# STRUCTURES OF FLAVONE AND FLAVONOL GLYCOSIDES

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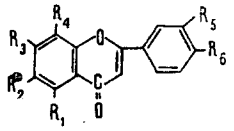
Flavonoid glycosides form a very large group of phenolic glycosides [1]. At the present time, flavone and flavonol glycosides have been studied most thoroughly. We have separated the known O-glycosides of flavones and flavonols into three groups: monoglycosidated and diglycosidated compounds and acylated glycosides.

The monoglycosidated flavones may contain two or three free hydroxy groups and one or two methoxy groups (as a rule, polymethoxylated flavones are not glycosidated). In Table 1, we have given the structures of several known natural monoglycosidated flavones. In these glycosides, the most widely distributed carbohydrate component is D-glucose, and then glucuronic acid. Glycosides containing D-galactose and L-rhamnose are found considerably more rarely. Pentoses (xylose and arabinose) are present only in biosides, and in this case arabinose is never attached directly to the aglycone. An exception is the glycoside salicaprin, in which arabogalactose is attached to chrysoeriol through the arabinose (see Table 1) [68]. The biosides most frequently contain rutinose [O-L-rhamnopyranosyl-(1→6) -β-D-glucopyranose] [2] and neohesperidose [O-α-D-rhamnopyranosyl-(1→2)-D-glucopyranose] [3, 6]. Biosides containing apioglucose [9, 32, 69], primeverose [1], sambubiose [1], and laminaribiose [42] are found. Glycosides containing triose and tetrose residues may also be found in plants [1].

Table 1 shows glycosides of very diverse aglycones: chrysin, baicalein, wogonin, apigenin, acacetin, genkwanin, scutellarein, hispidulin, dinatin, luteolin, diosmetin, chrysoeriol, tricin and others. The carbohydrate residue is most frequently attached to these aglycones in the $C_7$ position, and more rarely at $C_{4'}$ and $C_5$. If the glycoside contains a biose, it is predominantly present on the seventh carbon atom (rhoifolin, apiin, fortunellin, sorbifolin, diosmin, ornanthoside, palustroside, etc.). It is known that in dracocephaloside the sugar residue is in the $C_{3'}$ position [56], and in tetuim it is at $C_6$ [31].

The existence of C-glycosides is characteristic for luteolin, apigenin, chrysoeriol, and diosmetin. We shall not consider their structure in this communication.

TABLE 1. Structures of Monoglycosidated Flavones



$R_2=R_4=R_5=H$ $R_3=OH$ $R_1=$ D-Glucose–toringin [31],
$R_2=R_4=R_5=H$ $R_1=OH$ $R_3=$ D-Glucose–aequinoctin [32],
$R_2=R_4=R_5=R_6=H$ $R_1=OH$ $R_3=$ Glucuronic acid [32],
$R_4=R_5=R_6=H$; $R_1=R_2=OH$ $R_3=$ Glucuronic acid–baicalin [31],
$R_4=R_5=R_6=H$; $R_1=R_2=OH$ $R_3=$ Glucoside–oroxin A [35],
$R_4=R_5=R_6=H$; $R_1=R_2=OH$ $R_3=O$-Diglucoside–oroxin B [35],
$R_4=R_5=R_6=H$; $R_2=OH$; $R_3=OCH_3$ $R_1=O$-Glucuronoside–palustroside [37],
$R_4=R_5=R_6=H$; $R_1=R_3=OH$; $R_2=O-$Glucoside–tetuim [31,34],
$R_2=R_5=R_6=H$; $R_1=R_4=OH$; $R_3=O-$Glucuronide [44],
$R_2=R_4=R_5=H$; $R_3=R_6=OH$; $R_1=O-$Glucoside [31],
$R_2=R_4=R_5=H$; $R_1=R_3=OH$; $R_6=O-$Glucoside [33,38],
$R_2=R_4=R_5=H$; $R_1=R_6=OH$; $R_3=O-\beta$-Galactopyranoside–thalictiin [39].

