

## Flavonoid Components in Plants of the Genus *Scutellaria*

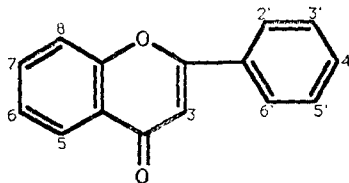
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**Abstract**—*Scutellariae* plants contain a large number of flavonoids and in addition, many of them are with unusual A- and/or B-ring substitutions. The total number of flavonoids reported up to the middle of 1991 are 137 including 89 of flavones, flavonols and their glycosides including 3 C-glycosides(1~89), 39 of flavanones, dihydroflavonols and their glycosides(90~128), 8 of chalcones(129~136) and one biflavonoid, 8,8''-bibaicalein(137). More than half of the flavonoids are with either unusual 5-methoxy(2'-methoxy in case of chalcones) in A-ring and/or 2'-oxygenation(2-oxygenation in case of chalcones) in B-ring substitutions. Four flavones, four flavanones and two chalcones are with methylation at 5-OH(2'-OH in case of chalcones) and six of them also have 2'-oxygenations(2- in case of chalcones). Sixtyeight out of total 137 flavonoids have oxygenated substitution at 2'-(2- in case of chalcones) position of B-ring and in addition, 27 of them have another oxygen function at 6'-(6- in case of chalcones) and 18 of them have additional oxygen substitutions either at 3'-, 5'-, 3',6'- or 3',4',5'-(3,4,5- in case of chalcones) positions. The distribution and isolation of flavonoid components of *Scutellariae* plants are tabulated with references.

*Scutellariae* plants are either annual or perennial herbs of the family Labiatae, which is distributed in the wide geographical region. Several *Scutellariae* plants have been used for various purposes in many countries as traditional medicines. Especially the roots of *Scutellaria baicalensis* have been considered as one of the most important medicines in the traditional oriental medicines and used for the treatment of various inflammatory diseases, suppurative dermatitis, fever, allergic, hyperlipemia and arteriosclerosis related diseases. The leaves of *S. discolor* and *S. scadens* have been used for colds, cuts and insect stings, the whole herb of *S. indica* as an antidotic, analgesic and hemostatic for the treatment of hemoptysis, hematemesis and other diseases and the whole herb of *S. rivularis* for the treatment of tumors, hepatitis, liver cirrhosis

*etc.* During the course of our study on the isolation of the biologically active flavonoid components from *S. baicalensis*, it was learned that *Scutellariae* plants contain a large number of flavonoids and in addition, several of them are with unusual A- and/or B-ring substitutions. The purpose of this review is to present the distribution of various flavonoids in plants of the genus *Scutellaria* and particularly the distribution of the unusually substituted flavonoids. The total number of flavonoids reported up to the middle of 1991 are 137 and they are tabulated in Tables I ~ III. They include 89 flavones, flavonols and their glycosides including 3 C-glycosides(1~89 in Table I), 39 of flavanones, dihydroflavonols and their glycosides(90~128 in Table II), 8 of chalcones(129~136) and one biflavonoid, 8,8''-bibaicalein(137). In the Tables,

Table I. Flavones and flavonols of *Scutellariae* plants

Comp.	Trivial name	3	5	6	7	8	2'	3'	4'	5'	6'
Di-Oxygen substituted											
1	chrysin		OH		OH						
2			OH		OglA						
3			OH		Oglu						
Tri-Oxygen substituted											
4	baicalein		OH	OH	OH						
5			OH	OglA	OH						
6	baicalin		OH	OH	OglA						
7	galeroside		OH	OH	Orha						
8			OH	OH	Oglu						
9	oroxylin A		OH	OMe	OH						
10	oroxyloside		OH	OMe	OglA						
11			OH	OMe	Oglu						
12*			OH	OH	OMe						
13	oratin		OMe	OMe	Oglu						
14	norwogonin		OH		OH	OH					
15			OH		OglA	OH					
16			OH		OH	OglA					
17	wogonin		OH		OH	OMe					
18			Oglu		OH	OMe					
19	wogonoside		OH		OglA	OMe					
20			OH		OMe	OMe					
21			OMe		OH	OMe					
22			OMe		OglA	OMe					
23			OH		OH		OH				
24			OH		OglA		OH				
25			OH		OH		OMe				
26			OH		OglA		OMe				
27	apigenin		OH		OH				OH		
28			OH		OglA				OH		
29	cosmosiin		OH		Oglu				OH		
30	isoroifolin		OH		Orha-(1→6)-Oglu				OH		
31	tilianin		OH		Oglu				OMe		
32	linarin		OH		Orut				OMe		
Tetra-Oxygen substituted											
33			OH	OMe	OMe	OH					
34	ikonnikoside		OH	OH	OglA		OH				
35	tenaxin II		OH	OMe	OH		OH				
36	scutellarein		OH	OH	OH				OH		
37	scutellarin		OH	OH	OglA				OH		

