone (Tricetin)		
7-Glucoside-3′-[6″-(3-hydroxy-3-methylglutaryl)glucoside]	*Frullania polysticta* whole plant (Frullaniaceae)	121

Table 3 (*cont.*)

Flavone	Source	Ref.
Tricetin 3′,5′-dimethyl ether (Tricin)		
7-Rhamnosyl(1→2)glucoside	*Phoenix humilis* var. *lanceana* leaf (Palmae)	145
7-[X″-(3-Hydroxy-3-methylglutaryl)glucoside]	*Frullania polysticta* whole plant (Frullaniaceae)	121
6-Hydroxytricetin		
5-Rhamnoside	*Argyreia speciosa* leaf (Convolvulaceae)	146
5-Glucoside		
5,7,2′,5′-Tetrahydroxy-8,6′-dimethoxyflavone (Viscidulin III)		
2′-Glucoside	*Scutellaria baicalensis* roots (Labiatae)	147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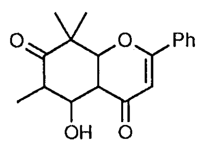
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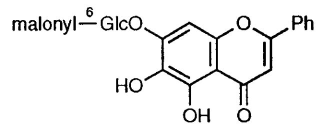
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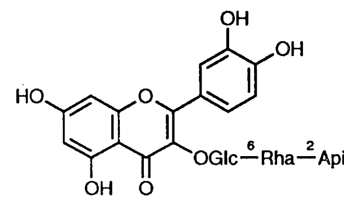
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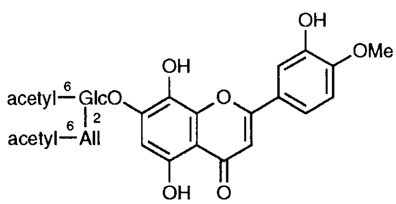
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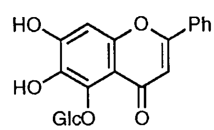
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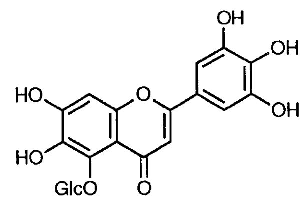

(58)

from the fruit of *Citrus reticulata* cv. *blanco*,[111] which is not unusual in the Rutaceae, where such structures are frequently encountered. Similarly, the finding of isojacareubin (52), another pyranoflavone, in the whole plant of *Hypericum japonicum*[112] is not surprising since many related prenylated xanthones have been recorded from the Guttiferae.

Some known flavones and flavonols (*e.g.* quercetin) show useful antitumour activity but unfortunately not all new structures are immediately tested for bioactivity. Positive results have been reported in some cases. Dasytrichone (53) from *Dasymaschiton* inhibited the metabolism of the carcinogen benzopyrene in hamster embryo cell cultures.[66] Similarly, the prenylflavones (40)–(42) from *Artocarpus* showed strong cytotoxic activity against leukaemia cells in tissue culture.[67] The *Vellozia* flavonols, *e.g.* (18), show structural resemblance to antifungal isoflavones from *Lupinus* and were tested for such activity but proved to be negative. Screening *Vellozia coronata* for antifungal compounds revealed instead the presence of active resveratrol derivatives.[104]

4 Flavone and Flavonol Glycosides

In the period 1992–94, 55 new flavone glycosides[113–147] and 125 new flavonol glycosides[148–223] have been reported. These are listed in Tables 3 and 4 together with plant sources and references. Acylated and sulfated derivatives and any bound form of a flavone or flavonol are included under this heading as well as those with only sugar.

Among the more unusual new simple flavone glycosides are baicalein 7-(6″-malonylglucoside) (54), which co-occurs with the corresponding flavanone conjugate,[113] and 6,7-dihydroxy-5-methoxyflavone 7-glucoside[114] from chitin-induced cell cultures of the old man cactus, *Cephalocereus senilis*. Seven other known flavone glycosides, identified in chitin-induced cultures of the same plant, all have the same 5,6,7-oxygenation pattern in ring A and an unsubstituted B ring. None of these glycosides was detected in unelicited cell cultures.[113,114]

No new monosaccharides were discovered in glycosidic combination with flavones or flavonols during the period under review but there are some new reports of the two rarer sugars apiose and allose. Thus, two apiose-containing glycosides, rhamnocitrin 3-[5‴-*p*-coumarylapiosyl(1→2)glucoside] and the corresponding ferulyl derivative have been identified in seeds of *Astragalus complanatus*,[174] quercetin 3-apiosyl(1→2)-rhamnosyl(1→6)glucoside (55) has been reported from aerial parts of *Baccharis thesioides*,[185] and a mixture of isorhamnetin 3-apiosylglucoside and 3-apiosylgalactoside from *Barbacenia conicostigma* (Velloziaceae).[196]

The new allosides include kaempferol 7-alloside, which was isolated from leaves of *Indigofera hebepetala* (Leguminosae).[148] The 3-allosides of kaempferol, its 7-methyl ether, and quercetin have all been described previously[7] but this is the first record of a flavonol 7-alloside. The three other allose-containing glycosides are all 6-hydroxyflavones isolated from the aerial parts of various *Sideritis* species, *i.e.* isoscutellarein 4′-methyl ether 7-allosyl(1→2)glucoside[131] and two acetylated derivatives, scutellarein 4′-methyl ether 2″,6″-diacetylalloside[123] and 8-hydroxyluteolin 4′-methyl ether 7-(6‴-acetylallosyl) (1→2)(6″-acetylglucoside) (56).[143] Apigenin, luteolin, and 8-hydroxyluteolin 7-allosyl (1→2)glucosides have been reported previously from other *Sideritis* species and some acetylated allosides from *Stachys* species, all members of the Labiatae.[7]

5-*O*-Glycosylation of flavones and flavonols is still comparatively rare in nature, presumably because of the hydrogen bonding that exists between the 5-hydroxyl and the 4-carbonyl. There are five new reports in the present listings. These include one flavone and one flavonol 5-glycoside from the Rosaceae, *viz* norwogonin 5-glucoside (57) from roots of *Pyracantha coccinea*[116] and isorhamnetin 5-galactoside from aerial parts of *Pyrus bourgaena*,[194] respectively. The 5-glucoside of another flavonol, quercetagetin 3,6,3′-trimethyl ether (jaceidin), has been recorded from twigs of *Eucryphia glutinosa* (together with another 5-substituted flavonol, quercetin 3,5-dimethyl ether) (caryatin) 7-glucoside.[104] However, the most interesting finding is that of the 5-glucoside (58) and 5-rhamnoside of the 6-hydroxylated flavone 6-hydroxytricetin, from leaves of *Argyreia*

Table 4 New flavonol glycosides reported in the period 1992–1994

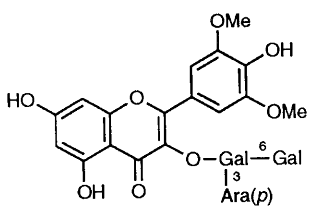
Flavone	Source	Ref.
Kaempferol 7-alloside	*Indigofera hebepetala* leaf (Leguminosae)	148
3-Glucosyl(1→2)rhamnoside	*Ginkgo biloba* leaf (Ginkgoaceae)	149, 150
7-Glucosyl(1→4)xyloside	*Crotalaria laburnifolia* (Leguminosae)	151
7-Neohesperidoside	*Caralluma tuberculata* (Asclepiadaceae)	152
3,7-Diarabinoside	*Indigofera hebepetala* leaf (Leguminosae)	148
3,4′-Diglucoside	*Picea abies* needles (Pinaceae)	153
3-(2^{Gal}-Rhamnosylrobinobioside)	*Sesbania sesban* (Leguminosae)	154
3-Rhamnosyl(1→2)[glucosyl(1→3)-glucoside]	*Impatiens balsamina* petals (Balsaminaceae)	155
3-Rhamnoside-7-glucosyl(1→2)rhamnoside	*Siraita grosvenori* fresh fruit (Cucurbitaceae)	156
3-Glucosyl(1→2)galactoside-7-glucoside	*Nicotiana* spp. flowers (Solanaceae)	157
3-Sophoroside-7-glucuronide	*Allium cepa* guard cells (Alliaceae)	158
4′-Rhamnosyl(1→3)rhamnosyl(1→6)-galactoside	*Rhamnus thymifolius* fruits (Rhamnaceae)	159
3-Rhamnosyl(1→4) rhamnosyl (1→6)galactoside-7-rhamnoside (3-Isorhamninoside-7-rhamnoside)	*Vigna* spp. whole plant (Leguminosae)	160
3-Rutinoside-7-sophoroside	*Equisetum* spp. (Equisetaceae)	161
3-Glucosyl(1→2)[rhamnosyl(1→6)galactoside]-7-rhamnoside	*Cephalocereus senilis* whole young plants (Cactaceae)	162
3-[6″-(3-hydroxy-3-methylglutaryl)glucoside]	*Citrus aurantifolia* callus cultures (Rutaceae)	163
3-(2″-Galloylarabinoside)	*Eucalyptus rostrata* leaf (Myrtaceae)	164
3-(2″-*E*-*p*-Coumarylrhamnoside)	*Platanus orientalis* buds	165
	P. acerifolia buds (Platanaceae)	166
3-(2″-*Z*-*p*-Coumarylrhamnoside)	*Platanus acerifolia* buds (Platanaceae)	166
3-(6″-Ferulylglucoside)	*Polylepis incana* leaf (Rosaceae)	167
7-(6″-*p*-Coumarylglucoside)	*Buddleia coriacea* aerial parts (Loganiaceae)	168
3-(2″,3″-di-*E*-*p*-Coumarylrhamnoside)	*Platanus orientalis* buds (Platanaceae)	165
3-(2″,6″-di-*E*-*p*-coumarylglucoside)	*Quercus canariensis* (Fagaceae)	169
3-(2″-*Z*-*p*-Coumaryl-6″-*E*-*p*-coumarylglucoside)		
3-[6″-(3-Hydroxy-3-methylglutaryl)glucoside]-7-glucoside	*Citrus aurantifolia* callus cultures (Rutaceae)	163
3-(6″-Malonylglucoside)-7-glucoside	*Equisetum* spp. (Equisetaceae)	161
3-(2″-*p*-Coumarylrhamnoside)-7-rhamnoside	*Cheilanthes fragrans* aerial parts (Sinopteridaceae)	170
3-(6″-*p*-Coumarylglucoside)-7-glucoside	*Anaphalis contorta* flowers (Compositae)	171
3-[2‴,3‴,4‴-Triacetyl-α-L-arabinopyranosyl(1→6)glucoside	*Calluna vulgaris* flowers (Ericaceae)	172
3-Rhamnosyl(1→3)-4‴-acetylrhamnosyl(1→6)galactoside	*Rhamnus thymifolius* fruits (Rhamnaceae)	159
3-(2‴-*E*-*p*-Coumarylsophoroside)-7-glucoside	*Brassica oleracea* leaf (Cruciferae)	173
3-(2‴-*E*-Caffeylsophoroside)-7-glucoside		
3-(2‴-*E*-Ferulylsophoroside)-7-glucoside		
3-[2″,6″-{*p*-(7″″-glucosyl)coumaryl}glucosyl]-rhamnoside	*Ginkgo biloba* leaf (Ginkgoaceae)	150
Kaempferol 7-methyl ether (Rhamnocitrin)		174
3-[5‴-*p*-Coumarylapiosyl(1→2)glucoside]	*Astragalus complanatus* seeds (Leguminosae)	
3-[5‴-Ferulylapiosyl(1→2)glucoside]		
3-Glucoside-4′-(3‴-dihydrophaseoylglucoside)		
Kaempferol 4′-methyl ether (Kaempferide)		
3-Rhamnoside	*Agrimonia eupatoria* aerial parts (Rosaceae)	175
3-Rhamnoside-7-xyloside	*Cassia biflora* leaf (Leguminosae)	176
Kaempferol 3,7-dimethyl ether		
4′-Glucoside (Camaroside)	*Lantana camara* leaf (Verbenaceae)	177
6-Hydroxykaempferol		
3-Glucoside	*Carthamnus tinctorius* petals (Compositae)	178
3,6-Diglucoside		
3,6,7-Triglucoside		
3-Rutinoside-6-glucoside		
7-(6″-Caffeylglucoside)	*Eupatorium glandulosum* leaf (Compositae)	179
6-Hydroxykaempferol		
6,4′-Dimethyl ether 3-glucoside	*Arnica montana* flowers (Compositae)	180
8-Hydroxykaempferol (Herbacetin)		
Herbacetin 8-methyl ether (sexangularetin)		
3-Neohesperidoside	*Crataegus monogyna* pollen (Rosaceae)	181
6,8-Dihydroxykaempferol		
3-Rutinoside	*Withania somnifera* leaf (Solanaceae)	182
Quercetin		
3-Xylosyl(1→6)glucoside	*Cistus ladanifer* pollen (Cistaceae)	183
3-Glucosyl(1→2)rhamnoside	*Ginkgo biloba* leaf (Ginkgoaceae)	184
3-Apiosyl(1→2)rhamnosyl(1→6)glucoside	*Baccharis thesioides* aerial parts (Compositae)	185
3-Xylosyl(1→2)glucoside-7-rhamnoside	*Lathyrus chrysanthus*, *L. chloranthus* flowers (Leguminosae)	186
3-Glucoside-7-glucosyl(1→4)rhamnoside		
3-Galactoside-7-glucosyl(1→4)rhamnoside		
3-Neohesperidoside-7-glucoside	*Nicotiana* spp. flowers (Solanaceae)	157
3-Sophoroside-7-glucuronide	*Allium cepa* guard cells (Alliaceae)	158
3-(2″-Caffeylglucuronide)	*Scolymus hispanicus* (Compositae)	187
4′-(6″-Galloylglucoside)	*Eucalyptus rostrata* leaf (Myrtaceae)	164
3-(3″,6″-Diacetylgalactoside)	*Tagetes elliptica* aerial parts (Compositae)	188
3-(2″,3″,4″-Triacetylgalactoside)		
3-[2‴,3‴,4‴-Triacetyl-α-L-arabinopyranosyl(1→6)glucoside]	*Calluna vulgaris* flowers (Ericaceae)	189
3-[2‴,3‴,4‴-Triacetyl-α-L-arabinopyranosyl(1→6)galactoside]	*Calluna vulgaris* flowers (Ericaceae)	190
3-[2‴,3‴,5‴Triacetyl-α-L-arabinofuranosyl(1→6)glucoside]	*Calluna vulgaris* flowers (Ericaceae)	172
3-(*p*-Coumarylsambubioside)-7-glucoside	*Ranunculus* spp. leaf (Ranunculaceae)	191

