

MANGIFERIN AND ISOMANGIFERIN IN ACYSTOPTERIS, CYSTOPTERIS, GYMNOCARPIUM, AND WOODSIA

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C-glycosylxanthones are pharmacologically active phenolic compounds that occur sporadically in higher plants (1). Their occurrence in ferns is not well known, and so far they have been reported from only 11 genera (2-4). A continuing survey at New York Botanical Garden has detected mangiferin and isomangiferin in several further taxa. In the present paper, we wish to report the discovery of mangiferin and isomangiferin in four new fern genera, namely *Acystopteris*, *Cystopteris*, *Gymnocarpium*, and *Woodsia* in the Athyrioideae. Only one species of *Woodsia* has previously been examined for C-glycosylxanthones, and the result proved to be negative (3). The only other member of the Athyrioideae known to contain any xanthones is *Athyrium mesosorum* Mak. (5).

EXPERIMENTAL

The complete list of taxa examined for mangiferin is listed in table 1. All samples were taken from herbarium specimens at New York Botanical Garden. Small amounts (0.5-1.0 g) of frond material were extracted in 80% aqueous methanol with a Polytron homogenizer (6). The solutions were chromatographed unidimensionally on Whatman No. 1 paper in water and 15% acetic acid (glacial acetic acid-water, 15:85). Mangiferin and isomangiferin appeared as orange spots in uv light, turning fluorescent yellow in ammonia vapor. Extracts that were positive for the presence of these compounds were then chromatographed two-dimensionally on Whatman No. 3 paper in *t*-butanol-acetic acid-water (TBA) (3:1:1) and 15% acetic acid. The compounds were eluted in 80% aqueous methanol and co-chromatographed in TBA; *n*-butanol-acetic acid-water (BAW) (4:1:5, upper layer); 15% acetic acid and water with authentic mangiferin and isomangiferin isolated from *Asplenium montanum* Willd. (7). Acid hydrolysis (2 N HCl, 100°, 30 min) indicated that the compounds were neither xanthone-O-glycosides nor xanthone-C-glycosides with further substitutions. Co-chromatography in four solvents with authentic

mangiferin and isomangiferin indicated that the compounds were not dilatatin and isodilatatin, the only other known xanthone-C-glycosides which lack further substitutions.

DISCUSSION

A small number of the investigated species was found to contain mangiferin and isomangiferin. These were *Acystopteris setosa*, *A. tenuisecta*, *Cystopteris diaphana*, *C. douglasii*, *C. fragilis*, *Gymnocarpium gracilipes*, and *Woodsia plummereae*. There was some geographic variation in the chemical composition of *A. tenuisecta*, *C. fragilis*, and *W. plummereae*. Two species of *Dryoathyrium* and one of *Lunathyrium* appeared not to contain mangiferin and isomangiferin. When C-glycosylxanthones occur in a fern genus they typically occur in very few of the species examined (2-4). This is also the case in the present study, with mangiferin and isomangiferin occurring in only 7 of the 41 species examined. The sporadic occurrence of these compounds within genera suggests that they are more likely to be detected by an intensive systematic search than by random sampling of families and genera. The reason for the sporadic occurrence remains a mystery. However, the occurrence of xanthones has proved to be of taxonomic interest in the fern genus *Asplenium* (7,8), and it is in these and similar situations that the occurrence of xanthones will be of greatest value. For example, the *Cystopteris fragilis* complex has recently been described as "perhaps the most formidable biosystematic problem in the ferns" (9). *C. fragilis* occurs in tetraploid, hexaploid, and octoploid forms and has a worldwide distribution. It is highly likely that chemical studies, including the occurrence of xanthones,

