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FLAVONOIDS OF THE COTTON PLANT AND PLANTS CLOSE TO IT

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This review gives information on the distribution of flavonoids (flavonol and anthocyanin glycosides, catechins, and proanthocyanidins in plants of the family Malvaceae, namely the various species of the genera Gossypium, Hibiscus, Altheae, etc. It is shown that the flavonols are represented by glycosides of kaempferol, quercetin, myricetin, herbacetin. gossypetin, and hibiscetin, the most widespread being glycosides of quercetin and kaempferol. Characteristic for the majority of representatives of the families that were studied are flavonols having a hydroxy group in the C-8 position. Anthocyanins are represented by glycosides of cyanidin and of delphinidin. However, together with these, glycosides of methoxylated anthocyanins have also been detected — peonidin, petinidin, and malvidin. Sources of a food dye have been revealed among representatives of the family. Literature sources up to 1991 have been included.

Plants of the family Malvaceae are widely distributed over the terrestial globe and are represented by 85 genera consisting of 2880 species [1]. There are reckoned to be 11 genera on the territory of Central Asia, including about 50 species, of which eight are endemic [2, 3]. This family includes such plants of practical importance as cotton, kenaf, althaea, etc.. Plants of the genera *Gossypium* L. (*G. hirsutum* L., *G. barbadense* L., *G. arboreum*, *G. herbaceum* L., *G. tricuspidatum*), *Hibiscus* L. (*H. cannabinus*, *H. sabdariffa* L.), *Althaea* L. (*A. officinalis*), and *Alcea* L. are widely cultivated as technical, dye, and medicinal crops. Some representatives of this family — for example, shrub althea (*H. syriacus*), Chinese hibiscus (*H. rosea sinensis* L.), scarlet rosemallow (*H. coccineus* Malt.), common rosemallow (*H. moscheutes* L.), hollyhock (*Alcea rosea* L.), and high mallow (*Malva sylvesstris*) — are cultivated as decorative plants.

The phenolic compounds of plants of this family are represented mainly by flavonoids. Tables 1, 2, and 4 give information on the distribution of flavonoid compounds — flavonol glycosides, anthocyanins, catechins, and proanthocyans — plants of the Malvaceae family.

The most studied group of flavonoids of plants of the Malvaceae family are the flavonol glycosides. Out of 85 genera of this family it is plants of the genera *Gossypium* L. and *Hibiscus* L. that have been studied mainly for the presence of flavonols, and these were used as objects of chemical investigation as early as the twenties by Perkin [4], who isolated from the flowers of several varieties of the cotton plant *G. arboreum* and *G. herbaceum* gossypitrin, quercimeritrin, and isoquercitrin. Seshadri and his colleagues [5-10] showed the presence in flowers of Indian varieties of the cotton plant of, together with already known flavonol glycosides, two new compounds (gossypin and herbacitrin (Table 1). The flavonols of Central Asian varieties of the cotton plant have been investigated by A. S. Sadykov et al. [11-18]. From the flowers and leaaves of medium- and fine-fibered varieties of the cotton plant, in adition to quercimeritrin, isoquercitrin, and gossypetrin, they isolated hirsutin, quercetin 3-O-glucoside, quercetin 3-O-sophoroside, and two new glucosides - isoastragalin (kaempferol 3-O-β-*D*-glucofuranoside) and hybridin [quercetin 3-O-[O-β-*D*-galactfuranosyl-(1→3)-O-β-*D*-glucopyranosyl-(1→3)-β-*D*-xylopyranoside].

The seeds of American varieties of the cotton plant have been shown to contain quercetin 3-O-sophoroside, rutin, isoquercitrin, kaempferol 3-O-rutinoside [19, 20], and methylated flavonols — tamarixetin and kaempferide [21], while the flowers contain, in addition to compounds known prefiously, trifolin, quercetin 3-O-galactoside, tamarixetin 7-O-glucoside,

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TABLE 1. Distribution of Flavonal Glycosides in Plants of the Malvacaeae

