

On the occurrence of flavonol and flavone glycosides in vegetables

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Über das Vorkommen von Flavonol- und Flavon-Glykosiden in Gemüse

Zusammenfassung. Flavonol- und Flavon-glykoside kommen in allen Gemüsearten vor, hauptsächlich als Quercetin- oder Kämpferol- und weniger häufig als Luteolin- oder Apigenin-glykoside. Da ihre Bildung lichtabhängig ist, sind sie im äußeren Gewebe angereichert. Die Konzentration ist in freistehenden Blättern mit Ausnahme der Küchenzwiebel erheblich höher als in anderen Teilen der gleichen Pflanze.

Summary. Flavonol and flavone glycosides occur in common vegetables, mainly as the quercetin or kaempferol glycosides and less frequently as the luteolin or apigenin glycosides. Their formation normally depends on light, so they are mainly concentrated in the outer tissues. Their concentration in free-standing leaves is considerably greater than that in any other part of the same plant, with the exception of the onion.

Introduction

Flavonoids [1, 2] which have the common skeleton of diphenylpropanes ($C_6C_3C_6$), occur in a wide range of plants. Apart from flavanols (catechins, proanthocyanidins), they consist mainly of the glycosides of anthocyanidins, flavones, flavonols and flavanones. Other classes of flavonoids are known, e.g. the isoflavonoids in some *Leguminosae*.

Flavonols and flavones occur in an almost bewildering array of derivatives with extra hydroxylation and/or methylation. Flavonol and flavone glycosides have been found in practically all types of plants, whereas flavonols are more frequently found in vegetables than flavones.

Chemical structure and general occurrence

Flavonols can be regarded as 3-hydroxyflavones and flavones, conversely, as 3-deoxy-flavonols. Individ-

ual differences arise in the number and distribution of the hydroxyl groups as well as the nature and extent of alkylation and/or glycosylation of these groups. In common with other flavonoids, the flavones and flavonols most frequently found in plants are those with B-ring hydroxylation in the 3'- and 4'-positions, followed by those with a hydroxyl group in the 4'-position only. Quercetin and kaempferol are typical flavonols of this type.

The preferred bonding site of the sugar radical to the flavonols is the 3 position, less frequently the 7-position, and only in rare cases the 4'-, 3'-, or 5'-positions. In the case of diglycosides, 3-O-biosides and 3,7-bis-O-glycosides occur most frequently. Flavones occur mainly as 7-O-glycosides, while other glycosides occur only rarely. D-Glucose is the most frequent sugar residue, although D-galactose, L-rhamnose, L-arabinose, D-xylose, D-apiose are also found, as well as D-glucuronic acid. In general, the sugars of the D-series occur as the β -glycoside, while those of the L-series have the alpha configuration.

Acylation occurs with hydroxycinnamic and hydroxybenzoic acids, as well as with benzoic, malonic, acetic and other acids. In these cases the acids are esterified with the sugars and are not attached to phenolic hydroxyl groups.

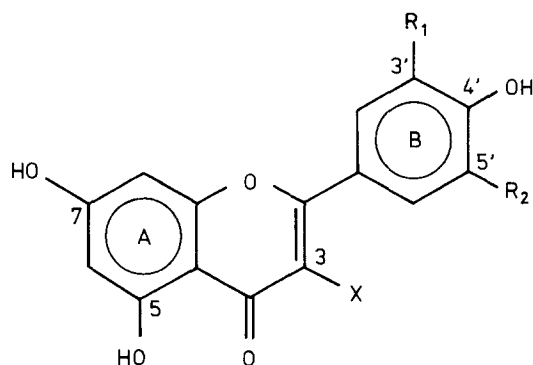


Fig. 1. Flavonols X OH. Kaempferol: R_1 H, R_2 H; Quercetin: R_1 OH, R_2 H; Myricetin: R_1 OH, R_2 OH; Isorhamnetin: R_1 OCH₃, R_2 H. Flavones X H. Apigenin: R_1 H, R_2 H; Luteolin: R_1 OH, R_2 H; Chrysoeriol: R_1 OCH₃, R_2 H

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C-Glycosyl flavones, which carry a sugar residue attached directly to an aromatic carbon atom, are also known and are often accompanied by either flavanol or flavone glycosides.

