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Novel Oxidative Phenol-coupling Reaction with Phosphomolybdic Acid on Silica Gel Support : Regioselective Biomimetic Synthesis of Dimeric Phenanthrene Derivatives

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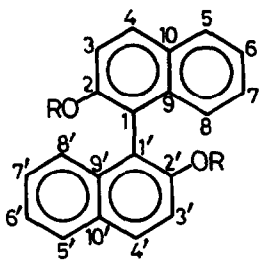
Abstract· *Biomimetic synthesis of the naturally occurring dimeric phenanthrene derivatives, cirrhopetalanthrin (3a) and flavanthrin (7a), and their structural analogues 3c, 3e, 5a and 7c was achieved in very high yields by regioselective oxidative coupling of their respective phenolic monomers 2a, 6a, 2c, 2e, 4a and 6c with phosphomolybdic acid on a silica gel support. Unlike coelonin (6a) and lusianthridin (6c), 2,7-dihydroxy-3,4,6-trimethoxy-9,10-dihydrophenanthrene (6e) gave, on similar oxidation, the phenanthrene dimer 3e, instead of the expected 9,10-dihydrophenanthrene dimer 7e. β-Naphthol afforded the corresponding 1,1′-dimer 1a in almost quantitative yield. The structures of the new dimeric compounds were established from various spectral data of the compounds and their respective acetyl derivatives.*

The isolation of a few dimeric phenolic phenanthrene derivatives[1-3] from a number of Indian orchids in our laboratory in recent years prompted us to synthesize them mimicing their probable biogenetic pathway[4a-c] which is assumed to involve oxidative coupling of their respective phenolic monomers. But all attempts to synthesize these compounds using the most commonly used oxidant, alkaline $K_3[Fe(CN)_6]$[5-8], yielded only heterogeneous gummy materials presumably due to extensive polymerization and nonregioselectivity of the reaction. In a search for a suitable alternative oxidant for the biomimetic synthesis of the natural phenanthrene dimers we have tried phosphomolybdic acid which is commonly used as a reagent for detection of phenolic and readily oxidizable functional groups. The Mo(VI) in PMA oxidizes the phenolic compounds, and itself is reduced to Mo(V) producing an intense blue colouration which is due to a mixture of Mo(VI) and Mo(V). But there appears to be no chemical work for the characterization of the oxidation products of the phenolic compounds with PMA. We report in this paper the isolation and characterization of the oxidation products of β-naphthol, the naturally occurring monomeric phenolic phenanthrene derivatives, flavanthrinin[9] (**2a**), nudol[10] (**2c**), **2e**[11], cirrhopetalin[12] (**4a**), and the 9,10-dihydrophenanthrenes, coelonin[13,1] (**6a**), lusianthridin[14] (**6c**) and **6e**[15,16] with PMA (on silica gel support) which

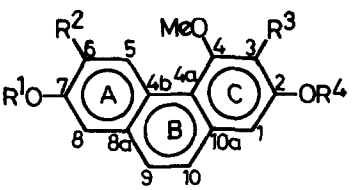
turned out to be the ideal oxidant we have been looking for the regioselective dimerization of the above types of phenolic compounds in very high yields.

From trial experiments of the reaction of β-naphthol and coelonin (**6a**) with PMA in aqueous acetone solution or ammoniacal aqueous acetone medium at room temperature and even at *ca* 90°, it was found that the rate of oxidation in each case was extremely slow, although the products of oxidation were mainly the corresponding dimers **1a** and **7a** formed in very poor yields. For a possible improvement in the yields of the oxidation products, the reaction was then carried out on a silica gel (100-200 mesh) support in the following manner. The phenolic compound to be oxidized was adsorbed on silica gel uniformly impregnated with PMA (slightly more than 1 equivalent of the phenolic compound). The whole material was then placed on a bed of fresh silica gel in a chromatographic column and kept soaked with light petroleum ether (B.p. 60-80°). The reaction was complete within *ca* 5-6h, and the oxidation product was then eluted with appropriate organic solvent leaving behind the inorganic materials mostly adsorbed in the column. Applying this method, β-naphthol was converted to the corresponding 1,1′ dimer **1a** in almost quantitative yield, and coelonin (**6a**) and flavanthrinin (**2a**) were induced to form the corresponding 1,1′-dimers **7a** and **3a** as the sole oxidation products in 80% and 85% yields respectively. The identity of **7a** and **3a** with flavanthrin[1] and cirrhopetalanthrin[2], respectively, was established by direct comparison with authentic samples (both the compounds were isolated recently in our laboratory). The above oxidative phenol-coupling with PMA on silica gel support thus provided a very convenient and elegant method for the regioselective biomimetic synthesis of the natural phenanthrene dimers **7a** and **3a** in exceptionally high yields.