Comp.	Trivial name	3	5	6	7	8	2'	3'	4'	5'	6'
38			OH	OH	Oglu				OH		
39	hispidulin(dinatin)		OH	OMe	OH				OH		
40			OH	OMe	OglA				OH		
41			OH	OMe	Oglu				OH		
42	pectolarigenin		OH	OMe	OH				OMe		
43	salvigenin		OH	OMe	OMe				OMe		
44			OH		OglA	OH	OH				
45	scutevulin		OH		OH	OMe	OH				
46			OH		OglA	OMe	OH				
47			OH		OMe	OH	OH				
48			OH		OH	OMe	OMe				
49			OH		Oglu	OMe	OMe				
50 <sup>18)</sup>	skullcapflavon I** (panicolin)		OH		OMe	OMe	OH				
51			OH		OMe	OMe	OMe				
52			OMe		OH	OMe	OMe				
53	isoscutellarein		OH		OH	OH			OH		
54			OH		OglA	OH			OH		
55			OH		OH	OglA			OH		
56			OH		OH	OMe			OH		
57			OH		OH		OH	OH			
58			OH		OH		OH				OH
59			OH		OH		OH				OMe
60	luteolin		OH		OH			OH	OH		
61			OH		OglA			OH	OH		
62	cynaroside		OH		Oglu			OH	OH		
Penta-Oxygen substituted											
63	viscidulin I	OH	OH		OH		OH				OH
64			OH	OH	OMe	OMe	OH				
65			OH	OMe	OMe	OMe	OH				
66	tenaxin I		OH	OMe	OMe	OMe	OH				
67			OH	OH	OH			OH	OH		
68			OH	OH	OglA			OH	OH		
69			OH	OMe	OH			OH	OH		
70	cirsilineol		OH	OMe	OMe			OMe	OH		
71 <sup>19)</sup>	rehderianin I**		OH		OMe	OMe	OH			OH	
72			OH		OH	OMe	O-(2-C-caffeoyl)glu				OH
73			OH		OH	OMe	OH				OMe
74	viscidulin II		OH		OMe	OMe	OH				OH
75			OH		OMe	OMe	OglA				OH
76			OH		OH	OMe	OMe				OMe
77	rivularin		OH		OMe	OMe	OH				OMe
78			OH		OMe	OMe	OglA				OMe
79	altisin		OH		OMe	OMe	OMe				OMe
Hexa-Oxygen substituted											
80	koganebananin		OH	OMe	OH	OMe	OMe	OMe			
81			OH	OMe	OMe	OMe	OH			OH	

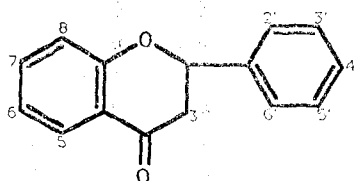
Comp.	Trivial name	3	5	6	7	8	2'	3'	4'	5'	6'
82			OH	OH	OMe	OMe	OH				OH
83			OH	OH	OMe	OMe	OH				OMe
84			OH	OMe	OMe	OMe	OH				OH
85	skullcapflavone II (neobaicalein)		OH	OMe	OMe	OMe	OH				OMe
86 <sup>19)</sup>	ganhuangenin** (viscidulin III)		OH		OH	OMe	OMe	OH			OH
C-Glycosyl											
87			OH	Ara	OH	Glu					
88			OH	Glu	OH	Ara					
89	vicenin II		OH	glu	OH	glu			CH		

glA : glucuronic acid, glu : glucose, rha : rhamnose, rut : rutinose.