The formation of flavone and flavanol glycosides normally depends on light [3–5]. In general, the highest concentrations of these compounds occur in the leaves, while only trace amounts are found in those parts of the plant below the soil surface. The common onion is, however, a well-known exception. In general, the influence of light is the predominant factor in determining the flavanol level, with enriched levels being found in the epidermis [6–9].

Growing plants in glasshouses also reduces the flavanol content, particularly in the outer leaves of kale, brussels sprouts, lettuce, kohlrabi and small radishes [10, 11], as well as in beans [12].

Quercetin glycosides predominate in vegetables or in the leaves of various vegetables. Frequently the glycosides of kaempferol, luteolin and apigenin are also present. In contrast, spinach shows another pattern (see Table 1) and only ripe tomatoes contain the flavanone naringenin [13]. The occurrence of flavanol and flavone glycosides in vegetables is shown in Table 1. The concentrations of flavanol and flavone glycosides, as with all plant secondary metabolites, vary within certain limits and are dependent on a number of factors, such as growing conditions and the variety and degree of ripeness.

Table 1. Flavanol and flavone glycosides of common vegetables^a

<i>Cichoriaceae</i>	
Lettuce (<i>Lactuca sativa</i> L. var. <i>capitata</i>), leaves:	
Quercetin 3-O- β -D-glucuronide	[14]
Quercetin 3-O- β -D-glucoside	[14]
Quercetin 3-O-(malonyl)- β -D-glucoside	[14]
Luteolin 7-O- β -D-glucuronide	[14]
Endive (<i>Cichorium endivia</i> L. var. <i>crispum</i>), leaves:	
Kaempferol 3-O- β -D-glucuronide	[14]
Kaempferol 3-O- β -D-glucoside	[14]
Kaempferol 3-O-(malonyl)- β -D-glucoside(?)	[14]
In the epigeal part of common chicory (<i>Cichorium intybus</i> L.) quercetin 3-O- β -D-galactoside, quercetin 3-O-rhamnoside, apigenin 7-O-arabinoside and luteolin 7-O- β -D-glucoside have been found	[15]
<i>Chenopodiaceae</i>	
Spinach (<i>Spinacia oleracea</i> L.), leaves:	
Patuletin 3-O-glucoside	[16, 17]
Patuletin 3-O- β -gentiobioside	[18]
Patuletin 3-O- β -D-glucopyranosyl-(1 \rightarrow 6)-[β -D- apiofuranosyl-(1 \rightarrow 2)]- β -D-glucopyranoside	[18]
Patuletin 7-O-glucoside (?) called patulitrin	[19]
Spinacetin 3-O-glucoside	[16, 17]
Spinacetin 3-O- β -gentiobioside	[18]
Spinatoid (3,6-dimethoxy-5,7,3',4'-tetrahydroxyflavone- 4'-O- β -D-glucopyranoside)	[18]
5,7,4'-Trihydroxy-3,6,3'-trimethoxyflavone-4'-O-glucuronide	[20]
5,3',4'-Trihydroxy-3-methoxy-6:7-methylenedioxy- flavone-4'-O-glucuronide	[20]
5,4'-Dihydroxy-3,3'-dimethoxy-6:7-methylenedioxy- flavone-4'-O-glucuronide	[20]
Patuletin = 3,5,7,3',4'-pentahydroxy-6-methoxyflavone Spinacetin = 3,5,7,4'-tetrahydroxy-6,3'-dimethoxyflavone	
Beetroot (<i>Beta vulgaris</i> L. var. <i>conditiva</i> Alef.), leaves: Kaempferol and quercetin glycosides	[21]

Table (continued)