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TABLE 1 continued

$R_2$=$R_4$=$R_5$=H; $R_1$=$R_6$=OH; $R_3$=O—β-D-Glucopyranoside—cosmosiin [32,33],
$R_2$=$R_4$=$R_5$=H; $R_3$=$R_6$=OH; $R_1$=Rhamnoglucoside—cephalotaxoside [36],
$R_2$=$R_4$=$R_5$=H; $R_1$=$R_6$=OH, $R_3$=O-β-Neohesperidoside—rhoifolin [40],
$R_2$=$R_4$=$R_5$=H; $R_1$=$R_6$=OH, $R_3$=O-Sambubioside [42],
$R_2$=$R_4$=$R_5$=H; $R_1$=$R_6$=OH, $R_3$=O-Apioglucoside—apiin [32],
$R_2$=$R_4$=$R_5$=H; $R_1$=$R_6$=OH; $R_3$=O-Diglucoside [43],
$R_2$=$R_4$=$R_5$=H; $R_1$=$R_3$=OH; $R_6$ = O-Rhamnoglucoside [44],
$R_2$=$R_4$=$R_5$=H; $R_1$=$R_6$=OH, $R_3$=O-Glucuronoside [32],
$R_2$=$R_4$=$R_5$=H; $R_1$=$R_6$=OH, $R_3$= O-Glucuronoxyloside—apigenin 7-glucuronoxyloside [45],
$R_2$=$R_4$=$R_5$=H; $R_1$=OH; $R_6$=$OCH_3$ $R_3$=O-β-D-Glucoside—tilianin [166],
$R_2$=$R_4$=$R_5$=H; $R_1$=OH; $R_6$=$OCH_3$; $R_3$=O-Glucurono-(1→2)-glucuronide—apigenin 7-glucuronoglucuronide [47],
$R_2$=$R_4$=$R_5$=H; $R_1$=OH; $R_6$=$OCH_3$; $R_3$= O-Rutinoside—linarin (acaciin) [46],
$R_2$=$R_4$=$R_5$=H; $R_1$=OH, $R_6$=$OCH_3$, $R_3$=O-Rhamnoglucoside—fortunellin [32],
$R_2$=$R_4$=$R_5$=H; $R_1$=OH; $R_6$=$OCH_3$ $R_3$= O-Diglucoside—acacetin 7-diglucoside [47],
$R_2$=$R_4$=$R_5$=H; $R_1$=OH; $R_6$=$OCH_3$; $R_3$= O-Xylosylrhamnosylglucoside [31],
$R_2$=$R_4$=$R_5$=H; $R_6$=OH; $R_3$=$OCH_3$ $R_1$=O-Glucoside—glucogenkwanin [32],
$R_2$=$R_4$=$R_5$=H; $R_1$=OH; $R_3$=$OCH_3$ $R_6$=O-Glucoside—genkwanin 4-glucoside [48],
$R_2$=$R_4$=$R_5$=H; $R_1$=OH; $R_3$=$OCH_3$ $R_6$=β-D-Glucopyranoside—phegopolin [38],
$R_4$=$R_5$=H; $R_1$=$R_2$=$R_6$=OH; $R_3$=7-O-Glucuronoside—scutellarin [49],
$R_4$=$R_5$=H; $R_1$=$R_2$=$R_6$=OH; $R_3$= 7-O-Glucoside—plantaginin [50],
$R_4$=$R_5$=H; $R_1$=$R_2$=$R_6$=OH, $R_3$=O-Rhamnoside—sorbarioside [51],
$R_4$=$R_5$=H; $R_1$=$R_2$=$R_6$=OH; $R_3$=O-α-L-Rhamnofuranosyl-(4→1)-xylopyranoside—sorbifolin [52],
$R_4$=$R_5$=H; $R_1$=$R_6$=OH; $R_2$=$OCH_3$ $R_3$=O-Glucoside—homoplantagnin [53],
$R_4$=$R_5$=H; $R_1$=OH; $R_2$=$R_6$=$OCH_3$ $R_3$=O-Rutinoside—pectolinarin [9,32],
$R_4$=$R_5$=H; $R_1$=$R_2$=OH, $R_6$=$OCH_3$ $R_3$=O-Glucoside—dinatin 7-glucoside [54],
$R_4$=$R_5$=H; $R_1$=$R_2$=OH, $R_6$=$OCH_3$ $R_3$=O-Glucobioside—dinatin 7-glucobioside [54],
$R_4$=$R_5$=H; $R_1$=$R_2$=OH; $R_6$=$OCH_3$ $R_3$=O-Glucuronoside—dinatin 7-glucuronide [54],
$R_4$=$R_5$=H; $R_1$=$R_6$=OH, $R_2$=$OCH_3$, $R_3$=O-Glucobioside—hispidulin 7-glucobioside [54],
$R_4$=$R_5$=H; $R_1$=OH, $R_2$=$R_3$=$OCH_3$, $R_6$=O-Glucoside—cirsimarin [55],
$R_2$=$R_4$=H; $R_3$=$R_5$=$R_6$=OH; $R_1$=O-Glucoside—galuteolin [1,32],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$=β-D-Glucopyranoside—glucoluteolin [1,32],
$R_2$=$R_4$=H; $R_1$=$R_3$=$R_5$=OH; $R_6$=O-Glucoside—luteolin 4-glucoside [1],
$R_2$=$R_4$=H; $R_1$=$R_3$=$R_6$=OH; $R_5$=β-D-Glucopyranoside—dracocephaloside [56],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$=O-Glucuronide [107],
$R_2$=$R_4$=H; $R_1$=$R_3$=$R_5$=OH; $R_6$=O-Glucuronoxyloside [45],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$=O-Apioglucoside [9,32],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH, $R_3$=O-Glucolactoside [57,52],
$R_2$=$R_4$=H, $R_1$=$R_5$=$R_6$=OH; $R_3$=O-β-Laminaribioside [42],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$= O-Rutinoside [52],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$=O-Neohesperidoside—veronicastroside [60],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH, $R_3$=O-Primeveroside [61],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$=O-Rhamnoglucoside—lonicerin [62],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$= O-Xyloglucoside [1],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$=O-Glucosidoglucuronoside [1],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$=O-Glucuronoside [1],
$R_2$=$R_4$=H; $R_1$=$R_5$=$R_6$=OH; $R_3$=O-Tetraglucoside [1],
$R_2$=$R_4$=H; $R_1$=$R_5$OH; $R_3$=$OCH_3$, $R_6$=O-α-D-Glucofuranoside [63],
$R_2$=$R_4$=H; $R_1$=$R_5$=OH, $R_3$=$OCH_3$, $R_6$=O-β-L-Rhamnopyranoside—spinoside [63,147],
$R_2$=$R_4$=H; $R_1$=$R_5$=OH; $R_6$=$OCH_3$, $R_3$=O-Rutinoside—diosmin [32,95],
$R_2$=$R_4$=H; $R_1$ =$R_5$=OH; $R_6$=$OCH_3$, $R_3$=O-Glucoside [148],
$R_2$=$R_4$=H; $R_1$=$R_5$=OH; $R_6$=$OCH_3$, $R_3$=O-α-L-Arabinofuranosyl-(1→6)-β-D-glucopyranoside—capreoside [67],
$R_2$=$R_4$=H; $R_1$=$R_5$=OH; $R_6$=$OCH_3$, $R_3$=O-β-L-Arabinofuranosyl-(1→6)-β-D-glucopyranoside—salicapreoside
$R_2$=$R_4$=H; $R_1$=$R_5$=OH; $R_6$=$OCH_3$; $R_3$=O-β-L-Arabinopyranosyl-(1→6)-β-D-glucopyranoside—palustroside [64],
$R_2$=$R_4$=H; $R_1$=$R_6$=OH; $R_5$=$OCH_3$; $R_3$=O-β-D-Galactobioside—ornanthobioside [65],
$R_2$=$R_4$=H; $R_1$=$R_6$=OH; $R_5$=$OCH_3$; $R_3$=O-Glucoarabinoside—bakkoside [66],
$R_2$=$R_4$=H; $R_1$=$R_6$=OH; $R_5$=$OCH_3$, $R_3$=O-Apioglucoside—graveobioside B [69],
$R_2$=$R_4$=H; $R_1$=$R_6$=OH; $R_5$=$OCH_3$; $R_3$=O-β-D-Galactopyranoside—salicapriin [68],

