Chem. Pharm. Bull. 30(10)3640—3646(1982)

Chemical and Chemotaxonomical Studies of Ferns. XXXIX.[1] Chemical Studies on the Constituents of *Pteris bella* Tagawa and *Pteridium aquilinum* subsp. *wightianum* (Wall) Shich

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(Received May 26, 1982)

From the fronds of *Pteris bella*, three new pterosin-type compounds, I, III and XI, were isolated along with pterosins B (VI), C (II), Q (VII) and T (IV), setulosopterosin (X), pterosin C 3-*O*-*β*-D-glucoside (IX) and pterosin Q 3-*O*-*β*-D-glucoside (VIII). From the fronds of *Pteridium aquilinum* subsp. *wightianum*, two new pterosin-type compounds, XVI and XVII, were isolated along with pterosins C (II), D (XVIII), F (XXII), H (XX), I (XXI) and Z (XIX) and astragalin (XXIII). The structures of the new compounds were determined on the basis of chemical and spectral data.

Keywords——*Pteris bella*; *Pteridium aquilinum* subsp. *wightianum*; Pteridaceae; chemotaxonomy; pterosins; 1-indanones; ^{13}C-NMR

In the previous papers,[2] we reported the occurrence of pterosin-type compounds in many ferns belonging to the genus *Pteris* and related genera of the Pteridaceae. Recent extensive studies have revealed that *Pteris bella* and *Pteridium aquilinum* subsp. *wightianum* also contain pterosin-type compounds including several new compounds. This paper deals with the isolation of these compounds and the structural elucidation of the new compounds.

From the fronds of *Pteris bella* Tagawa (Japanese name: Nagae-hachijoshida, Pteridaceae), three new pterosin-type compounds, I, III and XI, were isolated along with pterosins B (VI), C (II), Q (VII) and T (IV), setulosopterosin (X), pterosin C 3-*O*-*β*-D-glucoside (IX) and pterosin Q 3-*O*-*β*-D-glucoside (VIII).

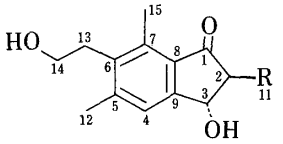
Compound I, $C_{14}H_{18}O_4$, colorless needles, mp 69—72°C, $[\alpha]_D^{28}$ +76° (c=0.4, MeOH), showed ultraviolet (UV) [λ_{max}^{MeOH} nm (log ε): 218 (4.14), 261 (3.79), 303 (2.81)] and infrared (IR) [ν_{max}^{KBr} cm^{-1}: 1695, 1605] absorptions characteristic of pterosin-type compounds.[3] In the ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum of I, signals due to two aromatic methyl groups at $\delta_{pyr.-d_5}$ 2.40 (3H, s) and 2.81 (3H, s), one aromatic proton at δ 7.61 (1H, s), one ethylene group at δ 3.11 (2H, t, J=7 Hz) and 3.94 (2H, t, J=7 Hz), one methylene group at δ 4.44 (1H, dd, J=11 and 4 Hz) and 4.65 (1H, dd, J=11 and 4 Hz), and two methine groups at δ 3.13 (1H, q, J=4 Hz) and 5.93 (1H, d, J=4 Hz) were observed. These signals are similar to those of pterosin C (II) except that the signals due to the methyl group ($\delta_{pyr.-d_5}$ 1.51, 3H, d, J=7 Hz) and proton (δ 2.88, 1H, m) at C-2 of pterosin C change to the signals due to a methylene group at δ 4.44 and 4.65 and a methine group at δ 3.13. These observations indicate that compound I is the 2-hydroxymethyl derivative of pterosin C (=11-hydroxypterosin C).

On the other hand, compound III, $C_{14}H_{18}O_5$, colorless amorphous powder, $[\alpha]_D^{28}$ +54° (c=0.3, MeOH), showed the following signals in its ^{1}H-NMR spectrum; $\delta_{pyr.-d_5}$ 2.80 (3H, s), 3.15 (1H, q, J=4 Hz), 3.21 (2H, t, J=7 Hz), 4.01 (2H, t, J=7 Hz), 4.44 (1H, dd, J=11 and 4 Hz), 4.65 (1H, dd, J=11 and 4 Hz), 5.18 (2H, s), 5.97 (1H, d, J=4 Hz) and 8.36 (1H, s). These signals similar to those of compound I except that the signal at δ 2.40 (3H, s) in the

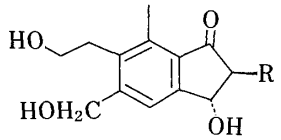
spectrum of I, assignable to the methyl group at C-5, changes to the methylene signal at δ 5.18. The chemical shift of this methylene group is almost the same as that of the hydroxymethyl group at C-5 of pterosin T (IV), $\delta_{\text{pyr.-}d_5}$ 5.16 (2H, s). Therefore, compound III was considered to be the 5-hydroxymethyl derivative of compound I, namely the 2-hydroxymethyl derivative of pterosin T (=11-hydroxypterosin T).

The structures of I and III were confirmed by comparison of the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) data of I and III with those of pterosins C and T, respectively (see Table I). The differences of chemical shifts between I and pterosin C and between III and pterosin T are similar to those observed between pterosin G (V)[2] and pterosin B (VI), as shown also in Table I. The results of these comparisons supported the above-mentioned structures of I and III. The absolute configurations of I and II were established as (2*S*) and (3*S*) on the basis of the circular dichroism Cotton effect:[3] I, $[\theta]^{28}_{326}$ +8810 (MeOH); II, $[\theta]^{28}_{325}$ +6990 (MeOH).

