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Chemical and Toxicological Studies on Bracken Fern, *Pteridium aquilinum* var. *latiusculum*. II.[1] Structures of Pterosins, Sesquiterpenes having 1-Indanone Skeleton

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The structures of twenty-four sesquiterpenes isolated from the young fronds were disclosed by chemical and physical methods. The stereostructures were established as **1**—**22** by degradation and correlation reactions and physical data.

Keywords——*Pteridium aquilinum* var. *latiusculum*; pterosins; pterosides; 1-indanone derivatives; sesquiterpenes; norsesquiterpenes

In the preceding paper[1] extraction and fractionation of methanol extracts of young fronds of bracken, *Pteridium aquilinum* Kuhn var. *latiusculum* Underwood (Pteridaceae), along with toxicological tests were reported. In the course of work norsesquiterpenes, named pterosins B, C, E, F, G, I, J, O and N, and the esters and the glucosides, and sesquiterpenes, *i.e.*, pterosins A, D, K, L and Z, and the ester and the glucoside, were isolated from the extracts. This paper describes in full detail the evidence which leads to the structures of these compounds. All these compounds are 5,7-dimethyl-1-indanone derivatives and belong to illudoid C_{14} and C_{15}-sesquiterpenes, as reported in our earlier communications.[3]

While our works were in progress, the group of Professor Takemoto isolated a series of glucosides designated pterosides B,[4] A,[5] C,[5] D[6] and Z[6] from the same source. The aglycones of these compounds were identified with our sesquiterpenes, tentatively designated BK-3,[3a] BI-2,[3a] Ac-3,[3b] BJ-4,[3a] and HQ-2,[3a] respectively, but the proposed structure (I, R= glucose) for pteroside B,[4] the first member appeared in the literatures, was proved to be erroneous by our precise examination of the structure of pterosin B (*vide infra*).[3a] The group of Professor Sakan[7] also isolated the same type of compounds, hypolepins, from *Hypolepis punctata* Mett. and identified hypolepin B with pterosin Z.[3a] In order to avoid the confusion in trivial names, 1-indanone derivatives from ferns were decided to be named pterosins for free sesquiterpenes and pterosides for the glucosides by the consultation with other two groups.[3b]

1) Part I: K. Yoshihira, M. Fukuoka, M. Kuroyanagi, S. Natori, M. Umeda, T. Morohoshi, M. Enomoto, and M. Saito, *Chem. Pharm. Bull.* (Tokyo), **26**, 2346 (1978).
2) Location: *Kamiyoga-1-chome, Setagaya-ku, Tokyo.*
3) *a*) K. Yoshihira, M. Fukuoka, M. Kuroyanagi, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **19**, 1491 (1971); *b*) K. Yoshihira, M. Fukuoka, M. Kuroyanagi, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **20**, 426 (1972); *c*) M. Fukuoka, M. Kuroyanagi, M. Tōyama, K. Yoshihira, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **20**, 2282 (1972); *d*) M. Kuroyanagi, M. Fukuoka, K. Yoshihira, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **22**, 723 (1974); *e*) M. Kuroyanagi, M. Fukuoka, K. Yoshihira, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **22**, 2762 (1974). These works were presented at the 92nd, 93rd, 94th, and 95th Annual Meetings of the Pharmaceutical Society of Japan, April 1972, April 1973, April 1974, and April 1975, and at the 16th Symposium on the Chemistry of Natural Products, Osaka, October 1972.
4) H. Hikino, T. Takahashi, S. Arihara, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 1488 (1970).
5) H. Hikino, T. Takahashi, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **20**, 210 (1972).
6) H. Hikino, T. Takahashi, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **19**, 2424 (1971).
7) Y. Hayashi, M. Nishizawa, S. Harita, and T. Sakan, *Chemistry Letters*, **1972**, 375.

In this paper the chemistry of pterosin B, the major constituent, will be precisely described first and, subsequently, the structures of other congeners will be discussed on the basis of the structure of pterosin B.

Pterosin B (**1a**), mp 109—110°, $[\alpha]_D$ −31.9°, has the molecular formula of $C_{14}H_{18}O_2$ as shown by elemental analysis and high resolution mass spectrum. The infrared (IR) spectrum showed the presence of hydroxyl and conjugated carbonyl groups and an aromatic ring as shown in Table I. The ^{1}H-nuclear magnetic resonance (PMR) spectrum showed signals due to one secondary methyl group at δ 1.25 (3H, d, J=8 Hz), two aromatic methyl groups at δ 2.41 (3H, s) and at δ 2.67 (3H, s), one aromatic ring proton at δ 6.99 (1H, br. s), two benzylic protons at δ 3.23 (1H, dd, J=9.5, 18 Hz) and in range δ 2.3—3.5 (1H), one methine proton overlapped in the range δ 2.3—3.5, and one hydroxyethyl group at δ 2.99 (2H, t, J= 8 Hz) and δ 3.72 (2H, t, J=8 Hz). The secondary methyl group was confirmed to be at the α position in relation to a carbonyl group by the fact that the doublet signal of the secondary methyl group changed into singlet by standing at room temperature for 24 hr in deuterated trifluoroacetic acid, indicating deuteration of the methine proton. In addition to the above physical properties, the ultraviolet (UV) absorptions at 217, 260 and 303 nm of **1a**, being characteristic for 1,2-benzocyclenone chromophore,[8] indicated 1-indanone nucleus to **1a**.

To confirm the framework following reactions were carried out. Pterosin B (**1a**) was subjected to acetylation with acetic anhydride and pyridine to afford an acetate (**1b**), which showed no absorption due to the hydroxyl group in its IR spectrum and a downfield shift of the methylene signal of the hydroxyethyl group in the PMR spectrum (δ 4.09). The selenium dioxide oxidation of **1b** afforded an indenone derivative (**2**), the structure of which was assigned from the UV absorptions[9,10] at 244, 250 and 335 nm and the PMR signals[10] at δ 6.51 (1H, s) (aromatic proton), δ 6.86 (1H, q, J=1.7 Hz) and δ 1.82 (3H, d, J=1.7 Hz) (vinyl proton and vinyl methyl group respectively).

Pterosin B (**1a**) was further subjected to reduction with sodium borohydride to afford a mixture of diols (**3a** and **3b**), in which the newly formed carbinyl protons at δ 4.75 (1H, d, J=3 Hz) and 4.93 (1H, d, J=5.2 Hz) showed coupling with the neighbouring methine proton. Dehydration of the mixture with *p*-toluensulfonic acid gave an indene derivative (**4a**), the structure of which was supported from the UV absorptions[11] at 220, 226 and 265 nm, and the PMR signals[12] at δ 6.44 (1H, br. s) and 2.09 (3H, br. s) due to –CH=C–CH_3 group, δ 6.94 (1H, br. s) due to an aromatic proton, and δ 3.19 (2H, br. s) due to a benzylic proton. From these facts it was proved that pterosin B (**1a**) was a 2-methyl-1-indanone derivative.

The orientation of substituents in the aromatic ring of pterosin B (**1a**) was established from the following evidences. The signals of the two aromatic methyl groups in the reduction products (**3a** and **3b**) appeared at higher fields (δ 2.35 and 2.39) when compared with those of **1a**. Moreover the Clemmensen reduction[13] of **1a** afforded an indan (**5**), in which the signals of the two methyl groups were more shielded (δ 2.20 and 2.30). On the other hand the anisotropic effect[14] of the carbonyl group was not observed for the aromatic proton and

8) R. Huisgen, G. Seidl, and I. Wimmer, *Liebigs Ann. Chem.*, **677**, 21 (1964).
9) H.O. House and D.J. Reif, *J. Am. Chem. Soc.*, **79**, 6491 (1957); H.O. House, V. Paragamian, R.S. Ro and D.J. Wlika, *ibid.*, **82**, 1452 (1960).
10) N.S. Bhacca and G.H. Williams, "Applications of NMR spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, 1964, p. 108; G. Maury and N.H. Cromwell, *Bull. Soc. Chim. France*, **1968**, 4573; M.B. Floyd and G.R. Allen, Jr., *J. Org. Chem.*, **35**, 2647 (1970).
11) E. Haselbach and E. Heilbronner, *Helv. Chem. Acta.*, **51**, 16 (1968).
12) J.A. Elrvidge and R.G. Foster, *J. Chem. Soc.*, **1963**, 590.
13) S.A. Galton, M. Kalafer, and F.M. Beringer, *J. Org. Chem.*, **35**, 1 (1970); S.A. Galton and R. Abbas, *ibid.*, **38**, 2008 (1973).
14) J.-L. Imbach, A.E. Pohland, E.D. Weiler, and N.H. Cromwell, *Tetrahedron*, **23**, 3931 (1967); J.W. Ap-Simon, P.V. Demarco, D.W. Mathieson, W.G. Craig, A. Karim, L. Saunders, and W.B. Whalley, *Tetrahedron*, **26**, 119 (1970).

the hydroxyethyl group. Thus one of the two methyl groups in **1a** showing the lower field signal (δ 2.67) was suggested to be in the deshielded sphere of the carbonyl group, *i.e.* the 7 position in 1-indanone. From this evidence, there remained six possible isomeric structures (I to VI) for pterosin B (**1a**). Decoupling experiment on **1a** suggested that the aromatic methyl group other than that at the 7 position was *ortho* to the aromatic proton, since the irradiation at the higher methyl signal at δ 2.41 exhibited the nuclear Overhauser effect on the aromatic proton at δ 6.99 (the increase of area, 12.6%), while that at the lower methyl signal at δ 2.67 did not show the effect on the aromatic proton. The above observation excluded the possibility of the formula I, proposed by Hikino, *et al.*,[4] and also of formula III and IV, and favoured the formulae II, V and VI. This point was definitely clarified by oxidation of **1a** with nitric acid. Chromatographic separation of the acidic oxidation products, after methylation with diazomethane, gave two compounds, trimethyl benzene–tricarboxylate (**6a**) and its nitro compound (**6b**). The PMR spectrum of **6a** showed signals of two aromatic methyl groups (δ 2.25 (3H, s) and 2.32 (3H, s)), three methoxycarbonyl groups (δ 3.84 (3H, s) and 3.90 (6H, s)) and an aromatic proton (δ 7.60 (1H, s)), excluding the possibility of the symmetric structure (**7**) expected to be formed from the formula I. The nitro compound (**6b**) was then hydrolysed with alkali and decarboxylated with copper and quinoline. The gas chromatography using two kinds of columns of the neutral decarboxylated product showed the identical retention time with that of 4-nitro-*m*-xylene (**8**) but different from those of 2-nitro-*m*-xylene, 2-nitro-*p*-xylene and 3-nitro-*o*-xylene. Thus the tricarboxylic acids, **6a** and **6b**, were proved to be 3,5-dimethyl-1,2,4-benzenetricarboxylic acid (**6a**) and its nitro derivative (**6b**).

Therefore the structure of pterosin B (**1a**) was firmly established as the formula V, 6-hydroxyethyl-2,5,7-trimethyl-1-indanone.

The absolute configuration of **1a** was proved to be 2*R* by oxidation with ozone furnishing methylsuccinic acid, which showed mp 109—110°, $[\alpha]_D$ +3.7° (MeOH) (lit.[15] +8.8° (H_2O)) and the positive plain curve to 218 nm in optical rotatory dispersion as reported for the (*R*)-acid.[15]

The circular dichroism (CD) curve of **1a** showed a positive Cotton effect associated with $n\rightarrow\pi^*$ transition, *i.e.* $[\theta]_{326}$ +1771 in methanol, $[\theta]_{366}$ −999, $[\theta]_{348}$ −1161, $[\theta]_{334}$ −687, $[\theta]_{326}$ +332 in cyclohexane, and $[\theta]_{360}$ −350, $[\theta]_{343}$ −117, $[\theta]_{321}$ +1028 in chloroform.[16]

Pterosin F (**1c**), mp 66—67°, $[\alpha]_D$ −14.6°, was isolated as a chlorine containing compound, $C_{14}H_{17}ClO$, as shown by a high resolution mass spectrum, and was quite similar to pterosin B (**1a**) regarding the UV (219, 259 and 303 nm) and IR (1695 and 1600 cm^{-1}) absorptions and the PMR signals due to one secondary methyl at δ 1.27 (3H, d, J=7 Hz) and two aromatic methyl groups at δ 2.42 and 2.66, and one aromatic proton at δ 6.98 (Tables I and II). The two multiplet signals at δ 3.2 (2H, m) and 3.4 (2H, m) along with the molecular formula suggested that the hydroxyl group of the hydroxyethyl group in pterosin B (**1a**) was substituted by a chlorine atom. The assumption was confirmed by the formation of a racemic pterosin F by chlorination of **1a** with thionyl chloride in pyridine. The stereochemistry of pterosin F (**1c**) was established as 2*R* configuration by the CD Cotton effect ($[\theta]_{362}$ −111 and $[\theta]_{322}$ +846 in methanol, and $[\theta]_{357}$ −218, $[\theta]_{343}$ −87 and $[\theta]_{320}$ +677 in chloroform)[16] compared with that of pterosin B (**1a**).

15) K. Balenovic and N. Bregant, *J. Chem. Soc.*, **1965**, 5131; A. Fredga, J.P. Jennings, W. Klyne, P.M. Scopes, B. Sjöberg, and S. Sjöberg, *ibid.*, **1965**, 3928.

16) In the previous communications[3d,e] we adopted erroneous $[\theta]$ values without knowing that the instrument had been adjusted with the internal parts not to need the factor 3300. With regret all the values reported in the papers should be corrected as shown in this paper. The relationship between the CD curves and the configurations and the conformations of the indanones will be reported in details in a forth-coming paper.[17]

The samples of pterosin B were not optically pure. The problem of optical purities of the pterosin series will also be reported in the following paper.[17]

17) M. Kuroyanagi, M. Fukuoka, K. Yoshihira, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), in the press.

Pterosin O (**1d**), mp 45—46°, $[\alpha]_D$ ±0°, $C_{15}H_{20}O_2$, exhibited similar UV and IR absorptions to pterosin B (**1a**) (Table I) and the PMR signals indicated the presence of one secondary methyl and two aromatic methyl groups, and one aromatic proton as **1a** (Table II). However one singlet at δ 3.36 (3H, s) and two multiplet signals at δ 3.50 (2H, m) and 3.05 (2H, m) suggested the presence of a methoxyethyl group instead of the hydroxyethyl group in pterosin B (**1a**) and the assumption was confirmed by methylation of **1a** with methyl iodide and sodium hydride to give pterosin O (**1d**), together with pterosins I (**21c**) and Z (**21a**) (*vide infra*).