Name	Structure	Plant	Plant organ from which the flavonoid was isolated	Literature
Kaempferol	3,4',5,7-Tetrahydroxyflavone			
1. Kaempferide	4'-O-Methylkaempferol	*Gossypium sp.*		21
2. Kaempferol	3-O-rutinoside Kaempferol 3-O-rutinoside	*Gossypium sp.*	Flowers Seeds	20, 22
3. Astragalin	Kaempferol 3-O-ß-D-glucopyranoside	*Athea rosea* *Althea mediflora*	Flowers Flowers	30 42
4. Isoastragalin	Kaempferol 3-O-α-D-glucofuranoside	*Gossypium hirsutum*	Flowers	14
5. Altheanin (flavanonol)	Dihydrokaempferol 3-O-glucoside	*Althea rosea*	Flowers	41
6. Trifolin	Kaempferol 7-O-ß-D-galactoside	*Gossypium sp.* *Hibiscus tiliacus*	Flowers Flowers	22, 23 27
7. Populnin	Kaempferol 3-O-ß-D-glucoside	*Thespesia populnea*	Flowers	40
8. Kaempferol 3,7-dirhamnoside	Kaempferol-3-O-α-L-rhamnopyranoside 7-O-α-L-rhamnofuranoside	*Hibiscus cannabinus*	Leaves	33
9. Kaempferitrin	Kaempferol 3,7-di-O-α-L-rhamnofuranoside	*Hibiscus cannabinus*	Leaves	34
10. Kaempferol 7-rhamnoside	Kaempferol 7-O-α-L-rhamnofuranoside	*Hibiscus cannabinus*	Leaves	34
11. Kaempferol 3-xyloglucoside	Kaempferol 3-O-xyloglucoside	*Hibiscus rosasinensis*	Flowers	23
12. Tiliroside	Kaempferol 3-O-(6''-p-coumaroyl-ß-D-glucoside)	*Althea officinalis*	Leaves	82
13. Kaempferol 5-glucoside	Kaempferol 5-O-ß-D-glucoside	*Thespesia populnea*	Flowers	88
Quercetin	3,3',4',5,7-Pentahydroxyflavone			
14. Tamarixetin	4'-O-Methylquercetin	*Gossypium sp.*	Flowers	21
15. Isoquercitrin	Quercetin 3-O-ß-D-glucofuranoside	*G. barbadense* *G. herbaceum* *G. arboreum* *G. hirsutum* *Althea rosea*	Flowers Flowers Seeds Flowers	4 13 19 30
16. Quercimeritrin	Quercetin 7-O-ß-D-pyranoside	*Gossypium sp.* *Hibiscus esculentus*	Flowers Flowers	4 13
17. Quercetin 3'-glucoside	Quercetin 3'-O-glucopyranoside	*Gossypium hirsutum*	Flowers	11, 12
18. Hirsutrin	Quercetin 3-O-ß-D-glucopyranoside	*Gossypium hirsutum* *Gossypium hirsutum* *G. barbadense*	Leaves Flowers Leaves	13, 16 17
19. Spiraeoside	Quercetin 4'-O-glucoside	*H. esculentus* *G. hirsutum*	Flowers Seeds	25 17, 20
20. Quercetin 3-sophoroside	Quercetin 3-O-[O-ß-D-glucosyl-(1→2)-ß-D-glucoside]	*G. barbadense* *H. esculentus* *H. rosea sinensis*	Flowers Flowers Flowers	23 25
21. Hyperoside	Quercetin 3-O-ß-D-galactoside	*G. barbadense*	Flowers	23

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Name	Structure	Plant	Plant organ from which the flavonoid was isolated	Literature
22. Rutin	Quercetin 3-O-rutinoside	*Gossypium sp.* *H. esculentus*	Seeds Flowers	19, 22 25
23. Hybridin	Quercetin 3-O-[O-ß-D-galactofuranosyl-(1→3)-O-ß-D-glucopyranosyl-(1→3)-ß-D-xylopyranoside]	*G. hirsutum* *G. barbadense* Hybrid of hibiscus with the cotton plant	Leaves Leaves Flowers	18 15 18, 35
24. Tamarixicitrin 7-glucoside	4'-O-Methylquercetin 7-O-glucoside	*Gossypium sp.*	Flowers	22
25. Quercetin 5-glucoside	Quercetin 5-O-glucoside	*H. esculentus*	Flowers	25
26. Quercetin 4¢-diglucoside	Quercetin 4'-O-glucosidoglucoside	*H. esculentus*	Flowers	25
27. Quercetin 3-triglucoside	Quercetin 3-O-sophorosidoglucoside	*H. esculentus*	Flowers	25
28. Quercetin 3,7-diglucoside	Quercetin 3,7-di-O-glucoside	*H. rosea sinensis*	Flowers	23
29. Hibiscatin	Quercetin 3',7-di-O-methylquercetin 4'-O-glucoside	*H. furcatus*	Flowers	38
30.	Quercetin 3-O-sambubioiside	*H. mutabilis var. versicolor*	Flowers	84
31. Guaijaverin	Quercetin 3-O-α-L-arabinopyranoside	*H. mutabilis*	Flowers	84
32.	Quercetin 5-rhamnoglucoside	*H. esculentus*	Flowers	25
33.	7-O-Methylmyricetin 5'-diglucoside	*H. esculentus*	Flowers	25
Herbacetin	3,4'5,7,8-Pentahydroxyflavone			
34. Herbacitrin	Herbacetin 7-O-glucoside	*G. arboreum* *G. herbaceum*	Flowers Flowers Flowers	5 6 8
35. Herbacin	Herbacetin 8-O-glucoside	*Althea rosea*	Flowers	39
36. Sexangularetin 3-glucoside 7-rhamnoside	8-O-Methylherbacetin 3-O-glucoside 7-O-rhamnoside	*G. hirsutum*	Buds	24
Gossypetin	3,3',4',5,7,8-Hexahydroxyflavone			
37. Gossypin	Gossypetin 8-O-glucoside	*G. arboreum* *G. herbaceum* *H. esculentus* *H. vitifolius*	Flowers Flowers Flowers Flowers	9 10 25 23
38. Gossypitrin	Gossypetin 7-O-glucoside	*H. tiliacus* *H. sabdariffa* *H. surattensis* *G. arboreum* *G. herbaceum*	Flowers Flowers Flowers Flowers Flowers	4 6 7 26, 23 28
39. Gossytrin	Gossypetin 3-O-glucoside	*H. tiliacus* *H. sabdariffa*	Flowers Flowers	26 29
40. Gossypetin 8-rutinoside	Gossypetin 8-O-rutinoside	*H. esculentus*	Flowers	25

