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PHOTOCHEMICAL ISOMERIZATION OF ISOFLAVONES TO ISOCOUMARINS

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Abstract—Irradiation of 2-phenylisoflavones through a Pyrex filter gave 3,4-diphenylisocoumarins and phenanthro[9,10-c]isocoumarins, of which the latter is formed via photochemical oxidation of the former. Mechanism involving the indanone oxide as intermediate was proposed. Photolysis of 2-methylisoflavones or flavone through a Pyrex filter produced no reaction.

Although the photochemical behavior, particularly isomerization of the 4-pyrones[1-3] and pyrylium salts[4,5] has received much attention in recent years, relatively little is known about the photochemistry of the chromone system, the benzo analogue of 4-pyrones. Matsuura, *et al.*[6] found the photorearrangement of the flavones to indandiones. The photochemistry of chromanones, the dihydro derivatives of chromone, was investigated extensively and evidence was presented which demonstrated that the photoisomerization of these compounds proceeds through their enol form.[7,8]

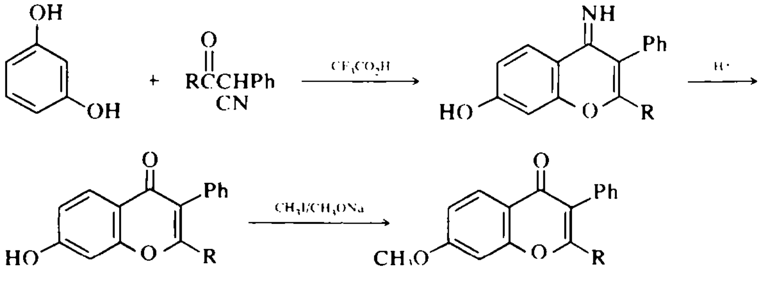
As part of our continuing studies dealing with the photochemistry of heterocyclic 2,5-dienones,[2,9,10] we have undertaken an investigation of the excited behavior of the isoflavones (**1**).[11] Extending our studies to this system, we have found that the photoreactivity of isoflavones is sensitive to the extent of substitution in the heterocyclic ring.

RESULTS AND DISCUSSION

7-Hydroxyisoflavones (**1** and **2**) were prepared by condensation-cyclization of resorcinol with α-acylbenzylcyanide in trifluoroacetic acid to the imine, followed by acid hydrolysis.[12] Methylation of **2** with methyl iodide yielded **3**. The structure assigned to the isoflavones rests on their spectral data and the chemical reaction of **2**. Their mass spectra showed two intense peaks, one of which corresponds to the parent ion and the other of which is consistent with the fragment $[M-CO]^+$. Their UV spectra exhibited strong absorption at 240–270 and 335 nm, a pattern indicative of isoflavones.[13] Confirmative evidence on the structure of isoflavone was obtained from oxidative degradation of **2** by permanganate, from which benzil, benzoic acid and 2,4-dihydroxybenzoic acid were identified.

Irradiation of 2-phenyl-7-methoxyisoflavone, **3**, through a Pyrex filter using a medium-pressure mercury lamp was carried out in methanol under nitrogen. Three products were formed, two of which were identified 3,4-diphenyl-6-methyoxyisocoumarin, **4**, and phenanthro - [9,10 - c] - 6 - methoxyisocoumarin, **6**. The third product whose yield never exceeded 10% in any photolysis, appeared to have the structure of either 9 - (2 - carbomethoxy - 5 - methoxyphenyl)phenanthrene or of 9 - (3 - methoxyphenyl)phenanthryl - 10 - acetate on the basis of its spectra.[†]

The isocoumarin, **4**, which was isolated from photolysis by silica gel column chromatography was identified on the basis of spectral properties and chemical reactions. Mass spectroscopy indicated that **4** was an isomer of the starting material and showed the strong peaks due to dehydrogenation and decarbonylation from the parent peak. The UV spectrum exhibited an intense band at 267 nm and a less intense band at 335 nm and its IR spectrum showed the CO stretch at 1760 cm^{-1}. Cold methanolic alkali on this product appeared to form a yellow solution of salt from which the heterocyclic lactones was regenerated by prompt treatment with dil. hydrochloric acid. These results clearly indicate that this