TABLE 1 continued

$R_2=R_4=H$; $R_1=R_6=OH$; $R_5=OCH_3$; $R_3$=O-β-D-Galactopyranosyl-(1→2)-α-L-arabinofuranoside—salicaprin [68]

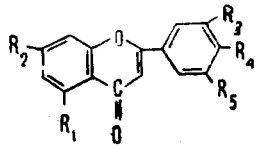
$R_2=R_4=H$; $R_1=R_6=OH$, $R_5=OCH_3$; $R_3$=O-Glucuronide [107],

$R_2=R_4=H$; $R_1=R_6=OH$; $R_5=OCH_3$, $R_3$=O-Rutinoside [107],

$R_2=R_4=H$; $R_1=OH$; $R_3=R_5=OCH_3$, $R_6$=O-Glucoside—yadorinin B [71],

$R_4=H$; $R_1=R_5=R_6=OH$; $R_2=OCH_3$, $R_3$=O-Glucoside—pedalin [32],

$R_4=H$; $R_1=R_3=R_6=OH$; $R_2=R_5=OCH_3$, $R_3$=O-Glucopyranoside—jaceoside [70],



$R_2=R_4=OH$; $R_3=R_5=OCH_3$; $R_1$=O-Glucoside [1],

$R_2=R_4=OH$; $R_3=R_5=OCH_3$; $R_1$=O-Glucobioside [1],

$R_1=R_4=OH$; $R_3=R_5=OCH_3$; $R_2$=O-Glucuronide [1],

$R_1=R_4=OH$; $R_3=R_5=OCH_3$; $R_2$=O-Diglucuronide [1].

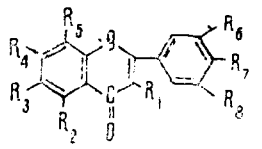
Table 1 shows the following facts:

| Position of the carbohydrate residue | 5 | 6 | 7 | 8 | 3' | 4' | 5' |
|---|---|---|---|---|---|---|---|
| Number of glycoside structures | 8 | 1 | 60 | - | 1 | 10 | - |

| Carbohydrate residue | Position of the carbohydrate substituent | | | | |
|---|---|---|---|---|---|
| | 5 | 6 | 7 | 3' | 4' |
| Monoses: | | | | | |
| D-glucose | 5 | 1 | 10 | 1 | 9 |
| D-galactose | - | - | 2 | - | - |
| L-rhamnose | 1 | - | 1 | - | 1 |
| D-xylose | - | - | - | - | 1 |
| Glucuronic acid | 2 | - | - | - | - |
| Bioses: | | | | | |
| Rutinose | - | - | 5 | - | - |
| Neohesperidose | - | - | 2 | - | - |
| Sambubiose | - | - | 1 | - | - |
| Primeverose | - | - | 1 | - | - |
| Laminaribiose | - | - | 1 | - | - |
| Total | 8 | 1 | 23 | 1 | 11 |

It is also interesting to note characteristic features of the flavonol glycosides. Table 2 gives the structures of some glycosides of di- to pentaflavonols and their methoxylated derivatives. In this case, in contrast to the flavone glycosides, glycosides of trimethoxylated aglycones (limocitrin and isolimocitrol [139, 142], centaurein [124], jacein [125]) are found in plants. In view of the fact that the structures of the aglycones are more diverse, the number of known flavonol glycosides is greater than that of flavone glycosides. In the monoglycosidated compounds, the carbohydrate residues are found most frequently in position 3 (in 80 out of the 108 given in Table 2), and then in position 7.