TABLE 1. Distribution of Flavonal Glycosides in Plants of the Malvacaeae

Name	Structure	Plant	Plant organ from which the flavonoid was isolated	Literature
41. Gossypetin 8-O-rhamnoside	Gossypetin 8-O-rhamnoside	*G. arboreum*	Flowers	83
42. Gossypetin 8-O-glucuronide	Gossypetin 8-O-glucuronide	*H. vitiflorus*	Flowers	85
43. Gossypetin 8-O-glucuronide 3-sulfate	Gossypetin 8-O-glucuronide 3-sulfate	*Malva sylvestris*	Leaves	86
44. Gossypin 3-sulfate	Gossypetin 8-O-D-glucoside 3-sulfate	*Malva sylvestris*	Leaves	87
45.	Gossypetin 3-glucoside 8-glucuronide	*M. sylvestris*	Leaves	87
Hypolaetin	3′,4′,5,7,8-Pentahydroxyflavone			
46.	Hypolaetin 8-O-ß-D-glucoside3′-sulfate	*M. sylvestris*	Leaves	89
47.	4′-O-Methylhypolaetin 8-glucuronide	*M. sylvestris*	Leaves	89
48.	Hypolaetin 8-glucuronide	*M. sylvestris*	Leaves	89
Naringenin	4′,5,7-Trihydroxyflavanone			
49.	5,7-Di-O-methylnaringenin 4′-O-ß-D-arabinoside	*H. mutabilis*	Stems	90
Eriodictyol	3′,4′,5,7-tetrahydroxyflavanone			
50.	5,7-Dimethyleriodictyol 4′-O-ß-D-arabinoside	*H. mutabilis*	Stems	91
Isoscutellarein	4′,5,7,8-Tetrahydroxyflavanone			
51.	Isoscutellarein 8-glucuronide	*M. sylvestris*	Leaves	89
Myricetin	3,3′,4′,5,5′,7,8-Heptahydroxyflavone			
52. Cannabiscitrin	Myricetin 3′-O-glucoside	*H. abelmoschus* *H. cannabinus*	Flowers Flowers	30
Hibiscetin	3,3′,4′,5,5′,7,8-Heptahydroxyflavone			
53. Hibiscitrin	Hibiscetin 3-O-glucoside	*H. sabdariffa*	Flowers	36, 37
Luteolin (flavone)	3′,4′,5,7-Tetrahydroxyflavone			
54.	8-Glucosyloxy-4′-O-methylluteolin	*Althea officinalis*	Leaves	82
55.	8-Glucosyloxy-4′-O-methylluteolin 3′-sulfate	*Althea officinalis*	Leaves	82

TABLE 2. Distribution of Anthocyanin Glycosides in Plants of the Malvacaeae

Name	Structure	Plant	Literature
Pelargonidin	3,4′,5,7-Tetrahydroxyflavylium		
1. Callistephin	Pelargonidin 3-O-glucoside	*Hibiscus syriacus*	68
2.	Pelargonidin 3-O-malonylglucoside	*Hibiscus syriacus*	68
Cyanidin	3,3′,4′,5,7-Pentahydroxyflavylium		
3. Chrysanthemin	Cyanidin 3-O-ß-D-glucoside	*Gossypium hirsutm*	58, 60, 66
		G. barbadense	60
		G. arboreum	60
		G. herbaceum	60
		Hibiscus syriacus	68
		H. sabdariffa var. sabdariffa	
		Hibiscus sp.	81
		Varieties: *M. Gor'kii*	64, 66
		Alenushka	64, 66
		Kolkhoznitsa	64, 66
		Krasnyi partizan	64, 66
		Gladiolus vidnyi	64, 66
		Kizil Uzbekistan	64, 66
		Alcea rosea	66, 75
		Abelmoschus manihot	73
		(L.) Medicus	73
		A. moscchatus Medicus	73
		Hibiscus archboldiamus	73
		Borss	73
		H. macrophyllus Roxb	73
		H. tiliaceous L.	73
		H. grewiifolius Hassk	73
		H. sabdariffa L.	73
4. Gossypicyanin	Cyanidin 3-O-ß-D-xylosyl-ß-glucoside	*Gossypium hirsutum*	58
		Hibiscus syriacus	
		Hibiscus sp.	
		Varieties: *M. Gorkii*	64, 65
		Gladiolus vidnyi	64, 65
		Alenushka	64, 65
		Kolkhoznitsa	64, 65
		Krasnyi partizan	64, 65
		Kizil Uzbekestan	64, 65
5.	Cyanidin 4′-O-glucoside	*H. esculentus*	25
6.	Cyanidin 3,4′-di-O-glucoside	*H. esculentus*	25
7. Cyanin	Cyanidin 3,5-di-O-glucoside	*H. mutabilis L.*	51
8. Mecocyanin	Cyanidin 3-O-gentiobioside*	*H. rosea sinensis*	43
9. Keracyanin	Cyanidin 3-O-rutinoside	*Abutilon indicum*	23
		Thespesia populnea (L) Sol.	68
10.	Cyanidin 3-O-sophoroside	*Hibiscus roas-sinensis L.*	73
		H. schizopetalus (Mast) Hook.	73
11.	Cyanidin 3-O-sophoroside 5-O-glucoside	*Hibiscus roas-sinensis L.*	23
12.	Cyanidin 3-O-ß-(2gl-glucosylrutinoside)	*Hibiscus sabdariffa L.*	23
13.	Cyanidin 3-O-malonylglucoside	*Hibiscus syriacus*	68
14.	Cyanidin 3-O-sambubioside	*Abelmoschus esculentus (L.)*	73
		A. manihot (L.)	73
		Medicus	
		A. moschatus Medicus	73
		H. archboldiamus	73
		Borss	73
		H. grewiifolius Hassk	73
		H. sabdariffa L.	73
		H. surattensis L.	73
		H. mutabilis L.	73
		H. brackinridgei	81
		H. sabdariffa var. sabdariffa	
15. Ilicicyanin	Cyanidin 3-O-xylosylglucoside	*G. hirsutum*	84, 92
		H. mutabilis	
16.	Cyanidin 3-rutinoside 5-glucoside	*H. mutabilis*	92
Peonidin	3,4′,5,7-Tetrahydroxy-3′-O-methylflavylium		

