Ring closing and photooxidation in nitrogen analogues of 3-hydroxyflavone

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An epoxide intermediate in the Algar–Flynn–Oyamada (AFO) synthesis of flavones is reaffirmed through the use of quinolone analogues to 3-hydroxyflavone (3HF). Stepwise synthesis of analogues 3-hydroxy-2-phenyl-1,4-dihydro-4-quinolone 11 and 3-hydroxy-1-methyl-2-phenyl-1,4-dihydro-4-quinolone 12, *via* chalcone formation, epoxidation, ring closing and final oxidation, has been accomplished. The intermediacy of an epoxide is further supported by blocking cyclization with methoxy substitution at the 2′-position (1A). Absorption/emission spectroscopy of 11 and 12 shows large red shifts, as seen in 3HF, indicative of an excited state intramolecular proton transfer mechanism. Nitrogen analogues demonstrate photooxidative stability similar to that of 3HF.

Flavonols are conveniently synthesized by the Algar–Flynn–Oyamada (AFO) reaction.[1–4] In the AFO reaction alkaline hydrogen peroxide converts 2′-hydroxychalcone **1** first into 3-hydroxyflavanone **3** and then into flavone **4**, provided there is an excess of hydrogen peroxide (Scheme 1).[5] The mechanism of the ring closure, to form 3-hydroxyflavanone, has been under debate for some time, however. It was initially believed[6–8] that an epoxide intermediate **2** is formed first and undergoes spontaneous internal attack by phenoxide (PhO^-) at the β position giving 3-hydroxyflavanone (Path 1), which is followed by the formation of flavones on further oxidation.

Dean and Podimuang[9] challenged this mechanism, citing the inability of 4′-hydroxychalcone to form an epoxide under the same conditions. However, recent work on the synthesis and subsequent cyclization of 2′-hydroxychalcone epoxides[10–12] has again pointed towards the possibility of epoxide intermediates. Since much study on chalcone cyclization, including recent work[11,13] has focussed on the propensity for 6′-substituted chalcones and chalcone epoxides to yield aurones rather than flavones,[6,9,14] we wished to readdress the question of epoxide intermediacy in the AFO reaction using appropriately substituted chalcones, as well as 2′-amino analogues of 2′-hydroxychalcone which, as shown by Donnelly and Farrell,[15] yield isolable epoxides under AFO conditions.

Nitrogen analogues of 3-hydroxyflavone have potential use in scintillator applications,[16–20] where a very large red-shift between absorption and emission, due to an excited state intramolecular proton transfer mechanism (ESIPT),[21,22] leads to low self-adsorption of emitted light. Dyes based on 3-hydroxyflavone derivatives may thus be employed in scintillating fibres for the detection of high-energy radiation,[23] although photooxidation limits the lifetime of these systems.[24] We thus undertook an empirical comparison of the photooxidative stability of the N-analogues synthesised.

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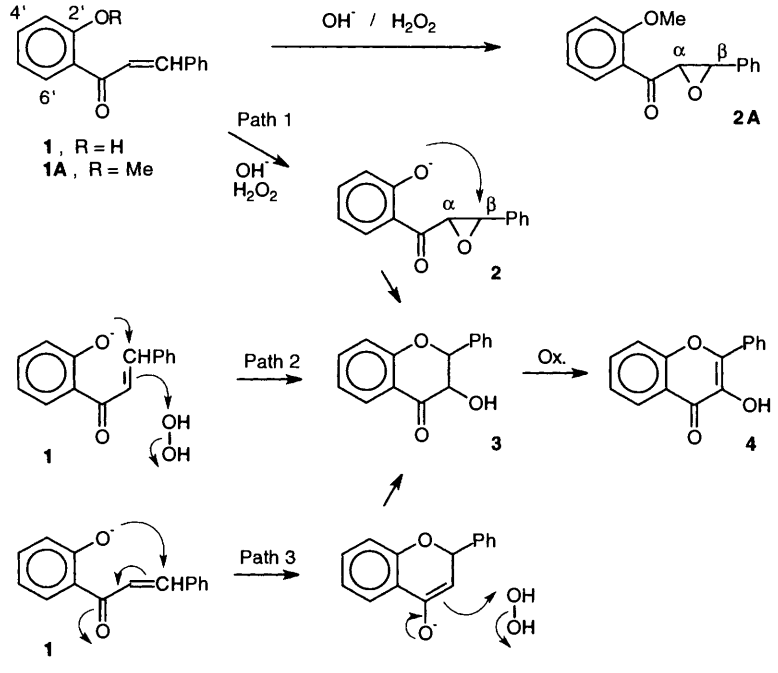
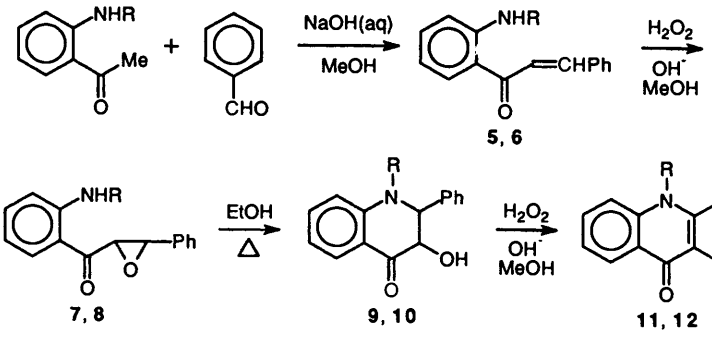