Table 4 (*cont.*)

Flavone	Source	Ref.
Quercetin (*cont.*)		
3-(Caffeylarabinosylglucoside)-7-glucoside	*Ranunculis* spp. leaf (Ranunculaceae)	191
3-(2‴-Caffeylsambubioside)-7-glucoside		
3-(Ferulylsambubioside)-7-glucoside		
3-(*p*-Coumarylsophoroside)-7-glucoside		
3-(Caffeylarabinosylglucoside)-7-glucoside	*Ranunculus biternatus* leaf (Ranunculaceae)	191
3-(2‴-*E*-Caffeylsophoroside)-7-glucoside	*Brassica oleracea* leaf (Cruciferae)	173
3-(2‴-*E*-Ferulylsophoroside)-7-glucoside		
3-[2″-(6‴-*p*-Coumaryl)glucosyl]rhamnoside-7-glucoside	*Ginkgo biloba* leaf (Ginkgoaceae)	184
3-[2″,6″-{*p*-(7‴-glucosyl)coumaryl}-glucosyl]rhamnoside		
Quercetin 7-methyl ether (Rhamnetin)		
3-Robinobioside	*Cassia siamea* stem bark (Leguminosae)	192
3-(3⁗-*p*-Coumarylrhamninoside)	*Rhamnus petiolaris* fruit (Rhamnaceae)	193
Quercetin 3′-methyl ether (Isorhamnetin)		
5-Galactoside	*Pyrus bourgaeana* aerial parts (Rosaceae)	194
3-Xylosyl(1→2)glucoside	*Lathyrus chrysanthus* and *L. chloranthus* flowers (Leguminosae)	186
3-Xylosyl(1→6)glucoside	*Cistus ladanifer* pollen (Cistaceae)	183
3-Glucosyl(1→3)galactoside	*Achlys triphylla* underground parts (Berberidaceae)	195
3-Apiosylglucoside	*Barbacenia conicostigma* leaf (Velloziaceae)	196
3-Apiosylgalactoside		
3-Galactoside-7-rhamnoside	*Lathyrus chrysanthus* and *L. chloranthus* flowers (Leguminosae)	186
4′-Rhamnosyl(1→2)glucoside (Crosatoside A)	*Crocus sativus* pollen (Iridaceae)	197
3-Galactosyl(1→2)[rhamnosyl(1→6)glucoside]	*Calotropis gigantea* aerial parts (Asclepiadaceae)	198
3-Xylosyl(1→2)glucoside-7-rhamnoside	*Lathyrus chrysanthus* and *L. chloranthus* flowers (Leguminosae)	186
3-Glucosyl(1→6)galactoside-7-glucoside	*Heterotropa aspera* leaf (Aristolochiaceae)	199
3-[6″-(2-*E*-Butenoyl)glucoside]	*Zygophyllum simplex* aerial parts (Zygophyllaceae)	200
7-(6″-*p*-Coumarylglucoside)	*Buddleia coriacea* aerial parts (Loganiaceae)	168
3-(6″-Acetylglucosyl)(1→3)galactoside	*Achlys triphylla* underground parts (Berberidaceae)	195
3-(4″,5″-diacetylglucosyl)(1→3)galactoside		
Quercetin 4′-methyl ether (Tamarixetin)		
3-Galactoside	*Cynanchum thesioides* whole plant (Asclepiadaceae)	201
3-Glucosyl(1→2)galactoside		
3-Rutinoside-7-rhamnoside	*Cassia italica* aerial parts (Leguminosae)	202
3-Glucoside-7-sulfate	*Polygonum hydropiper* leaf (Polygonaceae)	203
Quercetin 3,5-dimethyl ether (Caryatin)		
7-Glucoside	*Eucryphia glutinosa* twigs (Eucryphiaceae)	204
Quercetin 7,4′-dimethyl ether (Ombuin)		
3-Glucoside	*Gynostemma yixingense* (Cucurbitaceae)	205
Quercetin 3′,4′-dimethyl ether		
3-Neohesperidoside	*Crotalaria verrucosa* stems (Leguminosae)	206
3,7-Diglucoside	*Calamintha grandiflora* leaf and flower (Labiatae)	207
3,7,3′,4′,5′-Pentahydroxyflavone (Robinetin)		
7-Glucoside	*Alternanthera sessilis* (Amaranthaceae)	208
Quercetagetin 6-methyl ether (Patuletin)		
3,7-Diglucoside	*Arnica montana* flowers (Compositae)	180
3-Rhamnoside-7-(2″-acetylrhamnoside)	*Kalanchoe brasiliensis* stem and leaf (Crassulaceae)	209
3-(4″-acetylrhamnoside)-7-rhamnoside		
3-(4″-Acetylrhamnoside)-7-(2″-acetylrhamnoside)		
Quercetagetin 3,6,3′-trimethyl ether (Jaceidin)	*Eucryphia glutinosa* twigs (Eucryphiaceae)	204
5-Glucoside		
Quercetagetin 6,3′,4′-trimethyl ether		
3-Glucoside	*Arnica montana* flowers (Compositae)	180
Gossypetin 7,8-dimethyl ether		
3-Glucoside	*Erica cinerea* flowers (Ericaceae)	210
4′-Glucoside		
3,5,7,3′,4′,5′-Hexahydroxyflavone (Myricetin)		
3-Galactoside-3′-rhamnoside	*Buchanania lanzan* leaf (Anacardiaceae)	211
3,4′-Diglucoside	*Picea abies* needles (Pinaceae)	212
3-Rhamnosyl(1→3)glucosyl(1→6)glucoside	*Oxytropis glabra* (Leguminosae)	213
3-(3″-Galloylrhamnoside)	*Myrica esculenta* bark (Myricaceae)	214
3-(2″-Galloylgalactoside)		
Myricetin 3′,5′-dimethyl ether (Syringetin)		
3-(6″-Acetylglucoside)(1→3)galactoside	*Achlys triphylla* underground parts (Berberidaceae)	195
3,5,7,2′,3′,4′-Hexahydroxyflavone		
3-Glucoside	*Eupatorium sternbergianum* whole plant (Compositae)	215
5,8-Dihydroxy-3,6,7,4′-tetramethoxyflavone	*Peperomia pellucida* (Piperaceae)	216
8-Neohesperidoside		
5,7,8-Trihydroxy-3,6,4′-trimethoxyflavone	*Galeana pratensis* aerial parts (Compositae)	217
8-Tiglate		
5,8,4′-Trihydroxy-3,6,7-trimethoxyflavone		
8-(2-methylbutyrate)		
3,5,7,4′-Tetrahydroxy-6,8,3′-trimethoxyflavone		
3-α-L-Arabinopyranosyl(1→3)galactoside	*Pongamia pinnata* (Leguminosae)	218
3-α-L-Arabinopyranosyl(1→3)[galactosyl(1→6)galactoside]		