\* Detected only by TLC<sup>1)</sup>

\*\* Structural revisions were made from the first assigned structures.

Table II. Flavanones and dihydroflavonols of Scutellariae plants

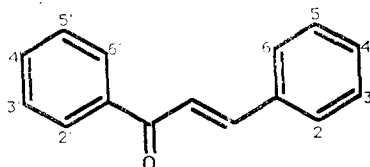


Comp.	Trivial name	3	5	6	7	8	2'	3'	4'	5'	6'
Di-Oxygen substituted											
90	pinocembrin		OH		OH						
91	alpinetine		OMe		OH						
Tri-Oxygen substituted											
92	(2R, 3R)	OH	OH		OH						
93	dihydrobaicalein		OH	OH	OH						
94	dihydrobaicalin		OH	OH	OglA						
95	dihydrooroxylin A		OH	OMe	CH						
96	dihydronorwogonin(2S)		OH		OH	OH					
97			OH		OglA	OH					
98	(2S)		OH		OH		OH				
99	naringenin		OH		OH				OH		
Tetra-Oxygen substituted											
100	(2R, 3R)	OH	OH		OH		OH				
101	isocarthamidin		OH	OH	OH				OH		
102			OH	OH	OglA				OH		
103			OH	OMe	OH				CH		
104	(2S)		OH		OH	OMe	OH				
105	(2S)		OH		OH	OMe	OMe				
106	(2S)		OMe		OH	OMe	OMe				
107	carthamidin		OH		OH	OH			OH		
108	(2S)		OH		OglA	OH			OH		
109	(±)		OH		OH	OMe			OH		

Comp.	Trivial name	3	5	6	7	8	2'	3'	4'	5'	6'
110	(2 <i>S</i> )		OH		OH		OH				OH
111	scuteamoenin(2 <i>S</i> )		OH		OMe		OH				OH
112	scuteamoenoside		OH		OMe		Cglu				OH
113	(2 <i>S</i> )		OMe		OH		OH				OH
114	eriodictyol		OH		OH			OH	OH		
Penta-Oxygen substituted											
115	(2 <i>R</i> , 3 <i>R</i> )	CH	OH		OH		OH				OH
116	(2 <i>S</i> )		OH	OMe	OH		OH			OH	
117	(2 <i>S</i> )		OH	OMe	OH		Oglu			OH	
118			OH	OMe	OH		(2-O-feruloyl)glu			OH	
119			OH	OMe	OH		(2-O-sinapoyl)glu			OH	
120			OH	OMe	OH		(2-O-vanilloyl)glu			OH	
121	(±)		OH	OMe	OMe		OH				OMe
122	(2 <i>S</i> )		OH		OMe	OMe	OH			OH	
123			OH		OMe	OMe	Cglu			OH	
124	(2 <i>S</i> )		OH		OMe	OMe	OH				OMe
125	(2 <i>S</i> )		OH		OMe	OMe	CglA				OMe
126			OH		OMe	OMe	CglA Bu ester				OMe
127	(2 <i>S</i> )		CH		OMe	OMe	OMe				OMe
Hepta-Oxygen substituted											
128	(2 <i>S</i> )		OMe	OMe	OMe		OMe	OMe	OMe	OMe	

glA; glucuronic acid, glu; glucose

Table III. Chalcones of Scutellariae plants



Comp.	Trivial name	2'	3'	4'	5'	6'	2	3	4	5	6
129	caldamomin	OH		OH		OMe					
130		OH	OMe	OH		OMe	OMe				
131		OH		OH		OMe	OH				OH
132		OH		OMe	OMe	OMe	OMe	OMe	OMe	OMe	
133		OMe		OMe	OMe	OMe	OMe	OMe	OMe	OMe	
134		OH		OCH <sub>2</sub> O		OMe	OH	OMe	OMe	OMe	
135		OH		OCH <sub>2</sub> O		OMe	OMe	OMe	OMe	OMe	
136		OMe		OCH <sub>2</sub> O		OMe	OMe	OMe	OMe	OMe	

