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Circular Dichroism and Conformations of Pterosins, 1-Indanone Derivatives from Bracken[1)]

Masanori Kuroyanagi,[2a)] Masamichi Fukuoka, Kunitoshi Yoshihira, and Shinsaku Natori[2)]

National Institute of Hygienic Sciences[2)]

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Pterosins and pterosides, 1-indanone derivatives isolated from bracken (*Pteridium aquilinum* var. *latiusculum*), and the derivatives exhibit CD Cotton effects associated with n→π^* transition of conjugated ketones in the range of 310—370 nm.

Snatzke's rule was applied to the compounds and the conformations of the indanones were discussed from the observations by the CD.

The conformation of pterosin A type compounds having a hydroxymethyl group at the 2-position is affected by the intramolecular hydrogen bonding. In pterosin C and L type compounds bearing a hydroxyl group at the 3-position, the hydroxyl group exists in pseudoaxial conformation irrespective of the configuration at the 2-position. The results obtained by the compounds of the established stereochemistry by chemical methods were applied for the determination of the absolute configurations of pterosin D type compounds.

Keywords——*Pteridium aquilinum* var. *latiusculum*; pterosins; pterosides; 1-indanone derivatives; illudoid sesquiterpenes; CD; conformation of 1-indanones

In the previous papers[3,4)] the structures of more than twenty kinds of sesquiterpenes, named pterosins, and the glucosides, named pterosides, from bracken fern, *Pteridium aquilinum* var. *latiusculum*, were reported. All these compounds have 1-indanone nucleus and most of them bear chiral centers at the 2- and 3-positions and exhibit the circular dichroism (CD) Cotton effects in the range of 310—370 nm associated with n→π^* transition of the conjugated ketones.

As an extension of CD and optical rotatory dispersion (ORD) studies of chiral conjugated ketones, CD of α,β-unsaturated ketones[5)] and aryl ketones[6)] were extensively studied and the empirical rule for the relationship between the helicity of the carbonyl group to the double bond and the sign of CD associated with n→π^* transition of conjugated ketones was introduced by Snatzke.[7)] According to the rule originally proposed for cyclopentenones, the relationship between the helicity and the sign of CD is inverse to those in cyclohexenones and cyclopentenones; *i.e.* transoid ketones in five-membered ring exhibit positive Cotton effect in the case of right-handed helicity, while negative in the case of left-handed helicity. On the contrary cisoid ketones exhibit negative Cotton effect in the case of right-handed

1) This paper constitutes Part V of "Chemical and Toxicological Studies on Bracken Fern, *Pteridium aquilinum* var. *latiusculum*." Part IV: M. Fukuoka, M. Kuroyanagi, K. Yoshihira, S. Natori, M. Nagao, Y. Takahashi, and T. Sugimura, *J. Pharm. Dyn.*, **1**, 324 (1978).

2) Location: *Kamiyoga-1-chome, Setagaya-ku, Tokyo*; *a*) Present address: *Shizuoka College of Pharmacy, Oshika, Shizuoka.*

3) M. Fukuoka, M. Kuroyanagi, K. Yoshihira, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **26**, 2365 (1978).

4) M. Kuroyanagi, M. Fukuoka, K. Yoshihira, and S. Natori, *Chem. Pharm. Bull.* (Tokyo), **27**, 592 (1979).

5) W.B. Whally, *Chem. and Ind.* (London), **1962**, 1024; K. Kuriyama, E. Kondo, and K. Tori, *Tetrahedron Lett.*, **1963**, 1485; J.R. Hanson, T.D. Organ, G.A. Sim, and D.N.J. White, *J. Chem. Soc.* (*C*), **1970**, 2111; K. Tori, Y. Terui, M. Moriyama, and K. Kuriyama, *Tetrahedron Lett.*, **1969**, 1657; K. Kuriyama, M. Moriyama, T. Iwata, and K. Tori, *ibid.*, **1968**, 1661.

6) R.C. Cambie, L.N. Mender, A.K. Bose, and M.S. Manhas, *Tetrahedron*, **20**, 409 (1964).

7) G. Snatzke, *Tetrahedron*, **21**, 413, 421, 439 (1965).

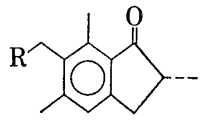
helicity, while positive in the case of lefthanded helicity. Formally 1-indanone derivatives have cisoid and transoid double bond to the carbonyl at the same time and the opposite helicity due to the cisoid and transoid relationships give the same contribution for the CD-sign. Octant type projections of 1-indanone are shown in Fig. 1. Although the exceptions to the rule for cyclopentenones have since been reported,[8] one related series of compounds, such as our pterosins and pterosides, should indicate the same relationship between the helicity and the sign of CD. Some informations on the CD or ORD of 1-indanone derivatives are found in literatures,[9] but the conformation of the five-membered ring has not much been discussed.

(+) (−)

Fig. 1. Octant Type Projection of 1-Indanone Derivatives

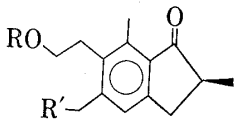
As reported in the previous papers[3,4] the absolute configurations of pterosins and pterosides were unequivocally established by degradation and correlation reactions. In this paper the conformation of the five-membered ring in forty kinds of 1-indanone derivatives listed in Chart 1 will be discussed by the observations from their CD Cotton effects. In some

pterosin B type



(2*R*)

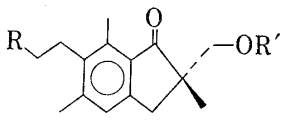
pterosin B	R=CH_2OH (**1**)
	R=CH_2OAc (**2**)
pterosin F	R=CH_2Cl (**3**)
benzoylpterosin B	R=CH_2O–COC_6H_5 (**4**)
palmitylpterosin B	R=CH_2O–palm. (**5**)
pteroside B	R=CH_2O–glu. (**6**)
	R=CH_2O–glu.–Ac_4 (**7**)
pterosin E	R=COOH (**8**)



(2*S*)