Table 4 (*cont.*)

Flavone	Source	Ref.
5,2′-Dihydroxy-3,6,7,4′,5′-pentamethoxyflavone (Brickellin)		
2′-Glucoside	*Chrysosplenium grayanum* (Saxifragaceae)	219
6″,6″-Dimethylpyrano(2″,3″:7,8)-4′-methoxykaempferol		
3-Rhamnoside	*Epimedium acuminatum* (Berberidaceae)	220
8-Prenylkaempferol [Noranhydroicaritin, 3,5,7,4′-tetrahydroxy-8-(3″,3″-dimethylallyl)flavone]		
3,7-Diglucoside	*Vancouveria hexandra* underground and aerial parts (Berberidaceae)	221
8-Prenylkaempferol 4′-methyl ether (Anhydroicaritin)		
7-Glucosyl(1→4)glucoside (Cuhuoside)	*Epimedium acuminatum* (Berberidaceae)	222
3-Glucosyl(1→3)rhamnoside-7-glucoside	*Vancouveria hexandra* underground and aerial parts (Berberidaceae)	221
3-Rhamnosyl(1→2)rhamnoside-7-glucosyl(1→2)glucoside (Acuminatoside)	*Epimedium acuminatum* aerial parts (Berberidaceae)	223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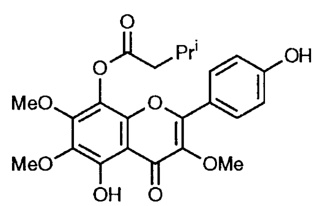
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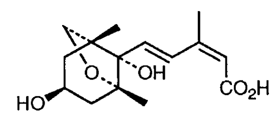
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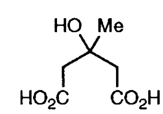

(62)

speciosa (Convolvulaceae), since it represents the first report of this aglycone in glycosidic combination.[146]

During the last three years, four new disaccharides have been characterized as components of flavone or flavonol glycosides. These are two flavonol hexose–hexose combinations from the Berberidaceae: glucosyl(1→3)galactose found attached to the 3-hydroxyl of rhamnetin in underground parts of *Achlys triphylla*[195] and a new diglucoside with a (1→4) linkage in combination with 8-prenylkaempferol 4′-methyl ether at the 3-position from *Epimedium acuminatum*.[222] The latter compound co-occurs with a 3,7-tetraglycoside of the same aglycone containing rhamnosyl(1→2)rhamnose at the 3-position which is reported only for the second time.[223] The other two new reports of disaccharides are both pentose–hexose namely: a scutellarein 7-xylosyl(1→6)galactoside from the leaf of *Semecarpus kurzii* (Anacardiaceae)[119] and syringetin 3-α-L-arabinopyranosyl(1→3)galactoside from heartwood of *Pongamia pinnata* (Leguminosae).[218] The latter structure co-occurs with syringetin 3-α-L-arabinopyranosyl(1→3)[galactosyl (1→6)galactoside] (59), which has a new branched trisaccharide. The only other new trisaccharide is linear, a rhamnosyl(1→3)glucosyl(1→6)glucose found attached to myricetin at the 3-hydroxyl in *Oxytropis glabra* (Leguminosae).[213]

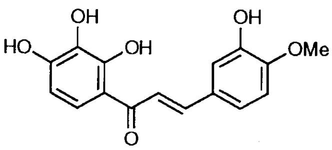
It is remarkable that over a third of the new flavonoid glycosides reported in the years 1992–94 have acylated structures (18 flavones and 52 flavonols). However, no new acylating acids were identified during this period. Acetic acid was again the most frequent acyl substituent but some more unusual acids were also reported. For example, 3-methylbutyric acid was found attached to the 6″-hydroxyl of luteolin 7-glucoside in flowers of *Arnica chamissonis* (Compositae)[136] and directly attached to the 8-hydroxyl of 5,8,4′-trihydroxy-3,6,7-trimethoxyflavone (60) in aerial parts of another composite, *Galeana pratensis*.[217] This acid has been reported only once previously from leaves of *Patersonia* (Iridaceae) attached at an unknown position to isorhamnetin 3-rutinoside.[7] Another aliphatic acid reported for only the second time is crotonic acid, (2*E*)-but-2-enoic acid, which was recently recorded from aerial parts of *Zygophyllum simplex* (Zygophyllaceae)[200] attached to the 6″-hydroxyl of isorhamnetin 3-glucoside. Similarly, the sesquiterpene dihydrophaseic acid (61) has been reported for the second time from seeds of *Astragalus complanatus* but with a different sugar linkage. The authors previously described rhamnocitrin 3-glucoside-4′-(2″-dihydrophaseoylglucoside)[7] and now report the occurrence of the 3″-isomer.[174]

However, the most abundant finding is of eight flavone glycosides acylated with the dibasic acid 3-hydroxy-3-methylglutaric acid (62) in the thallus of the liverwort *Frullania muscicola*.[121] Here (62) is located at the 6″-position of scutellarein, luteolin, diosmetin, 6-hydroxyluteolin, and tricetin 7-glucosides, additionally at the 3″ and 4″-hydroxyls of diosmetin 7-glucoside, and at an undetermined position in tricin 7-glucoside. This aliphatic acid has been detected also in callus cultures of *Citrus aurantifolia* (Rutaceae) at the 6″-hydroxyl of kaempferol 3-glucoside and at the same position in the co-occurring kaempferol 3-glucoside-7-glucoside.[63] As is sometimes the case with plant cell cultures, these glycosides were different from any of the flavonoid glycosides present in leaf and fruit tissues of the normal plant.

The biological activities of some of these new glycosides have been evaluated, although generally little is still known of their functions in the plant. In our experience, flavonol glycosides with two or more aromatic substituents such as kaempferol 3-(di-*p*-coumarylrhamnoside) from *Platanus*[165] and the corresponding di-*p*-coumarylglucoside from *Quercus*[169] show lipophilic solubility and are likely to be antimicrobial.[224] Indeed, the *Platanus* rhamnoside was found to have antibacterial properties.[165] Flavonoid glycosides otherwise are not noted for their antimicrobial activities.[225] Flavonol glycosides are often located in the upper epidermal cells of leaves and are thus readily detected by phytophagous insects. In addition to affecting feeding behaviour, they may also affect oviposition in the adult female. Nishida[199] has demonstrated that the new isorhamnetin glycoside, the 3-glucosylgalactoside-7-glucoside, of *Heterotropa aspera* is an oviposition stimulant to the swallowtail butterfly *Luchdorfia japonica*.

5 Chalcones and Flavanones

The yellow chalcones were originally discovered in plants as the yellow flower pigments of *Coreopsis* and other yellow-rayed Compositae. They have subsequently been found in other plant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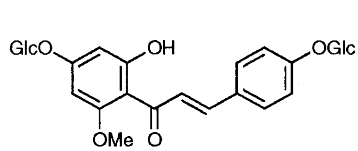
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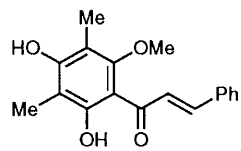
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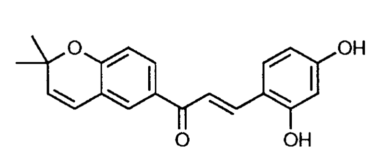
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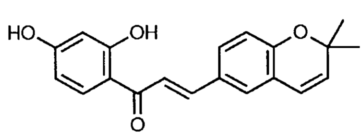
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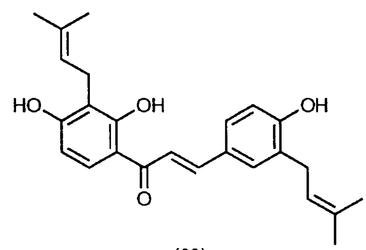
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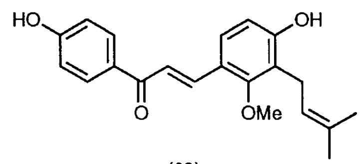
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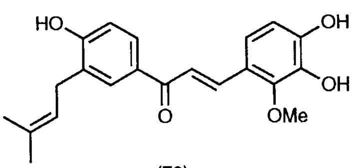
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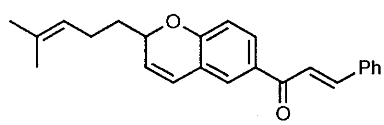
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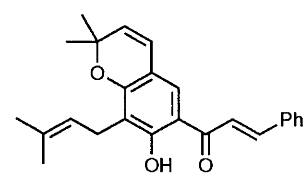
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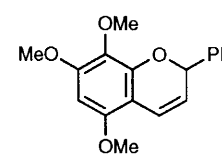
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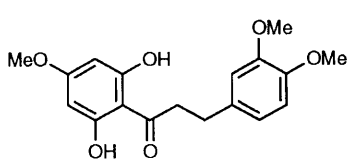
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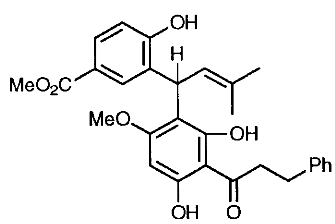
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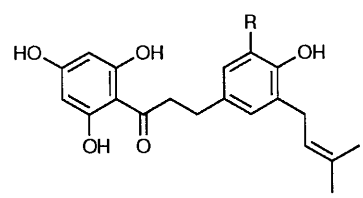
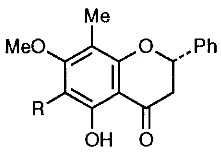

(76) R = prenyl
(77) R = geranyl

families and in other tissues[7] but none of the new reports of chalcones refer directly to their ability to impart yellow floral colour. Three new glycosides of okanin 4-methyl ether (63) were found in the aerial parts of *Bidens campylotheca* (Compositae) but it is not clear if they were located in the floral rays.[226] The compounds were the 4′-glucoside, the 4′-(6″-acetylglucoside), and the 4′-primveroside. Again, the 4,4′-diglucoside (64) of 4,2′,4′-trihydroxy-6′-methoxychalcone was found in the flowers of *Clerodendron phlomidis* (Verbenaceae) but its possible contribution to flower colour is not mentioned.[227]

