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Chemical and Toxicological Studies on Bracken Fern, *Pteridium aquilinum* var. *latiusculum*. III.[1] Further Characterization of Pterosins and Pterosides, Sesquiterpenes and the Glucosides having 1-Indanone Skeleton, from the Rhizomes

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Four pterosins, illudoid sesquiterpenes, and nine pterosides, the glucosides, were isolated from the rhizomes of *Pteridium aquilinum* var. *latiusculum*. The stereostructures of the new compounds were elucidated by chemical and physical methods based on the structures established for the compounds obtained from the fronds.[1,3]

Keywords——*Pteridium aquilinum* var. *latiusculum*; pterosins; pterosides; 1-indanone derivatives; illudoid sesquiterpene glucosids; optical purities

In the previous paper,[3] extraction and fractionation of constituents of young fronds of bracken fern, *Pteridium aquilinum* var. *latiusculum* (Pteridaceae), were reported along with toxicity tests aiming at characterization of the carcinogenic principle(s). In the course of works more than twenty kinds of sesquiterpenes having 1-indanone nucleus, named pterosins, and the glucosides, named pterosides, were isolated and the structures were elucidated as reported in the preceding paper.[1] Since the rhizomes of the plant were proved to exhibit stronger carcinogenicity for rats[4] and toxicity for cattles[5] than young fronds, systematic surveys on the constituents of the rhizomes were performed and several pterosins and pterosides were characterized. This paper deals with the structures of these compounds in special reference to the occurrence of diastereomers of those isolated from the young fronds.[6]

The dried rhizomes were extracted with methanol and the extract was separated first by charcoal column and then by silica gel column and preparative thin-layer chromatographies to give four pterosins and nine glucosides. Among these compounds, three of four pterosins, (2*S*)-pterosin A (**1**), (2*R*)-pterosin B (**2**) and (2*R*)-pterosin F (**3**), were identified with those obtained from young fronds[1] by infrared (IR), ultraviolet (UV), and nuclear magnetic resonance (NMR) spectra, and the same sign of optical rotations. The other one, (2*R*, 3*R*)-pterosin C (**4**), $[\alpha]_D$ −65.3°, was proved to be antipodal to (2*S*, 3*S*)-pterosin C (**4'**) isolated from the fronds.[1] Among the nine glucosides (2*S*)-pteroside A (**5**) and (2*R*)-pteroside B (**6**) were identified with those from the fronds.[1] (2*S*)-Pteroside B (**7**), (2*R*, 3*R*)-pteroside C (**8**) and (2*S*, 3*R*)-pteroside C (**9**) are diastereoisomers of those from the fronds.[1] (3*S*)-Pteroside D (**10**), (2*S*)-pteroside K (**11**), and pteroside Z (**12**) are new glucosides, though their aglycones or the enantiomers have been obtained from the fronds.[1] (2*S*)-Pteroside P (**13**) is a new

1) Part II: M. Fukuoka, M. Kuroyanagi, K. Yoshihira, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **26**, 2365 (1978).
2) Location: *Kamiyoga-1-chome, Setagaya-ku, Tokyo.*
3) K. Yoshihira, M. Fukuoka, M. Kuroyanagi, S. Natori, M. Umeda, T. Morohoshi, M. Enomoto, and M. Saito, *Chem. Pharm. Bull.* (Tokyo), **26**, 2346 (1978).
4) I. Hirono, K. Fushimi, H. Mori, T. Miwa, and M. Haga, *J. Natl. Cancer Inst.*, **50**, 1367 (1973).
5) J. Iwata and K. Yamaguchi, The paper presented at Annual Meeting of Japanese Society of Veterinary Sciences, 1974.
6) A part of the work was reported in the preliminary communication (M. Kuroyanagi, M. Fukuoka, K. Yoshihira, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **22**, 2762 (1974).

member of the group. Total amount of the glucosides in the rhizomes is more than that in the fronds, while that of the free forms, pterosins, is smaller. The following is the details of the structure elucidation of these glucosides.[6]

(2*S*)-Pteroside A (**5**), mp 116—118°, $C_{21}H_{30}O_8$, $[\alpha]_D$ −49.6,° was identical with that isolated from the young fronds.[1] The IR and UV spectra showed the presence of a glycosyl residue (ν_{max} 3320, 1100—1010 cm^{-1}) and the pterosin skeleton (ν_{max} 1678, 1605 cm^{-1} and λ_{max} 216, 260, 305 nm).[1] In NMR spectrum (CD_3OD) of **5** there disclosed the presence of an aliphatic tertiary methyl group (δ 1.07 (3H, s)), methylene protons (δ 2.65 (1H, d, J=17.5 Hz) and δ 3.25 (1H, d, J=17.5 Hz)), an aromatic proton (δ 7.06 (1H, s)), and two aromatic methyl groups (δ 2.41 (3H, s) and δ 2.62 (3H, s)). Pteroside A (**5**) gave pentaacetate (**14**) and was hydrolyzed to give glucose and (2*S*)-pterosin A (**1**).[1] The anomeric protons in **5** and **14** (Table I) suggested that the glycoside linkage is β. Consequently pteroside A (**5**) was concluded to be (2*S*)-pterosin A 2′-O-β-D-glucopyranoside. The same conclusion was obtained by Hikino, *et al.* for the compound obtained from the whole plant of the same species.[7]

Table I. The NMR of Anomeric Proton of Pterosides and Their Acetates

Compound	Chemical shift (δ, ppm)	Coupling constant (Hz)	Solvent
Pteroside A (**5**)	4.27	6.5	CD_3OD
Pteroside B (**6**)	4.28	6.5	CD_3OD
Pteroside C (**8**)	4.26	6.5	CD_3OD
Pteroside D (**10**)	4.27	6.5	CD_3OD
Pteroside K (**11**)	4.17	7.0	CD_3OD
Pteroside P (**13**)	4.28	6.5	CD_3OD
Pteroside A peracetate (**14**)	4.48	7.0	$CDCl_3$
Pteroside B peracetate (**15**)	4.42	7.5	$CDCl_3$
Pteroside C peracetate (**16**)	4.44	7.0	$CDCl_3$
Pteroside K peracetate (**20**)	4.44	7.5	$CDCl_3$
Pteroside P peracetate (**23**)	4.44	7.5	$CDCl_3$

(2*R*)-Pteroside B (**6**), mp 120—122,° $[\alpha]_D$ −48.8,° $C_{20}H_{28}O_7$, was identified with the compound obtained from the young fronds[1] and also with that isolated from the same source by Hikino, *et al.*[8] Pteroside B (**6**) gave tetraacetate (**15**) by acetylation and glucose and (2*R*)-pterosin B[1] (**2**), by hydrolysis.