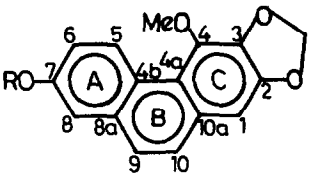
The reaction appeared to be quite general and was found to be equally satisfactory with a number of naturally occurring monomeric phenolic phenanthrene derivatives. Thus, nudol (**2c**), 2,7-dihydroxy-3,4,6-trimethoxyphenanthrene (**2e**), cirrhopetalin (**4a**) and lusianthridin (**6c**), on similar oxidation with PMA (with slightly more than 1 equivalent of the phenolic compounds), afforded the corresponding dimers **3c**, **3e**, **5a** and **7c** in 80%, 82%, 84% and 78% yields, respectively, as the exclusive characterizable products. Curiously, unlike the structurally similar 9,10-dihydrophenanthrene derivatives **6a** and **6c**, 2,7-dihydroxy-3,4,6-trimethoxy-9,10-dihydrophenanthrene (**6e**) on treatment with slightly more than 1 equivalent of PMA gave, besides some unchanged **6e**, the corresponding phenanthrene **2e** and its dimer **3e** in *ca* 25% and 20% yields respectively, instead of the expected 9,10-dihydrophenanthrene dimer **7e**. When the above reaction was carried out with



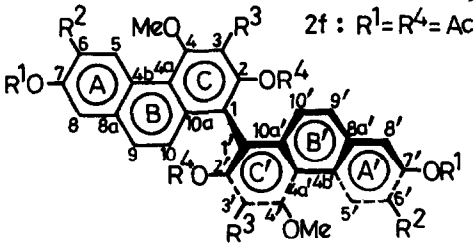
1a : R = H
1b : R = Ac



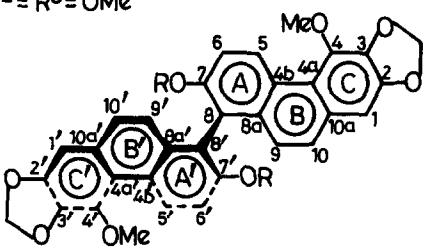
2a : $R^1 = R^2 = R^3 = R^4 = H$
2b : $R^1 = R^4 = Ac$, $R^2 = R^3 = H$
2c : $R^1 = R^2 = R^4 = H$, $R^3 = OMe$
2d : $R^1 = R^4 = Ac$, $R^2 = H$, $R^3 = OMe$
2e : $R^1 = R^4 = H$, $R^2 = R^3 = OMe$
2f : $R^1 = R^4 = Ac$, $R^2 = R^3 = OMe$



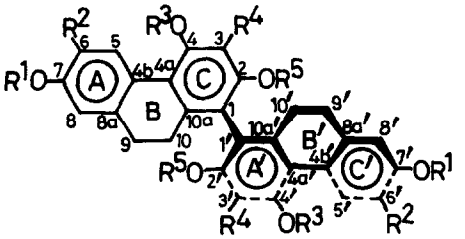
4a : R = H
4b : R = Ac



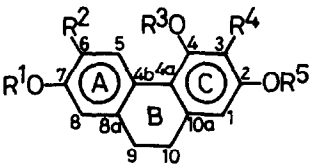
3a : $R^1 = R^2 = R^3 = R^4 = H$
3b : $R^1 = R^4 = Ac$, $R^2 = R^3 = H$
3c : $R^1 = R^2 = R^4 = H$, $R^3 = OMe$
3d : $R^1 = R^4 = Ac$, $R^2 = H$, $R^3 = OMe$
3e : $R^1 = R^4 = H$, $R^2 = R^3 = OMe$
3f : $R^1 = R^4 = Ac$, $R^2 = R^3 = OMe$



5a : R = H
5b : R = Ac



7a : $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = Me$
7b : $R^1 = R^5 = Ac$, $R^2 = R^4 = H$, $R^3 = Me$
7c : $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = Me$
7d : $R^1 = R^3 = Ac$, $R^2 = R^4 = H$, $R^5 = Me$
7e : $R^1 = R^5 = H$, $R^2 = R^4 = OMe$, $R^3 = Me$