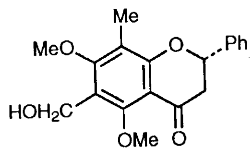
The Leguminosae, like the Compositae, are a family which produce a variety of chalcone structures. A di-*C*-methylchalcone (65) has been encountered in *Dalea caerulea*,[228] while a dimethylpyranochalcone (66) has been identified in the bark of *Mundulea sericea*.[229] Roots of *Glycyrrhiza eurycarpa* have yielded kanzonol B (67) and kanzonol C (68)[96] while the roots of *G. inflata* have produced licochalcones C (69) and D (70).[230] Again the roots of *Tephrosia spinosa* have given four closely related chalcones diprenylated in the A ring, 3′,5′-diprenyl-2′,4′-dihydroxychalcone, in the *E* and *Z* forms, spinochalcone B (71), and spinochalcone C (72).[231–233] One final new chalcone that should be mentioned is the simple 2-monohydroxy-3,4,6-trimethoxy derivative which occurs in another family, the Annonaceae, in *Uvaria dependens*, where it is present together with 5,7,8-trimethoxyflav-3-ene (73).[234]

Dihydrochalcones lack the conjugation between the two aromatic rings present in chalcones and hence are colourless. They have many similar structural features to the chalcones but generally have a different natural distribution. Four dihydrochalcones need some mention here. One is the simple dihydroxytrimethoxy derivative (74) which has been found in the frond exudate of the fern *Pityrogramma tartarea*, where it occurs as a complex mixture with other flavonoids.[235] Another is the benzyl-substituted compound (75) from leaves of *Piper aduncum* (Piperaceae).[236] The other two, (76) and (77), occur with prenyl and geranyl substituents in aerial parts of *Boronia inconspicua* (Rutaceae).[237]

The new flavanones and flavanonols (dihydroflavonols) discovered between 1992 and 1994 are conveniently considered together here. Because of the considerable number of new structures reported, they will be divided into three groups: simple structures with hydroxy/methoxy substitution; compounds with prenyl or geranyl substituents; and compounds with pyrano or furano substitution. A simple new flavanone is pinocembrin (5,7-diOH) 7-rhamnosylglucoside, reported from the fern *Onychium japonicum* (Sinopteridaceae) as a cytotoxic principle.[238] The 7-benzoate of pinocembrin itself has been



(78) R = CHO
(79) R = CH_2OH



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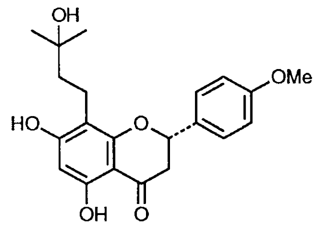

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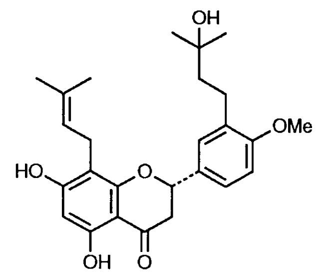

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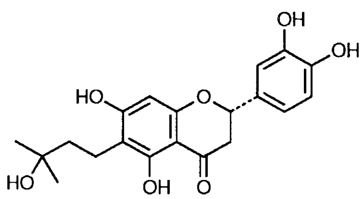

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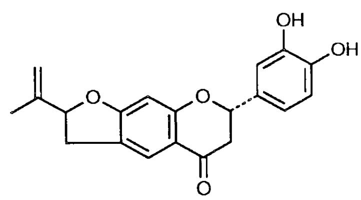

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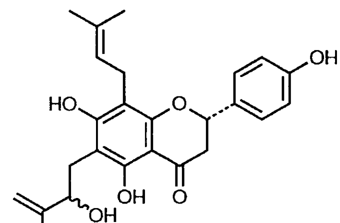

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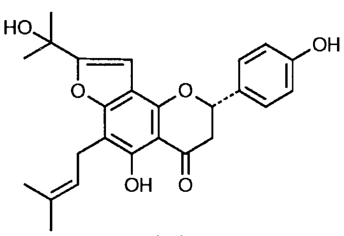

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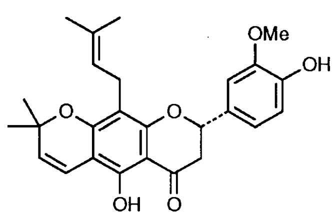

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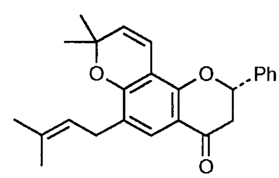

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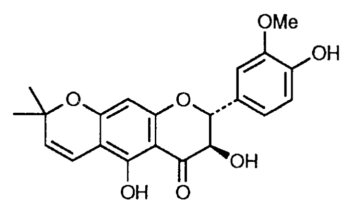

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found in aerial parts of *Pachylaena atriplicifolia* (Compositae).[239] Three pinocembrin derivatives with formyl or hydroxymethyl substitution at C-6, (78)–(80), have been identified in leaves of *Petiveria alliacea* (Phytolaccaceae).[240] The 5-glucoside of pinocembrin 7-methyl ether has been isolated from the roots of *Pyracantha coccinea* (Rosaceae), together with dihydrokaempferol 5-methyl ether.[241]

5,6,7-Trihydroxyflavanone 7-glucoside and its 5-methyl ether have been described from chitin-treated suspension cell cultures of *Cephalocereus senilis* (Cactaceae).[52] 8-Hydroxy-5,6,7-trimethoxyflavanone has been isolated from bark of *Fissistigma kwangiense* (Annonaceae),[242] while 5,7,8,4′-tetrahydroxyflavanone 7-rhamnoside has been found in Spanish broom, *Spartium junceum* (Leguminosae).[293] 5-Hydroxy-7,3′,4′-trimethoxy-6-*C*-methylflavanone has been reported from *Vellozia coronata* (Velloziaceae).[82] The more distinctive 5,2′-dihydroxy-6,7,8,6′-tetramethoxyflavanone has been detected in roots of *Scutellaria oxystegia* (Labiatae)[244] and the equally distinctive 5,7-dihydroxy-6,5′-dimethoxy-3′,4′-methylenedioxyflavanone occurs in aerial parts of *Agave americana* (Agavaceae).[245]

Two novel dihydroflavonols have been isolated from heartwood of the plum tree, *Prunus domestica* (Rosaceae). They are the 3-methyl ether of dihydrokaempferol and 6,4′-dimethyl ether of 6-hydroxydihydrokaempferol.[246] The 7,8-dimethyl ether of dihydrogossypetin has been found in *Erica cinerea* (Ericaceae), a genus known to produce gossypetin.[247] The novel 3,5,2′-trihydroxy-7,5′-dimethoxyflavanone has been encountered in *Blumea balsamifera* (Compositae)[248] while from the same family, the 3-isobutyroyl ester of 3,5,7,3′-tetrahydroxyflavanone has been found in *Flourensia retinophylla*.[249]

The twenty-three new prenylated flavanones are listed in Table 5.[250–262] Most of these have been found in plants of the Leguminosae. Prenylation is most common at C-6 and or C-8, but B-ring prenylation also occurs. Flavanone geranyl or prenyl esters are distinctively present in *Boronia caerulescens* of the Rutaceae.[252]

Prenylated flavanones may be accompanied by the corresponding structures in which the unsaturated side chain has accepted a molecule of water to produce a hydroxyisopentanyl substituent. This is true of 8-*C*-prenylnaringenin 4′-methyl ether which is accompanied in *Bosistoa brassii* by the flavanone (81).[251] Similarly, in *Azadirachta indica* (Meliaceae) 8,3′-diprenylnaringenin 4′-methyl ether occurs with the hydrated derivative (82).[263] In *Vellozia nanuzae*, the situation is slightly different, in that 6,8-diprenyleriodictyol is accompanied by the 6-monoprenylated derivative (83), which has the double bond hydrated. An unusual feature of the flavanones of *Vellozia* is the occurrence of the furano derivative velloeriodictyol (84), presumably formed from the 6-prenyl compound by ring closure on the 7-hydroxyl.[82]

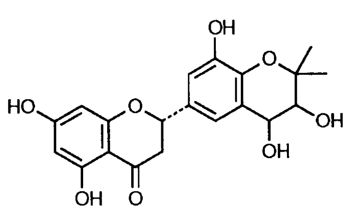
Oxidation of the prenyl side chain can, of course, occur without loss of the double bond, and this may give rise to stereoisomeric structures, as in the case of lupiniol A_1 and A_2 (85), which have been obtained from the roots of the yellow lupin, *Lupinus luteus* (Leguminosae).[264] This plant is a rich source of terpenoid-substituted flavanones and isoflavonoids; one other novel structure of interest is the furano-substituted naringenin derivative lupinenol (86). Many of these lupin root flavanones show significant antifungal activity.[264]

Prenylated flavanones which undergo subsequent ring closure on adjacent phenolic groups commonly yield tetracyclic structures with a pyrano rather than a furano fused ring. Four such compounds recently described are: 3′-methoxylupinifolin (87) from *Derris laxifolia*;[97] maxima flavanone A_2 (88) from *Tephrosia maxima*;[265] eriotrinol (89) from *Erythrina erio-*

Table 5 New prenylated flavanones reported in the period 1992–1994

Flavanone Substitution Pattern[a]	Prenylation[b]	Source	Ref.
5,4′-diOH	6-*C*-prenyl	*Crotalaria ramossissima* (Leguminosae)	250
5,7-diOH, 4′-OMe	8-*C*-prenyl	*Bosistoa brassii* (Rutaceae)	251
5,7,4′-triOH	4′-geranyl ester	*Boronia coerulescens* (Rutaceae)	252
5,4′-diOH, 7-OMe	4′-prenyl ester		
5,7-diOH, 4′-OMe, 8-*C*-Me	6,3′-di-*C*-prenyl	*Lespedeza formosa* (Leguminosae)	253
5,7-diOH, 4′-OMe, 6-*C*-Me	8,3-di-*C*-prenyl		
5,7,3′,4′-tetraOH	5′-*C*-prenyl	*Glycyrrhiza uralensis* (Leguminosae)	254
5,7,3′,4′-tetraOH	6,8-di-*C*-prenyl	*Vellozia coronata* (Velloziaceae)	82
5,2′,4′-triOH, 7-OMe	8-*C*-prenyl	*Echinosophora koreensis* (Leguminosae)	255
5,7,2′,4′-tetraOH	8-*C*-geranyl		
5,2′,4′-triOH, 7-OMe	8,5′-di-*C*-prenyl	*Maackia amurensis* (Leguminosae)	
5,7,2′,4′,6′-pentaOH	6-*C*-geranyl	*Echinosophora koreensis* (Leguminosae)	257
5,7,2′,4′,6′-pentaOH	8-*C*-geranyl		
5,7,2′,4′,6′-pentaOH	6,8-di-*C*-prenyl		
5,2′,6′-triOH, 7,4′-diOMe	8-*C*-prenyl	*Echinosophora koreensis* (Leguminosae)	258
5,7,2′,6′-tetraOH, 4′-OMe	8-*C*-prenyl		
5,7-diOH, 2′,4′,6′-triOMe	8-*C*-prenyl	*Artocarpus heterophyllus* (Moraceae)	259, 260
5-OH, 7,2′,4′,6′-tetraOMe	8-*C*-prenyl		
3,5,7,4′-tetraOH	7-geranyl ester	*Boronia caerulescens* (Rutaceae)	252
3,5,7,2′-tetraOH, 4′-OMe	8-*C*-prenyl	*Echinosophora koreensis* (Leguminosae)	261
3,5,7,2′-tetraOH, 4′-OMe	6-*C*-geranyl		
3,5,7,2′,6′-pentaOH, 4′-OMe	6-*C*-geranyl, 8-*C*-prenyl		
3,5,4′-triOH, 7,3′-diOMe	8-*C*-prenyl	*Paracalyx scariosa* (Leguminosae)	262