TABLE 2. Distribution of Anthocyanin Glycosides in Plants of the Malvacaeae

Name	Structure	Plant	Literature
17.	Peonidin 3-O-glucoside	*Hibiscus syriacus* *Alcea rosea*	68
18.	Peonidin 3-O-malonylglucoside	*Hibiscus syriacus*	68
Delphinidin	3,3′,4′,5,5′,7-Hexahydroxyflavylium		
19. Myrtillin	Delphinidin 3-O-ß-D-glucoside	*H. cannabinus var. simplex* *H. cannabinus var. purpureus* *H. cannabinus var. viridis* *H. cannabinus var. vulgaris* *H. manihot* *H. trionum* *H. faradei* *H. syriacus* *H. sabdariffa* *H. sabdariffa var. sabdariffa* *Alcea rosea* *Alcea rosea var. nigra* *Malva sylvestris* *Alceae broussonetifolia*	64 64 64 64 64 64 64 64 73 81 62, 66, 75 80 61 61
20. Cannabinin	Delphidinin 3-O-[O-ß-D-xylopyranosyl-(1→4)-ß-D-glucoside]	*Hibiscus cannabinus* *H. manihot* *H. trionum*	64 64 64
21. Delphin	Delphinidin 3,5-di-O-glucoside	*Alcea rosea* *Alcea rosea var. nigra* *Anoda hastata*	62, 66, 75 80
22.	Delphinidin 3-O-malonylglucoside	*Hibiscus syriacus*	68
23.	Delphinidin 3-O-sambubioside	*H. cannabinus L.* *H. sabdariffa L.* *H. brackinridgei*	73 73 73
Petunidin	3,4′,5,5′,7-pentahydroxy-3′-O-methylflavylium		
24.	Petunidin 3-O-glucoside	*Hibiscus syriacus* *Alcea rosea*	68
25.	Petunidin-3-O-malonylglucoside	*Alcea rosea var. nigra* *H. syriacus* *Alcea rosea**	68, 80
Malvidin	3,4′,5-Tetrahydroxy-3′,5′-di-O-methylflavylium		
Oenin	Malvidin 3-O-ß-D-glucoside	*Hibiscus syriacus* *Alcea rosea* *Malva sylvestris* *Alcea rosea var. nigra*	68 62, 66, 75 61, 62 80
27. Malvin	Malvidin 3,5-di-O-ß-D-glucoside	*Alcea rosea var. nigra* *Malva sylvestris* *Alcea rosea*	80 61, 62 62, 66
28.	Malvidin 3-O-malonylglucoside	*Hibiscus syriacus* *Alcea rosea*	68
29.	Malvidin 3-O-(6ð-malonylglucoside) 5-O-glucoside	*Malva sylvestris L. var. mauritiana*	69

*Now believed to be the 3-O-sophoroside — Translator.

**Peonidin 3-O-malonylglucoside, petunidin-3-O-glucodside petunidin-3-O-malonylglucoside, and malvidin 3-O-malonylglucoside were detected by the authors in *Alcea rosea*, but no details were published.

and quercetin 4'-O-glucoside [22-24]. In total, at the present time, the presence of 21 flavonols and their glycosides in the cotton plant has been shown.

Of plants of the genus *Hibiscus* [1, 2], which are represented by more than 600 species, only nine have been studied for the presence of flavonols; in addition to glycosides of kaempferol, quercetin, and gossypetin, their flowers have yielded glycosides of myricetin and of hibiscetin [18, 23, 25, 26-38].

Besides plants of the genera *Gossypium* and *Hibiscus*, some representatives of the genera *Thespesia*, *Altheae*, and others have been studied for the presence of flavonols [23, 30, 39-42] (Table 1). It must be mentioned that Table 1 includes a number of flavonol glycosides the structures of the sugar moities of which have not been definitively established.

Thus, flavonols of plants of the Malvaceae family are represented by glycosides of kaempferol, quercetin, myricetin, herbacetin, gossypetin, and hibiscetin, the most widespread being those of quercetin and kaempferol. Characteristic for the majority of the representatives of this family that have been studied are flavonols containing a hydroxy group in the C-8 position. It must be mentioned that glycosides of herbacetin and of hibiscetin are found most frequently in plants of the genus *Hibiscus* and some species of the genus *Gossypium*.

