An efficient synthesis of bibenzylic oxygen heterocycles

Virendra B. Kumbhar[a], Augustine R. Joseph[a], Arun D. Natu[a], Radhika S. Kusurkar[b] and Madhusudan V. Paradkar[a]*

[a]*Department of Chemistry, Post-Graduate and Research Centre, Abasaheb Garware College, Karve road, Pune 411 004. Maharashtra, India*

[b]*Department of Chemistry, University of Pune, Ganeshkhind Road, Pune, India*

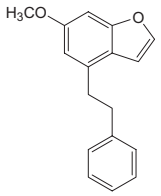
The first total syntheses of naturally occurring 6-methoxy-4-(2-phenylethyl)benzofuran **(1)** and 2,2-dimethyl-7-methoxy-5-(2-phenylethyl)chroman **(2)** and the non-natural 7-methoxy-5-(2-phenylethyl)chromen-2-one **(3)** are described from 3,5-dimethoxyphenylacetic acid in good yields.

Keywords: bibenzylic oxygen heterocycles, Wittig reaction, Friedel–Crafts acylation

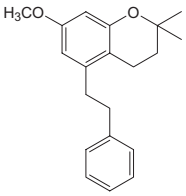
Bibenzyls and their derivatives containing oxygen heterocyclic ring systems are of synthetic importance because they constitute an important class of natural and non-natural products, many of which exhibit useful biological activities. They have been employed as 5-lipoxygenase inhibitors,[1] antifungal agents,[2] antimicrobial agents[2] and vasopressin antagonists.[2]

Owing to the natural occurrence and important biological properties, several interesting synthetic methods have been developed[1,3-4] for bibenzyls and their oxygen heterocyclic derivatives. 2,2-dimethyl-7-methoxy-5-(2-phenylethyl) chromene, for example, isolated from *R. kojana* was synthesised from 3-hydroxy-5-methoxy-2-(3-methylbutenyl)bibenzyl and Asakawa *et al.* have reported[1] two synthetic routes for 2,2-dimethyl-7-hydroxy-5-(2-phenylethyl)chroman. However, the drawbacks of these methods are the significantly low yields of desired products and the formation of unwanted by-products. In recent years we have initiated efforts on the development of convenient synthetic methods for various natural and non-natural oxygen heterocycles as well as their biological activity screening. Our interest in bibenzylic compounds stems from the occurrence of these systems in biologically active oxygen heterocyclic compounds and natural products.

Herein, we report the first total synthesis of 6-methoxy-4-(2-phenylethyl)benzofuran **(1)** and 2,2-dimethyl-7-methoxy-5-(2-phenylethyl)chroman **(2)**, both of which are known to occur in nature and a non-natural coumarin derivative viz. 7-methoxy-5-(2-phenylethyl)chromen-2-one **(3)** for the purpose of screening for potential bioactivity.



(1)



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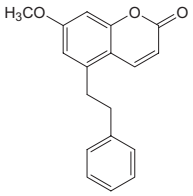


(3)

Initially, we focused on synthesising 6-methoxy-4-(2-phenylethyl)benzofuran **(1)** starting from 3,5-dimethoxyphenylacetic acid **(4)** as depicted in Scheme 1. The acid chloride of **(4)** was reacted with dry benzene in presence of anhydrous $AlCl_3$ and the ensuing ketone **(5)** was reduced under Wolf–Kishner reduction conditions to provide 1,3-dimethoxy-5-(2-phenylethyl)benzene[4] **(6)**. Vilsmeier–Haack formylation of **(6)** followed by demethylation reaction using anhydrous $AlCl_3$ afforded 2-hydroxy-4-methoxy-6-(2-phenylethyl)benzaldehyde **(8)**, which was treated with ethyl bromoacetate to obtain the aryloxy derivative **(9)**. Saponification of **(9)** and treatment of the resultant acid **(10)** with sodium acetate in Ac_2O:AcOH (1:1) provided the required natural product **(1)**.