[a] Where determined, these flavanones have the (2*S*)-configuration and the flavanonols the (2*R*,3*R*)-configuration; [b] Substitution by geranyl (C_{10}) groups are included as well as those substituted with prenyl (C_5) groups. Linkage is directly to the aromatic nucleus of the flavanone, except where an ester link is indicated (*i.e.* through a phenolic hydroxyl group)



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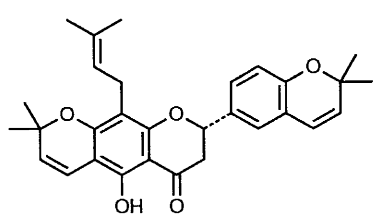

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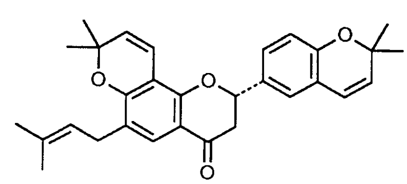

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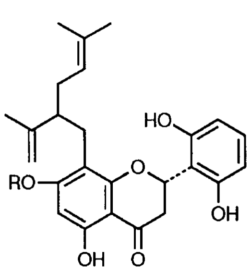
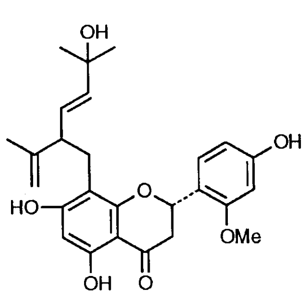


(93) R = H
(94) R = Me



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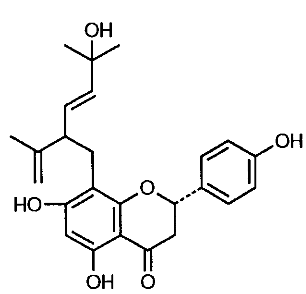

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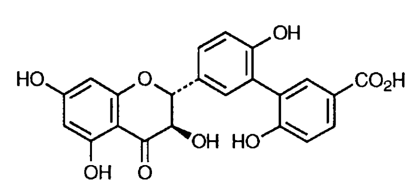

(97)

tricha;[266] and sigmoidin G (90) from *Erythrina sigmoidea*.[266] Two flavanones with two pyrano ring systems, (91) and (92), have been encountered in *Euchresta tubulosa*.[267] All these plants with pyrano-substituted flavanones are once more in the same family, Leguminosae.

One variation on the *C*-prenylation of flavanones is *C*-geranylation, where two isoprene units are linked head-to-tail to the flavonoid nucleus; some examples are given in Table 5. A modification of *C*-geranylation is where the isoprene units are asymmetrically linked to produce flavanones substituted with lavandulyl residues. Four such flavanones, (93)–(96), have been reported from *Sophora exigua*[268] or *S. leachiana* (Leguminosae).[269]

In Section 2 of this review, the presence of a unique 3-desoxyanthocyanidin riccionidin A (15) in the cell wall of the liverwort *Ricciocarpos natans* was noted. It seems appropriate to close this review with another unique structure from the kingdom of bryophytes: the occurrence of the flavanonol (97) in the gametophytic tissue of the moss *Hypnum cupressiforme*. This is surely the first time that dihydrokaempferol has been found with a *p*-hydroxybenzoic acid unit linked to the molecule.[270]

6 References

1 T. Kondo, K. Yoshida, A. Nakagawa, T. Kawai, H. Tamura, and T. Goto, *Nature* (*London*), 1992, **358**, 515.
2 'Food phytochemicals for cancer prevention', ed. M. T. Kuana, J. Osawo, C. T. Ho, and R. T. Rosen, ACS Symposium Series, Vol. 546 and 547, ACS, Washington DC, 1994.
3 D. R. Ferry, 1994, personal communication.
4 D. Leake, *The Biochemist*, 1995, **17**, 12.
5 C. A. Williams, J. R. S. Hoult, J. B. Harborne, J. Greenham, and J. Eagles, *Phytochemistry*, 1995, **38**, 267.
6 J. R. S. Hoult, L. H. Pang, P. A. Bland-Ward, R. A. Forder, C. A. Williams, and J. B. Harborne, *Pharm. Sci.*, 1995, **1**, 71.
7 'The Flavonoids: Advances in Research since 1986', ed. J. B. Harborne, Chapman and Hall, London, 1993.
8 D. M. X. Donnelly and G. M. Boland, *Nat. Prod. Rep.*, 1995, **12**, 321.
9 R. Robinson and G. M. Robinson, *Biochem. J.*, 1934, **28**, 1712.
10 J. B. Harborne and D. M. Smith, *Biochem. Syst. Ecol.*, 1978, **6**, 127.
11 N. Saito and J. B. Harborne, *Phytochemistry*, 1992, **31**, 3009.
12 J. B. Harborne, in 'Advances in Labiate Science', ed. R. M. Harley and T. Reynolds, Royal Botanic Gardens, Kew, 1992, p. 307.
13 T. Goto, *Fortschr. Chemie Organ. Naturst.*, 1987, **52**, 113.
14 N. Saito, T. S. Lu, M. Yokoi, A. Shigihara, and T. Honda, *Phytochemistry*, 1993, **33**, 245.
15 T. S. Lu, N. Saito, M. K. Yokoi, A. Shigihara, and T. Honda, *Phytochemistry*, 1992, **31**, 659.
16 T. S. Lu, N. Saito, M. Yokoi, A. Shigihara, and T. Honda, *Phytochemistry*, 1992, **31**, 289.
17 O. Dangles, N. Saito, and R. Brouillard, *Phytochemistry*, 1993, **34**, 119.
18 K. Toki, N. Saito, K. Kawano, T. S. Lu, A. Shigihara, and T. Honda, *Phytochemistry*, 1994, **36**, 609.
19 K. Takeda, M. Yamagisawa, T. Kifane, T. Kinoshita, and C. F. Timberlake, *Phytochemistry*, 1994, **35**, 1167.
20 K. Takeda, J. B. Harborne, and P. G. Waterman, *Phytochemistry*, 1993, **34**, 421.
21 K. Toki, N. Saito, K. Iimura, T. Suzuki, and T. Honda, *Phytochemistry*, 1994, **36**, 1181.
22 K. Takeda, S. Sato, H. Kobeyashi, Y. Kanaitsuka, M. Ueno, T. Kinoshita, H. Zazeki, and T. Fujimori, *Phytochemistry*, 1994, **36**, 613.
23 K. Brandt, T. Kondo, H. Aoki, and T. Goto, *Phytochemistry*, 1993, **33**, 209.
24 J. B. Harborne, *Phytochemistry*, 1986, **25**, 1987.
25 N. Terahara, M. A. Yamaguchi, and T. Honda, *Biosci. Biotech. Biochem.*, 1994, **58**, 1324.
26 F. Tatsuzaura, N. Saito, M. Yokoi, A. Shigihara, and T. Honda, *Phytochemistry*, 1994, **37**, 1179.
27 N. Terahara, K. Toki and T. Honda, *Z. Naturforsch.*, *Teil C*, *Biosci.*, 1993, **48**, 430.
28 G. Mazza and L. Gao, *Phytochemistry*, 1994, **35**, 237.
29 J. B. Harborne, N. Saito, and C. H. Detoni, *Biochem. Syst. Ecol.* 1994, **22**, 835.
30 C. A. Williams, J. B. Harborne, and P. Goldblatt, *Phytochemistry*, 1986, **25**, 2135.
31 K. Toki, N. Saito, T. Ueda, T. Chibana, A. Shigihara, and T. Honda, *Phytochemistry*, 1994, **37**, 885.
32 S. B. Ji, N. Saito, M. Yokoi, A. Shigihara, and T. Honda, *Phytochemistry*, 1992, **31**, 655.
33 S. B. Ji, M. Yokoi, N. Saito, and L. S. Mao, *Biochem. Syst. Ecol.*, 1992, **20**, 771.
34 D. Strack, V. Wray, J. W. Metzger, and W. Grosse, *Phytochemistry*, 1992, **31**, 989.
35 K. N. Rai, M. P. Singh, and B. K. Sinhar, *Asian J. Chem.*, 1994, **6**, 696.
36 O. M. Andersen, *Biochem. Syst. Ecol.*, 1992, **20**, 145.
37 S. Kunz, G. Burkhardt, and H. Becker, *Phytochemistry*, 1994, **35**, 233.
38 W. E. Glassgen, V. Wray, D. Strack, J. W. Metzger, and H. W. Seitz, *Phytochemistry*, 1992, **31**, 1593.
39 N. Terahara, N. Saito, K. Toki, Y. Sakata, and T. Honda, *Phytochemistry*, 1992, **31**, 1446.
40 Y. Asada, K. Sakamoto, and T. Furnya, *Phytochemistry*, 1994, **35**, 1471.
41 T. A. Holton, F. Brugliera, D. R. Lester, Y. Tanaka, C. D. Hyland, J. G. T. Menting, C. Y. Lu, E. Farey, T. W. Stevenson, and E. C. Cornish, *Nature* (*London*), 1993, **366**, 276.
42 I. Ino, H. Nishiyama, and M. A. Yamaguchi, *Phytochemistry*, 1993, **32**, 1425.
43 I. Ito and M. A. Yamaguchi, *Phytochemistry*, **33**, 1415.
44 K. V. Wood, C. C. Bonham, J. Ng, J. Hipskind, and R. L. Nicholson, *Rapid Comm. Mass Spectrom.*, 1993, **7**, 400.
45 K. V. Wood, C. C. Bonham, J. Hipskind, and R. L. Nicholson, *Phytochemistry*, 1994, **37**, 557.
46 H. Tamura, Y. Hayashi, H. Sugisawa, and T. Kondo, *Phytochem. Analysis*, 1994, **5**, 190.
47 W. Nerdal and O. M. Andersen, *Phytochem. Analysis*, 1992, **3**, 182.
48 T. Hosino, *Phytochemistry*, 1992, **31**, 647.
49 C. C. Merlin, A. Statona, J. P. Cornard, M. Saidi-Idrissi, and R. Brouillard, *Phytochemistry*, 1994, **35**, 227.
50 O. Dangles, M. C. Wigand, and R. Brouillard, *Phytochemistry*, 1992, **31**, 3811.
51 M. C. Wigand, O. Dangles, and R. Brouillard, *Phytochemistry*, 1992, 31, 4317.
52 Q. Liu, K. R. Markham, P. W. Paré, R. A. Dixon, and T. J. Mabry, *Phytochemistry*, 1993, **32**, 925.
53 P. K. Guha and A. Bhattacharyya, *Phytochemistry*, 1992, **31**, 1833.
54 V. U. Ahmad and N. Ismail, *Z. Naturforsch.*, *Teil B*, *Chem. Sci.*, 1991, **46**, 950.
55 R. D. Encarnacion, N. A. Ochoa, U. Anthoni, C. Christophersen, and P. H. Nielsen, *J. Nat. Prod.*, 1994, **57**, 1307.
56 V. S. Parmar, K. S. Bisht, S. K. Sharma, R. Jain, P. Taneja, S. Singh, O. Simonsen, and P. M. Boll, *Phytochemistry*, 1994, **36**, 507.
57 N. Xie, Z. Min, and S. Zhao, *Zhongguo Yaoke Daxue Xuebao*, 1990, **21**, 376.
58 R. S. Bhakuni, Y. N. Shukla, and R. S. Thakur, *Phytochemistry*, 1992, **31**, 2917.
59 N. Kaneda, J. M. Pezzuto, D. D. Soejarto, A. D. Kinghorn, N. R. Farnsworth, T. Santisuk, P. Tuchinda, J. Uddachon, and V. Reutrakul, *J. Nat. Prod.*, 1991, **54**, 196.
60 J. S. Mossa, M. M. El-Domiaty, I. A. Al-Meshal, F. S. El-Feraly, C. D. Hufford, D. R. McPhail, and A. T. McPhail, *Phytochemistry*, 1992, **31**, 2863.
61 T. Horie, H. Tominaga, and Y. Kawamura, *Phytochemistry*, 1993, **32**, 1076.
62 J. G. Diaz, B. Barba, W. Herz, and M. W. Bierner, *Phytochemistry*, 1992, **31**, 3471.
63 L. Quijano, F. Gómez-Garibay, G. Garcia-Perez, and T. Rios, *Phytochemistry*, 1992, **31**, 2859.
64 H. Häberlein and K. P. Tschiersch, *Phytochemistry*, **35**, 765.
65 J. Wu, S. Liao, H. Liang, and S. Mao, *Chin. Chem. Lett.*, 1994, **5**, 211.
66 Y. L. Liu, D. K. Ho, J. M. Cassady, C. E. Cottrell, J. Liang, J. Clardy, V. M. Cook, and W. M. Baird, *Nat. Prod. Lett.*, 1992, **1**, 161.
67 K. Kajiyama, S. Demizu, Y. Hiraga, K. Kinoshita, K. Koyama, K. Takahashi, T. Tamura, K. Okada, and T. Kinoshita, *J. Nat. Prod.*, 1992, **55**, 1197.
68 G. Delle Monache, R. Scurria, A. Vitali, B. Botta, B. Monacelli, G. Pasqua, C. Palocci, and E. Cernia, *Phytochemistry*, **37**, 893.
69 M. Kaouadji, S. Chiron, J. Garcia, F. Thomasson, M. Tissut, and P. Ravanel, *Phytochemistry*, 1992, **31**, 2131.
70 E. Wollenweber, K. Mann, F. J. Arriaga-Giner, J. N. Roitman, and J. G. West, *Phytochemistry*, 1993, **33**, 871.
71 G. Nakashima, W. Vichnowski, J. G. Diaz, and W. Herz, *Phytochemistry*, 1994, **37**, 285.
72 M. Hattori, X. L. Huang, Q. M. Che, Y. Kawata, Y. Tezuka, T. Kikuchi, and T. Namba, *Phytochemistry*, 1992, **31**, 4001.
73 A. A. Ahmed, A. A. Mahmoud, T. Tanaka, and M. Iinuma, *Phytochemistry*, 1994, **35**, 241.
74 E. Wollenweber, S. Armbruster, and J. N. Roitman, *Phytochemistry*, 1994, **37**, 455.
75 M. A. Rashid, J. A. Armstrong, A. I. Gray, and P. G. Waterman, *Phytochemistry*, 1992, **31**, 1265.
76 R. L. Hazarika, J. N. Baruah, P. C. Deka, C. S. Sharmah, and J. C. S. Kataky, *Indian J. Heterocycl. Chem.*, 1993, **3**, 139.
77 T. S. Wu, Y. Y. Chan, Y. L. Leu, and S. C. Huang, *Phytochemistry*, 1994, **37**, 287.
78 J. J. Lichius, O. Thoison, A. Montagnac, M. Païs, F. Guéritte-