6a : $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = Me$
6b : $R^1 = R^5 = Ac$, $R^2 = R^4 = H$, $R^3 = Me$
6c : $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = Me$
6d : $R^1 = R^3 = Ac$, $R^2 = R^4 = H$, $R^5 = Me$
6e : $R^1 = R^5 = H$, $R^2 = R^4 = OMe$, $R^3 = Me$
6f : $R^1 = R^5 = Ac$, $R^2 = R^4 = OMe$, $R^3 = Me$

slightly more than 2 equivalents of PMA, **6e** was converted into the phenanthrene dimer **3e** in 80% yield as the sole product. Thus **6e** possibly undergoes dehydrogenation at a faster rate than oxidative coupling to give at first the corresponding monomeric phenanthrene derivative **2e** which then dimerized to **3e** by oxidative coupling. Further, treatment of **6f**, the diacetyl derivative of **6e**, with slightly more than 1 equivalent of PMA afforded a mixture of unchanged **6f**, **6e** (formed by hydrolysis of **6f** by PMA in the acidic solid support), the corresponding phenanthrene **2e** and its dimer **3e** in the ratio of *ca* 1:1:1:1, while on carrying out the same reaction of **6f** with 2.5 equivalents of PMA, the phenanthrene dimer **3e** was obtained in 80% yield as the exclusive product. The facile dehydrogenation of **6e** may be attributed to increased electron density at C-8a and C-10a caused by the methoxyl groups at C-6 and C-3 respectively.

The structures of the dimers **3c**, **3e**, **5a** and **7c** were established from various spectral data of the compounds and their respective acetyl derivatives **3d**, **3f**, **5b** and **7d**. The molecular formulae of these dimers and their acetyl derivatives were ascertained from elemental analysis and confirmed by EI and, in most cases, by high resolution CI mass spectrometry. The appearance of fairly intense peaks corresponding to doubly charged molecular-ion peaks in the EI mass spectra of these compounds also indicates their dimeric formulation. The symmetrical dimeric structures of the above compounds were confirmed by the appearance of the same sets of signals in the ^{1}H NMR spectra of the dimers and the corresponding acetyl derivatives as those of their respective monomeric counterparts, except the signals corresponding to the protons at the site of dimerization (Table 1). Thus, the ^{1}H NMR spectra of the dimers **3c**, **3d**, **3e**, **3f**, **7c** and **7d** are essentially similar to those of their respective monomers **2c**, **2d**, **2e**, **2f**, **6c** and **6d**, except that the signals at δ 7.33, 7.55, 7.09, 7.37, 6.41 and 6.53 corresponding to H-1 respectively of the latter compounds are missing in the spectra of their respective dimers. A similar resemblance of the ^{1}H NMR spectra of **5a** and **5b** with those of their respective monomeric counterparts **4a** and **4b** is discernible, except that the spectra of **5a** and **5b** are devoid of the signals at δ 7.18 and 7.54 of **4a** and **4b**, respectively, corresponding to their H-8. The above spectral data show while the site of dimerization in **3c**, **3d**, **3e**, **3f**, **7c** and **7d** is 1,1′, as in **3a**^{2}, **3b**^{2}, **7a**^{1} and **7b**^{1}, that in **5a** and **5b** is 8,8′. The appearance of the signals for H-6 and H-6′ of **5a** and **5b** as clear doublets at δ 7.40 (J=9Hz) and 7.60 (J=8Hz), respectively, corresponding to coupling between two *ortho* aromatic protons compared to those of the H-6 of **4a** (δ 7.14, dd, J_1=9Hz and J_2=2.8Hz) and **4b** (δ 7.30, dd, J_1=9.4Hz and J_2=2.6Hz) exhibiting coupling with both *ortho* (H-5) and *meta* (H-8) protons lent further support for the 8,8′-coupling in **5a** and

5b. Similarly, the collapse of the doublet signals of H-3 of **6c** (δ 6.33, J=3Hz) and **6d** (δ 6.70,J=2.5Hz) corresponding to *meta*-coupling with H-1 to singlets in **7c** (δ 6.55;H-3,H-3′) and **7d** (δ 6.60;H-3,H-3′) affirmed the site of dimerization in the latter compounds to be at the 1,1′-position. The ^{1}H NMR spectra of **3c**, **3d**, **3e**, **3f**, **5a**, **5b**, **7c** and **7d** also revealed some other interesting features which, in the light of our earlier observations with **3a**[2], **3b**[2], **7a**[1], **7b**[1] and related compounds[3], are diagnostic of the site of dimerization of this type of compounds. Construction of Dreiding models

Table 1. ^{1}NMR Spectral Data of **3c**, **3d**, **3e**, **3f**, **5a**, **5b**, **7c**, **7d**, **2c**, **2d**, **2e**, **2f**, **4a**, **4b**, **6c** and **6d**.