Scheme 1



5, 7, 9, 11: R = H; **6, 8, 10, 12**: R = Me.

Scheme 2

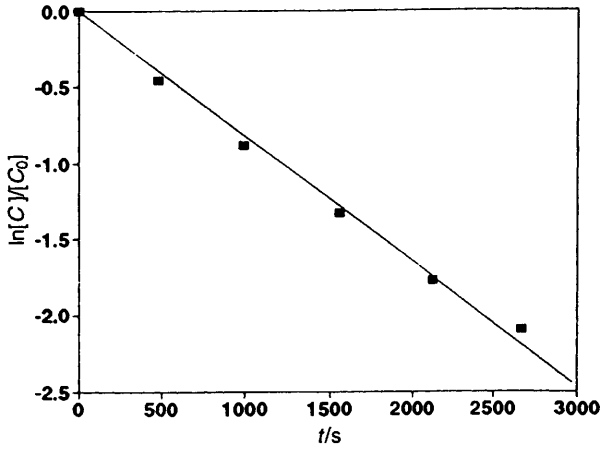


Fig. 1 Pseudo first-order kinetics for oxidation of **5** to **7** by an excess of H_2O_2 in basic alcoholic solution at room temperature. The concentration of **5** was monitored by UV–VIS absorption at 300 nm. Rate constant, $k = 7.8 \times 10^{-4}$ s^{-1}.

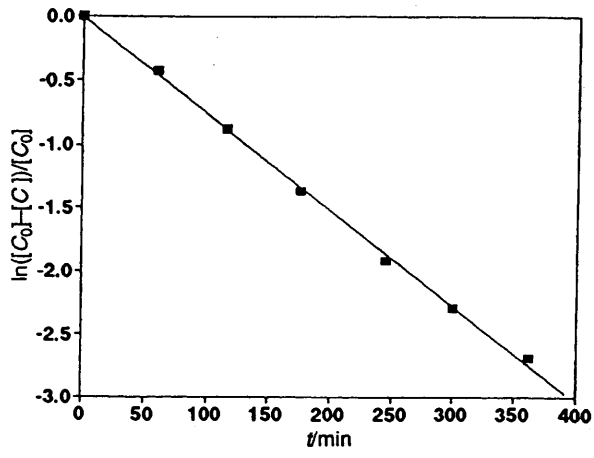


Fig. 2 Pseudo first-order plot of cyclization of **7** to **9** in refluxing butanol. The concentration of **9** was determined by fluorescence emission at 490 nm; $k = 1.3 \times 10^{-4}$ s^{-1}.

Results and discussion

The first piece of evidence to support an epoxide intermediate is the stepwise synthesis of β-hydroxy-2-phenyl-1,4-dihydro-4-quinolone **11** *via* 2′-aminochalcone epoxide **7** which was obtained from 2′-aminochalcone using alkaline hydrogen peroxide (AFO conditions) (Scheme 2). 2′-Aminochalcone epoxide, a yellow solid, was stable, and no evidence for further reaction (to **9** or **11**) was observed in this step. The stability of **7**, noted by Donnelly and Farrell,[15] contrasts with that of 2′-hydroxychalcone derivatives under AFO conditions. For example, Main and Old[25] observed a fast pseudo first-order cyclization of 2′-hydroxychalcone (at pH 11, $k = 2.5 \times 10^2$, corresponding to a lifetime of *ca.* 4 ms). The amino group apparently has a significantly lower nucleophilicity than the corresponding –OH group (PhO^-) under basic conditions. The epoxide may be converted into the quinolone by thermal treatment. 2′-Methylaminochalcone **6**, with nucleophilicity intermediate between PhO^- and $PhNH_2$, yielded mainly epoxide **8** with some quinolone **10** (a 5 : 2 ratio).

