

THE FLAVONOIDS: ADVANCES IN  
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# Flavone and flavonol glycosides

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## 8.1 INTRODUCTION

In our first review of the naturally occurring flavone and flavonol glycosides, we reported some 360 structures (Harborne and Williams, 1975). In the two subsequent reviews, we listed 720 and 1000 structures respectively (Harborne and Williams, 1982, 1988). The pace of discovery of the present period of review (1986–91) has increased and we describe in this chapter about 500 new glycosides. This is inevitably a conservative estimate of the known glycosidic variation since a number of partly characterized glycosides have not been included in our lists. As before, we use the term 'glycoside' to include any bound form of flavone or flavonol, and acylated and sulfated derivatives are described as well as those with only sugar. A novelty in this chapter is a listing of the glycosides of isoprenylated flavonols. Very few such substances were known at one time, but now some 36 glycosides have been reported. Flavone and flavonol C-glycosides are only discussed here incidentally, since they are covered in detail in Chapter 3.

A considerable array of new compounds have been

described during 1986 to 1991, and five representative structures are illustrated in Fig. 8.1. Two novel apigenin glycosides are the 7-(2"-glucosyllactate) from *Marrubium vulgare* leaf (Nawwar *et al.*, 1989a) and the 7-(6"-crotonylglucoside) from *Thermopsis alternifolia* (Yuldashev *et al.*, 1989). They represent two alternative structures – one in which a glucosylated acylating acid is directly linked to the flavone and one where the acylating acid is more usually linked via a glucose residue in the 7-position of the flavone. Lactic acid (2-hydroxypropionic acid) has been described before as an acylating acid in the flavone series, but crotonic acid (*trans*-2-butenic acid) is a new discovery.

The novel feature of the 3-(3",4"-diacetyl-2",6"-di-*p*-coumarylglucoside) of kaempferol, recently described from *Quercus* leaves (Romussi *et al.*, 1991), is the fact that all the free hydroxyls of the glucose unit are substituted by acyl groups. Such substitution changes the solubility properties of the original flavonol glycoside, converting it into a lipophilic substance. Such glycosides are likely to occur in the cytoplasm or on the leaf surface in the same cellular location as *O*-methylated flavones. Indeed, in our own laboratory, we have isolated the same diacetyl di-*p*-coumarate (or one of its isomers) from the leaf surface washings of *Quercus* and found that it has fungitoxic properties. The same point about lipophilic properties applies to a diacylated quercetin 3-rhamnoside reported by Markham *et al.* (1990b) from the gymnosperm *Libocedrus bidwillii* (see Section 8.6).

Another new flavonol glycoside with some degree of lipophilic solubility is rhamnocitrin 3-glucoside-4'-(2"-dihydrophaseylglucoside), from *Astragalus complanatus* (Cui *et al.*, 1991). The novelty here is the attachment to the 4'-glucose unit of the sesquiterpene, dihydrophaseic acid. This sesquiterpene is a natural metabolite of the growth hormone, abscisic acid, and presumably it has some growth-regulating properties.

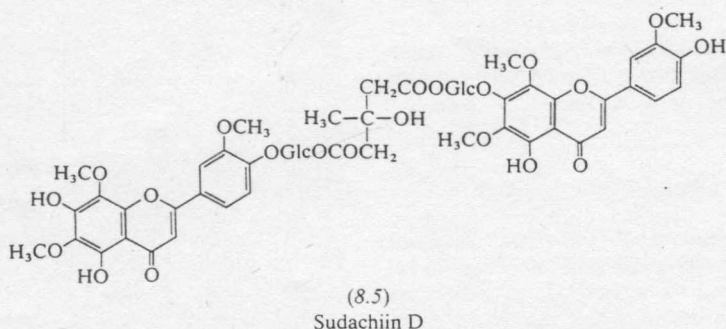
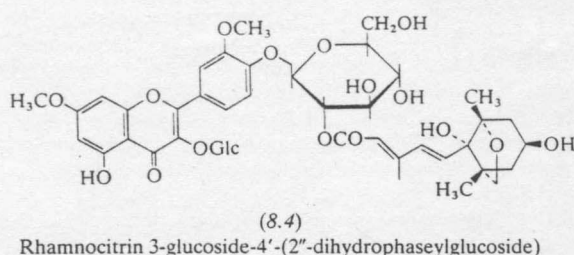
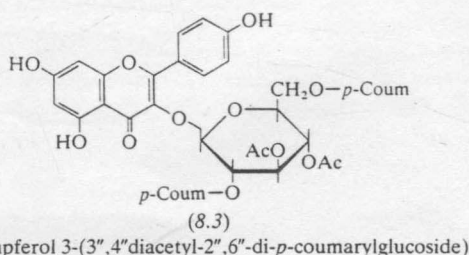
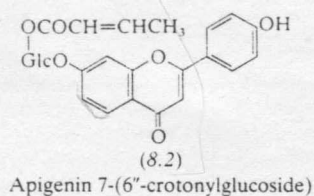
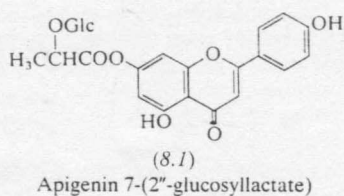


Fig. 8.1 Some new flavone and flavonol glycosides reported between 1985 and 1991 (Glc = glucosyl, Ac = acetyl, *p*-Coup = coumaryl).

The discovery of this compound attached to a flavonol glycoside is the first report of a plant hormone occurring in such a bound form.

The final structure, selected to indicate the range of new glycosides discovered in the last five or six years, is sudachiin D, from the green peel of *Citrus sudachi* (Horie *et al.*, 1976). This is only the second flavone glycoside to be found in which two flavone glycoside units are separately substituted on the carboxyl groups of an organic dicarboxylic acid. A diacetin-7-glucoside linked to malonic acid was described earlier from *Agostache rugosa* by Itokawa *et al.* (1981). This new compound from *Citrus* has a rare flavone, sudachitin (6,8-dimethoxyluteolin 3'-methyl ether), linked through glucose units attached to the 7- and 4'-positions to 3-hydroxy-3-methylglutaric acid. It co-occurs with the two monomeric glycosides, sudachiin B and C (see

Table 8.6). It is a highly unusual structure and might be considered loosely as belonging to the biflavonoid series (see Chapter 4).

## 8.2 SEPARATION AND PURIFICATION

Methods for separating and purifying flavone and flavonol glycosides have been reviewed by Markham (1989) and by Harborne (1992). Most recent research has been concerned with further refining the application of high-performance liquid chromatography (HPLC) to these substances (Daigle and Conkerton, 1988). For example, Hostettmann *et al.* (1984) described an HPLC system for the post-column derivatization of flavonoid glycosides so that ultraviolet (UV) spectra and shifts could be measured by a diode-array detector immediately following column separation. The method worked

well at the time, but the reaction coil required for the procedure went out of commercial production. An improved system for post-column derivatization using 10  $\mu$ l Viscomixers has now been described by Mueller-Harvey and Blackwell (1991). Post-column reactions with KOH, Na<sub>2</sub>HPO<sub>4</sub> and H<sub>3</sub>BO<sub>3</sub> reagents produced spectra and shifts that closely matched those of literature data.

The relatively new technique of centrifugal partition chromatography (CPC) has been applied to the preparative separation of flavonol glycosides (Marston *et al.*, 1990). Thus a 15 mg mixture of rutin, hyperin and quercitrin was separated with the solvent mixture ethyl acetate/ethanol/water (2:1:2) at a flow rate of 3 ml min<sup>-1</sup> in less than 2.5 h (Marston *et al.*, 1988). CPC has been applied successfully to the separation of the flavonol glycosides of *Ginkgo biloba* leaves. In conjunction with HPLC, CPC separated seven glycosides from 500 mg of leaf extract (Van Haelan and Van Haelan-Faste, 1988). Flavonol glycosides are often purified by gel filtration on Sephadex LH20, either in a preliminary clean-up of a crude plant extract or for final purification before spectral analysis. Hiemann (1986) claims better results if Fractogel PGM 2000 (manufactured by Merck) is used instead of LH20; elution is achieved by means of methanol.

### 8.3 IDENTIFICATION

The increase in the number (*ca* 500) of new glycoside reports during the period under review is due to two main factors: the advances in methods of separation, e.g. the excellent resolution of closely related structures by HPLC; and the wider use of proton and carbon-13 nuclear magnetic resonance (NMR) spectroscopy for glycoside identification. A book on the <sup>13</sup>C NMR spectroscopy of flavonoids has appeared (Agrawal, 1989), and this includes an extensive listing of NMR signals for most types of flavone and flavonol glycosides. Recent developments in NMR spectroscopy are reviewed elsewhere in this volume, so that no more need be included here.

The mass spectrometry (MS) of these glycosides continues to be explored as a means of structural identification. Most researchers use fast atom bombardment mass spectrometry (FAB-MS), since this method usually provides a strong molecular-ion peak, which indicates clearly the number and type of sugar units present. Sakushima *et al.* (1989) have examined the desorption chemical ionisation mass spectrometry (DCI-MS) at a low reagent gas pressure as an alternative method for analysing the sugar moieties. The molecular weights of the glycosides are indicated by the presence of negatively charged molecular ions, with a reasonable abundance for monoglycosides, a low abundance for diglycosides and a barely detectable (0.01%) abundance

for triglycosides. In addition to fragmentation to aglycone ions due to loss of sugars, anions are produced by the stepwise elimination of water from the sugar moiety at *m/z* 290 or 306 for 1 → 6 linked biosides, at *m/z* 127, 145 and 163 for deoxyglucosides, and at *m/z* 161 and 143 for hexosides. Hence, the technique is useful for recognizing the presence of 1 → 6 linked diglycosides such as robinobiosides, gentiobiosides and rutinobiosides.