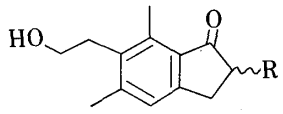
Compound XI, $C_{14}H_{18}O_4$, colorless needles, mp 166—167°C, $[\alpha]_D^{28}$ +132° (c=1.1, MeOH), showed the following signals in its ^{1}H-NMR spectrum: $\delta_{\text{pyr.-}d_5}$ 1.78 (3H, s), 2.42 (3H, s), 2.86



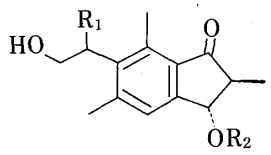
I : R=CH_2OH
II : R=CH_3



III : R=CH_2OH
IV : R=CH_3



V : R=β-CH_2OH
VI : R=α-CH_3



VII : R_1=OH, R_2=H
VIII : R_1=OH, R_2=β-D-glucosyl
IX : R_1=H, R_2=β-D-glucosyl

Fig. 1

TABLE I. ^{13}C Chemical Shifts in Pyridine-d_5

	I	II	δ(I) $-\delta$(II)	III	IV	δ(III) $-\delta$(IV)	V	VI	δ(V) $-\delta$(VI)	X	XI
C-1	205.0	205.4	−0.4	205.2	205.8	−0.6	208.1	209.4	−1.3	207.5	207.4
C-2	62.2	54.2	+8.0	62.3	54.4	+7.9	51.1	42.6	+8.5	83.1	83.1
C-3	69.9	74.9	−5.0	70.1	75.2	−5.1	29.0	33.8	−4.8	77.1	77.0
C-4	125.5	124.9	+0.6	122.8	122.3	+0.5	126.0	125.9	+0.1	123.7	125.3
C-5	144.7	144.5		149.0	148.8		144.4	144.4		149.5	145.3
C-6	136.5	136.4		136.7	136.7		136.1	136.4		137.0[b]	137.1
C-7	137.7	137.4		136.7	136.7		137.2	137.4		137.1[b]	138.0
C-8	133.0	131.5	+1.5	133.6	132.5	+1.1	133.5	132.3	+1.2	130.6	129.9
C-9	155.7	153.9	+1.8	156.0	154.5	+1.5	153.7	152.2	+1.5	152.3	152.0
C-10[a] or C-11[a]	59.5	13.2	+46.3	59.5	13.3	+46.2	62.2	16.6	+45.6	21.3	21.3
C-12	21.3	21.1		63.1	62.9		21.2	21.2		62.9	21.3
C-13	33.0	32.8		32.1	32.0		32.8	32.9		32.1	33.1
C-14	61.1	60.8		61.3	61.3		61.1	61.2		61.2	61.0
C-15	14.0	13.9		13.9	13.9		13.7	13.7		14.0	14.2

a) C-10, α-CH_3; C-11, β-CH_3.
b) Assignment of chemical shifts may be reversed.

(3H, s), 3.12 (2H, t, J=7 Hz), 3.95 (2H, t, J=7 Hz), 5.62 (1H, s) and 7.62 (1H, s). The signals at δ 1.78 and 5.62 are practically the same as those of the methyl group at C-2 and the proton at C-3 of setulosopterosin (X). The other signals are analogous to those of I or pterosin C (II). These findings indicate the structure of XI to be 2,3-dihydroxy-6-(2-hydroxyethyl)-2,5,7-trimethylindan-1-one (=2-hydroxypterosin C).

To confirm the structure, the *cis*-glycol XIII, mp 197—198°C, was prepared (as a mixture of XIII and its antipode) by OsO_4 oxidation of dehydropterosin B (XIV). XIII was not identical with compound XI and formed the isopropylidene ketal XV with acetone in the presence of a catalytic amount of sulfuric acid at room temperature. On the other hand, XI did not form an isopropylidene ketal under the same conditions, but, when the reaction mixture was heated under reflux, XI formed XV gradually. These chemical transformations indicate that XI has a 2,3-*trans*-glycol system and forms XV probably through dehydroxylation at C-2 under the above-mentioned conditions (Fig. 2). On the basis of these results, the structure was determined as XI in Fig. 2. The absolute configuration of XI was determined as (2*S*) and (3*R*) from the circular dichroism Cotton effect, $[\theta]^{22}_{335}$ +18800 (MeOH).[3]

In the previous paper,[4] we reported the structure of setulosopterosin as XII in Fig. 2. The presence of the *cis*-glycol system had been deduced from the formation of the isopropylidene ketal in acetone solution containing a catalytic amount of sulfuric acid under reflux. As discussed above, such a conclusion is invalid for pterosin-type compounds. In the ^{13}C-NMR spectrum (Table I), setulosopterosin showed signals at $\delta_{\text{pyr.-}d_5}$ 207.5, 83.1, 77.1 and 21.3 assignable to C-1, C-2, C-3 and C-11, respectively. The chemical shifts of these signals are practically the same as those of compound XI. This finding indicates that the correct structure of setulosopterosin is X in Fig. 2.