A kinetic study of the epoxidation of chalcone **5** was performed by following the decrease of the absorption maximum at 300 nm in basic alcoholic solution with an excess of H_2O_2. A pseudo first-order rate constant of 7.8×10^{-4} s^{-1} was obtained at room temperature, as shown in Fig. 1. A first-order reaction (k 1.3×10^{-4} s^{-1}) for cyclization of **7** to **9** was observed (Fig. 2) in refluxing butanol by monitoring the fluorescence at 490 nm (the fluorescence efficiency of **9** is about 70 times that of **7**).

Although substitution of –OH by –NRH makes ring closing the rate limiting step, 2′-hydroxychalcone epoxides have been prepared recently in good yield *via* an acid-cleavable protecting group for –O–, and *via* direct epoxidation by dimethyldioxirane.[10,12] These epoxides yield flavones on cyclization or, if substituted at the 6′ positions, mostly aurones.

Further evidence to support an epoxide intermediate was provided by the synthesis and ready epoxidation of 2′-methoxychalcone **1A** under AFO conditions. Ring closure is prevented by the methyl group. We contrast this result with that of Dean and Podimuang,[9] who observed only 'slow, general oxidation' of 4′-hydroxychalcone: the finding that epoxides were not produced in a system chosen to avoid ring-closure was offered as strong evidence in challenging the intermediacy of epoxides. We are unable to explain the rather puzzling difference in behaviour between 2′-methoxychalcone and 4′-hydroxychalcone, but we believe the facile epoxidation of the former reaffirms the epoxide route.

The spectroscopic properties of **11** and **12** are similar to those of 3-hydroxyflavone **4**, as shown by the spectra in Fig. 3, and include a very large red-shift indicative of intramolecular proton-transfer fluorescence.[21,22] The absorption maximum of both **11** and **12** occurs at 366 nm with ε/dm^3 mol^{-1} cm^{-1} 10 000 and 9000, respectively. Quinolone **11** emits at 516 nm and **12** at 526 nm with quantum yield $\varphi = 0.38$, *ca.* 1.4 times that of 3-hydroxyflavone under the same conditions. A test of relative stability against photooxidation using dilute solutions of **11**, **12** and **4** in CH_2Cl_2 revealed that **11** was photooxidized at a significantly faster rate than 3-hydroxyflavone, whereas the rate of photooxidation of **12** was similar (Fig. 4). The relative behaviour of these dyes is consistent with a mechanism of photooxidation of 3-hydroxyflavone described by Chou and Martinez[24] where the proton-transferred tautomer was considered the species reacting with triplet oxygen. Scheme 3 summarizes this mechanism for the quinolones studied here.

Since the ring heteroatom does not participate directly in the

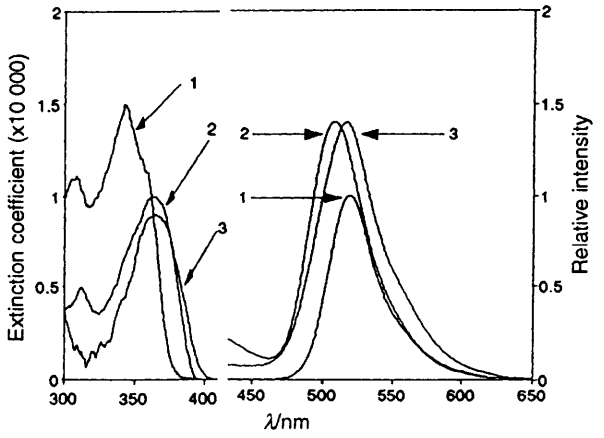


Fig. 3 UV–VIS absorption and emission spectra of dyes in CH_2Cl_2. Curve 1, 3 HF; curve 2, compound **11**; curve 3, **12**.