Benzoylpterosin B (**1e**), mp 68—70°, $[\alpha]_D$ −20.0°, $C_{21}H_{22}O_3$, and palmitylpterosin B (**1f**), mp 51—52°, $[\alpha]_D$ −3.3, $C_{30}H_{48}O_3$, are esters of pterosin B (**1a**) exhibiting the UV absorptions at 218, 230, 259 and 302 nm, and at 217, 260 and 303 nm, respectively. The IR spectra showed no absorption due to the hydroxyl group and the high resolution mass spectra showed the base peak at *m/e* 200, corresponding to the fragment ion, $C_{14}H_{16}O$, of $[M^+-C_6H_5CO_2H]$ and $[M^+-C_{15}H_{31}CO_2H]$, respectively. The PMR spectrum of **1e** showed the additional signals of the aromatic protons due to benzoate at δ 7.88—8.05 (2H) and 7.32—7.50 (3H). In the case of **1f** primary methyl group at δ 0.85 (3H, t, J=5 Hz), methylene protons at δ1.25 (26H, br. s) and a methylene group adjacent to an oxycarbonyl-carbon at δ 2.26 (2H, t, J=6.8 Hz) due to palmitate appeared other than the all signals except the hydroxyl group in **1a**. In comparison with signals of pterosin B (**1a**) (Table II) the methylene signal adjacent to the acyloxy group showed lower shifts to δ 4.37 (2H, t, J=8 Hz) for **1e** and δ 4.09 (2H, t, J=8 Hz) for **1f** respectively. The structures and the absolute configurations of **1e** and **1f** were established as formulae (**1e** and **1f**, both 2*R* configurations) by direct acylation of **1a** with benzoyl chloride and palmityl chloride in pyridine respectively.

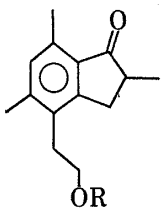
Isocrotonylpterosin B (**1g**), oil, $[\alpha]_D$ −3.5°, $C_{18}H_{22}O_3$, was similar to pterosin B acylates (**1e** and **1f**) regarding the UV and IR absorptions and the PMR signals (Tables I and II) except the signals due to an acyl group (*vide infra*). Moreover the fragment ion $[M^+-C_4H_6O_2]$ at *m/e* 200 in the mass spectrum of **1g** suggested the substitution of a crotonyl or isocrotonyl group as the acyl group. As for the choice between the crotonyl or isocrotonyl group, the latter was assumed to be preferable by the coupling constants of the olefinic protons.[18] The PMR signals of the -CH=CH-CH_3 group in the natural product (**1g**) appeared at δ 5.72 (1H, dq, J=11 and 1.5 Hz), 6.25 (1H, dq, J=11 and 8 Hz) and 2.12 (3H, dd, J=8 and 1.5 Hz). For the sake of comparison, a crotonate (**1h**), $[\alpha]_D$ −7.5°, was prepared from pterosin B (**1a**). The PMR of **1h** showed signals at δ 5.77 (1H, dq, J=15 and 1.5 Hz), 6.33 (1H, dq, J=15 and 8 Hz) and 2.34 (3H, dd, J=8 and 1.5 Hz).[18] The absolute configuration of **1g** was established as 2*R* by comparing the molecular rotation with those of **1a**, **1b**, **1c**, **1e** and **1f**.

Pteroside B (**1i**) isolated from the fronds was identified in all respects with the specimen obtained by Hikino, *et al.*[4] and the structure was revised to the formurla (**1i**) by the fact that **1i** was hydrolyzed by emulsin to afford (2*R*)-pterosin B (**1a**) and D-glucose (This will be discussed in detail in a forth-coming paper[17]).

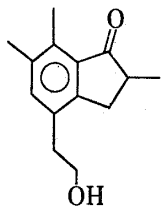
Pterosin E (**1j**), mp 160—162°, $[\alpha]_D$ ±0°, $C_{14}H_{16}O_3$, was similar to pterosin B (**1a**) in the UV and PMR spectra (Tables I and II) except a singlet signal at δ 3.74 (2H) instead of those of the hydroxyethyl group. The IR absorptions showed the presence of a carboxyl and a carbonyl function at 3000—2400, 1695 and 1680 cm^{-1}. Therefore the singlet signal at δ 3.74 was assignable as a methylene between the aromatic ring and the carboxyl group. This formulation (**1j**) for pterosin E was substantiated by the direct derivation from pterosin B (**1a**) by oxidation with chromic anhydride. The absolute configuration was established as 2*R* by the CD Cotton effect[16] ($[\theta]_{327}$ +94) compared with that of the synthetic specimen prepared from (2*R*)-pterosin B (**1a**). However, the optical purity of natural pterosin E was proved to be low, since the synthetic pterosin E showed stronger CD Cotton effect ($[\theta]_{324}$ +1648).[16]

18) F.A. Bovey, "NMR Data Tables for Organic Compounds," Vol. 1, Compound No. 428 and 429, Interscience Publishers, New York, 1967.

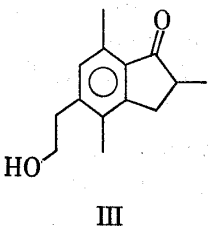
After our preliminary communications[3] Nambudiry and Rao[19] synthesized pterosin E as the racemic form starting from α-bromomesitylene and identified with our specimen. This provided a first synthetic confirmation of the structures of pterosin E and related compounds.



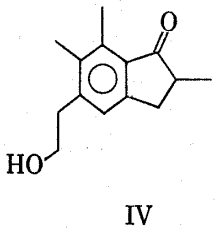
I : R=glucose
=H



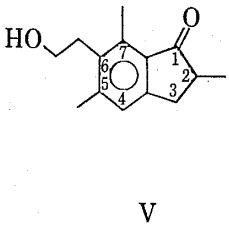
II



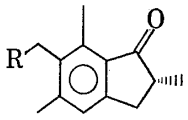
III

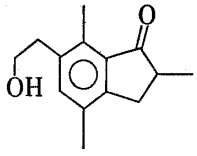


IV



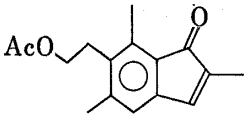
V





VI

1a : R=CH_2OH pterosin B
1b : =CH_2OAc
1c : =CH_2Cl pterosin F
1d : =CH_2OMe pterosin O
1e : =CH_2O-benzoyl
1f : =CH_2O-palmityl
1g : =CH_2O-isocrotonyl
1h : =CH_2O-crotonyl
1i : =CH_2O-glucose pteroside B
1j : =COOH pterosin E



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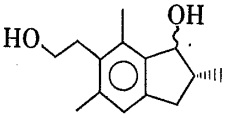
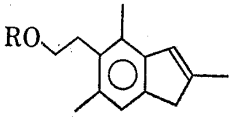
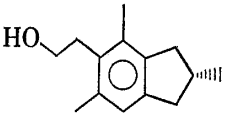


3a : 1-α OH
3b : 1-β OH



4a : R=H
4b : R=Ac



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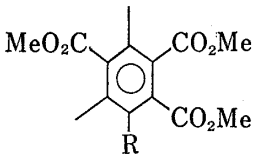
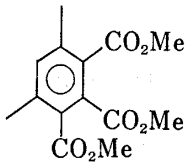


6a : R=H
6b : R=NO_2



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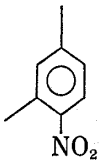
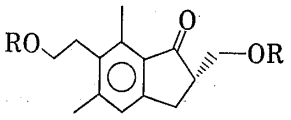
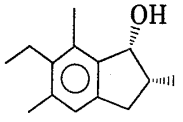


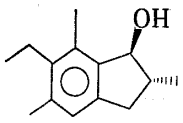
8



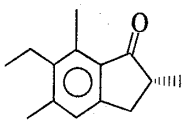
9a : R=H pterosin G
9b : =Ac
9c : =Tosyl



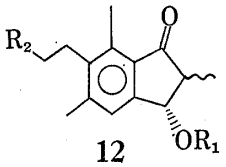
10a



10b



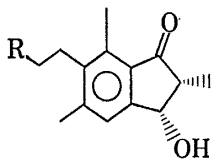
11



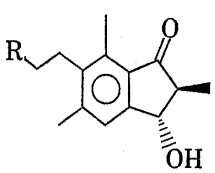
12

12a : R_1=H, R_2=OH pterosin C
12b : R_1=Ac, R_2=OAc
12c : R_1=H, R_2=Cl pterosin J
12d : R_1=H, R_2=OAc
12e : R_1=H, R_2=O-phenylacetyl
12f : R_1=glucose, R_2=OH wallichoside

12 series is the mixture having 2α-methyl and 2β-methyl groups but the major constituent has 2β-methyl group.



13a : R=OH
(2*R*, 3*S*)-pterosin C
13c : R=O-palmityl
13e : R=O-glucose



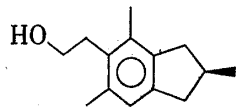
13b : R=OH
(2*S*, 3*S*)-pterosin C
13d : R=O-palmityl

Chart 1

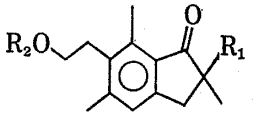
19) M.E.N. Nambudiry and G.S.K. Rao, *J. Chem. Soc. Perkin-I*, **1974**, 317.

Pterosin G (**9a**), mp 152—153°, $[\alpha]_D$ −14.6°, $C_{14}H_{18}O_3$, showed the similar UV and IR absorptions (Table I) to those of pterosin B (**1a**). The PMR spectrum (Table II) disclosed the presence of two aromatic methyl groups, one hydroxyethyl group, one methylene group (δ 3.77, 2H, d, J=5.5 Hz), one aromatic proton, and two benzylic protons and one methine proton (in the range of δ 2.9—3.1), but was devoid of aliphatic methyl groups. On acetylation with acetic anhydride and pyridine **9a** gave a diacetate (**9b**) in which the signal at δ 3.77 in **9a** was shifted to downfield at δ 4.35 (2H, s) as well as the methylene signal (δ 4.15, 2H, t, J=7.5 Hz) in the hydroxyethyl group. Thus the former methylene group was proved as a portion of the hydroxymethyl group and moreover assumed to exist at the 2 position in place of the methyl group in pterosin B (**1a**). The structure was established by the following correlation with pterosin B (**1a**).

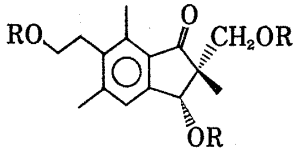
Pterosin B (**1a**) was subjected to tosylation followed by reduction with lithium aluminum hydride to afford 1-indanols (**10a** and **10b**), the structures of which were assigned on the



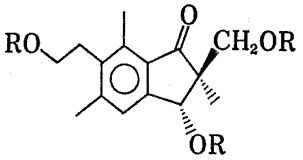
14



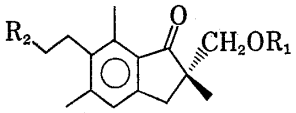
15a : R_1=OH R_2=H pterosin N
15b : =OH =Ac
15c : =Ac =Ac
15d : =OAc =Ac



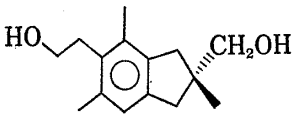
16a : R=H pterosin L
16b : =Ac



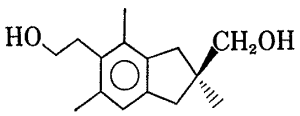
17a : R=H epipterosin L
17b : =Ac



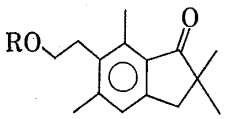
18a : R_1=H R_2= OH pterosin A
18b : =H =OAc
18c : =Ac =OH
18d : =Ac =OAc
18e : =H =Cl pterosin K
18f : =H =O-palmityl
18g : =palmityl =O-palmityl
18h : =H =O-glucose pteroside A



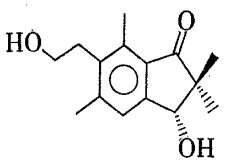
19



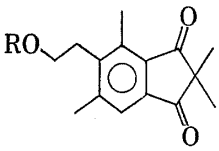
20



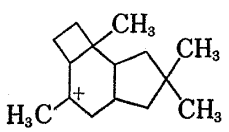
21a : R=H pterosin Z
21b : =Ac
21c : =Me pterosin I



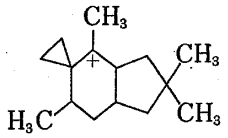
22 pterosin D



23a : R=H
23b : =Ac



A



B

Chart 2

basis of the coupling constants[20] between the carbinyl protons at the 1 position and the methine protons at the 2 position, *i.e.* the *cis*-related hydrogens having the larger coupling constant (δ 4.91, 1H, d, J=5.3 Hz) for **10a** and the *trans*-related hydrogens (δ 4.75, 1H, d, J=2.8 Hz) for **10b**. The indanol (**10a**) was oxidized with chromic anhydride to afford a ketone (**11**) ($[\theta]_{322}$ +906 in methanol). The two hydroxyl groups in pterosin G (**9a**) were also removed by the same successive reactions, *i.e.* tosylation with *p*-toluensulfonyl chloride and pyridine, reduction with lithium aluminum hydride and oxidation with chromic anhydride, to afford the same ketone (**11**) ($[\theta]_{322}$ +303 in methanol). This correlation proved the structure of pterosin G (**9a**) and, at the same time, established the absolute configuration as 2*S*, *i.e.* α-orientation of the hydroxymethyl group.

