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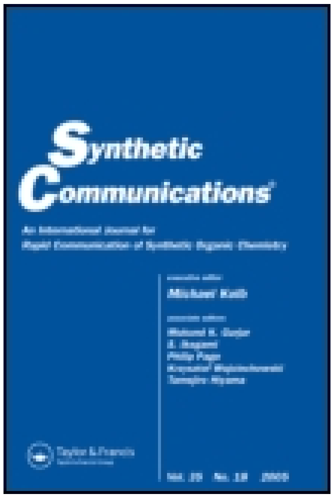

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PHOTOCHEMICAL REACTION OF PHENANTHRENEQUINONE WITH SOME NEW AURONES DERIVED FROM KHELLIN AND VISNAGIN

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PHOTOCHEMICAL REACTION OF PHENANTHRENEQUINONE WITH SOME NEW AURONES DERIVED FROM KHELLIN AND VISNAGIN

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ABSTRACT

Phenanthrenequinone **2** and aurones **5a–h** are potentially capable of undergoing an interesting photochemical reaction leading to the formation of the adducts **6a–h**. The structures of the 1,4-dioxine derivatives **6a–h** were firmly established on the basis of analytical data and spectroscopic evidences.

The naturally occurring furocoumarin khellin **1a** and visnagin **1b** show remarkable pharmacological properties.[1–4] Khellin for example, has attracted interest, being an antispasmodic and a coronary vasodilator of promise, in the treatment of angina pectoris and bronchial asthma.[5] Their photoreactions have been extensively studied.

The photoreactions of phenanthrenequinone **2** have also been extensively studied (vide infra). Thus, it appeared of interest to us to synthesize some derivatives having the furochromone moiety and to carry out the

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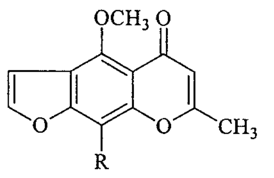
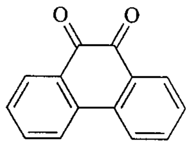
*Corresponding author.

photoreactions of these compounds with phenanthrenequinone to obtain an insight into the photoreaction behavior of these products and to produce compounds with wider medicinal spectra and of new potentialities.[6,7]

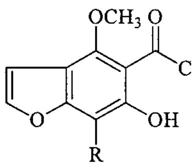


1 a: R = OCH_3
b: R = H

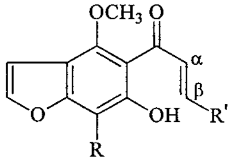


2

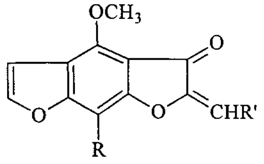
Thus, khellinone **3a**[8] and visnaginone **3b**[9] were prepared by the action of alkali on khellin **1a** and visnagin **1b**, respectively. Condensation of khellinone **3a** with the *p*-chlorobenzaldehyde, *p*-nitrobenzaldehyde, *p*-methoxybenzaldehyde and 2,4-dimethoxy benzaldehyde produced the corresponding chalcones **4a–d** respectively. Similarly, chalcones **4e–h** were produced by condensation of visnaginone **3b** with the respective aldehyde.



3 a: R = OCH_3
b: R = H



4a: R = OCH_3; R' = C_6H_4Cl-p
b: R = OCH_3; R' = $C_6H_4NO_2$-p
c: R = OCH_3; R' = $C_6H_4OCH_3$-p
d: R = OCH_3; R' = $C_6H_3(OCH_3)_2$
e: R = H; R' = C_6H_4Cl-p
f: R = H; R' = $C_6H_4NO_2$-p
g: R = H; R' = $C_6H_4OCH_3$-p
h: R = H; R' = $C_6H_3(OCH_3)_2$