the flavonoids are listed according to the increasing number of hydroxyl groups and the respective methyl ethers and glycosides are placed next to their corresponding hydroxylated flavonoids. The structures are arranged by

number and position, in ascending order, of substituents in ring A, followed by those in ring B. The detection of comp. 12 (7-methoxybaicalin) by TLC was reported from the EtOAc extract of the roots of *S. baicalensis*,<sup>1)</sup> however

Table IV. Flavonoid components isolated from plants of the genus *Scutellaria*

Plants/Part	Comp. number	Ref. number
<i>S. alpina</i>		
roots	1, 2, 4, 6, 9, 10, 14, 17, 19, 39, 45, 56, 84, 85, 137	20
leaves	1, 2, 23, 27, 28, 36, 37	20
<i>S. altissima</i>		
roots	4, 6, 9, 10, 17, 19, 79	21
<i>S. amoena</i>		
roots	1, 9, 14, 35, 58, 63, 85, 92, 96, 100, 110, 111, 112, 115	22, 23
ns	4, 6, 17, 19, 39	24
<i>S. baicalensis</i>		
leaves	1, 17, 27, 28, 36, 43, 53, 55, 101, 102, 107, 108	25, 26
roots	1, 4, 6, 8, 9, 14, 17, 18, 19, 20, 23, 33, 35, 45, 47, 50, 56, 57, 58, 59, 63, 65, 66, 73, 74, 81, 85, 86, 87, 88, 94, 95, 103, 110, 113, 115, 131	27~39
ns	6, 19, 80, 85	40~43
<i>S. barbata</i>		
whole plant	36, 101, 107	44
ns	37	45
<i>S. cretica</i>		
flower	27, 29, 36, 37, 60	46
leaves	27, 29, 36, 37, 60, 62	46
roots	4, 6, 36, 37, 39, 40	46
<i>S. discolor</i>		
aerial parts	1, 2, 16, 17, 27, 48, 56, 60, 72, 76	47
roots	14, 15, 17, 19, 21, 45, 48, 52, 56, 73, 76, 90, 105, 106, 121, 124, 130	48, 49
<i>S. epilobifolia</i>		
ns	93	50
<i>S. galericulata</i>		
aerial parts	4, 6, 7, 27, 29	51
flower, roots, stems	2	52
leaves	1, 2, 4, 6, 7, 9, 10, 17, 19, 27, 28, 36, 37, 60, 61, 67, 68, 93, 94, 96, 97	53
<i>S. granulosa</i>		
roots	25, 26	54
<i>S. grossa</i>		
roots	1, 2, 4, 5, 6, 9, 10, 14, 15, 17, 19, 36, 37, 51, 60, 64, 79, 127	4
<i>S. ikonnikovii</i>		
whole herb	2, 6, 15, 16, 24, 34, 37	55
<i>S. indica</i>		
aerial parts	1, 2, 27, 28, 36, 37, 38, 53, 55, 60, 128, 132, 133, 134, 135, 136	56
roots	17, 19, 45, 48, 49, 56, 74, 77, 91, 98, 104, 121, 122, 123, 124, 125, 126, 129	57, 58
<i>S. karjagini</i>		
roots	27, 37, 61	59
<i>S. likiangensis</i>		
roots	1, 4, 9, 17, 35, 63	60

