Secondary Mould Metabolites. Part 13.[1] Fungal Perylenequinones: Phleichrome, Isophleichrome, and their Endoperoxides

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The helix-shaped, fungal pigment phleichrome has been isomerized to isophleichrome. The axial chirality and absolute configuration of the side-chain carbons of both perylenequinones have been established. Photo-oxidation of both compounds occurs stereospecifically to give their endoperoxides, whose structure and stereochemistry results from a detailed analysis of their n.m.r. spectra.

The mycelium of the phytopathogenic fungus *Cladosporium phlei* shows a deep red pigmentation, due to the presence of the secondary metabolite phleichrome [(1a) or tautomers†], the structure of which was elucidated by Yoshihara *et al.* in 1975.[3] Phleichrome is a close analogue of another fungal perylene-quinone, cercosporin (2a),[4] the only gross structural difference between the two substances being the two methoxy groups in positions 6 and 7 of phleichrome (1a) instead of the methylene-dioxy group of cercosporin (2a). Cercosporin is a helix-shaped molecule, which is converted into the diastereoisomer isocercosporin (2b), with opposite axial chirality.[5,6] It is therefore surprising that Yoshihara *et al.* did not investigate in detail the stereochemistry of phleichrome.

As a part of our current work on the chemistry of fungal perylenequinones,[7] we report here on the conversion of phleichrome into isophleichrome [(1b) or tautomers†], on their stereochemistry, and on their reactivity with oxygen.
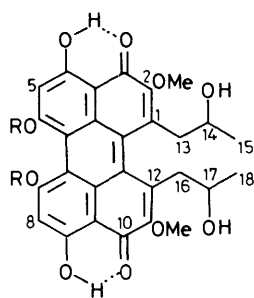
(1a and b) R = Me
(2a and b) RR = CH₂

Phleichrome was isolated from *Cladosporium phlei* in high yield, and rapidly converted, by heating in xylene, into an equilibrium mixture with isophleichrome. The close similarity in behaviour and physical data with those of the couple cercosporin–isocercosporin leaves no doubt that phleichrome and isophleichrome are also diastereoisomers, with out-of-plane distorted perylenequinone chromophores of opposite helicity. This also requires that the two asymmetric carbons of the side chains have the same configuration.[5,6] Thermal interconversion of the isomers is accompanied by a change in

the conformation of the side chains, as is evidenced by the chemical shifts and coupling constants of the $CH_3CH(OH)CH_2-$ groups, very similar to those of the couple cercosporin–isocercosporin.[5,6] It appears therefore that both the bulky side chains and the two methoxy groups in positions 6 and 7 contribute to a rather high barrier to interconversion.

Consistent with these conclusions are our results from a comparison of the circular dichroism (c.d.) spectra of compounds (1a) and (1b) with those of cercosporin and isocercosporin (2b) (Figure 1). As the absorption is mainly due to the inherently dissymmetrical chromophore of the perylenequinone ring,[5,6] it follows that the natural isomer phleichrome (only one isomer is produced by the fungus) has axial chirality *opposite* to that of cercosporin, *i.e.* (*S*), that of cercosporin (*R*) having been established by X-ray analysis.[6]

The absolute configuration of the side-chain carbons was then established as *S* by the application of Horeau's method of kinetic resolution to isophleichrome (1b) and to the methyl ethers (3b) and (4b), and also by direct comparison with cercosporin trimethyl ether.

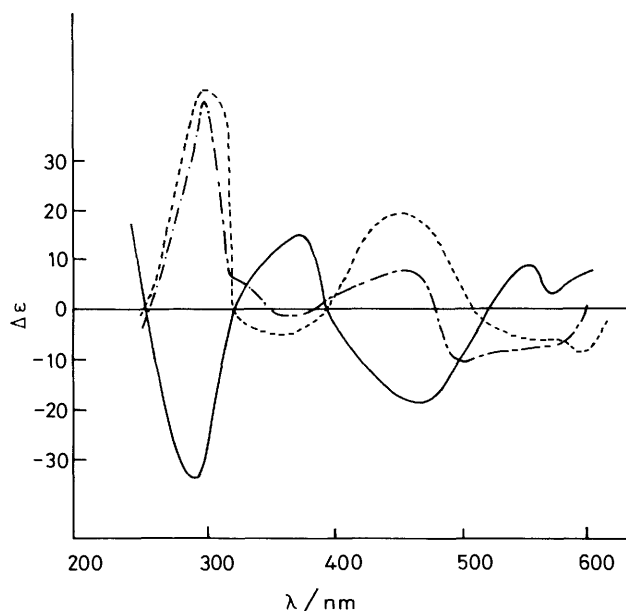Phleichrome and isophleichrome, like other compounds of