(2*S*)-Pteroside B (**7**), mp 164—166°, $[\alpha]_D$ −13.6°, showed superimposable IR and UV spectra with (2*R*)-pteroside B (**6**) but the signs of the optical rotation and the circular dichroism (CD) Cotton effect were opposite to those of **6**. The glucoside (**7**) was hydrolyzed to give glucose and (2*S*)-pterosin B (**2′**), which showed the same physical properties with (2*R*)-pterosin B (**2**) except the opposite sign of the optical rotation and the CD curve. Thus the glucoside (**7**) was concluded to be (2*S*)-pteroside B.

Though two glucosides (**6** and **7**) exhibit entirely close natures as observed in IR, NMR and UV spectra, the two isomers, in which the chiral center in the aglycone portion is apart from the glucosyl group, were separable by chromatography under some conditions.

(2*R*, 3*R*)-Pteroside C (**8**), mp 162—165,° $[\alpha]_D$ −70.3°, $C_{20}H_{28}O_8$, was suggested to be a glucoside of pterosin C from IR, UV and NMR spectra. Acetylation of **8** gave a pentaacetate

7) H. Hikino, T. Takahashi, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **20**, 210 (1972).
8) H. Hikino, T. Takahashi, S. Arihara, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 1488 (1970).

(**16**). Hydrolysis of **8** gave glucose and an aglycone (**4**), which showed identical mp, IR and NMR spectra but opposite signs in $[\alpha]_D$ and CD to (2*S*, 3*S*)-pterosin C[1] (**4'**). These observations indicated the stereochemistry of the pteroside C (**8**) as 2*R*, 3*R*. The same conclusion was obtained by Hikino, *et al.*[7] for the same compound from the same source. As precisely discussed in the previous paper[1] the sample of the glucoside (**8**) contained a small amount of the epimer at C-2 (**9**) as suggested by NMR.

(2*S*, 3*R*)-Pteroside C (**9**), mp 174—176°, $[\alpha]_D$ −46.6°, had similar IR and UV spectra to (2*R*, 3*R*)-pteroside C (**8**). The NMR signals of **9** were superimposable with those of **8** except the secondary methyl group [δ 1.20 (3H, d, J=7.5 Hz)] and the carbinyl proton at C-3 [δ 5.07 (1H, d, J=6.7 Hz)], in which the coupling constant was larger than that of **8** [δ 4.59 (1H, d, J=4.5 Hz)]. Hydrolysis of the pteroside (**9**) gave glucose and an aglycone (**17**), $[\alpha]_D$ −37.1°, showing nearly an identical IR spectrum to (2*S*, 3*S*)-pterosin C (**4'**).[1] In the NMR of **17** the secondary methyl group [δ 1.16 (3H, d, J=7 Hz)] and the carbinyl proton at C-3 [δ 5.13 (1H, d, J=6.8 Hz)] appeared in slightly higher fields but other signals were superimposable to those of *trans*-pterosin C (**4** and **4'**). Treatment of **17** with alkaline methanol caused the epimerization at C-2 to give the *trans*-pterosin C (**4**) containing small amount of the original compound (**17**). Thus the *cis*-configuration in **17** and **9** was confirmed. *cis*-Pteroside C (**9**) and *cis*-pterosin C (**17**) showed negative CD-curves associated with n→π^* transition as same as *trans*-pteroside C (**8**) and *trans*-pterosin C (**4**), indicating (2*S*, 3*R*)-configurations as precisely discussed in the previous paper.[1] The pteroside (**9**) was again concluded to be β-D-glucopyranoside at C-2' from the NMR, especially from the anomeric proton signal [δ 4.26 (1H, d, J=6.5 Hz)] and from the ease for hydrolysis with emulsin. The sample of the glucoside (**9**) was contaminated with the epimer (**8**) as in the case of the related compounds.

In this connection the stereochemistry of another isomer (**18**) of pteroside C, isolated from the fronds,[1] was firmly established to be (2*R*, 3*S*)-pteroside C from the following evidence: Hydrolysis of **18** gave glucose and an aglycone (**17'**), $[\alpha]_D$ +40.3,° showing identical IR and NMR but opposite signs of CD and optical rotation to (2*S*, 3*R*)-pterosin C (**17**). The NMR spectrum suggested contamination of a small amount of the epimer at C-2 in **18**.

Table II. The Optical Properties of Pterosin C Derivatives

Compound[a]	*trans-cis* ratio (by NMR)	CD (n→π^*) [θ] (in MeOH)	$[M]_D$ (in MeOH)
Pterosin C(a)	5.5 : 6	+18870	+130.3°
Pterosin C(b)	2 : 1	+22135	+217.9°
Pterosin C(c)	7.5 : 10	+22371	+171.2°
Pterosin C(d)	2.1 : 1	+20688	+192.8°
Pterosin C(d)−OH^-	4.4 : 1	+22939	+229.3°
Pterosin C(e)	9 : 1	−5542	−55.2°
Pterosin C(f)	9 : 1	−1561	−14.3°
Pterosin C(g)	4 : 1	−12320	−152.8°
Pterosin C(h)	10 : 1	−11722	−122.9°
Pterosin C(i)	7.3 : 1	−2240	−29.7°
Pterosin C(j)	8.3 : 1	−13566	−134.8°
Pterosin C(k)	8 : 1	−24453	−222.3°
Pterosin C(l)	1 : 10	−20415	−86.8°
Pterosin C(l)−OH^-	4 : 1	−22902	−201.9°
Palmitylpterosin C	*trans*	+20978	+229.9°
Palmitylpterosin C	*cis*	+18902	+74.6°
Pterosin L	*cis*	+18291	+62.6°
epi-Pterosin L	*trans*	+18480	+203.3°

a) Pterosin C(a)—(d) were isolated from the fronds, (e)—(g) were isolated from the rhizomes, and (h)—(l) were obtained from pteroside C isolated from the rhizomes. Pterosin C(d)−OH^- and (l)−OH^- were derived from pterosin C (d) and (l) respectively by alkaline epimerization.

As shown in the previous paper[1] pterosin C (**4'**) isolated from the fronds was proved to be (3*S*), though the ratio of *trans* (2*S*, 3*S*) and *cis* (2*R*, 3*S*) isomers varied from one sample to another. On the contrary pterosin C (**4**) and pterosides C (**8**, **9**) from the rhizomes are chiefly composed of (3*R*)-isomers and again the ratio of the diastereoisomers varies from one lot to another. They are practically inseparable, but the samples of pterosides C, chiefly composed of (2*R*, 3*R*)-isomer (**8**) and (2*S*, 3*R*)-isomer (**9**), were isolated as shown above and the corresponding aglycones (**4** and **17**) were prepared. The optical properties of these pterosin C derivatives are cumulatively shown in Table II. As shown in the previous paper[1] the NMR signals of the carbinyl protons at C-3 are good guides for the *trans-cis* ratio. Table II indicates that the sign and the amplitude of CD reflect the stereochemistry at C-3 and the optical purities respectively.