	Chemical shifts : δ values (multiplicity; J in Hz)						
	H-1 (H-1′)	H-3 (H-3′)	H-5 (H-5′)	H-6 (H-6′)	H-8 (H-8′)	H-9(H-9′)/ H_2-9(H_2-9′)	H-10(H-10′)/ H_2-10(H_2-10′)
3c[a]	-	-	9.48(d;9)	7.21(dd; 9,3)	7.26(d;3)	7.33(d;9)	7.03(d;9)
2c[b]	7.33(s)	-	9.33(d; 10)	7.30(dd; 10,3)	7.35(d;3)	7.77(d;8)	7.55(d;8)
3d[b]	-	-	9.73(d;8)	7.44-7.59(4H,m; (H-6,H-6′,H-8,H-8′)		7.36(d;8)	7.04(d;8)
2d[b]	7.55(s)	-	9.38(d; 10)	7.55(dd; 10,3)	7.80(d;3)	7.90 (2H,s; H-9 and H-10)	
3e[a]	-	-	9.21(s)	-	7.20(s)	7.31(d;9)	6.93(d;9)
2e[b]	7.09(s)	-	8.91(s)	-	7.22(s)	7.37 (2H,s; H-9 and H-10)	
3f[b]	-	-	9.35(s)	-	7.44(s)	7.32(d;8)	6.89(d;8)
2f[b]	7.37(s)	-	9.23(s)	-	7.52(s)	7.55(d;9)	7.49(d;9)
5a[a]	7.05(s)	-	9.58(d;9)	7.40(d; 9)	-	6.98(d;9)	7.37(d;9)
4a[b]	7.01(s)	-	9.41(d;9)	7.14(dd; 9,2.8)	7.18(d; 2.8)	7.46(d;8.8)	7.53(d;8.8)
5b[b]	7.04(s)	-	9.75(d;8)	7.60(d;8)	-	7.04(d;8)	7.44(d;8)
4b[b]	7.04(s)	-	9.53(d; 9.4)	7.30(dd; 9.4,2.6)	7.54(d; 2.6)	7.57 (2H,s; H-9 and H-10)	
7c[a]	-	6.55(s)	8.23(d; 8.5)	6.66-6.68 (m)	6.63(d; 1.5)	2.48-2.50 (m)	2.28-2.30 (m)
6c[b]	6.41(d; 3)	6.33(d; 3)	7.93(d;9)	6.72-6.75 (2H,m; H-6 and H-8)		2.71 (4H,s; H_2-9 and H_2-10)	
7d[b]	-	6.60(s)	7.89(d;9)	6.90-6.98 (4H,m; H-6,H-6′,H-8,H-8′)		2.55-2.62 (m)	2.35-2.45 (m)
6d[b]	6.53(d; 2.5)	6.70(d; 2.5)	7.87(d;9)	6.93-6.96 (2H,m; H-6 and H-8)		2.77 (4H,s; H_2-9 and H_2-10)	

Table 1 (contd.)

	Chemical shifts : δ values (multiplicity; assignments) OH/OAc/OMe/-OCH_2O-		OH/OAc/OMe/-OCH_2O-
3c[a]	7.87 and 8.57 (each s; 4xOH), 4.09 (s; 4xOMe)	**2c**[b]	8.0 and 8.65 (each s; 2xOH), 4.0 and 4.05 (each s; 2xOMe)
3d[b]	1.92 (s, OAc at C-2 and C-2′), 2.36 (s; OAc at C-7 and C-7′), 4.08 (s; 4xOMe)	**2d**[b]	2.38 and 2.45 (each s; 2xOAc), 4.0 and 4.05 (each s; 2xOMe)
3e[a]	7.84 and 7.94 (each s; 4xOH), 4.09 (s; 4xOMe), 4.14 (s; 2xOMe)	**2e**[b]	5.90 (s; 2xOH), 3.93, 4.0 and 4.04 (each s; 3xOMe)
3f[b]	1.92 (s; OAc at C-2 and C-2′), 2.38 (s; OAc at C-7 and C-7′), 4.08 (s; 4xOMe), 4.12 (s; 2xOMe)	**2f**[b]	2.40 (s; 2xOAc), 4.02, 4.03 and 4.04 (each s; 3xOMe)
5a[a]	7.89 (s; 2xOH), 4.18 (s; 2xOMe), 6.16 (s; 2x-OCH_2O-)	**4a**[b]	5.06 (s; OH), 4.11 (s; OMe), 6.08 (s; -OCH_2O-)
5b[b]	1.84 (s; OAc at C-7 and C-7′), 4.24 (s; 2xOMe), 6.16 (s; 2 x -OCH_2O-)	**4b**[b]	2.37 (s; OAc), 4.12 (s; OMe), 6.12 (s; -OCH_2O-)
7c[a]	8.10 and 8.42 (each s; 4xOH), 3.58 (s; OMe at C-2 and C-2′)	**6c**[b]	5.47 and 5.11 (each s; 2xOH), 3.78 (s; OMe)
7d[b]	2.25 and 2.29 (each s; 4xOAc), 3.65 (s; OMe at C-2 and C-2′)	**6d**[b]	2.28 and 2.29 (each s; 2xOAc), 3.80 (s; OMe)

[a] Spectra were run in d_6-acetone; [b] Spectra were run in $CDCl_3$.