	R=R′=H (**1′**)
pteroside B	R=glu., R′=H (**6′**)
pteroside P	R=glu., R′=OH (**9**)
pterosin P	R=H, R′=OH (**10**)

pterosin A type

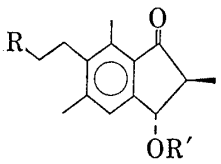


(2*S*)

pterosin A	R=OH, R′=H (**11**)
pteroside A	R=O–glu., R′=H (**12**)
	R=OAc, R′=H (**13**)
palmitylpterosin A	R=O–palm., R′=H (**14**)
pterosin K	R=Cl, R′=H (**15**)
	R=OAc, R′=Ac (**16**)
	R=O–palm., R′=palm. (**17**)
pteroside K	R=Cl, R′=glu. (**18**)
	R=Cl, R′=glu.–Ac_4 (**19**)

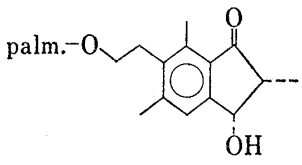
8) G. Snatzke, L. Hruban, F. Snatzke, R. Schmidt, and E. Hecker, *Israel J. Chem.*, **15**, 46 (1976/77).
9) M.J. Brienne, G. Ouannes, and J. Jaques, *Bull. Soc. Chim. France*, **1967**, 613; J. Almy and D.J. Cram, *J. Am. Chem. Soc.*, **91**, 4459 (1969); E. Dornhege and G. Snatzke, *Tetrahedron*, **26**, 3059 (1970); M.J. Luche, A. Marquet, and G. Snatzke, *Tetrahedron*, **28**, 1677 (1972); J.H. Brewster and R.T. Prudence, *J. Am. Chem. Soc.*, **95**, 1217, 1229 (1963).

pterosin C type



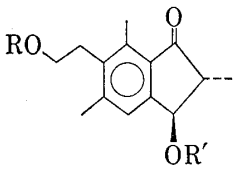
(2*S*,3*S*)

pterosin C R=OH, R′=H (**20**)
R=O-Ac, R′=Ac (**21**)
acetylpterosin C R=O-Ac, R′=H (**22**)
palmitylpterosin C R=O-palm., R′=H (**23**)
phenylacetylpterosin C R=O-Ph-Ac, R′=H (**24**)
pterosin J R=Cl, R′=H (**25**)



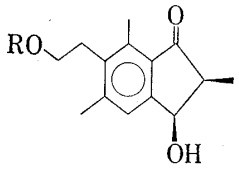
(2*R*,3*S*)

cis-palmitylpterosin C (**26**)



(2*R*,3*R*)

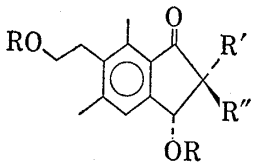
pterosin C R=R′H (**20′**)
pteroside C R=glu., R′=H (**27**)
R=glu.-Ac_4, R′=Ac (**30**)



(2*S*,3*R*)

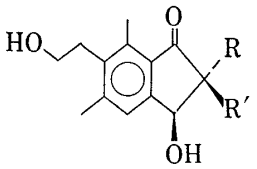
cis-pterosin C R=H (**28**)
cis-pteroside C R=glu. (**29**)

pterosin L type



(2*R*,3*R*) or (2*S*,3*R*)

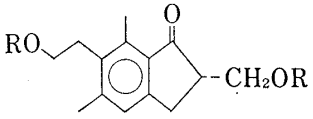
pterosin L R=H, R′=CH_2OH, R″=CH_3 (**31**)
R=H, R′=CH_3, R″=CH_2OH (**32**)
R=Ac, R′=CH_2OAc, R″=CH_3 (**33**)
R=Ac, R′=CH_3, R″=CH_2OAc (**34**)



(2*S*,3*S*) or (2*R*,3*S*)

R=CH_3, R′=CH_2OH (**31′**)
R=CH_2OH, R′=CH_3 (**32′**)

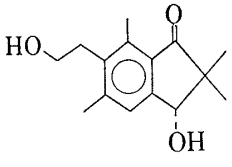
pterosin G type



(2*S*)

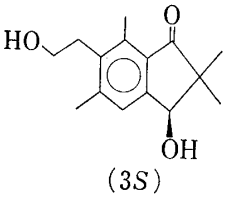
pterosin G R=H (**35**)
R=Ac (**36**)

pterosin D type



(3*R*)

pterosin D (**37**)



(3*S*)

pterosin D (**37′**)

Chart 1

cases ^{1}H-nuclear magnetic resonance (PMR) and infrared (IR) spectral observations will complimentarily be discussed.

Pterosins and pterosides were classified into six types according to the substituents at the 2- and 3-positions in the five membered ring of 1-indanone skeleton as shown in Chart 1; *i.e.* 1) Pterosin B type, 2) Pterosin A type, 3) Pterosin C type, 4) Pterosin L type, 5) Pterosin G type, and 6) Pterosin D type, and the discussion will be made following this order.

Pterosin B Type

The compounds of this type (**1**—**10**, **1′**, **6′**) bear only one chiral center at C-2 where a methyl group is substituted. Except (2*S*)-pteroside P(**9**), (2*S*)-pterosin P(**10**), (2*S*)-pterosin B(**1′**), and pteroside B(**6′**), all the compounds have (2*R*)-configuration.[3,4] Pterosin B(**1**), pterosin B acetate (**2**), pterosin F(**3**), benzoylpterosin B(**4**), palmitylpterosin B(**5**), pteroside B(**6**), the peracetate (**7**), and pterosin E(**8**), having (2*R*)-configuration, exhibited the positive Cotton effects associated with n→π^* transition in methanol in the vicinity of 320 nm (Fig. 2a) and bisignated CD-curves in chloroform (Fig. 2b). However in a nonpolar solvent such as cyclohexane, these compounds exhibited the CD bands both of negative and positive signs in the range of 310—360 nm as shown Fig. 2c. These observations indicated that the Cotton effects are affected by the solvent polarity.[10]