The other natural product viz. 2,2-dimethyl-7-methoxy-5-(2-phenylethyl)chroman **(2)** was synthesised (Scheme 2) by regiospecific introduction of an acetyl group into 1,3-dimethoxy-5-(2-phenylethyl)benzene[4] **(6)** by using glacial acetic acid in the presence of trifluoroacetic anhydride (TFAA) to give 2-acetyl-1,5-dimethoxy-3(-2-phenylethyl)benzene **(11)**. Selective demethylation of **(11)** by anhydrous $AlCl_3$ in dry DCM provided 2-acetyl-1-hydroxy-5-methoxy-3-(2-phenylethyl)benzene **(12)** which was reacted with an excess of acetone in the presence of pyrrolidine and the resultant chromone **(13)** was subjected to Wolf–Kishner reduction to furnish the target chroman **(2)**.

Finally, the non-natural coumarin derivative 7-methoxy-5-(2-phenylethyl)chromen-2-one **(3)** was obtained by reacting the previously synthesised 2,4-dimethoxy-6-(2-phenylethyl) benzaldehyde **(7)** with (carbethoxymethylene)triphenylphosphorane in dry toluene as depicted in Scheme 3.

To conclude, we have accomplished the first total synthesis of two natural products, 6-methoxy-4-(2-phenylethyl) benzofuran **(1)** and 2,2-dimethyl-7-methoxy-5-(2-phenylethyl) chroman **(2)** and the non-natural 7-methoxy-5-(2-phenylethyl) chromen-2-one **(3)** in good yields by using easily accessible starting materials and involving simple reaction conditions and convenient workup procedures.