TABLE 2. Structures of Monoglycosidated Flavonols



$R_3=R_5=R_6=R_7=R_8=H$; $R_2=OH$; $R_4=OCH_3$ $R_1$=O-Rutinoside—cannabin [72],

$R_2=R_3=R_6=R_8=H$; $R_4=R_5=R_7=OH$, $R_1$=O-β-D-Glucopyranoside[73],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1$=O-Xyloside [75],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$, $R_1$=O-L-Arabinoside—juglanin [32,74],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7OH$; $R_1$=O-β-D-Glucopyranoside—astragalin [32],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1$=O-L-Rhamnoside—afzelin [74,76],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1$=O-β-D-Galactoside—trifolin [32],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1$=O-α(β)-D-Galactofuranoside—α(β)-galactorobin [77],

TABLE 2 continued

$R_3=R_5=R_6=R_8=H$; $R_1=R_2=R_7=OH$; $R_4=O$-β-D-Glucoside—populnin [32],

$R_3=R_5=R_6=R_8=H$; $R_1=R_2=R_7=OH$, $R_4=O$-L-Rhamnoside [31, 167],

$R_3=R_5=R_6=R_8=H$; $R_1=R_2=R_7=OH$; $R_4=O$-α(β)-L-Rhamnofuranoside—α(β)-rhamnorobin [77],

$R_3=R_5=R_6=R_8=H$; $R_1=R_2=R_7=OH$; $R_4=O$-α-L-Rhamnopyranoside—α-rhamnoisorobin [77],

$R_3=R_5=R_6=R_8=H$; $R_1=R_2=R_4=OH$ $R_7=O$-D-Glucoside —laminooside [164],

$R_3=R_5=R_6=R_8=H$; $R_1=R_2=R_4=OH$, $R_7=O$-L-Arabinoside [76],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-Sophoroside sophoraflavonoloside [32,78],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-Rutinoside [32]

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-Gentiobioside [79],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-β-D-Glucosylxyloside—rustoside [80],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-Glucogalactoside—panasenoside [81],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-Glucuronoside [82],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-β-D-Galactofuranosyl-6-β-L-rhamnofuranoside—nikitiflorin [80],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-β-D-Galactofuranosyl-6-β-L-rhamnofuranoside biorobin [83],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$, $R_1=$Rhamnolaminaribioside [84],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-Glucoapioside [87],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=$Galactoglucorhamnoside—virectafloridoside [85],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_7=OH$; $R_1=O$-Rhamnodiglucoside [32],

$R_3=R_5=R_6=R_8=H$; $R_2=R_7=OH$: $R_1=OCH_3$; $R_4=O$-Rutinoside [88],

$R_3=R_5=R_6=R_8=H$; $R_1=R_2=OH$; $R_7=OMH_3$; $R_4=O$-Glucoside— mumenin [31,95],

$R_3=R_5=R_6=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-α-L-Arabinofuranoside—avicularin [32],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-α-L-Arabinopyranoside—guaijaverin [89],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-β-L-Arabinofuranoside—polystachoside [90,91],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=$ L-Arabinoside—foeniculin [32],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Glucuronide—miquelianin [32,110,154],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Xyloside—reynoutrin [9,32],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$,$R_1=O$-β-D-Galactopyranoside—hyperoside [32],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-L-Rhamnoside—quercitrin [32,92,93],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-β-D-Glucopyranoside—isoquercitrin [94,168],

$R_3=R_5=R_8=H$; $R_1=R_2=R_6=R_7=OH$; $R_4=O$-β-D-Glucopyranoside—quercimeritrin [32, 95],

$R_3=R_5=R_8=H$; $R_1=R_2=R_4=R_6=OH$; $R_7=O$-Glucoside—spyraeoside [32],

$R_3=R_5=R_8=H$; $R_1=R_2=R_4=R_6=OH$; $R_7=O$-Diglucoside [129],

$R_3=R_5=R_8=H$; $R_1=R_2=R_4=R_7=OH$; $R_6=O$-Glucopyranoside [168],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$: $R_1=O$-Diglucoside—meratin [32,96],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Rutinoside—rutin [32,45],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-α-L-Arabopyranosyl-(1→2)-α-L-rhamnofuranoside—zhealin [97],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Sophoroside [98, 99],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Gentiobioside [5],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Glucoglucuronide—nelumboside [111],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Triglucoside [100],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Digalactoside [101],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-β-L-Rhamnofuranosyl-β-D-glucofuranoside—flassilin [77],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Glucogalacturonide [102],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-β-D-Galactofuranosyl-6-β-L-rhamnopyranoside—bioquercetin [103],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-β-D-Xylopyranosyl-(1→3)-β-D-glucopyranosyl galactofuranoside—hybridin [104],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-Rhamnoside [106],

$R_3=R_5=R_8=H$; $R_2=R_4=R_6=R_7=OH$; $R_1=O$-α-L-Arabinopyranosyl-(1→6)-β-D-galactopyranoside—rumarin [105],

$R_3=R_5=R_8=H$; $R_1=R_4=R_6=R_7=OH$; $R_2=O$-Rhamnoglucoside [129],

$R_3=R_5=R_8=H$; $R_4=R_6=R_7=OH$; $R_2=OCH_3$, $R_1=O$-Rhamnoside—azalein [138],