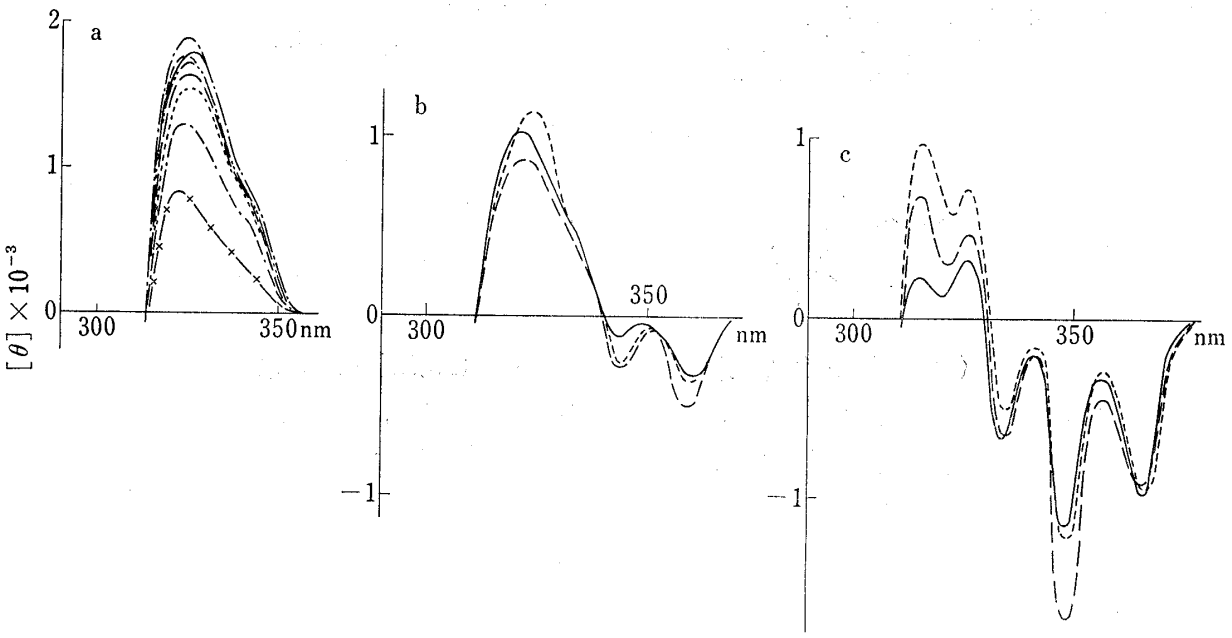


Fig. 2

a: 1 (————), 2 (·····), 3 (—×—×—), 4 (—··—··—), 5 (————), 6 (·—·—·—·), 7 (—·—·—), 8 (– – – – –) in MeOH.
b: 1 (————), 2 (– – – – –), 4 (————) in $CHCl_3$.
c: 1 (————), 2 (– – – – –), 4 (————) in cyclohexane.

Compounds having (2*S*)-configuration (**9**, **10**, **1′**, **6′**) exhibited the negative effects, opposite to (2*R*)-compounds, around 320 nm in methanol.

The PMR spectral data is informative to the conformation of the five-membered ring.[11] In pterosin B type compounds the proton in the methylene group at the 3-position trans to the methyl group at the 2-position exhibited the PMR signal at δ 3.23 (dd, J=9.5, 18 Hz) in $CDCl_3$. The coupling constant, 18 Hz, was attributed to the geminal coupling and

10) H. Falk, W. Fröstl, H. Hofer, and K. Schlögl, *Monatsh. Chem.*, **105**, 598 (1974).
11) G. Agahigian, H. Plant, and G.D. Vickes, *Anal. Chem.*, **39**, 1583 (1967); J.B. Lambert and F.R. Koeng, *Org. Mag. Resonance*, **3**, 389 (1971); E. Lustig and E.P. Ragelis, *J. Org. Chem.*, **32**, 1398 (1967).

another one, 9.5 Hz, to the vicinal coupling.[3] The Karplus equation[12] was applied to the latter value, 9.5 Hz, to conclude that the dihedral angle or the puckering angle is about 25°. This observation along with the results obtained by X-ray analysis for spiro-bisindan-1, 1′-dione[13] clearly indicated that the cyclopentenone ring is not coplanar and the angle of twist is appreciable.

Thus the original inverse rule[7] has been proved to be valid to the compounds of pterosin series and the pterosin B type compounds were shown to exist in an equilibrium of two conformers (Fig. 3), in which the conformer bearing a pseudoequatorial methyl group exists predominantly in methanol and the other with a pseudoaxial methyl in cyclohexane.

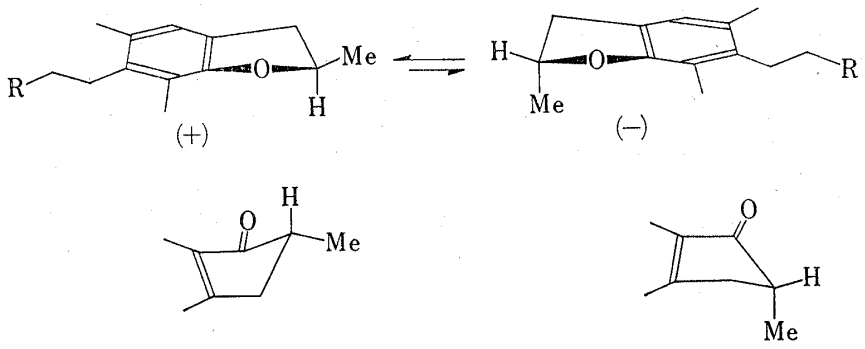


Fig. 3. Octant Type Projection of Pterosin B Type Compounds

Pterosin A Type

The compounds of this type (**11—19**) have only one chiral center at the 2-position, where a hydroxymethyl and a methyl group are geminally substituted. The all compounds have (2*S*)-configuration.[3,4]

