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GLYCOSIDIC NATURE OF *EQUISETUM FLAVONOIDS*

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Key Word Index—*Equisetum*; *Sphenopsida*; flavonoid glycosides.

Plant and source: Ten *Equisetum* species were previously [1] collected in British Columbia, Canada. *Previous work*: *E. arvense* [2, 3], *E. palustre* [4], *E. sylvaticum* [3] and *E. telmateja* [3]. *Plant part examined*. In a previous study of *Equisetum* flavonoids [1], the nature of the sugar moities were not completely elucidated. The present report is a continuation of these studies in which the identity of eight glycosides is determined. Standard procedures were followed as previously reported [1], and further studies including controlled acid and enzymatic hydrolyses [5], periodate oxidation [6] and hydrogen peroxide oxidation [7] were also applied. The results are outlined in Table 1.

Kaempferol-3-β-sophoroside-7-β-glucopyranoside has been reported in the flowers of *Petunia hybrida* [8] and of *Galanthus nivalis* [5, 9], but no m.p. was given. Apigenin-4′-glucoside, on the other hand, was first reported as an unseparable mixture with apigenin-7-glucoside in *Dahlia variabilis* [10]. It was later identified in some *Pyrus* species [11], but no m.p. was given. Apigenin-4′-glucopyranoside has been synthesized by Farkas *et al.* [12], but the m.p. reported (234–5) was lower than that isolated in the present study (267–9). (m.p. of apigenin-5-glucoside = 295° [13], and apigenin-7-glucoside = 232–3° [14], 217–9° [15]). Finally, it is clear that the *Equisetum* diglucosides have a 1—2 linkage, giving rise to sophorosides.

REFERENCES

1. Saleh, N. A. M., Majak, W. and Towers, G. H. N. (1972) *Phytochemistry* **11**, 1095.
2. Nakamura, H. and Hukuti, G. (1940) *J. Pharm. Soc. Japan* **60**, 449.
3. Harborne, J. B. (1967) *Phytochemistry* **6**, 1569.
4. Beckmann, S. and Geiger, H. (1963) *Phytochemistry* **2**, 281.
5. Harborne, J. B. (1965) *Phytochemistry* **4**, 107.
6. Guthrie, R. D. (1962) *Methods in Carbohydrate*, (Whistler, R. L. and Wolfrom, M. L. eds), Vol. 1, p. 432, Academic Press, London.

Table 1.

Identified flavonoids	Positions of glycosylation (from UV data) (1)	H_2O_2 oxidation (1)(2)	Controlled acid hydrolysis (1)(3)	β-glucosidase	Periodate oxidation (4)	m.p. (Uncorrected) (°C) (5)	m.p. (Literature) (°C)
Kaempferol -3-β-sophoroside-7-β-glucopyranoside	3,7	Sophorose	K, K7G and K37G	Kaempferol-3-sophoroside	5	220–222	–
Kaempferol-3,7-β-di-glucopyranoside	3,7	Glucose	K and K7G	Kaempferol and kaempferol-3-glucoside	4	235	233 [16]
Kaempferol-3-β-sophoroside*	3	Sophorose	K and K3G	-*re*	–	194–6	197–8 [17], 198 [18]
Kaempferol-3-β-glucopyranoside	3	Glucose	K	Kaempferol	2	180	180 [8], 176–7 [16]
Kaempferol-7-β-glucopyranoside	7	–	K	Kaempferol	2	271	271 [8]
Kaempferol-3-rutinoside	3	Rutinose	K and K3G	-*re*	–	186–8	182–5 [19]
Quercetin-3-β-sophoroside	3	Sophorose	Q and Q3G	-*re*	–	202	203 [8, 17]
Apigenin-4′-β-glucopyranoside	4′	–	Ap	Apigenin	2	267–9	234–5 [12]

(1) Results from previous study [1].
(2) Repeated using authentic sophorose from kaempferol-3-sophoroside.
(3) Ap = apigenin; K = kaempferol; K3G = kaempferol-3-glucoside; K7G = kaempferol-7-glucoside; K37G = kaempferol-3,7-diglucoside; Q = quercetin; Q3G = quercetin-3-glucoside.
(4) Mol periodate/mol flavonoid, under mild oxidation conditions.
(5) Crystallized from ethanol–water mixtures.
* Co-chromatographed with an authentic sample of kaempferol-3-sophoroside kindly supplied by Prof. Dr. H. Wagner, München University.