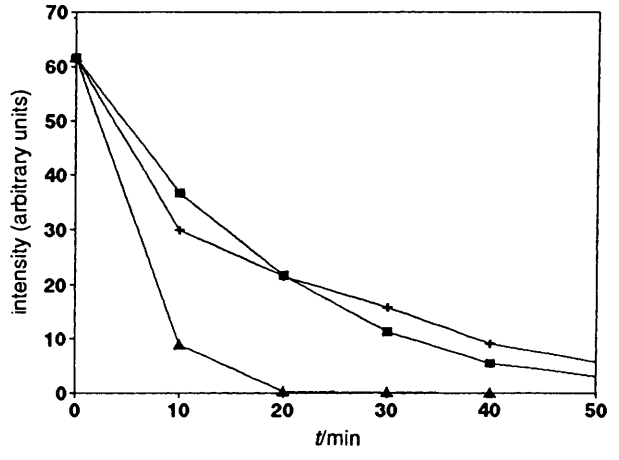
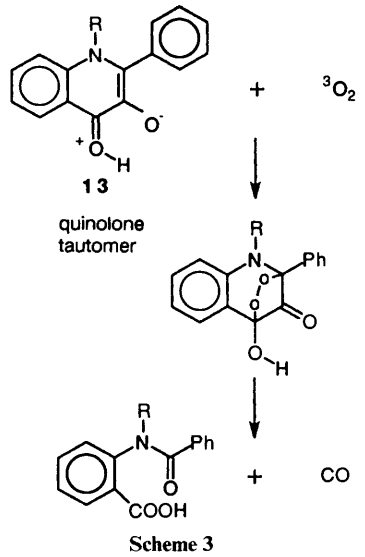


Fig. 4 Stability of dyes against photooxidation. Normalized emission intensity *vs.* time for UV irradiation in CH_2Cl_2 (10^{-5} mol dm^{-3}) under ambient conditions. ■, 3 HF; ▲, N-analogue **11**; +, methylated analogue **12**.



Scheme 3

photooxygenation one would not expect significant difference in reactivity between flavone and quinolones based on ground-state structure alone. Hückel calculations on the two classes of dyes show the same distribution in charge at the carbonyl and alcohol oxygen and at neighbouring carbons. However, time resolved fluorescence measurements[20] show a fluorescence lifetime of *ca.* 3 ns for **4** and **12**, whereas the lifetime for **11** is twice as long (6 ns). Since the lifetime of the tautomer **13** (R = H) is longer, one expects, and observes, faster photooxygenation for **11**.

In conclusion, when amino analogues of 2-hydroxyacetophenone are subjected to AFO conditions the intermediates, which include epoxychalcones, are stable and may be converted into N-analogues of 3-hydroxyflavone. This evidence, together with the synthesis of a cyclization-inhibited methoxy epoxide derivative, reaffirms the intermediacy of epoxides in the generalized AFO synthesis of flavones. The N-analogues synthesized exhibit large, efficient red shifting of absorbed light, making them suitable for use as scintillator dyes, although no improvement in photooxidative stability over 3HF was observed.

Experimental

^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer using Me_4Si as internal standard in $CDCl_3$. *J* Values are given in Hz. ^{13}C assignments were made following Agrawal.[26] IR spectra were recorded on a Nicolet 520 FTIR spectrometer. Mass spectral analyses were obtained using a Finnigan 4500 GC–MS system. UV–VIS and fluorescence spectra were measured on Shimadzu 520 or Varian Cary 3E UV–VIS and Perkin Elmer LS50 Luminescence spectrometers, respectively. Melting points were determined with a Thomas Unimelt apparatus and are uncorrected. Kinetic studies on epoxidation and ring closing were carried out by monitoring solution concentration changes with UV–VIS or fluorescence emission spectroscopy. Relative rates of photooxidation by ambient oxygen were determined in oxygen saturated CH_2Cl_2 solutions (10^{-5} mol dm^{-3}) contained in quartz cuvettes using a mercury vapour pen lamp (Spectroline SCT1A) as a source. The degree of photooxygenation was given by the decrease in the fluorescence intensity. All materials were used directly as received from commercial vendors unless otherwise stated. 2′-Aminochalcone **5**, 2′-amino-α-epoxychalcone **7**, and 3-hydroxy-2-phenyl-1,2,3,4-tetrahydro-4-quinolone **9** were synthesised following the procedure of Donnelly and Farrell.[15]