## 8.4 SUGARS AND OTHER CONJUGATES

### 8.4.1 Monosaccharides

The number of monosaccharides known to occur in association with flavones and flavonols has risen from nine to ten with the reinclusion of mannose (Table 8.1). This sugar was removed from the 1981–85 list because its identification was not carried out unambiguously. Recently, Gupta and Singh (1991) have reported two new diglycosides containing mannose: chrysoeriol 7-mannosyl-(1 → 2)-alloside and quercetin 7-methyl ether 3-mannosyl-(1 → 2)-alloside from seeds of *Cassia alata* (Leguminosae). In that study, identification of mannose and allose was based on paper chromatography (PC) and gas chromatography of trimethylsilyl (TMSi) derivatives and both <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, so that the reinclusion of mannose is probably justified. However, as the authors do not indicate how many PC solvent systems they used, its identification is still not absolutely certain.

Allose, once thought to be a rare plant sugar, is now appearing quite regularly linked to various flavones. Five further new glycosides containing allose have been identified since 1985. These include luteolin and apigenin 7-allosyl-(1 → 2)-glucoside (Tomás-Barberán *et al.*, 1988a) and three unusual acetylated derivatives of hypolaetin 7-allosyl-(1 → 2)-glucoside (Lenherr and Mabry, 1987).

Among other rare sugars, apiose is still uncommon, with only one new report of its occurrence in monoglycosidic combination with quercetagenin (Fang *et al.*,

Table 8.1 Monosaccharides of flavone and flavonol glycosides

Pentoses	Hexoses	Uronic acids
D-Apiose	D-Allose	D-Galacturonic acid‡
L-Arabinose†	D-Galactose	D-Glucuronic acid‡
L-Rhamnose	D-Glucose	
D-Xylose	D-Mannose*	

\*Newly reported in two disaccharides with allose.

†Known to occur in both pyranose and furanose forms; all other sugars (except apiose) are normally in the pyranose form.

‡Also reported to occur as the methyl and ethyl esters.



1986a). However, two trisaccharides and one acylated and one non-acylated disaccharide containing apiose have been characterized recently (see Section 8.4.3).

#### 8.4.2 Disaccharides

Since 1985 some 11 new disaccharides have been fully characterized as components of flavone or flavonol glycosides, bringing the total number of known disaccharides to 41 (Table 8.2). From the literature of the last six years it is apparent that FAB-MS and  $^{13}\text{C}$  NMR spectroscopy can be regarded as standard techniques for determining the linkages in oligosaccharides, and there has been a noticeable reduction in the number of reports of partially characterized diglycosides.

Among the newly identified disaccharides the most noteworthy are three isomers of rhamnosylrhamnose (Table 8.2), as there is only one previous report of a myricetin 3-dirhamnoside from *Azara microphylla* (Flacourtiaceae) by Sagareishvili *et al.* (1983), who gave no indication of the sugar linkage. Since then, rhamnetin 3-rhamnosyl-(1→4)-rhamnoside has been characterized in tubers of *Cyperus rotundus* (Cyperaceae) by Singh and Singh (1986), and also this sugar has been found attached to the 3-hydroxyl of kaempferol 7-rhamnoside in leaves of *Cassinopsis madagascariensis* (Icacinaceae) by Rasoanaivo *et al.* (1990). More recently, 8-prenylkaempferol 4'-methyl ether (anhydroicaritin) 3-rhamnosyl-(1→3)-rhamnoside-7-glucoside has been identified from underground parts of *Van couveria hexandra* (Berberidaceae) (Mizuno *et al.*, 1991c). A third isomer, rhamnosyl-(1→2)-rhamnose, was identified attached to the 3-hydroxyl of isorhamnetin in the inflorescence of the common marigold *Calendula officinalis* (Compositae) by Komissarenko *et al.* (1988), and Kang *et al.* (1991) have reported the 3-rhamnosyl-(1→2)-rhamnosides of both 8-prenylkaempferol and its 4'-methyl ether in underground parts of *Epimedium koreanum* (Berberidaceae).

The only other report of a new combination of two sugars is a quercetin 3-glucosyl-(1→2)-xyloside from *Kalanchoe prolifera* (Crassulaceae) by Razanamahefa *et al.* (1990). However, several new isomers of known disaccharides have been found, including xylosyl-(1→3)-rhamnose, xylosyl-(1→6)-glucose, glucosyl-(1→2)-rhamnose and galactosyl-(1→3)-rhamnose (Table 8.2). The unusual combination, mannosyl-(1→2)-allose, has already been discussed under monosaccharides (see above).

#### 8.4.3 Trisaccharides

In the last six years, 11 new trisaccharides, four linear and seven branched, have been fully characterized (Table 8.3). All are components of flavonol glycosides. This advance in knowledge again reflects the greater

Table 8.2 Disaccharides of flavone and flavonol glycosides

Structure	Trivial name
<b>PENTOSE-PENTOSE</b>	
<i>O</i> - $\beta$ -D-Apiofuranosyl-(1→2)-xylose	
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→2)-arabinose	
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→2)-rhamnose*	
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→3)-rhamnose*	
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→4)-rhamnose*	
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→4)-xylose	
<i>O</i> - $\beta$ -D-Xylosyl-(1→2)-rhamnose	
<i>O</i> - $\beta$ -D-Xylosyl-(1→3)-rhamnose*	
<b>PENTOSE-HEXOSE</b>	
<i>O</i> - $\alpha$ -L-Arabinosyl-(1→6)-glucose	Vicianose
<i>O</i> - $\alpha$ -L-Arabinosyl-(1→6)-galactose	
<i>O</i> - $\alpha$ -D-Xylosyl-(1→2)-glucose	Sambubiose
<i>O</i> - $\beta$ -D-Xylosyl-(1→6)-glucose*	
<i>O</i> - $\beta$ -D-Xylosyl-(1→2)-galactose	Lathyrose
<i>O</i> - $\beta$ -D-Apiofuranosyl-(1→2)-glucose	
<i>O</i> - $\beta$ -D-Apiofuranosyl-(1→2)-galactose	
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→2)-glucose	Neohesperidose
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→3)-glucose	Rungiose
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→6)-glucose	Rutinose
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→2)-galactose	
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→6)-galactose	Robinobiose
<b>HEXOSE-PENTOSE</b>	
<i>O</i> - $\beta$ -D-Glucosyl-(1→2)-rhamnose*	
<i>O</i> - $\beta$ -D-Glucosyl-(1→3)-rhamnose*	
<i>O</i> - $\beta$ -D-Glucosyl-(1→4)-rhamnose	
<i>O</i> - $\beta$ -D-Glucosyl-(1→2)-xylose*	
<i>O</i> - $\beta$ -D-Galactosyl-(1→3)-rhamnose†	
<i>O</i> - $\beta$ -D-Galactosyl-(1→4)-rhamnose	
<b>HEXOSE-HEXOSE</b>	
<i>O</i> - $\beta$ -D-Glucosyl-(1→2)-glucose	Sophorose
<i>O</i> - $\beta$ -D-Glucosyl-(1→3)-glucose	Laminaribiose
<i>O</i> - $\beta$ -D-Glucosyl-(1→6)-glucose	Gentiobiose
<i>O</i> - $\beta$ -D-Glucosyl-(1→2)-galactose	
<i>O</i> - $\beta$ -D-Glucosyl-(1→6)-galactose	
<i>O</i> - $\beta$ -D-Galactosyl-(1→4)-glucose	Lactose
<i>O</i> - $\beta$ -D-Galactosyl-(1→6)-glucose§	
<i>O</i> - $\beta$ -D-Galactosyl-(1→4)-galactose	
<i>O</i> - $\beta$ -D-Galactosyl-(1→6)-galactose	
<i>O</i> - $\beta$ -D-Allosyl-(1→2)-glucose	
<i>O</i> - $\beta$ -D-Mannosyl-(1→2)-allose*	
<b>PENTOSE-URONIC ACID</b>	
<i>O</i> - $\alpha$ -L-Rhamnosyl-(1→2)-galacturonic acid*	
<b>URONIC ACID-URONIC ACID</b>	
<i>O</i> - $\beta$ -D-Glucuronosyl-(1→2)-glucuronic acid*	

\*Newly discovered in diglycosidic combination, in the period 1985-91.

†Present as 4'-rhamnoside.

§Present as 7-dirhamnoside.