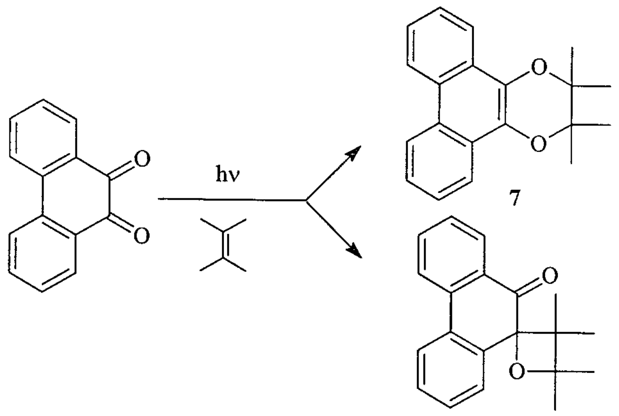
5a-h (R, R' as in **4a-h**)

The chalcone structures **4a–h** were assigned to the products by analytical and spectroscopic evidences as well as by analogy.[10] Thus, the IR spectra of the reaction products revealed the presence of C=O absorption at $\simeq 1730\,cm^{-1}$, and OH absorption at $\simeq 3460\,cm^{-1}$ (cf. Exp.). The ^1H NMR spectrum of compound **4g** taken as a representative example, showed two singlets at $\delta = 3.70$, 4.20 ppm, due to the two methoxyl groups. And a singlet appeared at 6.75 ppm for visnagin proton, 6.90 and 7.60 ppm due to two doublets for AB system, $J = 6$ Hz for the aromatic protons of the 1,4-disubstituted ring. While two doublets at 6.85 and 7.80 ppm, $J = 2$ Hz for the furan ring, 7.50 ppm due to one doublet for β-olefinic proton, a doublet at 7.70 ppm due to α-olefinic proton and a signal at 12.85 ppm due to OH proton. The ^{1}H NMR spectra of chalcone structures **4a–h** were confirmed (cf. Exp.).

The preparation of aurones **5a–h** was carried out via oxidation treatment of compounds **4a–h** utilizing hydrogen peroxide in alkaline medium. Analytical and spectroscopic evidences characterized the resulting aurones **5a–h**. In the mass spectra, molecular ion peaks observed for all the aurones **5a–h** showed $m/z = [M^+]$ corresponding to the molecular weight of the products. The IR spectrum of compound **5a** reveals the presence of absorption bands at 1700 cm^{-1} due to the frequency of the carbonyl group of the coumaranone ring and at 1650 cm^{-1} due to conjugated unsaturated ketone. Its mass spectrum, taken as a representative example showed an ion peak at $m/e = 356.5$ [M$^+$]. The ^{1}H NMR spectrum of this compound showed two singlets at $\delta = 4.16$ and 4.21 ppm due to two methoxy protons and a singlet centered at $\delta = 6.85$ ppm due to the CHR$'$ group. The two doublets 7.30 and 8.05 ppm are due to the two CH protons of the furan ring, $J = 2$ Hz. The aromatic protons appeared as two doublets at $\delta = 7.60$ and 7.95 ppm, 4H; AB system, $J = 6$ Hz for the 1,4-disubstituted benzene ring. The IR and ^{1}H NMR spectrum of compounds **5a**,**c**,**e**,**f–h** are given in the experimental section. Moreover, compounds **5a–h** are insoluble in alkali and give negative ferric chloride reaction. It gave a deep red color with concentrated sulfuric acid.[10]

Phenanthrenequinone **2** and aurones **5a–h** are potentially capable of undergoing an interesting photochemical reaction leading to the formation of the adducts **6a–h**. This reaction is carried out in a Pyrex vessel using high-pressure Hg lamp (Philips HPK 125 W) in toluene as a solvent. The progress of the reaction was followed by thin layer chromatography on silica plates. The products obtained were separated by column chromatography on a silica gel column. The 1,4-dioxine structure **6a–h** was assigned to the products according to analytical and spectroscopic evidences.

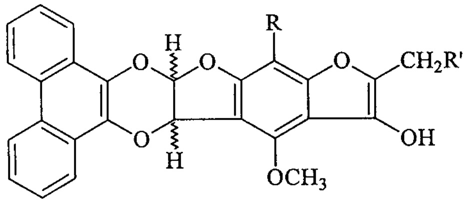
Information found in the literature regarding the photochemical reaction of phenanthrenequinone **2** with olefins is not in full agreement. Some papers[11,12] proved the formation of 1,4-dioxine derivatives **7**, while others[13] assigned the ketooxetane structure **8** to some of these adducts. However, it was reported that both addition products (dioxine and oxetanes) were produced simultaneously in other reactions.[14–17] Stilbene, alicyclic olefins, furocoumarines and xanthotoxin were investigated in these photoreactions.