Voegelein, T. Séveret, J. P. Cósson, and A. H. A. Hadi, *J. Nat. Prod.*, 1994, **57**, 1012.
79 L. Muschinetti, V. Martino, G. Ferraro, and J. Coussio, *Phytochemistry*, 1994, **36**, 1085.
80 E. Malan, *Phytochemistry*, 1993, **32**, 1631.
81 J. B. Harborne, C. A. Williams, J. Greenham, and J. Eagles, *Phytochemistry*, 1994, **35**, 1475.
82 J. B. Harborne, J. Greenham, C. A. Williams, J. Eagles, and K. R. Markham, *Phytochemistry*, 1993, **34**, 219.
83 C. A. Williams, J. Greenham, J. B. Harborne, J. Eagles, and K. R. Markham, *Phytochemistry*, 1992, **31**, 555.
84 R. S. Hou, C. Y. Duh, S. K. Wang, and T. T. Chang, *Phytochemistry*, 1994, **35**, 271.
85 T. Tanaka, M. Iinuma, K. Yuki, Y. Fujii, and M. Mizuno, *Phytochemistry*, 1992, **31**, 993.
86 J. B. Harborne, J. Greenham, C. A. Williams, J. Eagles, and K. R. Markham, *Phytochemistry*, **31**, 305.
87 C. A. Williams, J. B. Harborne, J. Greenham, J. Eagles, and K. R. Markham, *Phytochemistry*, 1993, **32**, 731.
88 S. Tahara, Y. Hashidoko, and J. Mizutani, *Agric. Biol. Chem.*, 1987, **51**, 1039.
89 S. S. Jia, D. Liu, X. P. Xheng, Y. Zhang, and Y. K. Li, *Yaoxue Xuebao*, 1993, **28**, 28.
90 S. S. Jia, C. M. Ma, and J. M. Wang, *Yaoxue Xuebao*, 1991, **25**, 758.
91 M. A. Nia, K. V. Rao, K. Sreeramulu, and D. Gunasekar, *J. Nat. Prod.*, 1992, **55**, 1152.
92 M. Rodsory, N. A. Ali, and D. Gunasekar, *Iran J. Chem. Eng.*, 1992, **11**, 20.
93 Y. Hano, R. Inami, and T. Nomura, *J. Chem. Res.*, 1994, **9**, 348.
94 I. C. Parsons, A. I. Gray, P. G. Waterman, and T. G. Hartley, *J. Nat. Prod.*, 1993, **56**, 46.
95 M. Ahsan, J. A. Armstrong, S. Gibbons, A. I. Gray, and P. G. Waterman, *Phytochemistry*, 1994, **37**, 259.
96 T. Fukai, J. Nishizawa, and T. Nomura, *Phytochemistry*, 1994, **35**, 515.
97 Y.-L. Lin, Y.-L. Chen, and Y.-H. Kuo, *Chem. Pharm. Bull.*, 1991, **39**, 3132.
98 S. Kitanaka and M. Takido, *Phytochemistry*, 1992, **31**, 2927.
99 S. Kitanaka and M. Takido, *Chem. Pharm. Bull.*, **39**, 1991, 3254.
100 F. Gómez-Garibay, L. Quijano, C. Hernández, and T. Rios, *Phytochemistry*, 1992, **31**, 2925.
101 C.-C. Chen, Y.-L. Huang, J.-C. Ou, C.-F. Lin, and T.-M. Pan, *J. Nat. Prod.*, 1993, **56**, 1594.
102 C.-M. Lu and C.-N. Lin, *Phytochemistry*, 1994, **35**, 781.
103 C. N. Lin and W. L. Shieh, *Phytochemistry*, 1992, **31**, 2922.
104 Y. Fujimoto, X. X. Zhang, M. Kirisawa, J. Uzawa, and M. Sumatra, *Chem. Pharm. Bull.*, 1990, **38**, 1787.
105 F. Asai, M. Iinuma, T. Tanaka, and M. Mizuno, *Heterocycles*, 1992, **33**, 229.
106 F. Asai, M. Iinuma, T. Tanaka, M. Takenaka, and M. Mizuno, *Phytochemistry*, 1992, **31**, 2487.
107 F. Asai, M. Iinuma, T. Tanaka, and M. Mizuno, *Phytochemistry*, 1991, **30**, 3091.
108 M. Iinuma, T. Tanaka, F. Asai, K.-I. Miyauchi, and E. Wollenweber, *Phytochemistry*, 1993, **33**, 1247.
109 M. Arisawa, H. Ba, M. Shiojima, T. Hayashi, Y. Tezuka, T. Taga, Y. Miwa, Y. Ito, T. Kikuchi, and N. Morita, *Chem. Pharm. Bull.*, 1993, **41**, 571.
110 B. T. Ngadjui, J. F. Ayafor, B. L. Sondengam, J. D. Connolly, D. S. Rycroft, and F. Tillequin, *Phytochemistry*, 1993, **32**, 1313.
111 V. K. Saxena and P. Shrivastava, *Phytochemistry*, 1994, **36**, 1039.
112 K. Ishiguro, S. Nagata, H. Fukumoto, M. Yamaki K. Isoi, and Y. Oyama, *Phytochemistry*, 1993, **32**, 1583.
113 Q. Liu, R. A. Dixon, and T. J. Mabry, *Phytochemistry*, 1993, **34**, 167.
114 Q. Liu, K. R. Markham, P. W. Paré, R. A. Dixon, and T. J. Mabry, *Phytochemistry*, 1993, **32**, 925.
115 R. N. Yadava and Y. Syeda, *Fitoterapia*, 1994, **65**, 554.
116 A. R. Bilia, S. Catalano, L. Pistelli, and I. Morelli, *Phytochemistry*, **33**, 1449.
117 T. Tomimori, Y. Imoto, and Y. Miyaichi, *Chem. Pharm. Bull.*, 1990, **38**, 3488.
118 T. Iwashina, S. Matsumoto, and Y. Yoshida, *Phytochemistry*, 1993, **32**, 1629.
119 M. S. Alam and N. Jain, *Fitoterapia*, 1993, **64**, 239.
120 K. Yoshida, K. Kameda, and T. Kondo, *Phytochemistry*, 1993, **33**, 917.
121 L. Kraut, R. Mues, and M. Sim-Sim, *Phytochemistry*, 1993, **34**, 211.
122 V. Ragunathan and N. Sulochana, *Indian J. Chem. Sect. B: Org. Chem. Ind. Med. Chem.*, 1994, **33**, 507.
123 N. Ezer, M. K. Sakar, B. Rodriguez, and M. C. De La Torre, *Int. J. Pharmacog.*, 1992, **30**, 61.
124 N. H. El Sayed, E. A. M. El-Khrisy, M. A. Khadiga, and T. J. Mabry, *Rev. Latinoam. Quim.*, 1991, **22**, 89.
125 H. Otsuka, *J. Nat. Prod.*, 1992, **55**, 1252.
126 M. F. Lahloub, *Mansoura J. Pharm. Sci.*, 1992, **8**, 78.
127 B. Das and A. K. Chakravarty, *Phytochemistry*, 1993, **33**, 493.
128 M. Aqil, I. Z. Khan, A. K. Yakaka, and F. A. Rahman, *Sci. Phys. Sci.*, 1994, **6**, 131.
129 R. J. Grayer-Barkmeijer and F. A. Tomás-Barberán, *Phytochemistry*, 1993, **34**, 205.
130 Z.-T. Chen, S.-W. Lee, and C.-M. Chen, *Heterocycles*, 1994, **38**, 1399.
131 J. L. Rios, S. Mañez, M. Paya, and M. T. Alcaraz, *Phytochemistry*, 1992, **31**, 1947.
132 Z.-T. Chen, S.-W. Lee, and C.-M. Chen, *Heterocycles*, 1994, **38**, 1399.
133 S. K. Chaturvedi and V. K. Saxena, *Acta Cienc. Indica Chem., Sect. C*, 1991, **17**, 155.
134 M. C. Recio, M. C. Terencio, J. A. Arenas, R. Ginar, M. J. Sanz, S. Manez, and J. L. R. Canavale, *Pharmazie*, 1993, **48**, 228.
135 P. Borai and R. Dayal, *Phytochemistry*, 1993, **33**, 731.
136 I. Merfort and D. Wendisch, *Planta Medica*, 1992, **58**, 355.
137 N. Okamura, H. Haraguchi, K. Hashimoto, and A. Yagi, *Phytochemistry*, **37**, 1463.
138 S. Kitanaka and M. Takido, *Chem. Pharm. Bull.*, 1992, **40**, 249.
139 J. A. Del Rio, O. Benavente, J. Castillo, and F. Borrego, *Phytochemistry*, 1992, **31**, 723.
140 S. J. Kellam, K. A. Mitchell, J. W. Blunt, M. H. G. Munro, and J. R. L. Walker, *Phytochemistry*, 1993, **33**, 867.
141 A. Hiermann, *Planta Medica*, 1982, **45**, 59.
142 M. Kamil, N. Jain, and M. Ilyas, *Fitoterapia*, 1992, **63**, 230.
143 A. Abdel Sattar, V. Bankova, S. Spassov, and H. Duddeck, *Fitoterapia*, 1993, **64**, 278.
144 J. B. Harborne, J. Greenham, C. A. Williams, J. Eagles, and K. R. Markham, *Phytochemistry*, 1993, **34**, 219.
145 A. Asami, Y. Hirai, and J. Shoji, *Chem. Pharm. Bull.*, 1991, **39**, 2053.
146 M. Ahmad, N. Jain, Shafiullah, M. S. Khan, and M. Ilyas, *J. Chem. Res. Synop.*, 1993, **7**, 248.
147 Y.-Y. Zhang, Y.-Z. Guo, M. Onda, K. Hashimoto, Y. Ikeya, M. Okada, and M. Maruno, *Phytochemistry*, 1994, **35**, 511.
148 A. Hasan, M. Farman, and I. Ahmed, *Phytochemistry*, 1994, **35**, 275.
149 K. R. Markham, H. Geiger, and H. Jaggy, *Phytochemistry*, 1992, **31**, 1009.
150 A. Hasler, G.-A. Gross, B. Meier, and O. Sticher, *Phytochemistry*, 1992, **31**, 1391.
151 R. N. Yadava, and A. Singh, *J. Indian Chem. Soc.*, 1993, **70**, 273.
152 G. H. Rizwani, K. Usmanghani, M. Ahmad, and V. U. Ahmad, *Pakistan J. Pharm. Sciences*, 1990, **3**, 27.
153 D. Strack, J. Heilemann, V. Wray, and H. Dirks, *Phytochemistry*, 1989, **28**, 2071.
154 N. H. El-Sayed, *Pharmazie*, 1991, **46**, 679.
155 H. Fukumoto, K. Ishiguro,T. Murashima, M. Yamaki, and K. Isoi, *Phytochemistry*, 1994, **37**, 1486.
156 J. Y. Si, D. H. Chen, Q. Chang, and L. G. Shen, *Yaoxue Xuebao*, 1994, **29**, 158.
157 M. E. Snook, O. T. Chortyk, V. A. Sisson, and C. E. Costello, *Phytochemistry*, 1992, **31**, 1639.
158 S. Urushibara, T. Okuno, and T. Matsumoto, *Tetrahedron Lett.*, 1992, **33**, 1213.
159 T. Satake, K. Hori, K. Kamiya, Y. Saiki, Y. Fujimoto, Y. Kimura, C. Maksut, and T. Mekin, *Chem. Pharm. Bull.*, 1993, **41**, 1743.
160 E. M. Zallocchi and A. B. Pomilio, *Phytochemistry*, 1994, **37**, 449.
161 M. Veit, F. C. Czygan, L. Witte, K. R. Markham, and H. Geiger, *Z. Naturforsch., Teil B, Chem. Sci.*, 1993, **48**, 1398.
162 Q. Liu, M. Liu, T. J. Mabry, and R. A. Dixon, *Phytochemistry*, 1994, **36**, 229.
163 M. A. Berhow, R. D. Bennett, S. M. Poling, S. Vannier, T. Hidaka, and M. Omura, *Phytochemistry*, 1994, **36**, 1225.
164 H. Okamura, A. Mimura, M. Niwano, Y. Takahara, H. Yasuda, and H. Yoshida, *Phytochemistry*, 1993, **33**, 512.
165 D. Mitrokotsa, S. Mitaku, C. Demetzos, C. Harvala, A. Mentis, S. Perez, and D. Kokkinopoulos, *Planta Medica*, 1993, **59**, 517.
166 M. Kaouadji, J.-M. Morand, and J. Garcia, *J. Nat. Prod.*, 1993, **56**, 1618.

