

Flavonoids in the Leaves of *Mastixia trichotoma*, *Camptotheca acuminata*, *Alangium platanifolium* var. *trilobum*, *A. premnifolium*, and *Davidia involucrata*, and Their Implication with the Genus *Cornus*

Tsukasa IWASHINA* and Hiroaki HATTA*

岩科 司*・八田洋章* : *Mastixia trichotoma*, キジュ, ウリノキ,
シマウリノキおよびハンカチノキの葉に含まれるフラボノイドと
ミズキ属植物のものとの類似性

The Cornaceae and related families have morphologically been variously defined (e.g., Wangerin 1910; Hutchinson 1967; Takhtajan 1980; Cronquist 1981; Eyde 1988). They have chemotaxonomically been discussed using iridoids and quinol glucosides (Jensen *et al.* 1975), iridoids, and hydrolyzable and condensed tannins (Bate-Smith *et al.* 1975), fatty acids (Hohn and Meinschein 1976; Breuer *et al.* 1987). However, the flavonoids compounds were roughly surveyed at aglycone level by Bate-Smith *et al.* (1975).

As a part of chemotaxonomical studies of the Cornaceae and related taxa, we have surveyed the flavonoid glycosides in the leaves of many *Cornus* species (Iwashina and Hatta 1990, 1992, 1993, 1994). Recently, the flavonoids of *Aucuba japonica* Thunb. including var. *borealis* Miyabe & Kudo and *Helwingia japonica* (Thunb.) F. G. Dietrich including subsp. *liukiensis* (Hatusima) Hara, which are other genera in Cornaceae, were also reported (Iwashina *et al.* 1997).

In this survey, the flavonoid glycosides in the leaves of *Mastixia trichotoma* Blume (Cornaceae), *Camptotheca acuminata* Decne (Nyssaceae), *Alangium platanifolium* (Sieb. & Zucc.) Harms var. *trilobum* (Miq.) Ohwi and *A. premnifolium* Ohwi (Alangiaceae) are reported for the first time, and that of *Davidia involucrata* (Davidiaceae) is re-observed. These taxa were considered as to be related to the genus *Cornus* by many authors. The flavonoid compositions were chemotaxonomically compared with those of the *Cornus*, *Aucuba* and *Helwingia* species in Cornaceae.

Materials and Methods

Plant materials

Mastixia trichotoma Blume was collected in Java Island, Indonesia, *Camptotheca acuminata* Decne in the Forests of Kyushu University, Miyazaki Pref., Japan (cultivated), *Alangium platanifolium* (Sieb. & Zucc.) Harms var. *trilobum* (Miq.) Ohwi in Hakone, Kanagawa Pref., Japan, *Alangium premnifolium* Ohwi in Ishigaki Island, Okinawa Pref., Japan, and *Davidia involucrata* Baill. in Tsukuba Botanical Garden, National Science Museum, Ibaraki Pref., Japan (cultivated). Voucher specimens were deposited in National Science Museum, Tokyo (TNS).

*Tsukuba Botanical Garden, National Science Museum, Tsukuba, 305-0005. 国立科学博物館 筑波研究資料センター 筑波実験植物園.

Isolation of flavonoids

Dry (*M. trichotoma*, 12.7g) or fresh leaves (*C. acuminata*, 90g; *A. platanifolium* var. *trilobum*, 130g; *A. premnifolium*, 108g; and *D. involucrata*, 70g) were extracted with MeOH, filtered and concentrated to small volumes, respectively. After shaken with petroleum ether, the extracts were applied to preparative paper chromatography (PPC) using BAW (n-BuOH/AcOH/H₂O = 4 : 1 : 5, upper phase), 15% AcOH and BEW (n-BuOH/EtOH/H₂O = 4:1:2.2). Isolated flavonoids were purified by Sephadex LH-20 column chromatography (solvent system: 70% MeOH). The flavonoids were obtained as crystals, powders or pure solutions.

Identification of flavonoids

The flavonoids were identified by UV spectra (Mabry *et al.* 1970), characterization of acid hydrolysates from the original glycosides, and PC and HPLC comparisons with authentic specimens. PC, HPLC and UV spectral data of isolated flavonoids from *Mastixia*, *Camptotheca*, *Alangium* and *Davidia* species are follows.