2′-Methylaminoacetophenone

Literature preparations for this compound[27] were simplified to the following one-step synthesis: a mixture of 2′-aminoacetophenone (9.34 g, 69.1 mmol), dimethyl sulfate (18.45 g, 146 mmol) and K_2CO_3 (24.7 g, 178 mmol) was maintained under reflux in tetrahydrofuran (THF) (150 cm^3) for 28 h and then poured into water. The mixture was extracted with CH_2Cl_2 and the organic phase dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was separated on a SiO_2 column with light petroleum–CH_2Cl_2 (1 : 1) which yielded the desired compound (3.59 g, 35%), mp 32–34 °C; δ_H($CDCl_3$; 300 MHz) 8.81 (1 H, br s, NH), 7.75 (1 H, d, $J_{5',6'}$ 8.1, 6′-H), 7.39 (1 H, t, $J_{3',4'} = J_{4',5'} = 8.1$, 4′-H), 6.72 (1 H, d, $J_{3',4'}$ 8.1, 3′-H), 6.61 (1 H, t, $J_{4',5'} = J_{5',6'} = 8.1$, 5′-H), 2.91 (3 H, s, NCH_3) and 2.58 (3 H, s, $COCH_3$); δ_C 200.9 (*C*=O), 152.1, 135.0, 132.7, 117.6, 113.8, 111.1 (Ar*C*), 28.8 (*C*H_3C=O) and 27.4 (*C*H_3N); ν(KBr)/cm^{-1} 3439, 3329 (N–H), 3077, 2997, 2904, 2864, 2818 (C–H), 1636 (C=O), 1572 and 1521; *m/z* [PCI, (M^+ + 1)/e] 150 (M^+ + 1) and 150 (100%) (Found: C, 72.55; H, 7.4; N, 9.35. Calc. for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.3%).

2′-Methylaminochalcone 6

2′-Methylaminoacetophenone (2.00 g, 13.4 mmol), benzaldehyde (1.87 g, 17.6 mmol) and NaOH (4.50 g in 10 cm^3 water) were stirred in MeOH (100 cm^3) for 25 h before the mixture was poured into water. The solid was collected by filtration and recrystallized from EtOH to give the title compound (1.97 g, 62%), mp 111–113 °C; δ_H($CDCl_3$; 300 MHz) 9.02 (1 H, br s, NH), 7.93 (1 H, d, $J_{5',6'}$ 8.1, 6′-H), 7.74 (1 H, d, J_{vinyl} 15.3, =CHPh), 7.66 (1 H, d, J_{vinyl} 15.3, COCH=), 7.66–7.63, 7.47–7.39 (6 H, m, other ArH), 6.82 (1 H, d, $J_{3',4'}$ 8.1, 3′-H), 6.70 (1 H, t,

$J_{4',5'} = J_{5',6'} = 8.1$, 5'-H) and 2.97 (3 H, s, CH_3); δ_C 191.9 (*C*=O), 153.0, 142.6, 135.6, 135.2, 131.8, 130.1, 129.0, 128.3, 123.5, 118.5, 114.1, 111.5 (Ar and vinyl *C*) and 29.2 (*C*H_3); ν(KBr)/cm^{-1} 3449, 3309 (N–H), 3077, 2997, 2904, 2864, 2818 (C–H), 1644 (C=O), 1576 and 1524 (C=C), *m*/*z* [PCI, (M^+ + 1)/e] 238 (M^+ + 1) and 238 (100%) (Found: C, 80.7; H, 6.5; N, 5.8. Calc. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90%).

2'-Methylamino-α-epoxychalcone 8 and 3-hydroxy-1-methyl 2-phenyl-1,2,3,4-tetrahydro-4-quinolone 10