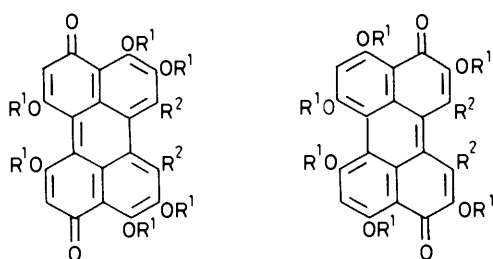**Figure 1.** C.d. curves (EtOH) of - - - - phleichrome (1a), ——— isophleichrome (1b), and – · – · – · – isocercosporin (2b)

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† A detailed study of the tautomerism of these systems is in advanced progress and results will be published shortly (ref. 2).

(3a and b)   R^1 = Me   (4a and b)

R^2 = CH$_2$CH(OH)Me

Table 1. ^{1}H N.m.r. chemical shifts (δ) and coupling constants (J/Hz) of compounds (5a) and (5b) in CDCl$_3$

Proton[a]	(5a)	(5b)
3-OH	12.09	11.92
9-OH	11.50	11.43
5-H	5.93	5.85
8-H	6.31	6.13
13-H$_a$	3.06	2.94
13-H$_b$	2.75	2.61
14-H	3.51	3.58
15-H$_3$	0.94	1.12
14-OH⎫ 17-OH⎭	2.10	2.60
16-H$_a$	3.16	3.12
16-H$_b$	2.38	2.37
17-H	4.17	4.13
18-H$_3$	1.27	1.24
19-H$_3$	3.93	3.85
20-H$_3$	3.96	3.90
21-H$_3$	3.82	3.67
22-H$_3$	4.10	4.08
J	(5a)	(5b)
13$_a$,13$_b$	13.2	12.8
13$_a$,14	7.6	2.8
13$_b$,14	5.0	9.0
14,15	6.1	6.1
16$_a$,16$_b$	12.9	12.9
16$_a$,17	9.2	4.6
16$_b$,17	2.9	7.2
17,18	6.2	6.2

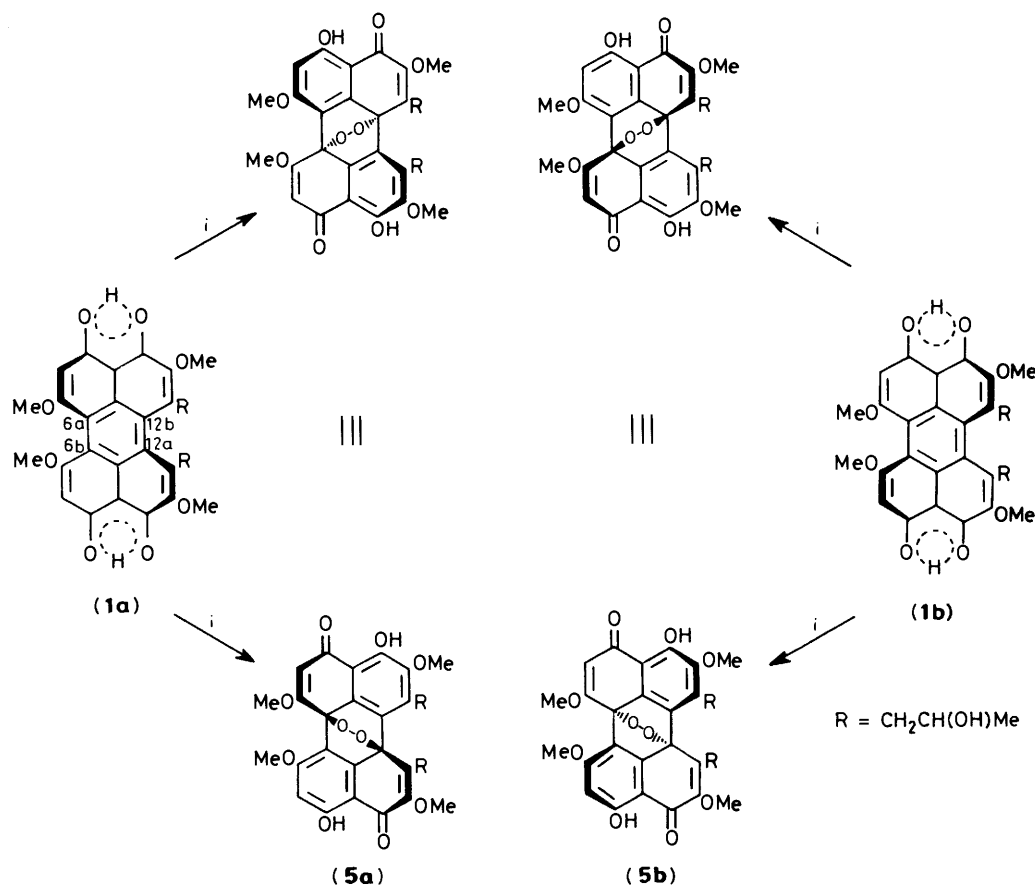[a] Positions 19—22 are shown in Figure 2.