1: R = CH$_3$
2: R = Ph
3: R = Ph

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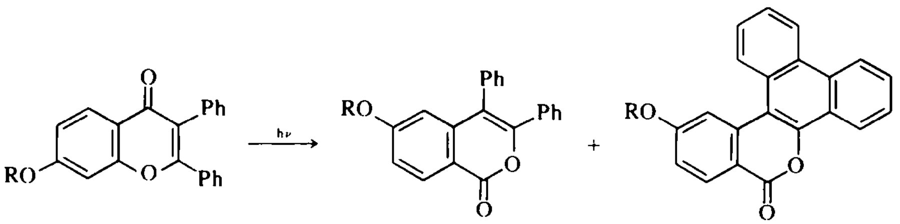
[†] M.p. 134.0–134.5: IR (KBr) 1730, 1610, 1500, 1380, 1290, 1210, 1100, 1015, 850, 825, 760 cm^{-1}; NMR (CDCl$_3$) δ 3.56 (s, 3H), 3.97 (s, 3H), 7.0–8.3 (m, 11H), 8.5–8.7 (m, 1H); UV (MeOH) λ_{max} 252 (log ϵ 3.88), 260 (3.87), 280 (3.81), 300 (3.63), 310 (3.67), 340 (3.19), 358 nm (3.07); mass spectrum at *m/e* (relative intensity) 343 (25), 342 (100, M$^+$), 312(10), 311(46), 239(16). (Found: C, 81.02; H, 5.38; O, 13.75. Calc. for $C_{23}H_{18}O_3$: C, 80.92; H, 5.31; O, 14.06%).

The presence of two OMe groups strongly suggests preference of 9 - (2 - carbomethoxy - 5 - methoxyphenyl)phenanthrene over 9 - (3 - methoxyphenyl)phenanthryl - 10 - acetate as the structure of third product. We thank a referee for suggestion on the structure and the mechanism.



3: R = Me
2: R = H

4: R = Me
5: R = H

6: R = Me
7: R = H

photoproduct has the structure of either coumarin or isocoumarin.[14] Structural preference of the isocoumarin rather than the coumarin was achieved by isolation of α - (2 - carboxyl - 5 - methyoxy)phenyldeoxybenzoin from prolonged exposure of this photoproduct to methanolic alkali and acidification of the resulting solution with dil hydrochloric acid. This result confirmed the structure of photoproduct to be **4** because similar treatment on the coumarin should give a cinnamic acid derivative.[14,15]

The structure of **6** was deduced from its elemental analysis, spectral data and the chemical reaction. The mass spectrum of **6** displayed the parent peak at *m/e* 326, whereas the parent peak of **4** was at *m/e* 328. The UV spectrum of **6** in methanol showed band at 257, 278(sh), 288(sh), 300(sh), 330 and 351 nm, a pattern similar to that of phenanthrene.[16] Its IR spectrum exhibited a strong carbonyl stretch at 1710 $\mathrm{cm^{-1}}$, in agreement with the structure of phenanthroisocoumarin rather than phenanthrocoumarin.† In addition to the UV similarity noted above, the NMR spectrum of **6** showed a Me singlet at δ 3.75, aromatic protons at δ 6.7–8.0 and 8.6–8.8. The multiplet at δ 8.6–8.8 can be assigned to the resonating protons at C-4 and C-5 of the phenanthrene moiety because of marked deshielding by all three benzene rings.[17] The acid hydrolysis of **6** in methanol afforded 9 - hydroxy - 10 - (3 - methoxy - 6 - carboxyphenyl) - phenanthrene.‡

When a dilute solution of 2 - phenyl - 7 - hydroxyisoflavone, **2**, in methanol was irradiated through a Pyrex filter, the conventional isolation procedures gave 3,4 - diphenyl - 6 - hydroxyisocoumarin, **5** and phenanthro[9,10-c]-6-hydroxyisocoumarin, **7**. Treatment of **5** with alkali formed a yellow solution of the ring opened product from which **5** was regenerated upon addition of acid. The acid hydrolysis of **7** also appeared to give 9 - hydroxy - 10 - (3 - hydroxy - 6 - carboxy)phenanthrene as in the case of **6**.