Pterosin C (**12a**), mp 153—156°, $[\alpha]_D$ +93.4°, $C_{14}H_{18}O_3$, was generally isolated as chromatographically pure crystals and was an analogue of pterosin B (**1a**) as suggested by the UV and IR absorption shown in Table I. The PMR spectrum (Table II) disclosed the presence of two aromatic methyl groups, one hydroxyethyl group, one methine proton, one deshielded aromatic proton (δ 7.24), protons of one methyl group appeared in a pair of doublet signals (altogether 3H, δ 1.15 and 1.26, each J=8 Hz), and one carbinyl proton appeared in a pair of doublet signals (altogether 1H, δ 4.59, d, J=3.8 Hz and 5.09, d, J=6.8 Hz) (*vide infra*). On treatment of **12a** with sodium deuterium methoxide in deuterium methanol at room temperature for 5 mins, the both pairs of the doublet signals now appeared as the pairs of signlet singnals (δ 1.15 and 1.28, and 4.60 and 5.04). This observation suggested the vicinal relation between the two pairs, *i.e.* the carbinyl and the methyl groups. On acetylation with acetic anhydride and pyridine pterosin C (**12a**) gave the corresponding diacetate (**12b**), in which a pair of signals for one proton appeared at the downfield (δ 5.78, d, J=3 Hz and 6.14, d, J=7 Hz). Therefore the pair of signals was traceable to a carbinyl proton. The mild base treatment of the acetate (**12b**) afforded a pure 1-indenone derivative (**2**), which was identified with the specimen obtained from pterosin B (**1a**). The formation of **2** suggested the elimination of acetoxyl group in the 3 position. Thus pterosin C (**12a**) was proved to be the 3-hydroxy derivative of pterosin B (**1a**) and existed as a mixture of the *cis* and *trans* isomers. Referring to the vicinal coupling constants reported for 1-indanone derivatives,[21] the minor component in **12a**, showing a larger coupling constant (δ 5.09, d, J=6.8 Hz), was assigned as the *cis* isomer (**13a**) and the major component showing a smaller value (δ 4.59, d, J=3.8 Hz) was assigned as the *trans* isomer (**13b**). The ratio of the *cis* and *trans* isomers was not constant but the *trans* isomer was in general predominant in the diastereomeric mixture and was also a more stable form in an alkaline condition. For example, the treatment of the mixture with 2% sodium hydroxide in methanol changed the ratio from 1:2 to 1:4. The CD curves of the mixtures exhibited nearly the same ellipticity values, irrespective of the ratio of *cis* and *trans*, *i.e.* $[\theta]_{326}$ +20688 for the mixture of 1:2 ratio and $[\theta]_{326}$ +22939 for the mixture of 1:4 ratio. If the mixture is composed of the isomers at the 3-position, the epimerization by alkaline at 2-position must induce a partial racemization and a decrease of the $[\theta]$ value. Thus the behaviour of the CD values by the epimerization indicated that the stereochemistry of the hydroxyl group at the 3-position contributes to the sign of the Cotton effects (a positive effect for 3α-hydroxypterosins and negative for 3β-hydroxypterosins; see the forthcoming paper[17]) and, hence, pterosin C (**12a**) is a mixture of epimers at the 2-position. On the Clemmensen reduction[13] pterosin C (**12a**, *cis*:*trans*; 1:2) gave an indan derivative (**14**). The specific optical rotation ($[\alpha]_D$ +1.86°) of the product indicated the contamination of the enantiomeric indan, when compared with that ($[\theta]_D$ −3.45°) of the 2α-methyl indan (**5**) derived from pterosin B (**1a**). Accordingly, the major component of the enantiomeric mixture (**14**) was proved

20) W.E. Rosen, L. Dorfman, and M.P. Linfield, *J. Org. Chem.*, **29**, 1723 (1964).

21) J.B. Lambert and F.R. Koeng, *Org. Magn. Resonance*, **3**, 389 (1971); E. Lusting and E.P. Ragelis, *J. Org. Chem.*, **32**, 1398 (1967).

to bear a 2β-methyl group and, hence, the configuration of the methyl and the hydroxyl groups in pterosin C (**12a**) were established as the 2α- and 3α-orientations (2*R*, 3*S*-configuration) for the minor *cis*-related component (**13a**), and the 2β- and 3α-orientations (2*S*, 3*S*-configuration) for the major *trans* component (**13b**), respectively.

Pterosin J (**12c**), mp 136—137°, $[\alpha]_D$ +83.5°, was isolated as a chlorine containing compound, $C_{14}H_{17}ClO_2$. The UV, IR and PMR spectra were similar to those of pterosin C (**12a**) as shown in Table I and II, but the signals due to two methylene groups at δ 3.15 (2H, m) and 3.55 (2H, m) showed the characteristic chemical shifts and coupling patterns as those of pterosin F (**1c**) bearing a chloroethyl group (Table II). Thus pterosin J (**12c**) was showed to be a mixture of the *cis* and *trans* isomers of the 6-chloroethyl derivative of pterosin C (**12a**). The stereochemistry of **12c** was established as 2*S*, 3*S*-configuration with respect to the major *trans* form by the CD Cotton effect, $[\theta]_{325}$ +15487, and by the coupling constant of the carbinyl proton, compared with those of **12a**.

Acetylpterosin C (**12d**), mp 115—118°, $[\alpha]_D$ +86.1°, $C_{16}H_{20}O_4$, and phenylacetylpterosin C (**12e**), mp 67—68°, $[\alpha]_D$ +38.6°, $C_{22}H_{24}O_4$, were isolated as acyl derivatives which showed the similar UV and IR absorption (Table I) to those of **12a**. The nature of the acyl groups was assigned acetyl and phenylacetyl group for **12a** and **12e** respectively by the following evidences. In the high resolution mass spectra, the both compounds (**12d** and **12e**) showed the base peak at *m/e* 216 ($C_{14}H_{16}O_2$), corresponding to the [M^+-CH_3COOH or $C_6H_5CH_2COOH$] fragment ion. The PMR spectra showed the additional signals due to acetyl group at δ 2.03 (3H, s) for **12d** and phenylacetyl group at δ 7.25 (5H, br. s) and 3.57 (2H, s) for **12e**, respectively, together with the all signals observed in **12a** except the methylene signals adjacent to the hydroxyl group in the hydroxyethyl group, showing low field shifts at δ 4.10 (2H, t, J=8 Hz) and δ 4.12 (2H, t, J=7 Hz), respectively. Acetylpterosin C (**12d**) was obtained from pterosin C (**12a**) by boiling in acetic acid, and directly identified with the natural specimen. Therefore the two acylpterosins, **12d** and **12e**, were proved to be diastereoisomeric mixtures having an acetoxyethyl and a phenylacetoxyethyl group at the 6-position in **12a**, respectively. The stereochemistries of **12d** and **12e** were assigned as the same (2*S*, 3*S*)-configurations for the major *trans*-related components by the CD Cotton effects, $[\theta]_{325}$ +16268 and $[\theta]_{324}$ +22439 respectively, and by the coupling constants of the carbinyl proton (Table II) compared with those of **12a**.

Palmitylpterosin C (**13d**), mp 95—97°, $[\alpha]_D$ +52.8°, $C_{30}H_{48}O_4$, showed the UV and IR absorptions (Table I) similar to those of pterosin C (**12a**) and its acylates (**12c**, **12d** and **12e**). The PMR spectrum (Table II) disclosed the presence of one primary methyl, one secondary

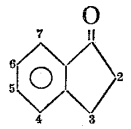
Table I. Physical Properties of Pterosins and Pterosides

Compound	mp (°C) (Recrystn. solvent)[a]	Formula	Mass spectrum (Calcd.) Analysis (%) (Calcd.)	UV λ_{max}^{EtOH} nm (log ε)	IR ν_{max}^{KBr} cm^{-1}	$[\alpha]_D$ (Solvent)
Pterosin A (**18a**)	125—127 (B)	$C_{15}H_{20}O_3$	M^+: *m/e* 248.140 (248.141) C: 72.51(72.55) H: 8.25 (8.12)	217(4.54), 261(4.19), 305(3.39)	3240, 1700, 1603	−45.3° (*c*=0.13, MeOH)
Pterosin B (**1a**)	109—110 (C-H)	$C_{14}H_{18}O_2$	M^+: *m/e* 218.132 (218.131) C: 76.90(77.03) H: 8.23 (8.31)	217(4.57), 260(4.21), 303(3.40)	3300, 1705, 1670 (3630, 1704, 1601 in CCl_4)	−31.9° (*c*=0.31, MeOH)
Pterosin C (**12a**)	153—156 (A)	$C_{14}H_{18}O_3$	M^+: *m/e* 234.124 (234.126) C: 71.82(71.77) H: 7.75 (7.74)	217(4.51), 259(4.12), 301(3.23)	3350, 1680, 1600	+93.4° (*c*=0.20, MeOH)
Pterosin D (**22**)	189—190 (M-C)	$C_{15}H_{20}O_3$	M^+: *m/e* 248.142 (248.141)	217(4.51), 260(4.23), 302(3.28)	3260, 1716, 1600	+4.8° (*c*=0.20, EtOH)

Compound	mp (°C) (Recrystn. solvent)[a]	Formula	Mass spectrum (Calcd.) Analysis (%) (Calcd.)	UV λ_{max}^{EtOH} nm (log ε)	IR ν_{max}^{KBr} cm^{-1}	$[\alpha]_D$ (Solvent)
Pterosin E (**1j**)	160—162 (T)	$C_{14}H_{16}O_3$	M$^+$: *m/e* 232.107 (232.109)	217(4.53), 260(4.20), 303(3.40)	1695, 1680, 1600	±0°
Pterosin F (**1c**)	66—67 (H)	$C_{14}H_{17}ClO$	M$^+$: *m/e* 236.096 (236.097) 238.096 (238.094)	219(4.66), 259(4.24), 303(3.49)	1695, 1600	−14.6° (*c*=0.44, MeOH)
Pterosin G (**9a**)	152—153 (T)	$C_{14}H_{18}O_3$	M$^+$: *m/e* 234.126 (234.126)	217(4.43), 261(4.14), 305(3.30)	3540, 1690, 1600	−14.6° (*c*=0.24, MeOH)
Pterosin J (**12c**)	136—137 (B-H)	$C_{14}H_{17}ClO_2$	M$^+$: *m/e* 252.087 (252.092) 254.088 (254.089)	218(4.46), 257(4.17), 299(3.37)	3380, 1715, 1600	+83.5° (*c*=0.17, $CHCl_3$)
Pterosin K (**18e**)	85—87 (H)	$C_{15}H_{19}ClO_2$	M$^+$: *m/e* 266.107 (266.108) 268.101 (268.105)	218(4.61), 259(4.21), 303(3.41)	3350, 1704, 1600	−37.5° (*c*=0.14, MeOH)
Pterosin L (**16a**)	139—141 (B)	$C_{15}H_{20}O_4$	M$^+$: *m/e* 264.131 (264.136)	218(4.51), 259(4.15), 301(3.30)	3360, 1690, 1603	+23.7° (*c*=0.16, MeOH)
Ptorosin N (**15a**)	165—167 (A)	$C_{14}H_{18}O_3$	M$^+$: *m/e* 234.123 (234.126)	218(4.49), 262(4.18), 308(3.39)	3430, 1700, 1605	−18.8° (*c*=0.10, MeOH)
Pterosin O (**1d**)	45—46 (H)	$C_{15}H_{20}O_2$	M$^+$: *m/e* 232.146 (232.146)	218(4.52), 260(4.20), 305(3.42)	1700, 1603	±0°
Pterosin Z (**21a**)	86—88 (H)	$C_{15}H_{20}O_2$	M$^+$: *m/e* 232.157 (232.160)	217(4.48), 260(4.12), 304(3.36)	3320, 1680, 1600	—
Benzoylpterosin B (**1e**)	68—70 (M)	$C_{21}H_{22}O_3$	M$^+$: *m/e* 322.157 (322.160)	218(4.51), 259(4.11), 302(3.27) 230(inflection) (4.12)	1715, 1693, 1603	−20.0° (*c*=0.11, $CHCl_3$)
Isocrotonyl-pterosin B (**1g**)	oil	$C_{18}H_{22}O_3$	M$^+$: *m/e* 286.154 (286.157)	217(4.56), 260(4.11), 303(3.27)	1718, 1703, 1604	−3.5° (*c*=0.20, $CHCl_3$)
Palmitylpterosin B (**1f**)	51—52 (H)	$C_{30}H_{48}O_3$	M$^+$: *m/e* 456.357 (456.360)	217(4.53), 260(4.18), 303(3.34)	1745, 1702, 1600	−3.3° (*c*=0.20, hexane)
Palmitylpterosin A (**18f**)	50—51 (H)	$C_{31}H_{50}O_4$	M$^+$: *m/e* 486.369 (486.371)	217(4.57), 258(4.20), 304(3.44)	3400, 1743, 1697, 1600	−37.8° (*c*=0.10. MeOH)
Palmithyl-pterosin C (**13d**)	95—97 (H)	$C_{30}H_{48}O_4$	M$^+$: *m/e* 472.351 (472.355)	217(4.56), 258(4.18), 300(3.42)	3380, 1743, 1713, 1600	+52.8° (*c*=0.11, $CHCl_3$)
Acetylpterosin C (**12d**)	115—118 (B-H)	$C_{16}H_{20}O_4$	M$^+$: *m/e* 276.133 (276.136)	216(4.55), 257(4.17), 298(3.30)	3360, 1740, 1713, 1600	+86.1° (*c*=0.23, $CHCl_3$)
Phenylacetyl-pterosin C (**12e**)	67—68 (H)	$C_{22}H_{24}O_4$	M$^+$: *m/e* 352.161 (252.167)	216(4.58), 257(4.14), 299(3.34)	3380, 1743, 1713, 1600	+38.6° (*c*=0.07, MeOH)
Pteroside A (**18h**)	116—118 (A)	$C_{21}H_{30}O_8$	M$^+$: *m/e* 410.198 (410.194)	216(4.37), 260(4.25), 305(3.46)	3320, 1678, 1603	−49.6° (*c*=0.34, MeOH)
Pteroside B (**1i**)	120—122 (M)	$C_{20}H_{28}O_7$	M$^+$: *m/e* 380.186 (380.184)	218(4.40), 260(4.04), 305(3.18)	3360, 1683, 1605	−48.8° (*c*=0.17, MeOH)
pteroside C (**13e**)	Amorphous	$C_{20}H_{28}O_8$	M$^+$: *m/e* 396.176 (396.178)	219(4.53), 260(4.16), 302(3.30)	3400, 1708, 1600	

a) Solvent of recrystallization: A=acetone; B=benzene; C=chloroform; H=*n*-hexane; M=methanol; T=carbon tetrachloride.