(3*S*)-Pteroside D (**10**), amorphous powder, $[\alpha]_D$ −52.4°, $C_{21}H_{30}O_8$, showed the characteristic IR and UV for the pterosides. NMR of **10** exhibited the signals of a geminal dimethyl group at C-2 [δ 1.01 (3H, s) and δ 1.15 (3H, s)], a carbinyl proton at C-3 [δ 4.67 (1H, s)] and a deshielded aromatic proton [δ 7.25 (1H, s)], but other signals were similar to those of pteroside B (**6**) including the anomeric proton [δ 4.27 (1H, d, J=6.5 Hz)]. Pteroside D (**10**) was hydrolyzed with emulsin or an acid to give glucose and (3*S*)-pterosin D (**19**), having opposite configuration to the (3*R*)-isomer (**19'**) isolated from the fronds.[1]

(2*S*)-Pteroside K (**11**), mp 94—96,° $[\alpha]_D$ −26.4,° $C_{21}H_{29}O_7Cl$, is a glycoside (ν_{max} 3300, 1100—1010 cm^{-1}) of a pterosin derivative containing a chlorine atom. In NMR (CD_3OD) the aglycone part was shown to be similar to pterosin A (**1**); an aliphatic methyl at C-2 (δ 1.11 (3H, s)), a higher field proton of methylene at C-3 (δ 2.68 (1H, d, J=17.5 Hz)), an aromatic proton (δ 7.13 (1H, s)), and two aromatic methyl groups (δ 2.42 (3H, s) and δ 2.62 (3H, s)) are present in **11**. Pteroside K (**11**) gave tetraacetate (**20**), $C_{29}H_{37}O_{11}Cl$. The NMR of **20** was again consonant to a glucoside of a pterosin A derivative having a chlorine atom.

Pteroside K (**11**) was hydrolyzed with emulsin to give glucose and the aglycone, which was identified with natural (2*S*)-pterosin K[1] (**21**) by every means including $[\alpha]_D$ and CD spectra. In NMR of **11** the anomeric proton appeared at δ 4.17 (1H, d, J=7 Hz). The NMR data (Table I) and hydrolysis of **11** by emulsin indicated β-D-glucopyranoside linkage in **11**. Therefore the structure of pteroside K (**11**) was confirmed to be (2*S*)-pterosin K β-D-glucopyranoside.

Most of the pterosin glycosides so far reported have the sugar residue at the hydroxyethyl group at C-6 and some others at the hydroxyl group at C-3;[9] thus pteroside K (**11**) is a first example of the glycosides bearing the sugar portion at the hydroxymethyl at C-2.

Pteroside Z (**12**) showed characteristic IR for the pterosides. The NMR of **12** exhibited the presence of an equivalent geminal dimethyl group at C-2 [δ 1.18 (6H, s)] and a methylene at C-3 [δ 2.93 (2H, br.s)] besides characteristic aromatic methyl groups, an aromatic proton, and protons of a glucosyl residue of pterosides. **12** was hydrolyzed by acid to give glucose and pterosin Z (**22**).[1] These data indicated to be the glucoside of pterosin Z[1] for **12**.

Pterosides D (**10**) and Z (**12**) were obtained from the same source and the same structures were proposed by Hikino, *et al.*[10]

(2*S*)-Pteroside P (**13**), mp 191—193,° $[\alpha]_D$ −14.8,° $C_{20}H_{28}O_8$, showed the presence of a glycosyl group (ν_{max} 3360, 1100—1010 cm^{-1}) and the 1-indanone nucleus (ν_{max} 1705, 1603 cm^{-1}, λ_{max} 217, 258, 305 nm). When the NMR spectrum of **13** was compared with the signals of other pterosides, the presence of one aliphatic methyl group at C-2 (δ 1.23 (3H, d, J=7 Hz)), a deshielded aromatic proton (δ 7.40 (1H, s)) similar to those of pterosins C and D bearing a

9) P. Sengupta, M. Sen, S.K. Niyogi, S.C. Pakrashi, and E. Ali, *Phytochemistry*, **15**, 995 (1976); N. Tanaka, M. Hata, T. Murakami, Y. Saiki, and C.-M. Chen, *Chem. Pharm. Bull.* (Tokyo), **23**, 1890 (1975); T. Murakami, N. Tanaka, K. Tanaka, and C.-M. Chen, *Chem. Pharm. Bull.* (Tokyo), **22**, 2758 (1974).

10) H. Hikino, T. Takahashi, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **19**, 2424 (1971).

hydroxyl group at C-3,[1] and an aromatic methyl group at C-7 (δ 2.65 (3H, s)) was clearly disclosed but the signal of the methyl group at C-5[1] was not observed. Pteroside P (**13**) gave a pentaacetate (**23**) by acetylation.

Pteroside P (**13**) was hydrolyzed with emulsin to give glucose and the aglycone, pterosin P (**24**), mp 115—117,° $C_{14}H_{18}O_3$. The NMR spectrum of **24** showed the presence of one aromatic methyl at C-7 (δ 2.69) and of a hydroxymethyl group (δ 4.72 (2H, s)) on the aromatic ring, and other signals were quite similar to those of pterosin B (**2**). The aglycone (**24**) gave a diacetate (**25**), the NMR of which showed the presence of an acetoxymethyl group (δ 2.03 (3H, s), 5.21 (2H, s)) and an acetoxyethyl group at C-6 (δ 2.12 (3H, s), 3.08 (2H, d, J=7 Hz), 4.17 (2H, d, J=7 Hz)). These facts indicated that a hydroxymethyl group was substituted at C-5 instead of the methyl group in other pterosins and pterosides. Comparison of the NMR spectra of **13**, **23**, **24**, and **25** disclosed a down field shift of the methylene signal of the hydroxylmethyl group by acetylation (in **23**, δ 5.16 (2H, s)), indicating the glycoside bond in the hydroxylethyl at C-6.