Irradiation of 2-methylisoflavone or 2-methyl-7-hydroxyisoflavone, **1**, in methanol with a medium-pressure mercury lamp equipped with either a Pyrex or Vycor filter resulted in the recovery of the starting materials. Flavone was also not affected by the prolonged UV irradiation. While at present we cannot explain the difference of photoreactivity among isoflavones against light, the photoreaction of 4-pyrones has been found to be remarkably dependent on the number and position of substituents present in the pyrone ring.[2,5] The similar photochemical reactivity sensitive to the extent of substituent was also observed with the 4-thiopyrones[9] and 4-pyridones.[10]

The products distribution during the UV irradiation of **2** was followed by comparing the R_f values of the reaction mixture with those of authentic samples on silica gel TLC plates. At very short period of time **4** was sole product¶ and **6** appeared to accumulate with time. The hydroxy compound, **5**, behaved similarly against UV irradiation. These results suggest that the isocoumarin is an initial product and is oxidized to the phenanthro[9,10-c]isocoumarin. UV irradiation of either **4** or **5** in methanol through a Pyrex filter under nitrogen gave **6** or **7**, respectively. Prolonged irradiation resulted in the formation of polymeric materials. Photolysis of either **6** or **7** under nitrogen did not form the isocoumarin (**4** or **5**), but produced only polymeric compound. 9 - (3 - Methoxyphenyl) - phenanthryl - 10 - acetate† was not affected by the prolonged UV irradiation. These results clearly indicate that the isocoumarin is a precursor for the formation of the phenanthro[9,10-c]isocoumarin.

The formation of the phenanthro[9,10-c]isocoumarins (**6** and **7**) might be rationalized by the photocyclization of the isocoumarins (**4** and **5**) to the dihydro intermediate, followed by the oxidation to the phenanthro[9,10-c]isocoumarins, since oxidative photocyclization of *cis*-stilbene and related systems to phenanthrene derivatives is studied extensively.[19] Irradiation of **2** in the presence of iodine did not furnish **5**, but afforded **7** and another unidentified product. Photolysis of **2** in methanol exposed to air gave only polymeric compound. Iodine appeared to accelerate the oxidative photocyclization since iodine served a good oxidizing reagent of dihydrophenanthrene.[18] **7** was not formed from **2** in aerobic methanol because of the photoisomerization of **2** to **5** was quenched by oxygen. The similar photooxidative cyclization was observed in 2,3,5,6 - tetraphenyl - 4 - pyrone.[2]

A mechanism consistent with the observed rearrangement of the hindered isoflavones (**2** and **3**) is outlined in the following scheme. The hindered isoflavone initially is photoisomerized to the indenone oxide, **8**, followed by the photochemical rearrangement to the isocoumarain which is then oxidized to phenanthro[9,10-c]isocoumarin. The photoisomerization of the epoxyindanones to the isocoumarin was investigated by Ullman[20] and Zimmerman[21] who also found yellow to red coloration due the