$R_3=R_5=R_8=H$; $R_4=R_6=R_7=OH$; $R_2=OCH_3$, $R_1=O$-β-D-Galactoside [109, 117],

$R_3=R_5=R_8=H$; $R_4=R_6=R_7=OH$; $R_2=OCH_3$, $R_1=O$-Diglucoside [109],

$R_3=R_5=R_8=H$; $R_4=R_6=R_7=OH$; $R_2=OCH_3$, $R_1=O$-Glucuronoside [110],

$R_3=R_5=R_8=H$; $R_1=R_2=R_7=OH$; $R_6=OCH_3$, $R_4=$ β-Glucopyranoside—transilin [112],

TABLE 2 continued

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_6$=$OCH_3$, $R_1$=O-α-L-Arabinoside–distichin [32],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_6$=$OCH_3$, $R_1$=O-Gentiobioside–astragaloside [113],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_6$=$OCH_3$, $R_1$=O-Rutinoside–narcissin [114],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_6$=$OCH_3$, $R_1$=O-Galactoside–cacticin [115,128],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_6$=$OCH_3$, $R_1$=O- Rhamnogalactoside [116],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_6$=$OCH_3$, $R_1$=O-β-D-Galacto-β-D-glucopyranoside [65],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_6$=$OCH_3$, $R_1$=α-L-Arabinopyranosyl-(1→2)-α-L-rhamnofuranoside–alliosidin [117],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_6$=$OCH_3$, $R_1$=O-Glucosylrhamnosylgalactoside [32],

$R_3$=$R_5$=$R_8$=H; $R_4$=$R_6$=$R_7$=OH; $R_1$=$OCH_3$, $R_2$=O-Glucoside–stizoloside [118],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_6$=$R_7$=OH; $R_4$=$OCH_3$, $R_1$=α-L-Rhamnoside–rhamnitrin [141],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_4$=$R_6$=OH; $R_7$=$OCH_3$, $R_1$=O-Glucoside–tamarixin [119],

$R_3$=$R_5$=$R_8$=H; $R_1$=$R_2$=$R_6$=OH; $R_7$=$OCH_3$, $R_4$=O-Rutinoside [146],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_6$=OH; $R_4$=$R_7$=$OCH_3$, $R_1$=O-Rutinoside–ombuoside [120],

$R_3$=$R_5$=$R_8$= H; $R_2$=$R_4$=$R_6$=$R_7$=OH; $R_1$=Trioside from glucose and arabinose–primflavoside [121],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_7$=OH; $R_4$=$R_6$=$OCH_3$, $R_1$=O-Glucoside–Flavoyadorinin A [123],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_7$=OH; $R_4$=$R_6$=$OCH_3$, $R_1$=O-β-D-Glucoside–alboside [122],

$R_3$=$R_5$=$R_8$=H; $R_2$=$R_7$=OH; $R_4$=$R_6$=$OCH_3$, $R_1$=O-Rhamninoside [106],

$R_3$=$R_5$=H; $R_2$=$R_4$=$R_6$=$R_7$=$R_8$=OH; $R_1$=O-Rhamnoside–myricitrin [32,93],

$R_3$=$R_5$=H; $R_2$=$R_4$=$R_6$=$R_7$=$R_8$=OH; $R_1$=O-β-D-Glucopyranoside–isomyricitrin [31,27]

$R_3$=$R_5$=H; $R_2$=$R_4$=$R_6$=$R_7$=$R_8$=OH; $R_1$=O-Digalactoside [145],

$R_3$=$R_5$=H; $R_2$=$R_4$=$R_6$=$R_8$=OH; $R_7$=$OCH_3$, $R_1$=O-Rhamnoside–mearnsitrin [140],

$R_5$=$R_8$=H; $R_1$=$R_2$=$R_3$=$R_6$=$R_7$=OH; $R_4$=O-Glucoside–quercetagitrin [108],

$R_5$=$R_8$=H; $R_2$=$R_3$=$R_4$=$R_6$=$R_7$=OH; $R_1$=O-Glucoside–tagetiin [32],

$R_5$=$R_8$=H; $R_1$=$R_2$=$R_6$=$R_7$=OH; $R_3$=$OCH_3$, $R_4$=O-Glucoside–patuletrin [32],

$R_5$=$R_8$=H; $R_2$=$R_3$=$R_4$=$R_6$=$R_7$=OH; $R_1$=O-Galactoside [108],

$R_5$=$R_8$=H; $R_2$=$R_3$=$R_4$=$R_5$=$R_7$=OH; $R_1$=O-Gentiotrioside [108],

$R_5$=$R_8$=H; $R_2$=$R_3$=$R_6$=$R_7$=OH; $R_1$=$OCH_3$, $R_4$=O-Glucoside [107],

$R_5$=$R_8$=H; $R_2$=$R_6$=OH; $R_1$=$R_3$=$R_7$=$OCH_3$, $R_4$=β-D-Glucoside–centaurein [124],

$R_5$=$R_8$=H; $R_2$=$R_7$=OH; $R_1$=$R_3$=$R_6$=$OCH_3$, $R_4$=O-β-D-Glucopyranoside [125],