Hydrolysis of **13** by emulsin and the chemical shift and the coupling constant of the anomeric protons in **13** and **23** (Table 1) indicated β-D-glucoside linkage for pteroside P (**13**). From these data the structure of pteroside P (**13**) was established as 2,7-dimethyl-6-hydroxyethyl-5-hydroxymethyl-1-indanone 2′-β-D-glucopyranoside. Pteroside P (**13**) and its aglycone (**24**) exhibit negative CD-curves associated with n→π^* transition, $[\theta]_{328}$ −682 and $[\theta]_{327}$ −415, respectively.[11] The values indicate (2*S*)-configurations for **13** and **24**, antipodal to (2*R*)-pterosin B (**2**) and (2*R*)-pteroside B (**6**), whose absolute configurations were firmly established as reported in the previous paper.[1]

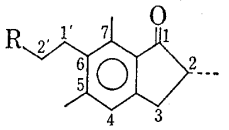
Here optical purities of pterosin derivatives reported in the previous paper and this paper will be considered. In pterosin B derivatives there exists only one chiral center at C-2 and the compounds are obtained in various optical purities ($[\alpha]_D$ ±0—31.9° in the case of pterosin B). Pterosin B, isolated from *Histiopteris incisa* (Japanese name, yunomineshida), was reported to show higher optical rotation ($[\alpha]_D$ −50° ($CHCl_3$)).[12] On the other hand all lots of pterosin A(**1**) and pteroside A (**5**) isolated from the fronds and the rhizomes showed almost same optical purities as shown by optical rotations and are considered to be optically pure. Such difference of the optical purities in the both series is assumed to be due to presence and absence of the enolizable hydrogen at C-2. As reported in the previous paper[1] the Clemmensen reduction products (**26**) of (2*S*)-pterosin A (**1**) and of (2*R*, 3*R*)-L (**27**) show almost same amplitudes of optical rotations ($[\alpha]_D$ −3.20 and $[\alpha]_D$ −3.40, respectively), indicating nearly 100% optical purity of pterosin L (**27**). Natural pterosin L (**27**) and synthetic sample prepared from (2*S*, 3*S*)-pterosin C (**4′**) show nearly the same optical rotations ($[\alpha]_D$ +23.7° and $[\alpha]_D$ +23.2°, respectively), which indicate nearly 100% optical purity of (2*S*, 3*S*)-pterosin C (**4′**) though it contains the epimer at C-2 (2*R*, 3*S*). The optical purity of the indan derivative (**28**) showing $[\alpha]_D$ +1.86,° prepared from (3*S*)-pterosin C (2*S*: 2*R*=2: 1), should retain 33% optical purities by the loss of the chiral center at C-3. On the other hand the antipodal indan derivative (**28′**) prepared from (2*R*)-pterosin B (**2**) ($[\alpha]_D$ −31.9°) shows $[\alpha]_D$ −3.45.° Thus the optical purity of the sample of pterosin B (**2**) is calculated as 61% as far as the epimerization has not occurred in the course of reactions. Thus (2*R*)-pterosin B (**2**) ($[\alpha]_D$ −20.9°) used in ozonolysis is calculated as 40% optical purity, which shows good accord to the lower optical purity ($[\alpha]_D$ +3.7°) of (*R*)-methylsuccinic acid (**29**) obtained by ozonolysis.[1]

More than thirty 1-indanone derivatives have so far been characterized from bracken fern and the illudoid sesquiterpenes are now assumed as the characteristic constituents of the Pteridaceae.[1] The constituents of the rhizomes of bracken differ from those of the fronds in the relative amount of the glucosides and the stereochemistry at C-2 and C-3 of the several

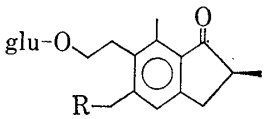
11) The details of CD and conformations of pterosin derivatives will be reported in a forth-coming paper.
12) J.W. Ronaldson, *Chem. and Ind.*, **1972**, 764.

compounds as shown in Chart 1. Although there exists no experimental proof for the biosynthetic relationship between these compounds, such difference of the constituents may render some suggestions for hydroxylation and demethylation stages expected in the course of biosynthesis of the various compounds from the proto-type compound, pterosin Z (**22**).

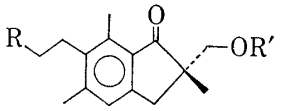
constituents of rhizomes



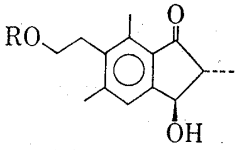
R=OH(**2**), Cl(**3**), O-glu(**6**)



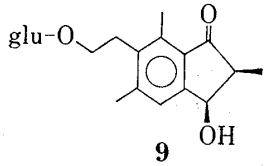
R=H(**7**), OH(**13**)



R=OH, R'=H(**1**); R=O-glu, R'=H(**5**),
R=Cl, R'=glu(**11**)



R=H(**4**), glu(**8**)



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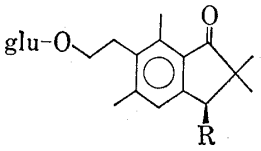
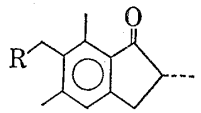
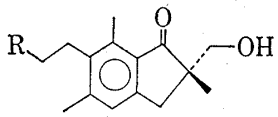


R=OH(**10**), H(**12**)

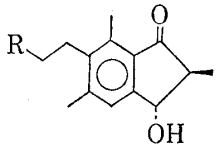
constituents of fronds



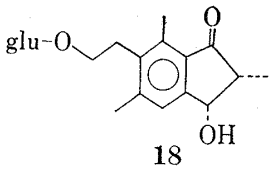
R=CH_2OH(**2**), CH_2Cl(**3**), CH_2O-benzoyl,
CH_2O-palmityl, CH_2O-isocrotonyl, CH_2OCH_3,
CH_2O-glu(**6**), COOH



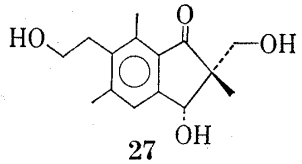
R=OH(**1**), O-glu(**5**), Cl(**21**), O-palmityl



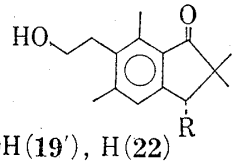
R=OH(**4'**), O-palmityl, O-acetyl, O-phenylacetyl, Cl



18



27



R=OH(**19'**), H(**22**)

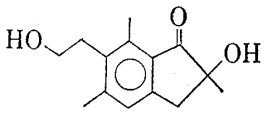
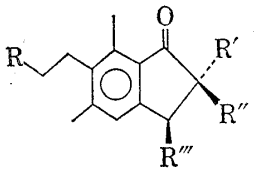


Chart 1

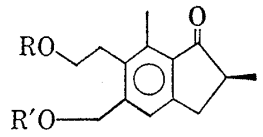
In the course of work ponasterone A,[13] ponasteroside A,[13] and protocatechualdehyde were isolated from the rhizomes and identified.

As reported in the previous paper,[1] pteroside B (**6**), the major constituent of the rhizomes, did not exhibit carcinogenicity to rat by feeding experiments. Further attempts for the characterization of the carcinogen(s) are in progress in our laboratory.

