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The Flavonoid Glycosides in the Leaves of *Cornus* Species IV. The Distribution of Flavonoids in Genus *Cornus*

By

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岩科　司*・八田洋章*：ミズキ属植物の葉に含まれるフラボノイド配糖体
IV.ミズキ属におけるフラボノイドの分布

The genus *Cornus* (family Cornaceae) contains about 100 species (Hatta 1994). The center of geographic distribution of the genus is mainly in the Temperate Zone of the northern hemisphere. Until now, iridoid glycosides are widely used in chemotaxonomic studies of the genus (Bate-Smith *et al.* 1975; Jensen *et al.* 1975). On the other hand, a foliar flavonoid has reported from *Cornus controversa* Hemsl. (quercetin 3-*O*-glucoside, Nakaoki and Morita 1958). We observed the flavonoids in *Cornus* species as a series of chemotaxonomic studies. Thus, some flavonal glycosides based on quercetin and kaempferol, e.g. 3-*O*-glucoside, 3-*O*-galactoside, 3-*O*-rhamnoside, 3-*O*-rutinoside or 3-*O*-xylosylgalactoside, were found from nine *Cornus* species, *C. controversa, C. brachypoda* Wall., *C. darvasica* (Pojark.) Pilip., *C. drummondii* C.A. Mey., *C. canadensis* L., *C. suecica* L., *C. capitata* Wall., *C. oblonga* Wall. and *C. macrophylla* Wall. (Iwashina and Hatta 1990, 1992, 1993).

In this paper, the flavonoid profiles of thirty-three *Cornus* taxa including newly surveyed twenty-five species are described for chemotaxonomic studies.

Materials and Methods

Plant Materials

Twenty-five *Cornus* taxa which were newly analyzed in this experiment were collected in place as follows:

Cornus florida L., *C. kousa* Hance, *C. mas* L. and *C. officinalis* Sieb. et Zucc.: Tsukuba Botanical Garden, National Science Museum, Tsukuba, Japan.

C. alternifolia L., *C. amomum* Mill., *C. asperifolia* Michx., *C. australis* C.A. Mey., *C. bretschneideri* Henry, *C. coreana* Wang., *C. foemina* Mill., *C. glabrata* Benth., *C. hemsleyi* C.K. Schneid. & Wang., *C. horseyi* Rehd., *C. iberica* Woronow., *C. obliqua* Raf., *C. paucinervis* Hance, *C. poliophylla* C.K. Schneid. & Wang., *C. racemosa* Lam., *C. sanguinea* L., *C. sericea* L. and *C. walteri* Wang.: Arnold Arboretum, Massachusetts, USA.

C. hongkongensis Hemsl. subsp. *hongkongensis*: Hongkong, Collected by H. Hatta.

C. hongkongensis subsp. *melanotrica* (Pojark.) Q.Y. Xiang and *C. multinervosa* (Pojark.) Q.Y. Xiang: Mt. Emei, Sichuan, China, Collected by H. Hatta.

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Isolation of flavonoids

Fresh leaves of *Cornus* species except *C. hongkongensis* subsp. *hongkongensis* of which dry leaves were used, were extracted with MeOH, concentrated to a small volume and applied to preparative paper chromatography (PPC) using solvent systems, BAW, 15%AcOH and then BEW (see Table 2). Isolated flavonoids were eluted with MeOH and finally purified by sephadex LH-20 column chromatography (solvent system: 70% MeOH).

UV spectra

UV spectra of flavonoids were measured in MeOH according to Mabry *et al.* (1970).

Acid hydrolysis

Complete and mild acid hydrolyses were performed with 12% aq.HCl and 1.2% HCl:MeOH (1:1) according to Iwashina and Hatta (1993).

High performance liquid chromatography (HPLC)

HPLC was carried out according to Hayashi *et al.* (1989).