Quercetin 3-*O*-glucoside (**1a**). PC: Rf 0.60 (BAW), 0.60 (BEW), 0.34 (15% AcOH), 0.20 (5% AcOH); UV - dark purple, UV/NH₃ - yellow. HPLC: retention time (Rt) 6.37 min. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 257, 266sh, 356; + NaOMe 274, 331, 411 (inc.); + AlCl₃ 275, 434; + AlCl₃/HCl 269, 300, 363, 399; + NaOAc 273, 325, 396; + NaOAc/H₃BO₃ 262, 379.

Quercetin 3-*O*-galactoside (**1b**). PC: Rf 0.60 (BAW), 0.60 (BEW), 0.32 (15% AcOH), 0.24 (5% AcOH); UV - dark purple, UV/NH₃ - yellow. HPLC: Rt 6.16 min. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 257, 266sh, 358; + NaOMe 272, 330, 408 (inc.); + AlCl₃ 275, 435; + AlCl₃/HCl 269, 298, 362, 402; + NaOAc 273, 325, 391; + NaOAc/H₃BO₃ 261, 378.

Quercetin 3-*O*-arabinoside (**6**). PC: Rf 0.58 (BAW), 0.70 (BEW), 0.25 (15% AcOH), 0.15 (5% AcOH); UV - dark purple, UV/NH₃ - yellow. HPLC: Rt 7.46 min. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 256, 264sh, 358; + NaOMe 273, 329, 409 (inc.); + AlCl₃ 274, 437; + AlCl₃/HCl 268, 299, 367, 405; + NaOAc 274, 323, 394; + NaOAc/H₃BO₃ 261, 295, 377.

Quercetin 3-*O*-rutinoside (**3**). PC: Rf 0.40 (BAW), 0.42 (BEW), 0.45 (15% AcOH), 0.33 (5% AcOH); UV - dark purple, UV/NH₃ - yellow. HPLC: Rt 5.13 min. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 257, 265sh, 358; + NaOMe 274, 329, 413 (inc.); + AlCl₃ 274, 430; + AlCl₃/HCl 269, 300, 363, 400; + NaOAc 273, 325, 401; + NaOAc/H₃BO₃ 262, 377.

Kaempferol 3-*O*-glucoside (**2a**). PC: Rf 0.66 (BAW), 0.77 (BEW), 0.35 (15% AcOH), 0.21 (5% AcOH); UV - dark purple, UV/NH₃ - dark greenish yellow. HPLC: Rt 8.93 min. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 266, 350; + NaOMe 275, 325, 399 (inc.); + AlCl₃ 274, 304, 352, 393; + AlCl₃/HCl 275, 302, 347, 393; + NaOAc 274, 304, 382; + NaOAc/H₃BO₃ 266, 354.

Kaempferol 3-*O*-galactoside (**2b**). PC: Rf 0.63 (BAW), 0.77 (BEW), 0.31 (15% AcOH), 0.20 (5% AcOH); UV - dark purple, UV/NH₃ - dark greenish yellow. HPLC: Rt 7.83 min. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 266, 349; + NaOMe 275, 326, 399 (inc.); + AlCl₃ 274, 304, 352, 395; + AlCl₃/HCl 275, 302, 345, 396; + NaOAc 274, 309, 386; + NaOAc/H₃BO₃ 266, 353.

Kaempferol 3-*O*-rutinoside (**4a**). PC: Rf 0.52 (BAW), 0.60 (BEW), 0.51 (15% AcOH), 0.38 (5% AcOH); UV - dark purple, UV/NH₃ - dark greenish yellow. HPLC: Rt 7.66 min. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 266, 350; + NaOMe 276, 325, 401 (inc.); + AlCl₃ 274, 305, 355, 396; + AlCl₃/HCl 275, 303, 348, 393; + NaOAc 275, 315, 392; + NaOAc/H₃BO₃ 266, 352.

Kaempferol 3-*O*-rhamnosylgalactoside (**4b**). PC: Rf 0.51 (BAW), 0.60 (BEW), 0.53 (15% AcOH), 0.40 (5% AcOH); UV - dark purple, UV/NH₃ - dark greenish yellow. HPLC: Rt 6.57

min. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 266, 352; +NaOMe 275, 324sh, 398 (inc.); +AlCl₃ 273, 304, 360, 399; +AlCl₃/HCl 275, 302, 353, 396; +NaOAc 275, 401; +NaOAc/H₃BO₃ 266, 355.