The 1,4-dioxine derivatives **6a–h** were obtained from the photochemical reaction of **2** and aurones **5a–h**. This structure was firmly established on the basis of analytical data, IR, ^{1}H NMR and ^{13}C NMR. The IR spectrum of **6f**, taken as a representative example, reveals the presence of an absorption band at 3460 due to hydroxyl group and at 1660 due to (C=O) group. The ^{1}H NMR of this compound showed a singlet at $\delta = 4.03$ ppm due to the methylene protons. The two doublets for the bridgehead methine protons overlapped in a complex pattern center at $\delta = 4.61$ ppm and the singlet at 4.37 ppm is due to the OCH_3 protons. The aromatic protons of the 1,4-disubstituted benzene ring appeared as two doublets at $\delta = 7.25$ and 8.12 ppm as AB system, $J = 6$ Hz, whereas the 8 H of the phenanthrene appeared as two triplets at 7.50 and 7.63 ppm and two doublets at 7.75 and 7.68 ppm. A signal appeared at $\delta = 7.55$ ppm (1H) due to the aromatic visnagin proton.

Moreover, compounds **6c**,**f**,**g** were analyzed by ^{13}C NMR using Bruker AM-500, for further confirmation. The ^{13}C NMR spectrum of compound **6f** taken as a representative example, showed in a clear pattern the assignment of all carbon atoms in these molecules (cf. Experimental). Interestingly, the bridged carbon atoms of these molecules were obtained in the range of $\delta \sim 130$ and 131 ppm.

Further evidence for the proposed structure comes from the mass spectral data. The 1,4-dioxine derivatives **6a–h** were characterized by a similar fragmentation pattern. The mass spectra of these photoadducts showed clearly a loss of benzylic group substituents and hydroxyl group. The *m*/*z* equals the composition of M^{+}-$C(OH)CH_2C_6H_5(p)X$ and dominates the



6a-h (R, R' as in **4a-h**)

electron impact and spectrum chart. The spectra of these compounds revealed the presence of the biphenyl moiety at $m/z = 152$ and the phenanthrenequinone fragment at $m/z = 208$. The formation of the 1,4-dioxine derivatives **6a–h** could be explained by assuming that the photoexcited phenanthrenequinone reacted with aurones in a stepwise fashion most probably via a biradical intermediate. The latter is stabilized to give **6**. The reduction of aurones may be achieved by hydrogen abstraction from the solvent.

EXPERIMENTAL

All melting points uncorrected were determined on an Electrothermal Engineering LKD 6891 apparatus. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AM-500 spectrometers with 5-mm dual frequency ^{1}H-^{13}C for compound **6c**,**f**,**g**. The proton spectra were acquired at 500.14 MHz on the AM-500. CF_3COOD was used as a solvent, unless otherwise noted. The internal standard residual COOH signal in CF_3COOD at 11.5 ppm. The chemical shifts were reported in delta (δ) units (ppm) upfield from CF_3COOD. The multiplicity patterns are s = singlet, d = doublet, t = triplet, m = multiplet. For compounds **5a–h** the ^{1}H NMR spectra were recorded on JEOL EX 270 NMR system for ^{1}H NMR (NRC, Cairo, Egypt). Typical conditions: spectral width = 4000 Hz for 1H and a flip angle of 45°C. The chemical shifts are recorded in δ ppm. Deuterated dimethyl sulfoxide, which was, used as a solvent, referring to the internal standard residual $(CD_3)_2$ signal in $(CD_3)_2$ SO_2 at 2.50 ppm. ^{13}C NMR spectra were acquired at 125.76 MHz on the AM-500. Analytical thin layer chromatography (TLC) was conducted by using plastic-backed, Fluka DC-Alufolien Kieslgel, 0.2 mm silica plates. Preparative chromatographic separations was carried out using column chromatography on silica gel G. Mesh size 0.2–0.5 mm, 37–70 mesh (ASTM) E Merch, Darmstadt through elution with toluene–ethylacetate (6 : 1 v/v), in a suitable condition. Infrared

(IR) spectra were recorded on Zeiss Infrared spectrophotometer IMR 16 and were reported in wave numbers (cm^{-1}).