TABLE II. PMR Spectra of Pterosins and Pterosides[a)]



Compound (solvent)	C_2	C_3	C_4	C_5	C_6	C_7
Pterosin A (**18a**) (CD_3OD)	$-CH_3$ 1.27 (s) $-CH_2$ 3.49 (d, J=10) OH 3.75 (d, J=10) 2.38	$-H_2$ 2.65 (d, J=17) 3.09 (d, J=17)	-H 7.05 (s)	$-CH_3$ 2.46 (s)	$-CH_2-CH_2-OH$ 2.97 (t, J=8), 3.67 (t, J=8), 2.38	$-CH_3$ 2.62 (s)
Pterosin B (**1a**) ($CDCl_3$)	$-CH_3$ 1.25 (d, J=8) -H *b)*	-H 3.23 (dd, J=18, 9.5) -H *b)*	-H 6.99 (s)	$-CH_3$ 2.41 (s)	$-CH_2-CH_2-OH$ 2.99 (t, J=8), 3.72 (t, J=8), 1.30	$-CH_3$ 2.67 (s)
Pterosin C (**12a**) 2*S*, 3*S* (CD_3OD)	$-CH_3$ 1.26 (d, J=8) -H 2.3—2.8	-H 4.59 (d, J=3.7) -OH —	-H 7.24 (s)	$-CH_3$ 2.45 (s)	$-CH_2-CH_2-OH$ 2.94 (t, J=8), 3.57 (t, J=8)	$-CH_3$ 2.61 (s)
2*R*, 3*S*	$-CH_3$ 1.15 (d, J=8)	-H 5.09 (d, J=6.8)				
Pterosin D (**22**) (CD_3OD)	$-CH_3$ 1.03 (s) $-CH_3$ 1.17 (s)	-H 4.7 (overlapped to a signal of solvent).	-H 7.32 (s)	$-CH_3$ 2.46 (s)	$-CH_2-CH_2-OH$ 2.97 (t, J=8), 3.61 (t, J=8)	$-CH_3$ 2.62 (s)
Pterosin E (**1j**) ($CDCl_3$)	$-CH_3$ 1.27 (d, J=7) -H *b)*	-H 3.27 (dd, J=17, 9) -H *b)*	-H 7.02 (s)	$-CH_3$ 2.40 (s)	$-CH_2-COOH$ 3.74 (s)	$-CH_3$ 2.67 (s)
Pterosin F (**1c**) ($CDCl_3$)	$-CH_3$ 1.27 (d, J=7) -H *b)*	$-H_2$ *b)*	-H 6.98 (s)	$-CH_3$ 2.42 (s)	$-CH_2-CH_2-Cl$ 3.2 (m), 3.4 (m)	$-CH_3$ 2.66 (s)
Pterosin G (**9a**) (CD_3OD)	$-CH_2$ 3.77 (d, J=5.5) OH — -H 2.9—3.1	$-H_2$ 2.9—3.1	-H 7.05 (s)	$-CH_3$ 2.39 (s)	$-CH_2-CH_2-OH$ 2.90 (t, J=8), 3.53 (t, J=8)	$-CH_3$ 2.60 (s)
Pterosin J (**12c**) 2*S*, 3*S* ($CDCl_3$)	$-CH_3$ 1.34 (d, J=8) -H 2.3—2.8	-H 4.74 (d, J=4) -OH 2.05	-H 7.30 (s)	$-CH_3$ 2.47 (s)	$-CH_2-CH_2-Cl$ 3.15 (m), 3.55 (m)	$-CH_3$ 2.67 (s)
2*R*, 3*S*	$-CH_3$ 1.20 (d, J=8)	-H 5.15 (d, J=6.2)				
Pterosin K (**18e**) ($CDCl_3$)	$-CH_3$ 1.20 (s) $-CH_2$ 3.75 (d, J=10) OH 3.50 (d, J=10) 2.13 (s)	$-H_2$ 2.65 (d, J=17) 3.08 (d, J=17)	-H 7.01 (s)	$-CH_3$ 2.41 (s)	$-CH_2-CH_2-Cl$ 3.10 (m), 3.47 (m)	$-CH_3$ 2.54 (s)
Pterosin L (**16a**) (CD_3OD)	$-CH_3$ 1.13 (s) $-CH_2$ 3.67 (s) OH —	-H 4.75 (s) -OH —	-H 7.28 (s)	$-CH_3$ 2.45 (s)	$-CH_2-CH_2-OH$ 2.95 (t, J=8), 3.58 (t, J=8)	$-CH_3$ 2.64 (s)
Pterosin N (**15a**) (CD_3OD)	$-CH_3$ 1.33 (s) -OH —	$-H_2$ 3.04 (br. s)	-H 7.09 (s)	$-CH_3$ 2.44 (s)	$-CH_2-CH_2-OH$ 2.96 (t, J=7.5), 3.02 (t, J=7.5)	$-CH_3$ 2.64 (s)
Pterosin O (**1d**) ($CDCl_3$)	$-CH_3$ 1.27 (d, J=7.5) -H *b)*	$-H_2$ *b)*	-H 7.06 (s)	$-CH_3$ 2.43 (s)	$-CH_2-CH_2-O-CH_3$ 3.05 (m), 3.50 (m), 3.36 (s)	$-CH_3$ 2.68 (s)
Pterosin Z (**21a**) ($CDCl_3$)	$-(CH_3)_2$ 1.32 (s)	$-H_2$ 2.84 (s)	-H 7.01 (s)	$-CH_3$ 2.44 (s)	$-CH_2-CH_2-OH$ 2.99 (t, J=8), 3.75 (t, J=8), 1.59	$-CH_3$ 2.67 (s)

Compound (solvent)	C_2	C_3	C_4	C_5	C_6	C_7
Benzoylpterosin B (**1e**) ($CDCl_3$)	$-CH_3$ 1.28(d, J=8) -H *b)*	$-H_2$ *b)*	-H 7.04(s)	$-CH_3$ 2.48(s)	$-CH_2-CH_2-OCO-C_6H_5$ 3.17(t, J=8), 4.37(t, J=8), 7.88—8.05(2H), 7.32—7.50(3H)	$-CH_3$ 2.75(s)
Isocrotonylpterosin B (**1g**) ($CDCl_3$)	$-CH_3$ 1.26(d, J=8) -H *b)*	-H 3.22(dd, J=18, 9) -H *b)*	-H 7.02(s)	$-CH_3$ 2.43(s)	$-CH_2-CH_2-OCO-CH=CH-CH_3$ 3.03(t, J=8), 4.15(t, J=8), 5.72(dq, J=11, 1.5), 6.25(dq, J=11, 8), 2.12(dd, J=8, 1.5)	$-CH_3$ 2.69(s)
Palmitylpterosin B (**1f**) ($CDCl_3$)	$-CH_3$ 1.25(d, J=8) -H *b)*	-H 3.33(dd, J=18, 9) -H *b)*	-H 7.02(s)	$-CH_3$ 2.40(s)	$-CH_2-CH_2-OCO-CH_2-(CH_2)_{13}-CH_3$ 3.00(t, J=8), 4.09(t, J=8), 2.26 (t, J=6.8), 1.25(br. s), 0.85 (t, J=5)	$-CH_3$ 2.66(s)
Palmitylpterosin A (**18f**) ($CDCl_3$)	$-CH_3$ 1.23(d, J=7) $-CH_2$ 3.54(d, J=10) OH 3.80(d, J=10)	$-H_2$ 2.69(d, J=17) 3.10(d, J=17)	-H 7.08(s)	$-CH_3$ 2.45(s)	$-CH_2-CH_2-OCO-CH_2-(CH_2)_{13}-CH_3$ 3.04(t, J=8), 4.14(t, J=8), 2.31 (t, J=6.8), 1.27(br. s), 0.88 (t, J=5)	$-CH_3$ 2.59(s)
Palmitylpterosin C (**13d**) ($CDCl_3$)	$-CH_3$ 1.32(d, J=7) -H 2.6—2.9)	-H 4.73(d, J=3.8) -OH —	-H 7.29(s)	$-CH_3$ 2.45(s)	$-CH_2-CH_2-OCO-CH_2-(CH_2)_{13}-CH_3$ 3.04(t, J=8), 4.12(t, J=8), 2.31 (t, J=6.8), 1.25(br. s), 0.88 (t, J=5)	$-CH_3$ 2.67(s)
Acetylpterosin C (**12d**) ($CDCl_3$) 2*S*, 3*S*	$-CH_3$ 1.32(d, J=8) -H 2.3—2.8	-H 4.70(d, J=4) -OH —	-H 7.27(s)	$-CH_3$ 2.45(s)	$-CH_2-CH_2-OCO-CH_3$ 3.02(t, J=8), 4.10(t, J=8), 2.03 (s)	$-CH_3$ 2.66(s)
2*R*, 3*S*	$-CH_3$ 1.22(d, J=8)	-H 5.14(d, J=6.8)				
Phenylacetyl-pterosin C (**12e**) ($CDCl_3$) 2*S*, 3*S*	$-CH_3$ 1.32(d, J=8) -H 2.3—2.8	-H 4.70(d, J=4) -OH 2.16	-H 7.25(s)	$-CH_3$ 2.43(s)	$-CH_2-CH_2-OCO-CH_2-C_6H_5$ 3.01(t, J=7), 4.12(t, J=7), 3.57 (s), 7.25(br. s)	$-CH_3$ 2.63(s)
2*R*, 3*S*	$-CH_3$ 1.22(d, J=8)	-H 5.13(d, J=6.8)				
Pteroside A (**18h**) (CD_3OD)	$-CH_3$ 1.07(s) $-CH_2$ 3.60(d, J=11) OH 3.86(d, J=11)	$-H_2$ 2.65(d, J=17.5) 3.25(d, J=17.5)	-H 7.06(s)	$-CH_3$ 2.41(s)	$-CH_2-CH_2-O$-glucose 3.06(t, J=7.5), 3.68(t, J=7.5), 4.27(d, J=6.5) *c)*	$-CH_3$ 2.62(s)
Pteroside B (**1i**) (CD_3OD)	$-CH_3$ 1.19(d, J=7) -H *b)*	$-H_2$ *b)*	-H 7.05(s)	$-CH_3$ 2.41(s)	$-CH_2-CH_2-O$-glucose 3.05(t, J=7), 3.80(t, J=7), 4.28 (d, J=6.5) *c)*	$-CH_3$ 2.60(s)
Pteroside C (**13e**) (CD_3OD)	$-CH_3$ 1.20(d, J=7.5) -H 2.3—2.8	-H 5.07(d, J=6.7) -OH —	-H 7.28(s)	$-CH_3$ 2.49(s)	$-CH_2-CH_2-O$-glucose 3.10(t, J=7.5), 3.83(t, J=7.5), 4.24(d, J=6.5) *c)*	$-CH_3$ 2.65(s)

a) The PMR spectra are determined at 60 MHz in $CDCl_3$ or CD_3OD and expressed in δ value in ppm from the internal standard TMS. Coupling pattern and coupling constant (Hz) of signals are shown in parentheses.

b) Overlapping signals around δ 2.3—3.5.

c) Signal of the anomeric proton.

methyl, thirteen methylene, one methylene adjacent to an oxycarbonyl-carbon atom, two aromatic methyl, one methine proton at the range of δ 2.6 to 2.9 (1H, m), one ethylene of acyloxyethyl group, one carbinyl proton and one aromatic proton. The palmityl group on the PMR spectrum was consistent with observation of the $[M^+-C_{15}H_{31}CO_2H]$ fragment ion, $C_{14}H_{16}O_2$, at *m/e* 216 by the high resolution mass spectrum. The structure of **13d** was established as the palmitate of *trans*-pterosin C (**13b**) by the following reaction. Pterosin C (**12a**) was treated with palmityl chloride and pyridine to afford the chromatographically separable monopalmitates (**13c**) and (**13d**). In the PMR spectra, the former component (**13c**) showed the signal due to the carbinyl proton at δ 5.21 having a larger coupling constant, $J=$ 6.7 Hz, while the latter (**13d**) showed the signal at δ 4.73 having a smaller coupling constant,[21] $J=3.8$ Hz. Therefore the synthetic samples (**13c**) and (**13d**) were respectively identified as the *cis* and *trans* isomers and the sterochemistries were established as 2*R*, 3*S*- and 2*S*, 3*S*-configurations. The natural product was proved to be identical with the latter by the direct comparison with the synthetic sample by a mixed mp, by IR, UV and PMR spectra, and by the CD Cotton effect, $[\theta]_{326}$ +16782.

Pteroside C[5] (**13e**) and wallichoside (**12f**) were isolated as the glucosides of pterosin C from the methanol extracts of the fronds. The structure of pteroside C was established as the formula (**13e**) by the fact that the hydrolysis of **13e** with emulsin gave (2*R*, 3*S*)-pterosin C (**13a**) and D-glucose. Wallichoside (**12f**) was identified with the authentic sample[22] in all respects. (These will be discussed in detail in a forth-coming paper.[17])

Pterosin N (**15a**), mp 165—167°, $[\alpha]_D$ −18.8, $C_{14}H_{18}O_3$, was proved to be a hydroxyl derivative of pterosin B (**1a**) from the UV, IR and PMR spectra (Tables I and II), in which two singlet signals at δ 1.33 (3H) and 3.04 (2H) took the place of those of a doublet methyl and two splitted benzylic protons in **1a**. On acetylation with acetic anhydride and pyridine **15a** gave a monoacetate (**15b**), the IR spectrum of which still showed the absorption due to the hydroxyl group at 3450 cm^{-1}. The above evidences suggested the presence of a tertiary hydroxyl group at the 2 position on the framework of **1a**. The assumption was confirmed by the following derivation from **1a**. Pterosin B (**1a**) was converted to the C,O-diacetylpterosin B (**15c**) with acetic anhydride and *p*-toluenesulfonic acid. The Baeyer–Villiger reaction of **15c** gave the O,O-diacetate (**15d**), which was hydolysed to the compound (**15a**) and identified with the natural product, pterosin N, in all respects.