Identification of flavonoids

The flavonoids were identified by paper chromatographic and HPLC comparisons with authentic specimens, UV spectra and acid hydrolysis as described above.

Results and Discussion

Identification of flavonoids

Thirty-seven flavonoid glycosides were isolated from *Cornus* leaves and twenty-four were completely identified in this experiment (Table 1). Among their glycosides, twelve, i.e. quercetin 3-*O*-glucoside, 3-*O*-galactoside, 3-*O*-glucuronide, 3-*O*-rhamnoside, 3-*O*-rutinoside, 3-*O*-diglucoside and 3-*O*-xylosylgalactoside, and kaempferol 3-*O*-glucoside, 3-*O*-galactoside, 3-*O*-rhamnoside, 3-*O*-rutinoside and 3-*O*-xylosylgalactoside, have been reported in *Cornus* species (Iwashina and Hatta 1990, 1992, 1993; Nair and Rudloff 1960; Delaveau et Paris 1961; Egger und Keil 1969). Remained twelve glycosides which are described below were found from *Cornus* species for the first time.

Myricetin 3-*O*-rhamnoside. UV spectra of the flavonoid, which was isolated from five *Cornus* species, *C. amomum, C. asperifolia, C. glabrata, C. hemsleyi* and *C. horseyi* belonging to subgenus *Kraniopsis*, showed the presence of free 5-, 7-, 3'-, 4'-, 5'- or 5-, 7-, 3'-, 4'-hydroxyl groups (Table 2). By acid hydrolysis, myricetin and rhamnose which were identified by direct PC comparisons with authentic specimens were liberated. Finally, the original flavonoid was identified as myricetin 3-*O*-rhamnoside (myricitrin) by PC and HPLC comparison with authentic specimen. Myricetin glycoside (Fig. 1) was found in *Cornus* species for the first time.

Quercetin 3-*O*-arabinoside and 3-*O*-xyloside. Flavonoids were also isolated from *C. amomum, C. asperifolia, C. glabrata, C. hemsleyi* and *C. horseyi*. UV spectra of the glycosides showed the presence of free 5-, 7-, 3'- and 4'-hydroxyl and a substituted 3-hydroxyl groups (Table 2) (Mabry *et al.* 1970). By acid hydrolysis, quercetin and arabinose, and quercetin and xylose which were identified by direct PC comparisons with authentic specimens were liberated, respectively. Finally, original glycosides were

Table 1. Occurrence of foliar flavonoid glycosides in *Cornus* species

Subgenera / Species		Flavonoids			Reference
		3-monoside	3-bioside	3,7-glycoside	
Mesomora					
C. alternifolia	quercetin	3-glucoside	3-rutinoside*		
		3-rhamnoside			
		3-glycoside			
C. controversa	quercetin	3-glucoside			Iwashina and Hatta (1990)
					Nakaoki and Morita (1958)
Kraniopsis					
C. amomum	myricetin	3-rhamnoside			
	quercetin	3-glucoside	3-rutinoside		
		3-galactoside			
		3-glucuronide			
		3-rhamnoside			
		3-arabinoside			
		3-xyloside			
	kaempferol	3-galactoside			
C. asperifolia	myricetin	3-rhamnoside			
	quercetin	3-glucoside	3-rutinoside		
		3-galactoside			
		3-glucuronide			
		3-rhamnoside			
		3-arabinoside			
		3-xyloside			
	kaempferol	3-galactoside			
C. australis	quercetin	3-glucoside			
	kaempferol	3-glucoside			
C. bretschneideri	quercetin	3-glucoside			
	kaempferol	3-glucoside			
C. coreana	quercetin	3-glucuronide	3-rutinoside		
	kaempferol	3-glucoside			
		3-galactoside			
		3-glucuronide			
C. darvasica	quercetin	3-glucoside			Iwashina and Hatta (1990)
	kaempferol	3-glycoside			
C. drummondii	quercetin	3-glucoside			Iwashina and Hatta (1990)
C. foemina	quercetin	3-glucoside			
C. glabrata	myricetin	3-rhamnoside			
	quercetin	3-glucoside	3-rutinoside		
		3-galactoside			
		3-glucuronide			
		3-rhamnoside			
		3-arabinoside			
		3-xyloside			
	kaempferol	3-galactoside			

