

## 水蕨與姬蕨極性成分之研究

### Studies on the polar components of *Ceratopteris Thalictroides* (L.) Brongn. And *Hypolepis punctata* (Thunb.) Mett.

#### 中文摘要

本論文以初步活性篩選顯示具抗癌活性之姬蕨與水蕨為主題，並做進一步化學成分之分離與探討。水蕨全草以甲醇冷浸萃取，浸液經減壓濃縮後，以 n-hexane、Ethyl acetate 及 H<sub>2</sub>O 分配萃取，經初步藥理活性篩選確定活性部分為 n-Hexane 及 Ethyl acetate 層，利用各種不同之層析法，經分離與純化後得 22 個化合物：quercetin 3-O- $\beta$ -D-glucopyranoside (174.2 mg) (CT-1)、ferulic acid (356.9 mg) (CT-2)、p-coumaric acid (11.7 mg) (CT-3)、3-(4-hydroxy-phenyl)-acrylic acid methyl ester (23.8 mg) (CT-4)、p-hydroxy benzaldehyde (7.5 mg) (CT-5)、 $\beta$ -sitosterol and  $\beta$ -stigmasterol mixture (19.8 mg) (CT-6)、stigmast-5-ene-3,7-dione (6 mg) (CT-7)、pterodin Z (8.1 mg) (CT-8)、pterodin A (4 mg) (CT-9)、pterodin V (6 mg) (CT-10)、pterodin K (3.5 mg) (CT-11)、pterodin Z (80 mg) (CT-12)、pterodin D 3-O- $\beta$ -D-glucopyranoside (209 mg) (CT-13)、12-chloro-pterodin D 3-O- $\beta$ -D-glucopyranoside (14mg) (CT-14)\*、ceratopterodin B (38 mg) (CT-15)、ceratopterodin C (36.6 mg) (CT-16)、ceratopterodin D (3.5 mg) (CT-17)\*、ceratopterodin E (6 mg) (CT-18)\*、6-O-p-coumaroyl-D-glucopyranoside (28 mg) (CT-19)、3-O-p-coumaroyl-D-glucopyranoside (33.3 mg) (CT-20)、4-O-p-coumaroyl-D-glucopyranoside (5 mg) (CT-21)、kaempferol 3-O- $\beta$ -glucopyranoside (20 mg) (CT-22)。其中 CT-14、CT-17、CT-18 為 pterodin 類中之新化合物。其他如 CT-1、CT-2、CT-3、CT-4、CT-5、CT-6、CT-7、CT-14、CT-17、CT-18、CT-20、CT-21、CT-22 皆為本植物中首次發現之化合物。姬蕨全草鮮品之甲醇萃取物，經以 n-Hexane、Ethyl acetate 及 H<sub>2</sub>O 分配萃取，並取具有活性之水層，藉由各種層析法，共分離出 6 個化合物。利用各種光譜分析鑑定其主要架構，分別為：Caffeic acid (14 mg) (HP-1)、2R,3R pterodin-L-13-O- $\beta$ -D-glucopyranoside (26.8 mg) (HP-2)、7', 8' -Dihydro-7' - (4'-hydroxy-3'-methoxyphenyl)-3-(hydroxymethyl)-1-benzofuranpropanol 4'-O- $\beta$ -glucopyranoside (29.1 mg) (HP-3)、6, 7' -dihydroxysolariciresinol 4' -O- $\beta$ -glucopyranoside (49.1 mg) (HP-4)\*、(+)-Lariciresinol 4' -O- $\beta$ -D-glucopyranoside (56.3 mg) (HP-5)、(+)-Pinoresinol 4' -O- $\beta$ -D-glucopyranoside (6 mg) (HP-6)。其中 HP-4 為新化合物。其他如 HP-1、HP-2、HP-3、HP-5、HP-6 為本植物中首次發現之化合物，活性部分則尚待評估。

## 英文摘要

In the course of our preliminary anticancer screening program, we found that the MeOH extract of *Ceratopteris thalictroides* (L.) Brongn and *Hypolepis punctata* (Thumb.) Mett. exhibited cytotoxic activity. Thus, it intrigued us to further chemical investigation of these two plants. The MeOH extract of whole fresh ferns of *C. thalictroides* was divided into fractions soluble in hexane, ethyl acetate, and H<sub>2</sub>O. From EtOAc fraction 22 compounds were isolated by Diaion, Sephadex LH-20, ODS, and silica gel column chromatography. Based on the 1D, 2D NMR and HRMS spectroscopic techniques, the structures were characterized as: quercetin 3-O- $\beta$ -D-glucopyranoside (CT-1), ferulic acid (CT-2), p-coumaric acid (CT-3), 3-(4-hydroxyphenyl)-acrylic acid methyl ester (CT-4), p-hydroxy benzaldehyde (CT-5),  $\beta$ -sitosterol and  $\beta$ -stigmasterol mixture (CT-6), stigmast-5-ene-3,7-dione (CT-7), pterosin Z (CT-8), pterosin A (CT-9), pterosin V (CT-10), pterosin K (CT-11), pteroside Z (CT-12), pterosin D 3-O- $\beta$ -D-glucopyranoside (CT-13), 12-chloro-pterosin D 3-O- $\beta$ -D-glucopyranoside (CT-14), ceratopteroid B (38 mg) (CT-15), ceratopteroid C (CT-16), ceratopteroid D (CT-17), ceratopteroid E (CT-18), 6-O-p-coumaroyl-D-glucopyranoside (CT-19), 3-O-p-coumaroyl-D-glucopyranoside (CT-20), 4-O-p-coumaroyl-D-glucopyranoside (CT-21), kaempferol 3-O- $\beta$ -glucopyranoside (CT-22). Among these, compounds CT-14, CT-17, and CT-18 are newly discovered. The others, CT-1~CT-7, CT-14, CT-17~CT-18, CT-20~CT-22 were isolated from *C. thalictroides* (L.) Brongn. for the first time.

Similarly, the MeOH extract of fresh plant of *Hypolepis punctata* was divided into fractions soluble in n-hexane, ethyl acetate and H<sub>2</sub>O. These fractions were subjected to various chromatography and cytotoxic screening. Totally, six compounds were isolated from this fern, and their structures were determined to be caffeic acid (HP-1), 2R,3R pterosin-L 13-O- $\beta$ -D-glucopyranoside (HP-2), 7',8'-Dihydro-7'-(4'-hydroxy-3'-methoxyphenyl)-3-(hydroxymethyl)-1-Benzofuranpropanol 4'-O- $\beta$ -glucopyranoside (HP-3), 6,7'-dihydroxyisolariciresinol 4'-O- $\beta$ -glucopyranoside (HP-4), (+)-Lariciresinol 4'-O- $\beta$ -D-glucopyranoside (HP-5), (+)-Pinoresinol 4'-O- $\beta$ -D-glucopyranoside (HP-6). Compound HP-4 is newly discovered, and the rest five compounds were first found in this fern.