old).[9] The serum LH concentrations were measured by radioimmunoassay according to Niswender, *et al.*[10]

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10) G.D. Niswender, A.R. Midgley, Jr., S.E. Monroe and E. Reichert, Jr., *Proc. Soc. Exptl. Biol. Med.*, **128**, 807 (1968).

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The Absolute Configurations of Pterosins, 1-Indanone Derivatives from Bracken, *Pteridium aquilinum* var. *latiusculum*[1]

In the previous communications[2–4] the isolation and the structural elucidations of seventeen pterosins, sesquiterpenoids having 1-indanone nucleus, from methanol extract of air-dried young leaves of bracken were reported. This communication concerns with the absolute configurations of these compounds.[1]

Pterosin B[2] (**1**) was proved to be identical with the aglycone of pteroside B[5] (**2**) and the absolute configuration at C-2 was proposed to be *R* on the basis of the circular dichroism (CD) curve by Hikino.[5] Since the direct application of the method to the indanone system is assumed to have some limitation,[6] the confirmation by an unequivocal method was carried out as follows.

The ozonolysis of pterosin B (**1**) afforded methylsuccinic acid (**3**), mp 109—111°, which showed $[\alpha]_D$ +7.8° (H_2O) and a positive Cotton effect (peak, 218 nm), indicating its *R*-configuration.[7] This result showed the *R*-configuration of the 2-position of pterosin B (**1**).

The *trans*-configuration of the methyl at C-2 and the hydroxyl at C-3 in pterosin C[3] (**4**) was shown in the previous communications.[3,4] The Clemmensen reduction of pterosin C (**4**) gave a product (**5**), mp 68°, $[\alpha]_D$ +3.0°, $[\alpha]_{350}$ +10.5° (MeOH), which was proved to be identical with the Clemmensen reduction product[2] (**6**) of pterosin B, mp 67—68°, $[\alpha]_D$ −2.0°,

1) A part of this work was presented at 16th Symposium on the Chemistry of Natural Products, Osaka, October 1972, Symposium Papers, p. 55.
2) K. Yoshihira, M. Fukuoka, M. Kuroyanagi, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **19**, 1491 (1971).
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5) H. Hikino, T. Takahashi, S. Arihara, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **18**, 1488 (1970).
6) G. Snatzke, *Tetrahedron*, **21**, 413, 421, 439 (1965); M.J. Luche, A. Marquet, and G. Snatzke, *Tetrahedron*, **28**, 1677 (1972) and the references cited therein.
7) A. Fredga, J.P. Jennings, W. Klyne, P.M. Scopes, B. Sjöberg, and S. Sjöberg, *J. Chem. Soc.*, **1965**, 3928.

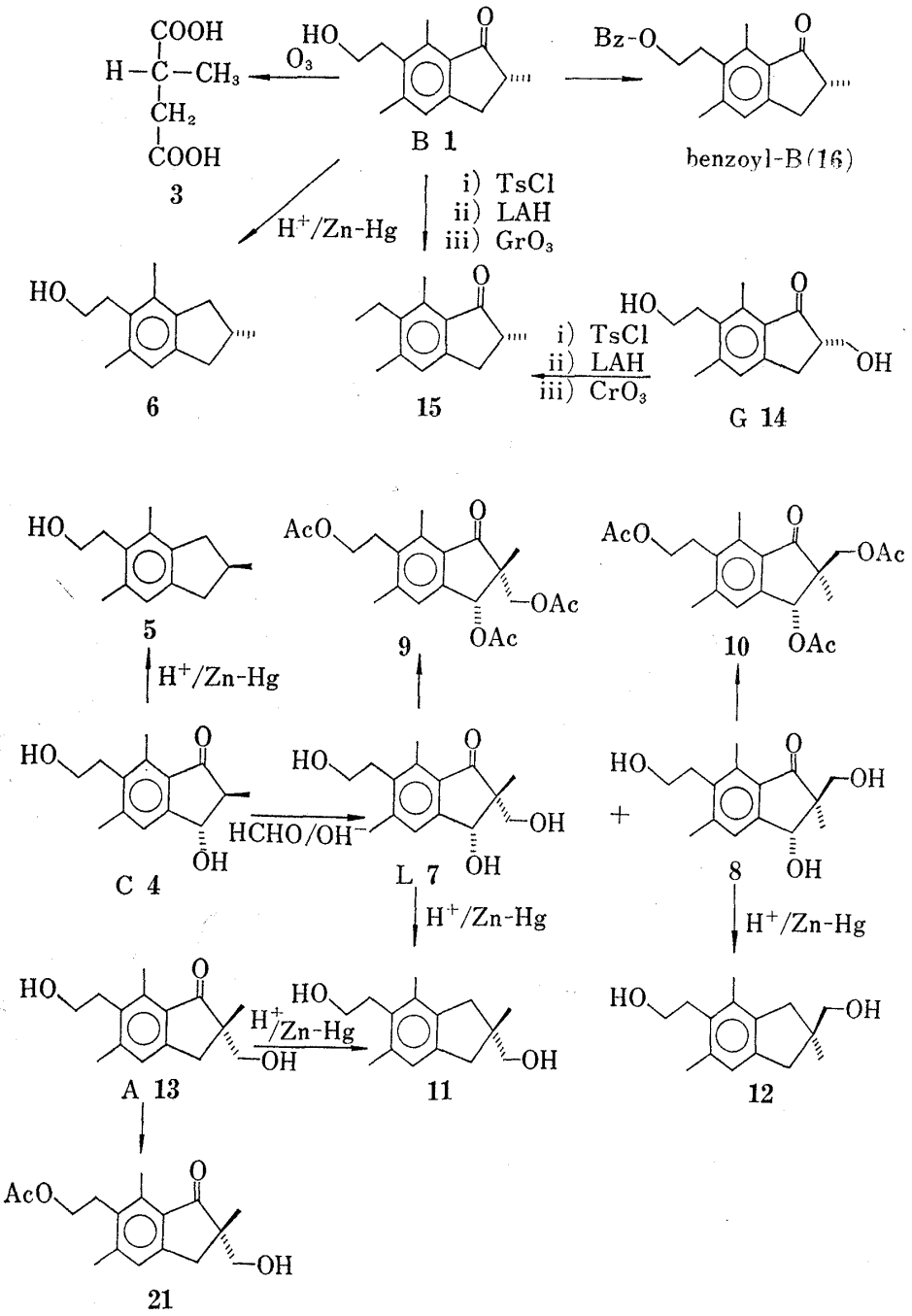
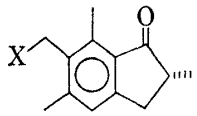