Low resolution EI mass spectra (LRMS) were obtained using a Shimadzu GC/MS-QP 1000 EX spectrometers at electron energy = 70 eV. The microanalysis were carried out at the microanalytical center, NRC, Cairo. The microanalysis for the new compounds were in good agreement with calculated values [C, H, ±0.1]. Photolysis experiments were carried out in Pyrex vessels using high-pressure lamps (Philips HPK 125 W) in toluene as solvent and control experiments were carried out in the dark under identical conditions.

The Preparation of Chalcones 4a–h

General procedure: To a solution of **3a** or **3b** (0.01 mole) in 30 ml aqueous potassium hydroxide (50%); a solution of the appropriate aldehyde (0.02 mole) in ethanol (30 ml) was added. After stirring at room temperature for 12 h, the solution was neutralized with dilute acetic acid (10%). The separated product was collected, washed with water and crystallized. **4a:** m.p. 128°C; brownish *crystals* (from MeOH); 99% yield; ν_{max} (cm^{-1}) (KBr) 3450 (OH); δ_H ($CDCl_3$) 4.10 (s, 3H, OCH_3), 4.15 (s, 3H, OCH_3), 7.40 and 7.85 (2d, 4H; AB system, $J = 6$ Hz, aromatic protons of 1,4-disubstituted benzene ring), 7.45–7.70 (4H; 1H, α-olefinic proton; 1H, β-olefinic proton and 2H furan in a complex pattern), 12.6 (s, 1H, OH proton); *m/z* 358 (Found: C, 63.61; H, 4.18. $C_{19}H_{15}O_5Cl$ requires C, 63.59; H, 4.18%). **4b:** m.p. 185°C; orange *crystals* (from MeOH); 99% yield; ν_{max} (cm^{-1}) (KBr) 3460 (OH); *m/z* 369 (Found: C, 61.78; H, 4.08. $C_{19}H_{15}O_7N$ requires C, 61.78; H, 4.06%). **4c:** m.p. 124°C; orange *crystals* (from benzene); 98% yield; ν_{max} (cm^{-1}) (KBr) 3470 (OH); δ_H [$(CD_3)_2SO$] 3.75 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 6.60 (s, 1H, aromatic proton), 7.10 (d, 1H, β-olefinic proton), 7.25 (d, 1H; $J = 2$ Hz furan proton), 7.55 (s, 1H, aromatic protons), 7.65 (d, 1H; $J = 2$ Hz for furan proton), 7.70 (d, 1H, α-olefinic proton), 7.90 (s, 1H, aromatic proton), 10.15 (s, 1H, OH proton); *m/z* 354 (Found: C, 67.81; H, 5.08. $C_{20}H_{18}O_6$ requires C, 67.79; H, 5.08%). **4d:** m.p. 105°C; reddish *crystals* (from benzene); 95% yield; ν_{max} (cm^{-1}) (KBr) 3455 (OH); *m/z* 384; (Found: C, 65.62; H, 5.20. $C_{21}H_{20}O_7$ requires C, 65.62; H, 5.20%). **4e:** m.p. 127°C; orange *crystals* (from MeOH); 95% yield; ν_{max} (cm^{-1}) (KBr) 3435 (OH); *m/z* 328.5; (Found: C, 65.77; H, 3.93. $C_{18}H_{13}O_4Cl$ requires C, 65.75; H, 3.95%). **4f:** m.p. 250°C; yellow *crystals* (from MeOH-benzene); 99% yield; ν_{max} (cm^{-1}) (KBr) 3450 (OH); *m/z* 339 (Found: C, 63.73; H, 3.99. $C_{18}H_{13}O_6N$ requires C, 63.71; H, 3.98%). **4g:** m.p. 105°C; yellow *crystals* (from benzene); 97% yield; ν_{max} (cm^{-1}) (KBr) 3460 (OH); δ_H (CDCl$_3$) 3.70 (s, 3H, OCH$_3$), 4.20 (s, 3H, OCH$_3$), 6.75 (s, 1H; visnagin proton), 6.90 and 7.60 [(2d, 4H; AB system, $J = 6$ Hz) aromatic protons of 1,4-disubstituted benzene ring], 6.85 and 7.80 (2d, 2H; $J = 2$ Hz, furan ring), 7.5 (d, 1H, β-olefinic proton), 7.70 (d, 1H, α-olefinic proton), 12.85 (s, 1H, OH proton); *m/z* 324 (Found: C, 70.37; H, 4.93. $C_{19}H_{16}O_5$ requires C, 70.37; H, 4.93%). **4h:** m.p. 135°C; orange *crystals* (from benzene); 96% yield; ν_{max} (cm^{-1}) (KBr) 3460 (OH); *m/z* 354 (Found: C, 67.73; H, 5.08. $C_{20}H_{18}O_6$ requires C, 67.79; H, 5.08%).