TABLE 1. Members of the Athyrioideae examined for mangiferin and isomangiferin

Species	Geographic location	Collector's name and number or date
<i>Acystopteris japonica</i> Nakai	Japan	Masamure 7.8.1928
<i>A. setosa</i> Bedd.	*Taiwan	Rosenstock 340
<i>A. tenuisecta</i> (Blume) Mett.	*China	Henry 11539
	Phillipines	Williams 2491
<i>Cystopteris alpina</i> Desv.	Faroos	Seidenfaden 21
<i>C. dentata</i> Desv.	Switzerland	July 1841. Meisner Herb.
<i>C. diaphana</i> (Bo.) Blasdell	*Canaries	Cook 431
<i>C. douglasii</i> Hk.	*Hawaii	Mann & Brigham 480
<i>C. fragilis</i> (L.) Bernh.	Iceland	Seidenfaden 956
	*Madeira	Kuntze 17488
	*Mongolia	Chaney 237
	India	MacLeod July 1891
	New Zealand	Murray January 1848
<i>C. grandis</i> C. Chr.	China	Maire 6046
<i>C. montana</i> (Lam.) Bernh.	Sweden	Moldenke 20966
	India	Koelz 21225
<i>C. moupinensis</i> Franch.	China	H. Smith 12098
<i>C. regia</i> Desv.	Switzerland	St. Lager 7.29.1895
<i>C. schizochlamys</i> Ching	China	H. Smith 10995
<i>C. setosa</i> Bedd.	India	Mann 181
<i>C. sudetica</i> A. Br. and Milde	Norway	Samuelson & Zander 7.22.1934
	Manchuria	Komarov 8
<i>Cystopteris</i> sp.	Austro-Hungary	Voss 2776
<i>Dryoathyrium boryanum</i> (Willd.) Ching	Borneo	Clemens 32563
<i>D. henryi</i> (Bak.) Ching	China	Chow 76106
<i>Gymnocarpium dryopteris</i> (L.) Newm.	Oregon	Marhala 2499
	Greenland	Feilberg 5095
	Norway	Kemp 7.11.1922
	Manchuria	Dorsett 6321
	China	Smith 12664
<i>G. gracilipes</i> (Copel.) Ching	*Phillipines	Copeland 112
<i>G. pulchella</i> (Salisb.) Hayek	Siberia	Sergievskaja 7.27.1923
<i>G. remotum</i> Ching	Himalayas	Koelz 644
<i>G. robertianum</i> (Hoffm.) Newm.	Himalayas	Stewart 22532a
	Sweden	Moldenke 20965
	Siberia	Reverdatto
<i>Lunathyrium japonicum</i> (Thunb.) Kurata	Japan	Danserau 527
<i>Woodsia alpina</i> (Bolton) Gray	Labrador	Platt and Boucot 5a
	Sweden	Moldenke 20996
	Kashmir	Stewart 21796
<i>W. crenata</i> (Kze.) Hier.	Bolivia	Brooke 6091
<i>W. delavayi</i> Christ.	China	Delavay 3
<i>W. elongata</i> Hk.	Himalayas	Stewart 21276
	Himalayas	Stewart 11333
<i>W. glabella</i> R. Br.	Quebec	Rousseau and Roureau 50
	Tyrol	Ronniger 8.3.1912
<i>W. hancockii</i> Bak.	China	Cowdry August 1963
<i>W. hyperborea</i> R. Br.	Sweden	Elfstrand 1879
<i>W. ilvensis</i> (L.) R. Br.	Greenland	Porsild 7.19.1924
	Czechoslovakia	Deyl 200
	Manchuria	Komaiov 4
<i>W. manchuriensis</i> Hk.	Japan	Tryas 72
<i>W. mexicana</i> Fee	New Mexico	Kipley and Barneby 3034
	Mexico	Correll and Johnston 20083

TABLE 1. *Continued*

Species	Geographic location	Collector's name and number or date
<i>W. mollis</i> (Klf.) J. Sm.	Mexico	Lott and Wendt 12. 14. 1980
<i>W. montevidensis</i> (Spr.) Hier.	Peru	Lopez 3713
	Colombia	Killif and Smith 17633
<i>W. obtusa</i> (Spr.) Torrey	New Hampshire	Eggleston 6. 27. 1898
	Bolivia	Rusby 338
<i>W. oregana</i> Ear.	Michigan	Richards 3784
<i>W. peruviana</i> Hk.	Mexico	Unknown 6
	Dominican Republic	Ekman 13644
<i>W. plummereae</i> Lemmon	New Mexico	Spellenberg 5138
	*Mexico	Gentry 19331
<i>W. polystichoides</i> Eat.	Japan	Stanford August 1894
	Japan	Uno 21664
	Japan	Toyasi 365
<i>W. scopulina</i> Eat.	Quebec	Fernald and Pease 24800

Mangiferin is 2-C-β-D-glucosyl-1,3,6,7-tetrahydroxyxanthone, and isomangiferin is the 4-C-glucosyl isomer.

*= positive.

will be helpful in elucidating or confirming the relationships of the various taxa in this complex.

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