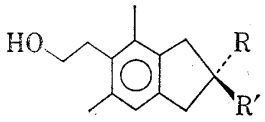
13) H. Hikino, S. Arihara, and T. Takemoto, *Tetrahedron*, **25**, 3909 (1969).



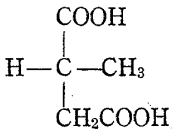
R=OH, R′=H, R″=CH_3, R‴=H(2′)
R=O-glu-Ac_4, R′=CH_2OAc, R″=CH_3, R‴=H(**14**)
R=O-glu-Ac_4, R′=CH_3, R″=H, R‴=H(**15**)
R=O-glu-Ac_4, R′=CH_3, R″=H, R‴=OAc(**16**)
R=OH, R′=H, R″=CH_3, R‴=OH(**17**)
R=OH, R′=R″=CH_3, R‴=OH(**19**)
R=Cl, R′=CH_2O-glu-Ac_4, R″=CH_3, R‴=H(**20**)



R=glu-Ac_4, R′=Ac(**23**)
R=H, R′=H(**24**)
R=Ac, R′=Ac(**25**)



R=CH_2OH, R′=CH_3(**26**)
R=H, R′=CH_3(**28**)
R=CH_3, R′=H(28′)



(**29**)

Chart 2

Experimental[14]

Isolation of Constituents——Dried powders (30 kg) of the rhizomes of bracken fern, *Pteridium aquilinum* var. *latiusculum* (Pteridaceae), collected at Nayoro, Hokkaido, in August 1971, were extracted successively with benzene and MeOH at a room temperature for 3 days. The methanolic extracts were suspended in water, chromatographed over charcoal column, and eluted with water at first and then MeOH to give several methanolic eluates, which were combined to two fractions, Fr. 1 (128 g) and Fr. 2 (50 g). The fraction 1 was chromatographed over silicagel column using a $CHCl_3$–MeOH gradient system as the developer to give several fractions, which were combined to six fractions, I—VI, according to TLC patterns using the samples obtained from the fronds[1] as the standards. The fraction I was chromatographed on silicagel column and/or PLC to give pterosins B (**2**) (0.4 g), A (**1**) (0.8 g) and C (**4**) (0.3 g), protocatechualdehyde (50 mg), pteroside K (**11**) (0.2 g), ponasterone A (0.2 g), and pteroside Z (**12**) (0.2 g). By the similar methods the fraction II afforded pterosins F (**3**) (0.05 g) and B (**2**) (0.2 g), (2*R*)-pteroside B (**6**) (1 g), pteroside Z (**12**) (0.1 g), ponasterone A (0.1 g), and pteroside A (**5**) (0.1 g); the fraction III gave (2*R*)-pteroside B (**6**) (1.2 g), pteroside A (**5**) (3 g) and pteroside D (**10**) (0.3 g); the fraction IV, pterosides A (**5**) (5 g), D (**10**) (0.8 g), and (2*R*,3*R*)-C (**8**) (7 g) and ponasteroside A (0.15 g); the fraction V, pterosides A (**5**) (1.2 g), D (**10**) (0.3 g) and (2*R*,3*R*)-C (**8**) (6.9 g); the fraction VI, (2*R*,3*R*)-pteroside C (**8**) (0.7 g).

The fraction 2 was chromatographed over silicagel column to give three fractions, VII-IX. From the fraction VII (2*S*)-pteroside B (**7**) (3 g) was obtained by filtration. The filtrate was chromatographed on silicagel column and/or PLC to give (2*S*)-pteroside B (**7**) (10 g). From fraction VIII (2*S*)-pteroside B (**7**) (2 g) was obtained and the filtrate was chromatographed on silicagel column and/or PLC to give pterosides A (**5**) (0.5 g), P (**13**) (0.2 g), and (2*S*,3*R*)-C (**9**) (4 g). Fraction IX was chromatographed on silicagel column and/or PLC to give pteroside D (**10**) (0.2 g) and (2*S*,3*R*)-pteroside C (**9**) (1 g).

(2*S*)-Pterosin A (**1**)——mp 125—127° (from AcOEt), $[\alpha]_D$ −47.8° (c=0.25). IR ν_{max} cm^{-1}: 3240, 1700, 1603; NMR ($CDCl_3$) δ: 1.27 (3H, s), 2.38 (2H, s, OH×2), 2.46 (3H, s), 2.62 (3H, s), 2.65 (1H, d, J=17 Hz, –CH– at C-3), 2.97 (2H, t, J=8 Hz), 3.09 (1H, d, J=17 Hz, –CH– at C-3), 3.49 (1H, d, J=10 Hz, –CHOH), 3.67 (2H, t, J=8 Hz), 3.75 (1H, d, J=10 Hz, –CHOH), 7.05 (1H, s); identified with (2*S*)-pterosin A (**1**) isolated from the fronds.[1]

14) mps are uncorrected. All spectra were recorded under the following conditions unless otherwise stated; UV in EtOH solution, IR in KBr disc, NMR at 60 MHz in CD_3OD and $CDCl_3$ with Me_4Si as an internal standard, optical rotation and circular dichroism in MeOH, and MS using direct inlet system at 70 eV. Column chromatographies were carried out on silicic acid (Mallinckrodt) and charcoal (Wako). Preparative TLC (PLC) were carried out using Kieselgel HF_{254} nach Stahl (Merck, 20×20×0.7 mm). Analytical TLC were carried out on Kieselgel 60 F_{254} (Merck).

(2*R*)-Pterosin B (2)——mp 107—109° (from hexane), $[\alpha]_D$ −6° (c=0.20). IR ν_{max} cm^{-1}: 3300, 1705, 1670, 1600; $\nu_{max}^{CCl_4}$ cm^{-1}: 3630, 1704, 1601; NMR ($CDCl_3$) δ: 1.25 (3H, d, J=8 Hz), 2.41 (3H, s), 2.61 (3H, s), 2.99 (2H, t, J=8 Hz, $-C\underline{H}_2-CH_2-OH$), 3.23 (1H, dd, J=18, 9.5 Hz, $-\underline{C}H-$ at C-3), 3.72 (2H, t, J=8 Hz, $-CH_2-C\underline{H}_2-OH$), 6.99 (1H, s); identified with (2*R*)-pterosin B (2) from the fronds.[1]

(2*R*)-Pterosin F (3)——mp 66—67° (from hexane), $[\alpha]_D$ −17.6° (c=0.49). IR ν_{max} cm^{-1}: 1695, 1600; NMR ($CDCl_3$) δ: 1.27 (3H, d, J=7 Hz, $-CH_3$ at C-2), 2.42 (3H, s, arom. CH_3), 2.66 (3H, s, arom. CH_3), 3.2 (2H, m, $C\underline{H}_2-CH_2-Cl$), 3.4 (2H, m, $CH_2-C\underline{H}_2-Cl$), 6.98 (1H, s, arom. H); identified with (2*R*)-pterosin F (3) from the fronds.[1]

(2*R*,3*R*)-Pterosin C (4)——mp 162—164° (from AcOEt), $[\alpha]_D$ −65.3° (c=0.59). IR ν_{max} cm^{-1}: 3350, 1680, 1600; NMR (CD_3OD) δ: 1.26 (3H, d, J=8 Hz), 2.45 (3H, s), 2.61 (3H, s), 2.94 (2H, t, J=8 Hz), 3.57 (2H, t, J=8 Hz), 4.59 (1H, d, J=3.8 Hz, carbinyl H at C-3), 7.24 (1H, s); identified with (2*S*,3*S*)-pterosin C isolated from the fronds[1] in all respects except the opposite sign of the optical rotation.