Pterosin L (**16a**), mp 139—141°, $[\alpha]_D$ +23.7°, $C_{15}H_{20}O_4$, was proved to belong to the same series from the UV, IR and PMR spectra as shown in Table I and II. It formed a triacetate (**16b**), indicating the presence of three hydroxyl groups in **16a**. Characteristic signals in the PMR spectrum of **16a** were four singlet signals due to a deshielded aromatic proton at δ 7.28, to a tertiary methyl group at δ 1.13, and three carbinyl protons at δ 3.67 (2H, s) and 4.75 (1H, s). The downfield shift of the aromatic proton signal was assignable to the presence of a hydroxyl group at the 3-position, when compared with the signal at δ 7.24 in pterosin C (**12a**) and that at δ 6.99 in pterosin B (**1a**). The three carbinyl protons were deshielded in the triacetate (**16b**); the two protons at δ 3.67 shifted to δ 4.14 (1H, d, $J=10.5$ Hz) and 4.39 (1H, d, $J=10.5$ Hz) as AB quartet signals[23] and the other proton at δ 4.75 to 6.05 (1H, s). These observations suggested that one of the three carbinyl protons was a methine proton at the 3 position and the other two protons were those of a methylene in a hydroxymethyl group on the carbon bearing a methyl group, *i.e.* at the 2 position. Moreover the hydroxyl group at the 3 position was supposed to be α-orientation from the fact that the CD curve of **16a** showed the same positive Cotton effect ($[\theta]_{330}$ +18291) as that of **12a** having the 3α-hydroxyl group. Thus pterosin L (**16a**) must be a compound in which a hydroxymethyl group is inserted to the framework of pterosin C (**12a**). The insertion of the hydroxymethyl group was carried out

22) P. Sengupta, M. Sen, S.K. Niyogi, S.C. Pakrashi, and E. Ali, *Phytochemistry*, **15**, 995 (1976).
23) N. Sugiyama, K. Yamada, and H. Aoyama, *J. Chem. Soc.* (*C*), **1971**, 830; I. Yosioka, S. Saijoh, and I. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), **20**, 564 (1972).

as follows: Treatment of **12a** with alkaline formaldehyde gave pterosin L (**16a**), $[\alpha]_D$ +23.2°, and its epimer (**17a**). $[\alpha]_D$ +77°, and the former was identified with the natural product in all respects. The epimer was also converted to the corresponding triacetate (**17b**). The stereochemistry of **16a** was established as bearing methyl group *cis* to the carbinyl proton at the 3 position, *i.e.* 2*R*,3*R*-configuration, and the epimer (**17a**) 2*S*,3*R*-configuration by the irradiation experiments on the both triacetates; the irradiation at the tertiary methyl group (δ 1.32) at the 2 position in **16b** exhibited the nuclear Overhauser effect (increase of the area of 15%) on the carbinyl proton (δ 6.05) at the 3 position, while that at the methyl group (δ 1.07) in **17b** did not show the effect on the proton (δ 6.18) (3.0%).

Pterosin A (**18a**), mp 125—127°, $[\alpha]_D$ −45.3°, $C_{15}H_{20}O_3$, showed the common UV and IR absorptions (as in Table I) to pterosins. The PMR spectrum as shown in Table II was similar to that of pterosin B (**1a**) except a tertiary methyl group (δ 1.27) instead of the secondary methyl group, with additional signals due to one methylene group (δ 3.49, 1H, d, J=10 Hz and 3.75, 1H, d, J=10 Hz). On acetylation with acetic anhydride in benzene or in pyridine, **18a** gave two monoacetates (**18b** and **18c**) and the diacetate (**18d**). In the monoacetate (**18c**) and diacetate (**18d**) the signals of the methylene group in **18a** shifted to the lower field at δ 4.1 as a singlet signal. The above evidences suggested an insertion of a hydroxymethyl group to the framework of pterosin B (**1a**) for the structure of pterosin A (**18a**). The structure was substantiated by hydroxymethylation at the 2 position of **1a** with formaldehyde in methanolic potassium hydroxide. The product was obtained as a racemic mixture and identified with the natural product by mixed mp, and the UV, IR and PMR spectra. The Clemmensen reduction[13] of pterosin L (**16a**) and its synthetic epimer (**17a**) gave the corresponding indan derivatives (**19**) ($[\alpha]_D$ −3.20°) and (**20**) ($[\alpha]_D$ +3.44°) respectively. Pterosin A (**18a**) was subjected to the same reduction and the product was identified by the mp, the IR, UV and PMR spectra, and the optical rotation ($[\alpha]_D$ −3.40°) with the indan (**19**) derived from **16a**. Therefore the the stereochemistry of pterosin A (**18a**) was established as 2*S*-configuration.

Pterosin A (**18a**) showed the CD Cotton effect, $[\theta]_{352}$ +116, $[\theta]_{343}$ −83 and $[\theta]_{328}$ −298 in methanol, and $[\theta]_{350}$ +1424 (inflection), $[\theta]_{332}$ +2267 and $[\theta]_{325}$ +2258 in chloroform, respectively.[16]

Pterosin K (**18e**), mp 85—87°, $[\alpha]_D$ −37.5° was isolated as a chlorine containing compound, $C_{15}H_{19}ClO_2$, and showed the similar UV and IR absorptions to those of pterosin A (**18a**) as shown in Table I. The PMR signals were superimposable with those of **18a** except those of the ethylene protons at δ 3.10 (2H, m) and 3.47 (2H, m), which suggested the presence of a chloroethyl group as in pterosin F (**1c**) and J (**12c**). Thus pterosin F (**1c**) was subjected to hydroxymethylation with alkaline formaldehyde to afford a racemic mixture, which was identified with the natural pterosin K (**18e**) by mixed mp, and the IR and PMR spectra. Therefore the structure of pterosin K was established as a formula (**18e**), in which the hydroxyl group of the hydroxyethyl group in pterosin A (**18a**) was substituted by a chlorine atom. The stereochemistry of **18e** was established as 2*S*-configuration by the similar CD Cotton effect ($[\theta]_{352}$ +143, $[\theta]_{344}$ −32, and $[\theta]_{329}$ −273 in methanol, and $[\theta]_{360}$ +1533, $[\theta]_{344}$ +2570, $[\theta]_{328}$ +2254 and $[\theta]_{317}$ +1443 in cyclohexane)[16] to that of pterosin A (**18a**).

Palmitylpterosin A (**18f**), mp 50—51°, $[\alpha]_D$ −37.8°, $C_{31}H_{50}O_4$, showed the similar UV and IR absorptions (Table I) to those of pterosin A (**18a**) except the absorption at 1743 cm^{-1} due to an ester function. The nature of the acyl group was assigned as the palmityl group by the following evidences. In the high resolution mass spectrum, **18f** showed the base peak at *m/e* 230 ($C_{15}H_{18}O_2$), corresponding to $[M^+-C_{15}H_{31}CO_2H]$. The PMR spectrum showed the additional signals due to palmityl group at δ 0.88 (3H, t, J=5 Hz), 1.27 (26H, br, s) and 2.31 (2H, t, J=6.8 Hz) other than those of pterosin A (**18a**), and the ethylene signal of the acyloxyethyl group appeared at δ 4.14 (2H, t, J=8 Hz) and 3.04 (2H, t, J=8 Hz). Therefore **18f** was assigned as the structure having the palmitoxyethyl group at the 6 position. The structure was established by the direct acylation of pterosin A (**18a**) with palmityl chloride in pyri-

dine to form the palmitate (**18f**) accompanied with a dipalmitate (**18g**). The stereochemistry of **18f** was established as 2*S*-configuration by the CD Cotton effect ($[\theta]_{357}$ +979, $[\theta]_{341}$ +1779, $[\theta]_{327}$ +1688 and $[\theta]_{313}$ +1067 in cyclohexane),[16] compared with that of the synthetic specimen (See Experimental).

Pteroside A (**18h**) was a glucoside isolated from the methanol extracts of the fronds and identified with the authentic specimen[5] by the specific optical rotation $[\alpha]_D$,and the IR and PMR spectra. The structure was established as the formula (**18h**) by the fact that the hydrolysis of **18h** with emulsion gave D-glucose and pterosin A (**18a**) (This will be discussed fully in a forth-comong paper[17]).

Pterosin Z (**21a**), mp 86—88°, $[\alpha]_D$ ±0°, $C_{15}H_{20}O_2$, was homologous to pterosin B (**1a**) in the UV and IR spectra as shown in Table I. The PMR spectrum (Table II) disclosed the presence of a *gem*-dimethyl group instead of the secondary methyl group. The structure (**21a**) was substantiated by methylation at the 2 position of **1a** with methyl iodide and sodium hydride in benzene. This reaction was accompanied by the methylation of the hydroxyethyl group at the 6 position to afford pterosin O (**1d**) (*loc. cit.*) and the C,O-dimethyl derivative (**21c**), which was later isolated as a natural product, named pterosin I, by Hayashi, *et al.*[7] from *Hypolepis punctata*.

Pterosin D (**22**), mp 189—190°, $[\alpha]_D$ +4.8°, $C_{15}H_{20}O_3$, showed the common UV and IR spectra (as in Table I) to pterosin B series. The PMR spectrum showed the presence of a *gem*-dimethyl group instead of the secondary methyl group, and the deshielded aromatic proton, when compared with that of pterosin B (**1a**) (Table II). Particularly the signal at δ 7.35 of the aromatic proton suggested the presence of a hydroxyl group at the 3 position as in pterosins C (**12a**) and L (**16a**). From the above evidences a formula (**22**) borne a methyl group at the 2 position on the framework of pterosin C (**12a**) was anticipated for the structure of pterosin D. The assumption was confirmed by the following reactions. Oxidation with chromic anhydride and pyridine of **22** gave a diketone (**23a**), in which the aromatic proton signal showed the lower field shift at δ 7.55. Thus the secondary hydroxyl group in **22** was

Table III

Substance	Plant or source	Reference
Pterosin A (**18a**)	*Dennstaedia scabra*	32
Pterosin B (**1a**)	*Histiopteris incisa*	25
	Pteris inaequalis var. *aequata*	26
	P. wallichiana	27
	Culture of gametophytes of *Pteridium aquilinum*	35
Pterosin C (**12a**)	*Pteris inaequalis* var. *aequata*	28
	P. kiuschiuensis	29
	Culture of gametophytes of *Pteridium aquilinum*	36
Pterosin D (**22**)	*Pteris wallichiana*	27
	Hypolepis punctata	30
Pterosin F (**1c**)	*Pteris fauriei*	31
Pterosin G (**9a**)	*Pteris kiuschiuensis*	29
Pterosin K (**18e**)	*Pteris wallichiana*	27
	Hypolepis punctata	30
	Dennstaedia scabra	32
Pterosin L (**16a**)	*Hypolepis punctata*[a]	30
Epipterosin L (**17a**)	*Hypolepis punctata*[a]	30
Pterosin N (**15a**)	*Pteris oshimensis*	33
	P. wallichiana	27
Pterosin O (**1d**)	*Pteris inaequalis* var. *aequata*	26
Pterosin Z (**21a**)	*Hypolepis punctata*	5
	Pteris wallichiana	27
	Onychium auratum	34
Acetylpterosin C (**12d**)	*Pteris inaequalis* var. *aequata*	28

a) Isolated as the glucoside.

proved to locate at the 3 position. Moreover, the diketone (**23a**) was subjected to acetylation to afford the corresponding acetate (**23b**) which was identified with the specimen obtained from acetylpterosin Z (**21b**) with chromic anhydride in acetic acid.

The stereochemistry of pterosin D (**22**) was established as 3*R*-configuration by the CD Cotton effect ($[\theta]_{324}$ +1064), in which a contribution of the hydroxyl group at the 3 position appears predominant as mentioned in the cases of pterosins C and L. However, the isolated pterosin D (**22**) was proved to show a low optical purity by comparing with its antipode of 3*S*-configuration ($[\alpha]_D$ −15.4°, $[\theta]_{330}$ −4094), obtained from pteroside D isolated from the rhizomes.[18]

Our preliminary examination by thin-layer chromatography of the extracts of 140 species of the Pteridophyta to learn the distribution of pterosins and the glycosides revealed the presence of pterosins or related compounds in 15 out of 18 species in the Pteridaceae.[24] After our preliminary communications[3a-e] the pterosins have been indeed isolated from other ferns of the family and identified with our compounds as shown in Table III.[25-36] Besides these compounds nearly twenty kinds of new members of the group have also been isolated and the group of compounds has grown up rapidly to the characteristic constituents of the family.

Following the synthesis of pterosin E[19] several members of the group such as pterosin B,[37,38] D,[39] F,[37] and Z[7,37] have also been synthesized and identified with the natural products.

As anticipated from the structure the pterosins belong to illudoid sesquiterpenes and are expected to be formed from a humulene-type precursor through the intermediate like (A) or (B). The incorporation of [2-^{14}C] mevalonate into the aglycone of pteroside B has been reported.[40]

The constituents of the rhizomes of the same plant and the examination by the CD curves of the conformation of the indanone nucleus will be reported in forth-coming papers.[17]

Experimental[41]

Pterosins and Pterosides——The isolation of pterosins and pterosides from the young fronds was reported in the preceding paper.[1] The phycical properties of the isolated pterosins and pterosides were cumulatively shown in Tables I and II.

24) Unpublished data of our laboratory.
25) J.W. Ronaldson, *Chem. and Ind.*, **1972**, 764.
26) A. Kobayashi, H. Egawa, J. Koshimizu, and T. Mitsui, *Agr. Biol. Chem.*, **39**, 1851 (1975).
27) T. Murakami, K. Aoyama, N. Tanaka, and C.-M. Chen, *Chem. Pharm. Bull.* (Tokyo), **24**, 173 (1976).
28) T. Murakami, N. Tanaka, T. Tezuka, and C.-M. Chen, *Chem. Pharm. Bull.* (Tokyo), **23**, 1634 (1975).
29) T. Murakami, T. Satake, and C.-M. Chen, *Chem. Pharm. Bull.* (Tokyo), **23**, 936 (1975).
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33) T. Murakami, N. Tanaka, K. Tanaka, and C.-M. Chen, *Chem. Pharm. Bull.* (Tokyo), **22**, 2758 (1974).
34) A. Banerji, Private Communication.
35) K. Nakanishi, Private Communication.
36) T.C. McMorris, Private Communication.
37) T.C. McMorris, M. Liu, and R.H. White, *Lloydia*, **40**, 221 (1977).
38) T.K. John, Thesis, Indian Institute of Science, Bangalore (1977).
39) Y. Hayashi, M. Nishizawa, and T. Sakan, *Chemistry Letters*, **1974**, 945.
40) H. Hikino, T. Miyase, and T. Takemoto, *Phytochemistry*, **15**, 121 (1976).

41) Melting points were measured in a Yanagimoto mp apparatus and are uncorrected. UV spectra were determined in ethanol solution and IR spectra in KBr discs unless otherwise specified. PMR spectra were measured in $CDCl_3$ or CD_3OD with Me_4Si as an internal standard and chemical shifts are given in δ value (ppm). Abbreviations are s=singlet, br. s=broad singlet, d=doublet, t=triplet, q=quartet, and m=multiplet. ORD and CD curves were measured on a JASCO ORD-UV 5 Optical Rotatory Dispersion with a CD attachment. Extracts were dried over Na_2SO_4. At each stage of the separation and purification, thin-layer chromatography (TLC) was adopted for monitorring the purity of the specimen. For thin-layer plates Kieselgel HF_{254} nach Stahl (Merck) was used. Optical rotations were determined with a JASCO DIP-180 automatic polarimeter. The mass spectra were determined on a JEOL 01SG-2 High Resolution Mass Spectrometer with direct inlet system.