The Preparation of Aurones 5a–h

General procedure: To a sodium hydroxide solution (20 ml, 10%), a solution of the chalcone derivatives **4a–h** (1 g) in pyridine (10 ml) was added. Hydrogen peroxide solution (15 ml, 20 vol. %) was gradually added to the externally cooled alkaline solution and the reaction mixture was left in the refrigerator for 4 days. The precipitated material was filtered, washed with water, dried and crystallized from a suitable solvent. **5a:** m.p. 235°C; yellow *crystals* (from benzene); 65% yield; ν_{max} (cm^{-1}) (KBr) 1700 (C=O), 1650 (conjugated unsaturated ketones); δ_H [(CD$_3$)$_2$SO] 4.16 (s, 3H, OCH$_3$), 4.21 (s, 3H, OCH$_3$), 6.85 (s, 1H, for CHR′), 7.30 (d, 1H, furan proton, $J = 2$ Hz), 7.60 and 7.95 [(2d, 4H; AB system, $J = 6$ cps) for aromatic protons of 1,4-disubstituted benzene ring], 8.05 (d, 1H, furan proton, $J = 2$ Hz); *m/z* 365.5 (Found: C, 63.95; H, 3.64. $C_{19}H_{13}O_5Cl$ requires C, 63.95; H, 3.64%). **5b:** m.p. 304°C; yellow *crystals* (from benzene); 85% yield; ν_{max} (cm^{-1}) (KBr) 1700 (C=O), 1655 (conjugated unsaturated ketones); *m/z* 367 (Found: C, 62.14; H, 3.56. $C_{19}H_{13}O_7N$ requires C, 62.12; H, 3.54%). **5c:** m.p. 155°C; brown *crystals* (from MeOH); 75% yield; ν_{max} (cm^{-1}) (KBr) 1710 (C=O), 1650 (conjugated unsaturated ketones); *m/z* 352 (Found: C, 68.18; H, 4.54. $C_{20}H_{16}O_6$ requires C, 68.18; H, 4.54%). **5d:** m.p. 185°C; brownish *crystals* (from benzene); 75% yield; ν_{max} (cm^{-1}) (KBr) 1700 (C=O), 1650 (conjugated unsaturated ketones); *m/z* 382 (Found: C, 65.94; H, 4.69. $C_{21}H_{18}O_7$ requires C, 65.96; H, 4.71%). **5e:** m.p. 188°C; yellow *crystals* (from benzene); 65% yield; ν_{max} (cm^{-1}) (KBr) 1700 (C=O), 1655 (conjugated unsaturated ketones); *m/z* 362.5 (Found: C, 66.15; H, 3.36. $C_{18}H_{11}O_4Cl$ requires C, 66.15; H, 3.36%). **5f:** m.p. 275°C; orange *crystals* (from benzene); 95% yield; ν_{max} (cm^{-1}) (KBr) 1705 (C=O), 1645 (conjugated unsaturated ketones); δ_H (CDCl$_3$) 4.45 (s, 3H, OCH$_3$), 6.75 (s, 1H, visnagin proton), 7.00 (d, 1H; $J = 2$ Hz furan proton), 7.55 (d, 1H; $J = 2$ Hz furan proton), 8.00 and 8.30 [(2d, 4H; AB system, $J = 6$ Hz) aromatic protons of 1,4-disubstituted benzene ring], 8.10 (s, 1H, CHR′); *m/z* 337 (Found: C, 64.09; H, 3.26. $C_{18}H_{11}O_6N$ requires C, 64.09; H, 3.26%). **5g:** m.p. 201°C; orange *crystals* (from benzene); 70% yield; ν_{max} (cm^{-1}) (KBr) 1705 (C=O), 1650 (conjugated unsaturated ketones); δ_H [$(CD_3)_2SO$] 3.85 (s, 3H, OCH_3), 4.30 (s, 3H, OCH_3), 6.75 (s, 1H, CHR′), 7.05 and 7.93 [(2d, 4H; AB system, $J = 6$ Hz) aromatic protons of 1,4-disubstituted benzene ring], 7.30 (d, 1H, furan proton, $J = 2$ Hz), 7.35 (s, 1H, visnagin proton), 8.00 (d, 1H, furan proton, $J = 2$ Hz); *m/z* 322 (Found: C, 70.80; H, 4.34. $C_{19}H_{14}O_5$ requires C, 70.80; H, 4.34%). **5h:** m.p. 205°C; orange *crystals* (from benzene); 70% yield; ν_{max} (cm^{-1}) (KBr) 1695 (C=O), 1645 (conjugated unsaturated ketones); δ_H [$(CD_3)_2SO$] 3.75 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 4.35 (s, 3H, OCH_3), 6.65 (d, 1H, furan proton, $J = 2$ Hz), 6.70 (s, 1H, visnagin proton), 7.00 (s, 1H, CHR′ proton), 7.40 (s, 1H, aromatic proton), 7.30 and 8.15 [(2d, 4H; AB system, $J = 6$ Hz) aromatic protons 1,4-disubstituted benzene ring], 7.95 (d, 1H, furan proton, $J = 2$ Hz); *m/z* 352 (Found: C, 68.20; H, 4.56. $C_{20}H_{16}O_6$ requires C, 68.18; H, 4.51%).