<i>Apiaceae</i>	
Carrot (<i>Daucus carota</i> L. ssp. <i>sativus</i>), leaves:	
Luteolin 7-O- β -D-glucoside	[22–24]
Luteolin 4'-O- β -D-glucoside	[24]
Luteolin 7-O-rutinoside	[24]
Luteolin 7-O- β -D-glucuronide	[24]
Apigenin 7-O- β -D-glucoside	[23, 24]
Apigenin 7-O-rutinoside	[24]
Chrysoeriol 7-O- β -D-glucoside	[24]
Carrot roots contain only traces of luteolin and apigenin glycosides	[25]
Celery (<i>Apium graveolens</i> L. var. <i>rapaceum</i>), leaves:	
Apigenin 7-O-apiosyl- β -D-glucoside (<i>apiin</i>)	[26]
Apigenin 7-O- β -D-glucoside	[26]
Luteolin 7-O-apiosyl- β -D-glucoside	[26]
Luteolin 7-O- β -D-glucoside	[26]
Chrysoeriol 7-O-apiosyl- β -D-glucoside	[26, 27]
Chrysoeriol 7-O- β -D-glucoside (?)	[26]
Celery, tubers:	
Apigenin 7-O-apiosyl- β -D-glucoside (<i>apiin</i>)	[26]
Luteolin 7-O-apiosyl- β -D-glucoside and probably apigenin and luteolin 7-O-glucosides	[26]
Fennel (<i>Foeniculum vulgare</i> Mill. var. <i>azoricum</i>): Quercetin 3-O- β -D-glucuronide and traces of other glycosides of quercetin, kaempferol and probably isorhamnetin	[28]
Parsnip (<i>Pastinaca sativa</i> L. var. <i>sativa</i>), leaves:	
Quercetin 3-O-glucoside	[22, 29]
Quercetin 3-O-rutinoside	[29]
Isorhamnetin 3-O-glucoside	[29]
Isorhamnetin 3-O-glucoside-7-O-rhamnoside	[29]
<i>Solanaceae</i>	
Tomato (<i>Lycopersicon lycopersicum</i> (L.) Karst ex Farw.), fruit:	
Quercetin 3-O-rutinoside	[9, 30]
Quercetin 3-O- β -D-glucoside	[30]
Kaempferol 3-O-rutinoside	[30]
and probably other quercetin and kaempferol glycosides	[31]
Leaves contain high concentration of the same flavanol glycosides	
Sweet pepper (<i>Capsicum annum</i> L.), leaves:	
Luteolin 7-O-glucoside	[32]
Luteolin 7-O-apiosylglucoside	[32]
Luteolin 7-O-digluconide	[32]
Luteolin and quercetin glycosides have been found in the fruits of sweet pepper [9] and luteolin 7-O-glucoside and apigenin 7-O- apiosylglucoside in the fruits and leaves of <i>Capsicum annum</i>	[33]
<i>Fabaceae</i>	
Bean (<i>Phaseolus vulgaris</i> ssp. <i>vulgaris</i> var. <i>nanus</i> (L.) Aschers), leaves:	
Quercetin 3-O- β -D-glucuronide	[34–36]
Quercetin 3-O-rutinoside	[35–36]
Quercetin 3-O-xylosylglucoside	[36]
Kaempferol 3-O- β -D-glucuronide	[35, 36]
Kaempferol 3-O-rutinoside	[35, 36]
Pea (<i>Pisum sativum</i> L. ssp. <i>sativum</i>), leaves:	
Quercetin 3-O-tri- β -D-glucoside and its p-coumaric acid ester	[37–39]
Kaempferol 3-O-tri- β -D-glucoside and its p-coumaric acid ester	[37–39]
Quercetin 3-O-glucoside (traces), 2 quercetin 3,7-O-bis-glycosides, ferulates of kaempferol and quercetin 3-O-trigluconides and caffeate of quercetin 3-O-trigluconide are named in a two- dimensional paper chromatogram	[38]
Broad bean (<i>Vicia faba</i> L.), leaves:	
Kaempferol 3-O- β -D-glucoside-7-O-rhamnoside	[40, 41]
Kaempferol 3-O-galactoside-7-O-rhamnoside	[42]
Kaempferol 3,7-O-bis- β -D-glucoside	[41]
Quercetin 3-O- β -D-glucoside-7-O-rhamnoside	[41]
Quercetin 3-O-rutinoside	[41]
Seeds: glycosides of kaempferol, quercetin and myricetin	[43]
Chickpea (<i>Cicer arietinum</i> L.), arial parts:	
Kaempferol 3-O- β -D-glucoside	[44]
Kaempferol 3-O- β -D-glucosylapioside and glycosides of kaempferol, quercetin and isorhamnetin as minor constituents	[44]
In soya-bean leaves (<i>Glycine max</i> L.) the products of the controlled hydrolysis and oxidation of the flavanol 3-O-glycosides were studied. The kaempferol and quercetin glycosides were identified as the glucoside, sophoroside, gentiobioside, rutinoside, neohesperidoside, 2G-glucosylrutinoside, 2G-glucosylgentiobioside, 2G-rhamnosylrutinoside and 2G-rhamnosylgentiobioside	[45, 46]