(2S)-Pteroside A (5)——mp 116—118° (from acetone), $[\alpha]_D$ −49.6° (c=0.34). MS m/e: 410.198 (M^+) (Calcd. for $C_{21}H_{30}O_8$, 410.194). UV λ_{max} nm (log ε): 216 (4.37), 260 (4.25), 305 (3.46); IR ν_{max} cm^{-1}: 3320, 1678, 1605, 1100—1010; NMR (CD_3OD) δ: 1.07 (3H, s), 2.41 (3H, s), 2.62 (3H, s), 2.65 (1H, d, J=17.5 Hz, $-\underset{H}{C}H-$ at C-3), 3.06 (2H, t, J=8 Hz), 3.25 (1H, d, J=17.5 Hz, $-\underset{H}{C}\underline{H}-$ at C-3), 3.60 (1H, d, J=10.5 Hz, $-\underset{H}{C}H-OH$), 3.69 (1H, d, J=10.5 Hz, $-\underset{H}{C}\underline{H}-OH$), 3.81 (2H, t, J=8 Hz), 4.27 (1H, d, J=6.5 Hz, anomeric H), 7.06 (1H, s), 3.2—3.4, 3.6—3.9 (br.m, glucosyl); CD: $[\theta]_{370}$+52, $[\theta]_{354}$+210, $[\theta]_{345}$−92, $[\theta]_{330}$−524; identified with (2*S*)-pteroside A[1] (5) isolated from the fronds.

(2*R*)-Pteroside B (6)——mp 120—122° (from MeOH), $[\alpha]_D$ −48.8° (c=0.17). MS m/e: 380.186 (M^+) (Calcd. for $C_{20}H_{28}O_7$, 380.184). UV λ_{max} nm (log ε): 218 (4.40), 260 (4.04), 305 (3.18); IR ν_{max} cm^{-1}: 3360, 1683, 1605, 1100—1010; NMR (CD_3OD) δ: 1.19 (3H, d, J=7 Hz), 2.41 (3H, s), 2.62 (3H, s), 3.05 (2H, t, J=7 Hz, $-C\underline{H}_2-CH_2-O$-glu), 3.80 (2H, t, J=7 Hz, $-CH_2-C\underline{H}_2-O$-glu), 4.28 (1H, d, J=6.5 Hz, anomeric H), 7.05 (1H, s), 3.2—3.35, 3.6—3.9 (br.m, glucosyl); CD: $[\theta]_{324}$ +1874; identified with (2*R*)-pteroside B (6) isolated from the fronds.[1]

(2*S*)-Pteroside B (7)——mp 164—166° (from acetone), $[\alpha]_D$ −13.6° (c=0.29); CD: $[\theta]_{323}$ −1225 (MeOH); *Anal.* Calcd. for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 62.69; H, 7.36. NMR and IR spectra were superimposable with those of **6**.

(2*R*,3*R*)-Pteroside C (8)——mp 162—165° (from EtOH), $[\alpha]_D$ −70.3° (c=0.16). MS m/e: 396.176 (M^+) (Calcd. for $C_{20}H_{28}O_8$, 396.178). UV λ_{max} nm (log ε); 219.5 (4.53), 260.5 (4.16), 302 (3.30); IR ν_{max} cm^{-1}: 3400, 1708, 1600, 1100—1010; NMR (CD_3OD) δ: 1.28 (3H, d, J=7 Hz), 2.44 (3H, s), 2.60 (3H, s), 3.06 (2H, t, J=8 Hz), 3.81 (2H, t, J=8 Hz), 4.26 (1H, d, J=6.5 Hz, anomeric H), 4.59 (1H, d, J=4.5 Hz, carbinyl H at C-3), 7.25 (1H, s), 3.2—3.35, 3.6—3.9 (br.m, glucosyl); CD: $[\theta]_{325}$ −16542.

(2*S*,3*R*)-Pteroside C (9)——mp 174—176° (from EtOH), $[\alpha]_D$ −46.6° (c=0.15). *Anal.* Calcd. for $C_{20}H_{28}O_8 \cdot C_2H_5OH$: C, 59.71; H, 7.75. Found: C, 59.46; H, 7.38. IR ν_{max} cm^{-1}: 3400, 1705, 1600, 1100—1020; NMR (CD_3OD) δ: 1.20 (3H, d, J=7 Hz), 5.07 (1H, d, J=6.7 Hz, carbinyl H at C-3); other signals are superimposable with those of **8**; CD: $[\theta]_{330}$ −18346.

(3)*S*-Pteroside D (10)——Amorphous, $[\alpha]_D$ −52.4° (c=0.41). MS m/e: 410.190 (M^+) (Calcd. for $C_{21}H_{30}H_8$, 410.194). UV λ_{max} nm (log ε): 216 (4.46), 258 (4.07), 300 (3.27); IR ν_{max} cm^{-1}: 3390, 1690, 1600, 1100—1010; NMR (CD_3OD) δ: 1.01 (3H, s), 1.15 (3H, s), 2.45 (3H, s), 2.61 (3H, s), 3.08 (2H, t, J=7.5 Hz), 3.80 (2H, t, J=7.5 Hz), 4.27 (1H, d, J=6.5 Hz, anomeric H), 4.67 (1H, s, carbinyl H at C-3), 7.25 (1H, s), 3.2—3.35, 3.6—3.9 (br. m).

