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FERNS

ASPIDIACEAE

THE PHLOROGLUCINOL DERIVATIVES OF *DR YOPTERZS POL YLEPZS*

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Plant. Dryopteris polylepis (Fr. et Sav.) C. Chr.

Uses. Medicinal.[1]

Previous work. On the sister species.[2]

Rhizomes. Dried material was percolated with Et_2O, and the extract was evaporated. The raw filicin obtained by method of Aebi[3] was dissolved in Et_2O. Upon concentration, crystalline material precipitated. Flavaspidic acid A B (major compound): $C_{22}H_{26}O_8$, yellow needles, m.p., mixed m.p. with synth. flavaspidic acid A B, NMR, UV, IR, TLC (solvent. $CHCl_3$–MeOH–H_2O, 7 : 3 : 1, lower) and alkaline cleavage. Mother liquor after removal of flavaspidic acid A B was evaporated and was dissolved in EtOAc.

Upon concentration, crystalline material precipitated. Dryocrassin : m.p., mixed m.p. with dryocrassin from ***D. crassirhizoma,***[4] IR and TLC. Mother liquor after removal of dryocrassin was chromatographed on silica, eluted by cyclohexane–$CHCl_3$ (3 : 2). Albaspidin B B: m.p., mixed m.p. with authentic sample, IR and TLC. Filixic acid: m.p., mixed m.p. with authentic sample, IR and TLC.

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[1] S. HISADA, *Syoyakuguku zasshi* **16,** 46 *(1962).*
[2] S. HISADA and Y. NORO, *Yakugaku zasshi* **81,** 1270 (1961).
[3] A. AEBI, J. BÜCHI and A. KAPOOR, *Helv. Chim. Acta 40,266 (1957).*
[4] *G.* SHIMADA, *Y.* NORO, K. OKUDA, I. INAGAKI, S. HISADA, T. TANAKA and H. YOKOHASHI, Abstracts of papers, Meeting of The Pharmacognostical Society of Japan, p. 33, Fukuoka (1968).

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GYMNOSPERMAE

CEPHALOTAXACEAE

OCCURRENCE OF BIFLAVONYLS IN *CEPHALOTAXUS*

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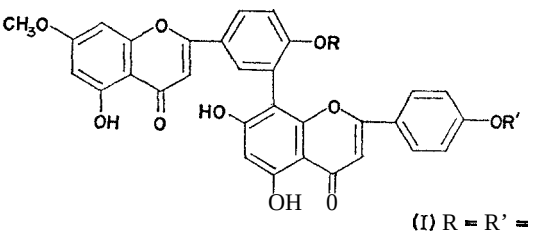
THE FACT that biflavonyls are restricted mainly to gymnosperms and that they are very important for their chemical classification stimulated us to investigate *Cephalotaxus* for

biflavonyls. *Cephalotaxus drupacea* Sieb. & Zucc and C. *nana* Nakai have already been reported to contain kayaflavone[1] as the sole biflavonyl constituent along with apigenin-5-rhamnoglucosyl in the former.[2] We now wish to report the isolation and characterization of sequoiaflavone(I), ginkgetin(II), sciadopitysin(III) and amentoflavone (in traces only) from the leaf extracts of C. *drupacea* Sieb. and Zucc. An apigenin glycoside was also obtained as a major component, but was not further investigated.

Extraction of fresh leaves followed by solvent fractionation, column chromatography and preparative TLC gave four biflavonyls. All gave the same hexamethyl ether which was identical with an authentic sample of amentoflavone hexamethyl ether. NMR studies of the acetates of each component characterized the three individual biflavonyls as mentioned above.



(I) R = R' = H
(II) R = Me. R' = H
(III) R = R' = Me

The presence of sciadopitysin in *Cephlotaxus* is noteworthy and is in contrast to the previous observation' that the Taxaceae are characterized by the presence of sciadopitysin whereas *Cephalotaxus* yield kayaflavone. Furthermore, the non-coniferous[3] plants of cycadales, Ginkgoales, Taxaceae and Cephlatotaxaceae produce biflavonyls of only amentoflavone series while the true conifers, with the notable exception of Pinaceae,[1] are characterized by the presence of biflavonyls belonging to more than one series.[4]

It may, therefore, be inferred that morpholigical divergence in the non-coniferous[3] plants is accompanied by chemical convergence. It is perhaps possible that similar enzyme systems present in them are syntherizing analogous biflavonyls.

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[1] W. BAKER and W. D. OLLIS, *Recent Developments in the Chemistry of Natural Phenolic Compounds* (edited by W. D. OLLIS), p. 181, Pergamon Press (1961).
[2] VICTOR PLOUVIER, C. *R. Acad. Sci. Paris*, **263**, 1529 *(1966)*.
[3] H. ERDTMAN and T. NORIN, *Progress in the Chemistry of Organic Natural Products* (edited by L. ZECHMEISTER) p. *248*, Springer-Verlag (1966).
[4] W. RAHMAN et *al.*, unpublished work.