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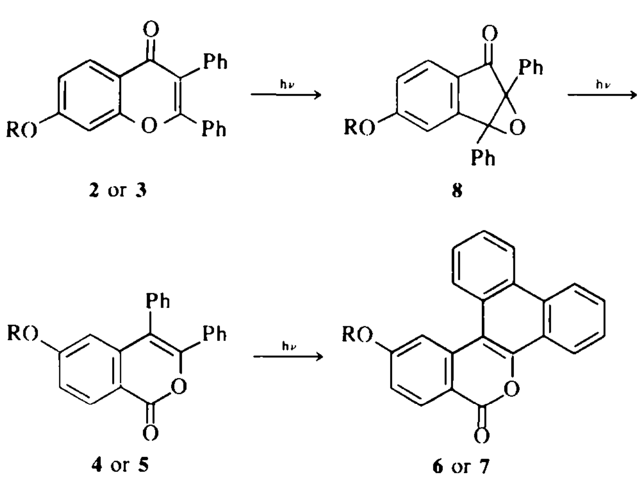
†The spectral data could not exclude the coumarin as the structure of the photoproduct. The fact that **4** is a precursor for the formation of **6** as shown in the text indicates that **4** has the structure of isocoumarin because the thermal or/and photochemical isomerization of isocoumarin to coumarin and vice versa is not feasible.§

‡The possible alternative structures are phenanthro[9,10-c]-6-methoxycoumarin for **6** and 9 - carboxyl - 10 - (3 - methoxy - 6 - hydroxyphenyl)phenanthrene for the acid hydrolysis product of **6**, respectively. These assignments are, however, ruled out from the fact that **6** is formed from the photooxidation of **4** (see text).

§Photodimerization of coumarins is studied extensively.[18]

¶The unidentified product described in text and previous footnote appeared to be an initial product, judging from TLC. UV irradiation of either **4** or **6** did not form this unidentified product. Photolysis of this unidentified compound also gave neither **4** nor **6**.



formation of the pyrylium-3-oxide.[22] The colored pyrylium-3-oxide which reverts to the epoxyindanone, was eliminated as the precursor of the isocoumarin.[21,22] Apparent yellow to red coloration was not observed during the photolysis of either 2 or 3. An attempt to trap a transient pyrylium-3-oxide with dimethyl acetylene dicarboxylate in the photolysis of 3 was unsuccessful. Photolysis of 3 through a Pyrex filter was monitored by visible absorption spectroscopy. Examination of the visible spectra, however, did not show an absorption band corresponding to the pyrylium-3-oxide which was detected in the photolysis of 2,3-diphenylindenone oxide.[20] Oxidative photocyclization of 3,4-diphenyliscoumarin to the phethanthro[9,10-c]isocoumarin was confirmed by independent irradiation of the former in the presence of iodine.

EXPERIMENTAL

M.ps were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory, Kyoto University, Kyoto, Japan. PMR spectra were recorded with Jeol PS-100 and Varian T-60A spectrometers, with TMS as an internal standard. Mass spectra were obtained on a Hitachi RMU-6L spectrometer at 70 eV unless otherwise noted, IR spectra were taken with a Hitachi Model 123 spectrophotometer.

Flavone[23] and 2-methylisoflavone[24] were prepared according to the reported methods.

7-Hydroxy-2-methylisoflavone (1). A mixture of 2-phenylacetyl acetonitrile (8 g), resorcinol (5.5 g) and trifluoroacetic acid (12.5 g) was refluxed for 3 hr. After cooled to the room temp, the mixture was poured into water (100 ml) and the ppt was filtered off. These crystals were dissolved into a mixture of conc. HCl (15 ml) and water (50 ml) and refluxed for 24 hr. After the soln was chilled, the ppt was collected on a filter funnel and recrystallized from 80% EtOH to give colorless crystals, m.p. 236–237° (lit.[12] 237–238°); IR (KBr) 3200, 1670, 1590, 1440, 1370, 1225, 1150, 1125, 1070, 980, 860, 780, 750 cm^{-1}; NMR (acetone-d$_6$) δ 2.28 (s, 3H), 2.86 (s, 1H), 6.7–7.8 (m, 8H); UV (MeOH) λ_{max} 237 (log ϵ 4.49), 329 nm (4.87); mass spectrum at *m/e* (relative intensity) 253(20), 252(100, M$^+$), 251(26), 224(84), 223(41). (Found: C, 76.05; H, 4.91; O, 18.96. Calc. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80; O, 19.02%).