Isorhamnetin 3-*O*-rhamnosylglucoside (**5a**) and 3-*O*-rhamnosylgalactoside (**5b**). PC: Rf 0.46 (BAW), 0.56 (BEW), 0.51 (15%AcOH), 0.38 (5%AcOH); UV - dark purple, UV/NH₃ - yellow. HPLC: Rt 8.33 (3-rhamnoglucoside) and 7.83 (3-rhamnogalactoside). UV $\lambda_{\max}^{\text{MeOH}}$ nm: 256, 265sh, 355; +NaOMe 273, 328sh, 405 (inc.); +AlCl₃ 272, 303, 362sh, 407; +AlCl₃/HCl 269, 299, 361, 399; +NaOAc 268, 324sh, 407; +NaOAc/H₃BO₃ 257, 360.

Chlorogenic acid. PC: Rf 0.58 (BAW), 0.31 (BEW), 0.67 (15%AcOH), 0.61 (5%AcOH); UV-blue, UV/NH₃ - blue green. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 244sh, 300, 328; +NaOMe 262sh, 311, 376 (inc.); +AlCl₃ 260, 312, 358; +AlCl₃/HCl 243sh, 301sh, 329; +NaOAc 297sh, 331, 377sh; +NaOAc/H₃BO₃ 255, 305, 350.

Ellagic acid. PC: Rf 0.28 (BAW), 0.24 (BEW), 0.04 (15%AcOH); UV - mauve. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 255, 350sh, 365; +NaOMe 256, 288, 406; +AlCl₃ 248, 270, 314sh, 383; +AlCl₃/HCl 255, 348sh, 366; +NaOAc 253, 277, 355, 366sh; +NaOAc/H₃BO₃ 263, 366sh, 381.

High performance liquid chromatography (HPLC)

HPLC was performed with Tosoh TSKgel ODS 80TM column (i.d. 4.6mm × 150mm). The flavonoids were dissolved in MeOH, filtered through Maishoridisc H-13-5, 0.45 μm (Tosoh) pre-cartridge, and eluted with MeCN/H₂O/H₃PO₄ (22:78:0.2). Detection was at 195-350nm and flow-rate was 1.0ml min⁻¹.

Results

Flavonoids from Mastixia trichotoma

Two flavonoid glycosides (**1a** and **2a**) were isolated from the leaves of *Mastixia trichotoma*. These compounds liberated quercetin and glucose, and kaempferol and glucose by acid hydrolysis, respectively. Since UV spectra of original glycosides showed the presence of free 5, 7, 3', 4' -tetraOH (**1a**) or 5, 7, 4' -triOH (**2a**) and a substituted 3-OH groups, a glucosyl group must be attached to 3-hydroxyl group of quercetin or kaempferol. Finally, they were identified as quercetin 3-*O*-glucoside (**1a**) and kaempferol 3-*O*-glucoside (**2a**) by direct PC and HPLC comparisons with authentic isoquercitrin and astragalins. In the case of kaempferol 3-*O*-glucoside, it was shown by HPLC that kaempferol 3-*O*-galactoside (**2b**) was accompanied as very minor compound.

As other phenolic compounds, chlorogenic acid, and ellagic acid or hexahydrodipheic acid (HHDP) and these derivatives were also characterized by PC and UV spectra.

Flavonoids from Camptotheca acuminata

MeOH extract from the leaves of *Camptotheca acuminata* apparently gave three flavonoid spots (**1-3**) on the two-dimensional chromatogram. Major flavonoid **1** was obtained as yellow powders, and liberated quercetin, glucose and a trace of galactose by acid hydrolysis. UV spectra of **1** showed the presence of free 5,7,3',4' -tetraOH and a substituted 3-OH groups. PC properties of original glycoside agreed with those of authentic isoquercitrin. However, flavonoid **1** was divided into two peaks, major **1a** and minor **1b**. These retention times by HPLC agreed with those of authentic quercetin 3-*O*-glucoside and quercetin 3-*O*-galactoside, respectively. Thus, it was shown that flavonoid **1** was a mixture of isoquercitrin (**1a**) and hyperin (**1b**).