As already mentioned, the majority of flavonoid compounds are found in plants in the form of glycosides. An important stage in their investigation is, therefore, the determination of the structure of the carbohydrate moiety of the molecule and its relationship to the aglycon. Chemical and spectral methods are used for this purpose [43-46]. The most informative method in the determination of the structures and stereochemistries of the flavonoid glycosides is PMR spectroscopy. Thus, on the basis of a systematic study of the PMR spectra of a whole series of flavonoid glycosides (O-arabinosides, -xylosides, and -rhamnosides) and of their trimethylsilyl ethers and acetates, G. G. Zapesochnaya [47-49] has found a correlation between the parameters of the PMR spectra and the structures and stereochemistries of these compounds. As a result, the structures of the aglycons and of the carbohydrate moieties and the configurations of their bonds, the sizes of the rings, and the conformations of the carbohydrate moieties of more than 50 compounds, including natural acyl derivatives, have been established. On the basis of the results obtained [47-49] and information in the literature [50], she put forward a hypothesis of the predominance of the existence of carbohydrate residues (rhamnose, xylose, glucose, and galactose) in glycosides in the pyranose form. For aldoses of the *L*-series an α-glycosidic bond of the carbohydrate moiety with the aglycon is preferable, and for aldoses of the *D*-series, a β-glycosidic bond [4, 9]. In view of this, the structures of the sugar moieties of a number of flavonol glycosides given in Table 1 (4, 8, 9, 10, 13, 21) are improbable and require further investigation.

Mass spectrometry, especially field desorption mass spectrometry, also give useful information in the structural analysis of flavonoid glycosides and, especially, their acyl derivatives [49]. In the spectra of acetyl derivatives of monoglycosides, the main peak of the molecular ion is accompanied by the peak of a fragmentary ion with the mass of the acetylated carbohydrate fragment, the intensity of this peak depending on the size of the sugar ring and on the position of its attachment to the aglycon. In the case of flavonoid glycosides acylated by phenolic acids, in their mass spectra, the ions of the deacylated analogues are formed in addition to the molecular ions, the ions of the aglycons, and those of the acylated sugar.

Particularly interesting is the fact that in the ionization of the glycosides acylated by cinnamic acid the acyl residue migrates from the carbohydrate moiety to the aglycon, leading to the formation of ions with the mass values of the acylated aglycon. The corresponding rearrangement peak, and also the peak of the acylated sugar, may be diagnostic in the spectroscopy of natural glycosides acylated in the carbohydrate moiety [49].

The next group of flavonoids of plants of the Malvaceae family to be studied was the anthocyanins. Anthocyanins — some of the most widely distributed group of flavonoids in the plant kingdom — are water-soluble nonplastid pigments imparting various colors to plant tissues — from pink to black-violet. They are present in almost all parts of the plants but accumulate mainly in the flower petals, the fruit and the leaves. At the present time, the anthocyanins of numerous species of plants belonging to more than 100 families have been investigated, and already more than 20 anthocyanidins and about 250 of their glycosides are known [51-55].

The anthocyanins of plants of the *Malvaceae* family have remained little studied. There are only a few publications on this question in the literature. Thus, cyanidin 3,5-di-O-glucoside has been isolated from flowers of *Hibiscus mutabilis* [56], cyanidin 3-O-gentiobioside from *H. rosea sinensis* [51]. and cyanidin 4'-O-glucoside and cyanidin 3-O-glucoside 4'-O-glucoside from *H. esculentus* [25]. In addition, the presence of cyanidin 3-O-sophoroside 5-O-glucoside in the flowers of *H. rosea sinensis*, of cyanidin 3,5-di-O-glucoside and cyanidin-3-(2^{gl}-glucosylrutinoside in the flowers of *H. sabdariffa*, and of cyanidin 3-O-rutinoside in the flowers of *Abutilon indicum* has been shown chromatographically [23].

A systematic investigation of the anthocyans of plants of the Malvaceae family and, in particular, the cotton plant of various species (*Gossypium* sp.), kenaf (*Hibisus cannabinus*), hollyhock (*Alcea rosea*), high mallow (*Malva sylvestris*),

TABLE 3. Total Amounts of Flavonoids (Catechins, Leucoanthocyanidins, Proanthocyanidins, and Anthocyanins) in some Plants of the Malvaceae Family

Genus, species, and variety of plant	Catechins, leucoanthocyanidins, and proanthocyanidins, %					Anthocyanins, %
	Bark of the stems	Bark of the roots	Valves of the capsules	Seed coats	Leaves	Flowers
1. *G. hirsutum mexicanum* var.	11.64	15.16	7.30	—	—	—
nervosum Watt.						
var: 108-F	5.78	7.63	5.80	6.34	3.15	2.0
152-F	5.59	7.34	6.43	7.12	3.9	—
8196	5.86	8.37	6.72	7.12	3.54	—
315-F	4.98	6.36	5.59	5.86	3.84	5.5
2. *G. barbadense* L.						
var.: 5904-I	5.60	6.87	6.35	7.32	3.66	0.8
Paraguay (Cuba)	7.96	10.18	—	—	—	—
Carpylla BA-4-28	8.00	9.42	—	—	—	—
3. *G. arboreum* var.: C-7065	4.65	6.36	6.20	5.86	4.00	3.1
4. *G. herbaceum* var.: C-7082	5.17	7.12	5.80	6.15	3.80	0.7
5. Hibiscus cannabinus:						
var. *simplex L.*	1.27	2.00	2.84	2.15	—	5.8
var. *purpureus*	1.55	1.63	2.15	—	2.08	3.9
var. *viridis*	1.86	2.45	2.13	—	—	2.8
var *vulgaris* var. 3876	2.45	2.62	2.84	3.00	1.15	2.6
6. *H. manihot L.*	—	—	—	0.80	—	—
7. *H. syriacus*	—	—	—	1.30	—	—
8 *H. esculentus*	—	—	—	2.10	—	—
9. *Hibiscus sp.*						
var.: M. Gorkii	3.70	4.34	3.20	3.26	4.00	10.6
Kolkhoznita	3.35	5.00	2.80	3.84	2.75	5.1
Krasnyi partizan	2.62	4.75	—	4.12	3.54	4.5
Kisil Uzbekistan	2.84	4.60	3.00	—	3.20	4.8
10. *Alcea rosea*	—	—	—	—	—	11.8
11. *Malva sylvestris*	—	—	—	—	—	8.1
12. *Althe broussonetifolia*	—	—	—	—	—	2.1
13. *Anoda hastata*	—	—	—	—	—	3.2