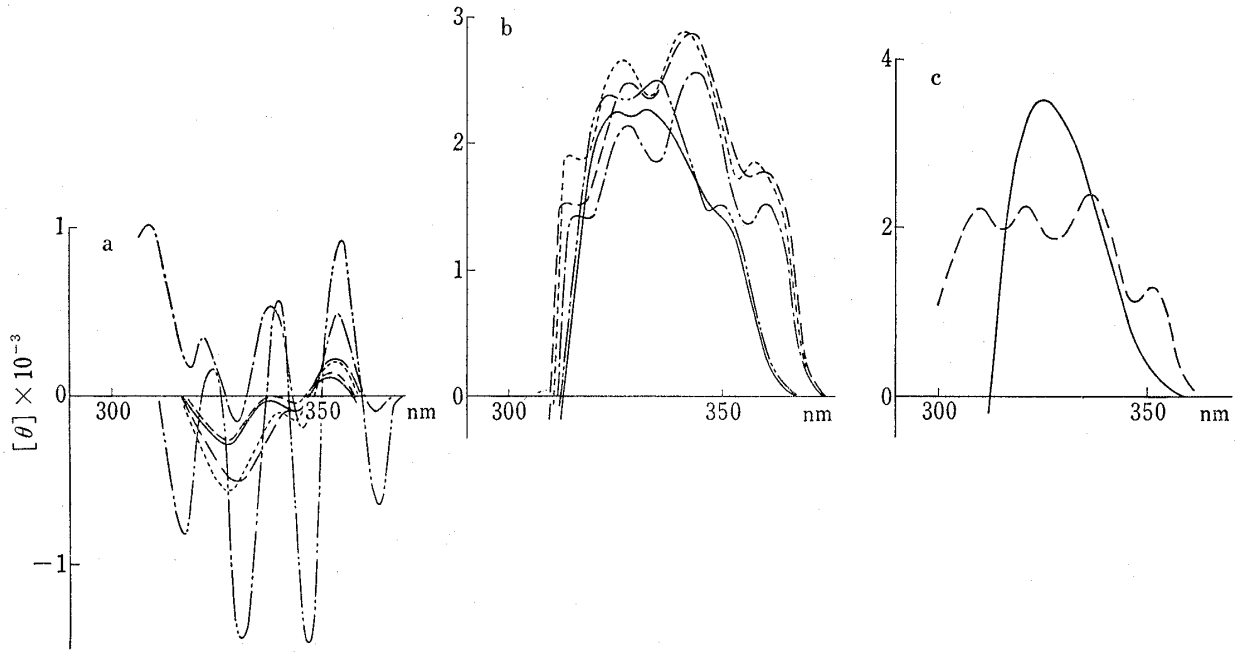


Fig. 4

a: **11** (————), **12** (– – – – –), **13** (·····), **15** (– – – – – –), in MeOH and **16** (·—·—·—·), **17** (—··—··—) in cyclohexane.
b: **11** (————), **13** (—··—··—), in $CHCl_3$ and **13** (·····), **14** (– – – – –), **15** (·—·—·—·), in cyclohexane.
c: **18** (————) in MeOH and **19** (– – – – –) in cyclohexane.

12) R.J. Abraham and K.A. McLanchlan, *Mol. Phys.*, **5**, 513 (1962); R.J. Abraham and J.S.E. Holker, *J. Chem. Soc.*, **1963**, 806; K. Kuriyama, E. Komoda, and K. Tori, *Tetrahedron Lett.*, **1963**, 1485.
13) K.B. Peterson and J. Danielsen, *Acta Crystl*, **30B**, 338 (1974).

In MeOH pterosin A(**11**), pteroside A(**12**), pterosin A monoacetate (**13**), palmitylpterosin A(**14**), and pterosin K(**15**) exhibited the weak bisignated CD-curves associated with n→π^* transition in the range of 310—360 nm. However these compounds having free hydroxymethyl group at C-2 exhibited the strong positive Cotton effects in aprotic solvents, such as chloroform and cyclohexane (Fig. 4b). On the contrary pterosin A diacetate (**16**) and pterosin A dipalmitate (**17**) having no free hydroxymethyl group at the 2-position exhibited the similar bisignated CD-curves in cyclohexane (Fig. 4a) to those of the free hydroxymethyl compounds in methanol. Such bisignated CD-curves may be due to the conformational equilibrium shown in Fig. 5. The observation indicated that the hydroxymethyl group at the 2-position formed an intramolecular hydrogen bond to the carbonyl group at the 1-position in aprotic solvents. The formation of the intramolecular hydrogen bond in **13** was confirmed by the IR absorption, ν_{OH} 3500 cm^{-1}, in dilution method (0.005 mol/l in CCl_4).[14] An examination by a Dreiding model suggested that the hydroxymethyl group must adopt pseudoequatorial conformation to form the intramolecular hydrogen bond.

When the (2*S*)-pterosin A type compounds, showing strong positive CD-curves in cyclohexane or chloroform, were projected according to the empirical rule, the conformations of these compounds were shown in Fig. 5, where the hydrogen-bonded hydroxymethyl group existed as pseudoequatorial.

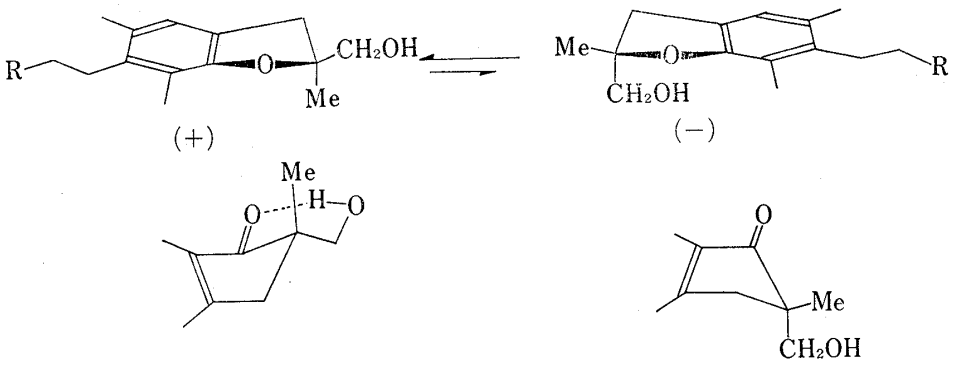


Fig. 5. Octant Type Projection of Pterosin A Type Compounds

(2*S*)-Pteroside K (**18**), having β-D-glucopyranosyloxymethyl group and methyl group at the 2-position, and its peracetate (**19**) exhibited strong positive CD-curves associated with n→π^* transition both in methanol and cyclohexane (Fig. 4c). The positive CD-curves will be explained by a pseudo-equatorial conformation due to bulkiness and high chirality of the glucopyranosyloxymethyl group.