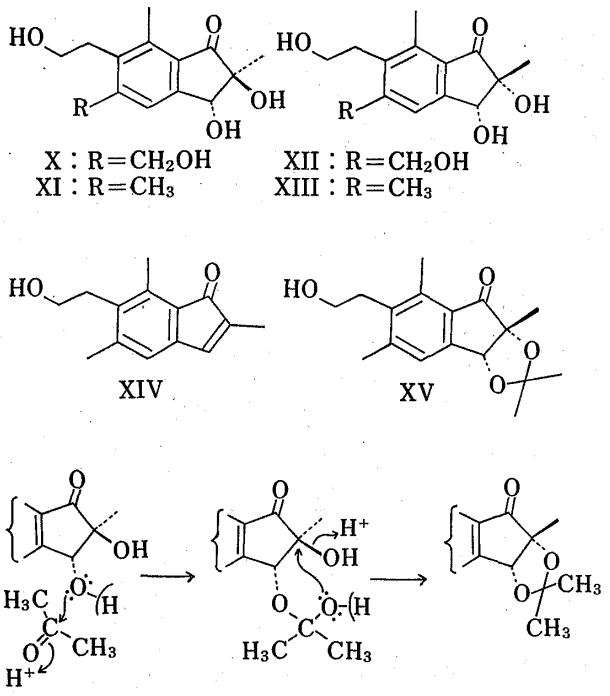


Fig. 2

From the fronds of *Pteridium aquilinum* subsp. *wightianum* (Wall) Shich (Japanese name: Randai-warabi, Pteridaceae), two new pterosin-type compounds, XVI and XVII, were isolated along with pterosins C (II), D (XVIII), F (XXII), H (XX), I (XXI) and Z (XIX) and astragalin (XXIII).

Compound XVI, $C_{21}H_{30}O_8$, colorless amorphous powder, $[\alpha]_D^{20}$ −22° (c=0.43, MeOH), showed UV [λ_{max}^{MeOH} nm (log ε): 219 (4.64), 260 (4.25), 304 (3.48)] and IR [ν_{max}^{KBr} cm^{-1}: 3400, 1690, 1600] absorptions and a mass spectrum (MS) [m/z: 410 (M^+), 248 ($M^+-C_6H_{10}O_5$), 231 (248—OH), 217 (248—CH_2OH)] indicating it to be a glycoside of a pterosin-type sesquiterpene. In the ^{1}H-NMR spectrum of XVI (in pyr.-d_5), an anomeric proton signal (δ 5.12: 1H, d, J= 8 Hz) and six overlapping proton signals (δ 3.72—4.58) due to a hexosyl moiety were observed along with the following signals comparable to those of pterosin D;[3] 1.38 (3H, s), 1.58 (3H, s), 2.29 (3H, s), 2.81 (3H, s), 3.08 (2H, t, J=8 Hz), 3.90 (2H, t, J=8 Hz), 5.09 (1H, s), 7.80 (1H, s).

On acid hydrolysis, XVI gave (3*R*)-pterosin D (XVIII) and D-glucose. On comparison of the ^{13}C-NMR spectrum of XVI with that of (3*R*)-pterosin D, a downfield shift (+8.8 ppm) of

the carbon signal at C-3 was observed. This observation indicates that the glucosyl moiety is linked with the hydroxy group at C-3.[5] The ^{13}C-NMR spectrum of XVI also showed signals at $\delta_{\text{pyr.-}d_5}$ 106.3, 78.8, 78.6, 75.3, 71.7 and 62.9 characteristic of the β-D-glucopyranosyl moiety linked to a secondary hydroxyl group.[5] These data and the large coupling constant (8 Hz) of the anomeric proton signal in the ^{1}H-NMR spectrum of XVI show that the D-glucosyl moiety has a β-linkage. This evidence established the structure of compound XVI as (3*R*)-pterosin D 3-*O*-β-D-glucopyranoside (XVI in Fig. 2). While pteroside D bearing a D-glucosyloxy group at C-14 has been isolated from several ferns,[6] this is the first example of pteroside D bearing a D-glucosyloxy group at C-3.

Compound XVII, $C_{15}H_{19}ClO_2$, colorless syrup, showed UV [λ_{max}^{MeOH} nm (log ε): 219 (4.84), 260 (4.42), 304 (3.69)] and IR [$\nu_{max}^{CHCl_3}$ cm^{-1}: 1700, 1600] absorptions suggesting it to be a pterosin-type compound. The ^{1}H-NMR spectrum of XVII showed signals assignable to geminal dimethyl groups at C-2 [δ_{CDCl_3} 1.11 (3H, s) and 1.24 (3H, s)], two aromatic methyl groups [δ 2.47 (3H, s) and 2.67 (3H, s)], one ethylene group at C-6 [δ 3.19 (2H, m) and 3.55 (2H, m)], one carbinyl proton at C-3 [δ 4.80 (1H, s)] and one aromatic proton [δ 7.32 (1H, s)]. These signals are similar to those of pterosin D (XIX) except for the ethylene proton signals. The chemical shifts of these ethylene protons coincide more closely with those of the chloroethyl group in such compounds as pterosins F (XXII) and H (XX). Further, MS of XVII showed intense ion peaks at *m/z* 231 (M^+—Cl) and 217 (M^+—CH_2Cl). These spectral data suggested the presence of a chloroethyl group in XVII. To confirm the structure, XVI was converted into XVII by chlorination with thionyl chloride in pyridine, followed by acid hydrolysis.