this group of natural substances, show phenol–quinone tautomerism.[2] This is also evidenced by the formation of two isomeric dimethyl ethers, one red and one yellow, by methylation of each isomer with CH$_3$I and Ag$_2$O. The symmetry of the ^{1}H n.m.r. spectra of these ethers is consistent only with structures possessing a C_2 symmetry axis, such as (3) or (4). The assignment of structures (3) and (4), to the yellow and red ethers respectively, is based on the chemical shift of the 5-H and 8-H protons. The quinonoid structure of the 'left' moiety of compound (3) is consistent with an upfield absorption of the protons α to the CO group in compound (3) with respect to those of compounds (4) and (1). Similar behaviour is shown by another group of pigments of this class, the elsinochromes.[8]

Phleichrome (1a), again like other 4,9-dihydroxyperylene-3,10-quinones, shows interesting photodynamic activity.[3,9] Recent reports of production of singlet oxygen by irradiation of

(1a)

(5a)   (5b)

(1b)

R = CH$_2$CH(OH)Me

Scheme. *Reagent*: i, O$_2$

Figure 2. Fully ¹H-coupled 75.47 MHz ¹³C n.m.r. spectrum of peroxyisophleichrome (**5b**) in CDCl₃

Table 2. ^{13}C N.m.r. chemical shifts (δ_C) and (C,H) coupling constants (J/Hz) of compounds (5a) and (5b) in CDCl$_3$

C	(5a)	(5b)	C	(5a)	(5b)	C	(5a)	(5b)
1	134.95	136.23	8	98.73	98.36	13	36.11	36.11
2	145.84	145.29	9	163.06	162.55	14	69.11	69.06
3	152.67	152.37	9a	107.21	107.40	15	23.37	24.27
3a	111.70	111.42	9b	145.28	145.49	16	39.97	40.12
4	189.65	189.71	10	182.88	183.40	17	67.90	68.26
5	104.47	104.42	11	153.26	153.52	18	24.49	23.72
6	168.72	168.69	12	133.36	132.52	19	60.63	60.46
6a	75.10	75.20	12a	81.56	81.09	20	56.70	56.70
6b	117.29	116.97	12b	129.10	129.85	21	56.56	56.40
7	159.42	158.93	12c	135.71	135.03	22	60.85	60.31