Acetylation of Pterosins A (18a), B (1a), C (12a), G (9a), L (16a), N (15a), Z (21a) and Epipterosin L (17a)

i) With Ac_2O in Pyridine——Pterosin B Acetate (**1b**): Pterosin B (**Ia**, 530 mg) was treated with Ac_2O (250 mg) in pyridine (1 ml) at room temperature overnight to afford a corresponding acetate (**1b**), in a quantitative yield. mp 56—57° (from hexane), $[\alpha]_D$ −24.5° (c=0.12, MeOH). CD (cyclohexane): $[\theta]_{366}$ −911, $[\theta]_{349}$ −1418, $[\theta]_{334}$ −675, $[\theta]_{326}$ +473, $[\theta]_{315}$ +608; UV λ_{max} nm (log ε): 216 (4.54), 258 (4.15), 301 (3.38); IR ν_{max} cm^{-1}: 1742, 1697, 1602, 1230; PMR ($CDCl_3$): 1.26 (3H, d, J=7.5 Hz), 2.06 (3H, s), 2.3—3.5 (2H, m), 3.22 (1H, dd, J=9, 18 Hz), 2.43 (3H, s), 2.69 (3H, s), 3.01 (2H, t, J=7.5 Hz), 4.09 (2H, t, J=7.5 Hz), 6.99 (1H, s). MS m/e: 260.143 (M^+) (Calcd. for $C_{16}H_{20}O_3$, 260.141).

By the same procedure the acetylpterosins were obtained having the following physical properties.

Pterosin A Diacetate (**18d**): An oil (350 mg) from **18a** (300 mg), $[\alpha]_D$ = −19.2° (c=0.19, MeOH). CD (cyclohexane): $[\theta]_{363}$ −98, $[\theta]_{354}$ +456, $[\theta]_{345}$ −190, $[\theta]_{338}$ +532, $[\theta]_{330}$ −152, $[\theta]_{322}$ +342, $[\theta]_{309}$ +1012; UV λ_{max} nm (log ε): 218 (4.51), 260 (4.16), 296 (3.33), 306 (3.36); IR ν_{max} cm^{-1}: 1743, 1700, 1600, 1230; PMR ($CDCl_3$): 1.21 (3H, s), 1.95 (3H, s), 2.07 (3H, s), 2.46 (3H, s), 2.70 (3H, s), 2.74 (1H, d, J=17 Hz), 3.04 (2H, t, J=7.5 Hz), 3.17 (1H, d, J=17 Hz), 4.12 (2H, t, J=7.5 Hz), 4.16 (2H, s), 7.05 (1H, s). MS m/e: 332.161 (M^+) (Calcd. for $C_{19}H_{24}O_5$, 332.162).

Pterosin C Diacetate (**12b**): An oil (120 mg) from **12a** (106 mg), $[\alpha]_D$ −5.6° (c=0.2, MeOH). CD (cyclohexane): $[\theta]_{360}$ +5869, $[\theta]_{343}$ +12961, $[\theta]_{330}$ +14426, $[\theta]_{320}$ +11746; UV λ_{max} nm (log ε): 218.5 (4.157), 258 (4.15), 290 (3.24), 300 (3.25); IR ν_{max} cm^{-1}: 1740, 1713, 1603, 1230; PMR ($CDCl_3$): 1.13 (3/10H, d, J=7.5 Hz), 1.34 (27/10H, d, J=7.5 Hz), 2.05 (3H, s), 2.14 (3H, s), 2.4—2.8 (1H, m), 2.46 (3H, s), 2.69 (3H, s), 3.02 (2H, t, J=8 Hz), 4.09 (2H, t, J=8 Hz), 5.78 (9/10H, d, J=3 Hz), 6.14 (1/10H, d, J=6 Hz), 7.16 (1H, s). MS m/e: 318.144 (M^+) (Calcd. for $C_{18}H_{22}O_5$, 318.147).

Pterosin G Diacetate (**9b**): mp 74—75° (from hexane, 53.5 mg) from **9a** (68.6 mg). $[\alpha]_D$ −20.4° (c=0.3 MeOH). CD (MeOH): $[\theta]_{318}$ +667. UV λ_{max} nm (log ε): 216 (4.46), 258 (4.10), 295 (3.37), 302 (3.36); IR ν_{max} cm^{-1}: 1740, 1695, 1602, 1230; PMR ($CDCl_3$): 2.01 (3H, s), 2.08 (3H, s), 2.48 (3H, s), 2.71 (3H, s), 3.04 (2H, br. s), 3.05 (2H, t, J=7.5 Hz), 4.15 (2H, t, J=7.5 Hz), 4.35 (2H), 7.10 (1H, s). MS m/e: 318.147 (M^+) (Calcd. for $C_{18}H_{22}O_5$, 318.147).

Pterosin L Triacetate (**16b**): An oil (45 mg) from **16a** (38 mg), $[\alpha]_D$ +26.9° (c=0.31, MeOH), CD (cyclohexane): $[\theta]_{360}$ +5760, $[\theta]_{343}$ +10893, $[\theta]_{329}$ +10643, $[\theta]_{317}$ +7128: UV λ_{max} nm (log ε): 218 (4.44), 260 (4.06), 304 (3.20); IR ν_{max} cm^{-1}: 1743, 1712, 1604, 1233; PMR ($CDCl_3$): 1.32 (3H, s), 1.92 (3H, s), 2.07 (3H, s), 2.13 (3H, s), 2.50 (3H, s), 2.74 (3H, s), 3.10 (2H, t, J=7.5 Hz), 4.14 (1H, d, J=10.5 Hz), 4.18 (2H, t, J=7.5 Hz), 4.39 (1H, d, J=10.5 Hz), 6.05 (1H, s), 7.20 (1H, s). MS m/e: 390.160 (M^+) (Calcd. for $C_{21}H_{26}O_7$, 390.168).

Epipterosin L Triacetate (**17b**): mp 92—94° (from hexane, 25 mg) from **17a** (28 mg). $[\alpha]_D$ +30.6° (c=0.13, MeOH). CD (cyclohexane): $[\theta]_{360}$ +5850, $[\theta]_{343}$ +11895, $[\theta]_{328}$ +12090, $[\theta]_{317}$ +8385; UV λ_{max} nm (log ε): 218 (4.50), 260 (4.10), 303 (3.35); IR ν_{max} cm^{-1}: 1743, 1705, 1602, 1238; PMR ($CDCl_3$): 1.07 (3H, s), 1.90 (3H, s), 2.04 (3H, s), 2.19 (3H, s), 2.47 (3H, s), 2.68 (3H, s), 3.04 (2H, t, J=7.5 Hz), 4.12 (2H, t, J=7.5 Hz), 4.13 (1H, d, J=10.5 Hz), 4.32 (1H, d, J=10.5 Hz), 6.18 (1H, s), 7.27 (1H, s). MS m/e: 390.163 (M^+) (Calcd. for $C_{21}H_{26}O_7$, 390.168).

Pterosin N Acetate (**15b**): mp 96—97° (from hexane, 10 mg) from **15a** (14 mg). IR ν_{max} cm^{-1}: 3380, 1740, 1690, 1220; PMR ($CDCl_3$): 1.24 (1H, s), 1.38 (3H, s), 2.03 (3H, s), 2.41 (3H, s), 2.63 (3H, s), 2.98 (2H, t, J=8 Hz), 3.06 (2H, s), 4.09 (2H, t, J=8 Hz), 6.99 (1H, s). MS m/e: 276.132 (M^+) (Calcd. for $C_{16}H_{20}O_4$, 276.136).

Pterosin Z Acetate (**21b**): An oil (60 mg) from **21a** (100 mg). IR ν_{max} cm^{-1}: 1741, 1702, 1604, 1235; PMR ($CDCl_3$): 1.21 (6H, s), 2.04 (3H, s), 2.42 (3H, s), 2.68 (3H, s), 2.82 (2H, s), 3.00 (2H, t, J=7.5 Hz), 4.10 (2H, t, J=7.5 Hz), 7.01 (1H, s). MS m/e: 274.154 (M^+) (Calcd. for $C_{17}H_{22}O_3$, 274.157).

ii) With Ac_2O in Benzene——Pterosin A Acetates (**18b, 18c** and **18d**): To a solution of pterosin A (**18a**, 1.5 g) in dried benzene (12 ml) was added Ac_2O (0.8 g) and the mixture was refluxed for 30 min and allowed to stand at room temperature overnight. The starting material (380 mg) was recovered by filtration of the reaction mixture and the filtrate was separated into four fractions by preparative TLC using a mixture of $CHCl_3$ and MeOH (20: 1) as the developer. Fraction 1 (150 mg) was identified with the diacetate (**18d**) described in i). Fraction 2 (650 mg) was recrystallized from hexane–benzene to give the monoacetate (**18b**, 410 mg), mp 83—84°, $[\alpha]_D$ −44.6° (c=0.18, MeOH). IR ν_{max} cm^{-1}: 3520, 1725, 1700, 1600; PMR ($CDCl_3$): 1.20 (3H, s), 2.03 (3H, s), 2.20 (1H, s, OH), 2.43 (3H, s), 2.66 (3H, s), 2.68 (1H, d, J=16.5 Hz), 3.02 (2H, t, J=7.5 Hz), 3.12 (1H, d, J=16.5 Hz), 3.52 (1H, d, J=10.5 Hz), 3.77 (1H, d, J=10.5 Hz), 4.11 (2H, t, J=7.5 Hz), 7.05 (1H, s). MS m/e: 290.156 (M^+) (Calcd. for $C_{17}H_{22}O_4$, 290.152). Fraction 3 gave a pure oily monoacetate (**18c**, 170 mg), $[\alpha]_D$ −18.8 (c=0.13, MeOH). UV λ_{max} nm (log ε): 218 (4.34), 261.5 (4.18), 299 (3.38), 306 (3.40); IR (liquid film) ν_{max} cm^{-1}: 3420, 1742, 1698, 1604; PMR ($CDCl_3$): 1.18 (3H, s), 1.80 (1H, s, OH), 1.93 (3H, s), 2.68 (3H, s), 2.78 (1H, d, J=16.5 Hz), 3.01 (2H, t, J=7.5 Hz), 3.15 (1H, d, J=16.5 Hz), 3.75 (2H, t, J=7.5 Hz), 4.14 (2H, s), 7.05 (1H, s). MS m/e: 290.154 (M^+) (Calcd. for $C_{17}H_{22}O_4$, 290.152).

iii) With Ac_2O and TsOH in Benzene——C,O-Diacetyl Pterosin B (**15c**): To a solution of pterosin B (**1a**, 70 mg) in benzene (1 ml) were added Ac_2O (0.5 ml) and TsOH (100 mg), and the mixture was refluxed for 6 hr. The reaction mixture was diluted with H_2O and extracted with benzene. The benzene layer was washed with aq. $NaHCO_3$ and H_2O, dried and evaporated. The residue was purified by preparative TLC to give an oily compound (**15c**, 68 mg). UV λ_{max} nm (log ε): 219 (4.46), 263 (4.19), 300 (3.42), 307 (3.42);

PMR ($CDCl_3$): 1.51 (3H, s), 2.03 (3H, s), 2.18 (3H, s), 2.43 (3H, s), 2.64 (3H, s), 2.65 (1H, d, J=16.5 Hz), 3.02 (2H, t, J=7.5 Hz), 3.65 (1H, d, J=16.5 Hz), 4.11 (2H, t, J=7.5 Hz), 7.07 (1H, s). MS *m/e*: 302.151 (M^+) (Calcd. for $C_{18}H_{22}O_4$, 302.152).

iv) **With AcOH**——Pterosin C Monoacetate (**12d**): Pterosin C (**12a**, 50 mg) was refluxed for 2 hr in 90% AcOH (2 ml) and the solvent was removed *in vacuo*. After extracted with benzene, the benzene layer was washed with H_2O, dried, and evaporated. The residue was separated into three fractions. Fraction 1 (5.8 mg): Acetyldehydropterosin B (**2**, *vide infra*), being identified with the specimen obtained from pterosin B (**1a**). Fraction 2: Recrystallization from benzene–hexane gave a monoacetate (28.6 mg), mp 115—118°, $[\alpha]_D$+92° (c=1.006, $CHCl_3$), which was identified with the natural acetylpterosin C (**12d**) in all respects. Fraction 3 (13.1 mg): The starting material.

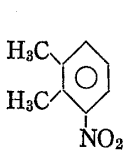
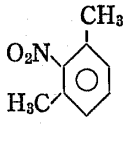
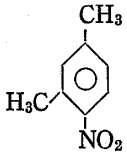
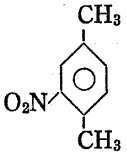
HNO_3 Oxidation of Pterosin B (1a)——A solution of pterosin B (**1a**, 382 mg) and HNO_3 (d, 1.38, 10 ml) was heated in a sealed tube for 20 hr. The reaction mixture was concentrated to 1/5 volumes and filtrated to afford a crystalline mass which, after methylation with CH_2N_2 in ether (20 ml), separated on preparative TLC into four fractions, *i.e.* a) a mixture of less polar products (28.6 mg), b) colourless compound (**6a**, 157.9 mg), c) yellowish compound (**6b**, 40.8 mg), and d) a mixture of overoxidized products (60.6 mg).

6a: an oil, IR ν_{max} cm^{-1}: 1740, 1601, 1437, 1250; PMR ($CDCl_3$): 2.25 (3H, s), 2.32 (3H, s), 3.84 (3H, s), 3.90 (6H, s), 7.60 (1H, s). MS *m/e*: 280.091 (M^+) (Calcd. for $C_{14}H_{16}O_6$, 280.095).

6b: mp 113° (from $CHCl_3$–MeOH), IR ν_{max} cm^{-1}: 1740, 1600, 1535, 1240—1210; PMR ($CDCl_3$): 2.28 (3H, s), 2.39 (3H, s), 3.85 (3H, s), 3.89 (3H, s), 3.96 (3H, s). MS *m/e*: 325.080 (M^+) (Calcd. for $C_{14}H_{15}NO_8$, 325.076).

Decarboxylation of the Nitro Derivative (6b)——The nitro compound (**6b**, 25 mg) was hydrolysed with 5% NaOH to give an acidic compound (19.1 mg). To a solution of an activated Cu powder[42] (8.63 mg) in fresh quinoline (1 ml) was added the compound and the mixture was heated for 3 hr at 185—195° and, after being diluted with H_2O, extracted with ether. The ethereal layer was washed with dil. HCl and H_2O, dried and evaporated. The residue was passed through silica-gel using hexane as the developer and the hexane eluate was applied for gas chromatography under the two conditions; Condition 1: Column: Carbowax 20 M (glass 1 m×3 mm), C.T. 200°, I.T. 210°, D.T. 215°, N_2 1.0 kg/cm², H_2 1.0 kg/cm², Air 1.0 kg/cm²; Condition 2: Column: Gorey Ucone 550 (glass 1 m×3 mm), C.T. 150°, I.T. 177°, D.T. 230°, N_2 1.8 kg/cm², H_2 1.0 kg/cm², Air 1.0 kg/cm².