Table 1. – (continued) –

Subgenera Species		Flavonoids 3-monoside	3-bioside	3,7-glycoside	Reference
C. hemsleyi	myricetin	3-rhamnoside			
	quercetin	3-glucoside	3-rutinoside		
		3-galactoside			
		3-glucuronide			
		3-rhamnoside			
		3-arabinoside			
		3-xyloside			
	kaempferol	3-galactoside			
C. horseyi	myricetin	3-rhamnoside			
	quercetin	3-glucoside	3-rutinoside		
		3-galactoside			
		3-glucuronide			
		3-rhamnoside			
		3-arabinoside			
		3-xyloside			
	kaempferol	3-galactoside			
C. iberica	quercetin	3-glucoside			
	kaempferol	3-glucoside			
		3-galactoside			
		3-glucuronide			
		3-glycoside			
C. macrophylla	quercetin	3-glucoside			Iwashina and Hatta (1993)
		3-galactoside			
		3-rhamnoside			
C. obliqua	quercetin	3-glucoside	3-rutinoside		
		3-galactoside			
		3-glucuronide			
C. oblonga	quercetin	3-glucoside	3-diglucoside		Iwashina and Hatta (1993)
		3-galactoside			
	kaempferol	3-glucoside			
		3-galactoside			
C. paucinervis	quercetin	3-glucoside	3-rutinoside		
C. poliophylla	quercetin	3-glucoside			
		3-glycoside			
C. racemosa	quercetin	3-glucoside	3-rutinoside		
	kaempferol	3-glucuronide			
C. sanguinea	quercetin	3-glucoside			
C. sericea	quercetin	3-glucoside	3-rutinoside		
	kaempferol	3-glucoside			
C. walteri	quercetin	3-glucoside	3-rutinoside		
		3-glucuronide			
	kaempferol	3-glucoside			
		3-galactoside			
		3-glucuronide			

Table 1. – (continued) –

Subgenera / Species		Flavonoids: 3-monoside	3-bioside	3,7-glycoside	Reference
Arctocrania					
C. canadensis	quercetin	3-galactoside	3-xylogalactoside		Iwashina and Hatta (1992)
			3-glycogalactoside		
	kaempferol	3-glucoside	3-rutinoside		
		3-galactoside	3-xylogalactoside		
		3-glycoside			
C. suecica	quercetin	3-glucoside			Iwashina and Hatta (1992)
		3-galactoside			
	kaempferol	3-glucoside			
		3-galactoside			
Cornus					
C. mas	quercetin	3-glucoside	3-rutinoside		
		3-galactoside	3-diglycoside		
		3-glucuronide			
		3-glycoside			
	kaempferol	3-glucuronide	3-diglycoside		
C. officinalis	quercetin	3-glucoside	3-xyloglucoside		
		3-glucuronide			
	kaempferol	3-glycosides (2)			
Benthamia					
C. capitata	quercetin	3-glucoside	3-xylogalactoside		Iwashina and Hatta (1993)
		3-galactoside			
		3-rhamnoside			
	kaempferol	3-glucoside	3-xylogalactoside		
		3-rhamnoside			
C. hongkongensis	quercetin	3-galactoside			
var. *hongkongensis*	kaempferol			3,7-diglycosides (2)**	
C. hongkongensis	quercetin	3-glucoside	3-rutinoside		
var. *melanotrica*	kaempferol	3-glucoside			
		3-galactoside			
		3-glycoside			
C. kousa	quercetin	3-glucoside	3-rutinoside		
		3-galactoside	3-diglucoside		
	kaempferol	3-glucoside	3-rutinoside		
		3-galactoside	3-diglucoside		
C. multinervosa	quercetin	3-glucoside	3-xylogalactoside	3-glucoside-7-rhamnoside	
		3-rhamnoside		3-galactoside-7-rhamnoside	
	kaempferol			3,7-dirhamnoside	
				3-dirhamnoside	
				3-glucoside-7-rhamnoside	
				3-galactoside-7-rhamnoside	
				3,7-diglycosides (2)	
Cynoxylon					
C. florida	quercetin	3-glucoside	3-xylogalactoside	3,7-diglucoside	