7-Hydroxy-2-phenylisoflavone (2). A mixture of α-benzoyl benzylcyanide (22 g) and resorcinol (11 g) in trifluoroacetic acid (25 ml) was refluxed for 4 hr. The mixture was cooled to room temp and poured into water. The ppt was thoroughly washed with water and refluxed in a mixture of conc. HCl (25 ml) and water (200 ml) for 48 hr. The ppt formed was recrystallized twice from 80% EtOH and twice from benzene-acetone (8:2) to give 2 (6 g), m.p. 297–298°: IR (KBr) 3400, 1685, 1600, 1550, 1490, 1440, 1355, 1270, 1130, 1010, 845, 755 cm^{-1}; NMR (acetone-d$_6$) δ 2.95 (s, 1H), 6.7–7.4 (m, 13H), UV (MeOH) λ_{max} 241 (log ϵ 4.77), 337 nm (4.88); mass spectrum at *m/e* (relative intensity) 315(25), 314(100, M$^+$), 313(46), 287(18), 286(73), 257(20). (Found: C, 80.12; H, 4.26; O, 15.00. Calc. for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49; O, 15.27%).

7-Methoxy-2-phenylisoflavone (3). 7-Hydroxy-2-phenylisoflavone (2 g) was dissolved in MeOH (100 ml) containing NaOMe (1 g). To this soln MeI was added under reflux. The mixture was poured into cold water, neutralized with dil. HCl and extracted with ether. After removal of the solvent under vacuum, the residual solid was chromatographed on a silica gel with benzene-EtOAc (9:1) as an eluent. Recrystallization from MeOH gave 3 (0.65 g), m.p. 177–179°; IR (KBr) 1700, 1600, 1545, 1490, 1440, 1360, 1330, 1265, 1155, 1130, 1020, 850, 780 cm^{-1}; NMR (CDCl$_3$) δ 3.82 (s, 3H), 6.7–7.4 (m, 13H); UV (MeOH) λ_{max} 243 (log ϵ 4.75), 270(4.91), 333 nm (4.59); mass spectrum at *m/e* (relative intensity) 329(14), 328(100, M$^+$), 327(43), 301(22), 300(48), 286(67), 228(13), 105(11), 77(14). (Found: C, 80.22; H, 5.01; O, 14.67. Calc. for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91; O, 14.62%).

Irradiation of 7-methoxy-2-phenlisoflavone (3). A soln of 3 (0.3 g) in MeOH (350 ml) was irradiated with a Ushio 500-W medium-pressure mercury lamp using a Pyrex filter. After 48 hr, the solvent was removed *in vacuo* and the resulting residue was chromatographed on silica gel with benzene as eluent. The first fraction, after recrystallization from MeOH, afforded colorless crystals (9%) whose structure was not identified. (For spectral data. see footnote in p. 4). The second fraction gave 4 (25%), m.p. 167–169°; IR (KBr) 1760, 1630, 1590, 1510, 1450, 1275, 1200, 1140, 1105, 1020, 970, 840, 750 cm^{-1}; UV (MeOH) λ_{max} 267 (log ϵ 4.67), 300 nm (3.39); mass spectrum at *m/e* (relative intensity) 328 (16, M$^+$) 327(16), 326(67), 299(21), 298(100), 297(52). (Found: C, 80.19; H, 4.94; O, 14.57. Calc. for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91; O, 14.62%).