Table 8.3 Trisaccharides of flavonol glycosides

Structure	Trivial name
<b>LINEAR</b>	
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 4)- <i>O</i> - $\alpha$ -arabinofuranosyl-(1 $\rightarrow$ 2)-arabinopyranose	Primflasine
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 2)- <i>O</i> - $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-glucose	2'-Rhamnosylrutinose
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 4)- <i>O</i> - $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-glucose*§	
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 2)- <i>O</i> - $\beta$ -glucosyl-(1 $\rightarrow$ 3)-glucose	2'-Rhamnosyllaminaribiose
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 3)- <i>O</i> - $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-glucose*	3 <sup>R</sup> -Glucosylrutinose
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 2)- <i>O</i> - $\beta$ -glucosyl-(1 $\rightarrow$ 2)-rhamnose*	
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 2)- <i>O</i> - $\beta$ -glucosyl-(1 $\rightarrow$ 2)-glucose	Sophorotriose
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 2)- <i>O</i> - $\beta$ -glucosyl-(1 $\rightarrow$ 6)-glucose	2'-Glucosylgentiobiose
<i>O</i> - $\alpha$ -Glucosyl-(1 $\rightarrow$ 4)- <i>O</i> -glucosyl-(1 $\rightarrow$ 6)-glucose	6'-Maltosylglucose
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 6)- <i>O</i> - $\beta$ -glucosyl-(1 $\rightarrow$ 4)-glucose	Sorborose
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 4)- <i>O</i> - $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-galactose*†	Isorhamninose
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 3)- <i>O</i> - $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-galactose†	Rhamninose
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 3)- <i>O</i> - $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-galactose‡	Sugar of faralatoside
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 6)- <i>O</i> - $\beta$ -glucosyl-(1 $\rightarrow$ 4)-rhamnose	
<b>BRANCHED</b>	
<i>O</i> - $\beta$ -Apiosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-glucose]	2 <sup>G</sup> -Apiosylrutinose
<i>O</i> - $\beta$ -Apiosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-galactose]*	2 <sup>Gal</sup> -Apiosylrobinobiose
<i>O</i> - $\beta$ -Xylosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-glucose]*	2 <sup>G</sup> -Xylosylrutinose
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-glucose]	2 <sup>G</sup> -Rhamnosylrutinose
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 6)- <i>O</i> -[ $\beta$ -apiosyl-(1 $\rightarrow$ 2)-glucose]*	
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 6)- <i>O</i> -[ $\beta$ -glucosyl-(1 $\rightarrow$ 2)-glucose]*	6 <sup>G</sup> -Rhamnosylsophorose
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\beta$ -glucosyl-(1 $\rightarrow$ 6)-glucose]	2 <sup>G</sup> -Rhamnosylgentiobiose
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-glucose]	2 <sup>G</sup> -Glucosylrutinose
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 3)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 2)-glucose]	3 <sup>G</sup> -Glucosylneohesperidose
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\beta$ -glucosyl-(1 $\rightarrow$ 6)-galactose]*	
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-galactose]*	2 <sup>Gal</sup> -Glucosylrobinobiose
<i>O</i> - $\beta$ -Galactosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-glucose]*	2 <sup>G</sup> -Galactosylrutinose
<i>O</i> - $\beta$ -Glucosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\beta$ -glucosyl-(1 $\rightarrow$ 6)-glucose]	2 <sup>G</sup> -Glucosylgentiobiose
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 4)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 2)-glucose]	4 <sup>G</sup> -Rhamnosylneohesperidose
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 2)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-galactose]	2 <sup>Gal</sup> -Rhamnosylrobinobiose
<i>O</i> - $\alpha$ -Rhamnosyl-(1 $\rightarrow$ 4)- <i>O</i> -[ $\alpha$ -rhamnosyl-(1 $\rightarrow$ 6)-galactose]	4 <sup>Gal</sup> -Rhamnosylrobinobiose

\* Newly discovered in period 1985–91.

† Revised structures.

‡ Only present with an acetyl group at the 4-hydroxyl of rhamnose.

§ Only present with a caffeoyl or *p*-coumaroyl group at the 6-hydroxyl of the second glucose.

ease in determining sugar linkages using FAB-MS and <sup>13</sup>C NMR spectroscopy.

Among the new linear trisaccharides are glucosyl-(1 $\rightarrow$ 3)-rhamnosyl-(1 $\rightarrow$ 6)-glucose, which has been found linked to the 3-position of both quercetin and kaempferol in leaves of the tea plant *Camellia sinensis* (Theaceae) (Finger *et al.* 1991b), and glucosyl-(1 $\rightarrow$ 2)-glucosyl-(1 $\rightarrow$ 2)-rhamnose, which is attached to the 3-hydroxyl of two acylated derivatives (montbretins A and B) of myricetin 4'-rhamnosyl-(1 $\rightarrow$ 4)-xyloside in corms of *Crocsmia crocosmiflora* (Iridaceae) (Asada *et al.*, 1988). A third novel linear trisaccharide, rhamnosyl-(1 $\rightarrow$ 4)-rhamnosyl-(1 $\rightarrow$ 6)-glucose, was found attached to the 3-position of kaempferol in leaves of some *Actinidia* species (Actinidiaceae) (Webby and Markham, 1990). The corresponding quercetin and

isorhamnetin triosides probably occur in the same plants, but their structures could not be confirmed because of insufficient material for <sup>13</sup>C NMR studies. Another new sugar, rhamnosyl-(1 $\rightarrow$ 4)-rhamnosyl-(1 $\rightarrow$ 6)-galactose, linked to the 3-position of both quercetin and kaempferol, was however fully characterized from *Actinidia*. This latter trisaccharide has been reported previously in glycosidic combination and referred to as rhamninose (Schmid *et al.*, 1972; Wagner *et al.*, 1974; Harborne and Williams, 1988). However, as a result of comparative <sup>13</sup>C NMR studies with synthetic rhamnosyl-(1 $\rightarrow$ 4)-rhamnosyl-(1 $\rightarrow$ 6)-galactose, Reiss-Maurer and Wagner (1982) revised the structure of the sugar in the then known rhamninosides to rhamnosyl-(1 $\rightarrow$ 3)-rhamnosyl-(1 $\rightarrow$ 6)-galactose, a triose previously listed as the sugar of alaternin



(Harborne and Williams, 1975). Thus, as a result of their findings, Reiss-Maurer and Wagner (1982) gave the name isorhamninose to rhamnosyl-(1→4)-rhamnosyl-(1→6)-galactose, which was then only known as a synthetic product. These revisions were regrettably omitted from our 1980–85 review (Harborne and Williams, 1988). However, in a recent paper Lin *et al.* (1991) have reported rhamnazin and rhamnocitrin 3-isorhamninosides (i.e. Rha(1→4)Rha(1→6)Gal) from the roots of *Rhamnus formosana*. This is surprising since Reiss-Maurer and Wagner (1982) corrected the structure of rhamnazin 3-rhamninoside (xanthorhamnin C) isolated from the fruit of *Rhamnus petiolaris* from 3-Rha(1→4)Rha(1→6)Gal to 3-Rha(1→3)Rha(1→6)Gal. So the question is now open whether both these trisaccharides occur in *Rhamnus* species, since the fruit of another *Rhamnus* plant, *R. leptophylla*, has been shown to contain kaempferol 3-rhamninoside (Rha(1→3)Rha(1→6)Gal) (Wang *et al.*, 1988a).

Two new branched trisaccharides containing apiose have been reported since 1985. One is apiosyl-(1→2)-[rhamnosyl-(1→6)-galactose] linked to the 3-position of kaempferol in seeds of *Chenopodium quinoa* (Chenopodiaceae) (De Simone *et al.*, 1990) and in the aerial parts of *Monnina sylvatica* (Polygalaceae) (Bashir *et al.*, 1991). The other is glucosyl-(1→6)-[apiosyl-(1→2)-glucose] attached to the 3-hydroxyl of patuletin from leaves of *Spinacia oleracea*, which is also in the Chenopodiaceae (Aritomi *et al.*, 1986). Another novel branched triside was found in leaves of tea, *Camellia sinensis* (Theaceae) (Sekine *et al.*, 1991), in combination with both kaempferol and quercetin at the 3-position. Three other novel sugar combinations based on glucose, galactose and rhamnose are: rhamnosyl-(1→2)-[glucosyl-(1→6)-galactose], attached to the 3-hydroxyl of quercetin, from leaves of the black nightshade, *Solanum nigrum* (Solanaceae) (Nawwar *et al.*, 1989b); 2<sup>Gal</sup>-glucosylrobinobiose, as a kaempferol derivative, from aerial parts of both *Monnina sylvatica* (Polygalaceae) (Bashir *et al.*, 1991) and *Anthyllis sericea* (Leguminosae) (Marco *et al.*, 1989); and 2<sup>G</sup>-galactosyl-rutinoside, again linked to the 3-position of kaempferol, from seeds of the tea plant, *Camellia sinensis* (Sekine *et al.*, 1991). Finally, a new isomer of 2<sup>G</sup>-rhamnosyl-gentiobiose, rhamnosyl-(1→6)-[glucosyl-(1→2)-glucose] or 6<sup>G</sup>-rhamnosylsophorose, occurs attached to the 3-hydroxyl of kaempferol in *Hosta ventricosa* (Liliceae) (Budzianowski, 1990a).

#### 8.4.4 Tetrasaccharides

The first known branched tetrasaccharide, [rhamnosyl-(1→4)-glucosyl-(1→6)]-sophorose, has been found attached to the 7-hydroxyl of acacetin and acetylated at the 6'''-position of the sophorose in leaves of *Peganum harmala* (Zygophyllaceae) by Ahmed and

Saleh (1987). Characterization of this glycoside was based on acid hydrolysis to aglycone and sugar, UV and <sup>1</sup>H NMR analyses, and the sugar linkage was determined by <sup>13</sup>C NMR measurements. Thus, the identification of this new tetrasaccharide appears to be complete. No linear tetrasaccharide has so far been reported. Several glycosides with four sugar units are known, but these have the sugars distributed between the 3- and 7-positions, e.g. kaempferol 3-galactosyl-(1→6)-glucoside-7-dirhamnoside, 3-sophorotrioside-7-glucoside and 3-rutinoside-4'-diglucoside, and quercetin 3-rhamnosyldiglucoside-7-glucoside, 3-rutinoside-7,3'-bisglucoside and 3-rutinoside-4'-diglucoside (see Harborne and Williams, 1988).

Higher glycosides in the flavone and flavonol series no doubt exist in nature, but none has yet been fully characterized. Evidence from two-dimensional paper chromatography and the detection of glycosides with very low *R<sub>f</sub>* in butanol/acetic acid/water (4:1:5) and high *R<sub>f</sub>* in 15% acetic acid would suggest that such higher glycosides (e.g. pentaglycosides, hexaglycosides, etc.) may occur with some frequency (Harborne, unpublished results). The study by Markham (1972) of one such component from the liverwort *Monoclea forsteri* revealed the presence of 8-methoxyluteolin covalently linked via galacturonic acid to a carbohydrate with about 18 monosaccharide units. Whether such flavone-polysaccharide complexes are also present in higher plants remains for future investigation.