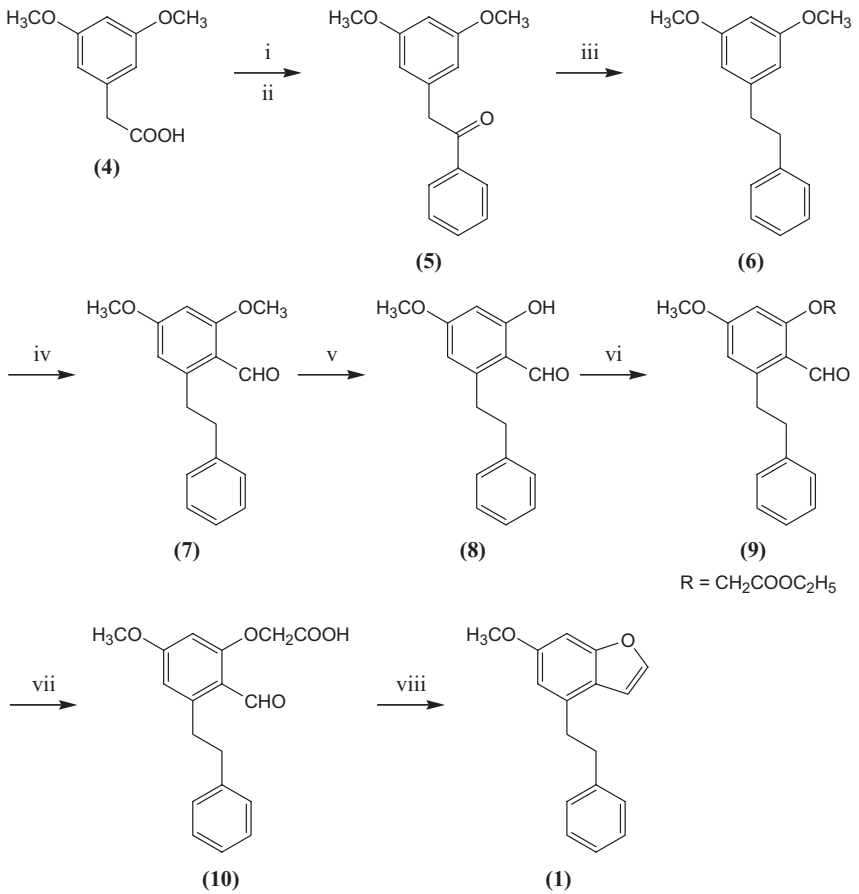
Experimental

Melting points were determined in capillaries and are uncorrected. ^{1}H NMR spectra were measured in $CDCl_3$ on a Varian Mercury 300 MHz FT-NMR spectrometer. The chemical shifts are expressed in parts per million (ppm) using TMS as an internal standard. Coupling constants are in Hz. IR spectra were recorded on a Perkin Elmer spectrum BX FTIR spectrometer and are reported in wave-numbers (cm^{-1}). Elemental analyses were acquired using a HOSLI semi-automatic CHN analyser.

2-(3,5-Dimethoxyphenyl)-1-phenylethanone (**5**): A slurry of finely powered anhydrous $AlCl_3$ (2.5 g, 18 mmol) in dry benzene (50 ml) was stirred at room temperature. To this mixture, a solution of 3, 5-dimethoxyphenylacetyl chloride [prepared by refluxing a mixture of 3,5-dimethoxyphenylacetic acid (1 g, 5 mmol) and $SOCl_2$ (1 ml, 14 mmol) in DCM (20 ml) for 1 h] in dry benzene (20 ml) was added drop-wise under stirring over a period of 15 min. To the resultant black-coloured mixture was added ice-cold water (50 ml) and conc. HCl (20 ml). The organic layer was separated and the aqueous layer was extracted with ether (2 × 20 ml). Combined organic layers were washed successively with water (2 × 20 ml), satd. $NaHCO_3$ solution (2 × 20 ml), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel using hexane-ethyl acetate as eluent to provide the ketone **(5)** (1 g) as white solid.

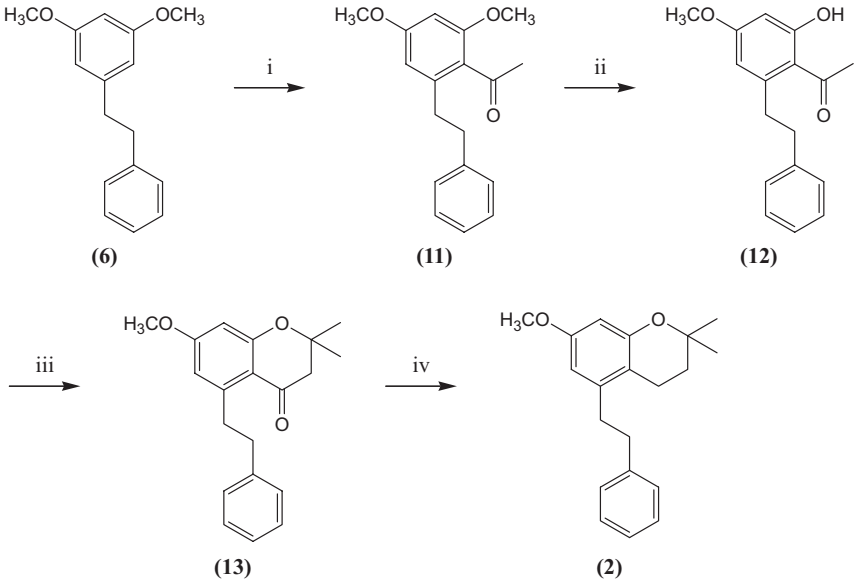
Yield: 77%; m.p. 66°C, (lit[5]. m.p. 65–66°C); IR: 1685 cm^{-1}; ^{1}H NMR: δ 3.74 (s, 6H), 4.18 (s, 2H), 6.40 (s, 3H), 7.46 (t, 3H), 7.98 (d, J = 8 Hz, 2H); Anal. calcd. for $C_{16}H_{16}O_3$: C, 75.00; H, 6.25. Found: C, 75.0; H, 6.45.