Table IV. Retention Times[a] of Decarboxylation Product and Four Nitroxylenes

					Decarboxylation product of **6b** (intensity)
Condition 1	4.53	2.49	4.30	3.65	
	When mixed the above four nitroxylenes: 2.42, 3.67, 4.30				2.60(1) 3.69(1) 4.30(10)
Condition 2	3.10	1.95	2.50	2.75	
	When mixed the above four nitroxylenes: 1.95, 2.50, 2.62, 3.05				1.70(1) 2.50(10) 3.10(1)

a) Retention times were determined on a Hitachi Perkin-Elmer Gas Chromatograph F6-D.

As shown in Table IV the decarboxylation product was proved to be **8**.

Indene Derivative (4b) from Pterosin B (1a)——i) $NaBH_4$ Reduction of **1a**: To a solution of **1a** (380 mg) in MeOH (6 ml) was added $NaBH_4$ (250 mg) and the mixture was stirred for 1 hr at room temperature. The reaction mixture was concentrated to afford a crystalline product (380 mg) and the product was recrystallized from MeOH–H_2O to afford a mixture (320 mg, mp 126—129°) of **3a** and **3b** (3: 5); IR ν_{max} cm^{-1}: 3320, 1040; PMR ($CDCl_3$) : 1.08 (15/8H, d, J=7 Hz), 1.20 (9/8H, d, J=7 Hz), 1.67 (2H, s, OH), 2.35 (3H, s), 2.39 (3H, s), 2.94 (2H, t, J=7.5 Hz), 3.24 (2H, dd, J=8.5, 16.5 Hz), 3.71 (2H, t, J=7.5 Hz), 4.75 (5/8H, d, J=3 Hz), 4.93 (3/8H, d, J=5.2 Hz), 6.89 (1H, s); MS *m/e*: 220.146 (M^+) (Calcd. for $C_{14}H_{20}O_2$, 220.146).

ii) Dehydration of the Mixture of **3a** and **3b**: To a solution of the reduction products (600 mg of **3a** and **3b**) in dried benzene (50 ml) was added TsOH (200 mg) and the mixture was azeotropically refluxed for 1 hr. The reaction mixture was diluted with benzene, washed with aq. $NaHCO_3$ and H_2O, dried and eva-

42) R.Q. Brewster and T. Groening, "Organic Synthesis," Vol. 14, ed. W.W. Hartman, John Wiley and Sons, Inc., New York, 1940, p. 67.

porated. The residue was, after purification by preparative TLC using $CHCl_3$–acetone (3: 1) as the developer, recrystallized from hexane–benzene to afford indene derivative (**4a**, 248 mg), mp 114—115° (from hexane–benzene), UV λ_{max} nm (log ε): 220 (4.33), 226 (4.35), 265 (4.03); IR ν_{max} cm^{-1}: 3250, 3070; PMR ($CDCl_3$): 1.56 (1H, s, OH), 2.09 (3H, br. s), 2.33 (6H, s), 2.93 (2H, t, J=7.5 Hz), 3.19 (2H, br. s), 3.69 (2H, t, J=7.5 Hz), 6.44 (1H, br. s), 6.94 (1H, s); MS *m/e*: 202.131 (M^+) (Calcd. for $C_{14}H_{18}O$, 202.136).

iii) Acetylation of **4a**: The indene (**4a**, 300 mg) was treated with Ac_2O–pyridine. Recrystallization from MeOH–H_2O gave **4b** (248 mg), mp 66—67°, UV λ_{max} nm (log ε): 220 (4.33), 225 (4.35), 264 (4.01); IR ν_{max} cm^{-1}: 2960, 2900, 1735, 1245; PMR ($CDCl_3$): 2.03 (3H, s), 2.11 (3H, br. s), 2.35 (6H, s), 2.98 (2H, t, J= 7.5 Hz), 3.21 (2H, br. s), 4.11 (2H, t, J=7.5 Hz), 6.47 (1H, br. s), 6.97 (1H, s). MS *m/e*: 244.143 (M^+) (Calcd. for $C_{16}H_{20}O_2$, 244.146).

Acetyl-1,3-indandione (23b)——i) From Pterosin D (**22**): A solution of pterosin D (**22**, 10.0 mg) in pyridine (0.5 ml) was added into a CrO_3 (11.1 mg)–pyridine (0.2 ml) complex solution and the mixture was allowed to stand for 5 hr at room temperature. The reaction mixture was diluted with H_2O to extract with benzene and the benzene layer was washed with dil. HCl and H_2O, dried, and evaporated. The residue was purified by preparative TLC using benzene–AcOEt (6: 4) as the developer to afford 1,3-diketone (**23a**, 8 mg), mp 111° (from CCl_4–hexane), PMR ($CDCl_3$): 1.26 (6H, s), 1.78 (1H, s, OH), 2.53 (3H, s), 2.77 (3H, s), 3.10 (2H, t, J=7 Hz), 3.79 (2H, t, J=7 Hz), 7.55 (1H, s). MS *m/e*: 246.127 (M^+) (Calcd. for $C_{15}H_{18}O_3$, 246.126). The diketone (**23a**, 7.5 mg) was acetylated with Ac_2O (0.1 ml) in pyridine (0.1 ml) at room temperature overnight. The reaction mixture was diluted with H_2O to extract with benzene and the benzene layer was washed with dil. HCl and H_2O, dried, and evaporated. The residue was purified by preparative TLC using benzene–AcOEt (2: 1) as the developer to afford acetyl-1,3-indandione (**23b**, 7 mg), mp 73—75°, IR ν_{max} cm^{-1}: 1738, 1704, 1590, 1228, PMR ($CDCl_3$): 1.22 (6H, s), 2.02 (3H, s), 2.52 (3H, s), 2.76 (3H, s), 3.12 (2H, t, J=8 Hz), 4.18 (2H, t, J=8 Hz), 7.60 (1H, s). MS *m/e*: 288.137 (M^+) (Calcd. for $C_{17}H_{20}O_4$, 288.136). *Anal.* Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.88; H, 7.10.

ii) From Pterosin Z Acetate (**21b**): To a solution of **21b** (10 mg), Ac_2O (0.5 ml) and AcOH (0.1 ml) was added CrO_3 (10 mg) and the mixture was warmed on a water bath for 1 hr. The reaction mixture was poured into an ice-water and extracted with ether. The ethereal layer was separated into a product (5 mg) and the starting material (3 mg) by preparative TLC using the above solvents system. The product was identified with the above acetyl-1,3-indandione (**23b**) in all respects.

Acetyldehydropterosin B (2)——i) From Pterosin B Acetate (**1b**): To a solution of **1b** (25 mg) in 90% AcOH (2 ml) was added SeO_2 (35 mg) and the mixture was refluxed for 2 hr. After removal of AcOH, the residue was extracted with $CHCl_3$. The $CHCl_3$ layer was washed with aq. $NaHCO_3$ and H_2O, dried and evaporated to afford a yellowish residue. The yellowish mixture (30 mg) was separated into major and minor fractions by preparative TLC using benzene–AcOEt (9: 1) as the developer. The major fraction was recrystallized from hexane–benzene to afford a yellowish compound (**2**, 15 mg), mp 71—72°, UV λ_{max} nm (log ε): 244 (4.53), 250 (4.63), 335 (3.42); IR ν_{max} cm^{-1}: 1740, 1700, 1600; PMR ($CDCl_3$): 1.82 (3H, d, J=1.7 Hz), 2.04 (3H, s), 2.30 (3H, s), 2.52 (3H, s), 3.04 (2H, t, J=7.5 Hz), 4.12 (2H, t, J=7.5 Hz), 6.51 (1H, s), 6.86 (1H, q, J=1.7 Hz). MS *m/e*: 258.124 (M^+) (Calcd. for $C_{16}H_{18}O_3$, 258.126). From the minor fraction pterosin G diacetate (**9b**) was isolated and was inferred from the comparison of PMR spectra.

ii) From Pterosin C Diacetate (**12b**): A solution of **12b** (100 mg) in dried benzene (1 ml) was added to a solution of NaH (200 mg) in dried benzene (1 ml) and the mixture was refluxed for 5 hr. The reaction mixture was diluted with H_2O and extracted with benzene. The benzene layer was washed with H_2O, dried, and evaporated. The residue was separated into the starting material (50 mg) and a product (31 mg) by preparative TLC. The product was recrystallized from hexane–benzene to afford **2** (20 mg).

Methylation of Pterosin B (1a): Pterosin I (21c), Pterosin O (1d) and Pterosin Z (21a)——To a solution of NaH (200 mg) and CH_3I (20 ml) in anhydrous benzene (2 ml) was added the solution of pterosin B (**1a**, 390 mg) in anhydrous benzene (6 ml) for a period of 1 hr and the mixture was refluxed for 5 hr. The reaction mixture was diluted with H_2O and extracted with benzene. The benzene layer was washed with H_2O, dried, and evaporated. The residue was separated into four fractions by preparative TLC using benzene–AcOEt (2: 1) as the developer. Fraction 1 (65 mg) was recrystallized from hexane to afford **21c** (45 mg), mp 56—57.5°, identified with the natural pterosin I[7] in all respects. Fraction 2 (110 mg) was recrystallized from hexane to afford (**1d**, 67 mg), mp 41—43°, identified with the natural pterosin O. Fraction 3 (40 mg) was recrystallized from hexane to afford **21a** (29 mg), mp 85—87°, identified with the natural pterosin Z. Fraction 4 (30 mg) was identified with the starting material.

Hydroxymethylation of Pterosins B (1a), C (12a) and F (1c) to Pterosins A (18a), K (18e) and L (16a)——i) Pterosin A (**18a**) from Pterosin B (**1a**): To a solution of **1a** (11.7 mg) and 10% methanolic KOH (1 ml) was added formaldehyde (0.2 ml) and the mixture was refluxed for 1 hr. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried and evaporated. The product was separated by preparative TLC from the starting material. Recrystallization from benzene gave a racemic pterosin A (5 mg), mp 105°, identified with the natural pterosin A by the mixed mp diagram, corresponding to a eutectic, and the IR and PMR spectra.

By the same procedure pterosin K (**18e**) and L (**16a**), and epipterosin L (**17a**) were obtained and pterosin K (**18e**) and L (**16a**) were identified with the natural products.

ii) Pterosin K (**18e**): mp 66—67°, 10 mg from pterosin F (**1c**, 18 mg).

iii) Pterosin L (**16a**): mp 133—135°, 27 mg, and epipterosin L (**17a**): mp 86—89°, 55 mg, from pterosin C (**12a**, 200 mg). Epipterosin L (**17a**): mp 86—89° (from benzene), $[\alpha]_D$+77.0° (c=0.13, MeOH), CD (MeOH): $[\theta]_{330}$+18480; UV λ_{max} nm (log ε): 216 (4.54), 258 (4.18), 301 (3.31); IR ν_{max} cm^{-1}: 3440, 3260, 1697, 1597; PMR (CD_3OD): 0.94 (3H, s), 2.45 (3H, s), 2.64 (3H, s), 2.93 (2H, t, J=7.5 Hz), 3.49 (1H, d, J=10.5 Hz), 3.58 (2H, t, J=7.5 Hz), 3.76 (1H, d, J=10.5 Hz), 5.10 (1H, s), 7.27 (1H, s). MS m/e: 264.135 (M^+) (Calcd. for $C_{15}H_{20}O_4$, 264.136).

Ozonolysis of Pterosin B (1a)——A stream of 1—2% ozonized oxygen was passed into a solution of **1a** ($[\alpha]_D$−20.9°, 850 mg) in MeOH (50 ml) at −40° at the rate of 2.5 l per min for 10 hr. The resulting solution was concentrated *in vacuo*, and diluted with 98% formic acid (15 ml) and 30% H_2O_2 (15 ml), and then allowed to stand for 40 hr at room temperature. After warming at 60° untill foams disappeared and evaporation of the solvent, the residue (600 mg) was repeatedly separated by preparative TLC using diisopropyl ether–formic acid–H_2O (90: 7: 3) as the developer to afford a major fraction (150 mg) and the fraction was repeatedly recrystallized from benzene to afford methylsuccinic acid (15 mg), mp 109—110°, $[\alpha]_D$+3.7° (c=0.14, MeOH), ORD (MeOH): positive plain curve to 218 nm, IR ν_{max} cm^{-1}: 3000—2500, 1720—1690, 1420, 1280—1200, 930, identified with an authentic specimen.

Pterosin E (1j) from Pterosin B (1a)——To a solution of **1a** ($[\alpha]_D$−31.9°, 80 mg) in AcOH (1 ml) was added CrO_3 (40 mg) and the mixture was allowed to stand for 3 hr at room temperature. The reaction mixture was diluted with an ice-water and extracted with AcOEt. The AcOEt layer was shaken with 5% Na_2CO_3. The aqueous layer was, after neutralization, reextracted with AcOEt. After removing the solvent, the residue was purified by preparative TLC and recrystallized from CCl_4 to afford pterosin E (**1j**, 26 mg), mp 162—163°, $[\alpha]_D$−32.9° (c=0.20, MeOH), CD (MeOH): $[\theta]_{324}$+1648°, identified with the natural product by mixed mp, TLC, and the IR and PMR spectra.

Chlorination of Pterosin B (1a) to Pterosin F (1c)——A solution of **1a** (90 mg) in $SOCl_2$ (5 ml) was refluxed for 4 hr. The reaction mixture was diluted with an ice-water and extracted with ether. The ether layer was washed with H_2O, dried, and evaporated. The residue was purified by preparative TLC to afford a crystalline product (50 mg). Recrystallization from hexane gave a racemic compound (**1c**, 20 mg), mp 70—71°, identified with pterosin F by mixed mp, TLC, and the IR spectrum.