shrub althaea (*Hibiscus syriacus*), hybrid forms of hibiscus (*Hibiscus* sp.), *Althaea broussonetifolia*, and *Anoda hastata*, etc., has been begun by A. S. Sadykov et al. [57-63].

Table 3 gives information on the amounts of anthocyans in the plants mentioned above. The amounts of the anthocyan pigments were determined by a colorimetric method from calibration graphs plotted on the basis of standard samples of anthocyans isolated from some source or other. The optical densities of the standard and trial solutions were measured on a FÉK-56 M photoelectric colorimeter in cells with a layer thickness of 1 cm, using a No. 6 filter.

As can be seen from Table 3, the flowers of shrub althea (*Hibisucs syriacus*), of high mallow (*Malva sylvestris*), of hybrid forms of hibiscus (*Hisbiscus* sp.), and of hollyhock (*Alcea rosea*) are distinguished by a higher content of anthocyan glycosides than other species of plants of this family.

The qualitative compositions of the anthocyanin pigments of plants of the Malvaceae family also differ fairly considerably from genus to genus. Thus, characteristic for plants of the genus *Gossypium* is the formation of cyanidin glycosides — chrysanthemin (cyanidin 3-O-β-*D*-glucopyranoside) and gossypicyanin (cyanidin 3-O-[O-β-*D*-xylopyranosyl-(1→4)-glucopyranoside]).

Many species of plants of the genus *Hibiscus* contain mainly delphinidin glycosides. Thus myrtillin (delphinidin 3-O-β-*D*-glucoside and cannabinin (delphinidin 3-O-[O-β-*D*-xylopyranosyl-(1→4)-β-*D*-glucopyranoside]) have been isolated from petals of various *Hibiscus* species (Table 2).

It must also be mentioned that anthocyanin glycosides of representatives of the genus *Gossypium* and some representatives of the genus *Hibiscus* (different varieties of kenaf), even though they differ by the structures of their aglycons, are characterized by the presence of similar types of carbohydrate residues. Thus, the main anthocyanin glycosides of various species of the cotton plant are cyanidin 3-O-β-*D*-glucopyranoside and cyanidin 3-O-[O-β-*D*-xylopyranosyl-(1→4)-β-*D*-glucopyranoside]. The anthocyanin glycosides of kenaf are represented by delphinidin 3-O-β-*D*-pyranoside and delphinidin 3-O-[O-β-*D*-pyranosyl-(1→4)-β-*D*-glucopyranoside. Delphinidin glycosides havae also been found in the flowers of *Althea broussonetifolia*, *Anoda hastata*, and *Malva sylvestris*.

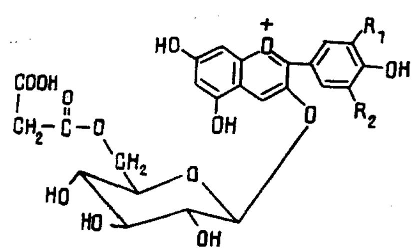
Some species of the genus *Gossypium* contain fairly considerable amounts of anthocyanin pigments. Thus, the flowers of cotton plants of the species *G. hirsutum* and *G. arboreum*, unlike the species *G. barbadense* and *G. herbaceum*, contain about 5.5% of anthocyanins.

Among the plant species investigated, the largest amount and the most complex set of anthocyanin glycosides have been found for the flowers of *Alcea rosea*, *Malva sylvestris*, and *Hisbiscus syriacus*. Thus, in the flowers of *Alcea rosea*, in addition to cyanidin glycosides, various glycosides of peonidin, delphinidin, and malvidin were found (see Table 2). From the flowers of *Hibiscus syriacus* were isolated and identified the 3-O-glucosides of cyanidin, peonidin, delphinidin, petunidin, pelargonidin, and malvidin, and also the 3-malonylglucosides of the aglycons mentioned. The main anthocyanidin pigments of the flowers of *Malva sylvestris* are glycosides of delphinidin and of malvidin.

The anthocyanins of the flowers of *Hisbiscus esculentus* are represented by glycosides of cyanidin — cyanidin 4′-O-glucoside and cyanidin 3,4′-di-O-glucoside, and the flowers of *H. rosea sinensis* by cyanidin 3-gentiobioside and cyanidin 3-O-sophoroside 5-O-glucoside.

A number of investigators [68-74] have shown the presence of malonylated anthocyanin glycosides in some species of plants of the Malvaceae and other families. Thus, the new anthocyanin malvidin 3-O-(6″-O-malonylglucoside) 5-O-glucoside has been detected in wild and cultivated forms of *Malva sylvestris* [69].