*rutinoside = rhamnosyl (1→6) glucoside.
**Identical with kaempferol 3,7-diglycoside from *C. multinervosa*.

Table 2. UV spectral data of newly isolated flavonol glycosides from *Cornus* species

Glycosides	λ max (nm)					
in	MeOH	+NaOMe	+$AlCl_3$	+$AlCl_3$/HCl	+NaOAc	+NaOAc/H_3BO_3
myricetin 3-rhamnoside	257 356	270 322 404*	273 430	271 300 362 399	272 322 390	261 376
quercetin 3-arabinoside	256 358	272 330 410*	274 437	268 298 363 404	273 324 395	261 378
quercetin 3-xyloside	257 354	272 326 403*	274 432	270 295sh 359 399	273 324 389	261 373
quercetin 3-xyloglucoside	256 356	274 325 411*	275 431	270 296sh 361 396	273 324 393	261 377
quercetin 3-glucoside-7-rhamnoside and 3-galactoside-7-rhamnoside	258 363	272 397*	275 439	270 297sh 368 403	263 393	262 385
quercetin 3,7-diglucoside	257 357	272 396*	275 439	270 297sh 362 400	264 410	261 376
kaempferol 3-glucuronide	266 349	275 324 395*	276 307 355 397	275 304 350 394	274 305 383	266 352
kaempferol 3-diglucoside	266 347	276 327 395*	274 304 353 385sh	275 303 345 386sh	274 309 381	267 351
kaempferol 3,7-dirhamnoside	265 344	272 378*	274 300 348 395	275 298 341 395	263 364	265 346
kaempferol 3-glucoside-7-rhamnoside and 3-galactoside-7-rhamnoside	266 351	273 387*	275 300 352 400	275 295sh 348 397	265 393	265 354

sh = shoulder.
*Remarkable increase in intensity of Band I relative to that in MeOH.

identified as quercetin 3-*O*-arabinoside (avicularin) and quercetin 3-*O*-xyloside by PC and HPLC comparisons with authentic specimens (Table 3).

Quercetin 3-*O*-xylosylglucoside. UV spectra of the flavonoid which was obtained from *C. officinalis* also showed the presence of free 5,7,3',4'-tetraOH and a substituted 3-OH groups (Table 2). PC data of the original glycoside was very similar to those of authentic quercetin 3-*O*-xylosylgalactoside which was isolated from *C. capitata* (Iwashina and Hatta 1993). However, retention time of HPLC was slightly different between their glycosides. Quercetin, xylose and glucose were liberated by complete

Table 3. PC and HPLC data of newly isolated flavonol glycosides from *Cornus* species