Thus, XVII was determined to be the 6-chloroethyl derivative of pterosin D (=(3*R*)-hydroxypterosin H). The absolute configuration of XVII was established as (3*R*) by the circular dichroism Cotton effect, $[\theta]_{328}^{25}$ +6700 (MeOH), as compared with that of (3*R*)-pterosin D.

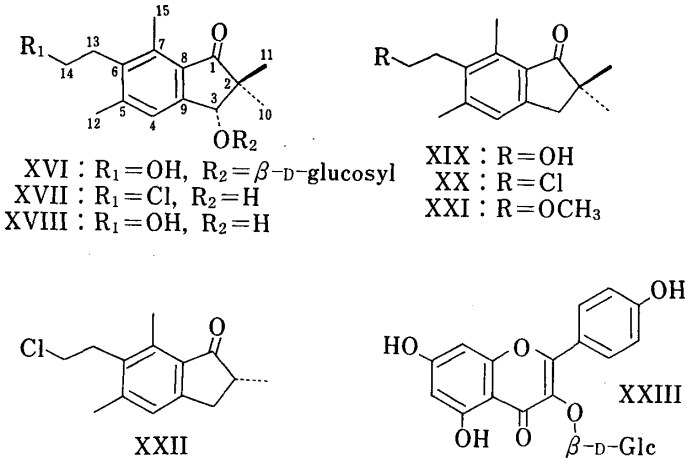


Fig. 3

Experimental

The instruments, materials and experimental conditions were the same as described in Part XXXVII[2] in this series.

Isolation Procedure——1) *Pteris bella* TAGAWA: The air-dried fronds (300 g) of *P. bella*, collected in Taiwan in December, were extracted 3 times with 1 l of methanol under reflux for 6 h. The extracts and then 5 l of methanol were passed over activated charcoal (50 g) packed in a column of 5 cm diameter. The resulting solution was concentrated to a syrup under reduced pressure. The syrup was mixed with silica gel (20 g) and applied to a silica gel column (70 g). The column was eluted successively with $CHCl_3$ (900 ml, frac. 1), 5% MeOH in $CHCl_3$ (500 ml, frac. 2), 5% MeOH in $CHCl_3$ (500 ml, frac. 3), 10% MeOH in $CHCl_3$

(300 ml, frac. 4) and 20% MeOH in $CHCl_3$ (300 ml, frac. 5). Frac. 1 was rechromatographed on alumina using $CHCl_3$ as an eluent followed by preparative layer chromatography (PLC) (solvent system, $CHCl_3$: ether=4: 1) to yield pterosin B (VI, 5 mg). Frac. 2 was rechromatographed on alumina using $CHCl_3$ and ether as eluents to yield pterosin C (II, 6 mg). Frac. 3 was rechromatographed on alumina using 10% MeOH in $CHCl_3$ as an eluent followed by PLC (solvent system, EtOAc only and $CHCl_3$: *tert*-BuOH=5: 1) to yield pterosin Q (VII, 56 mg), pterosin T (IV, 39 mg), compound I (8 mg) and compound XI (21 mg). Frac. 4 was subjected to droplet countercurrent chromatography (DCC) followed by PLC (solvent system, $CHCl_3$: MeOH=5: 1) to yield setulosopterosin (X, 17 mg) and compound III (7 mg). Frac. 5 was rechromatographed on polyamide using 20% MeOH in EtOAc as an eluent followed by PLC (solvent system, $CHCl_3$: MeOH=10: 3) to yield pterosin C 3-*O*-*β*-D-glucoside (IX, 4 mg) and pterosin Q 3-*O*-*β*-D-glucoside (VIII, 6 mg).

2) *Pteridium aquilinum* subsp. *wightianum* (Wall) Shich: The air-dried fronds (1.5 kg) of *P. aquilinum* subsp. *wightianum*, collected in Taiwan in December, were extracted with methanol (3 l×3) under reflux for 6 h. The combined extracts (9 l) and then fresh methanol (10 l) were passed over activated charcoal (120 g) packed in a column of 7 cm diameter. The resulting solution was concentrated to a syrup under reduced pressure. The syrup was then partitioned into the upper and lower layers of a mixture of $CHCl_3$ (400 ml), MeOH (400 ml) and water (300 ml). The lower layer was evaporated under reduced pressure to a syrup which was chromatographed on silica gel (120 g) using $CHCl_3$ (500 ml, frac. 1), 10% MeOH in $CHCl_3$ (500 ml), 20% MeOH in $CHCl_3$ (500 ml, frac. 2) and 30% MeOH in $CHCl_3$ (500 ml). Frac. 1 was rechromatographed on silica gel using *n*-hexane and $CHCl_3$ as eluents to yield pterosin F (XXII, 3 mg), pterosin H (XX, 8 mg) and pterosin I (XXI, 31 mg). Frac. 2 was rechromatographed on silica gel using $CHCl_3$ and ether as eluents followed by PLC (solvent system, $CHCl_3$: ether=4: 1) to yield pterosin D (XVIII, 5 mg), pterosin Z (XIX, 30 mg) and compound XVII (4 mg). The upper layer was concentrated to a syrup under reduced pressure. The syrup was subjected to DCC followed by silica gel column chromatography (eluent, EtOAc: $CHCl_3$=25: 1) to yield astragalin (XXIII, 48 mg) and compound XVI (200 mg).