From *Hibiscus syriacus* [73] have been isolate malonylated glycosides of delphinidin (1), cyanidin (2), petunidin (3), pelargonidin (4), peonidin (5), and malvidin (6):



	R_1	R_2
1	OH	OH
2	OH	H
3	OMe	OH
4	H	H
5	OMe	H
6	OMe	OMe

We have also isolated malonylated glycosides of anthocyanins from some species of *Hisbiscus* and from *Malva sylvestris* and *Alcea rosea* growing in Uzbekistan.

In total, six anthocyanidins (pelargonidin, cyanidin, peonidin, delphinidin, petunidin, and malvidin) and 24 of their glycosides have been isolated from plants of the Malvaceae family [57-67, 75]. A new anthocyanin — gossypicyanin (cyanidin 3-O-[O-β-D-xylopyranosyl-(1→4)-β-D-glucopyranoside]) has been isolated from the flowers of a hybrid form of hibiscus and the cotton plant. A new delphinidin glycoside — cannabinin (delphinidin 3-O-[O-β-*D*-xylopyranosyl-(1→4)-β-*D*-glucopyranoside]) has been isolated from flowers of kenaf, *H. cannabinus* var. *syriacus*.

This anthocyanin has also be detected in flowers of other species of kenaf — *H. cannibinus* var. *purpureus*, *H. cannabinus* var. *viridis*, and *H. cannabinus* var. *vulgaris*.

For the first time, myrtillin, oenin, and malvin have been isolated from the flowers of high mallow, and chrysanthemin, peonidin 3-O-β-*D*-glucoside, oenin, malvin, and delphin from the hollyhock. Myrtillin and delphin have also been isolated for the first time from the flowers of *Althea broussonetidifolia* and *Anoda hastata*.

As can be seen from the facts given, the main anthocyanins of the plants studied are glycosides of cyanidin and of delphinidin. However, in some plants of this family, such as *Malva sylvestris*, *Alcea rosea*, and *H. syriacus*, together with these, glycosides of methylated anthocyanidins — peonidin, petunidin, and malvidin — have been found. Malonylglycosides of anthocyanidins have also been found in the flowers of *Hibiscus syriacus*.

TABLE 4. Qualitative Compositions of the Flavonoids of Some Plants of the Malvaceae Family*

Genus, species, and variety of plant	Polyphenols detected and isolated				
	Bark of the stems	Bark of the roots	Seed coats	Valves of the capsules	Leaves
1. *G. hirsutum mexicanum* var. *nervosum* Watt. var: 108-F 152-F 8196 315-F	(+)—C, (±)—GC, PA, LC, LD The compounds indicated have also been found in other varieties and species of the cotton plant				(+)—C, (±)—GC, PA, LC, Chr
2. *G. barbadense* L. var. 5904-I Paraguay (Cuba) Carpylla BA-4-28					
3. *G. arboreum* L. var. C-7065					
4. *G. herbaceum* var. C-7082					
5. *Hibiscus cannabinus*: var. simplex L.	(±)—GC, PAs, Chr	(+)—C, (±), GC, PAs	(+)—C, PAs	—	
var. *purpureus* L.	(±)—GC, LC, Chr	(±)—GC, PA, LC	(±)—GC, LC, PAs	(±)—GC, PAs	Chr, LC, Chr
var. *viridis*	—	(—)—EC, PA	(±)—GC, PAs	—	—
var. *vulgaris*	—	(—)—EC, PA, LC, LD	(—)—EC, PA, LC, LD	(±)—GC, PAs	—
6. *H. manihot*	—	—	(±)—GC, PAs	—	—
7. *H. syriacus*	—	—	(±)—GC	—	
8. *H. esculentus*	—	—	(±)—GC, PA	—	—
9. *Hibiscus sp.* var. M. Gor'kii	(±)—GC, (—)—EC, PAs, LC, (+)—C	(+)—C, LC	(—)—EC, LC	(+)—C, PAs, LC	(±)—GC, (—)—EC, PA, LC, (+)—C
Kolkhoznitza	(±)—GC, (—)—EC, PAs, LC, (+)—C	(+)—C, LC	(—)—EC, LC	(+)—C, PAs, LC	(±)—GC, (—)—EC, (+)—C, PA, LC
Krasnyi partizan	(±)—GC, (—)—EC, (+)—C, PAs, LC	(+)—C, LC	(—)—EC, LC	(+)—C, PAs, LC	(±)—GC, (—)—EC
Kuzil Uzbekistan	(±)—GC, (—)—EC, (+)—C, PAs, LC	(+)—C, LC	(—)—EC, LC	(+)—C, PAs, LC	(±)—C, PA, LC

*(+)-C = (+)-catechin; (±)-GC = (±)-gallocatechin; (−)-EC = (−)-epicatechin; LK = leukoanthocyanodin; LD = leukodelphinidin; PAs = proanthocyanidins; Chr = chrysanthemin.

The main sugar components of monosides of anthocyans in plants of the Malvaceae family are glucose and xylose. However, in some plants biosides have also been found the carbohydrate moiety of which is represented by gentiobiose, rutinose, sophorose, etc.. In anthocyans of plants of the Malvacaeae family, glycosylation takes place most frequently at the OH group in the C-3 position.