A solution of **6**, (0.14 g, 0.59 mmol) NaOH (1.12 g in 3 cm^3 water), MeOH (50 cm^3) and H_2O_2 (30%; 4.5 cm^3) was stirred for 3 h and then poured into water. The mixture was extracted with CH_2Cl_2 and the organic phase was dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was separated using a SiO_2 column and CH_2Cl_2 which yielded **8** (75 mg, 50%) and **10** (30 mg, 20%). Data for **8**: δ_H($CDCl_3$; 300 MHz) 8.78 (1 H, br s, NH), 7.75 (1 H, d, $J_{5',6'}$ 8.1, 6'-H), 7.44–7.36 (6 H, m, other ArH), 6.73 (1 H, d, $J_{3',4'}$ 8.1, 3'-H), 6.57 (1 H, t, $J_{4',5'} = J_{5',6'} = 8.1$, 5'-H), 4.29 (1 H, d, J_{epoxy} 1.8, O=CCH), 4.03 (1 H, d, J_{epoxy} 1.8, CHPh) and 2.94 (3 H, s, CH_3); δ_C 193.4 (*C*=O), 152.5, 136.1, 135.9, 131.2, 128.9, 128.8, 125.1, 116.3, 114.3, 111.5 (Ar*C*), 60.7, 58.8 (epoxy *C*) and 29.0 (*C*H_3); ν(liquid)/cm^{-1} 3336 (N–H), 3064, 2904, 2818 (C–H), 1649 (C=O), 1576, 1523 (C=C) and 1171 (epoxide); *m*/*z* [PCI, (M^+ + 1)/e] 254 (M^+ + 1) and 134 (100%).‡ Data for **10**: δ_H($CDCl_3$; 300 MHz) 7.93 (1 H, d, $J_{5,6}$ 7.8, 5-H), 7.51–7.41 (6 H, m, other ArH), 6.90–6.83 (2 H, m, 6-H, 8-H), 4.55 (1 H, d, $J_{2,3}$ 13.2, 2-H), 4.30 (1 H, d, $J_{2,3}$ 13.2, 3-H), 3.78 (1 H, br s, OH) and 2.72 (3 H, s, CH_3); δ_C 194.7 (*C*=O), 153.4, 138.5, 136.8, 129.2, 128.8, 128.7, 128.2, 127.0, 118.1, 114.6 (Ar*C*), 75.1, 71.5 (C-2, C-3) and 29.5 (*C*H_3); ν(liquid)/cm^{-1} 3349 (O–H), 3064, 2924, 2858 (C–H), 1676 (C=O), 1616 and 1483 (C=C), *m*/*z* [PCI, (M^+ + 1)/e] 254 (M^+ + 1) and 254 (100%).‡

3-Hydroxy-2-phenyl-1,4-dihydro-4-quinolone 11

A mixture of **9** (0.23 g, 0.96 mmol) and NaOH (0.94 g in 4 cm^3 of water), 35 cm^3 MeOH and 15 cm^3 of 30% aq. H_2O_2 was stirred for 4.5 h. The resulting mixture was neutralized with dilute HCl and extracted with CH_2Cl_2. The solvent was removed from the organic phase after drying with Na_2SO_4. Recrystallization from toluene gave the desired compound (0.04 g, 17%), mp 260–262 °C; δ_H([$^2H_6$]DMSO; 300 MHz) 11.61 (1 H, br s, NH), 8.15 (1 H, d, *J* 8.4, 5-H), 7.71 (1 H, d, $J_{7,8}$ 8.4, 8-H), 7.80–7.78, 7.60–7.49 (6 H, m, other ArH), 7.26 (1 H, t, $J_{5,6} = J_{6,7} = 8.4$, 6-H) and 3.41 (1 H, br s, OH); δ_C([$^2H_6$]DMSO) 170.5 (*C*=O), 138.3, 138.0, 132.6, 131.8, 130.9, 129.6, 129.5, 128.6, 124.7, 122.3, 122.0 and 118.7 (Ar*C*); ν(KBr)/cm^{-1} 3469 (O–H), 3243 (N–H), 3110–2858 (C–H), 1635 (C=O), 1591 and 1489 (C=C); *m*/*z* [PCI, (M^+ + 1)/e] 238 (M^+ + 1) and 238 (100%) (Found: C, 75.1; H, 4.7; N, 5.8. Calc. for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.91%).

3-Hydroxy-1-methyl-2-phenyl-1,4-dihydro-4-quinolone 12

The same procedure for **8** and **10** was used except that the reaction was carried out for 10 h. Recrystallization from MeOH afforded the desired compound (70%), mp 260–263 °C; δ_H([$^2H_6$]DMSO; 300 MHz) 8.29 (1 H, d, $J_{5,6}$ 8.1, 5-H), 7.77 (1 H, d, $J_{7,8}$ 8.1, 8-H), 7.69 (1 H, t, $J_{6,7} = J_{7,8} = 8.1$, 7-H), 7.58–7.45 (5 H, m, ArH), 7.36 (1 H, t, $J_{5,6} = J_{6,7} = 8.1$, 6-H) and 3.55 (3 H, s, CH_3); ν(FTIR; KBr)/cm^{-1} 3205 (O–H), 2952, 2826 (C–H), 1616, 1581 and 1539 (C=C); *m*/*z* [PCI, (M^+ + 1)/e] 252 (M^+ + 1) and 252 (100%) (Found: C, 75.1; H, 5.3; N, 5.2. Calc. for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.58%).