Pterosin C Type

The compounds of this type (**20**—**30**) have two chiral centers at the 2- and 3-positions where a methyl group and a hydroxyl group are substituted respectively. Of these compounds pterosin C (**20**), acetylpterosin C (**22**), palmitylpterosin C (**23**), phenylacetylpterosin C (**24**), and pterosin J (**25**) isolated from the fronds have (2*S*, 3*S*)-configurations[3] and some of them contain small amounts of the epimer at the 2-position, (2*R*, 3*S*)-compounds.[3,4] The CD-spectra of these compounds and the derivative, pterosin C diacetate (**21**), exhibited the strong positive Cotton effects near 325 nm either in methanol or cyclohexane solution (Fig. 6a). (2*S*, 3*S*)-Palmitylpterosin C (**23**) and its epimer at the 2-position, (2*R*, 3*S*)-palmitylpterosin C (**26**), exhibited the same strong positive CD-curves of nearly same amplitudes, though that of the former is slightly larger than that of the latter (Fig. 6b). However the epimers at the 3-position (2*S*, 3*R*)-pterosin C (**28**) and (2*R*, 3*R*)-pterosin C (**20′**), containing small amounts

14) Chemical Society of Japan (ed.), "Jikkenkagaku Koza," Supplement Vol. 5, Maruzen, Tokyo, 1965, p. 345; K. Huitric, *J. Am. Chem. Soc.*, **78**, 1149 (1956).

of the epimers at the 2-position, exhibited the same strong negative CD-curves (Fig. 6c). Namely the sign of the CD-curves of this type of compounds was decided by the configuration at the 3-position regardless of the configuration at C-2 and the solvent.

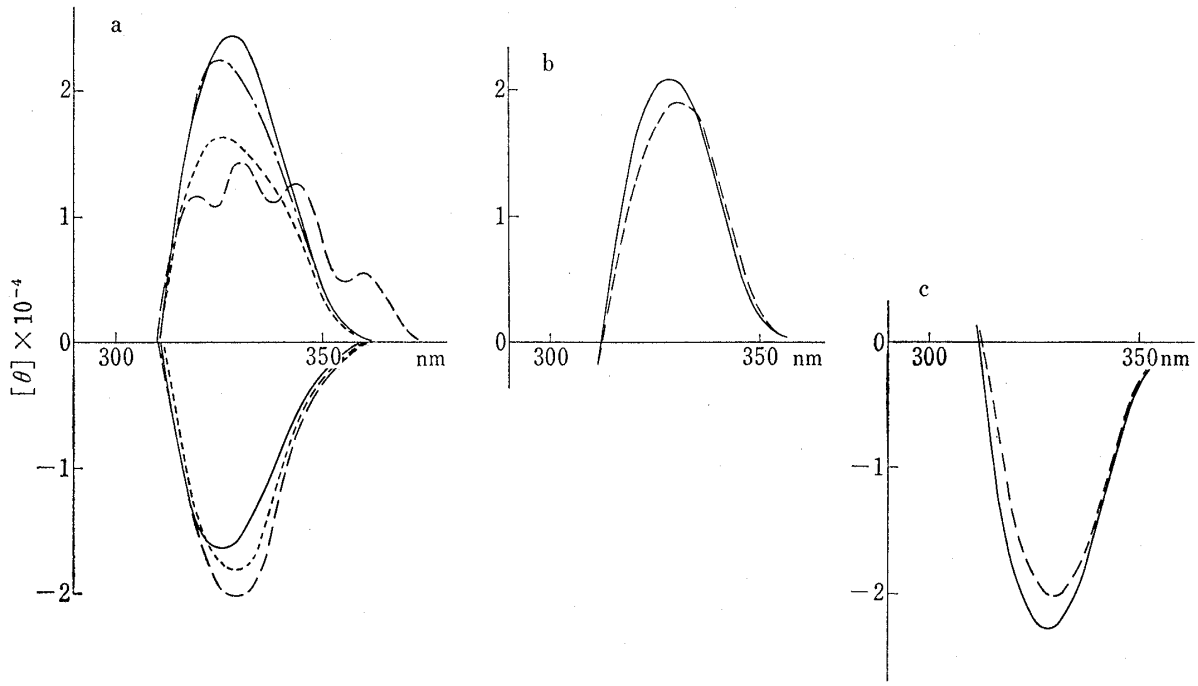


Fig. 6

a: 20 (————), 24 (·—·—·—·), 25 (– – – – –) in MeOH, 21 (– – – – –) in cyclohexane.
27 (————), 28 (– – – – –), 29 (– – – – –) in MeOH.
b: 23 (————), 26 (– – – – –) in MeOH.
c: 20′(————), 28 (– – – – –) in MeOH.

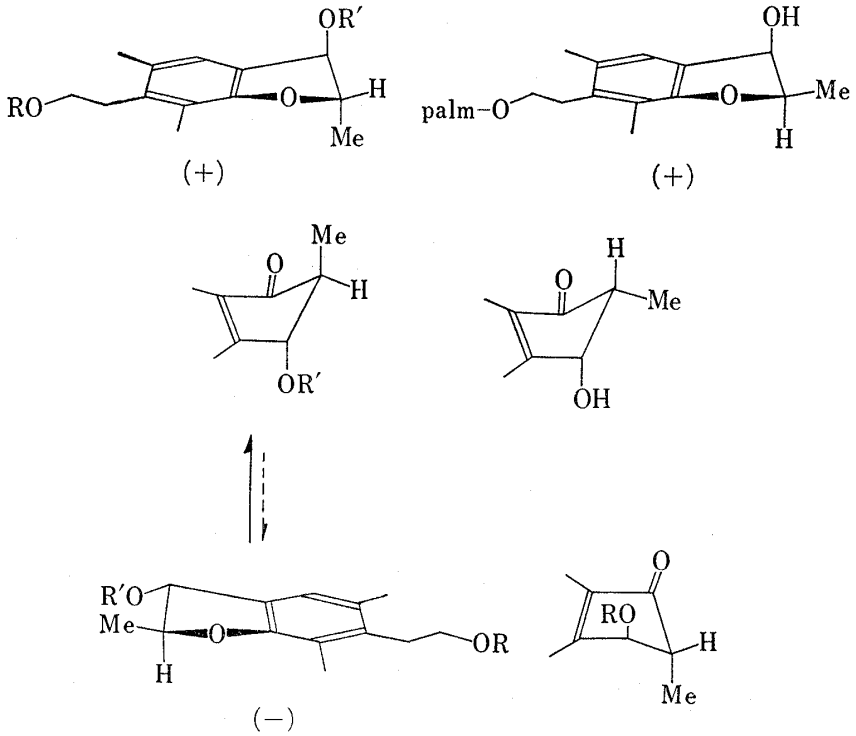


Fig. 7. Octant Type Projection of Pterosin C Type Compounds

The positive CD-curves of (2*S*, 3*S*)- or (2*R*, 3*S*)-pterosin C derivatives indicate that the hydroxyl or the acetoxyl group at C-3 exists in pseudo-axial conformation irrespective of the configuration at C-2 (Fig. 7).

