Phytochemistry, 1974, Vol. 13, pp. 509 to 511. Pergamon Press. Printed in England.

NEW INDANONE COMPOUNDS FROM *ONYCHIUM JAPONICUM*

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(*Received* 5 *July* 1973. *Accepted* 20 *July* 1973)

Key Word Index—*Onychium japonicum*: Pteridaceae: 4-hydroxy-1-indanone derivatives; pteroside M; pterosin M. M; pterosin M.

Abstract—A new indanone glucoside pteroside M has been isolated from fronds of *Onychium japonicum* (Pteridaceae). The structure of its aglycone pterosin M has been established by ^{13}C NMR, PMR spectra and degradation with nitric acid.

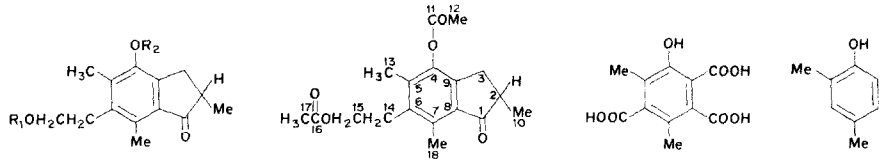
DURING the studies of chemotaxonomy of Pteridaceae,[1-3] we isolated a colourless crystalline compound (*ca* 0·01%) from the ethyl acetate extract of the fronds of *Onychium japonicum*. The compound was purified by recrystallization from EtOAc, m.p. 192°, λ_{max} 272 and 322 nm, which has the molecular formula of $C_{20}H_{28}O_8$. It gives monomethyl ether with diazomethane, this suggests the existence of a free phenolic hydroxyl group in the molecule. An aglycone and glucose are produced by acid or enzymatic hydrolysis. The aglycone, m.p. 187°, *m/e* 234, λ_{max} 271 and 322 nm, has the empirical formula $C_{14}H_{18}O_3$. In the presence of ethanolic sodium hydroxide the λ_{max} of the aglycone undergoes a pronounced bathochromic shift to 288 and 365 nm, indicating the presence of a phenolic hydroxyl group. The aglycone gives monomethyl ether, m.p. 114°, *m/e* 248, and diacetate, m.p. 77–79°, *m/e* 318. The presence of carbonyl group is indicated with 2,4-dinitrophenylhydrazine solution and IR spectrum. The absorption band 1675 cm^{-1} suggests that a carbonyl group exists in 5-membered ring.

The name of pteroside M (**1**) is proposed for the new glucoside, and pterosin M (**2**) for the aglycone due to their 1-indanone structure as indicated in further data of ^{13}C NMR and PMR spectra. We use the trivial names as the proposed system by Natori *et al.*[4]

The ^{13}C NMR spectrum of (**3**) (in $CDCl_3$, chemical shifts are relative to TMS) showed resonances at δ 209·00 (C-1 carbon), 170·78 (C-16), 168·42 (C-11), 144·63 (C-4), 144·21 (C-6), 135·77 (C-7, C-8), 135·599 (C-9), 132·92 (C-5), 62·42 (C-15), 42·17 (C-2), 30·46 (C-3), 28·28 (C-14), 20·75 (C-17), 20·33 (C-12), 16·26 (C-10) and 13·29 (C-13 and C-18).

[1] HASEGAWA, M. and AKABORI, Y. (1968) *Bot. Mag. Tokyo* **81**, 469.
[2] AKABORI, Y. and HASEGAWA, M. (1969) *Bot. Mag. Tokyo* **82**, 294.
[3] AKABORI, Y. and HASEGAWA, M. (1970) *Bot. Mag. Tokyo* **83**, 263.
[4] YOSHIHIRA, K., FUKUOKA, M., KUROYANAGI, M. and NATORI, S. (1972) *Chem. Pharm. Bull.* **20**, 426, footnote.

The PMR spectrum of (**3**) in $CDCl_3$ (reference, TMS) showed resonance absorptions at δ 1·26 ppm (*d*, *J* 8 Hz, 3H, C-10 methyl protons), 2·05 (*s*, 3H, acetyl protons), 2·43 (*s*, 3H, acetyl protons), 2·40 (*s*, 3H, C-5 methyl protons), 2·70 (*s*, C-7 methyl protons), 3·08 (*t*, *J* 8 Hz, 2H, C-14 methylene protons, 4.17 (*t*, *J* 8 Hz, 2H, C-15 methylene protons) and 2·2–3·4 (*m*, 3H, C-3 methylene protons and C-2 methin protons overlapped). The C-7 methyl protons appeared at 2·70, whereas C-5 methyl protons appeared at 2·40. This shows that C-7 methyl group is deshielded by the next carbonyl group forming 5-membered ring, accordance with the result of 6-hydroxyethyl-2,5,7-trimethyl-1-indanone (pterosin B). The location of the secondary methyl at C-2 was confirmed by the fact that the doublet methyl signal of (**3**) changed into singlet after 1 hr of standing at room temperature in CF_3COOD due to deuteration of the methin proton in coupling with the methyl protons through enolization.