Chart 1

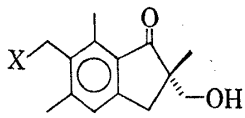
$[\alpha]_{350}$ −10.0° (MeOH), in every respects except the opposite sign of the optical rotatory dispersion (ORD) curve. Thus the stereochemistry of pterosin C (**4**) was established as 2*S*, 3*S*.[8]

As shown in the previous communication[4] the introduction of a hydroxymethyl group to pterosin C gave pterosin L[4] (**7**) and its epimer at the 2-position[4] (**8**). The both compounds were derived to the respective triacetates (**9** and **10**). When the tertiary methyl groups at the 2-position (1.32 ppm in **9** and 1.07 ppm in **10**) were irradiated, nuclear Oberhauser effects

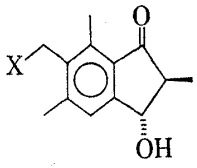
8) The conclusion is opposite (*i.e.* antipodal) to that proposed by Hikino, *et al.* from the CD.[9] This discrepancy will be solved in a forthcoming communication.[10]
9) H. Hikino, T. Takahashi, and T. Takemoto, *Chem. Pharm. Bull.* (Tokyo), **19**, 2424 (1971); *idem, ibid.*, **20**, 210 (1972).
10) in preparation.



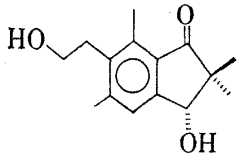
X=COOH E(17)
X=CH_2Cl F(18)
X=$CH_2OCOCH=CHCH_3$ isocrotonyl-B(19)
X=$CH_2OCOC_{15}H_{31}$ palmityl-B(20)
X=CH_2O-glucose pteroside B(2)



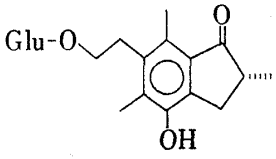
X=CH_2Cl K(22)
X=$CH_2OCOC_{15}H_{31}$ palmityl-A(23)
X=CH_2O-glucose pteroside A(28)



X=CH_2Cl J(24)
X=CH_2OAc acetyl-C(25)
X=$CH_2OCOC_{15}H_{31}$ palmityl-C(26)



D(27)



pteroside M(29)