In the PMR spectra of pterosin C type compounds, the carbinyl proton showing the vicinal coupling with the methine proton at C-2 appear at δ 4.59 (d, J=3.8 Hz) and δ 5.09 (d, J=6.5 Hz) in *trans*-(2*S*, 3*S*)- and *cis*-(2*R*, 3*S*)-pterosin C (**20**),[3] respectively. This observation also provided the information on the conformation. The effects of electronegative substituents on vicinal coupling constants were reported in several papers.[15] The *trans*-2,3-vicinal coupling constants of *trans*-1,2-dihalogenoindan derivatives were calculated as $J_{2a,3a}$=9.7 Hz and $J_{2e,3e}$=1.0 Hz respectively.[16] Since electronegativity of hydroxyl group is assumed to be not so much different from that of halogene atoms, the following equation might be applicable:

$$J = X_{AA}J_{AA} + (1-X_{AA})J_{EE}$$

where $J_{AA}=J_{2a,3a}$=9.7 Hz, $J_{EE}=J_{2e,3e}$=1.0 Hz, J=3.8 Hz (our observed value for *trans*-pterosin C), and X is the molar fraction of the diaxial conformer ($X_{AA}+X_{EE}=1$). From this equation the ratio of the conformer having diaxial protons at C-2 and C-3 was calculated as 32% and another having diaxial methyl and hydroxyl groups as 68%. The values indicate that the pseudoaxial conformation of the hydroxyl group at C-3 is predominant and agree with the results from the CD observation.

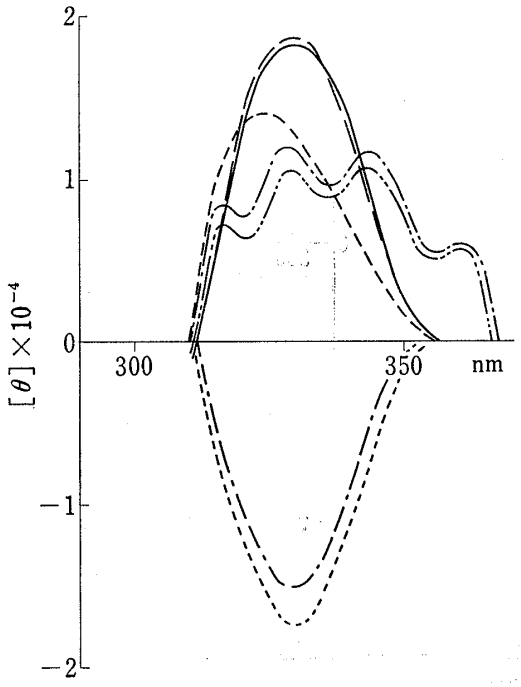
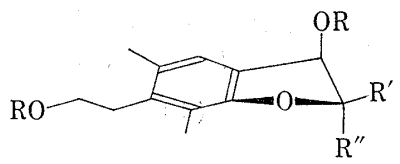
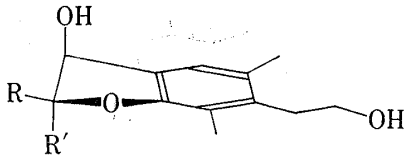


Fig. 8

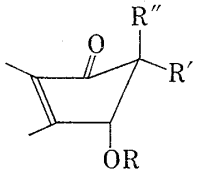
31 (————), 32 (– – – – –), 34 (— — — —) in MeOH and 33 (—·—·—), 34 (·—·—·—·) in cyclohexane.
31′(——·——·), 32′(— — — — —) in MeOH.



R′=CH_2OR, R″=Me or R′=Me, R″=CH_2OR
(+)



R=CH_2OH, R′=Me or R=Me, R′=CH_2OH
(−)



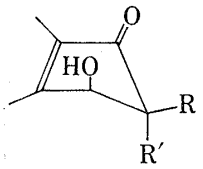


Fig. 9. Octant Type Projection of Pterosin L Type Compounds

15) D.H. Williams and N.S. Bhacca, *J. Am. Chem. Soc.*, **86**, 2742 (1964); H. Booth, *Tetrahedron Lett.*, **1965**, 411; K.L. Williamson, C.A. Lanford, and C.R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964); S.L. Smith and R.H. Cox, *J. Phys. Chem.*, **72**, 198 (1968); M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963); R.A. Arstin and C.P. Lillya, *J. Org. Chem.*, **34**, 1327 (1969).

16) H.R. Buys and E. Havinga, *Tetrahedron*, **24**, 4967 (1968).

Pterosin L Type

The compounds of this type have two chiral centers at C-2 and C-3; a methyl and a hydroxymethyl group are geminally substituted at the 2-position and a hydroxyl group does at the 3-position.

(2*R*, 3*R*)-Pterosin L (**31**) and its epimer (**32**) at C-2 having (2*S*, 3*R*)-configuration, derived from (2*S*, 3*S*)-pterosin C (**20**) by hydroxymethylation,[3] exhibited the same strong positive Cotton effects in methanol regardless of opposite configurations at C-2 (Fig. 8). Their triacetates (**33** and **34**) also exhibit positive CD-curves in cyclohexane (Fig. 8). The enantiomers of these, (2*S*, 3*S*)- and (2*R*, 3*S*)-pterosin L (**31′** and **32′**) exhibited the negative Cotton effects in methanol (Fig. 8)

Applying Snatzke's rule, it was concluded that the conformation of the hydroxyl or acetoxyl group at C-3 is predominantly in pseudoaxial as in the case of pterosin C type compounds regardless of the configuration at C-2 and the polarities of solvents (Fig. 9).