J^a	(5a)	(5b)	J	(5a)	(5b)	J	(5a)	(5b)
C-3,3-OH	4.7	4.7	C-9,9-OH	5.0	5.2	C-5,5-H	163.5	163.0
C-3a,5-H	3.9	3.8	C-9a,8-H	5.2	5.2	C-8,8-H	160.5	159.5
C-3a,3-OH	5.0	5.0	C-9a,9-OH	4.9	4.9	C-13,13-H$_2$	128.0	128.5
C-4,5-H	1.8	1.8	C-9b,9-OH	b	<1	C-14,14-H	145.0	145.0
C-6,5-H	2.8	2.8	C-11,22-H$_3$	b	4.0	C-15,15-H$_3$	125.5	125.0
C-6,20-H$_3$	4.2	4.2	C-11,16-H$_a$	3.5	3.8	C-16,16-H$_2$	129.5	128.5
C-6a,5-H	7.1	7.3	C-11,16-H$_b$	5.7	5.6	C-17,17-H	148.5	147.0
C-6a,8-H	1.6	1.6	C-12,16-H$_a$	5.6	5.6	C-18,18-H$_3$	126.0	125.0
C-6b,8-H	5.8	5.8	C-12,16-H$_b$	5.6	5.6	C-19,19-H$_3$	145.5	144.5
C-7,21-H$_3$	4.1	4.2	C-12,17-H	2.0	1.8	C-20,20-H$_3$	146.5	146.0
C-7,8-H	2.8	2.8	C-12a,16-H$_a$	4.7	4.6	C-21,21-H$_3$	146.0	145.5
C-7,9-OH	1.7	1.8	C-12a,16-H$_b$	3.3	3.4	C-22,22-H$_3$	146.0	145.5
C-8,9-OH	7.8	7.8	C-12b,13-H$_a$	5.7	5.5			
C-9,8-H	4.6	4.6	C-12b,13-H$_b$	3.9	3.6			

^{a} (C,H) Couplings relative to C-1 and C-2 may not be unequivocally determined. ^{b} Couplings not resolved.

cercosporin have increased the interest shown to these compounds.[10]

Photo-oxidation of either phleichrome or isophleichrome in CHCl$_3$ afforded, in good yield, the corresponding endoperoxide (5a) and (5b) respectively. Analogous behaviour is shown by another compound of the series, hypocrellin,[11] whereas cercosporin, isocercosporin, and elsinochrome A do not react under the same conditions.

Although the endoperoxides (5a and b) are thermally unstable, as they revert to the parent compounds even at room temperature, they could be isolated and characterized by elemental analysis and mass and n.m.r. spectra. These data are consistent with the addition of one mole of oxygen, which should most probably[11,12] occur across the central ring of the reactive anthracene moiety of the two degenerate (equivalent) 3,9-dihydroxyperylene-4,10-quinone tautomers of compounds (1a and b).

Owing to the close similarity between the two endoperoxides, the discussion of their ^{1}H and ^{13}C n.m.r. spectral parameters will be restricted to isomer (5b).

The 300.13 MHz ^{1}H n.m.r. spectrum of compound (5b) shows signals corresponding to 30 protons. The resonances at δ 11.92, 11.43, and 2.60 (four OH protons), 6.13 and 5.85 (two aromatic methine protons), and 4.08, 3.90, 3.85, and 3.67 (12 OMe protons) were readily attributed. The remainder of the ^{1}H n.m.r. spectrum exhibited extensive fine structure. First-order analysis of these multiplets yielded the values of proton chemical shifts and the ^{1}H–^{1}H coupling constants. Extensive ^{1}H–{^{1}H} and ^{13}C–{^{1}H} decoupling experiments allowed all the resonances to be unambiguously assigned. The ^{1}H n.m.r. data for endoperoxides (5a) and (5b) are given in Table 1.

The 75.47 MHz ^{13}C n.m.r. spectrum of compound (5b) (Figure 2) revealed that the 30 carbon resonances are due to 6 methyl, 2 methylene, 4 methine, and 18 quaternary carbon atoms. The chemical shifts observed in the proton-noise-decoupled ^{13}C n.m.r. spectra, the multiplicities observed in the single-frequency

off-resonance decoupled spectra, and the ^{1}H–^{13}C coupling constants obtained from the fully ^{1}H-coupled ^{13}C n.m.r. spectra of endoperoxides (5a) and (5b) are summarized in Table 2.