Photoreaction of Phenanthrenequinone 2 with Aurones 5a–h

General procedure: To a suspension of 0.2 g phenanthrenequinone **2** in toluene (200 ml) contained in a Pyrex photoreactor (>313 nm), 0.35 g of aurone **5a** was added. The mixture was exposed to UV light (HPK 125 W lamp). TLC followed the course of the reaction until the reaction mixture indicated substantial reaction of starting material (48 h). The solvent was evaporated and the product was separated using a column prepared by packing slurry of silica gel (30 g) is toluene. The column was eluated with toluene/ethyl acetate (1 : 1 v/v) whereby the photoaddition product **6a** was separated. In a similar manner, the photochemical reactions of phenanthrenequinone **2** with aurone **5b–h** were carried out whereby compounds **6b–h** were likewise separated. **6a:** m.p. 380°C; brown *crystals*; 20% yield; ν_{max} (cm^{-1}) (KBr) 3400 (OH); *m/z* 564.5; (Found: C, 70.15; H, 3.72. $C_{33}H_{21}O_7Cl$ requires C, 70.15; H, 3.72%). **6b:** m.p. 285°C; orange *crystals*; 60% yield; ν_{max} (cm^{-1}) (KBr) 3420 (OH); *m/z* 575; (Found: C, 68.86; H, 3.65. $C_{33}H_{21}O_9$ requires C, 68.86; H, 3.65%). **6c:** m.p. 294°C; brown *crystals*; 15% yield; ν_{max} (cm^{-1}) (KBr) 3400 (OH); δ_H (CF_3COOD), 3.99 (s, 3H, OCH_3), 4.00 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 4.08–4.12 (4H, two methylene protons and two bridgehead methine protons in a complex pattern), 7.25 and 8.10 [(2d, 4H; AB system, $J = 6$ Hz) aromatic protons 1,4-disubstituted benzene ring], 7.75 and 7.85 (2d, 4H), 7.53 and 7.70 (2t, 4H, phenanthrene protons); *m/z* 559 (Found: C, 72.98; H, 4.11. $C_{34}H_{23}O_8$ requires C, 72.98; H, 4.11%). **6d:** m.p. 275°C; brown *crystals*; 20% yield; ν_{max} (cm^{-1}) (KBr) 3420 (OH); *m/z* 590 (Found: C, 71.20; H, 4.42. $C_{35}H_{26}O_9$