of these dimers shows that in the most preferred conformation of each of these compounds the two monomeric halves are almost perpendicular to each other so that H-10, H-10′ of **3c**, **3d**, **3e** and **3f**, and H_2-10, H_2-10′ of **7c** and **7d** fall in the shielding zones of the neighbouring rings C′ and C respectively. The observed upfield shifts of H-10, H-10′ of **3c**, **3d**, **3e** and **3f**, and of H_2-10, H_2-10′ of **7c** and **7d** compared with the chemical shifts of the corresponding protons of their respective monomeric counterparts can thus be accounted for only in terms of 1,1′-coupling in all these compounds. The rings C′ and C of these compounds also exert long range shielding effect on H-9, H-9′ of **3c**, **3d**, **3e** and **3f** and on H_2-9, H_2-9′ of **7c** and **7d**. As a result, these protons are slightly shifted upfield compared with the corresponding protons of their respective monomers. Similar upfield shifts of H-9, H-9′, and H-10, H-10′ of **5a** and **5b** caused by the shielding effects of their rings A′ and A compared with the normal chemical shifts of the corresponding protons in the respective monomers **4a** and **4b** are in conformity with 8,8′-coupling in **5a** and **5b**. The two acetate methyls at C-2 and C-2′ of **3d** (δ 1.92) and **3f** (δ 1.92), and the methoxy methyls of **7c** (δ 3.58) and **7d** (δ 3.65) at the same positions likewise also fall in the shielding zones of their respective rings C′ and C, and consequently are shifted upfield compared with the normal

chemical shifts of these protons of their respective monomers. The relatively high field resonance of the two acetate methyls (δ1.84) of **5b** at C-7 and C-7′ is likewise due to similar shielding effects of its rings A′ and A. This type of diamagnetic anisotropic effect of the neighbouring aromatic rings on the acetoxyl and methoxyl groups attached to the carbon atoms *ortho* to the site of dimerization is a well-documented feature in similar[1-3] and related biaryl compounds[17,18].

The structures of the dimers **3c**, **3e** and **7c** were further supported by the ^{13}C NMR spectral data of their respective acetyl derivatives **3d**, **3f** and **7d**, and that of **5a** by the δ_C values of the compound itself (Table 2). The degree of protonation of each carbon atom was determined by DEPT experiments, and the assignments of the carbon chemical shifts were made by comparison with the δ_C values of their respective monomers[10,11,14,15]. The appearance of the carbon signals in the ^{13}C NMR spectra of the above compounds, which corresponded to just half the number of carbon atoms present in their

Table 2. ^{13}C NMR Spectral Data of **3d**, **3f**, **5a**, **7d**, **2d**, **2f**, **4a** and **6d**

C‡	δ_C (ppm)							
	3d[a]	**3f**[a]	**5a**[b]	**7d**[a]	**2d**[a]	**2f**[a]	**4a**[a]	**6d**[a]
1(1′)	121.92	122.63	102.25	121.39	117.12	116.98	101.85	111.91
2(2′)	145.15	144.69	141.78	156.46	144.89	144.30	140.93	158.74
3(3′)	142.53	142.46	139.72	104.34	143.18	143.03	138.66	107.36[c]
4(4′)	152.42	152.17	148.22	147.75	152.45	152.12	147.24	148.37[c]
4a(4a′)	123.21	121.91	121.05	119.38	123.01	122.34	120.03	119.60
4b(4b′)	129.22	129.37	125.05	129.94	129.42	129.61	124.89	129.58
5(5′)	129.22	109.48	129.53[c]	127.33	128.86	109.09	128.99	127.15[d]
6(6′)	119.63[c]	150.38	117.66	120.52[c]	119.59[c]	150.04	116.21	120.88[d]
7(7′)	149.01	139.76	154.28	148.83	148.72	139.36	152.95	148.99[c]
8(8′)	121.0[c]	121.07	123.94	119.02[c]	120.87[c]	120.91	111.41	119.27[d]
8a(8a′)	133.78	128.63	134.34	140.08[d]	133.71	128.37	133.78	141.54[e]
9(9′)	127.0	126.60	124.15	29.22	126.87[d]	126.27	125.36	29.51[f]
10(10′)	125.42	123.14	128.05[c]	26.64	127.38[d]	124.87	127.59	30.16[f]
10a(10a′)	127.59	127.48	128.34	140.70[d]	127.42	127.26	128.77	139.79[e]
$-OCH_2O-$	-	-	102.61	-	-	-	101.52	-
OMe	60.98	61.05	60.13	55.53	61.18	61.08	59.85	55.39
	59.98	60.10			60.05	60.06		
		55.78				55.72		
OCOMe	169.77	169.32	-	169.48	169.22	169.01	-	169.53
	168.54	168.45		168.96	169.55	20.59		169.01
	20.90	20.44		21.38	20.77			21.40
	19.91	19.95		21.0	21.27			21.16

[a] Spectra were run in $CDCl_3$ and the chemical shifts were measured with $\delta_{(TMS)} = \delta_{(CDCl_3)} + 76.9$ ppm.