Glycosides	PC						HPLC
	Rf values				Colors		
	BAW	BEW	15%AcOH	5%AcOH	U.V	UV/NH_3	Rt(min)
myricetin 3-rhamnoside	0.63	0.76	0.38	0.23	dark purple	yellow	6.22
quercetin 3-arabinoside	0.67	0.76	0.26	0.15	dark purple	yellow	10.61
quercetin 3-xyloside	0.76	0.87	0.32	0.19	dark purple	yellow	11.57
quercetin 3-xyloglucoside	0.32	0.26	0.61	0.40	dark purple	yellow	4.78
quercetin 3-glucoside-7-rhamnoside	0.44	–	0.63	–	dark purple	dark brown	3.53
quercetin 3-galactoside-7-rhamnoside	0.44	–	0.63	–	dark purple	dark brown	3.33
quercetin 3,7-diglucoside	0.42	0.44	0.56	0.37	dark purple	yellow	–
kaempferol 3-glucuronide	0.73	0.42	0.42	0.27	dark purple	greenish yellow	12.06
kaempferol 3-diglucoside	0.43	0.56	0.60	0.50	dark purple	greenish yellow	5.57
kaempferol 3,7-dirhamnoside	0.80	–	0.65	–	dark purple	greenish yellow	–
kaempferol 3-glucoside-7-rhamnoside	0.72	–	0.73	–	dark purple	greenish yellow	4.22
kaempferol 3-galactoside-7-rhamnoside	0.72	–	0.73	–	dark purple	greenish yellow	3.68

PC: Solvent systems; BAW = n-BuOH/AcOH/H_2O (4:1:5, upper phase), BEW = n-BuOH/EtOH/H_2O (4:1:2.2), 15%AcOH =AcOH/H_2O (15:85) and 5%AcOH =AcOH/H_2O (5:95).

HPLC: Eluent; $CH_3CN/H_2O/H_3PO_4$ (22:78:0.2), Column; TSKgel ODS-80Tᴍ (Tosoh), Flow rate; 1.0 ml/min and Detection; 345 nm.

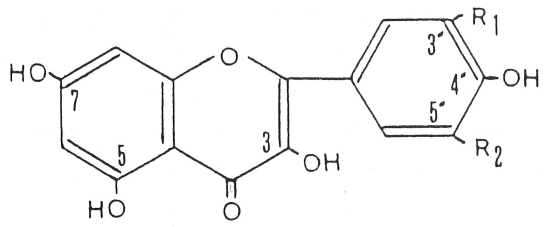

Fig. 1. Chemical structures of flavonol aglycones from *Cornus* species.
$R_1 = R_2 = H$: kaempferol
$R_1 = OH$, $R_2 = H$: quercetin
$R_1 = R_2 = OH$: myricetin

acid hydrolysis and quercetin 3-*O*-glucoside was by mild acid treatment. Accordingly, the glycoside was regarded as quercetin 3-*O*-xylosylglucoside.

Quercetin 3-*O*-glucoside-7-*O*-rhamnoside and 3-*O*-galactoside-7-*O*-rhamnoside. When their glycosides were isolated from *C. multinervosa* by PPC, they seemed to be single substance (Table 3). However, they were separated into two peaks by HPLC analysis. UV spectra of the mixture showed the presence of free 5-, 3'- and 4'-hydroxyl and substituted 3- and 7-hydroxyl groups (Table 2). By complete acid hydrolysis, quercetin, glucose, galactose and rhamnose were liberated. HPLC analysis of the intermediates, which were obtained by mild acid hydrolysis of the mixture, was appeared three peaks other than those of two original glycosides. Of their peaks, two were identified as quercetin 3-*O*-glucoside and 3-*O*-galactoside by HPLC comparisons with authentic specimens. Another one may be quercetin 7-*O*-rhamnoside. From the results described above, they were determined as the mixture of quercetin 3-*O*-glucoside-7-*O*-rhamnoside and quercetin 3-*O*-galactoside-7-*O*-rhamnoside.

Quercetin 3,7-di-*O*-glucoside. It was showed by UV spectral analysis that the flavonoid from *C. florida* had 5,3',4'-triOH and substituted 3,7-diOH groups (Table 2). Quercetin and glucose, and quercetin 3-*O*-glucoside were produced by complete and mild acid hydrolyses, respectively. Accordingly, the glycoside was regarded as quercetin 3,7-di-*O*-glucoside.