Brassicaceae

Horseradish (<i>Armoracia rusticana</i> Gaertn.), leaves:	
Quercetin 3-O-(2-O- β -D-xylopyranosyl)- β -D-galactopyranoside	[47]
Kaempferol 3-O-(2-O- β -D-xylopyranosyl)- β -D-galactopyranoside	[47]
Broccoli (<i>Brassica oleracea</i> L. var. <i>italica</i> Plenck.), leaves:	
3-O-Sophoroside-7-O-glucosides of quercetin, kaempferol and isorhamnetin	[48]
Chinese cabbage (<i>Brassica chinensis</i> L.), leaves:	
3-O-Monoglycosides and 3-O-diglycosides of quercetin and isorhamnetin	[48]
Vegetables of the other <i>Brassica oleracea</i> subspecies contain also glycosides of kaempferol and quercetin	[10]
Radish, small (<i>Raphanus sativus</i> L. var. <i>sativus</i>), tuber:	
Kaempferol and quercetin glycosides	[25]

Allium species

Onion (<i>Allium cepa</i> L.), bulb:	
Quercetin-4'-O- β -D-glucoside (<i>spiraeoside</i>)	[7, 35, 49–52]
Quercetin 3,4'-O-bis- β -D-glucoside	[35, 50–52]
Quercetin 7,4'-O-bis- β -D-glucoside	[35, 50, 52]
Quercetin 3-O- β -D-glucoside	[50–52]
Kaempferol 3-O-glucoside	[51, 52]
Kaempferol 4'-O-glucoside	[51, 52]
Isorhamnetin 4'-O-glucoside	[51]
Quercetin 7-glucoside, quercetin 3,7-bis-glucoside and kaempferol 7,4'-bis-glucoside were named in a two-dimensional thin-layer chromatogram after polyamide column purification	[52]
Onion green leaves see p. 4	
Shallot (<i>Allium ascalonicum</i> Strand), bulb:	
Quercetin 4'-O- β -D-glucoside (<i>spiraeoside</i>)	[49, 53]
Quercetin 3,4'-O-bis-glucoside	[53]
Quercetin 7,4'-O-bis-glucoside	[53]
Leek (<i>Allium porrum</i> L.), leaves and bulb:	
Kaempferol 3-O- β -D-glucoside	[54]
Kaempferol 3-O-xylosyl- β -D-glucoside	[54]
Quercetin 3-O-glucoside (traces)	[54]
See also [8]	
Chive (<i>Allium schoenoprasum</i> L.), leaves:	
Kaempferol di- and triglycosides predominate. 3-O- β -D-glucosides of kaempferol, quercetin and isorhamnetin are minor glycosides	[54]