Compound I——Colorless needles from a mixture of methanol and ethyl acetate, mp 69—72°C, $[\alpha]_D^{28}$ +76° (c=0.4, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.14), 261 (3.79), 303 (2.81). IR ν_{max}^{KBr} cm^{-1}: 3300, 1695, 1605, 1345, 1040, 900. ^{1}H-NMR (100 MHz, in pyr.-d_5) δ: 2.40 (3H, s), 2.81 (3H, s), 3.11 (2H, t, J=7 Hz), 3.13 (1H, q, J=4 Hz), 3.94 (2H, t, J=7 Hz), 4.44 (1H, dd, J=11 and 4 Hz), 4.65 (1H, dd, J=11 and 4 Hz), 5.93 (1H, d, J=4 Hz), 7.61 (1H, s). MS m/z: 250, 232, 219, 207, 201, 189. Calcd for $C_{14}H_{18}O_4$: 250.121 (M), Found: 250.120 (M$^+$). $[\theta]_{326}^{28}$ +8810 (MeOH).

Pterosin C (II)——Colorless needles from a mixture of $CHCl_3$ and CCl_4, mp 134—135°C, $[\alpha]_D^{23}$ +101° (c=0.2, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.53), 260 (4.13), 302 (3.25). IR ν_{max}^{KBr} cm^{-1}: 3350, 1680, 1600, 1005. ^{1}H-NMR (60 MHz, in pyr.-d_5) δ: 1.51 (3H, d, J=7 Hz), 2.41 (3H, s), 2.82 (3H, s), 2.88 (1H, m), 3.11 (2H, t, J=7 Hz), 3.96 (2H, d, J=7 Hz), 5.02 (1H, d, J=4 Hz), 7.57 (1H, s). MS m/z: 250, 232, 219, 201. This product was identical with an authentic sample on direct comparison (gas–liquid chromatography (GLC), IR and mixed fusion).

Compound III——Colorless amorphous powder, $[\alpha]_D^{28}$ +54° (c=0.3, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.12), 259 (3.75), 301 (2.80). ^{1}H-NMR (100 MHz, in pyr.-d_5) δ: 2.80 (3H, s), 3.15 (1H, q, J=4 Hz), 3.21 (2H, t, J=7 Hz), 4.01 (2H, t, J=7 Hz), 4.44 (1H, dd, J=11 and 4 Hz), 4.65 (1H, dd, J=11 and 4 Hz), 5.18 (2H, s), 5.97 (1H, d, J=4 Hz), 8.36 (1H, s). MS m/z: 266, 248, 217, 200, 163. Calcd for $C_{14}H_{18}O_5$: 266.115 (M), Found: 266.116 (M$^+$). $[\theta]_{325}^{28}$ +6990 (MeOH).

Pterosin T (IV)——Colorless amorphous powder, $[\alpha]_D^{28}$ +72° (c=2.0, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.52), 260 (4.12), 303 (3.24). ^{1}H-NMR (60 MHz, in pyr.-d_5) δ: 1.48 (3H, d, J=7 Hz), 2.79 (3H, s), 2.90 (1H, dq, J=7 and 4 Hz), 3.21 (2H, t, J=7 Hz), 4.01 (2H, t, J=7 Hz), 5.03 (1H, d, J=4 Hz), 5.16 (2H, s), 8.25 (1H, s). MS m/z: 250, 232, 219, 202. This product was identical with an authentic sample on direct comparison (TLC, GLC, IR and ^{1}H-NMR).

Pterosin B (VI)——Colorless prisms from a mixture of $CHCl_3$ and *n*-hexane, mp 103—105°C, $[\alpha]_D^{20}$ −32° (c=0.4, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.57), 260 (4.21), 303 (3.40). IR ν_{max}^{KBr} cm^{-1}: 3300, 1705, 1670. ^{1}H-NMR (60 MHz, in $CDCl_3$) δ: 1.26 (3H, d, J=7 Hz), 2.42 (3H, s), 2.67 (3H, s), 2.99 (2H, t, J=7 Hz), 3.75 (3H, t, J=7 Hz), 7.07 (1H, s). MS m/z: 218, 203, 187, 185, 173, 129, 128. This product was identical with an authentic sample on direct comparison (GLC, IR and mixed fusion).

Pterosin Q (VII)——Colorless amorphous powder, $[\alpha]_D^{28}$ +107° (c=2.8, MeOH). UV λ_{max}^{MeOH} nm (log ε): 219 (4.46), 260 (4.05), 300 (3.05). ^{1}H-NMR (60 MHz, in CD_3OD) δ: 1.26 (3H, d, J=7 Hz), 2.42 (1H, m), 2.53 (3H, s), 2.69 (3H, s), 3.59 (1H, dd, J=11 and 6 Hz), 3.95 (1H, dd, J=11 and 8 Hz), 4.65 (1H, d, J=4 Hz), 5.30 (1H, dd, J=8 and 6 Hz), 7.29 (1H, s). MS m/z: 250, 235, 232, 219, 217, 201. This product was identical with an authentic sample on direct comparison (GLC, MS and ^{1}H-NMR).

Pterosin Q 3-*O*-*β*-D-Glucoside (VIII)——Colorless amorphous powder, $[\alpha]_D^{28}$ +24° (c=0.5, MeOH). UV λ_{max}^{MeOH} nm (log ε): 219 (4.48), 260 (4.06), 300 (3.18). ^{1}H-NMR (60 MHz, in pyr.-d_5) δ: 1.51 (3H, d, J=7 Hz), 2.55 (3H, s), 3.04 (1H, m), 3.05 (3H, s), 3.6—4.2 (8H), 4.99 (1H, d, J=4 Hz), 5.04 (1H, d, J=7 Hz), 5.80 (1H, dd, J=8 and 6 Hz), 7.66 (1H, s). This product was identical with an authentic sample on direct comparison (TLC and ^{1}H-NMR).