$R_5$=$R_8$=H; $R_2$($R_1$)=OH; $R_3$=$R_4$=$R_6$=$OCH_3$, $R_1$ ($R_2$)=O-Glucoside–chrysosplenin [32],

$R_3$=$R_8$=H; $R_1$=$R_2$=$R_5$=$R_6$=$R_7$=OH; $R_4$=O-β-D-Glucopyranoside–gossypitrin [32,126,134],

$R_3$=$R_8$=H; $R_2$=$R_4$=$R_5$=$R_6$=$R_7$=OH: $R_1$=O-β-D-Glucoside–gossytrin [134,136],

$R_3$=$R_8$=H; $R_1$=$R_2$=$R_4$=$R_6$=$R_7$=OH; $R_5$=O-Glucoside–gossypin [126,129],

$R_3$=$R_8$=H; $R_1$=$R_2$=$R_4$=$R_6$=$R_7$=OH; $R_5$= O-Rhamnoglucoside [129],

$R_3$=$R_8$=H; $R_1$=$R_2$=$R_4$=$R_6$=$R_5$=OH; $R_7$=O-Glucoside [129],

$R_3$=$R_8$=H; $R_2$=$R_7$=OH; $R_1$=$R_4$=$R_6$=$OCH_3$, $R_3$=O-Glucoside–chrysosplenoside C [132],

$R_3$=$R_8$=H; $R_2$=OH; $R_1$=$R_3$=$R_4$=$R_5$=$OCH_3$, $R_7$=O-Glucoside–chrysosplenoside B [133],

$R_5$=$R_8$=H; $R_3$=$R_4$=$R_7$=OH; $R_2$=$OCH_3$, $R_1$=O-Glucoside–vogeloside [135],

$R_5$=$R_8$=H; $R_2$=OH; $R_1$=$R_3$=$R_4$=$OCH_3$, $R_1$=O-Glucoside–pendulin [131],

$R_3$=H; $R_2$=$R_4$=$R_5$=$R_6$=$R_7$=$R_8$=OH; $R_1$=O-Glucoside–hibiscitrin [32],

$R_3$=$R_6$=$R_8$=H; $R_1$=$R_2$=$R_5$=$R_7$=OH; $R_4$=O-Glucoside–herbacitrin [143],

$R_3$=$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_5$=$R_6$=$OCH_3$, $R_1$=O-β-D-Glucoside [139],

$R_3$=$R_8$=H; $R_2$=$R_4$=$R_7$OH; $R_5$=$R_6$=$OCH_3$, $R_1$=O-β-Arabinoglucoside [139],

$R_8$=H; $R_2$=$R_4$=$R_6$=OH; $R_3$=$R_5$=$R_7$=$OCH_3$, $R_1$=O-β-Glucoside [142],

$R_8$=H; $R_1$=$R_4$=$R_7$=OH; $R_3$=$R_5$=$R_6$=$OCH_3$, $R_1$=O-β-Glucoside [142],

$R_3$=$R_8$=H; $R_2$=$R_4$=$R_6$=$R_7$=OH; $R_5$=$OCH_3$, $R_1$=O-Galactoside–corniculatusin [137],

$R_8$=H; $R_2$=$R_4$=$R_7$=OH; $R_3$=$R_5$=$R_6$=$OCH_3$, $R_1$=O-Arabinodiglucoside [139],

Table 2 shows the following facts:

| Position of the carbohydrate residue | 3 | 5 | 6 | 7 | 8 | 3' | 4' |
|---|---|---|---|---|---|---|---|
| Number of glycosidic structures in the given position | 84 | 2 | 1 | 13 | 2 | 2 | 7 |

The numbers of glycosides containing carbohydrate residues in different positions of the flavonol nucleus are given below:

| Carbohydrate residue | Position of the carbohydrate substituent | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3 | 5 | 6 | 7 | 8 | 3' | 4' |
| Monoses: | | | | | | | |
| D-glucose | 13 | 2 | 1 | 10 | 1 | 2 | 2 |
| D-galactose | 8 | - | - | - | - | - | - |
| L-rhamnose | 4 | - | - | 1 | - | - | - |
| L-arabinose | 4 | - | - | - | - | - | 1 |
| D-xylose | 3 | - | - | - | - | - | - |
| Glucuronic acid | 2 | - | - | - | - | - | - |
| Bioses: | | | | | | | |
| Rutinose | 5 | - | - | 2 | - | - | - |
| Sophorose | 3 | - | - | | - | - | - |
| Gentiobiose | 3 | - | - | - | - | - | - |
| Leucoverose | 1 | - | - | - | - | - | - |

The carbohydrate components are found considerably more rarely in the $C_4'$ and $C_3'$ positions and very rarely at $C_5$ and $C_6$. Of the monosaccharides, glucose and galactose predominate and of the biosides rutinose. The bioses maltose [8], leucoverose [7], and gentiobiose [5] are found very rarely.

We have not included in Tables 1 and 2 some glycosides in which the position of the carbohydrate residue has not been determined (for example, moroside [130], alaternoside [139], etc.), and glycosides containing aliphatic radicals in the nucleus [32].

Diglycosidation is more characteristic for flavonols than for flavones, and usually takes place in positions 3 and 7, and rarely in positions 3' and 4', of the flavonol nucleus. Table 3 gives the structures of some diglycosides of kaempferol, quercetin, and isorhamnetin. Because of the different combinations of monoses and bioses, their structures are still more diverse.

