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

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

In the previous communications²⁻⁴⁾ 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 B²⁾ (**1**) was proved to be identical with the aglycone of pteroside B⁵⁾ (**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 $[\alpha]_D +7.8^\circ$ (H₂O) 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 C³⁾ (**4**) was shown in the previous communications.^{3,4)} The Clemmensen reduction of pterosin C (**4**) gave a product (**5**), mp 68°, $[\alpha]_D +3.0^\circ$, $[\alpha]_{350} +10.5^\circ$ (MeOH), which was proved to be identical with the Clemmensen reduction product²⁾ (**6**) of pterosin B, mp 67–68°, $[\alpha]_D -2.0^\circ$,

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Chart 1

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

As shown in the previous communication⁴⁾ the introduction of a hydroxymethyl group to pterisin C gave pterisin L⁴⁾ (7) and its epimer at the 2-position⁴⁾ (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=CH₂Cl F (18)X=CH₂OCOCH=CHCH₃ isocrotonyl-B (19)X=CH₂OCOC₁₅H₃₁ palmityl-B (20)X=CH₂O-glucose pteroside B (2)X=CH₂Cl K (22)X=CH₂OCOC₁₅H₃₁ palmityl-A (23)X=CH₂O-glucose pteroside A (28) X=CH₂Cl J (24)X=CH₂OAc acetyl-C (25)X=CH₂OCOC₁₅H₃₁ palmityl-C (26)

D (27)

pteroside M (29)

Chart 2

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

Compound	λ (nm)	$[\theta]$ (20—25°)	Solvent
Pterodin B (1)	320	+2870	MeOH
Pteroside B (2)	322	+3700	MeOH
Pterodin G (14)	320	+1700	MeOH
15	322	+2990	MeOH
		(from 1)	
	322	+1000	MeOH
		(from 14)	
Pterodin E (17)	327	+310 ^{a)}	MeOH
Pterodin F (18)	319	+2804	MeOH
	364	— 238	cyclohexane
	346	— 420	
	332	— 252	
Isocrotonylpterodin B (19)	ca. 320	positive ^{a)}	MeOH
Palmitylpterodin B (20)	320	+2130	MeOH
Pterodin A (13)	332	+7400	CHCl ₃
Pterodin A (13) from pteroside A (28)	332	+6200	CHCl ₃
21	357	+6080	cyclohexane
	341	+9570	
	327	+8810	
	314	+6380	
Pterodin K (22)	358	+3990	cyclohexane
	341	+6612	
	327	+5814	
	314	+4218	
Palmitylpterodin A (23)	357	+3230	cyclohexane
	341	+5870	
	327	+5570	
	313	+3520	
Pterodin C (4)	325	+70711	MeOH
Pterodin J (24)	325	+51106	MeOH
Acetylpterodin C (25)	325	+53684	MeOH
Palmitylpterodin C (26)	326	+55380	MeOH
Pterodin L (7)	327	+58490	MeOH
8	328	+60984	MeOH
Pterodin 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 pterisin L (**7**) was established as 2*R*, 3*R*.

When pterisin L (**7**) and the epimer (**8**) were reduced by the Clemmensen method, a diol (**11**), mp 117–119°, $[\alpha]_D -3.2^\circ$, $[\alpha]_{350} -10.5^\circ$ (MeOH), and the enantiomer (**12**), $[\alpha]_D +2.8^\circ$, $[\alpha]_{350} +9.4^\circ$ (MeOH), were obtained respectively. In the same way pterisin A²⁾ (**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 pterisin A (**13**) was shown to be 2*S*.

The tosylation, reduction with lithium aluminum hydride, and oxidation with chromium trioxide of pterisin B³⁾ (**1**) and pterisin G^{3,11)} (**14**) afforded a same 1-indanone derivative (**15**), oil, C₁₄H₁₈O, and the products obtained from the both starting materials showed a same positive Cotton effect (Table I), proving the 2*S*-configuration in pterisin G (**14**).

The synthetic sample of benzoylpterisin 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 solvents⁶⁾ (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 $n \rightarrow \pi^*$ Cotton effects of pterisin E (**17**), F (**18**), the B esters (**19** and **20**) are nearly superimposable with those of pterisin B (**1**), G (**14**), and the compound (**15**), suggesting the 2*R*-configurations. Those of pterisin K (**22**) and the A ester (**23**) are the same as that of pterisin A monoacetate (**21**), mp 83–84°, indicating the same 2*S*-configuration. In the same way pterisin J (**24**) and the C esters (**25** and **26**) were compared with pterisin C (**4**) and proved to be 2*S*, 3*S*. Pterisin 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 pterisin D (**27**) suggests the 3*R*-configuration.⁸⁾

The corresponding glucosides, pteroside A⁹⁾ (**28**) and B⁵⁾ (**2**) obtained from the young leaves,³⁾ were also proved to have the same configuration as pterisin A (**13**) and B (**1**) respectively. By these observations the stereochemistry of all known pterisin 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-hydroxypteriside B.¹²⁾ The positive CD of the compound indicated its 2*R*-configuration.¹³⁾

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11) In the previous communication³⁾ the optical activity of the compound was reported to be $\pm 0^\circ$ due to its weak rotation.

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13) The sample was kindly provided by Professor M. Hasegawa.