Table 1. Distribution of flavonoids in the leaves of *Mastixia* (Cornaceae), *Alangium* (Alangiaceae), *Davidia* (Davidiaceae), and *Camptotheca* (Nyssaceae)

Family	Taxa	Flavonoids
Cornaceae	<i>Mastixia trichotoma</i> Blume	Kaempferol 3-glucoside and 3-galactoside Quercetin 3-glucoside
Alangiaceae	<i>Alangium platanifolium</i> (Sieb. & Zucc.) Harms var. <i>trilobum</i> (Miq.) Ohwi	Kaempferol 3-rutinoside Quercetin 3-glucoside and 3-rutinoside
	<i>A. premnifolium</i> Ohwi	Kaempferol 3-rutinoside and 3-rhamnogalactoside Quercetin 3-glucoside, 3-galactoside and 3-rutinoside Isorhamnetin 3-rhamnoglucoside and 3-rhamnogalactoside
Davidiaceae	<i>Davidia involucrata</i> Baill.	Kaempferol 3-galactoside Quercetin 3-glucoside, 3-galactoside, 3-arabinoside and 3-rhamnoside*
Nyssaceae	<i>Camptotheca acuminata</i> Decne	Kaempferol 3-glucoside and 3-galactoside Quercetin 3-glucoside, 3-galactoside and 3-rutinoside

*Reported by Rast (1968), but could not be found in this experiment.

Table 2. Comparison of flavonoid characters among the genera *Cornus*, *Mastixia*, *Aucuba*, *Helwingia*, *Alangium*, *Camptotheca* and *Davidia*

Flavonoid character	<i>Cornus</i>	<i>Mastixia</i>	<i>Aucuba</i>	<i>Helwingia</i>	<i>Alangium</i>	<i>Camptotheca</i>	<i>Davidia</i>
Flavonol							
3-monoglycoside	+	+			+	+	+
3-diglycoside	+		+		+	+	
3,7-diglycoside	+		+				
7-glycoside			+				
Flavone							
7-glycoside				+			
C-glycoside				+			

*Found only from *C. hongkongensis*, *C. multinervosa* and *C. florida*.

It was proved by HPLC survey that flavonoid **2** was also a mixture of two glycosides, **2a** and **2b**. Kaempferol, glucose and galactose were liberated as acid hydrolysates of the mixture. Moreover, UV spectra of the mixture showed the presence of free 5,7,4'-triOH and a substituted 3-OH groups. Finally, it was shown by HPLC comparisons with authentic specimens that flavonoids **2a** and **2b** are kaempferol 3-*O*-glucoside and kaempferol 3-*O*-galactoside, respectively.

UV spectra of flavonoid **3** showed the presence of free 5-, 7-, 3' - and 4' -hydroxyl and a substituted 3-hydroxyl groups. By acid hydrolysis of the glycoside, quercetin, glucose and rhamnose were liberated. It was proved by direct PC and HPLC comparisons with authentic rutin that flavonoid **3** was quercetin 3-*O*-rutinoside.

Flavonoids from Alangium platanifolium var. *trilobum* and *A. premnifolium*

Three (**1a**, **3** and **4a**) and seven (**1a**, **1b**, **3**, **4a**, **4b**, **5a** and **5b**) flavonoid glycosides were detected from the leaves of *Alangium platanifolium* var. *trilobum* and *A. premnifolium*, respectively. Their flavonoid compositions were clearly different to each other.

Of three flavonoids which were isolated from *A. platanifolium* var. *trilobum*, two ones were quercetin 3-*O*-glycosides (**1a** and **3**) and another one was kaempferol 3-*O*-glycoside (**4a**) by UV spectra and characterization of aglycones. Glucose alone (**1a**), or glucose and rhamnose (**3** and **4a**) were detected as glycosidic sugars. Finally, these flavonoids were identified as quercetin 3-*O*-glucoside (**1a**), quercetin 3-*O*-rutinoside (**3**) and kaempferol 3-*O*-rutinoside (**4a**) by PC and HPLC comparisons with authentic specimens.

On the other hand, MeOH extract from *Alangium premnifolium* was appeared four flavonoid spots on 2D-chromatogram. Of these spots, major one (**1**) was shown to be a mixture of quercetin 3-*O*-glucoside (**1a**) and quercetin 3-*O*-galactoside (**1b**) by UV spectra, acid hydrolysis, and PC and HPLC comparisons with authentic specimens.

Flavonoid **4** was characterized as kaempferol 3-*O*-glycoside by UV spectra and identification of aglycone. The flavonoid liberated glucose, galactose (trace) and rhamnose as glycosidic sugars by acid hydrolysis. Though the glycoside **4** appeared as single spot on 2D-chromatogram, it was shown to be a mixture of kaempferol 3-*O*-rutinoside (**4a**) and kaempferol 3-*O*-rhamnosylgalactoside (**4b**) by HPLC.