The Clemmensen Reduction of Pterosins A (18a), B (1a), C (12a), L (16a) and Epipterosin L (17a)——Zinc amalgam (obtained from 1 g of Zn and 0.1 g of $HgCl_2$) was added to a solution of conc. HCl (2.5 ml), H_2O (1 ml) and toluene (5 ml). Into the two phase solution was dissolved **1a** ($[\alpha]_D$−31.9°, 44 mg) and the mixture was refluxed for 20 hr. The reaction solution was extracted with ether and the ethereal layer was washed with H_2O, dried, and evaporated. The residue (38 mg) was recrystallized from hexane to afford a hydrocarbon (**5**, 13 mg), mp 67—68° (from hexane), $[\alpha]_D$−3.45° (c=0.28, MeOH), UV λ_{max} nm (log ε): 242 (2.77), 248 (2.48), 252.5 (2.67), 260 (2.78), 270 (2.98), 275 (2.92), 279.5 (3.02); IR ν_{max} cm^{-1}: 3220, 2900, 1458, 1035; PMR ($CDCl_3$): 1.25 (3H, d, J=6 Hz), 1.52 (1H, s, OH), 2.20 (3H, s), 2.30 (3H, s), 2.50 (4H, br. s), 2.90 (2H, t, J=7.5 Hz), 3.69 (2H, t, J=7.5 Hz), 6.78 (1H, s). MS m/e: 204.155 (M^+) (Calcd. for $C_{14}H_{20}O$, 204.151).

By the same procedure the hydrocarbons (**14**, **19** and **20**) were obtained having the following physical properties.

14: mp 67—68° (from hexane), 25 mg from **12a** ($[\alpha]_D$+93.1°, $[\theta]_{328}$+22135°, *cis*: *trans*=1: 2, 70 mg), $[\alpha]_D$+1.86° (c=0.28, MeOH), identified with the hydrocarbon (**5**) by mp, and the UV, IR and PMR spectra.

19: mp 88—89° (from benzene), 35 mg from **18a** (72 mg), $[\alpha]_D$−3.40° (c=0.65, MeOH), UV λ_{max} nm (log ε): 251 (2.27), 256 (2.49), 263 (2.74), 268 (2.84), 272 (2.98), 277 (2.93), 281.5 (3.03); IR ν_{max} cm^{-1}: 3300, 2910, 1035, and in $CHCl_3$: 3440, 2950, 1030; PMR ($CDCl_3$): 1.17 (3H, s), 1.78 (2H, s, OH), 2.20 (3H, s), 2.29 (3H, s), 2.53 (2H, br. s), 2.65 (2H, br. s), 2.90 (2H, t, J=7.5 Hz), 3.47 (2H, s), 3.69 (2H, t, J=7.5 Hz), 6.76 (1H, s). MS m/e: 234.158 (M^+) (Calcd. for $C_{15}H_{20}O_2$, 234.162). **19** (11 mg) obtained from **16a** (40 mg): $[\alpha]_D$−3.20° (c=0.49, MeOH). On the Clemmensen reduction of **18a** and **16a** a chlorinated hydrocarbons was isolated as a minor product suggested by showing signals at δ 1.25 (3H, s), 1.70 (1H, s, OH), 2.18 (3H, s), 2.28 (3H, s), 2.65 and 2.75 (4H, br.), 2.9—3.2 (2H, m), 3.35—3.8 (2H, m), 3.45 (2H, s), 6.75 (1H, s).

20: mp 117—119° (from benzene), 15 mg from **17a** (60 mg), $[\alpha]_D$+3.44° (c=0.49, MeOH), showed the same UV, IR, PMR and mass spectra with those of **19**.

Correlation of Pterosin B (1a) and Pterosin G (9a)——i) Indanols (**10a** and **10b**): To a solution of **1a** (100 mg) in pyridine (1 ml) was added *p*-toluenesulfonyl chloride (120 mg) and the mixture was allowed to stand at room temperature overnight. The reaction solution was diluted with an ice-water and extracted with ether. The ether layer was washed with dil. HCl, 5% $NaHCO_3$ and H_2O, dried and evaporated. The residual oil (150 mg) was proved to be a corresponding tosylate by the IR spectrum (ν_{max} cm^{-1}: 1700, 1600) and the PMR spectrum (δ $CDCl_3$): 1.27 (3H, d, J=7.5 Hz), 2.36 (3H, s), 2.44 (3H, s), 2.52 (3H, s), 3.08 (2H, t, J=7.5 Hz), 3.28 (1H, dd, J=9, 18 Hz), 3.83 (2H, t, J=7.5 Hz), 7.07 (1H, s), 7.29 (2H, d, J=8.5 Hz), 7.73 (2H, d, J=8.5 Hz).

To a solution of the tosylate (150 mg) in tetrahydrofuran (3 ml) was added $LiAlH_4$ (150 mg) and the mixture was stirred at room temperature for 20 hr. After decomposition of the excess of $LiAlH_4$ with AcOEt, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with

H_2O, dried, and evaporated. The residue was separated into two indanols (**10a** and **10b**) by preparative TLC using $CHCl_3$–MeOH (40: 1) as the developer.

10a: mp 129—132° (from hexane), 17 mg, UV λ_{max} nm (log ε): 242 (2.33), 247.5 (2.50), 253.5 (2.66), 259.5 (2.73), 270 (2.98), 275 (2.78), 279 (2.87); IR ν_{max} cm^{-1}: 3220, 2890, 1453, 1435; PMR ($CDCl_3$): 1.08 (3H, t, J=7.5 Hz), 1.19 (3H, d, J=6.5 Hz), 1.40 (1H, s, OH), 2.28 (3H, s), 2.36 (3H, s), 2.64 (2H, q, J=7.5 Hz), 2.3—3.5 (2H), 4.91 (1H, d, J=5.3 Hz), 6.81 (1H, s). MS *m/e*: 204.147 (M^+) (Calcd. for $C_{14}H_{20}O$, 204.151).

10b: mp 123—124° (from hexane), 40 mg, UV λ_{max} nm (log ε): 241.5 (2.51), 247.5 (2.78), 253 (2.92), 269.5 (2.76), 275 (2.77), 279 (2.78); IR ν_{max} cm^{-1}: 3200, 2890, 1445; PMR ($CDCl_3$): 1.07 (3H, d, J=7 Hz), 1.10 (3H, t, J=7.5 Hz), 1.40 (1H, s, OH), 2.29 (3H, s), 2.36 (3H, s), 2.64 (2H, q, J=7.5 Hz), 3.21 (1H, dd, J=8, 16.5 Hz), 2.3—3.5 (2H), 4.75 (1H, d, J=2.8 Hz), 6.80 (1H, s). MS *m/e*: 204.140 (M^+) (Calcd. for $C_{14}H_{20}O$, 204.151).

ii) Indanone (**11**): To a solution of **10a** (50 mg) in pyridine (1 ml) was added CrO_3 (80 mg) and the mixture was stirred at room temperature overnight. The reaction mixture was diluted with an ice-water and extracted with ether. The ethereal layer was washed with dil. HCl and H_2O, dried and evaporated. The residue was purified by preparative TLC to afford an indanone (**11**, 30 mg), $[\alpha]_D$+42.0° (c=0.16, MeOH), UV λ_{max} nm (log ε): 218 (4.48), 260 (4.25), 305 (3.47); IR ν_{max} cm^{-1}: 1704, 1604; PMR ($CDCl_3$): 1.08 (3H, t, J=7.5 Hz), 1.27 (3H, d, J=7.5 Hz), 2.20 (2H, q, J=7.5 Hz), 2.35 (3H, s), 2.64 (3H, s), 2.3—3.5 (2H), 3.25 (1H, dd, J=9.5, 18 Hz), 7.01 (1H, s). MS *m/e*: 202.133 (M^+) (Calcd. for $C_{14}H_{18}O$, 202.135).

iii) Indanone (**11**) from Pterosin G (**9a**): Pterosin G (**9a**, $[\alpha]_D$−4.6°, 110 mg) was treated with the above procedures to afford the indanone without separation of the indanols as intermediate.

Pterosin N (15a) from C,O-Diacetylpterosin B (15c)——i) Baeyer–Villiger Oxidation of **15c**: To a solution of **15c** (84 mg) in $CHCl_3$ (4 ml) was added *m*-chloroperbenzoic acid (60 mg) in $CHCl_3$ (1 ml) and the mixture was allowed to stand at room temperature for 2 days. The reaction mixture was separated by preparative TLC into the starting material (40 mg) and a racemic compound (**15d**, 20 mg), mp 129—131° (from hexane), UV λ_{max} nm (log ε): 216 (4.47), 258 (4.17), 301 (3.34); IR ν_{max} cm^{-1}: 1740, 1715, 1600, 1250; PMR ($CDCl_3$): 1.42 (3H, s), 2.03 (3H, s), 2.06 (3H, s), 2.42 (3H, s), 2.72 (3H, s), 2.97 (1H, d, J=16.5 Hz), 3.02 (2H, t, J=7.5 Hz), 3.44 (1H, d, J=16.5 Hz), 4.14 (2H, t, J=7.5 Hz), 7.02 (1H, s).

ii) Hydrolysis of **15d**: The oxidation product (**15d**, 20 mg) was dissolved in 1% methanolic KOH (2 ml) and the mixture was, after warming for a few minutes, allowed to stand at room temperature for 30 min. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried and evaporated. The residue was recrystallized from acetone to afford pterosin N (**15a**), mp 162—163°, identified with the natural product by mixed mp, TLC, and the IR spectrum.

Palmitylpterosins A (18f), B (1f) and C (13c and 13d)——A solution of pterosin B (**1a**) ($[\alpha]_D$ −28.0°, 30 mg) and palmityl chloride (50 mg) in pyridine (1 ml) was allowed to stand at room temperature overnight. The reaction mixture was diluted with an ice-water and extracted with ether. The ethereal layer was washed with dil. HCl, 5% $NaHCO_3$ and H_2O, dried, and evaporated. The residue was purified by preparative TLC and recrystallization from MeOH to afford a palmitate (**1f**, 25 mg), mp 51.5—53°, $[\alpha]_D$−16.5° (c=0.23, MeOH), $[\theta]_{325}$+1598°, identified with the natural product in all respects. By the same procedure the palmitylpterosins were obtained having the following physical properties.

Pterosin A Monopalmitate (**18f**): mp 55—55.5°, 40 mg, from **18a** (130 mg), $[\alpha]_D$−20.7° (c=0.13, MeOH), identified with the natural palmitylpterosin A in all respects.

Pterosin A Dipalmitate (**18g**): mp 53—54.5° (from MeOH), 50 mg, from **18a** (130 mg), $[\alpha]_D$−11.0° (c=0.19, MeOH), CD (cyclohexane): $[\theta]_{364}$−653, $[\theta]_{355}$+924, $[\theta]_{347}$−1470, $[\theta]_{340}$+572, $[\theta]_{331}$−1429, $[\theta]_{324}$+164, $[\theta]_{317}$−816. IR ν_{max} cm^{-1}: 2930, 1740, 1690, 1603, 1300—1200; PMR ($CDCl_3$): 0.90 (6H, t, J=7 Hz), 1.21 (3H, s), 1.24 (48H, s), 1.5 (4H, m), 2.29 (4H, t, J=7 Hz), 2.43 (3H, s), 2.68 (1H, d, J=17.5 Hz), 2.67 (3H, s), 3.01 (2H, t, J=7.5 Hz), 3.11 (1H, d, J=17.5 Hz), 4.14 (2H, t, J=7.5 Hz), 4.16 (2H, s), 7.05 (1H, s). *Anal.* Calcd. for $C_{47}H_{80}O_5$: C, 77.85; H, 11.12. Found: C, 77.79; H, 11.21.

Pterosin C Monopalmitate (**13c** and **13d**): From **12a** ($[\alpha]_D$+73.2°, *cis*: *trans*=5: 4, 40 mg), **13d** (15 mg), mp 98.5—99°, $[\alpha]_D$+48.7° (c=0.09, MeOH), identified with the natural palmitylpterosin C in all respects; **13c** (20 mg), mp 111—112° (from hexane), $[\alpha]_D$+15.8° (c=0.13, MeOH), CD (MeOH): $[\theta]_{330}$+19012. UV λ_{max} nm (log ε): 216 (4.51), 260 (4.16), 296 (3.33), 306 (3.36); IR ν_{max} cm^{-1}: 3260, 2920, 1743, 1706, 1608, 1260—1200; PMR ($CDCl_3$): 0.92 (3H, t, J=7 Hz), 1.24 (3H, d, J=7 Hz), 1.25 (24H, s), 1.68 (2H, m), 2.28 (2H, t, J=7 Hz), 2.47 (3H, s), 2.67 (3H, s), 3.03 (2H, t, J=7.5 Hz), 4.13 (2H, t, J=7.5 Hz), 5.21 (1H, d, J=6.7 Hz), 7.35 (1H, s). MS *m/e*: 454.348 (M^+-H_2O) (Calcd. for $C_{30}H_{48}O_4$–H_2O, 454.345).

Benzoylpterosin B (1e)——To a solution of **1a** (100 mg) in pyridine (1 ml) was added benzoyl chloride (150 mg) and the mixture was allowed to stand at room temperature for 1.5 hr. The reaction mixture was diluted with an ice-water and extracted with ether. The ethereal layer was washed with dil. HCl, 5% $NaHCO_3$ and H_2O, dried and evaporated. The residue was recrystallized from MeOH to afford a benzoate (**1e**, 50 mg), mp 72—73°, $[\alpha]_D$−25.6° (c=0.13, MeOH); CD (cyclohexane): $[\theta]_{315}$+988, $[\theta]_{325}$+737, $[\theta]_{334}$−510, $[\theta]_{349}$−1211, $[\theta]_{366}$−956, identified with the natural product in all respects.

Pterosin B Crotonate (1h)——To a solution of **1a** (40 mg) in pyridine (1 ml) was added crotonic anhydride (0.5 ml) and the mixture was allowed to stand at room temperature for 4 hr. The reacted mixture was diluted with H_2O and extracted with ether. The ethereal layer was washed with H_2O, dried, and evaporated.

The residue was separated by preparative TLC using benzene–AcOEt (19: 1) as the developer into the starting material (6 mg) and an oily compound (**1h**, 25 mg), $[\alpha]_D$ −7.5° (c=0.12, $CHCl_3$); UV λ_{max} nm (log ε): 217 (4.55), 260 (4.05), 304 (3.46); IR ν_{max} cm^{-1}: 2930, 1723, 1704, 1650, 1605, 1444, 1312, 1176; PMR ($CDCl_3$): 1.25 (3H, d, J=7.5 Hz), 2.34 (3H, dd, J=1.5, 8 Hz), 2.42 (3H, s), 2.68 (3H, s), 3.02 (2H, t, J=8 Hz), 3.23 (1H, dd, J=8.5, 17.5 Hz), 2.3—3.5 (1H), 4.13 (2H, t, J=8 Hz), 5.77 (1H, dq, J=15, 1.5 Hz), 6.33 (1H, dq, J=15, 8 Hz), 7.01 (1H, s).

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