Chemical shift criteria and the observed multiplicities dictate that the resonances at δ_C 189.71 and 183.40 p.p.m. must be attributed to the two carbonyl carbon atoms. C-4 Appears as a doublet, the observed 1.8 Hz splitting being removed by irradiation of 5-H (δ 5.85) while C-10 shows no long-range coupling at all. A wealth of structural information was obtained by irradiation of 5-H. It causes the signal at δ_C 111.42 p.p.m. (C-3a), which appears as a doublet of doublets, to simplify to a doublet, the remaining coupling being the three-bond coupling to the 3-OH hydroxy proton at δ 11.92. It also causes the doublet of quartets at δ_C 168.69 p.p.m. (C-6) to change to a quartet, the residual coupling being the three-bond coupling to the 6-OMe protons. Furthermore its irradiation changes the doublet of doublets centred at δ_C 75.20 p.p.m. to a doublet, allowing its rigorous assignment to the quaternary oxygen-bearing sp^3-hybridized carbon C-6a, the remaining coupling being the four-bond coupling constant to 8-H. Irradiation of 3-OH affected C-3 and C-2, this latter carbon showing a broad multiplet which sharpens on irradiation of either the 2-OMe or the 13-H$_2$ protons.

Similar low-power specific ^{1}H-decoupling experiments permit the other resonances to be assigned. In particular, irradiation of the 16-H$_2$ protons causes collapse of the triplet at δ_C 81.09 p.p.m. to a sharp singlet, allowing its assignment to the other quaternary oxygen-bearing sp^3-hybridized carbon C-12a.*

* No carbon with even roughly similar chemical shift appears among the ^{13}C n.m.r. data reported by Breitmaier and co-workers[11] for peroxyhypocrellin. Therefore their data are not consistent with the structure of peroxyperoxyhypocrellin, which, however, we believe to be substantially correct (albeit not the only possible one, due to the lack of a C_2 axis in this compound).

Final confirmation of the structure comes from the three-bond coupling constant[13] (J 7.8 Hz) between C-8 and the remaining 9-OH phenolic proton at δ 11.43.

The photo-oxidation reactions occur with complete stereospecificity, which, however, is a consequence of the steric factors and the symmetry properties exhibited by compounds (1a and b). The same compound, (5a), results by O_2 attack either from the top face onto carbons 6a and 12a of the 3,9-dihydroxy-4,10-diketo tautomer or from the bottom face onto carbons 6b and 12b of the equivalent, 4,10-dihydroxy-3,9-diketo tautomer of phleichrome (1a), as shown in the Scheme.

Attack from the opposite side in each case is prevented by steric constraint due to the helical shape of the starting materials, and would be possible only by simultaneous inversion of the helicity of the ring. This, however, is ruled out by comparison of the c.d. curves (see Experimental section) of the isomers (5a) and (5b) with those of (1a) and (1b) respectively. Taking into account the interrupted conjugation between the two bicyclic moieties, no change appears to have occurred in the sign of the major chromophore. Moreover, the photo-oxidation and the retrograde O_2 expulsion proceed at room temperature, well below the temperature necessary for a fast equilibration of the two diastereoisomers (1a) and (1b).

As the axial chirality of peroxyphleichrome is the same as in phleichrome, i.e. S, the configuration of the two new asymmetric carbon atoms 6a and 12a in the endoperoxide (5a) is S and R respectively, and vice versa in the isomer (5b).

Experimental

U.v. spectra were measured in 95% EtOH on a Beckman DK-2 spectrophotometer. Flash chromatography was performed with Merck silica gel (0.040—0.063 mm), and t.l.c. with Merck HF_{254} silica gel. Unless otherwise indicated, the purity of products was checked by t.l.c. and n.m.r. and mass spectra, and deemed sufficient for structural elucidation. Mass spectra were taken with a Hitachi RMU6D instrument at 70 eV. [1]H (300.13 MHz) and [13]C (75.47 MHz) n.m.r. spectra were recorded on a Bruker CXP-300 spectrometer. Chemical shifts are in p.p.m. (δ) from $SiMe_4$ as internal standard. C.d. spectra were measured with a Jobin-Yvon dichrograph. M.p.s are uncorrected.