Similarly, flavonoid **5** was also divided into two peaks (**5a** and **5b**) by HPLC. Acid hydrolysis of the mixture liberated isorhamnetin, glucose, galactose and rhamnose. Since UV spectra of the mixture showed that the presence of free 5-, 7- and 4' -hydroxyl and substituted 3- and 3' -hydroxyl groups, glycosidic sugars must be attached to 3-hydroxyl group. Finally, retention time of major peak (**5a**) on HPLC agreed with that of authentic isorhamnetin 3-*O*-rhamnosylglucoside (probabry, 3-*O*-rutinoside) and minor peak (**5b**) was presumed as isorhamnetin 3-*O*-rhamnosylgalactoside.

Another minor flavonoid **3** was identified as quercetin 3-*O*-rutinoside by UV spectra, characterization of acid hydrolysates, PC and HPLC comparisons with authentic rutin.

Though flavonoids of two *Alangium* species were flavonol glycosides, flavonoid composition of *A. premnifolium* was clearly different with that of *A. platanifolium* var. *trilobum* by the presence of *O*-methylated flavonol, isorhamnetin.

Flavonoids from Davidia involucrata

Four flavonol glycosides (**1a**, **1b**, **2b** and **6**) were detected from the leaves of *Davidia involucrata*.

It was shown by UV, characterization of hydrolysates, and PC and HPLC comparisons with authentic specimens that major glycoside is quercetin 3-*O*-galactoside (**1b**), which is accompanied with quercetin 3-*O*-glucoside (**1a**).

Flavonoid **2b** was identified as kaempferol 3-*O*-galactoside by same manners.

Though another glycoside **6** was also quercetin 3-*O*-glycoside, it liberated arabinose as a glycosidic sugar by acid hydrolysis. Finally, flavonoid **6** was identified as quercetin 3-*O*-arabinoside by PC and HPLC comparison with authentic avicularin.

Ellagic acid and chlorogenic acid were also isolated and identified from *D. involucrata* as phenolic acids in addition to flavonoids.

The foliar flavonoids of *Davidia involucrata* have been reported to be quercetin 3-*O*-galactoside and 3-*O*-rhamnoside (Rast, 1968). However, we found kaempferol 3-*O*-galactoside, and quercetin 3-*O*-glucoside and 3-*O*-arabinoside, in addition to quercetin 3-*O*-galactoside, and failed to detect quercetin 3-*O*-rhamnoside in this experiment.

Discussion

It was proved by this study that the flavonoids in *Mastixia trichotoma*, *Camptotheca acuminata*, *Alangium platanifolium* var. *trilobum* and *A. premnifolium*, and *Davidia involucrata* were all flavonol 3-*O*-glycosides based on kaempferol, quercetin and isorhamnetin.

As described by us (Iwashina and Hatta 1994), the flavonoid characters of the *Cornus* species were also flavonol glycosides. Major glycosides were 3-*O*-mono- and di-glycosides of kaempferol and quercetin in almost species. Though flavonol 3,7-*O*-glycosides such as 3-*O*-glucoside-7-*O*-rhamnoside and 3-*O*-galactoside-7-*O*-rhamnoside of kaempferol and quercetin, were found from two Chinese evergreen *Cornus*, *C. hongkongensis* and *C. multinervosa*, and an American *C. florida*, flavonoid characters of many *Cornus* species were very similar to those of *Mastixia trichotoma*, *Camptotheca acuminata*, *Alangium platanifolium* var. *trilobum* and *A. premnifolium*, and *Davidia involucrata*.

The genera *Cornus*, *Aucuba*, *Helwingia* and *Mastixia* were classified into the family Cornaceae by Wangerin (1910) and Cronquist (1981). Among these genera, the flavonoid character of *Aucuba japonica* was the presence of flavonol glycosides attaching xylose as a sugar, such as kaempferol 3-*O*-xylosylglucoside and 3-*O*-xyloside-7-*O*-glucoside, quercetin 3-*O*-xylosylglucoside and 3-*O*-xyloside-7-*O*-glucoside (Iwashina *et al.* 1997), and also anthocyanins, pelargonidin and cyanidin 3-*O*-xylosylglucosides (Ishikura 1971). In addition, the species did not have any common flavonol 3-*O*-monoglycosides in difference with those of *Cornus* species.