(2*S*)-Pteroside K (11)——mp 94—96° (from EtOH), $[\alpha]_D$ −26.4° (c=0.10). MS m/e: 428.163 (M^+) (Calcd. for $C_{21}H_{29}O_7Cl$, 428.161). UV λ_{max} nm (log ε): 220.5 (4.52), 261 (4.17), 306 (3.35); IR ν_{max} cm^{-1}: 3300, 1685, 1600, 1100—1010; NMR (CD_3OD) δ: 1.11 (3H, s), 2.42 (3H, s), 2.62 (3H, s), 2.68 (1H, d, J=17.5 Hz, $-\underset{H}{C}\underline{H}-$ at C-3), 4.08 (1H, d, J=9 Hz, $-\underset{H}{C}\underline{H}-O-$), 4.17 (1H, d, J=7 Hz, anomeric H), 7.13 (1H, s), 3.2—3.35, 3.6—3.8 (br. m); CD: $[\theta]_{423}$ +3507.

Pteroside Z (12)——Amorphous. NMR (CD_3OD) δ: 1.18 (6H, s, $CH_3 \times 2$ at C-2), 2.50 (3H, s), 2.71 (3H, s), 2.93 (2H, br.s, $-CH_2-$ at C-3), 3.17 (2H, t, J=7.5 Hz), 7.24 (1H, s), 3.2—3.4, 3.6—3.9 (br. m).

(2*S*)-Pteroside P (13)——mp 191—193° (from MeOH-acetone), $[\alpha]_D$ −14.9° (c=0.19). MS m/e: 396.167 (M^+) (Calcd. for $C_{20}H_{28}O_8$, 396.178). UV λ_{max} nm (log ε): 217 (4.61), 258 (4.19), 305 (3.48); IR ν_{max} cm^{-1}: 3360, 1705, 1603, 1100—1010; NMR (CD_3OD) δ: 1.23 (3H, d, J=7 Hz), 2.65 (3H, s), 3.09 (2H, t, J=8 Hz), 3.87 (2H, t, J=8 Hz), 4.28 (1H, d, J=6.5 Hz, anomeric H), 7.40 (1H, s), 3.2—3.4, 3.6—3.85 (br.m); CD: $[\theta]_{328}$ −682.

Hydrolysis of Pterosides with Emulsin——General Methods: A glucoside (100 mg) in distilled water (30 ml) was incubated with emulsin (50 mg) for 36—48 hrs at 30°. When precipitates deposited, they were filtered off to obtain a crude pterosin. The filtrate or the reaction mixture was extracted with AcOEt.

The AcOEt layer was washed with water and dried over Na_2SO_4. The solvent was evaporated to leave a crude pterosin. The mother liquor was passed through a charcoal column and eluated with water. After evaporation of water the residue was applied on a silicagel plate and glucose was identified with an authentic sample.

(2*S*)-Pterosin A (**1**): mp 121—123° (from AcOEt), $[\alpha]_D$ −42.8° (c=0.25), identified with the authentic sample of (2*S*)-Pterosin A (**1**).[1] Yield, 250 mg from (2*S*)-pteroside A (**5**) (700 mg).

(2*R*)-Pterosin B (**2**): mp 106—107° (from $CHCl_3$–hexane), $[\alpha]_D$ −31.4° (c=0.14), identified with auhtentic (2*R*)-pterosin B (**2**).[1] Yield, 80 mg from (2*R*)-pteroside B (**6**) (300 mg).

(2*S*)-Pterosin B (**2′**): mp 106—108° (from $CHCl_3$–hexane), $[\alpha]_D$ +30.3° (c=0.29), identified with (2*R*)-pterosin B (**2**) by IR and NMR. Yield, 270 mg from (2*S*)-pteroside B (**7**) (1000 mg).

(2*R*,3*R*)-Pterosin C (**4**): mp 154—155° (from AcOEt), $[\alpha]_D$ −95.0° (c=0.46), identified with (2*S*,3*S*)-pterosin C[1] (**4′**) in all respect except the opposite sign of the optical rotation. Yield, 500 mg from (2*R*,3*R*)-pteroside C (**8**) (1700 mg).

(2*S*,3*R*)-Pterosin C (**17**): mp 163—166° (from AcOEt), $[\alpha]_D$ −37.1° (c=0.21). MS *m/e*: 236.134 (M^+) (Calcd. for $C_{14}H_{20}O_3$, 236.141); IR ν_{max} cm^{-1}: 3370, 1678, 1598; NMR (CD_3OD) δ: 1.16 (3H, d, J=7.5 Hz), 5.13 (1H, d, J=6.8 Hz); other signals were superimposable with *trans*-pterosin C (**4** and **4′**). CD: $[\theta]_{330}$ −20415. Yield, 64 mg from (2*S*,3*R*)-pteroside C (**9**) (300 mg).

(3*S*)-Pterosin D (**19**): mp 180—183° (from AcOEt), $[\alpha]_D$ −15.4° (c=0.09), identified with (3*R*)-pterosin D (**19′**)[1] isolated from the fronds by IR, TLC and NMR, and by opposite signs of CD and $[\alpha]_D$. CD: $[\theta]_{330}$ −4094. Yield, 20 mg from (3*S*)-pteroside D (**10**) (150 mg).

(2*S*)-Pterosin K (**21**): mp 87—88° (from hexane), $[\alpha]_D$ −40.9° (c=0.21), identified with (2*S*)-pterosin K[1] (**21**) isolated from the fronds in all respects. CD: $[\theta]_{360}$ +1507, $[\theta]_{344}$ +2512, $[\theta]_{328}$ +2153, $[\theta]_{317}$ +1435 (cyclohexane). Yield, 10 mg from (2*S*)-pteroside K (**11**) (50 mg).

(2*S*)-Pterosin P (**24**): mp 115—117° (from $CHCl_3$–benzene), $[\alpha]_D$ +6.6° (c=0.18). MS *m/e*: 234.121 (M^+) (Calcd. for $C_{14}H_{18}O_3$, 234.125). UV λ_{max} nm (log ε): 218 (4.46), 258 (4.31), 302 (3.69); IR ν_{max} cm^{-1}: 3360, 1675, 1600; NMR (CD_3OD) δ: 1.21 (3H, d, J=7 Hz), 2.69 (3H, s), 2.96 (2H, t, J=7 Hz), 3.30 (1H, dd, J=9, 18 Hz, –$\underset{H}{C}$H– at C-3), 3.68 (2H, t, J=7 Hz), 4.72 (2H, s, –CH_2OH at C-5), 4.25 (2H, s, OH×2), 7.38 (1H, s); CD: $[\theta]_{327}$ −415. Yield, 20 mg from (2*S*)-pteroside P (**13**) (130 mg).

Acid Hydrolysis of Pterosides——General Methods: A glucoside (100 mg) was dissolved in 3% HCl (4 ml) and heated for 1 hr on a water bath. The reaction mixture was extracted with AcOEt. The organic layer was washed with water and dried over Na_2SO_4. The solvent was evaporated to give a crude aglycone, which was crystallized from a suitable solvents. The aqueous layer was neutralized with $NaHCO_3$ and passed through a charcoal column. An aqueous elutant was concentrated and analyzed on TLC (Kieselgel 60 F_{254}, Merck) to identify with glucose.