Chart 2

TABLE I. $n\rightarrow\pi^*$ Cotton Effects of 1-Indanones

Compound	λ(nm)	[θ](20—25°)	Solvent
Pterosin B (**1**)	320	+2870	MeOH
Pteroside B (**2**)	322	+3700	MeOH
Pterosin G (**14**)	320	+1700	MeOH
15	322	+2990 (from **1**)	MeOH
	322	+1000 (from **14**)	MeOH
Pterosin E (**17**)	327	+ 310[a]	MeOH
Pterosin F (**18**)	319	+2804	MeOH
	364	− 238	cyclohexane
	346	− 420	
	332	− 252	
Isocrotonylpterosin B (**19**)	*ca.* 320	positive[a]	MeOH
Palmitylpterosin B (**20**)	320	+2130	MeOH
Pterosin A (**13**)	332	+7400	$CHCl_3$
Pterosin A (**13**) from pteroside A (**28**)	332	+6200	$CHCl_3$
21	357	+6080	cyclohexane
	341	+9570	
	327	+8810	
	314	+6380	
Pterosin K (**22**)	358	+3990	cyclohexane
	341	+6612	
	327	+5814	
	314	+4218	
Palmitylpterosin A (**23**)	357	+3230	cyclohexane
	341	+5870	
	327	+5570	
	313	+3520	
Pterosin C (**4**)	325	+70711	MeOH
Pterosin J (**24**)	325	+51106	MeOH
Acetylpterosin C (**25**)	325	+53684	MeOH
Palmitylpterosin C (**26**)	326	+55380	MeOH
Pterosin L (**7**)	327	+58490	MeOH
8	328	+60984	MeOH
Pterosin D (**27**)	324	+3510	MeOH
Pteroside M (**29**)	320	+2980	MeOH

a) Due to the scarcity of the sample, accurate measurement has not been carried out.

were observed on the signals of the benzylic protons at the 3-position (6.05 ppm in **9** and 6.18 ppm in **10**) (the increase of the areas, 15% in **9** and 3% in **10**), indicating the *cis* and the *trans* configuration respectively of the groups in **9** and **10**. Thus the absolute configuration of pterosin L (**7**) was established as 2*R*, 3*R*.

When pterosin L (**7**) and the epimer (**8**) were reduced by the Clemmensen method, a diol (**11**), mp 117—119°, $[\alpha]_D$ −3.2°, $[\alpha]_{350}$ −10.5° (MeOH), and the enantiomer (**12**), $[\alpha]_D$ +2.8°, $[\alpha]_{350}$ +9.4° (MeOH), were obtained respectively. In the same way pterosin A[2] (**13**) was reduced to a diol, which was proved to be identical with diol (**11**) in every respects including the optical rotation, and the configuration of pterosin A (**13**) was shown to be 2*S*.

The tosylation, reduction with lithium aluminum hydride, and oxidation with chromium trioxide of pterosin B[2] (**1**) and pterosin G[3,11] (**14**) afforded a same 1-indanone derivative (**15**), oil, $C_{14}H_{18}O$, and the products obtained from the both starting materials showed a same positive Cotton effect (Table I), proving the 2*S*-configuration in pterosin G (**14**).

The synthetic sample of benzoylpterosin B (**16**) showed the same optical rotation with the natural product.[4]

The CD curves of indanone system are influenced by the conformations of the five-membered ring depending on the temperature and the solvents[6] (*e.g.* **18** in Table I). Thus the application of the method was carried out using the compounds of the established stereochemistry as the reference compounds and employing the same solvents. As shown in Table I the n→π^* Cotton effects of pterosin E (**17**), F (**18**), the B esters (**19** and **20**) are nearly superimposable with those of pterosin B (**1**), G (**14**), and the compound (**15**), suggesting the 2*R*-configurations. Those of pterosin K (**22**) and the A ester (**23**) are the same as that of pterosin A monoacetate (**21**), mp 83—84°, indicating the same 2*S*-configuration. In the same way pterosin J (**24**) and the C esters (**25** and **26**) were compared with pterosin C (**4**) and proved to be 2*S*, 3*S*. Pterosin C (**4**), L (**7**), and the epimer (**8**) showed nearly the same Cotton effects. The fact indicates that the contribution of the substituents at the 3-position is greater than that at the 2-position and the same positive Cotton effect of pterosin D (**27**) suggests the 3*R*-configuration.[8]

The corresponding glucosides, pteroside A[9] (**28**) and B[5] (**2**) obtained from the young leaves,[3] were also proved to have the same configuration as pterosin A (**13**) and B (**1**) respectively. By these observations the stereochemistry of all known pterosin derivatives has been clarified.

Recently a phenolic compound named pteroside M (**29**) was isolated from *Onychium japonicum* Kunze and the structure was proved to correspond to 4-hydroxypteroside B.[12] The positive CD of the compound indicated its 2*R*-configuration.[13]

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11) In the previous communication[3] the optical activity of the compound was reported to be ±0° due to its weak rotation.
12) M. Hasegawa, Y. Akabori, and S. Akabori, *Phytochemistry*, in the press.
13) The sample was kindly provided by Professor M. Hasegawa.