#### 8.4.5 Acylated derivatives

An astonishing number of new acyl derivatives (42 flavones and 99 flavonols) have been reported in the literature between 1986 and 1991. Thirteen aliphatic and ten aromatic acids have now been identified as acyl substituents (Table 8.4). There are four new aliphatic acids: isobutyric, 2-methylbutyric, crotonic (*trans*-2-butenic) and 2-methylbutenoic. Thus, quercetin 3-, 3'- and 4'-isobutyrate were found in the leaf gum of *Traversia baccharoides* (Compositae) by Kulanthaivel and Benn (1986); isorhamnetin 3-(3-methylbutyryl-rutinoside) was discovered in two *Patersonia* species (Iridaceae); apigenin and chrysoeriol 7-(6"-crotonyl-glucoside)s were reported from *Thermopsis alternifolia* (Leguminosae) by Yuldashev *et al.* (1989); and 5,7,8-trihydroxy-3-methoxyflavone 8-(*Z*-2"-methyl-2-butenate) (together with the rare 8-(2"-methylbutyrate)) was characterized in the resinous leaf and stem exudate of *Gnaphalium robustum* (Compositae) by Arzua and Cuadra (1990). There is one new aromatic acid, cinnamic, and one new sesquiterpenoid acid, dihydrophaseic. Kaempferol 3-(6"-*cis*-cinnamoyl-glucoside) was found in the aerial parts of *Solanum elaeagnifolium* (Solanaceae) by Chiale *et al.* (1991), and rhamnocitrin 3-glucoside-4'-(2"-dihydrophaseyl-

Table 8.4 Acylating acids found in flavone and flavonol derivatives

Organic acid	Examples of occurrence	References
<b>ALIPHATIC ACIDS</b>		
Acetic	Apigenin 7-(2''-acetylglucoside)	Redaelli <i>et al.</i> (1980)
Malonic	Quercetin 3-(malonylglucoside)†	Woeldecke and Herrmann (1974)
2-Hydroxypropionic (lactic)	Kaempferol 3-(2-hydroxypropionylglucoside)-4'-glucoside	Aguinagalde and del Pero Martinez (1982)
Succinic	Kaempferol 7-(6''-succinylglucoside)	Hiraoka and Maeda (1979)
Butyric	Herbacetin 8-butyrate	Wollenweber <i>et al.</i> (1978)
Isobutyric*	Quercetin 3-, 3'- and 4'-isobutyrate	Kulanthaivel and Benn (1986)
2-Methylbutyric	Acacetin 7-[2'''-(2-methylbutyryl)rutinoside]	Chari <i>et al.</i> (1977)
3-Methylbutyric*	Isorhamnetin 3-(3-methylbutyrylrutinoside)	Williams <i>et al.</i> (1989)
Crotonic		
(E-2-butenic)*	Apigenin and chrysoeriol 7-(6''-crotonylglucoside) (8.2)	Yuldashev <i>et al.</i> (1989)
2-Methyl-2-butenic*	5,7,8-Trihydroxy-3-methoxyflavone 8-[(Z)-2-methyl-2-butenate]	Arzua and Cuadra (1990)
Tiglic	Quercetin 7-(6''-tiglylglucoside)	Ogawa and Ogihara (1975)
3-Hydroxy-3-methylglutaric	Sudachitin 7-(3-hydroxy-3-methylglutarate)-4'-glucoside	Kumamoto <i>et al.</i> (1985)
Quinic	Herbacetin 7-(6''-quinylglucoside)	Nawwar <i>et al.</i> (1984)
<b>AROMATIC ACIDS</b>		
Benzoic	Kaempferol 3-(benzoylglucoside)†	Schonsiegel <i>et al.</i> (1969)
p-Hydroxybenzoic	Kaempferol 3-(p-hydroxybenzoylglucoside)†	Schonsiegel <i>et al.</i> (1969)
Gallic	Quercetin 3-(6''-galloylglucoside)	Collins <i>et al.</i> (1975)
Cinnamic*	Luteolin 7-(6''-trans-cinnamylglucoside)	Mizuno <i>et al.</i> (1987a)
p-Coumaric	Apigenin 7-(4''-p-coumarylglucoside)	Karl <i>et al.</i> (1976)
Caffeic	Apigenin 7-glucoside-4'-caffeate	Gella <i>et al.</i> (1967)
Ferulic	Luteolin 7-glucuronide-3'-ferulylglucoside†	Markham <i>et al.</i> (1978)
Isoferulic	Quercetin 3-(isoferulylglucuronide)†	El-Ansari <i>et al.</i> (1976)
Sinapic	Kaempferol 3-(sinapylsophoroside)-7-glucoside†	Stengel and Geiger (1976)
<b>SESQUITERPENE ACID</b>		
Dihydrophaseic*	Rhamnocitrin 3-glucoside-4'-(2''-dihydrophaseylglucoside)* (8.4)	Cui <i>et al.</i> (1991)

\*Newly discovered in the period 1985-91.

†In this example, the position of attachment of acyl group to sugar has not been established.

glucoside) was identified in *Astragalus complanatus* (Leguminosae) by Cui *et al.* (1991).

However, most new reports concern acetic acid, as an acylating acid of sugar hydroxyl groups (16 new flavones and 44 new flavonol derivatives). Since acetic acid is volatile and acetyl groups are easily lost by mild acid hydrolysis, it is difficult to detect this acid as an acyl substituent using traditional PC and thin-layer chromatography (TLC) procedures. Thus, many acetylated derivatives have probably been overlooked in past flavonoid surveys, and no doubt the large number of new reports are due to the successful application of FAB-MS and <sup>13</sup>C NMR techniques. Among these new acetylated flavonoids, the most interesting are a triacetate, kaempferol 3-(2''',3''',5'''-triacyl)arabinofuranosyl-(1→6)-glucoside from flowers of *Calluna vulgaris* (Ericaceae) (Allais *et al.*, 1991), and two tetraacylated glucosides of kaempferol, which have two

acetyl and two p-coumaroyl substituents on the same glucose residue, from the leaves of the oak, *Quercus suber* (Fagaceae) (Romussi *et al.*, 1991). In aerial parts of *Kalanchoe gracilis* (Crassulaceae), Liu *et al.* (1989b) found as many as nine acetylated 3,7-dirhamnosides, two mono-, three di- and two triacetylated derivatives of quercetagenin and one mono- and one diacetylated derivative of eupafolin, together with eupafolin 4'-rhamnoside and 3,7-dirhamnoside (see Table 8.7). There are two series of isomers: the 3''- and 4''-monoacetylramnosides, and the 2'',4''- and 3'',4''-diacetylramnosides. From rhizomes of *Zingiber zerumbet* (Zingiberaceae) five novel acetylated kaempferol 3-rhamnosides have also been characterized: the 2'', 3''- and 4''-monoacetates and the 2'',4''- and 3'',4''-diacetates (Masuda *et al.*, 1991).

The number of new malonates discovered since 1985 is surprisingly small considering how many new



malonylated anthocyanins have been described (see Chapter 1). There are five flavone and two flavonol derivatives. The most unusual of these are the 5-(6''-malonylglucosides) of apigenin, genkwanin and luteolin, from the barren sprouts of the horsetail *Equisetum arvense* (Equisetaceae) (Veit *et al.*, 1990). Apigenin 7-(6''-malonylglucoside) from *Bryum capillare* (Stein *et al.*, 1985) is included because its characterization has only now been substantiated regarding the position of attachment of the malonyl group. In another moss, *Bryum pseudotriquetrum*, 6''-malonylglucose was found attached to the 7-position of scutellarein by Stein and Zinsmeister (1990), and isorhamnetin 3-(6''-malonylglucoside) was identified in leaves of the pear tree, *Pyrus communis* (Rosaceae), by Wald *et al.* (1989). The fifth new malonate, kaempferol 3-(apiosylmalonylglucoside) from aerial parts of chickpea, *Cicer arietinum* (Leguminosae), has not been completely characterized (Börger and Barz, 1988), but the authors assume, by analogy, that the malonic acid is probably at the 6-position of glucose.

Five other notable acylated derivatives are quercetin 3-[6''-(3-hydroxy-3-methylglutaryl)galactoside] from *Rubus* fruits (Rosaceae) (Wald *et al.*, 1986), three lactates (i.e. 2-hydroxypropionates) in leaves of the labiate *Marrubium vulgare* (Nawwar *et al.*, 1989a), and rhamnocitrin 3-rhamnoside-7-(6''-succinylglucoside) from the fern *Asplenium bulbiferum* (Imperato, 1987b).

#### 8.4.6 Sulfate conjugates

During the last six years, a further 25 sulfate conjugates, including seven new structural types, have been reported, bringing the total number of known flavone and flavonol sulfates to 80 (Table 8.5). The most interesting are four new conjugates in aerial parts of *Lippia nodiflora* and *L. canescens* (Verbenaceae), where the 6-sulfate of 6-hydroxyluteolin, the 6,7-disulfates of 6-hydroxyluteolin and nodifloretin, the 7,4'-disulfates of hispidulin and jaceosidin, and the 3',4'-disulfate of nepetin were identified (Tomás-Barberán *et al.*, 1987). Thus, assuming that the 5-hydroxyl is not normally available for sulfation, most of the other possible mono- and disulfates have now been described in the flavone series. Another new flavone derivative, 7-disulfatoglucoside, was found in combination with luteolin and chrysoeriol in fruit of the date *Phoenix dactylifera* (Palmae) by Ferreres and Tomás-Lorente (1988). Among the new flavonol sulfates are the 3'-sulfate and 3-glucuronide-3'-sulfate of quercetin, characterized in aerial parts of *Hypericum elodes* (Guttiferae) (Seabra and Alves, 1991), and the 3,3'-disulfates of quercetin and patuletin, identified in leaves of *Flaveria chloraefolia* (Compositae) by Barron and Ibrahim (1987a). Thus, apart from the absence of 5-sulfates, most of the possible di- and trisulfates of

quercetin have now been described from the genus *Flaveria* and the 3,7,3',4'-tetrasulfate is also present (Barron *et al.*, 1988).