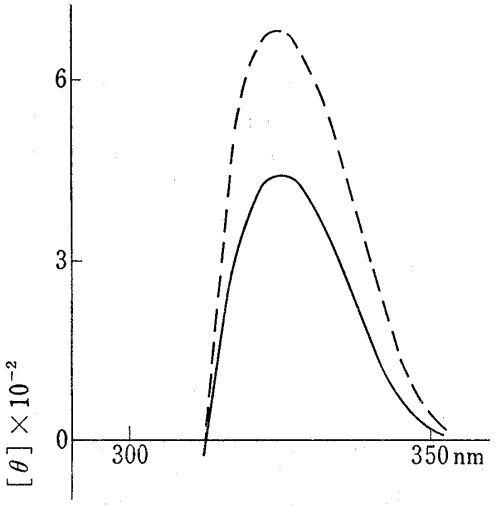


Fig. 10

35 (————) in MeOH, (– – – – –) in $CHCl_3$.

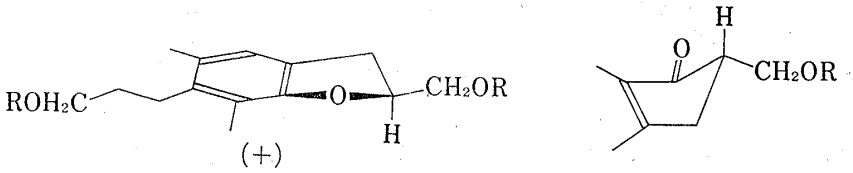


Fig. 11. Octant Type Projection of Pterosin G Type Compounds

Pterosin G Type

(2*S*)-Pterosin G (**35**) has one chiral center at the 2-position, where a hydroxymethyl group is substituted. Pterosin G (**35**) showed a positive CD-curve in methanol and a more stronger positive CD-curve in chloroform. This may be attributed to the intramolecular hydrogen bond as same as pterosin A type derivatives (Fig. 10). The diacetate (**36**) also exhibited a positive CD-curve.

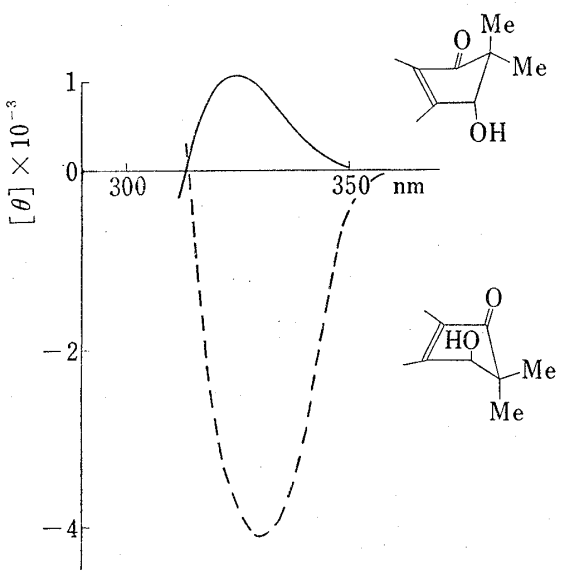


Fig. 12

37 (————) and **37′**(– – – – –) in MeOH.

As the results it was concluded that these compounds have the pseudo-equatorial hydroxymethyl or acetoxymethyl group predominantly and such conformation increases by the contribution of intramolecular hydrogen bond (Fig. 11).

Pterosin D Type

Pterosin D (**37**) has one chiral center at the 3-position, where a hydroxyl group is substituted. As mentioned above the sign of CD-curves of pterosin C type and pterosin L type compounds is decided by the configuration of the hydroxyl group at the 3-position, which exists predominatly in the pseudo-axial conformation. In the same way the hydroxyl

group at the 3-position of pterosin D type compounds is expected to exist in pseudo-axial conformation and, accordingly, the configurations of pterosin D (**37**) showing a positive CD-curve and pterosin D (**37'**) showing a negative CD-curve were assigned[4] as (3*R*) and (3*S*) respectively (Fig. 12).[17]

Conclusion

Since the conformation of the five-membered ring in 1-indanones is flexible, direct application of the sign of the Cotton effect associated with the n→π^* transition of the carbonyl group to the absolute configuration has some limitation. However determination of the CD both in protic and aprotic solvents and the consideration on the hydrogen bond formation will assure the application of the rule proposed by Snatzke[7] to the stereochemistry of naturally occurring 1-indanone sesquiterpenes.[3,4]

Experimental

The substances used in this study were compounds isolated from *Pteridium aquilinum* var. *latiusculum* or the derivatives prepared thereof.[3,4] As reported in the previous paper[4] the optical purities of many of these compounds are not 100%.

All CD spectra were recorded with JASCO ORD-UV 5 with a CD attachment in MeOH,[18] $CHCl_3$, or cyclohexane solutions at 20—25°. CD-data are given as $[\theta]$ for maxima.[19]

(2*R*)-Pterosin B(**1**): 326(+1771) in MeOH(c=0.24). 366(−999), 348(−1161), 334(−687), 326(+332), 315(+237) in cyclohexane(c=0.018). 362(−414), 346(−356), 322(+711) in cyclohexane–$CHCl_3$(4: 1) (c=0.015). 360(−390), 344(−283), 323(+744) in cyclohexane–$CHCl_3$(4: 2)(c=0.012). 359(−387), 344 (−168), 322(+800) in cyclohexane–$CHCl_3$(4: 4)(c=0.012). 360(−350), 343(−117), 321(+1028) in $CHCl_3$ (c=0.045). 360(−214), 327(+1648) in $CHCl_3$–MeOH(4: 1)(c=0.035). 359(−183), 327(+1648) in $CHCl_3$–MeOH(4: 1)(c=0.30). 358(−128), 325(+1752) in $CHCl_3$–MeOH(4: 3)(c=0.025). 357(−98), 328(+1758) in $CHCl_3$–MeOH(4: 4)(c=0.022).

(2*R*)-Acetylpterosin B(**2**): 323(+1805) in MeOH(c=0.018). 366(−911), 349(−1418), 334(−675), 326(+473), 315(+608) in cyclohexane(c=0.019). 358(−502), 343(−295), 322(+886) in $CHCl_3$(c=0.022).

(2*R*)-Pterosin F(**3**): 362(−111), 322(+846) in MeOH(c=0.053). 357(−218), 343(−87), 320(+677) in $CHCl_3$(c=0.054). 367(−470), 349(−713), 334(−379), 326(+159), 314(+273) in cyclohexane(c=0.077).