Pterosin C 3-*O*-*β*-D-Glucoside (IX)——Colorless needles from a mixture of methanol and water, mp

216—218°C, $[\alpha]_D^{28}$ +38° (c=0.3, MeOH). UV λ_{max}^{MeOH} nm (log ε): 219 (4.73), 260 (4.33), 302 (3.35). IR ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1603, 1080, 1015. ^{1}H-NMR (60 MHz, in pyr.-d_5) δ: 1.57 (3H, d, J=7 Hz), 2.27 (3H, s), 2.79 (3H, s), 3.08 (2H, t, J=7 Hz), 3.93 (2H, t, J=7 Hz), 3.9—4.7 (6H), 5.03 (1H, d, J=3.5 Hz), 5.18 (1H, d, J=7 Hz), 7.67 (1H, s). This product was identical with an authentic sample on direct comparison (TLC, IR, ^{1}H-NMR and mixed fusion).

Setulosopterosin (X)——Colorless needles from acetone, mp 178—179°C, $[\alpha]_D^{28}$ +106° (c=0.5, MeOH). UV λ_{max}^{MeOH} nm (log ε): 214 (4.48), 259 (4.03), 305 (3.17). IR ν_{max}^{KBr} cm^{-1}: 3400, 1710, 1605, 1335, 1167, 1085, 1030. ^{1}H-NMR (60 MHz, in CD_3OD) δ: 1.20 (3H, s), 2.63 (3H, s), 2.99 (2H, t, J=7 Hz), 3.66 (2H, t, J=7 Hz), 4.72 (2H, s), 4.88 (1H, s), 7.59 (1H, s). (60 MHz, in pyr.-d_5) δ: 1.80 (3H, s), 2.86 (3H, s), 3.24 (2H, t, J=8 Hz), 4.04 (2H, t, J=8 Hz), 5.23 (2H, s), 5.68 (1H, s), 8.42 (1H, s). MS m/z: 266, 248, 230, 233, 217, 200. This product was identical with an authentic sample on direct comparison (GLC, IR and mixed fusion).

Compound XI——Colorless needles from acetone, mp 166—167°C, $[\alpha]_D^{28}$ +132° (c=1.1, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.20), 262 (3.87), 304 (2.98). IR ν_{max}^{KBr} cm^{-1}: 3550, 3320, 1710, 1600, 1035. ^{1}H-NMR (60 MHz, in CD_3OD) δ: 1.21 (3H, s), 2.48 (3H, s), 2.63 (3H, s), 2.99 (2H, t, J=7 Hz), 3.62 (2H, t, J=7 Hz), 4.87 (1H, s), 7.31 (1H, s); (100 MHz, in pyr.-d_5) δ: 1.78 (3H, s), 2.42 (3H, s), 2.86 (3H, s), 3.12 (2H, t, J=7 Hz), 3.95 (2H, t, J=7 Hz), 5.62 (1H, s), 7.62 (1H, s). MS m/z: 250, 232, 217, 201, 149. Calcd for $C_{14}H_{18}O_4$: 250.121 (M), Found: 250.120 (M$^+$). $[\theta]_{335}^{22}$ +18800 (MeOH).

Dehydropterosin B (XIV)——Pterosin C (II, 50 mg) was dissolved in 10 ml of dioxane containing 0.25 ml of sulfuric acid. The mixture was warmed at 80°C for 4 h, then poured into water. The products were extracted with benzene. The extract was washed with water, dried over sodium sulfate, and concentrated under reduced pressure. The residue was chromatographed on silica gel using $CHCl_3$ and ether as eluents to yield dehydropterosin B (XIV, 33 mg). Yellow syrup. UV λ_{max}^{MeOH} nm (log ε): 245 (4.55), 252 (4.61), 330 (3.40). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1700, 1625, 1605, 1027, 900, 890. ^{1}H-NMR (60 MHz, $CDCl_3$) δ: 1.80 (3H, d, J=1 Hz), 2.30 (3H, s), 2.51 (3H, s), 2.88 (2H, t, J=7 Hz), 3.72 (2H, t, J=7 Hz), 6.57 (1H, s), 6.93 (1H, q, J=1 Hz). MS m/z: 216, 201, 185.

Compound XIII——A mixture of 30 mg of dehydropterosin B (XIV) and 40 mg of OsO_4 in 1 ml of pyridine was stirred at room temperature for 1.5 h. To this mixture, a solution of 120 mg of sodium bisulfite, 2 ml of water and 1.4 ml of pyridine was added. The mixture was stirred for 1 h, poured into water, and extracted with n-BuOH. The extract was washed with water and concentrated under reduced pressure. The residue was crystallized from MeOH to yield 9 mg of XIII. Colorless needles, mp 197—198°C. UV λ_{max}^{MeOH} nm (log ε): 218 (4.49), 262 (4.11), 300 (3.30). IR ν_{max}^{KBr} cm^{-1}: 3450, 3270, 1705, 1605, 1045, 905. ^{1}H-NMR (60 MHz, in CD_3OD) δ: 1.30 (3H, s), 2.47 (3H, s), 2.64 (3H, s), 3.00 (2H, t, J=7 Hz), 3.63 (2H, t, J=7 Hz), 4.66 (1H, s), 7.31 (1H, s). MS m/z: 250, 232, 217, 201. Calcd for $C_{14}H_{18}O_4$: 250.121, Found: 250.120 (M$^+$).