From the third fraction 6 was isolated in 51% yield; m.p. 207–209°; IR (KBr) 1700, 1620, 1590, 1515, 1445, 1370, 1285, 1240, 1200, 1160, 1110, 1035, 950, 845, 790, 760 cm^{-1}; NMR (pyridine-d$_5$) δ 3.73 (s, 3H), 6.6–8.0 (m, 9H), 8.6–8.8 (m, 2H); UV (MeOH) λ_{max} 257 (log ϵ 4.54), 278 (sh, 4.28), 288 (sh, 4.17), 300 (sh, 3.98), 330 (2.88), 351 nm (2.32); mass spectrum at *m/e* (relative intensity) 327(27), 326(100, M$^+$), 298(12), 283(34), 255(14), 226(19), 149(16), 113(19), 83(14), 77(27). (Found: C, 80.74; H, 4.15; O, 14.61. Calc. for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32; O, 14.71%).

Irradiation of 7-hydroxy-2-phenylisoflavone (2). Irradiation of 2 (0.5 g) in MeOH (950 ml) was conducted under N_2 for 11 hr using a 300-W Taika medium-pressure mercury lamp equipped with a Pyrex filter. Chromatography on silica gel with benzene-EtOAc (8:2) as an eluent afforded 5 (20%), m.p. 299–301° and 7 (15%), m.p. 305–309°. Their spectral data are as follow: 5, IR (KBr) (3250, 1670, 1610, 1445, 1375, 1320, 1295, 1250, 1170, 1150, 1120, 1010, 970, 855, 820, 790, 760 cm^{-1}; UV (MeOH) λ_{max} 248 (sh, log ϵ 4.69), 254(4.73), 289(4.24), 300 nm (4.19); mass spectrum at m/e (relative intensity) (20 eV) 314 (18, M$^+$), 313(25), 312(100), 285(16), 284(57), 255(14), 226(19). (Found: C, 80.25; H, 4.29; O, 15.06. Calc. for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49; O, 15.27%).

7, IR (KBr) 3350, 1700, 1610, 1445, 1375, 1320, 1250, 1155, 1120, 1010, 970, 845, 760 cm^{-1}; UV (MeOH) λ_{max} 254.5 (sh, log ϵ 4.41), 261(4.43), 289.5(sh, 4.16), 301.5(4.08), 340.5(3.75), 357.5(3.87), 376.5(3.89), 394.5 nm (3.84); mass spectrum at *m/e* (relative intensity) 313(24), 312(100, M^{+}) 285(15), 284(44), 255(13), 226(17), 142(20), 113(17), 79(21), 78(44), 77(76). (Found: C, 80.56; H, 3.74; O, 15.30. Calc. for $C_{21}H_{12}O_3$: C, 80.75; H, 3.87; O, 15.37%).

Independent irradiation of photoproducts **4**, **5**, **6** *and* **7**. Each photoproduct (**4**, **5**, **6** and **7**) (0.03–0.05 g) was dissolved in MeOH (50-100 ml). After N_2 gas was bubbled for 15 min, the soln was irradiated with a Ushio 500-W medium-pressure mercury lamp equipped with a Pyrex filter. Extent of the reaction was followed by a TLC method. After 30 min irradiation the mixture of **4** and **5** showed the spots corresponding to **6** and **7**, respectively, on silica gel TLC plates. After 60–90° min irradiation, **4** and **5** disappeared and **6** and **7** together with a polymeric compound were detected on silica gel TLC plate. The MeOH soln of **6** and **7** gave polymeric compound after 30 min irradiation and disappeared completely after 90–120 min irradiation.

Oxidative photocyclization of 2-phenyl-7-hydroxyisoflavone to phenanthro - [9,10 - c] - 6 - hydroxyisocoumarin. The soln containing **2** (0.2 g) and I_2 (0.18 g) in MeOH (350 ml) was irradiated under N_2 with a Ushio 500-W medium-pressure mercury lamp with a Pyrex filter for 4 hr. After removal of the solvent under vacuum, the residue was chromatographed on silica gel using EtOAc and benzene (1:9) to give **7** in 38% yield.

Photolysis of **2** (0.1 g) in MeOH (350 ml) was carried out on exposure to air for 1 hr using a Ushio 500-W medium pressure-mercury lamp with a Pyrex filter. TLC on silica gel indicated complete disappearance of **2** and the formation of only a polymeric compound.