Helwingia japonica was only one species of which the flavonoids are flavone *O*-glycosides with a small volume of *C*-glycosylflavones among the *Cornus* and related taxa. The genus *Helwingia* was regarded as an independent family, *Helwingiaceae* by Takhtajan (1980), or a member of *Araliaceae* by Hutchinson (1967). Recently, Xiang *et al.* (1993) showed by *rb*ĒL sequence data that *Helwingia* keeps aloof from *Cornus*.

In this study, it was chemotaxonomically proved that the genera *Mastixia*, *Camptotheca*, *Alangium* and *Davidia* were related to *Cornus* rather than *Helwingia* and *Aucuba* in Cornaceae.

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Summary

The flavonoid in the leaves of *Mastixia trichotoma* (Cornaceae), *Camptotheca acuminata* (Nyssaceae), *Alangium platanifolium* var. *trilobum* and *A. premnifolium* (Alangiaceae), and *Davidia involucrata*, of which the flavonoids were reported in this paper for the first time except latter one, were isolated by column and paper chromatography. These flavonoids were identified as kaempferol 3-*O*-rutinoside and 3-*O*-galactoside, and quercetin 3-*O*-glucoside (*M. trichotoma*), kaempferol 3-*O*-glucoside and 3-*O*-galactoside, and quercetin 3-*O*-glucoside, 3-*O*-galactoside and 3-*O*-rutinoside (*C. acuminata*), kaempferol 3-*O*-rutinoside, and quercetin 3-*O*-glucoside and 3-*O*-rutinoside (*A. platanifolium* var. *trilobum*), kaempferol 3-*O*-rutinoside and 3-*O*-rhamnosylgalactoside, quercetin 3-*O*-glucoside, 3-*O*-galactoside and 3-*O*-rutinoside, and isorhamnetin 3-*O*-rhamnosylglucoside and 3-*O*-rhamnosylgalactoside (*A. premnifolium*), and kaempferol 3-*O*-galactoside, and quercetin 3-*O*-glucoside, 3-*O*-galactoside and 3-*O*-arabinoside (*D. involucrata*) by UV, characterization of acid hydrolysates, and PC and HPLC comparisons with authentic specimens.

The flavonoids detected from these species are all flavonol 3-*O*-glycosides based on kaempferol, quercetin and isorhamnetin, and are very similar to those of almost *Cornus* species which have been surveyed by us. Thus, it was chemotaxonomically estimated that *Mastixia*, *Camptotheca*, *Alangium* and *Davidia* species were related to the genus *Cornus* rather than *Helwingia* and *Aucuba* in Cornaceae.

摘 要

Mastixia trichotoma Blume (ミズキ科), キジュ (*Camptotheca acuminata* Decne, ヌマミズキ科), ウリノキ (*Alangium platanifolium* (Sieb. & Zucc.) Harms var. *trilobum* (Miq.) Ohwi, ウリノキ科), シマウリノキ (*Alangium premnifolium* Ohwi, ウリノキ科) およびハンカチノキ (*Davidia involucrata* Baill., ハンカチノキ科) の葉に含まれるフラボノイド化合物がハンカチノキを除き、初めて報告された。

これらの植物に含まれているのはいずれもフラボノールの配糖体で, *M. trichotoma* からは kaempferol 3-*O*-glucoside と 3-*O*-galactoside および quercetin 3-*O*-glucoside, キジュからは kaempferol の 3-*O*-glucoside と 3-*O*-galactoside, および quercetin の 3-*O*-glucoside, 3-*O*-galactoside と 3-*O*-rutinoside, ウリノキからは kaempferol 3-*O*-rutinoside, および quercetin 3-*O*-glucoside と 3-*O*-rutinoside, シマウリノキからは kaempferol の 3-*O*-rutinoside, 3-*O*-rhamnosylgalactoside, quercetin の 3-*O*-glucoside, 3-*O*-galactoside と 3-*O*-rutinoside, および isorhamnetin の 3-*O*-rhamnosylglucoside と 3-*O*-rhamnosylgalactoside, そしてハンカチノキからは kaempferol の 3-*O*-galactoside, および quercetin の 3-*O*-glucoside, 3-*O*-galactoside と 3-*O*-arabinoside が分離同定された。