Isopropylidene Ketal (XV)——Compound XIII (6 mg) was dissolved in 5 ml of acetone containing 0.2% sulfuric acid. The mixture was kept at room temperature for 1 h, and then poured into 5% Na_2CO_3 solution. The products were extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was subjected to PLC (solvent system, $CHCl_3$: ether=2: 1) to yield 4 mg of XV, colorless syrup. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1715, 1605, 1380, 1020, 905. ^{1}H-NMR (60 MHz, in $CDCl_3$) δ: 1.17 (3H, s), 1.48 (3H, s), 1.52 (3H, s), 2.47 (3H, s), 2.68 (3H, s), 3.04 (2H, t, J=7 Hz), 3.79 (2H, t, J=7 Hz), 5.16 (1H, s), 7.30 (1H, s). MS m/z: 290, 275, 232, 217, 201.

Isopropylidene Ketal (XV) from Compound XI——Compound XI (5 mg) was dissolved in acetone containing 0.2% sulfuric acid (5 ml). The mixture was refluxed for 6 h, and then poured into 5% Na_2CO_3 solution. The products were extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was subjected to PLC (solvent system, $CHCl_3$: ether=2: 1) to yield 0.5 mg of XV, which was found to be identical with an authentic sample on direct comparison (TLC, GLC and MS).

Compound XVI——Colorless amorphous powder, $[\alpha]_D^{23}$ −22° (c=0.4, MeOH). UV λ_{max}^{MeOH} nm (log ε): 219 (4.64), 260 (4.25), 304 (3.48). IR ν_{max}^{KBr} cm^{-1}: 3400, 2910, 2850, 1690, 1600, 1505, 1465, 1380, 1320, 1070, 1030, 985, 900. ^{1}H-NMR (100 MHz, in pyr.-d_5) δ: 1.38 (3H, s), 1.58 (3H, s), 2.29 (3H, s), 2.81 (3H, s), 3.08 (2H, t, J=8 Hz), 3.90 (2H, t, J=8 Hz), 3.72—4.58 (8H), 5.09 (1H, s), 5.12 (1H, d, J=8 Hz), 7.80 (1H, s). ^{13}C-NMR (in pyr.-d_5) δ: 208.8 (s), 150.8 (s), 144.5 (s), 138.4 (s), 137.1 (s), 130.3 (s), 126.2 (d), 106.3 (d), 85.5 (d), 78.6 (d), 78.4 (d), 75.3 (d), 71.7 (d), 62.9 (t), 60.9 (t), 51.6 (s), 33.1 (t), 22.8 (q), 22.1 (q), 21.1 (q), 14.0 (q). MS m/z: 410, 248, 232, 231, 217, 216. Calcd for $C_{21}H_{30}O_8$: 410.194 (M), Found: 410.192 (M$^+$).

Acid Hydrolysis of Compound XVI——A solution of XVI (60 mg) in 50% MeOH containing 6% HCl was heated on a boiling water bath for 5 h. After cooling, the reaction mixture was neutralized with 3% Na_2CO_3 solution and extracted with ethyl acetate 3 times. The extracts were washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was chromatographed on silica gel (solvent system, $CHCl_3$: ether=7: 1) to yield pterosin D, colorless needles (20 mg) from a mixture of $CHCl_3$ and n-hexane, mp 189—190°C, $[\alpha]_D^{20}$ +6° (c=1.0, MeOH). This product was shown to be identical with an authentic sample by direct comparison (GLC, IR, ^{1}H-NMR and mixed fusion). The water layer was concentrated and the residue was chromatographed on silica gel using 30% MeOH in $CHCl_3$ as an eluent to yield 11 mg of D-glucose, $[\alpha]_D^{24}$ +42° (c=0.6, H_2O). Its trimethylsilyl ether was identical with an authentic sample on GLC, t_R 15.8 and 24.2 min. (column temp., 160°C).

Compound XVII——Colorless oil. UV λ_{max}^{MeOH} nm (log ε): 219 (4.84), 260 (4.42), 304 (3.69). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2930, 2850, 1700, 1600, 1460, 1090, 990. ^{1}H-NMR (100 MHz, in $CDCl_3$) δ: 1.11 (3H, s), 1.24 (3H, s), 2.47 (3H, s), 2.67 (3H, s), 3.19 (2H, m), 3.55 (2H, m), 4.80 (1H, s), 7.32 (1H, s). MS *m/z*: 268, 266, 253, 251, 231, 228, 217, 212, 199. Calcd for $C_{15}H_{19}ClO_2$: 268.104 and 266.107 (M), Found: 268.103 and 266.107 (M^+). $[\theta]_{328}^{20}$ +6700 (MeOH).