Other vegetables

Asparagus (<i>Asparagus officinalis</i> L. var. <i>officinalis</i>), Liliaceae, spears and leaves:	
Quercetin-3-O-rutinoside	[55, 56]
Quercetin and kaempferol glycosides are minor glycosides	[56]
Rhubarb (<i>Rheum raphaniticum</i> L.), Polygonaceae, petioles:	
Quercetin 3-O-glucoside	[57]
Quercetin 3-O-rhamnoside	[57]
Quercetin 3-O-rutinoside	[57]
+ another quercetin glucoside	[57]
Cornsalad (<i>Valerianella locusta</i> (L.) Lotenn.), Valerianaceae, leaves:	
Luteolin 7-O-rutinoside	
Luteolin 7-O- β -D-glucoside-4-O-arabinoside (?)	[41]
Quercetin 3-O-rutinoside, traces	[41]
Diosmetin glycoside	[58]
Artichoke (<i>Cynara scolymus</i> L.), Asteraceae, leaves:	
Luteolin 7-O- β -D-glucoside	[59–61]
Luteolin 4'-O- β -D-glucoside	[61]
Luteolin 7-O-rutinoside	[59, 61]
Luteolin 7-O-rutinoside-4'-O- β -D-glucoside	[59]
Luteolin 7-O-diglycoside	[60]

^a The underlined compound is the main glycoside of the vegetable in question

In a considerable number of vegetables, only fairly low concentrations of flavonol and flavone glycosides have been detected. We found concentrations of approximately 1 mg/kg fresh weight and lower amounts in carrot, radish, rutabaga, scorzonera, garlic, leek bulb, beet, white asparagus (without tips or with white tips), cabbage without the outer leaves (white, red,

Savoy cabbage), peeled kohlrabi, cauliflower (edible parts), chicory, pea, cucumber, eggplant and potato [10, 25, 43, 54, 56, 62; K. Herrmann u. W. Eloesser, unpublished data]. On the other hand, the leaves of root vegetables, such as potatoes and asparagus, frequently contained concentrations in excess of 1000 mg/kg.

Leaf vegetables

Flavonols are nearly always found in free-standing leaves. The concentration in the leaves is in general much higher than in other tissues of the same plant.

Where heads are formed from leaves, such as in lettuce [11, 62], endive [11] and in *Brassica* species (white, red and Savoy cabbage) [10] there is a significant decrease in the flavonol concentration from the outer to the inner leaves. Investigations of several varieties of lettuce and endives have shown that, probably due to sunlight, the outer (mainly green) leaves contain a much higher level of flavonols than the inner (mainly yellow) ones. In the case of lettuce and endives, these levels appear to vary with the chlorophyll content, as indicated by the green colour. The green outer leaves of the leek showed ten times more kaempferol and quercetin glycosides than in the edible white parts [54, 62].

Legumes

Investigations on peas and broad beans [43] have shown that the flavonol content is higher in leaves, lower in pods and extremely low in unripe seeds and is located almost exclusively in the skins. On abrasion of frozen pea leaves, large concentrations of flavonol glycosides are found in the upper and lower epidermis [6].

Legume plants, e.g., soya beans [1] and chickpeas [1, 63], contain a number of isoflavonoids. Further, several antifungal isoflavonoids have been found after fungal infection. These isoflavonoid phytoalexins are believed to play a primary role in stopping fungal growth in vivo. Especially in beans (*Phaseolus vulgaris*), a wide range of isoflavonoid phytoalexins are produced, e.g., phaseollin, phaseollidin, phaseolliniso-flavan, licoisoflavone A, kievitone and coumestrol [64], phaseoluteone and several other 5-hydroxyisoflavonoids [65].

Allium species

Unlike other vegetables and in contrast to white-skinned varieties, the flavonol content of onions with coloured skins is exceptional. The outer dry skins contain 2.5% and more of quercetin [49, 66, 67], which appears mainly in the free form, i. e. as the aglycone (67%–86% of total quercetin in ten samples) and only to a lesser extent as spiraeoside (quercetin-4'-O-

glucoside). The epidermis of onion scales exclusively contains quercetin glucosides, mainly spiraeoside. This is formed first, while the formation of diglucosides follows during storage and increases continuously. There appear to be no flavonols in the mesophyll.