Kaempferol 3-*O*-glucuronide. The flavonoid was obtained from *Cornus racemosa, C. iberica, C. coreana, C. walteri* and *C. mas* (Table 1). Rf value of the glycoside using solvent system, BEW was remarkably lower than that using BAW (Table 3), presumed that the glycoside was glucuronide or acylated with lipophilic acid. UV spectra of the original compound showed the presence of free 5-, 7- and 4'-hydroxyl and a substituted 3-hydroxyl groups (Table 2). Moreover, kaempferol and glucuronic acid were liberated by acid hydrolysis. Finally, PC and HPLC data completely agreed with those of authentic kaempferol 3-*O*-glucuronide which were obtained from fern, *Asplenium dalhousiae* (Iwashina *et al.* 1993).

Kaempferol 3-*O*-diglucoside. The glycoside was isolated from *Cornus kousa*. By acid hydrolysis, kaempferol and glucose were produced. Since UV spectra of the glycoside showed the presence of free 5-, 7- and 4'-hydroxyl groups, glucose moiety must be on 3-position. Moreover, PC data (Rf) of the original glycoside using aqueous solvent systems, 15%AcOH and 5%AcOH indicated to be the bioside but not monoside (Table 3). From the results described above, the flavonoid was identified as kaempferol 3-*O*-diglucoside.

Kaempferol 3,7-di-*O*-rhamnoside. UV spectra of the glycoside which was isolated from *Cornus*

multinervosa showed the presence of free 5,4'-diOH and substituted 3,7-diOH groups (Table 2). Since kaempferol and rhamnose were liberated by complete acid hydrolysis, glycosidic sugar attaching to both 3- and 7-position must be rhamnose. Accordingly, the flavonoid was identified as kaempferol 3,7-di-*O*-rhamnoside.

Kaempferol 3-*O*-glucoside-7-*O*-rhamnoside and 3-*O*-galactoside-7-*O*-rhamnoside. The glycosides were also obtained from *C. multinervosa* as the mixture. UV spectra of them showed the presence of free 5,4'-diOH and substituted 3,7-diOH groups. Kaempferol, glucose, galactose and rhamnose, and kaempferol 3-*O*-glucoside, kaempferol 3-*O*-galactoside and a trace of unknown intermediate (probably kaempferol 3-*O*-rhamnoside) were produced by complete and mild acid hydrolyses, respectively. From the results described above, the glycosides were identified as the mixture of kaempferol 3-*O*-glucoside-7-*O*-rhamnoside and kaempferol 3-*O*-galactoside-7-*O*-rhamnoside.

Distribution of flavonoids in Cornus

The foliar flavonoid compounds of twenty-five *Cornus* taxa were surveyed in this experiment. All flavonoids except one which was myricetin glycoside were flavonal glycosides based on quercetin and kaempferol (Table 1). Though procyanidin and prodelphinidin which were commonly present in woody plants (Porter 1994) have found from some *Cornus* species (Bate-Smith 1975), it was shown by this experiment that quercetin and kaempferol 3-*O*-glycosides were diagnostic flavonoids in the genus. They were glycosylated with various sugars, i.e. glucose, galactose, glucuronic acid, rhamnose, xylose and arabinose. In particular, *Cornus amomum, C. asperifolia, C. glabrata, C. hemsleyi* and *C. horseyi* belonging to subgenus *Kraniopsis* were occurred not only the all quercetin 3-*O*-monoglycosides of their sugars but also myricetin 3-*O*-rhamnoside which was reported from *Cornus* species for the first time. Moreover, they were accompanied with some unknown substances (**1–5**). Of them, four (**1–4**) which were soluble in petroleum ether, but insoluble in water may be non-flavonoids due to their UV spectral and PC data (Table 4). Remained one (**5**) was presumed to be quercetin 3-*O*-glycoside by UV spectra. Moreover, UV spectral data agreed with that of authentic quercetin 3-*O*-(2"-galloylglucoside), but Rf values on the paper chromatograms was distinctly different (Kawasaki *et al.* 1986). Accordingly, substance **5** may be quercetin 3-*O*-galloylglycoside. Until now, acylated flavonoid was not reported from *Cornus* species.