Conversion of XVI into XVII——A solution of XVI (15 mg) in pyridine (3 ml) was treated with $SOCl_2$ (3 ml), and the mixture was allowed to stand at room temperature overnight. The reaction mixture was diluted with ice-cold water and extracted with ether 3 times. The extracts were washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in 3 ml of 50% MeOH containing 5% HCl and heated on a boiling water bath for 5 h. After cooling, the reaction mixture was poured into ice-cold water and extracted with ether 3 times. The extracts were washed with water, dried over anhydrous Na_2SO_4 and concentrated. The residue was subjected to PLC (solvent system, $CHCl_3$: ether=4: 1) followed by column chromatography on alumina using 20% ether in $CHCl_3$ as an eluent to yield a colorless oil (5 mg), which was identified as compound XVII by direct comparison (GLC, ^{1}H-NMR, MS and IR).

Pterosin D (XVIII)——Colorless needles from a mixture of $CHCl_3$ and *n*-hexane, mp 190—191°C, $[\alpha]_D^{23}$ +6° (*c*=0.5, EtOH). UV λ_{max}^{MeOH} nm (log ε): 219 (4.10), 262 (3.73), 305 (3.00). IR ν_{max}^{KBr} cm^{-1}: 3400, 2920, 2860, 1710, 1690, 1600, 1060. ^{1}H-NMR (60 MHz, in $CDCl_3$) δ: 1.08 (3H, s), 1.25 (3H, s), 2.44 (3H, s), 2.64 (3H, s), 2.95 (2H, t, *J*=7 Hz), 3.60 (2H, t, *J*=7 Hz), 4.74 (1H, s), 7.22 (1H, s). MS *m/z*: 248, 233, 217, 199. This product was found to be identical with an authentic sample on direct comparison (GLC, IR, ^{1}H-NMR, MS and mixed fusion).

Pterosin Z (XIX)——Colorless needles from *n*-hexane, mp 84—86°C. UV λ_{max}^{MeOH} nm (log ε): 217 (4.75), 260 (4.31), 307 (3.53). IR ν_{max}^{KBr} cm^{-1}: 3430, 2960, 2920, 2870, 1675, 1600, 1460, 1375, 1045. ^{1}H-NMR (60 MHz, in a mixture of $CDCl_3$ and CD_3OD) δ: 1.25 (6H, s), 2.42 (3H, s), 2.65 (3H, s), 2.82 (2H, s), 2.98 (2H, t, *J*=8 Hz), 3.70 (2H, t, *J*=8 Hz), 7.00 (1H, s). MS *m/z*: 232, 218, 217, 201, 187. This product was identical with an authentic sample of direct comparison (GLC, IR, MS, ^{1}H-NMR and mixed fusion).

Pterosin H (XX)——Colorless needles from a mixture of $CHCl_3$ and *n*-hexane, mp 86—87°C. UV λ_{max}^{MeOH} nm (log ε): 210 (4.72), 260 (4.27), 305 (3.43). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2960, 2920, 2860, 1690, 1600, 1460, 1380, 1330, 1100, 990. ^{1}H-NMR (60 MHz, in $CDCl_3$) δ: 1.18 (6H, s), 2.42 (3H, s), 2.65 (3H, s), 2.84 (2H, s), 3.27 (2H, m), 3.54 (2H, m), 7.02 (1H, s). MS *m/z*: 252, 250, 237, 235, 215, 201. The properties and spectral data of this product are in good agreement with those reported.[3]

Pterosin I (XXI)——Colorless syrup. UV λ_{max}^{MeOH} nm (log ε): 217 (4.41), 260 (4.05), 305 (3.22). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2910, 2850, 1690, 1595, 1450, 1370, 1100. ^{1}H-NMR (60 MHz, in $CDCl_3$) δ: 1.20 (6H, s), 2.40 (3H, s), 2.65 (3H, s), 2.82 (2H, s), 2.95 (2H, t, *J*=7 Hz), 3.31 (3H, s), 3.41 (2H, t, *J*=7 Hz), 6.98 (1H, s). MS *m/z*: 246, 231, 217, 201, 187. The spectral data are in good agreement with those reported.[3]

Pterosin F (XXII)——Colorless syrup, $[\alpha]_D^{20}$ −15° (*c*=0.6, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.31), 261 (3.92), 304 (3.10). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2920, 2850, 1690, 1600, 1460, 1380, 1110. ^{1}H-NMR (100 MHz, in $CDCl_3$) δ: 1.29 (3H, d, *J*=8 Hz), 2.42 (3H, s), 2.68 (3H, s), 3.17 (2H, m), 3.50 (2H, m), 7.06 (1H, s). 2.4—3.6 (3H). MS *m/z*: 238, 236, 201, 187. This product was identical with an authentic sample on direct comparison (GLC, IR, MS and ^{1}H-NMR).

Astragalin (XXIII)——Yellow needles from methanol, mp 167—175°C, $[\alpha]_D^{23}$ −15° (*c*=0.1, MeOH). UV λ_{max}^{MeOH} nm (log ε): 267 (4.32), 354 (4.23). IR ν_{max}^{KBr} cm^{-1}: 3300, 1650, 1595, 1550, 1490, 1355, 1260, 1165, 1060, 1010, 820. ^{1}H-NMR of its trimethylsilyl ether (100 MHz, in $CDCl_3$) δ: 3.02—3.72 (6H, m), 5.88 (1H, d, *J*=7 Hz), 6.19 (1H, d, *J*=2 Hz), 6.47 (1H, d, *J*=2 Hz), 6.85 (2H, d, *J*=9 Hz), 7.90 (2H, d, *J*=9 Hz). MS *m/z*: 286 (aglycone). This product was identical with an authentic sample on direct comparison (TLC, IR and mixed fusion).

References and Notes

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