Isolation and Purification of Phleichrome (1a).—The mycelium of a strain of *Cladosporium phlei* Gregory, 358.69, obtained from Centraal Bureau voor Schimmelcultures, Baarn, grown on malt–peptone–glucose–agar (2–0.2–20–15 g l^{-1}) in Roux flasks, was extracted thrice with EtOAc after 2 weeks of growth at room temperature. The extracts were dried and evaporated under reduced pressure. Pure phleichrome (1a), m.p. 205—210 °C (500 mg l^{-1}; lit.,[2] 2 mg l^{-1}) was obtained after crystallization from CH_2Cl_2–hexane; δ_H($CDCl_3$) 15.78 (s, 2 chelated OH), 6.58 (s, 5- and 8-H), 4.20 (s, 2- and 11-OMe), 4.06 (s, 6- and 7-OMe), 3.42 (ddq, J 6.6, 6.4, and 6.2 Hz, 14-and 17-H), 3.60 (dd, J 12.9 and 6.6 Hz, 13-and 16-H_a), 2.95 (dd, J 12.9 and 6.4 Hz, 13-and 16-H_b), and 0.53 (d, J 6.2 Hz, 15- and 18-H_3).

Methylation of Phleichrome.—Phleichrome (1a) (400 mg), Ag_2O (500 mg), dry acetone (20 ml), and MeI (4 ml) were stirred for 4 days at room temperature in the dark. Flash chromatography on silica gel (with added 2% KH_2PO_4) with CH_2Cl_2–MeOH (30:1) as eluant gave two main products, the yellow dimethyl ether (3a) and the red dimethyl ether (4a).

Compound (3a) had m.p. 107—110 °C; $\lambda_{max.}$ 296, 360, and 445 nm (ϵ 13 900, 10 100, and 24 300); m/z 580 (M^+ + 2); δ_H*($CDCl_3$) 6.12 (s, 5- and 8-H), 4.12, 4.08, and 3.93 (s,

6 × OMe), 3.45 (m, 14- and 17-H), 3.63 and 3.06 (m, 13- and 16-H_2), and 0.42 (d, 15- and 18-H_3).

Isomer (4a) had m.p. 120—125 °C; $\lambda_{max.}$ 268, 336, 465, and 570sh nm (ϵ 36 700, 8 300, 23 900, and 8 900); m/z 580 (M^+ + 2); δ_H($CDCl_3$) 6.79 (s, 5- and 8-H), 4.18, 4.12, and 4.10 (s, 6 × OMe), 3.40 (m, 14- and 17-H), 3.35 and 2.68 (m, 13- and 16-H_2), and 0.67 (d, 15- and 18-H_3).

Isophleichrome (1b).—A solution of phleichrome (1a) (0.5 g) in xylene (100 ml) was refluxed for 1 h, the conversion being monitored by t.l.c. Chromatography of the reaction mixture on silica gel (with added 2% KH_2PO_4) with CH_2Cl_2–MeOH (15:1) as eluant gave isophleichrome (1b) (150 mg), m.p. 215—220 °C; $\lambda_{max.}$ 350, 475, 540sh, and 584 nm (ϵ 5 000, 24 100, 12 200, and 12 200); $\nu_{max.}$(Nujol) 1 610 cm^{-1} (conj. CO); m/z 550 (M^+); δ_H (c = 6.3 × 10^{-3}M in $CDCl_3$) 15.85 (s, 2 chelated OH), 6.44 (s, 5- and 8-H), 4.22 (s, 2- and 11-OMe), 3.99 (s, 6- and 7-OMe), 3.74 (ddq, J 3.3, 8.3, and 6.2 Hz, 14- and 17-H), 3.54 (dd, J 13.2 and 3.3 Hz, 13- and 16-H_a), 2.93 (dd, J 13.2 and 8.3 Hz, 13- and 16-H_b), and 0.95 (d, J 6.2 Hz, 15- and 18-H_3).