[b] Spectrum was run in d_6-acetone and the chemical shifts were measured with $\delta_{(TMS)} = \delta_{(d_6\text{-acetone})} + 29.6$ ppm.

[c,d,e,f] Values in each column are interchangeable.

‡ Numbers in the first bracket refer only to the dimers.

respective molecular formulae is again in conformity with their symmetrical dimeric formulations. Further, except for C-1, C-1′ and C-10, C-10′, the signals for all the carbon stoms of **3d**, **3f** and **7d** appeared essentially at the same positions as those for the corresponding carbon atoms of their respective monomers **2d**, **2f** and **6d**. Similarly, except C-8, C-8′ and C-9, C-9′, all the carbon atoms of **5a** resonated almost at the same positions as the corresponding carbon atoms of **4a**. The signals for the protonated C-1 of **2d** (δ_C 117.12), **2f** (δ_C 116.98) and **6d** (δ_C 111.91) are replaced by the relatively downfield nonprotonated carbon signals at δ_C 121.92, 122.63 and 121.39 in the spectra of **3d**, **3f** and **7d**, respectively. Similarly, the signal for the protonated C-8 of **4a** (δ_C 111.41) is replaced by the nonprotonated carbon signals at δ_C 123.94 in the spectrum of **5a**. These observations provide further evidence for the fact that while **3c**, **3e** and **7c** are symmetrical dimers of **2c**, **2e** and **6c**, respectively, linked at their C-1, **5a** is also a symmetrical dimer of **4a** joined through its C-8. Further, the upfield shifts of C-10, C-10′ of **3d**, **3f** and **7d** by *ca* 1.5-2.5 ppm compared with the δ_C values of their respective C-9, C-9′ which appeared essentially at the same positions as the C-9 of **2d**, **2f** and **6d** respectively, are typical of 1-substituted phenanthrene derivatives[1,2,19a], the substituents in these compounds being their respective monomeric units. Similarly, the upfield shifts of C-9, C-9′ of **5a** by 1.21 ppm compared with its C-10, C-10′ resonance which is almost the same as that of C-10 of **4a** is again a convincing evidence for the presence of a substituent[3,19b] at C-8 in **5a** in the form of its monomeric unit. The structure of **1a** was also established to be the 1,1′-dimer of β-naphthol from its various spectral data.

EXPERIMENTAL

M.p.s are uncorrected. UV spectra were measured in 95% aldehyde-free EtOH and IR spectra were run in KBr discs. ^{1}H NMR spectra were recorded in a Bruker 300 MHz supercon instrument using TMS as the internal standard. ^{13}C NMR were run at 75 MHz in the same instrument using the same internal standard. Chemical shifts were measured in δ ppm. Mass spectra were recorded at 70 eV using direct inlet system and the figures in the first bracket attached to m/z values represent relative intensities of peaks. Silica gel (100-200 mesh) was used for chromatography and silica gel G for TLC. All analytical samples were routinely dried over P_2O_5 for 24 hr *in vacuo* and were tested for purity by TLC and MS. Dry Na_2SO_4 was used for drying organic solvents and petrol used had b.p. 60-80°.

Oxidation of coelonin (**6a**) *and β-naphthol with PMA in aqueous acetone solution.* A solution of **6a** (0.05 g) and β-naphthol (0.05 g) in aq. acetone (20 ml) were separately stirred with 0.4 g and 0.65 g respectively of PMA at room temperature for 7 hr. The mixture in each case was extracted with Et_2O, dried and the solvent removed. The residues were separately chromatographed to give mostly unchanged **6a** and β-naphthol and only small amounts of **7a** (0.01 g) and **1a** (0.015 g). No perceptible improvement of yields in both the cases was observed by making the reaction medium ammoniacal or by heating at *ca* 90° for 6 hr.