The complexity of the glycosidic structures of flavones and flavonols is also due to the presence of acyl residues in their molecules. Acyl derivatives were first described by Willstätter et al. in 1915 [12], and then the structures of a series of acylated anthocyanins was established, their distinguishing feature proving to be the presence of an acyl residue in the carbohydrate component of the glycoside [12-18].

In 1959, the first acylated flavonol glycoside – tiliroside – was isolated from the flowers of Tilia argentea Desf. [19]. According to Hörhammer et al., this compound was kaempferol 7-p-coumaroyl 3-$\beta$-glucoside [19, 20].

In 1964, Harborne [12] established that in this glucoside the acid residue was attached to the carbohydrate residue and that, consequently, it is kaempferol 3-(p-coumaroyl-$\beta$-glucoside). Birkofer and his co-workers [21-23] have described the structures of two more acylglycosides: bignoside and petunoside (see Table 1) in which the acyl residue is attached to a sugar. Soviet workers have isolated a number of acylated flavone glycosides. In some of them the acyl residue is directly attached to the flavone nucleus (quinqueloside, piperoside, menthoside) [24, 25]. C-Glycosides may also be acylated. Thus, for example, King [26] has shown the existence in wheat germ of compounds similar to vitexin acylated with sinapic acid. From Crataegus curvisepala Lindm, V. S. Batyuk et al. [27, 28] have isolated the C-glycoside cratenacin, in which the carbohydrate moiety of the molecule contains an acetic acid residue (we do not consider their structure in the present paper).

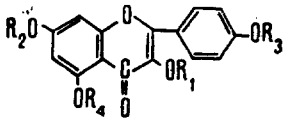
Such diversity of glycosides with accurately fixed positions of the carbohydrate residues in flavone and flavonol nuclei enables the theoretically possible number of structures to be calculated by the methods of combinatorial mathematics. To find the theoretically probable number of monoglycosidated flavonoids we have obtained the following formula:

$$S_1 = \lambda m k^{n-1}, \quad (1)$$

where λ is the number of possible structures of carbohydrates capable of forming part of a glycoside; m is the number of apices (positions in the flavonoid nucleus) at which there may be carbohydrate residues; k is the number of substituents on the carbon atoms in the flavonoid nucleus (H, OH, $OCH_3$); and n is the total number of apices at which there can be H, OH, and $OCH_3$ substituents and a carbohydrate residue.

TABLE 3. Structures of Diglycosidated Flavonols

Diglycosides of Kaempferol and Its Methyl Derivatives

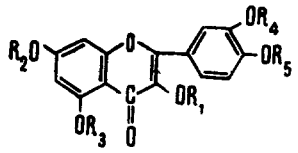


$R_3$=$R_4$=H; $R_1$ = rhamnose, $R_2$ = rhamnogalactose—swartzioside [150],
$R_3$=$R_4$=H; $R_1$ = rhamnogalactose, $R_2$ = glucose [151],
$R_3$=$R_4$=H; $R_1$ = rhamnoglucose, $R_2$ = glucose [152],
$R_2$=$R_4$=H; $R_1$ = rhamnose, $R_3$ = arabinose [153],
$R_3$=$R_4$=H; $R_2$ = Rhamnofuranose* [32],
$R_3$=$R_4$=H; $R_1$=$R_2$= α-L-Rhamnofuranose—lespedin [159],
$R_3$=$R_4$=H; $R_1$ = α-L-arabinofuranose, $R_2$ = α-L-rhamnofuranose—ternoside [156],
$R_3$=$R_4$=H; $R_1$ = galactorhamnose, $R_2$ = rhamnose—robinin [32, 149],
$R_3$=$R_4$=H; $R_1$ = rutinose, $R_2$ = rhamnose [149],
$R_3$=$R_4$=H; $R_1$ = arabinohamnose, $R_2$ = rhamnose [154],
$R_3$=$R_4$=H; $R_1$ = sophorose, $R_2$ = glucose [1, 154],
$R_3$=$R_4$=H; $R_1$ = glucose, $R_2$ = rhamnose [150],
$R_3$=$R_4$=H; $R_1$ = rutinose, $R_2$ = glucuronic acid [1],
$R_3$=$R_4$=H; $R_2$ = D-glucose, $R_1$ = D-glucose—peonoside [143],
$R_3$=$R_4$=H; $R_2$ = α-L-rhamnofuranose, $R_1$ = β-D-galactofuranosyl-(1→6)-β-D-rhamnofuranose—α-neorobin [83],
$R_3$=$R_4$=H; $R_1$ = β-D-galactofuranosyl-(1→6)-rhamnofuranose, $R_2$ = α-L-rhamnofuranose— β-neorobin [155],
$R_3$=$R_4$=H; $R_1$ = $R_1$ = D-xylose, $R_2$ = L-rhamnose—lepidoside [80],
$R_3$=$R_4$=H; $R_1$ = α-D-xylofuranose, $R_2$ = α-L-rhamnofuranose [160],
$R_2$=$R_3$=H; $R_1$ = $R_4$ Glucose [157],
$R_3$=$R_4$=H; $R_1$ = sophorose, $R_2$ = rhamnose [1],
$R_3$=$R_4$=H; $R_1$ = rhamnoarabinose, $R_2$ = arabinose [1],
$R_3$=$R_4$=H; $R_1$ = 3 moles of rhamnose, $R_2$ = rhamnose [151],
$R_3$=$R_4$=H; $R_1$ = lathyrose, $R_2$ = rhamnose [1],

*$R_1$ not given in Russian original – Publisher.