Plants/Part	Comp. number	Ref. number
<i>S. orientalis</i>		59, 61
roots	1, 2, 3, 4, 6, 17, 19, 27, 37, 39	
<i>S. oreophila</i>		
aerial parts	1, 4, 6, 60, 62	62
<i>S. ovata</i>		
flowers, roots, stems	1, 11, 13, 27, 39, 60, 69	63
<i>S. polyodon</i>		
flowers	30, 31, 32	64
flowers, leaves	36, 37	65
<i>S. prostrata</i>		
roots	1, 2, 4, 6, 9, 10, 15, 17, 19, 23, 25, 26, 45, 46, 50, 56, 77, 82, 83	66
<i>S. przewalskii</i>		
aerial parts	27, 28, 29, 36, 37, 38, 39, 40, 41, 42, 60, 62	67
roots	6	68
<i>S. rehderiana</i>		
roots	4, 6, 9, 17, 19, 71, 86	69, 70
<i>S. rivularis</i>		
aerial parts	17, 21, 27, 36, 39, 45, 56, 60, 77, 99, 103, 109, 114	71, 72
roots	6, 17, 19, 20, 22, 44, 45, 75, 77, 78, 102, 108	71, 73, 74
whole herb	1, 4, 21, 23, 27, 39, 48, 50, 60, 70, 74, 91, 109, 129	75, 76
<i>S. scadens</i>		
leaves	1, 2, 4, 6, 27, 28, 36, 37, 89, 93, 94, 101, 102	5
roots	1, 2, 4, 6, 9, 14, 17, 19, 93, 94, 95, 116, 117, 118, 119, 120	77
<i>S. scordiifolia</i>		
aerial parts	1, 2	54
roots, leaves	1, 2, 4, 6, 9, 17, 27, 36, 60	78
<i>S. squarrosa</i>		
roots	1, 4, 6, 9, 10, 17	79
<i>S. tenax</i>		
roots	4, 6, 9, 17, 19, 63, 66, 85	80
<i>S. viscidula</i>		
roots	4, 6, 9, 17, 19, 50, 63, 74, 85	81
ns	35, 86	82

\* ns: parts were not specified

there appears no report on the isolation of this compound from Scutellariae plants. In Table IV, the distribution of flavonoid components of Scutellariae plants are tabulated. Those flavonoids which were only detected by either HPLC or TLC methods are not included in Table IV. As mentioned above, high proportions of Scutellariae flavonoids are with unusual substitution patterns. Actually, more than half of the flavonoids are with either unusual 5-methoxy

(2'-methoxy in case of chalcones) in A-ring and/or 2'-oxygenation (2-oxygenation in case of chalcones) in B-ring substitutions. Four flavones (13, 21, 22, 52), four flavanones (91, 106, 113, 128) and two chalcones (133, 136) are with methylation at 5-OH (2'-OH in case of chalcones) and six of them (52, 106, 113, 128, 133, 136) also have 2'-oxygenations (2-oxygenation in case of chalcones). Sixtyeight out of total 137 flavonoids have oxygenated substitutions at 2'-(2- in case of

chalcones) position of B-ring and in addition, 27 of them have another oxygen function at 6'-(6- in case of chalcones) (58, 59, 63, 72~79, 82~86, 110~113, 115, 121, 124~127, 131) and 18 of them have additional oxygen substitutions either at 3'-(57, 80), 5'-(71, 81, 116~120, 122, 123), 3',6'-(86) or 3',4',5'-(3, 4, 5- in case of chalcones) positions (128, 132~136).

In his review of minor flavonoids, Bohm described that dihydromorin (5,7,2',4'-tetrahydroxyflavonol) was reported as a component of *S. baicalensis*, and 2',4'-dihydroxy-2,3,6'-trimethoxychalcone as a constituent of *S. discolor*.<sup>2)</sup> However, dihydromorin and any other 2',4'-B-ring substituted flavone or flavonol and any chalcone with 2,3- or 2,4-dioxygenation in B-ring have not been reported from Scutellariae plants upto the date of this review except one report describing the isolation of one flavanone (128) and five chalcones (132~136) with four oxygen substitutions at 2',3',4',5'-(2,3,4,5- in case of chalcones) positions of B-ring from the aerial parts of *S. indica*.

As regards the other constituents of these plants, few reports appeared. They included the isolation of catalpol type iridoids, stilbenes, aurantiamide and other minor phytosterols.<sup>3-6)</sup> More recently, the isolations of various neoclerodane type diterpenoids from *S. galericulata*, *S. rivularis* and *S. woronowii*<sup>7-16)</sup> and a new oleanane type triterpene from *S. rivularis*<sup>17)</sup> were reported.

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