167 S. Catalano, A. R. Bilia, M. Martinezzi, and I. Morelli, *Phytochemistry*, 1994, **37**, 1777.
168 I. Kubo and Y. Yokokawa, *Phytochemistry*, 1992, **31**, 1075.
169 G. Romussi, B. Parodi, and G. Caviglioli, *Pharmazie*, 1992, **47**, 877.
170 F. Imperato, *Phytochemistry*, 1992, **31**, 3291.
171 J. H. Lin, *J. Chin. Chem. Soc.* (*Taipei*),1993, **40**, 93.
172 A. Simon, A. J. Chulia, M. Kaouadji, D. P. Allais, and C. Delage, *Phytochemistry*, 1993, **33**, 1237.
173 J. K. Nielsen, C. E. Olsen, and M. K. Petersen, *Phytochemistry*, 1993, **34**, 539.
174 B. Cui, M. Nakamura, J. Kinjo, and T. Nohara, *Chem. Pharm. Bull.*, 1992, **40**, 1943.
175 A. R. Bilia, E. Palme, A. Marsili, L. Pistelli, and I. Morelli, *Phytochemistry*, 1993, **32**, 1078.
176 N. Jain and R. N. Yadava, *J. Indian Chem. Soc.*, 1994, **71**, 209.
177 W. D. Pan, L. T. Mai, Y. J. Li, X. L. Xu, and D. Q. Yu, *Yaoxue Xuebao*, 1993, **28**, 35.
178 M. Hattori, X.-L. Huang, Q.-M. Che, Y. Kawata, Y. Tezuka, T. Kikuchi, and T. Namba, *Phytochemistry*, 1992, **31**, 4001.
179 A. G. R. Nair, R. Jayaprakasam, R. Gunasekaran, C. Bayet, and B. Voirin, *Phytochemistry*, 1993, **33**, 1275.
180 I. Merfort and D. Wendisch, *Planta Medica*, 1992, **58**, 355.
181 J. C. Dauguet, M. Bert, J. Dolley, A. Bekaert, and G. Lewin, *Phytochemistry*, 1993, **33**, 1503.
182 F. E. Kandil, N. H. El Sayed, A. M., Abou-Douh, M. S. Ishak, and T. J. Mabry, *Phytochemistry*, 1994, **37**, 1215.
183 F. Tomas-Lorente, M. M. Garcia-Grau, J. L. Nieto, and F. A. Tomas-Barberan, *Phytochemistry*, 1992, **31**, 2027.
184 A. Hasler, G.-A. Gross, B. Meier, and O. Sticher, *Phytochemistry*, 1992, **31**, 1391.
185 Y. L. Lin, B. N. Timmermann, J. F. Hoffmann, and S. P. McLaughlin, *Phytochemistry*, 1993, **33**, 1549.
186 K. R. Markham, K. R. W. Hammett, and D. J. Ofman, *Phytochemistry*, 1992, **31**, 549.
187 M.-J. Sanz, M.-C. Terencio, S. Mañez, and J.-L. Rios, *J. Nat. Prod.*, 1993, **56**, 1995.
188 M. D'Agostino, F. De Simone, Z. L. Zhou, and C. Pizza, *Phytochemistry*, 1992, **31**, 4387.
189 A. Simon, A. J. Chulia, M. Kaouadji, D. P. Allais, and C. Delage, *Phytochemistry*, 1993, **32**, 1045.
190 A. Simon, A. J. Chulia, M. Kaouadji, and C. Delage, *Phytochemistry*, 1994, **36**, 1043.
191 K. Gluchoff-Fiasson, J. L. Fiasson, and J. Favre-Bonvin, *Phytochemistry*, 1994, **37**, 1629.
192 A. K. Tripathi and J. Singh, *Fitoterapia*, 1993, **64**, 90.
193 M. Ozipek, I. Calis, M. Ertan, and P. Ruedi, *Phytochemistry*, 1994, **37**, 249.
194 A. R. Bilia, J. M. Gonzalez, I. Morelli, E. Nieri, and M. E. Rubio, *Phytochemistry*, 1994 **35**, 1378.
195 M. Mizuno, S. Yoshida, M. Iinuma, Y. Yanaka, K. Ysuji, and F. A. Lang, *Phytochemistry*, 1992, **31**, 301.
196 C. A. Williams, J. B. Harborne, J. Greenham, and J. Eagles, *Phytochemistry*, 1994, **36**, 931.
197 C. Song and R. Zu, *Huaxue Xuebao* 1991, **49**, 917.
198 S. Sen, N. P. Sahu, and S. B. Mahato, *Phytochemistry*, 1992, **31**, 2919.
199 R. Nishida, *Phytochemistry*, 1994, **36**, 873.
200 H. A. Hassanean and E. K. Desoky, *Phytochemistry*, 1992, **31**, 3293.
201 H. Q. Yuan and C. X. Zuo, *Yaoxue Xuebao*, 1992, **27**, 589.
202 N. H. El-Sayed, A. M. Abu-Dooh, E. A. M. El-Khrisy, and T. J. Mabry, *Phytochemistry*, 1992, **31**, 2187.
203 A. Yaga, T. Uemura, N. Okamura, H. Haraguchi, T. Imoto, and K. Hashimoto, *Phytochemistry*, 1994, **35**, 885.
204 S. Sepulveda-Boza, S. Delhvi, and B. K. Cassels, *Phytochemistry*, 1993, **32**, 1301.
205 J. Si, D.Chen, Q. Chang, L. Shen, and Z. Zhu, *Zhiwu Xuebao* 1994, **36**, 239.
206 R. N. Yadava, and S. R. Mathews, *Fitoterapia*, 1994, **65**, 340.
207 C. Souleles, C. Harvala, and J. Chinou, *Int. J. Pharmacogn.*, 1991, **29**, 317.
208 B. R. Sahu and A. Chakrabarty, *Asian J. Chem.*, 1994, **5**, 1148.
209 S. S. Costa, A. Jossang, B. Bodo, M. L. M. Souza and V. L. G. Moraes, *J. Nat. Prod.*, 1994, **57**, 1503.
210 B. Bennini, A. J. Chulia, M. Kaouadji, and F. Thomasson, *Phytochemistry*, 1995, **38**, 259.
211 R. Arya, V. Babu, M. Ilyas, and K. T. Nasim, *Phytochemistry*, 1992, **31**, 2569.
212 R. Slimestad, W. Nerdal, G. W. Francis, and O. M. Anderson, *Phytochemistry*, 1993, **32**, 179.
213 R. Yu, X. Li, H. Zhang, L. Wu, T. Zhu, W. Li, L. Liu, and G. Zhang, *Zhiwu Xuebao*, 1992, **34**, 369.
214 D. Sun, Z. Zhao, L. Y. Foo, and H. Wong, *Linchan Huaxue Yu Gongye*, 1991, **11**, 251.
215 M. D'Agostino, V. D. Feo, C. Pizza, and F. De Simone, *Fitoterapia*, 1994, **65**, 472.
216 M. Aqil, F. A. Rahman, and M. B. Ahmad, *Sci. Phys. Sci.*, 1994, **6**, 141.
217 E. Maldonado, R. A. Roscano, C. Mancera, M. T. Tripp, and A. Ortega, *Phytochemistry*, 1992, **31**, 1003.
218 B. Agrawal, Hemlata, and J. Singh, *Int. J. Pharmacogn.*, 1993, **31**, 305.
219 M. Arisawa, H. Ba, M. Shiojima, T. Hayashi, Y. Tezuka, T. Taga, Y. Miwa, Y. Ito, T. Kikuchi, and N. Morita, *Chem. Pharm. Bull.*, 1993, **41**, 571.
220 B. H. Hu, L. D. Zhou, and Y. L. Liu, *Yaoxue Xuebao*, 1992, **27**, 397.
221 M. Mizuno, Y. Kanie, M. Iinuma, T. Tanaka, and F. A. Lang, *Phytochemistry*, 1992, **31**, 297.
222 H. Liang, L. Li and Y. Weimen, *J. Nat. Prod.*, 1993, **56**, 943.
223 B.-H. Hu, L.-D. Zhou, and Y.-L. Liu, *J. Nat. Prod.*, 1992, **55**, 672.
224 J. B. Harborne, in 'Polyphenolic Phenomena', ed. A. Scalbert, INRA, Paris, 1993, p. 19.
225 R. J. Grayer and J. B. Harborne, *Phytochemistry*, 1994, **37**, 19.
226 K. Redl, B. Davis, and R. Bauer, *Phytochemistry*, 1993, **32**, 218.
227 R. Roy and V. B. Pandey, *Phytochemistry*, 1994, **37**, 1775.
228 A. G. González, Z. E. Aguiar, J. G. Luis, A. Rivera, J. Calle, and G. Gallo, *Phytochemistry*, 1992, **31**, 2565.
229 L. Luyengi, I.-K. Lee, W. Mar, H. H. S. Fong, J. M. Pezzuto, and A. Douglas, *Phytochemistry*, 1994, **36**, 1523.
230 K. Kajiyama, S. Demizu, Y. Hiraga, K. Kinoshita, K. Koyama, K. Takahashi, Y. Tamura, K. Okada, and T. Kinoshita, *Phytochemistry*, 1992, **31**, 3229.
231 E. Venkata Rao and Y. Rajendra Prasad, *Phytochemistry*, 1992, **31**, 2121.
232 V. M. Sharma and P. S. Rao, *Phytochemistry*, 1992, **31**, 2915.
233 E. V. Rao and Y. R. Prasad, *Phytochemistry*, 1993, **32**, 183.
234 M. H. H. Nkunya, R. Waibel, and H. Achenbach, *Phytochemistry*, 1994, **34**, 853.
235 M. Iinuma, T. Tanaka, and F. Asai, *Phytochemistry*, 1994, **36**, 941.
236 J. Orjala, A. D. Wright, H. Behrends, G. Folkers, and O. Sticher, *J. Nat. Prod.*, 1994, **57**, 18.
237 M. Ahsan, J. A. Armstrong, and P. G. Waterman, *Phytochemistry*, 1994, **36**, 799.
238 Y. Xu, I. Kubo, and Y. Ma, *Phytochemistry*, 1993, **33**, 510.
239 M. Hoeneisen, M. Silva, J. Jakupovic, F. Papastergiou, and M. G. Peter, *Phytochemistry*, 1993, **34**, 1653.
240 F. Delle Monache and L. E. C. Suarez, *Phytochemistry*, 1992, **31**, 2481.
241 A. R. Bilia, S. Catalano, L. Pistelli, and I. Morelli, *Phytochemistry*, 1993, **33**, 1449.
242 L. Shang, B. Zhao, and X. Hao, *Yunnan Zhiwu Yanjiu*, 1994, **16**, 191.
243 A. R. Bilia, F. Flammini, G. Flamini, I. Morelli, and A. Marsili, *Phytochemistry*, 1993, **34**, 847.
244 I. I. Chemesova, M. Ilinuma, and A. L. Budantsev, *Rastit. Resur.*, 1993, **29**, 75.
245 V. S. Parmar, H. N. Jha, A. K. Gupta, and A. K. Prasad, *Phytochemistry*, 1992, **31**, 2567.
246 V. S. Parmar, A. Vardhan, G. R. Nagarajan, and R. Jain, *Phytochemistry*, 1992, **31**, 2185.
247 R. Bennini, A. J. Chulia, M. Kaouadji, and C. Delage, *Phytochemistry*, 1993, **33**, 1233.
248 N. C. Barua and R. P. Sharma, *Phytochemistry*, 1992, **31**, 4040.
249 H. Stuppner and E. P. Muller, *Phytochemistry*, 1994, **37**, 1185.
250 M. Khalilullah, V. M. Sharma, P. S. Rao, and K. Raghava Raju, *J. Nat. Prod.*, 1992, **55**, 229.
251 I. C. Parsons, A. I. Gray, and P. G. Waterman, *J. Nat. Prod.*, 1993, **56**, 46.
252 M. Ahsan, J. A. Armstrong, S. Gibbons, A. I. Gray, and P. G. Waterman, *Phytochemistry*, 1994, **37**, 259.
253 J. Li, H. Yuan, and M. Wang, *Phytochemistry*, 1992, **31**, 3664.
254 S. S. Jia, C. M. Ma, and J. M. Wang, *Yaoxue Xuebao*, 1991, **25**, 758.
255 M. Iinuma, M. Ohyama, T. Tanaka, M. Mizuno, and S.-K. Hong, *Phytochemistry*, 1993, **33**, 1241.