The structures of some 23 naturally occurring flavonoid sulfates have recently been confirmed by synthesis (cf. Barron *et al.*, 1988). This success is due largely to new improved methods of synthesis. The disadvantage of the older sulfamic acid method is that, while this successfully introduces a sulfate group at the 3'-position of 3',4'-dihydroxylated flavonoids, it otherwise leads to a complex mixture of mono- and disulfates and only very small amounts of the 3- and 7-sulfates are produced. The new method using *N,N'*-dicyclohexylcarbodiimide (DCC) and tetrabutylammonium hydrogensulfate (TBAHS) in dimethylformamide has allowed the synthesis of specifically sulfated flavonoids in good yield. Thus TBAHS and DCC under different reaction conditions lead to stepwise sulfation of the 3-, 7- and 4'-positions in the order 7 > 4' > 3 (Barron and Ibrahim, 1988a). However, in this method, the 3- and 3'-positions are still resistant to sulfation. Thus, the recent discovery that highly purified aryl sulfatase (i.e. with glucosidase and uronidase contaminants removed) mediates in the stepwise hydrolysis of all sulfate groups except that at the 3-position is a major breakthrough, since it allows the preparation of 3-sulfated flavonols in good yield. This enzymatic hydrolysis can be used in conjunction with and is thus complementary to the chemical methods.

#### 8.5 NEW REPORTS OF FLAVONE GLYCOSIDES

Some 120 new flavone glycosides have been discovered in the period 1986–91. These are listed in Table 8.6 with plant source and reference. A complete checklist of all the known flavone glycosides is given in the appendix at the end of the chapter. The number of compounds has increased by 37% since 1985, to give a total of 463 flavone glycosides. These include a further 23 apigenin, 20 luteolin and one tricin glycoside, bringing their totals to 81, 92 and 18 respectively. A number of flavone aglycones have been found in glycosidic combination for the first time, e.g. 7,2'-dihydroxyflavone 7-glucoside from *Primula macrophylla*, 5,7,8-trihydroxyflavone 7- and 8-glucuronides from *Scutellaria* spp., and 7,8,4'-trihydroxyflavone 8-neohesperidoside from *Sophora subprostrata* (see Table 8.6 for details).

The report of apigenin 7-(6''-malonylglucoside) from *Bryum capillare* by Stein *et al.* (1985) was accidentally omitted from our last review. Further work on mosses of the genus *Bryum* has revealed new malonylated derivatives such as the scutellarein analogue, together with apigenin and luteolin 7-(6'''-malonylneohesperidoside) (Stein and Zinsmeister, 1990). Related flavone 6''-malonylglucosides have been characterized from the

Table 8.5 Sulfate conjugates of flavones and flavonols

Type of conjugate	Known aglycones
<b>FLAVONES</b>	
6-Sulfate	6-OH luteolin*
7-Sulfate	Apigenin, luteolin, chrysoeriol, diosmetin, hispidulin*, 6-OH luteolin*, nepetin*, nodifloretin*, jaceosidin*
8-Sulfate	Hypolaetin
3'-Sulfate	Luteolin, diosmetin, tricetin, luteolin 7,4'-dimethyl ether*
4'-Sulfate	Luteolin, hispidulin*
6,7-Disulfate	6-OH luteolin*, nodifloretin*
7,3'-Disulfate	Luteolin, diosmetin, tricetin
7,4'-Disulfate	Hispidulin*, jaceosidin*
3',4'-Disulfate	Nepetin*
7-Sulfatoglucoside	Apigenin, luteolin, chrysoeriol, tricetin
7-Sulfatoglucuronide	Tricin, luteolin
7-Disulfatoglucoside	Luteolin*, chrysoeriol*
7-Disulfatoglucuronide	Tricin
7-Sulfatorutinoside	Luteolin
8-Glucoside-3'-sulfate	Hypolaetin, hypolaetin 4'-methyl ether
7-Sulfate-3'-glucoside	Luteolin
7-Sulfate-3'-rutinoside	Luteolin
<b>FLAVONOLS</b>	
3-Sulfate	Rhamnocitrin, kaempferol 7,4'-dimethyl ether, kaempferol, kaempferide*, eupafolin*, eupalitin*, quercetin, isorhamnetin, tamarixetin, rhamnetin, rhamnazin, ombuin*, gossypetin, patuletin, eupatoletin, eupatin, veronicafolin, spinacetin*
7-Sulfate	Kaempferol, isorhamnetin, patuletin, quercetagenin 3-methyl ether
3'-Sulfate	Quercetin*
3,7-Disulfate	Kaempferol, isorhamnetin
3,3'-Disulfate	Quercetin*, patuletin*
3,4'-Disulfate	Quercetin, isorhamnetin*
3,5,4'-Trisulfate	Rhamnetin
3,7,3'-Trisulfate	Quercetin
3,7,4'-Trisulfate	Quercetin, kaempferol, isorhamnetin
3,7,3',4'-Tetrasulfate	Quercetin
3-(3"-Sulfatoglucoside)	Quercetin, kaempferol
3-(6"-Sulfatoglucoside)	Kaempferol
3-Sulfatorhamnoside	Kaempferol, quercetin, myricetin
3-Sulfatorutinoside	Quercetin, isorhamnetin, kaempferol
3-(6"-Sulfatogentiobioside)	Kaempferol
3-Glucoside-7-sulfate	Patuletin
3-Glucuronide-7-sulfate	Kaempferol, quercetin, isorhamnetin
3-Glucuronide-3'-sulfate	Quercetin*
8-Glucuronide-3-sulphate	Gossypetin
3'-Glucuronide-3,5,4'-trisulfate	Rhamnetin

\*Newly discovered sulfate conjugate in the period 1985-91.

barren sprouts of the horsetail *Equisetum arvense*; these are derivatives of apigenin, genkwanin and luteolin with the malonated sugar attached to the 5- rather than the more usual 7-hydroxyl (Veit *et al.*, 1990).

Flavone glycosides acylated with *p*-coumaric acid are relatively uncommon in nature, so that the reports of the *cis* and *trans* forms of apigenin 7-(4"-*p*-coumarylglucoside), from *Echinops echinatus* and *Sideritis raeseri* respectively, during the period under review are note-

worthy. The more stable *trans* isomer is presumably identical to an apigenin 7-(4"-*p*-coumarylglucoside) reported from *Salix alba* leaf by Karl *et al.* (1976). It may be noted that the isomeric 7-(6"-*p*-coumarylglucoside) is also known, from *Pogostemon cablin* (Labiatae) (Itokawa *et al.*, 1981).

Some new glycosides of the rare 5,7,2',4',5'-penta-hydroxyflavone (isoetin) deserve mention, in relationship to the position of sugar substitution. Thus the 5'-



Table 8.6 New flavone glycosides

Glycoside	Source	Family	References
5,7-Dihydroxyflavone (chrysin) 7-Benzoyl	<i>Baccharis bigelovii</i> leaf and stem exudate	Compositae	Arriaga-Giner <i>et al.</i> (1986)
7,2'-Dihydroxyflavone 7-Glucoside	<i>Primula macrophylla</i> whole plant	Primulaceae	Ahmad <i>et al.</i> (1991d)
7,4'-Dihydroxyflavone 4'-Glucoside	<i>Sophora subprostata</i> roots	Leguminosae	Shirataki <i>et al.</i> (1986)
2',5'-Dihydroxyflavone 5'-Acetate	<i>Primula</i> sp. farinose exudate	Primulaceae	Wollenweber <i>et al.</i> (1988a)
5,7,8-Trihydroxyflavone (norwogonin) 7-Glucuronide	<i>Scutellaria discolor</i> roots	Labiatae	Tomimori <i>et al.</i> (1986)
8-Glucuronide	<i>Scutellaria ikonnikovii</i> whole plant	Labiatae	Wang <i>et al.</i> (1988b)
5-Hydroxy-7,8-dimethoxyflavone 5-Glucoside	<i>Andrographis paniculata</i> roots	Acanthaceae	Kuroyanagi <i>et al.</i> (1987)
5,7,2'-Trihydroxyflavone 7-Glucuronide	<i>Scutellaria ikonnikovii</i> whole plant	Labiatae	Wang <i>et al.</i> (1988b)
7,8,4'-Trihydroxyflavone 8-Neohesperidoside	<i>Sophora subprostata</i> roots	Leguminosae	Shirataki <i>et al.</i> (1986)
5,7,4'-Trihydroxyflavone (apigenin) 7- $\alpha$ -L-Arabinofuranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucoside 7- $\alpha$ -L-Arabinopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucoside 7-Xylosyl-(1 $\rightarrow$ 6)-glucoside 7-Dirhamnoside 7-Glucosylrhamnoside 7-Allosyl-(1 $\rightarrow$ 2)-glucoside	} <i>Dacrydium</i> spp.  } <i>Asplenium normale</i> fronds } <i>Sideritis</i> sp. aerial parts	Podocarpaceae	Markham <i>et al.</i> (1987)
7-Rhamnosyl-(1 $\rightarrow$ 2)-galacturonide		Compositae	Ahmed <i>et al.</i> (1989)
7-Rhamnoside-4'-rutinoside		Leguminosae	Messens <i>et al.</i> (1989)
7-Digalacturonide 7-Galacturonylglucoside 7-Digalacturonide-4'-glucoside 5-(6"-Malonylglucoside)		Umbelliferae	El-Negoumy and Mansour (1989)
7-(6"-Crotonylglucoside) (crotonylcosmosin) (8.2)		Equisetaceae	Veit <i>et al.</i> (1990)
7-(2"-Acetyl-6"-methylglucuronide)	<i>Thermopsis alternifolia</i>	Leguminosae	Yuldashev <i>et al.</i> (1989)
7-Lactate 7-(2"-Glucosyllactate) (8.1) 7-(2"-Glucuronosyllactate) 7-(6"-Malonylglucoside)	} <i>Calluna vulgaris</i> flowers  } <i>Marrubium vulgare</i> leaf  } <i>Bryum capillare</i> whole plant	Ericaceae	Allais <i>et al.</i> (1991)
7-(4"-Z-P-Coumarylglucoside)		Labiatae	Nawwar <i>et al.</i> (1989a)
	<i>Echinops echinatus</i> aerial parts	Bryaceae	Stein <i>et al.</i> (1985)
		Compositae	Chaudhuri and Thakur (1986)

Table 8.6 (Contd.)