requires C, 71.18; H, 4.40%). **6e:** m.p. 370°C; brown *crystals*; 20% yield; ν_{max} (cm^{-1}) (KBr) 3400 (OH); *m*/*z* 534.5; (Found: C, 71.88; H, 3.59. $C_{32}H_{19}O_6Cl$ requires C, 71.84; H, 3.55%). **6f:** m.p. 380°C; orange *crystals*; 65% yield; ν_{max} (cm^{-1}) (KBr) 3400 (OH); δ_H (CF_3COOD) 4.03 (s, 2H, methylene proton), 4.37 (s, 3H, OCH_3), 4.61 (2d, bridgehead methine protons overlapped in a complex pattern), 7.25 and 8.12 (2d, 4H; AB system, $J = 6\,Hz$) aromatic protons 1,4-disubstituted benzene ring), 7.55 (s, 1H, visnagin proton), 7.50 and 7.63 (2t, 4H; 7.75 and 7.68 (2d, 4H, phenenthrene protons); ^{13}C NMR: 58.9 (OCH_3), 98.0 (CH_2), [123.5, 127.0, 130.1, 130.9, 132.8, 134.2] (12C phenanthrenequinone), [130.9, 131.2] (2$\underline{C}$-H), [99.7, 102.5, 103.2, 158.0, 158.5, 158.5] (6C visnagin-phenyl ring), [123.5, 123.5, 127.8, 127.8, 145.6, 147.7] (6C visnagin 1,4-disubstituted phenyl ring), 145.6 (2$\underline{C}$-O phenanthrenequinone), 165.4 (O-$\underline{C}CH_2$), 165.1 ($\underline{C}$-OH); *m*/*z* 545 (Found: C, 70.45; H, 3.48. $C_{32}H_{19}O_8$ require C, 70.45; H, 3.48%). **6g:** m.p. 385°C; brown *crystals*; 15% yield; ν_{max} (cm^{-1}) (KBr) 3400 (OH); δ_H (CF_3COOD) 3.94 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 3.95 (s, 2H, methylene proton), 4.04 and 4.6 (2d, bridgehead methine protons), 7.26 (s, 1H, visnagin proton), 7.25 and 8.15 [(2d, 4H; AB system, $J = 6\,Hz$) aromatic protons 1,4-disubstituted benzene ring], 7.67 and 7.5 (2t, 4H), 7.7 and 7.95 (2d, 4H, phenanthrene protons); ^{13}C NMR: 57.6 (OCH_3), [129.9, 130.2, 132.7, 132.9, 132.3, 136.0] (12C phenanthrenquinone), [132.7, 132.9] (2$\underline{C}$-H), [107.6, 107.6, 158.7, 158.7] (visnagin-phenyl ring), [111.3, 129.8, 136.0] (visnagin 1,4-disubstituted phenyl ring), 145.7 (2$\underline{C}$-O phenanthrenequinone), 160.0 (O-$\underline{C}CH_2$), 160.3 ($\underline{C}$-OH); *m*/*z* 530 (Found: C, 74.71; H, 4.15. $C_{33}H_{22}O_7$ requires C, 74.71; H, 4.15%). **6h:** m.p. 370°C; brown *crystals*; 22% yield; ν_{max} (cm^{-1}) (KBr) 3410 (OH); *m*/*z* 560 (Found: C, 72.85; H, 4.28. $C_{34}H_{24}O_8$ requires C, 72.85; H, 4.28%).

There was a minor variation in the yield percentage of **6** due to the ring substitution in **5** (15–22% yield). However, a major variation was observed in both **6b** and **6f** (≃60% yield).

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