256 N. Matsuura, R. Nakai, M. Iinuma, T. Tanaka, and K. Inoue, *Phytochemistry*, 1994, **36**, 255.
257 M. Iinuma, M.Ohyama, T. Tanaka, M. Mizuno, and S.-K. Hong, *Phytochemistry*, 1992, **31**, 665.
258 M. Iinuma, M. Ohyama, T. Tanaka, M. Mizuno, and S.-K. Hong, *Phytochemistry*, 1992, **31**, 2855.
259 C.-M. Lu and C.-N. Lin, *Phytochemistry*, 1994, **35**, 781.
260 C.-M. Lu and C.-N. Lin, *Phytochemistry*, 1993, **33**, 909.
261 M. Iinuma, M. Ohyama, T. Tanaka, M. Mizuno, and S. K. Hong, *Phytochemistry*, 1993, **33**, 1241.
262 M. A. Nia, K. V. Rao, K. Sreeramulu, and D. Gunasekar, *J. Nat. Prod.*, 1992, **55**, 1152.
263 C. Balasubramanian, P. S. Mohan, K. Arumugasamy, and K. Udaiyan, *Phytochemistry*, 1993, **34**, 1194.
264 S. Tahara, Y. Katagiri, J. L. Ingham, and J. Mizutani, *Phytochemistry*, 1994, **36**, 1261.
265 E. V. Rao, Y. R. Prasad, and M. S. R. Murthy, *Phytochemistry*, 1994, **37**, 111.
266 A. E. Nkengfack, J. Kouam, W. T. Vouffo, Z. T. Fomum, E. Dagne, O. Sterner, L. M. Browne, and J. Guijun, *Phytochemistry*, 1993, **32**, 1305.
267 N. Matsuura, M. Iinuma, T. Tanaka, and M. Mizuno, *Phytochemistry*, 1993, **33**, 701.
268 N. Ruangrungsi, M. Iinuma, T. Tanaka, M. Ohyama, J. Yokoyama, and M. Mizuno, *Phytochemistry*, 1992, **31**, 999.
269 M. Iinuma, T. Tanaka, M. Mizuno, and F. A. Lang, *Phytochemistry*, 1992, **31**, 721.
270 H. Sievers, G. Burkhardt, H. Becker, and H. D. Zinsmeister, *Phytochemistry*, 1992, **31**, 3233.