Glycoside	Source	Family	References
7-(4"-E-p-Coumarylglucoside)	<i>Sideritis raeseri</i> aerial parts	Labiatae	Gabrieli and Kokkalou (1990)
5-Rhamnosyl-(1 → 2)- (6"-acetylglucoside)	<i>Eurya japonica</i> flowers	Theaceae	Inada <i>et al.</i> (1989)
7-[6'''-Acetylallosyl-(1 → 2)- glucoside]	<i>Stachys aegyptiaca</i> aerial parts	Labiatae	El-Ansari <i>et al.</i> (1991)
7-(6'''-Malonylneohesperidoside)	<i>Bryum pseudotriquetrum</i>	Bryales	Stein and Zinsmeister (1990)
7-Sulfatoglucuronide	<i>Fuchsia procumbens</i> leaf	Onagraceae	Williams <i>et al.</i> (1983)
Apigenin 4'-methyl ether (acacetin)			
7-[Rhamnosyl-(1 → 4")-glucosyl- (1 → 6")-6'''-acetylsophoroside]	<i>Peganum harmala</i> leaf	Zygophyllaceae	Ahmed and Saleh (1987)
Apigenin 7-methyl ether (genkwanin)			
4'-Glucosylrhamnoside	<i>Asplenium normale</i> fronds	Aspleniaceae	Iwashina <i>et al.</i> (1990)
5-(6"-Malonylglucoside)	<i>Equisetum arvense</i> barren sprouts	Equisetaceae	Veit <i>et al.</i> (1990)
6-Hydroxyapigenin (scutellarein)			
7-Glucoside	<i>Crocus chrysanthus</i> cv. 'Cream Beauty' leaf	Iridaceae	Harborne and Williams (1984)
6-Rhamnosyl-(1 → 2)-galactoside	<i>Ficus infectoria</i> leaf	Moraceae	Ahmad <i>et al.</i> (1991c)
7-Glucosyl-(1 → 4)-rhamnoside	<i>Thymus serpyllum</i> stems	Labiatae	Washington and Saxena (1986)
7-(6"-Malonylglucoside)	<i>Bryum pseudotriquetrum</i>	Bryales	Stein and Zinsmeister (1990)
Scutellarein 6-methyl ether (hispidulin)			
7-Sulfate	<i>Iphiona scabra</i> aerial parts	Compositae	Ahmed and Mabry (1987)
7-Sulfate	} <i>Lippia nodiflora</i> , <i>L. canescens</i> aerial parts	Verbenaceae	Tomás-Barberán <i>et al.</i> (1987)
4'-Sulfate			
7,4'-Disulfate			
Scutellarein 7-methyl ether			
6-Glucoside	<i>Crocus corsicus</i> , <i>C. minimus</i> leaf	Iridaceae	Harborne and Williams (1984)
6-Galactoside	<i>Garcinia andamanica</i> leaf	Guttiferae	Alam <i>et al.</i> (1986)
Scutellarein 6,4'-dimethyl ether (pectolarigenin)			
7-Rhamnoside	<i>Kichxia ramosissima</i> stem and leaf	Scrophulariaceae	Sing and Prakash (1987)
8-Hydroxyapigenin (isoscutellarein)			
7-Xyloside	<i>Libocedrus bidevillii</i> , <i>L. plumosa</i> leaf	Compositae	Markham <i>et al.</i> (1990b)
7-Glucoside	<i>Bryum argenteum</i> whole plants	Bryales	Markham and Given (1988)
7-Neohesperidoside	<i>Garcinia andamanica</i> leaf	Guttiferae	Alam <i>et al.</i> (1987)
7-[6'''-Acetylallosyl-(1 → 2)- 6"-acetylglucoside]	<i>Stachys anisochila</i> leaf	Labiatae	Lenherr and Mabry (1987)
8-Hydroxyapigenin 4'-methyl ether			
8-(2"-Sulfatoglucoside)	<i>Althaea officinalis</i> roots	Malvaceae	Gudej (1991)
5,6,7,2'-Tetrahydroxyflavone			
7-Glucuronide	<i>Scutellaria ikonnikovii</i> whole plant	Labiatae	Wang <i>et al.</i> (1988b)

(Contd.)



Table 8.6 (Contd.)

Glycoside	Source	Family	References
5,7,2'-Trihydroxy-8-methoxyflavone 7-Glucuronide	<i>Scutellaria prostrata</i> root	Labiatae	Kikuchi <i>et al.</i> (1991)
5,7-Dihydroxy-8,2'-dimethoxyflavone 7-Glucuronide	<i>Scutellaria indica</i> root	Labiatae	Miyaichi <i>et al.</i> (1987)
5-Hydroxy-7,8,2'-trimethoxyflavone 5-Glucoside	<i>Andrographis paniculata</i> root	Acanthaceae	Kuroyanagi <i>et al.</i> (1987)
5,7,3',4'-Tetrahydroxyflavone (luteolin) 7-Dirhamnoside	<i>Asplenium normale</i> fronds	Aspleniaceae	Iwashina <i>et al.</i> (1990)
7- $\alpha$ -L-Arabinofuranosyl- (1 $\rightarrow$ 6)- $\beta$ -D-glucoside	} <i>Dacrydium</i> spp.	Podocarpaceae	Markham <i>et al.</i> (1987)
7- $\alpha$ -L-Arabinopyranosyl- (1 $\rightarrow$ 6)- $\beta$ -D-glucoside			
7-Allosyl-(1 $\rightarrow$ 2)-glucoside	<i>Sideritis maura</i> aerial parts	Labiatae	Tomás-Barberán <i>et al.</i> (1988a)
7-Galacturonide-4'-glucoside	<i>Cuminum cyminum</i> seeds	Umbelliferae	El-Negoumy and Mansour (1989)
4'-Neohesperidoside	<i>Caralluma tuberculata</i>	Asclepiadaceae	Rizwani <i>et al.</i> (1990)
7-Rutinoside-3'-glucoside	<i>Campanula persicifolia</i> aerial parts	Campanulaceae	Teslov (1988)
3'-Acetylglucuronide	<i>Rosmarinus officinalis</i> leaf	Labiatae	Aeschbach <i>et al.</i> (1986)
5-(6"-Malonylglucoside)	<i>Equisetum arvense</i> barren sprouts	Equisetaceae	Veit <i>et al.</i> (1990)
7-Lactate	} <i>Marrubium vulgare</i> leaf	Labiatae	Nawwar <i>et al.</i> (1989a)
7-(2"-Glucosyllactate)			
7-(2"-Glucuronosyllactate)	} <i>Salix gilgiana</i> leaf	Salicaceae	Mizuno <i>et al.</i> (1987a)
7-(6"-Acetylglucoside)			
7-(6"-E-Cinnamylglucoside)			
7-(6"-p-Coumarylglucoside)			
7-(6"-Ferulylglucoside)	} <i>Stachys aegyptiaca</i> aerial parts	Labiatae	El-Ansari <i>et al.</i> (1991)
7-[6'''-Acetylallosyl-(1 $\rightarrow$ 2)-glucoside]			
7-(6'''-Acetylsophoroside)	<i>Veronica linariifolia</i> ssp. <i>dilatata</i>	Scrophulariaceae	Ma <i>et al.</i> (1991)
7-Neohesperidoside 6"-malonyl ester	<i>Bryum pseudotriquetrum</i>	Bryales	Stein and Zinsmeister (1990)
7-Disulfatoglucoside	<i>Phoenix dactylifera</i> fruit	Palmae	Ferreres and Tomás- Lorente (1988)
Luteolin 3'-methyl ether (chrysoeriol) 7-Xyloside	} <i>Carex nigromarginata</i> complex leaf/stem	Cyperaceae	Rettig and Giannasi (1990)
7,4'-Dixyloside			
7-Mannosyl-(1 $\rightarrow$ 2)-alloside	<i>Cassia alata</i> seeds	Leguminosae	Gupta and Singh (1991)
7-(3"-E-p-Coumarylglucoside)	<i>Phlomis lychnitis</i> aerial parts	Labiatae	Tomas <i>et al.</i> (1986)
7-(6"-Crotonylglucoside) (crotonylthermoposide)	<i>Thermopsis alternifolia</i>	Leguminosae	Yuldashev <i>et al.</i> (1989)
7-Disulfatoglucoside	<i>Phoenix dactylifera</i> fruit	Palmae	Ferreres and Tomás- Lorente (1988)
Luteolin 7-methyl ether 4'-Diglucoside	<i>Carex nigromarginata</i> complex leaf/stem	Cyperaceae	Rettig and Giannasi (1990)

Table 8.6 (Contd.)