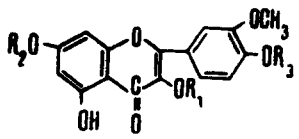
Table 3 (continued)

## Quercetin Glycosides



$R_3=R_4=R_5=H$; $R_1$ = β-D-glucopyranose, $R_2$ = α-L-rhamnopyranose–antoside [80],
$R_2=R_3=R_5=H$; $R_1=R_4$=Glucose [1],
$R_3=R_4=R_5=H$; $R_1=R_2$=Glucose [1],
$R_2=R_3=R_4=H$; $R_1=R_5$=Glucose [1],
$R_3=R_4=R_5=H$; $R_1$ = sophorose, $R_2$ = glucose [154],
$R_3=R_4=R_5=H$; $R_1$ = α-L-arabofuranose, $R_2$ = β-D-glucopyranose [161],
$R_3=R_4=R_5=H$; $R_1$ = rhamnogalactose, $R_2$ = glucose [166],
$R_3=R_4=R_5=H$; $R_1$ = xyloglucose, $R_2$ = glucose [154],
$R_3=R_4=R_5=H$; $R_1=R_2$= Glucuronic acid [1,154],
$R_3=R_4=R_5=H$; $R_1$ = rhamnoglucose, $R_2$ = galactose [151],
$R_3=R_4=R_5=H$; $R_1$ = glucose, $R_2$ = rhamnose–petiolaroside [164],
$R_2=R_4=R_5=H$; $R_1=R_3$=Galactose [162],
$R_3=R_4=R_5=H$; $R_1$ = α-D-xylose, $R_2$ = β-D-glucose [154],
$R_3=R_4=R_5=H$; $R_1$ = α-L-rhamnose, $R_2$ = β-D-glucose [164],
$R_3=R_4=R_5=H$; $R_1$ = rutinose, $R_2$ = glucuronic acid [154],
$R_3=R_4=H$; $R_1=CH_3$, $R_2$ = 2 moles of glucose, $R_5$ = rhamnose [171],
$R_4=H$; $R_2=R_5=CH_3$, $R_3(R_3)$ = glucose, $R_5(R_1)$ = rhamnose–rhodotyposide [163],
$R_3=R_5=H$; $R_2=CH_3$, $R_1$ = arabinose, $R_4$ = rhamnose–peumoside [170, 163].

## Isorhamnetin Glycosides



$R_3=H$; $R_1$ = β-D-glucofuranoside, $R_3$ = α-L-rhamnopyranoside–pasternoside [77],
$R_3=H$; $R_1$ = sophorose, $R_2$ = glucose–brassicoside [169],
$R_3=H$; $R_1$ = D-glucose, $R_2$ = α-L-rhamnose–brassidin [169],
$R_3=H$; $R_1$ = glucose, $R_2$ = rhamnose–boldoside [153],
$R_3=H$; $R_1=R_3$=Glucose–dactylin [32],
$R_3=H$; $R_1=R_2$=Glucose [1].

Let us assume that in the flavone nucleus there are substituents (H, OH, $OCH_3$) in positions $C_5$, $C_6$, $C_7$, $C_{3'}$, and $C_{4'}$, which is quite possible according to Table 1, and that one of the hydroxyls is glycosidated. What is the theoretically possible number of structures in this case?

We have $\lambda = 1$, $m = 3$, $k = 3$, and $n = 5$ and, from Formula (1), $S_1 = 243$. Since glycosidated tri- and tetramethoxylated flavones are not found in nature and there are no monohydroxyflavone glycosides, the number of theoretically possible structures according to our calculations must be decreased by 45, giving 198. Thus, there must be 198 glycosides of different aglycones containing one and the same sugar. It is known that flavones can give monoglycosides with different sugars. This leads to a corresponding increase in the number of combinations. Here we shall not take into account the sizes of the oxide rings and the configurations of the glycosidic bonds.

For flavonols we take the simplest case in which there can be an OH or $OCH_3$ group or a carbohydrate component at the $C_3$ position and in the other positions H, OH, $OCH_3$ or a carbohydrate residue of definite structure attached only to some definite "apex."

In this case, $\lambda = 1$, $m = 1$, $k = 3$, $n = 8$, and $S_1 = 2187$. Deducting the number of structures impossible for natural glycosides, we obtain $2187 - 108 = 2079$ probable structures.

To calculate the total number of theoretically possible diglycosidated flavonoids we have derived the formula

$$S_2 = \frac{1}{2}\lambda m (m-1) k^{n-2}, \qquad (2)$$

where the letter symbols are the same as in Formula (1).

## SUMMARY

Literature information on the structures of O-glycosides of flavones and flavonols has been generalized. Using the methods of combinatorial mathematics, the possibility of a great diversity of the structure of the glycosides has been shown without taking into account their acylation, the dimensions of the oxide rings of the sugars, and the nature of the glycosidic bonds.

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