これらのフラボノイドはいずれも kaempferol, quercetin および isorhamnetin の 3-*O*-モノ-あるいはジ-配糖体であり, 著者らが以前に分離同定を行った大多数のミズキ属 (*Cornus*) 植物のフラ

ボノイド組成と極めて類似していた。

以上のような点から、限られた種の分析ではあるものの、上記4科の種属はフラボノイドを指標とした化学分類学的観点からみると、ミズキ科のうちでもフラボノールでなくフラボンの配糖体を含むハナイカダ属 (*Helwingia*) や、糖として主にキシロースを結合しているフラボノールの3,7-O-配糖体が主要成分であるアオキ属 (*Aucuba*) よりもむしろミズキ属に近縁であると推定された。

References

- Bate-Smith, E. C., I. K. Ferguson, K. Hutson, S. R. Jensen, B. J. Nielsen and T. Swain, 1975. Phytochemical interrelationships in Cornaceae. *Biochem. Syst. Ecol.* **3**: 79-89.
- Breuer, B., T. Stuhlfauth, H. Fock and H. Huber, 1987. Fatty acids of some Cornaceae, Hydrangeaceae, Aquifoliaceae, Hamamelidaceae and Styracaceae. *Phytochemistry* **26**: 1441-1445.
- Cronquist, A., 1981. An Integrated System of Classification of Flowering Plants. Columbia Univ. Press, New York.
- Eyde, R. H., 1988. Comprehending *Cornus*: Puzzles and progress in the systematics of the dogwoods. *Bot. Rev.* **54**: 233-351.
- Hohn, M. Ed. and W. G. Meinschein, 1976. Seed oil fatty acids: Evolutionary significance in the Nyssaceae and Cornaceae. *Biochem. Syst. Ecol.* **4**: 193-199.
- Hutchinson, J., 1967. The Genera of Flowering Plants, Vol. 2. Clarendon Press, Oxford.
- Ishikura, N., 1971. Pelargonidin glycosides in fruits. *Experientia* **27**: 1006.
- Iwashina, T. and H. Hatta, 1990. The flavonoid glycosides in the leaves of *Cornus* species I. The flavonoids of *C. controversa*, *C. brachypoda*, *C. darvasica* and *C. drummondii*. *Ann. Tsukuba Bot. Gard.* **9**: 41-47 (in Japanese with English summary).
- and —, 1992. The flavonoid glycosides in the leaves of *Cornus* species II. The flavonoids of *C. canadensis* and *C. suecica*. *Ann. Tsukuba Bot. Gard.* **11**: 23-34.
- and —, 1993. The flavonoid glycosides in the leaves of *Cornus* species III. The flavonoids of three Himalayan *Cornus* species. *Ann. Tsukuba Bot. Gard.* **12**: 49-56.
- and —, 1994. The flavonoid glycosides in the leaves of *Cornus* species IV. The distribution of flavonoids in genus *Cornus*. *Ann. Tsukuba Bot. Gard.* **13**: 29-40.
- , K. Kamenosono and H. Hatta, 1997. Flavonoid glycosides from the leaves of *Aucuba japonica* and *Helwingia japonica* (Cornaceae): Phytochemical relationship with the genus *Cornus*. *J. Jpn. Bot.* **72**: 337-346.
- Jensen, S.R., A. Kjaer and B. J. Nielsen, 1975. The genus *Cornus*. Non-flavonoid glucosides as taxonomic markers. *Biochem. Syst. Ecol.* **3**: 75-78.
- Mabry, T. J., K. R. Markham and M. B. Thomas, 1970. The Systematic Identification of Flavonoids. Springer, Berlin.
- Rast, D., 1968. Hyperosid, das Hauptflavonolglykosid von *Davidia involucreta* Baill. *Planta* **80**: 154-158.
- Takhtajan, A. L., 1980. Outline of the classification of flowering plants (Magnoliophyta). *Bot. Rev.* **46**: 225-359.
- Wangerin, W., 1910. Cornaceae. In Engler, A. (ed.) *Das Pflanzenreich*. Series IV, Family 229 (Heft 41). W. Engelmann, Leipzig. pp.1-101.
- Xiang, Q.-Y., D. E. Soltis, D. R. Morgan and P. S. Soltis, 1993. Phylogenetic relationships of *Cornus* L. *sensu lato* and putative relatives inferred from *rbcL* sequence data. *Ann. Missouri Bot. Gard.* **80**: 723-734.