Glycoside	Source	Family	References
Luteolin 7,4'-dimethyl ether 3'-Glucoside	<i>Gelonium multiflorum</i> leaf	Euphorbiaceae	Parveen and Khan (1987)
6-Hydroxyluteolin 7-Rhamnoside	<i>Teucrium</i> spp. aerial parts	Labiatae	Harborne <i>et al.</i> (1986b)
7-Apioside	<i>Pleurostima</i> spp. leaf	Velloziaceae	Williams <i>et al.</i> (1991)
7-Rutinoside	<i>Crocus minimus</i> leaf	Iridaceae	Harborne and Williams (1984)
6-Glucoside-3'-rhamnoside	<i>Ficus infectoria</i> leaf	Moraceae	Jain <i>et al.</i> (1990b)
7-Sophoroside	} <i>Globularia elongata</i> aerial parts	Globulariaceae	Klimek (1988)
7-(6'''- <i>p</i> -Coumarylsophoroside)			
7-(6'''-Caffeylsophoroside)			
6-Sulfate	} <i>Lippia nodiflora</i> , <i>L. canescens</i> aerial parts	Verbenaceae	Tomás-Barberán <i>et al.</i> (1987)
7-Sulfate			
6,7-Disulfate			
6-Methoxyluteolin (nepetin)	} <i>Lippia nodiflora</i> , <i>L. canescens</i> aerial parts	Verbenaceae	Tomás-Barberán <i>et al.</i> (1987)
7-Sulfate			
3',4'-Disulfate			
6-Hydroxyluteolin 3'-methyl ether (nodifloretin)	} <i>Lippia nodiflora</i> , <i>L. canescens</i> aerial parts	Verbenaceae	Tomás-Barberán <i>et al.</i> (1987)
7-Sulfate			
6,7-Disulfate			
6-Hydroxyluteolin 4'-methyl ether 7-[6'''-Acetylallosyl-(1→2)- 6"-acetylglucoside]	<i>Stachys anisochila</i> leaf	Labiatae	Lenherr and Mabry (1987)
6-Hydroxyluteolin 6,3'-dimethyl ether (jaceosidin)	} <i>Lippia nodiflora</i> , <i>L. canescens</i> aerial parts	Verbenaceae	Tomás-Barberán <i>et al.</i> (1987)
7-Sulfate			
7,4'-Disulfate			
8-Hydroxyluteolin (hypolaëtin)	<i>Libocedrus bidwillii</i> , <i>L. plumosa</i> leaf	Cupressaceae	Markham <i>et al.</i> (1990b)
7-Xyloside			
8-Gentiobioside	<i>Althaea officinalis</i> leaf	Malvaceae	Gudej (1987)
7-[6'''-Acetylallosyl-(1→2)-glucoside]	} <i>Stachys anisochila</i> leaf	Labiatae	Lenherr and Mabry (1987)
7-[6'''-Acetylallosyl-(1→2)- 6"-acetylglucoside]			
7-[6'''-Acetylallosyl-(1→2)- 3"-acetylglucoside]			
8-Hydroxyluteolin 4'-methyl ether 8-Glucuronide	<i>Malva sylvestris</i> leaf	Malvaceae	Billeter <i>et al.</i> (1991)
7-Allosyl-(1→2)-glucoside	<i>Sideritis incana</i> ssp. <i>incana</i> aerial parts	Labiatae	Manez <i>et al.</i> (1986)
8-Hydroxyluteolin 8,3'-dimethyl ether 7-Glucoside	<i>Setaria italica</i> leaf	Gramineae	Jain <i>et al.</i> (1991)
6,8-Dihydroxyluteolin 8-methyl ether 7-Apioside	<i>Pleurostima</i> spp. leaf	Velloziaceae	Williams <i>et al.</i> (1991)

(Contd.)



Table 8.6 (Contd.)

Glycoside	Source	Family	References
6,8-Dihydroxyluteolin 6,8,3'-trimethyl ether (sudachitin)	Citrus sudachi green peel	Rutaceae	Horie <i>et al.</i> (1986)
7-[6''-(3-Hydroxy-3-methylglutaryl)-glucoside] (sudachiin C)			
4'-[6''-(3-Hydroxy-3-methylglutaryl)-glucoside] (sudachiin B)			
Sudachiin D (8.5)			
5,2',3'-Trihydroxy-7,8-dimethoxyflavone 3'-Glucoside	Andrographis paniculata roots	Acanthaceae	Kuroyanagi <i>et al.</i> (1987)
5-Hydroxy-7,8,2',3'-tetramethoxyflavone 5-Glucoside	Andrographic paniculata roots	Acanthaceae	Kuroyanagi <i>et al.</i> (1987)
5,7,3',4',5'-Pentahydroxyflavone (tricitin) 3'-Xyloside	Trema humbertii leaf	Ulmaceae	Rakotovao <i>et al.</i> (1988)
7,3'-Diglucuronide	Rhizomnium magnifolium, R. pseudopunctatum	Bryales	Mues <i>et al.</i> (1986)
Tricitin 3'-methyl ether 7,5'-Diglucuronide	Rhizomnium magnifolium, R. pseudopunctatum	Bryales	Mues <i>et al.</i> (1986)
Tricitin 3',4'-dimethyl ether (apometzgerin) 7-Glucuronide	Rhizomnium magnifolium, R. pseudopunctatum	Bryales	Mues <i>et al.</i> (1986)
Tricitin 3',5'-dimethyl ether (tricin) 7-Xyloside	Carex nigromarginata complex leaf/stem	Cyperaceae	Rettig and Giannasi (1990)
8-Hydroxytricitin 7-Glucuronide	Scoparia dulcis whole plant	Scrophulariaceae	Kawasaki <i>et al.</i> (1988)
5,7,2',4',5'-Pentahydroxyflavone (isoetin) 5'-Glucoside	Artemisia hispanica aerial parts	Compositae	Marco <i>et al.</i> (1988)
7-Arabinoside	Heywoodiella oligocephala flowers	Compositae	Harborne (1991)
7-Xylosylarabinosylglucoside			
2'-Xyloside	Hypochoeris spp. leaf	Compositae	Gluchoff-Fiasson <i>et al.</i> (1991)
7-Glucoside-2'-xyloside			
2'-(4''-Acetylxyloside)			
7-Glucoside-2'-(4''-acetylxyloside)			
5,4'-Dihydroxy-7,8,2',3'-tetramethoxyflavone 5-Glucoside	Andrographis paniculata root	Acanthaceae	Kuroyanagi <i>et al.</i> (1987)

glucoside was found in *Artemisia hispanica* by Marco *et al.* (1988), and the 2'-xyloside, with three other related derivatives, was reported from the leaf of *Hypochoeris* spp. by Gluchoff-Fiasson *et al.* (1991). The UV spectrum of the 2'-xyloside ( $\lambda_{\max}$  362 nm) was at variance with that of three 2'-glycosides ( $\lambda_{\max}$  375 nm) reported earlier from a related plant *Heywoodiella oligocephala* (Harborne, 1978). Since the structure of the 2'-xyloside was securely established by NMR

analysis, it became necessary to re-examine the *Heywoodiella* glycosides, and it is now clear that these are, in fact, 7- and not 2'-glycosides (see Table 8.6). The free flavone isoetin has  $\lambda_{\max}$  at 374 nm and it is apparent that substitution of sugar at the 2'- or 5'-position causes an unexpectedly large hyperchromic shift (-12 nm) in the neutral spectrum, while substitution of sugar at the 7-position has no such effect. Thus, substitution of a sugar on a B-ring hydroxyl in isoetin produces a dis-

tortion in the planar flavone structure comparable to that recorded by Fang and Mabry (1989) for 3,2'-dioxxygen substitution in the flavonol series.

The reliability of melting points for characterizing flavone glycosides has been raised by the work of Klimek (1988) on 6-hydroxyluteolin 7-sophoroside isolated from *Globularia elongata*. This author reported a m.p. of 299–302°C, which was at variance with the value of 210–214°C for the same compound from the bryophyte *Frutellania jackii* (Mues *et al.*, 1984). The situation is not aided by the fact that the isomeric 7-gentiobioside, as reported from *Lomatogonium corinthiacum* (Schaufelberger and Hostettmann, 1984), melts in the same region at 215–218°C. Since so much spectral and other data were available to these authors for structural characterization, it seems reasonable to assume that all the structural assignments are correct and that the m.p. discrepancy is due to the presence of impurities in a sample or to crystal dimorphism.

## 8.6 NEW REPORTS OF FLAVONOL GLYCOSIDES

Some 234 new flavonol glycosides have been reported in the period 1986–91, and these are shown in Table 8.7 with plant source and reference. A checklist of the 870 known flavonol glycosides is given at the end of the chapter. New simple glycosides still appear: kaempferol 3- $\alpha$ -D-galactoside from the fern *Adiantum malesiana* (Murakami *et al.*, 1986), eupafolin 3-rhamnoside from *Brickellia vernicosa* (Compositae) (Ahmed *et al.*, 1986), and myricetin 3- $\alpha$ -arabinofuranoside from creeping Jenny, *Lysimachia nummularia* (Yasukawa *et al.*, 1990). The majority, however, are more complex, with a disaccharide or trisaccharide with a novel interglycosidic linkage. At least a third are also acylated and among the new novelties is a flavonol acylated with cinnamic acid, i.e. kaempferol 3-(6''-cinnamyl-glucoside) from *Solanum elaeagnifolium* (Chiale *et al.*, 1991).