Oxidation of β-naphthol, coelonin (**6a**), *flavanthrinin* (**2a**), *nudol* (**2c**), **2e**, *cirrhopetalin* (**4a**), *lusianthridin* (**6c**) *and* **6e** *with PMA on silica gel support.* 0.05 g each of β-naphthol, **6a**, **2a**, **2c**, **2e**, **4a**, **6c** and **6e** were separately adsorbed uniformly on 10 g portions of silica gel (100-200 mesh) previously impregnated with aq. methanolic solution of 0.66 g, 0.4 g, 0.4 g, 0.35 g, 0.32 g, 0.35 g, 0.4 g, and 0.32 g of PMA, respectively (the silica gel after uniformly impregnated with PMA was dried in vacuum desiccator for 1 hr), and the solvent was removed by keeping the materials in vacuum desiccator for 30 min. The materials were then separately placed on beds of fresh silica gel (*ca* 20 g) in small chromatographic columns, and kept soaked with petrol for 5-6 hr. The silica gel layer containing PMA and phenolic compounds gradually turned intense blue in colour. The columns were then washed with petrol-EtOAc (3:1), when the organic materials migrated out (with small amounts of inorganic substances), leaving behind most of the inorganic materials adsorbed in silica gel in the columns. The eluates from the columns were separately washed with water, dried and the solvent removed to give **1a** (0.0489 g; 98.5%), **7a** (0.0398 g; 80%), **3a** (0.0423 g; 85%), **3c** (0.0398 g; 80%), **3e** (0.0408 g; 82%), **5a** (0.0418 g; 84%), **7c** (0.0388 g; 78%) and **3e** (0.0099 g; 20%) as the oxidation products of β-naphthol, **6a**, **2a**, **2c**, **2e**, **4a**, **6c** and **6e**. In the oxidation of **6e**, were also obtained 0.0124 g of **2e** and *ca* 0.023 g unchanged **6e**. Oxidation of **6e** (0.05 g) with PMA (0.65 g) by the above method gave **3e** (0.0396 g; 80%) as the sole product. **6f** (0.05 g), on similar oxidation with PMA (0.24 g), afforded *ca* 0.01 g each of **3e**, **2e**, **6e** and unchanged **6f**. The same oxidation of **6f** with PMA (0.65 g) gave **3e** (0.031 g; 80%).

1a, crystallized from petrol-EtOAc, m.p. 250°. (Found : C, 83.89; H, 4.87. $C_{20}H_{14}O_2$ requires : C, 83.91; H, 4.89%). λ_{max} nm : 218 and 230 (log ε 4.20 and 4.43); (in EtOH-0.1M NaOH) : 208, 228 and 252 (log ε 4.53, 4.23 and 3.98); ν_{max} (cm^{-1}) : 3400 and 3500 (OH), 1620, 1600, 830, 820, 780 and 750 (aromatic nucleus); ^{1}H NMR : δ 8.0 (2H, d, J=8.7Hz; H-4,H-4′), 7.88 (2H, br.d, J=8.2Hz; H-5,H-5′), 7.16 (2H, d, J=8.7Hz; H-3,H-3′), 7.28-7.40 (6H, m; H-6, H-6′, H-7,H-7′ and H-8,H-8′) and 5.04 (2H,s; 2xArOH); ^{13}C NMR : δ_C 110.65 (C-3, C-3′), 117.61 (C-1, C-1′), 123.91 (C-8, C-8′), 124.06 (C-6, C-6′), 127.76 (C-7, C-7′), 128.27 (C-4, C-4′), 129.31 (C-9, C-9′), 131.29 (C-5, C-5′), 133.25 (C-10, C-10′) and 152.59 (C-2, C-2′); MS (EI) m/z (rel.int.) : 286 (M^+, 100), 268 (10.2), 257 (19.7), 239 (21.1), 229 (12), 228 (12), 226 (13), 202 (6), 144 (17), 134 (11.9), 120 (48.8) and 115 (54.3).

7a, crystallized from petrol-EtOAc, m.p. 285°; tetraacetate (**7b**), m.p. 180°; **3a** crystallized from petrol-EtOAc, m.p. 296°; tetraacetate (**3b**), m.p. 282°. **7a**, **7b**, **3a** and **3b** were identified as flavanthrin, flavanthrin tetraacetate, cirrhopetalanthrin and cirrhopetalanthrin tetraacetate, respectively, by direct comparison (m.p., m.m.p, TLC and superimposable IR spectra) with authentic samples.

3c, crystallized from petrol-EtOAc, m.p. 250°. (Found : C, 71.34; H, 4.81. $C_{32}H_{26}O_8$ requires : C, 71.37; H, 4.83%). λ_{max} nm : 213, 265, 311 and 350 (log ε 4.67, 5.02, 4.31 and 3.62); (in EtOH-0.1M NaOH); 224, 270 and 273 (log ε 4.56, 4.91 and 4.92); ν_{max} (cm^{-1}) : 3400 (OH), 1610, 1570, 850, 830 and 780 (aromatic nucleus); MS (EI) m/z (rel.int.) : 538 (M^+,100), 269 (37), 253 (15), 241 (10), 224 (22), 210 (12), 189 (11), 169 (19), 146 (18) and 132 (39); CI : 539.1706 [538.168 (M^+) + 1.0078]; tetraacetate (**3d**), crystallized from petrol-EtOAc, m.p. 150°. (Found : C, 67.95; H, 4.80. $C_{40}H_{34}O_{12}$ requires : C, 67.99; H, 4.82%). λ_{max} nm : 218, 262, 296 and 309 (log ε 4.62, 4.93, 4.35 and 4.39); ν_{max} (cm^{-1}) : 1255 and 1760 (OAc), 1610, 885, 830 and 790 (aromatic nucleus); MS (EI) m/z (rel.int.) : 706 (M^+,15), 664 (82), 622 (100), 580 (65), 538 (30) and 269 (68); CI : 707.21283 [706.20503 (M^+) + 1.0078].