7. Chandler, B. V. and Harper, K. A. (1961) *Austral. J. Chem.* **14,** 586.
8. Birkofer, L. and Kaiser, C. M. (1962) *Z. Naturforsch.* **17b,** 359.
9. Hörhammer, L., Wagner, H. and Beck K. (1967) *Z. Naturforsch.* **22b,** 986.
10. Nordstrom, C. G. and Swain, T. (1953) *J. Chem. Soc.* 2764.
11 Challice, J. S. and Williams, A. H. (1968) *Phytochemistry* **7,** 1781. (1970) *Phytochemistry* **9,** 1271.
12. Farkas, L., Wolfner, A., Nógrádi, M., Wagner, H. and Hörhammer, L. (1968) *Chem. Ber.* **101,** 1630.
13. Zemplén, G. and Mesta, T. (1943) *Chem. Ber.* **76,** 776.
14. Aritomi, M. (1963) *Chem. Pharm. Bull.* **11,** 1225.
15. Seshadri, T. R. and Vydeeswarn, S. (1972) *Phytochemistry* **11,** 803.
16. Schönsiegel, I., Egger, K. and Keil, M. (1969) *Z. Naturforsch.* **24b,** 1213.
17. Wagner, H., Hörhammer, L., Dirscherl, R., Farkas, L. and Nógrádi, M. (1968) *Chem. Ber.* **101,** 1186.
18. Freudenberg, K., Knauber, H. and Cramer, F. (1951) *Chem. Ber.* **84,** 144.
19. Hörhammer, L., Wagner, H. and Luck, R. (1956) *Arch. Pharm.*, **289,** 613.

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XANTHONES IN THE FERN *CTENITIS DECOMPOSITA**

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Key Word Index—*Ctenitis decomposita*; Aspidiaceae; Filicopsida; xanthones; mangiferin; isomangiferin; polyphenols.

Plant. Ctenitis decomposita (R. Br.) Copeland. Leaves were taken from plants which have been maintained in our collection for several years. A voucher specimen has also been deposited in our herbarium.

Previous work. On *C. decomposita*, none, on other *Ctenitis* species [1,2].

Present work. In our continuing study of polyphenolic compounds in ferns an unhydrolyzed extract of *Ctenitis decomposita* leaves was examined. Two prominent golden-yellow fluorescent spots were observed along with lesser amounts of what appeared to be flavonoids. The prominent compounds were isolated by paper chromatography using 15% HOAc and BAW (4:1:5). Both compounds were resistant to acid hydrolysis under conditions known to cleave *O*-glycosides. Their UV spectra were identical to that of mangiferin (1,3,6,7-tetrahydroxy-2-*C*-glucosylxanthone) discussed by Harborne [3]. R_f values were identical to those reported for mangiferin and isomangiferin (the 4-*C*-glucosyl isomer) which were isolated from *Asplenium montanum* [4]. An authentic sample of mangiferin was isolated from leaves of *Mangifera indica* for comparison purposes. NMR of the trimethylsilyl ethers of the unknowns confirmed their identification as mangiferin and isomangiferin.

Herbarium material from six additional species of *Ctenitis* was examined chromatographically for the xanthones. None was found in *C. crinalis*, *C. dissecta*, *C. eatonii*, *C. maximowicziana*, *C. sinii* and *C. velutina* although flavonoid spots were seen in several extracts. Negative results of this sort can be misleading especially since several of the specimens were quite old. Some recent acquisitions, however, were also negative. One of these was a sample of *C. decomposita* from a New Zealand collection. The variation in the appearance of xanthones in this species can not be explained at this time, but it may represent another example of geographic variation in biosynthetic capacity.

In addition to the observation of xanthones in *Asplenium montanum* referred to above [4] manigiferin and other xanthones have been observed in *Athyrium mesosorum* by Ueno [5]. It is of interest to note that *Athyrium* and *Ctenitis* were placed in Aspidiaceae by Copeland [6]. Further searches for xanthones in this family might prove interesting.

* Part VII in the series "Phenolic Compounds in Ferns". For Part VI see *Phytochemistry* **9,** 2197.