Apart from almost *Cornus* species which exclusively produced quercetin and kaempferol 3-*O*-glycosides, it was interest that two Chinese evergreen *Cornus* species belonging to subgenus *Benthamia, C. multinervosa* and *C. hongkongensis* subsp. *hongkongensis*, and an American *Cornus florida* belonging to subgenus *Cynoxylon* made 3,7-di-*O*-glycosides such as quercetin 3-*O*-glucoside-7-*O*-rhamnoside, 3-*O*-galactoside-7-*O*-rhamnoside and 3,7-di-*O*-glucoside, and kaempferol 3-*O*-glucoside-7-*O*-rhamnoside, 3-*O*-galactoside-7-*O*-rhamnoside and 3,7-di-*O*-rhamnoside in addition to 3-*O*-glycosides. Moreover, two subspecies of *C. hongkongensis*, subsp. *hongkongensis* and subsp. *melanotrica* were distinguished by the presence of flavonol 3,7-diglycosides in former subspecies. Quercetin and kaempferol glycosides which attached uronic acid (glucuronic acid) were found from members in subgenera *Kraniopsis* and *Cornus*, but not *Arctocrania, Benthamia, Cynoxylon* and *Mesomora* (Table 5).

Two flavonol triglycosides, which attached 2 mol glucose and 1 mol rhamnose to 3-position of quercetin and kaempferol, but sugar-sugar sequence could not be determined, were isolated from *Cornus kousa*. Triglycoside has not been reported from other *Cornus* species.

Table 4. UV spectral and PC data of unknown substances from *C. amomum, C. asperifolia, C. glabrata, C. hemsleyi* and *C. horseyi*

Substances	PC (Rf and colors)					UV spectra λ max (nm)
	BAW	BEW	BPW	15%AcOH	UV	MeOH
1	0.78	0.78	0.80	0.06	blue[1)]	289
2	0.43	0.42	0.53	0.10	blue[2)]	263, 281
3	0.46	0.47	0.46	0.08	blue	260, 365sh
4	0.56	–	–	0.04	blue	260sh, 310sh
5	0.82	0.91	–	0.20	dark purple[3)]	266, 348[4)]

BPW = n-BuOH/Pyridine/H_2O (140:30:30).
Immediately changed to dull yellow[1)] and dull blue[2)] under UV light.
[3)]Changed to yellow under UV/NH_3.
[4)]+NaOMe: 273, 323, 399; +$AlCl_3$: 276, 431; +$AlCl_3$/HCl: 272, 303sh, 356, 390sh; +NaOAc: 273, 321, 383; +NaOAc/H_3BO_3: 261, 296, 366.

Table 5. Occurrence of 3-*O*-glycoside, 3,7-di-*O*-glycoside, 3-*O*-glucuronide and myricetin glycoside among subgenera in *Cornus*

Subgenera	3-*O*-glycoside	3,7-di-*O*-glycoside	3-*O*-glucuronide	myricetin glycoside
Mesomora (2)	2			
Kraniopsis (21)	21		10	5
Arctocrania (2)	2			
Cornus (2)	2		2	
Benthamia (5)	5	2		
Cynoxylon (1)	1	1		

( ) = number of species examined.

Synthetically, the difference of flavonoid composition was comparatively small among *Cornus* species except *C. multinervosa, C. hongkongensis* subsp. *hongkongensis* and *C. florida* which produced flavonol 3,7-*O*-glycosides and *C. amomum, C. asperifolia, C. glabrata, C. hemsleyi* and *C. horseyi* which had myricetin 3-*O*-rhamnoside, quercetin 3-*O*-galloylglycoside and diagnostic unknown non-flavonoid substances, showing to be the chemically discriminated genus. In order to estimate the speciation of genus *Cornus*, flavonoid profiles of other genera in Cornaceae such as *Helwingia, Aucuba* and *Mastixia*, and related other families, e.g. Davidiaceae, Alangiaceae, Nyssaceae, and Garryaceae, must be surveyed and now in progress.