A comparative analysis of the chemical compositions of the anthocyanin pigments of plants of the Malvaceae family has shown that many genera of plants differ considerably with respect to the composition of their anthocyans. The capacity of many species of plants of this family for elaborating a definite type of anthocyans is a biochemical marker of them that, as results that we have obtained have shown, can be used for the systematics of plants.

As a result of investigations performed together with the Institute of Botany of the Academy of Sciences of the Republic of Uzbekistan, promising sources for obtaining natural food dyes have been revealed and a technology for the production of a dye from hollyhock flowers has been developed and introduced into the Chartak experimental factory for food preparations of the Uzpishcheprom concern.

Plants of the Malvaceae family have also been studied for their content of catechins, leucoanthocyanidins, and proanthocyanidins. It has been shown that catechins are present in considerable amounts in the cotton plant, kenaf, and hybrid forms of hibiscus, while in plants of the genera *Malva* L., *Alcea* L., *Althea* L., and *Anoda* Cav. their amount is fairly low [76-78]. Five catechins have been isolated from the above-mentioned plants. On the basis of a study of the chemical and physicochemical properties of the substances themselves and the products of their cleavage, and also spectral characteristics, the substances isolated have been identified as (+)-catechin, (±)-gallocatechin, (−)-epigallocatechin, (−)-epicatechin, and (−)-epigallocatechin gallate. In addition, the presence of leukocyanidin and of leukodelphinidin has been shown in the plants studied (Table 4).

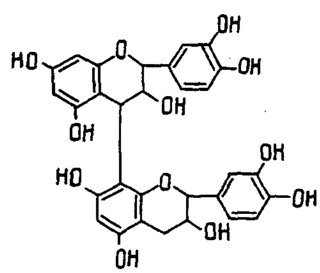
A study of the PMR spectra of the catechins and their acetyl derivatives also confirmed their structures. The parameters found for the signals of the protons of C_2 and C_3 (ring *C*) and the characteristic change on acetylation permitted an unambiguous assignment of the catechins isolated to the normal or the epi- series [78].

The catechins of the cotton plant were represented by (+)-catechin, (±)-gallocatechin, (−)-epigallocatechin, and (−)-epicatechin, the amount of the first two predominating [77].

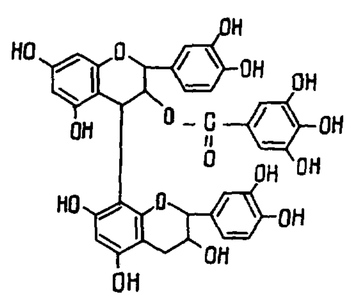
With respect to the compositions of the catechins, the hybrid hibiscuses were close to the cotton plant. In plants of the genus *Gossypium* (*G. hirsutum*, *G. barbadense*, *G. arboreum*, and *G. herbaceum*, in contrast to other genera of the Malvaceae family, in addition to catechins and glucoanthocyanins, considerable amounts of proanthocyanidins accumulated, their maximum amount being found in the bark of the roots, and the seed coats of wild species of cotton. The amount of proanthocyanidins in the flavonoid complex is more than 70%. The amount of catechins and proanthocyanidins in species of the genus *Hibiscus* are considerably lower than in the cotton plant.

Two proanthocyanidins have been isolated from the roots and stems of the cotton plant, and these are the products of the condensation of (+)-catechin (−)-gallocatechin, leucodelphinidin, and leucocyanidin, as has been shown by study of the products of hydrolysis under various conditions both of the proanthocyanidins themselves and of the products of their cleavage. The proanthocyanidins isolated were similar with respect to the compositions of their flavan units from which they were formed but differed in their degrees of condensation. Judging from the relative ease of hydrolysis with sulfuric acid, the bonds between the flavan units in both compounds were formed, in all probability, at the C_4 and C_8 or (C_6) positions.

Two proanthocyanidins, B-5 and B-6 [79] have been isolated from the roots of *Hibiscus cannabinus* [79] and for these, on the basis of a study of the products of their transformation and spectral characteristics, the most probable structures of (I) and (II), respectively, have been proposed:



I



II

Thus, the flavonoids of plants of the Malvaceae family are represented by flavonol and anthocyanin glycosides, catechins, leucoanthocyanidins, and the products of their condensation — proanthocyanidins. The flavones, in their turn, are represented by glycosides of kaempferol, quercetin, myricetin, herbacetin, gossypetin, and hibiscetin, the quercetin and kaempferol glycosides being the most widely distributed. Characteristic for the majority of representatives of this family that were studied are flavonols in which there is a hydroxy group in the C-8 position. It must be mentioned that glycosides of herbacetin, gossypetin, and hibiscetin are found most frequently in plants of the genus *Hibiscus* and some species of the genus *Gossypium*.

As a result of the study of the anthocyanin pigments of plants of the Malvaceae family, extremely valuable plants have been found which contain considerable amounts of anthocyanins and are recommended as raw material for obtaining a red food dye. One of them, the hollyhock, has been introduced into cultivation by the Institute of Botany of the Academy of Sciences of the Republic of Uzbekistan. The production of a dye from hollyhock flowers has been organized by a developed technology in the Chatak experimental factory for food concentrates of the Uzpishchiprom concern and is being marketed in the form of a concentrate and a powder and used for coloring nonalcoholic and liqueur-vodka beverages, confectionery, and sausage articles, and dry kiffels, and for marking meat carcases and eggs, and it is also used in the pharmaceutical and perfumery industries.

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