The flavonol concentration decreases from the outer to the inner scales, with higher levels in the outer than in the inner epidermis [7, 51] and an accumulation in the cell vacuole [68].

In the green leaves, the flavonol biosynthesis is known to be light dependent. Glucosides of both kaempferol and quercetin are formed, but no spiraeoside or diglucosides, found in the scales, are present. There is also no evidence for the presence of spiraeoside in leek and chive. Moreover, flavonols tend to accumulate when drying onion leaves as a consequence of the formation of free quercetin and spiraeoside. Free kaempferol does not appear to be formed under such conditions [7].

Onions with white skins (variety „Weisse Frühlingszwiebel“) showed only traces of flavonols, e.g., 10 mg/kg total quercetin in dry skins.

Green leaves of leek and chive contain mainly kaempferol glycosides, with mono- and di-glycosides dominating in leek and di- and tri-glycosides in chive. In the leek, glucose is the dominant sugar component; in chive, glucose and galactose were found. In both leek and chive, the green leaves contain much higher flavonol levels than the white leaf portions [54]. In the leek, the flavonols are strictly localized in the epidermis [8]. Garlic (*Allium sativum*) and leek bulbs contain only a few mg/kg of kaempferol and quercetin glycosides [54].

Potatoes

Reznik and Wietschel [69–71] studied the leaf flavonoid patterns of 107 tuber-bearing *Solanum* species, using column and thin-layer chromatography. Thirty-eight different flavonol glycosides, mainly of kaempferol and quercetin, and luteolin-7-glucoside, were fully or partly characterized by means of UV-spectroscopy and different hydrolysis methods.

Quercetin 3-O-glycosides predominate, accompanied by kaempferol and in some instances isorhamnetin and myricetin glycosides. Glucose and rhamnose are the most commonly occurring sugars; arabinose, galactose and xylose occur more rarely [72].

Quercetin and kaempferol 3-O-glycosides and 3-O-rutinosides are widespread. Quercetin 3-O-rutinoside, first identified in 1924 by Charaux [73], often occurs in the highest concentration. More complex triglycosides are also common. One of the most interesting of these triglycosides is quercetin 3-O-(2G-glu-

cosylrutinoside), which occurs in the flowers of 37% of wild *Solanum* species and 41% of cultivated taxa [74].

When potatoes were exposed to light for 1 month, such that they were coloured green by chlorophyll, the flavonol glycoside level in the outer tissue rose from below 1 mg/kg to approximately 50 mg/kg, with the major quantities being located in the skin [K. Herrmann u. W. Eloesser, unpublished data].

Remarks on the isolation and identification of flavonol and flavone glycosides

In the past, the isolation of flavonoid glycosides was carried out by column chromatographic and paper chromatographic methods [2, 75, 76]. The disadvantages of these methods are: the loss of time, an often inadequate separation and, therefore insufficient purity of the isolated glycoside. In contrast, preparative high-performance liquid chromatography (HPLC) is a time-saving and more efficient method and is also suitable for the isolation of sensitive substances. The preparative column efficiency is comparable with that of an analytical column filled with the same stationary phase. Hence, each analytical separation can be performed on a preparative scale and only the flow rate has to be altered.

A suitable method (after the necessary polyamide separation) was presented by Siewek et al. [77]. In analyses of phenolics, the polyamide must be free from any traces of iron.

In the past, the identification was performed after isolation in methanol by means of UV spectra and after the addition of shift reagents [78]. Acid and enzymatic hydrolyses were also performed [75].

The benzylation of sugars and liquid chromatographic separations are now very suitable methods for the identification and quantification of flavonol and flavone glycosides [77, 79]. After benzylation, HPLC and a diode-array detector allow reliable determination of the degree of glycosidation [80].

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