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Summary

The flavonoid profiles of 33 *Cornus* taxa, of which 25 have not been analyzed for flavonoid, were surveyed for chemotaxonomic studies. Twenty-four quercetin, kaempferol and myricetin glycosides which were glycosylated by combination of various sugars, such as glucose, galactose, glucuronic acid, rhamnose, xylose or arabinose, were identified. Major flavonoids in almost *Cornus* species were 3-*O*-monosides and 3-*O*-biosides. On the other hand, two Chinese evergreen *Cornus* species, *C. multinervosa* and *C. hongkongensis* subsp. *hongkongensis* (subgenus *Benthamia*), and an American *C. florida* (subgenus *Cynoxylon*) produced quercetin and kaempferol 3,7-di-*O*-glycosides in addition to common 3-*O*-glycosides. Of flavonol 3-*O*-glycosides, myricetin 3-*O*-rhamnoside, and quercetin 3-*O*-arabinoside, 3-*O*-xyloside and acylated (probably galloyl) 3-*O*-glycoside which rarely occurred in plants than 3-*O*-glucoside, 3-*O*-galactoside or 3-*O*-rutinoside, were present in five *Cornus* species, i.e. *C. amomum, C. asperifolia, C. glabrata, C. hemsleyi* and *C. horseyi* belonging to subgenus *Kraniopsis*. They were accompanied with other unknown compounds which may be phenolics but not flavonoids.

摘　　要

25種の今まで報告のなかったものも含めた33種のミズキ属（***Cornus***）植物の葉に含まれるフラボノイド配糖体の組成が調査された。1種類のmyricetin配糖体を除くすべてがquercetinとkaempferolをアグリコンとする配糖体で，その多くはグルコース，ガラクトース，ラムノース，キシロースあるいはアラビノースがモノシドまたはビオシドとして3-位の水酸基に結合したものであった。これらのフラボノール3-配糖体は今回分析の行われたすべての種で検出された一方で，中国産の常緑の2種，*C. multinervosa* と *C. hongkongensis* subsp. *hongkongensis*（*Benthamia* 亜属）およびアメリカ産のハナミズキ（*Cynoxylon* 亜属）からは3-位以外に7-位にも糖を結合するフラボノール3,7-配糖体が検出された。

最も多くの種を分析した *Kraniopsis* 亜属ではすべての種がフラボノール3-配糖体を基本としているが，その中で *C. amomum*, *C. asperifolia*, *C. glabrata*, *C. hemsleyi* および *C. horseyi* の5種からはグルコース，ガラクトース，ラムノース，キシロース，アラビノース，それにグルクロン酸のquercetin 3-*O*-モノシドがすべて検出されるばかりでなく，従来，ミズキ属では報告されていなかったmyricetinの配糖体（myricetin 3-*O*-rhamnoside）や没食子酸でアシル化されていると推定されるquercetinの配糖体，さらにはこの5種に特有のフラボノイドではないと考えられる未知の物質も存在することで他とは区別された。

しかしながら，総じてミズキ属では検出されたほとんどのフラボノイドがquercetinとkaempferolを基本とした配糖体であることなどから，その化学分類学的な差異は小さいと考えられ，今後はハナイカダ（*Helwingia*）やアオキ（*Aucuba*）属などの他のミズキ科植物や関連する他の科，例えばウリノキ科，ガリア科，ハンカチノキ科，ヌマミズキ科などとミズキ属との類縁関係を化学分類学的に解明する方向に向かわなければならないと考えられた。

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