(2*S*)-Pterosin A (**1**): mp 126—128° (from AcOEt), $[\alpha]_D$ −42.3° (c=0.41, MeOH), identified with **1**. Yield, 54 mg from (2*S*)-pteroside A (**5**) (220 mg).

(3*S*)-Pterosin D (**19**): mp 180—183° (from AcOEt), $[\alpha]_D$ −13.4° (c=0.17, MeOH). Yield, 20 mg from (3*S*)-pteroside D (**10**) (130 mg).

Acetylation of Pterosides and Pterosins——General Methods: A sample (100 mg) and Ac_2O (0.1 ml) in pyridine (1 ml) were kept standing overnight at room temperature. The reaction mixture was poured into ice-water and extracted with ether. The ether layer was successively washed with dil-HCl, $NaHCO_3$ solution and water, and dried over Na_2SO_4. The solvent was evaporated to leave an acetate which was purified by recrystallization or PLC.

(2*S*)-Pteroside A Pentaacetate (**14**): Amorphous, NMR ($CDCl_3$) δ: 1.18 (3H, s), 1.96 (6H, s, Ac×4), 2.01, 2.02, 2.08 (each 3H, s, Ac×3), 2.38 (3H, s), 2.63 (3H, s), 2.99 (2H, t, J=7 Hz), 2.67 (1H, d, J=16.5 Hz, –$\underset{H}{C}$H– at C-3), 3.13 (1H, d, J=16.5 Hz, –$\underset{H}{C}$H– at C-3), 4.48 (1H, d, J=7 Hz, anomeric H), 7.02 (1H, s); Other signals are overlapped in the range of 3.8—4.2, 4.7—5.2.

(2*R*)-Pteroside B Tetraacetate (**15**): mp 141° (from hexane–$CHCl_3$), $[\alpha]_D$ −55.5° (c=0.17). MS *m/e*: 548.216 (M^+) (Calcd. for $C_{28}H_{36}O_{11}$, 548.226). UV λ_{max} nm (log ε); 215 (4.65), 257 (4.19), 303 (3.40); IR ν_{max} cm^{-1}: 1748, 1705, 1603; NMR ($CDCl_3$) δ: 1.24 (3H, d, J=7 Hz), 1.90, 1.96, 1.98, 2.04 (each 3H, s, Ac×4), 2.35 (3H, s), 2.60 (3H, s), 2.96 (2H, t, J=7 Hz), 4.42 (1H, d, J=7.5 Hz, anomeric H), 6.98 (1H, s); other signals are overlapped each other. CD: $[\theta]_{323}$ +1761.

(2*R*,3*R*)-Pteroside C Pentaacetate (**16**): Viscous oil. NMR ($CDCl_3$) δ: 1.35 (3H, d, J=7.5 Hz), 1.92, 1.97, 1.99, 2.06, 2.13 (each for 3H, s, Ac×5), 2.40 (3H, s), 2.63 (3H, s), 3.01 (2H, t, J=7 Hz), 4.45 (1H, d, J=7 Hz, anomeric H), 5.83 (1H, d, J=3 Hz, carbinyl H at C-3), 7.20 (1H, s), 3.9—4.2, 4.8—5.2 (br. m); other signals are overlapped in the vicinity of 3.4—3.9.

(2*S*)-Pteroside K Tetraacetate (**20**): mp 123—126° (from hexane), $[\alpha]_D$ −27.7° (c=0.16). MS *m/e*: 596.202 (M^+) (Calcd. for $C_{29}H_{37}O_{11}Cl$, 596.203); UV λ_{max} nm (log ε): 220.5 (4.55), 261 (4.14), 306 (3.39); IR ν_{max} cm^{-1}: 1750, 1698, 1600, 1270, 1040; NMR ($CDCl_3$) δ: 1.15 (3H, s), 1.97 (3H, s, Ac), 1.98 (6H, s, Ac×2), 2.02 (3H, s,

Ac), 2.41 (3H, s), 2.64 (3H, s), 2.65 (1H, d, J=17 Hz, –C<u>H</u>– at C-3), 3.24 (1H, d, J=17 Hz, –C<u>H</u>– at C-3), 3.1—3.8 (4H, m, $-CH_2-CH_2-Cl$), 3.44 (1H, d, J=10 Hz, –C<u>H</u>–O– at C-2), 3.94 (1H, d, J=10 Hz, –C<u>H</u>–O at C-2), 4.44 (1H, d, J=7.5 Hz, anomeric H), 7.03 (1H, s), 3.7—4.2, 4.7—5.2 (br. m); CD: $[\theta]_{351}$ +1324, $[\theta]_{336}$ +2384, $[\theta]_{322}$ +2249, $[\theta]_{309}$ +2249, $[\theta]_{296}$ +629 (cyclohexane).

(2*S*)-Pteroside P Pentaacetate (**23**): Amorphous. NMR ($CDCl_3$) δ: 1.27 (3H, d, J=7 Hz), 1.92, 1.98, 1.99, 2.06, 2.11 (each for 3H, s, Ac×4), 2.66 (3H, s), 3.04 (2H, t, J=7 Hz), 3.65 (2H, t, J=7 Hz), 4.44 (1H, d, J=7.5 Hz, anomeric H), 5.16 (2H, s, arom. –C<u>H</u>$_2$–OAc at C-5), 7.25 (1H, s), 3.9—4.2, 4.8—5.2.

(2*S*)-Pterosin P Diacetate (**25**): Oil. NMR ($CDCl_3$) δ: 1.28 (3H, d, J=7 Hz), 2.03, 2.12 (each for 3H, s, Ac×2), 2.69 (3H, s), 3.08 (2H, d, J=7 Hz), 3.32 (1H, dd, J=9, 18 Hz, –C<u>H</u>–CH– at C-3), 4.17 (2H, t, J=7 Hz), 5.21 (2H, s, –C<u>H</u>$_2$–O–Ac at C-5), 7.27 (1H, s).

Identification of Known Compounds——Ponasterone A: mp 280—283° (from MeOH), $[\alpha]_D$ +63.2° (c=0.30); IR ν_{max} cm^{-1}: 3380, 2950, 1645, 1385, 1055; identified with the authentic sample.[13]

Ponasteroside A: mp 272—275° (from MeOH); IR ν_{max} cm^{-1}: 3338, 2940, 1648, 1385, 1158, 1070, 1028; identified with the authentic sample.[13]

Protocathechualdehyde: mp 155—156° (benzene–AcOEt); IR ν_{max} cm^{-1}: 3220, 1650, 1595, 1440, 1375, 1296, 1165; identified with the authentic sample.

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