Most flavonol glycosides have sugars attached at no more than two hydroxyl groups (usually 3-, 7- or 3,7-) of the flavonoid nucleus, so that the report of rhamnetin 3-galactoside-3',4'-bisglucoside in *Anthyllis onobrychioides* is noteworthy (Barberà *et al.*, 1986). It co-occurs in this plant with rhamnazin 3-galactoside and 3-galactoside-4'-glucoside. Another new related structure is isorhamnetin 3-rutinoside-4'-glucoside from the plant annual mercury, *Mercurialis annua* (Aquino *et al.*, 1987). It co-occurs with four known glycosides: rutin, isorhamnetin 3-rutinoside, isorhamnetin 3-rutinoside-7-glucoside and quercetin 3-(2''-glucosylrutinoside).

Rutinose (rhamnosyl-(1 $\rightarrow$ 6)-glucose), as in the glycosides of *Mercurialis*, is the most widespread of disaccharides based on glucose and rhamnose. Never-

theless, more and more isomeric forms are being discovered, especially where the order of sugars is reversed (see Table 8.2). For example, glucosyl-(1 $\rightarrow$ 2)-rhamnose occurs as quercetin 3-[glucosyl-(1 $\rightarrow$ 2)-rhamnoside]-7-rhamnoside in *Ochradenus baccatus* (Barakat *et al.*, 1991). An isomer, glucosyl-(1 $\rightarrow$ 4)-rhamnose, was reported attached to kaempferol and quercetin, and acylated with *p*-coumaric acid, in leaves of *Ginkgo biloba* by Nasr *et al.* (1986, 1987). The linkage in the *Ginkgo* glycosides has, however, been revised to the same (1 $\rightarrow$ 2) as that in the *Ochradenus* flavonoid, following NMR analysis of the glycoside peracetates (Kang *et al.*, 1990).

Structural analysis of flavonol glycosides can sometimes be based too heavily on NMR data. For example, Kalidhar (1990) revised the structure of eupalitin 3-rhamnoside from *Rudbeckia bicolor* to the 5-rhamnoside based entirely on proton NMR analysis. Location of the rhamnose at the 5- instead of the 3-position would equally have been apparent from the colour properties of the glycoside (fluorescent yellow instead of dark brown in UV light) and from the greater lability of the 5-O-glycosidic link to acid hydrolysis.

NMR analysis, however, can be invaluable in the determination of the stereochemistry of the sugars present in these glycosides. Bashir *et al.* (1991) found a kaempferol 3-[apiosyl-(1 $\rightarrow$ 2)-galactoside] in leaves of *Monnina sylvatica* (Polygalaceae), identical to a compound reported in the previous year to occur in seeds of *Chenopodium quinoa* (Chenopodiaceae) (De Simone *et al.*, 1990). By measuring nuclear Overhauser effect (NOE) differences in the NMR spectrum of the glycoside peracetate, Bashir *et al.* (1991) were able to show that the apiose occurs in these plants as the 3-C-hydroxymethyl- $\beta$ -D-erythrofuranoisomer.

A spate of acetylated flavonol glycosides have been reported recently (Table 8.7), but it is not entirely clear whether they all occur as such *in vivo*. Thus Liu *et al.* (1989b) reported the presence of the 3-rhamnoside-7-(3'''-acetylramnoside), the 3-rhamnoside-7-(4'''-acetylramnoside) and the 3-rhamnoside-7-(3'''',4'''-diacetylramnoside) of patuletin in *Kalanchoe gracilis*. Are the first two compounds possibly breakdown products of the third during the isolation procedure? Likewise, the plant is reported to contain the 3-(4''-acetylramnoside)-7-(3''',4'''-diacetylramnoside) and the 3-(4''-acetylramnoside)-7-(2''',4'''-diacetylramnoside) of patuletin. But did migration of the acetyl from the 3- to the 2-OH of rhamnose occur during isolation, or vice versa? Nakatani *et al.* (1991) characterized the 3-(3'',4''-diacetylramnoside) and the 3-(2'',4''-diacetylramnoside) of kaempferol from rhizomes of *Zingiber zerumbet*, but they do comment that the 3'',4''-diacetate could have been formed from the 2'',4''-diacetate during plant extraction. Clearly, more needs to be known about the stabilities of the different



Table 8.7 New flavonol glycosides

Glycoside	Source	Family	References
5,7,8-Trihydroxy-3-methoxyflavone 8-(Z-2-Methyl-2-butenate) 8-(2-Methylbutyrate)	<i>Gnaphalium robustum</i> leaf and stem resinous exudate	Compositae	Arzua and Cuadra (1990)
3,5,7,4'-Tetrahydroxyflavone (kaempferol)			
3- $\alpha$ -D-Galactoside	<i>Adiantum malesianum</i>	Filicales	Murakami <i>et al.</i> (1986)
3-Apiosyl-(1 $\rightarrow$ 2)-galactoside	<i>Monnina sylvatica</i> leaf	Polygalaceae	Bashir <i>et al.</i> (1991)
3-Xylosyl-(1 $\rightarrow$ 2)-rhamnoside	<i>Moghania faginea</i> leaf	Leguminosae	Soicke <i>et al.</i> (1990)
3-Robinoside	<i>Strychnos variabilis</i> leaf	Loganiaceae	Brasseur and Angenot (1986)
7-Galactosyl-(1 $\rightarrow$ 4)-rhamnoside	<i>Cassia biflora</i> leaf	Leguminosae	Ahmad <i>et al.</i> (1991a)
3-Rhamnoside-7-xyloside	<i>Chenopodium ambrosioides</i> fruits	Chenopodiaceae	Jain <i>et al.</i> (1990a)
3- $\alpha$ -D-Glucoside-7- $\alpha$ -L-rhamnoside	<i>Erythroxylon cuneifolium</i> aerial parts	Erythroxylaceae	Iñigo <i>et al.</i> (1988)
3-Rhamnoside-7-galacturonide	<i>Silybum marianum</i> flowers	Compositae	Ahmed <i>et al.</i> (1989)
3-Glucoside-7-glucuronide	<i>Tulipa gesneriana</i> cv. 'Paradae' perianths	Liliaceae	Budzianowski (1991)
3-Rhamnoside-4'-xyloside	<i>Chenopodium ambrosioides</i> fruits	Chenopodiaceae	Jain <i>et al.</i> (1990a)
3-Galactoside-4'-glucoside	<i>Bryum pseudotriquetrum</i>	Bryales	Stein and Zinsmeister (1990)
3-Rhamnosyl-(1 $\rightarrow$ 3)-rhamnosyl- (1 $\rightarrow$ 6)-galactoside (rhamninoside)	<i>Rhamnus leptophylla</i> fruits	Rhamnaceae	Wang <i>et al.</i> (1988a)
3-Rhamnosyl-(1 $\rightarrow$ 4)-rhamnosyl- (1 $\rightarrow$ 6)-galactoside (isorhamninoside)	<i>Actinidia</i> spp. leaf	Actinidiaceae	Webby and Markham (1990)
3-Rhamnosyl-(1 $\rightarrow$ 4)-rhamnosyl- (1 $\rightarrow$ 6)-glucoside			
3-Xylosylrutinoside	<i>Hosta ventricosa</i>	Liliaceae	Budzianowski (1990a)
3-Glucosyl-(1 $\rightarrow$ 3)-rhamnosyl- (1 $\rightarrow$ 6)-galactoside	<i>Camellia sinensis</i> tea	Theaceae	Finger <i>et al.</i> (1991a)
3-(3 <sup>R</sup> -Glucosylrutinoside)	<i>Camellia sinensis</i> tea	Theaceae	Finger <i>et al.</i> (1991b)
3-Apiosyl-(1 $\rightarrow$ 2)-[rhamnosyl- (1 $\rightarrow$ 6)-galactoside]	<i>Chenopodium quinoa</i> seeds	Chenopodiaceae	De Simone <i>et al.</i> (1990)
	<i>Monnina sylvatica</i> leaf	Polygalaceae	Bashir <i>et al.</i> (1991)
3-Glucosyl-(1 $\rightarrow$ 2)-[rhamnosyl- (1 $\rightarrow$ 6)-galactoside]	<i>Monnina sylvatica</i> leaf	Polygalaceae	Bashir <i>et al.</i> (1991)
3-Rhamnosyl-(1 $\rightarrow$ 2)-[rhamnosyl- (1 $\rightarrow$ 6)-galactoside] (mauritanin)	<i>Lysimachia mauritiana</i> whole plant	Primulaceae	Yasukawa and Takido (1987)
3-Galactosyl-(1 $\rightarrow$ 2)-[rhamnosyl- (1 $\rightarrow$ 6)-glucoside]	<i>Camellia sinensis</i> seeds	Theaceae	Sekine <i>et al.</i> (1991)
3-Xylosyl-(1 $\rightarrow$ 2)-rhamnosyl- (1 $\rightarrow$ 6)-glucoside]			
3-Rhamnosyl-(1 $\rightarrow$ 6)-[glucosyl- (1 $\rightarrow$ 2)-glucoside]	<i>Hosta ventricosa</i>	Liliaceae	Budzianowski (1990a)
3-Rhamnosyl-(1 $\rightarrow$ 4)-rhamnoside- 7-rhamnoside	<i>Cassinopsis madagascariensis</i> leaf	Icacinaceae	Rasoanaivo <i>et al.</i> (1990)
3-Xylosyl-(1 $\rightarrow$ 2)-rhamnoside- 7-rhamnoside (sagittatin A)	<i>Epimedium sagittatum</i> aerial parts	Berberidaceae	Oshima <i>et al.</i> (1989)
3-Rhamnosyl-(1 $\rightarrow$ 2)-galactoside- 7-rhamnoside	<i>Vicia faba</i> leaves	Leguminosae	Tomás-Lorente <i>et al.</i> (1989)