‡ Compounds **8** and **10** were not stable enough for satisfactory elemental analyses to be obtained.

2-Methoxychalcone 1A

2-Hydroxychalcone (1.00 g, 4.36 mmol), iodomethane (2.03 g, 14.3 mmol) and K_2CO_3 (9.76 g) were stirred in acetone (20 cm^3) for 28 h and then the mixture was poured into water (300 cm^3). The resulting solution was extracted with CH_2Cl_2. The solvent was removed under reduced pressure after drying with Na_2SO_4. The residue was separated on a SiO_2 column with a mixture of ethyl acetate and light petroleum (1:9), which yielded the title compound as an oil (0.63 g, 61%); δ_H($CDCl_3$; 300 MHz) 7.63 (1 H, d, J_{vinyl} 15.9, =CHPh), 7.62 (1 H, d, $J_{5',6'}$ 7.8, 6'-H), 7.41 (1 H, t, $J_{3',4'} = J_{4',5'} = 7.8$, 4'-H), 7.38 (1 H, d, J_{vinyl} 15.9, =CHCO), 7.53–7.51, 7.34–7.31 (5 H, m, other ArH), 6.99 (1 H, t, $J_{4',5'} = J_{5',6'} = 7.8$, 5'-H), 6.93 (1 H, d, $J_{3',4'}$ 7.8, 3'-H) and 3.79 (3 H, s, OCH_3); δ_C($CDCl_3$) 192.6 (*C*=O), 158.1, 142.8, 134.9, 132.8, 130.1, 130.0, 129.1, 128.7, 128.1, 126.9, 120.5, 111.5 (Ar and vinyl *C*) and 55.2 (*C*H_3); ν(neat)/cm^{-1} 3064, 3031, 2944, 2838 (C–H), 1656 (C=O), 1603 and 1484 (C=C); *m*/*z* [PCI, (M^+ + 1)/e] 239 (M^+ + 1) and 239 (100%) (Found: C, 80.7; H, 5.9. Calc. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%).

2'-Methoxy-α-epoxychalcone 2A

A solution of **1A** (0.32 g, 1.34 mmol), NaOH (0.5 g in 3 cm^3 water), MeOH (30 cm^3) and H_2O_2 (30%; 8 cm^3) was stirred for 13 h and then poured into water (200 cm^3). The white precipitate was washed with water until neutral and pumped to dryness, which yielded the desired product (0.26 g, 76%), mp 124–125 °C; δ_H($CDCl_3$; 300 MHz) 7.82 (1 H, d, $J_{5',6'}$ 7.8, 6'-H), 7.51 (1 H, t, $J_{3',4'} = J_{4',5'} = 7.8$, 4'-H), 7.40–7.36 (5 H, m, other ArH), 7.05 (1 H, t, $J_{4',5'} = J_{5',6'} = 7.8$), 6.93 (1 H, d, $J_{3',4'}$ 7.8, 3'-H), 4.30 (1 H, d, J_{epoxy} 1.8, O=CCH), 4.00 (1 H, d, J_{epoxy} 1.8, CHPh) and 3.60 (3 H, s, OCH_3); δ_C($CDCl_3$) 195.2 (*C*=O), 159.9, 136.8, 135.0, 130.9, 128.8, 128.7, 126.3, 125.9, 121.2, 111.7 (Ar*C*), 64.3 and 59.7 (epoxy C) and 55.5 (*C*H_3); ν(KBr)/cm^{-1} 3063, 2984, 2837 (C–H), 1675 (C=O), 1598, 1483, 1467, 1437 (C=C), 1164 and 899 (epoxy); *m*/*z* [PCI, (M^+ + 1)/e] 255 (M^+ + 1) and 135 (100%) (Found: C, 75.5; H, 5.6. Calc. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.55%).

Acknowledgements

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