3e, crystallized from petrol-EtOAc, m.p. 270°. (Found : C, 68.18; H, 4.98. $C_{34}H_{30}O_{10}$ requires : C, 68.22; H, 5.02%). λ_{max} nm : 224, 239, 264, 318, 347 and 365 (log ε 4.63, 4.64, 5.03, 4.32, 3.82 and 3.95); (in EtOH-0.1M NaOH) : 272, 275 and 376 (log ε 4.91, 4.91 and 3.94); ν_{max} (cm^{-1}) : 3400 (OH), 1630, 870 and 775 (aromatic nucleus); MS (EI) m/z (rel.int.) : 598 (M^+, 99.2), 300 (21.8), 299 (20.73), 283 (47.6), 271 (28.5), 254 (26.7), 239 (26.2), 225 (22.5), 211 (24.1), 197 (21.8), 183 (24.1), 169 (20.6), 155 (19.8), 140 (13), 125 (20.5), 105 (10.2) and 55 (100); CI : 599.1917 [598.1839 (M^+) + 1.0078]; tetraacetate (**3f**), crystallized from petrol-EtOAc, m.p. 180°. (Found : C,

65.76; H, 4.92. $C_{42}H_{38}O_{14}$ requires : C, 65.79; H, 4.96%). λ_{max}nm : 219, 262, 304 and 317 (log ε 2.78, 3.10, 2.57 and 2.61); $\nu_{max}(cm^{-1})$: 1230 and 1765 (OAc), 1620, 870, 850 and 780 (aromatic nucleus); MS (EI) m/z (rel.int.) : 766 (M^+,57.6), 724 (90.5), 682 (71.8), 640 (60.8), 598 (43.2), 283 (65.2), 271 (12.9), 254 (11) and 57 (100). CI : 767.2339 [766.2261 (M^+) + 1.0078].

5a, crystallized from petrol-EtOAc, m.p. 260°. (Found : C, 71.87; H, 4.09. $C_{32}H_{22}O_8$ requires : C, 71.91; H, 4.12%). λ_{max}nm : 250 (log ε 4.83); (in EtOH-0.1M NaOH) : 258 (log ε 4.92); $\nu_{max}(cm^{-1})$: 3465 (OH), 1610, 1590, 830, 810 and 770 (aromatic nucleus); MS (EI) m/z (rel.int.) : 534 (M^+,100), 268 (17.94), 267 (58.7), 251 (49.6), 239 (7.5), 222 (96.8), 200 (8), 149 (14.3), 137 (67) and 125 (8.1); diacetate (**5b**), crystallized from petrol-EtOAc, m.p. 230°. (Found : C, 69.87; H, 4.16. $C_{36}H_{26}O_{10}$ requires : C, 69.90; H, 4.20%). $\nu_{max}(cm^{-1})$: 1265 and 1760 (OAc), 1620, 1590, 850 and 800 (aromatic nucleus); MS (CI) : 619.1537 [618.1459 (M^+) + 1.0078].

7c, crystallized from petrol-EtOAc, m.p. > 300°. (Found : C, 74.65; H, 5.36. $C_{30}H_{26}O_6$ requires : C, 74.69; H, 5.39%). λ_{max}nm : 210, 275 and 300 (log ε 4.71, 4.47 and 4.30); (in EtOH-0.1M NaOH) : 220 and 285 (log ε 4.87 and 4.48); $\nu_{max}(cm^{-1})$: 3400 (OH), 1580, 850, 810 and 740 (aromatic nucleus); MS (EI) m/z (rel.int.) : 482 (M^+,100), 241 (74.8), 227 (8.9), 211 (6.6), 197 (9.7), 181 (10.2), 171 (20.9), 165 (5.7), 157 (21.9), 143 (5.7) and 129 (12.7); tetraacetate (**7d**), crystallized from petrol-EtOAc, m.p. 170°. (Found : C, 70.10; H, 5.20. $C_{38}H_{34}O_{10}$ requires : C, 70.15; H, 5.23%). λ_{max} nm : 210 and 278 (log ε 4.72 and 4.54); $\nu_{max}(cm^{-1})$: 1245 and 1750, 1770 (OAc), 1600 and 830 (aromatic nucleus); MS (EI) m/z (rel.int.) : 650 (M^+, 1.4), 608 (2.4), 566 (5.5), 524 (6.7), 482 (12.3), 283 (2.4), 256 (7), 241 (100), 227 (5.4), 211 (9.1), 197 (8.4), 174 (13.5), 157 (22), 145 (10), 129 (7) and 115 (6.7).

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