(2*R*)-Benzoylpterosin B(**4**): 324(+1717) in MeOH(c=0.034). 360(−332), 344(−295), 323(+1148) in $CHCl_3$(c=0.027). 366(−956), 349(−1211), 334(−510), 325(+737), 315(+988) in cyclohexane(c=0.027).

(2*R*)-Palmitylpterosin B(**5**): 324(+1648) in MeOH(c=0.024).

(2*R*)-Pteroside B(**6**): 324(+1874) in MeOH(c=0.036).

(2*S*)-Pteroside B(**6'**): 323(−1225) in MeOH(c=0.028).

(2*S*)-Pterosin B(**1'**): 324(−1180) in MeOH(c=0.055).

(2*R*)-Pteroside B Tetraacetate(**7**): 364(−122), 327(+1299) in MeOH(c=0.067). 358(−256), 321(+1059) in $CHCl_3$(c=0.075). 365(−729), 348(−1094), 333(−456), 325(+547), 315(+909) in cyclohexane(c=0.048).

(2*R*)-Pterosin E(**8**): 324(+1648) in MeOH(c=0.019).

(2*S*)-Pteroside P(**9**): 328(−682) in MeOH(c=0.035).

(2*S*)-Pterosin P(**10**): 327(−415) in MeOH(c=0.040).

(2*S*)-Pterosin A(**11**): 352(+116), 343(−83), 328(−298) in MeOH(c=0.19). 350sh(+1424), 332(+2267), 325(+2258) in $CHCl_3$(c=0.035).

(2*S*)-Pteroside A(**12**): 370(+52), 354(+210), 345(−92), 330(−524) in MeOH(c=0.078).

(2*S*)-Acetylpterosin A(**13**): 370(+51), 354(+204), 344(−115), 328(−574) in MeOH(c=0.057). 349 (+1523), 334(+2500), 323(+2385) in $CHCl_3$(c=0.025). 357(+1846), 341(+2900), 327(+2670), 314(+1933) in cyclohexane(c=0.032).

(2*S*)-Palmitylpterosin A(**14**): 359(+1796), 342(+2879), 328(+2483), 314(+1532) in cyclohexane (c=0.092).

(2*S*)-Pterosin K(**15**): 352(+143), 344(−32), 329(−273) in MeOH(c=0.041). 360(+1507), 344(+2512), 328(+2153), 317(+1435) in cyclohexane(c=0.018).

17) The optical purity of **37** is lower than that of **37'**.[4]

18) In order to examine hemiacetal or acetal formation in MeOH, the values in MeOH, EtOH, and CH_3CN were compared using pterosin B(**1**) and pterosin C(**20**). Since no sign of the acetal formation was observed, further determinations were carried out in MeOH.

19) The $[\theta]$ values reported in the preliminary communications were erroneous. The correct values are shown in the previous papers[3,4] and this report.

(2*S*)-Diacetylpterosin A(**16**): 348(+253), 334(+464), 316(+674) in MeOH(c=0.23). 363(−98), 354 (+456), 345(−190), 338(+532), 330(−152), 322(+342), 309(+1012) in cyclohexane(c=0.043).

(2*S*)-Dipalmitylpterosin A(**17**): 364(−653), 355(+924), 347(−1470), 340(+1572), 331(−1429), 324 (+164), 317(−816) in cyclohexane(c=0.073).

(2*S*)-Pteroside K(**18**): 324(+3507) in MeOH(c=0.045).

(2*S*)-Pteroside K Tetraacetate(**19**): 351(+1324), 336(+2384), 321(+2249), 310(+2249) in cyclohexane (c=0.031).

(2*S*,2*S*)-Pterosin C(**20**): 328(+24488) in MeOH(c=0.025).

(2*R*,3*R*)-Pterosin C(**20′**): 325(−17200) in MeOH(c=0.024).

(2*S*,3*S*)-Diacetylpterosin C(**21**): 360(+5869), 343(+12961), 330(+14426), 320(+11746) in cyclohexane (c=0.065).

(2*S*,3*S*)-Acetylpterosin C(**22**): 325(+16268) in MeOH(c=0.045).

(2*S*,3*S*)-Palmitylpterosin C(**23**): 328(+20978) in MeOH(c=0.018).

(2*S*,3*S*)-Phenylacetylpterosin C(**24**): 324(+22439) in MeOH(c=0.010).

(2*S*,3*S*)-Pterosin J(**25**): 325(+15487) in MeOH(c=0.022).

(2*S*,3*S*)-Palmitylpterosin C(**26**): 330(+19012) in MeOH(c=0.014).

(2*R*,3*R*)-Pteroside C(**27**): 325(−16542) in MeOH(c=0.045).

(2*S*,3*R*)-Pterosin C(**28**): 330(−20415) in MeOH(c=0.033).

(2*S*,3*R*)-Pteroside C(**29**): 330(−18346) in MeOH(c=0.039).

(2*R*,3*R*)-Pteroside C Pentaacetate(**30**): 324(−10563) in MeOH(c=0.045).

(2*R*,3*R*)-Pterosin L(**31**): 330(+18291) in MeOH(c=0.035).

(2*S*,3*S*)-Pterosin L(**31′**): 329(−15136) in MeOH(c=0.012).

(2*S*,3*R*)-Pterosin L(**32**): 330(+18480) in MeOH(c=0.010).

(2*R*,3*S*)-Pterosin L(**32′**): 329(−17600) in MeOH(c=0.024).

(2*R*,3*R*)-Acetylpterosin L(**33**): 360(+5760), 343(+10893), 326(+16043), 317(+7128) in cyclohexane (c=0.062).

(2*S*,3*R*)-Acetylpterosin L(**34**): 324(+17306) in MeOH(c=0.040). 360(+5850), 343(+11895), 328 (+12090), 317(+8385) in cyclohexane(c=0.040).

(2*S*)-Pterosin G(**35**): 325(+443) in MeOH(c=0.35). 324(+682) in $CHCl_3$(c=0.030).

(2*S*)-Diacetylpterosin G(**36**): 316(+660) in MeOH(c=0.026).

(3*R*)-Pterosin D(**37**): 324(+1064) in MeOH(c=0.021).

(3*S*)-Pterosin D(**37′**): 330(−4094) in MeOH(c=0.02).

PMR spectra were recorded at 60 MHz in $CDCl_3$ or CD_3OD solution with TMS as an internal standard. IR spectra were measured in $CHCl_3$ or CCl_4 solution.

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