Oxidation of 2-phenyl-7-hydroxyisoflavone with potassium permanganate. A mixture of **2** (0.5 g) and $KMnO_4$ (2 g) in water (200 ml) was refluxed for 48 hr. After the mixture was filtered off the filtrate was acidified with dil. HCl and extracted with ether. After removal of the solvent under vacuum, the residue was chromatographed on silica gel with a mixture of chloroform and MeOH (8:2) to give benzil, benzoic acid and 2,4-dihydroxybenzoic acid. The structure of these products were confirmed by comparison of their IR spectra with those of authentic samples and by no depression of their mixture m.ps.

Alkaline hydrolysis of 3,4-diphenyl-6-methoxyisocoumarin. To stirred soln of **4**. (0.07 g) in MeOH (10 ml) was added 30% NaOH (5 ml). The mixture was allowed to stir for 24 hr at room temp. and then poured onto an ice-10% HCl mixture to neutralize. The mixture was extracted with ether and the extract was dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica gel thick-layer plate using a 1:9 MeOH–$CHCl_3$ mixture as eluent. The product was identified as α - (2 - carboxyl - 5 - methoxy)phenyldeoxybenzoin, m.p. 120–122°; IR (KBr) 3250, 2700, 1700, 1600, 1510, 1430, 1285, 1200, 1160, 1100, 1030, 955, 830, 740 cm^{-1}; NMR ($CDCl_3$) δ 3.85 (s, 3H), 5.33 (s, 1H), 6.6–7.8 (m, 13H), 9.80 (s, 1H); mass spectrum at *m/e* (relative intensity) 346(10, M^{+}), 330(20), 328(100), 300(60). (Found: C, 76.02; H, 5.13; O, 18.19. Calc. for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24; O, 18.47%).

Acid hydrolysis of phenanthro[9, 10 - c] - 6 - methoxyisocoumarin. To a soln of **6** (0.1 g) in MeOH (10 ml) was added a few drops of conc. H_2SO_4. The mixture was refluxed for 10 hr and poured onto cold water (100 ml). The ppt formed was recrystallized from MeOH to give 9 - hydroxy - 10 - (3 - methoxy - 6 - carboxylphenyl)phenanthrene (30%), m.p. 176–179°; IR (KBr) 3300, 2700, 1710, 1610, 1445, 1375, 1295, 1250, 1170, 1150, 1120, 1035, 860, 760, 726 cm^{-1}; NMR ($CDCl_3$) δ 2.16 (s, 1H), 3.90 (s, 3H), 6.8–8.1 (m, 8H), 8.4–8.5 (m, 3H), 10.5 (s, 1H); UV (MeOH) λ_{max} 260 (log ϵ 4.87), 280 (4.64), 290 (4.61), 302(4.52), 337(4.24), 355(4.37), 375(4.36), 390 nm (4.38). (Found: C, 76.54; H, 4.49; O, 18.47. Calc. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68; O, 18.58%).

Acid hydrolysis of phenanthro[9,10-c]-6-hydroxyisocoumarin. Compound **7**, was hydrolyzed by the similar method employed for acid hydrolysis of **6**. Recrystallization from MeOH gave 9 - hydroxy - 10 - (3 - hydroxy - 6 - carboxyphenyl)phenanthrene, m.p. 277–280°; IR (KBr) 3200, 2700, 1670, 1610, 1550, 1455, 1375, 1320, 1290, 1240, 1165, 1120, 1000, 850, 785, 755 cm^{-1}. UV (MeOH) λ_{max} 262 (log ϵ 4.83), 280(4.55), 290(4.53), 303(4.44), 340(4.19), 355(4.29), 380(4.28), 393 nm (4.27). (Found: C, 76.49; H, 4.23; O, 19.08. Calc. for $C_{21}H_{14}O_4$: C, 76.51; H, 4.28; O, 19.41%).

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