(**1**) R_1 = glucose; R_2 = H
(**2**) R_1 = R_2 = H

(**3**) (**4**) (**5**)

The aglycone was oxidized with dilute nitric acid[5] giving an oxidation product (**4**), which, without purification, was decarboxylated with copper in quinoline affording 2,4-xylenol (**5**). The phenolic compounds of the reaction mixture were checked by GLC and a peak showing the same retention time with an authentic sample was observed. Therefore the oxidation product must be 3,5-dimethyl-6-hydroxybenzene-1,2,4-tricarboxylic acid (**4**) and the structure of pterosin M is established as 4-hydroxy-6-hydroxyethyl-2,5,7-trimethyl-1-indanone (**2**). The structure of pteroside M is (**1**).

Many 1-indanone derivatives have been detected in *Pteridium aquilinum*[4–8] and *Histiopteris incisa*,[9] which have no hydroxyl group at 4 position. The compounds having 4-hydroxy-1-indanone structure have been reported first in ferns.

EXPERIMENTAL

Isolation. The fronds of *Onychium japonicum* (1·8 kg) collected at Yamakita (Kanagawa Prefecture) on 19 September 1971 were extracted with hot MeOH. After evaporation of MeOH, the residue was dissolved in hot H_2O (300 ml), from which EtOAc soluble fraction prepared by the ordinary method.[1] The combined ethyl acetate extracts were concentrated under reduced pressure. The residue dissolved in 30 ml EtOH was added 30 g polyamide powder (Woelm), which was dried at 100°. The dried powder added to polyamide column (3 × 40 cm) was eluted with H_2O, 300 ml each eluate was collected and examined by PC (6% HOAc). The 3rd and 4th fractions contained pteroside M, which were concentrated to syrup and extracted with EtOAc. After evaporation of the EtOAc, a crystalline mass appeared, yield 1·5 g, which was recrystallized from EtOAc to give pure **1**.

Pteroside M. From EtOH, m.p. 192°; $[\alpha]_D^{18}$ + 129° (Me_2CO + H_2O, *c* 1·2) (Found: C, 60·49 and H, 7·38. $C_{20}H_{28}O_8$ requires: C, 60·59 and H, 7·12%). λ_{max}: (EtOH) 233, 277, 322 nm (ϵ 4·31, 4·05, 3·51). This compound gave one spot on TLC (Wakogel B-5UA, EtOAc–$CHCl_3$–HCOOH–H_2O, 19:1:1:1, R_f 0·28) and PC (6% HOAc, R_f 0·76; BAW, 0·73). Pteroside M monomethyl ether was prepared with CH_2N_2, m.p. 68°. λ_{max}: 265, 312 nm (EtOH). ν_{max}^{KBr}: 3400, 2900, 1685, 1640, 1588. The hydrolysis product with β-glucosidase was identified with pterosin M monomethyl ether by a m.m.p. test and IR.

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[9] RONALDSON, J. W. (1972) *Chem. Ind. (London)* **72**, 764.

Hydrolysis of pteroside M. Pteroside M (0·6 g) was hydrolyzed with β-glucosidase (0·4 g), or with hot 5% H_2SO_4. Pterosin M was recrystallized from hot H_2O or from EtOAc, m.p. 187°. λ_{max}: 271, 323 nm (EtOH) (Found: C, 71·62 and H, 7·94. $C_{14}H_{18}O_3$ requires: C, 71·77 and H, 7·74%). ν_{max}^{KBr}: 3390, 2950, 2900, 1675, 1600, 1590. Diacetate was prepared with pyridine and acetic anhydride, recrystallized from EtOH, m.p. 77–79°. ν_{max}^{KBr}: 2975, 2940, 1750, 1700, 1604; *m/e* 318.

Pterosin M monomethyl ether. Pterosin M was methylated with diazomethane, recrystallized from H_2O and then from dil. MeOH, m.p. 114°; λ_{max} 255, 311 nm (EtOH); *m/e* 248.

Acknowledgement—The authors thank Dr. Shinsaku Natori of the National Institute of Hygienic Science for his valuable help during this study.