Acetylation of Isophleichrome (1b).—To pyridine (2 ml) were added isophleichrome (1b) (100 mg) and acetic anhydride (4 ml), the solution was left overnight and then poured in ice, and the precipitate was collected and chromatographed by preparative t.l.c. (p.l.c.) using CH_2Cl_2–MeOH (15:1) as developer to give the tetra-acetate of isophleichrome (1b) (80 mg), δ_H($CDCl_3$) 6.87 (s, 5- and 8-H), 4.70 (m, 14- and 17-H), 4.07 (s, 4 × OMe), 3.26 and 2.68 (m, 13- and 16-H_2), 2.53 (s, 2 ArO*Ac*), 1.06 (d, 15- and 18-H_3), and 0.87 (s, 14- and 17-OAc).

Isophleichrome Dimethyl Ethers (3b) *and* (4b).—Isophleichrome (200 mg) was methylated with Ag_2O–MeI as above. Flash chromatography of the product in the usual way gave two products, (3b) and (4b). Compound (3b) had m.p. 147—150 °C; $\lambda_{max.}$ 295, 360, and 450 nm (ϵ 13 100, 8 800, and 21 800); $\nu_{max.}$(KBr) 1 610 cm^{-1} (conj. CO); δ_H($CDCl_3$) 5.97 (s, 5- and 8-H), 4.14, 4.06, and 3.83 (s, 6 × OMe), 3.8 (m, 14- and 17-H), 3.46 and 3.02 (m, 13- and 16-H_2), and 1.01 (d, 15- and 18-H_3).

Compound (4b) had m.p. 185—188 °C; $\lambda_{max.}$ 267, 336, 465, and 570sh nm (ϵ 33 100, 7 200, 21 200, and 7 900); $\nu_{max.}$(KBr) 1 610 cm^{-1} (conj. CO); δ_H($CDCl_3$) 6.60 (s, 5- and 8-H), 4.11, 4.09, and 3.76 (s, 6 × OMe), 3.7 (m, 14- and 17-H), 3.34 and 2.87 (m, 13- and 16-H_2), and 1.01 (d, 15- and 18-H_3).

Reactions with (±)-2-*Phenylbutyric Anhydride.*—(±)-2-Phenylbutyric anhydride (70 mg) was added to a solution of the perylenequinone (50 mg) in dry pyridine (1 ml). The solution was kept for 20 h at room temperature. 2-Phenylbutyric acid was obtained upon work-up of the reaction mixture according to the literature method.[14] The following values of optical rotation of the acid were obtained: from (1b) $[\alpha]_D^{20}$ − 1.9°, from (4a) − 1.6°, from (4b) − 2.2°, from cercosporin dimethyl ether[5] +2.8°, and from cercosporin trimethyl ether +4.2°.

Peroxyphleichrome (5a) *and Peroxyisophleichrome* (5b).—A solution of phleichrome (1a) (100 mg) in $CHCl_3$ (50 ml) was saturated with O_2 and left in the air and light (200-W lamp) for 3 days. After evaporation of the solvent, the less polar compound [*peroxyphleichrome* (5a), 60 mg] was separated from the reaction mixture by p.l.c. in C_6H_6–Et_2O–formic acid (50:5:1). Compound (5a) had m.p. 135—140 °C (Found: C, 61.3; H, 5.1. $C_{30}H_{30}O_{12}$ requires C, 61.85; H, 5.19%); $\lambda_{max.}$ 267 and 366 (ϵ 22 900 and 6 900); $\nu_{max.}$(CHCl_3) 1 645 and 1 610 cm^{-1} (conj. CO); m/z 582 (M^+), 578, 564, and 550 (M^+ − 32); c.d. (EtOH, c 4.1 × 10^{-4} g ml^{-1}) 395, 320, and 290 nm ($\Delta\epsilon$ + 12, + 39, and − 8.5).

Compound (1b) was treated in the same way to obtain

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* Numbering scheme as for compounds (1) and (2).

peroxyisophleichrome (**5b**), m.p. 135—140 °C; $\lambda_{max.}$ 267 and 366 nm (ε 23 500 and 6 750); $\nu_{max.}$(CHCl$_3$) 1 645 and 1 610 cm^{-1} (conj. CO); m/z 582 (M^+); c.d. (EtOH, c 4.02 $\times$ 10^{-4} g ml^{-1}) 395, 320, and 290 nm ($\Delta\varepsilon$ −10.1, −40.5, and +18). For the n.m.r. spectra of compounds (**5a** and **b**), see the Tables.

Acknowledgements

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