* Correspondent. E-mail: madhusudanparadkar@yahoo.co.in

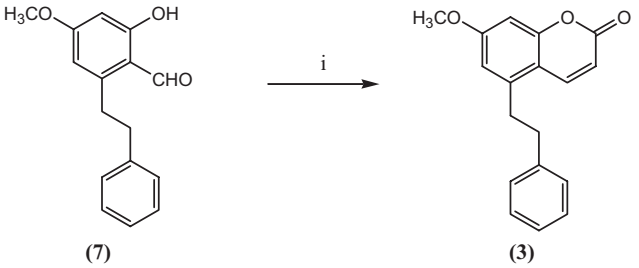


Scheme 1 *Reagents and conditions*: (i) $SOCl_2$, DCM, 1 h, reflux; (ii) dry benzene, $AlCl_3$; (iii) $NH_2NH_2.H_2O$, ethylene glycol, KOH, reflux, 3 h; (iv) DMF, $POCl_3$, 50°C, 5 h; (v) $AlCl_3$, DCM, 1 h, r.t.; (vi) ethyl bromoacetate, DMF, K_2CO_3, 1 h, r.t.; (vii) 5% aq. NaOH, heat, 0.5 h, followed by conc. HCl; (viii) NaOAc, Ac_2O–AcOH, heat, 1 h.

1,3-Dimethoxy-5-(2-phenylethyl)benzene (**6**): A mixture of 2-(3,5-dimethoxyphenyl)-1-phenylethanone **(5)** (2 g, 7.8 mmol) and hydrazine hydrate (4 ml) was heated on a water bath. To this ethylene glycol (40 ml) was added and the mixture was refluxed until a homogenous solution resulted. KOH (6 g, 107 mmol) was carefully added into this refluxing solution in small portions over a period of 2 h. The reaction mixture was refluxed for an additional 1 h when TLC indicated completion of reaction. After cooling the reaction mixture to room temperature it was poured into a beaker containing ice-cold conc. HCl (10 ml) and extracted with ether (2 × 50 ml). The ether layer was washed thoroughly with water, dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the crude residue was purified by column chromatography over silica gel using hexane as eluent to obtain the required 1,3-dimethoxy-5-(2-phenylethyl)benzene **(6)** (1.46 g) as pale yellow viscous oil.



Scheme 2 *Reagents and conditions*: (i) glacial AcOH, TFAA, r.t. 3 h; (ii) $AlCl_3$, DCM, R.T., 1 h; (iii) acetone, pyrrolidine, dry benzene, reflux, 48 h; (iv) $NH_2NH_2.H_2O$, ethylene glycol, KOH, reflux, 3 h.



(7) (3)

Scheme 3 *Reagents and conditions*: (i) Ph_3P =CHCOOEt, dry toluene, reflux, 48 h.

Yield: 77%; m.p. oil, (lit[4]. m.p. oil); ^{1}H NMR: δ 2.86 (brs, 4H), 3.72 (s, 6H), 6.29 (m, 3H), 7.17 (m, 5H); Anal. calcd. for $C_{16}H_{18}O_2$: C, 79.65; H, 8.39. Found: C, 79.3; H, 8.1.

2,4-Dimethoxy-6-(2-phenylethyl)benzaldehyde (**7**): To a complex prepared from dry DMF (0.7 ml, 9.1 mmol) and $POCl_3$ (0.9 ml, 9.62 mmol) at 0ºC was added 1,3-dimethoxy-5-(2-phenylethyl) benzene **(6)** (2 g, 8.26 mmol). The mixture was stirred and heated at 50°C for 5 h. The reaction mixture was poured into a beaker containing a satd. solution of NaOAc (50 ml) and the resultant oil was extracted with ethyl acetate (2 × 20 ml), washed successively with water (10 ml), satd. $NaHCO_3$ solution (10 ml) and again with water (10 ml). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure and the crude reside was purified by silica gel column chromatography using hexane as eluent to afford the required compound **(7)** (1.34 g) as colourless solid.

Yield: 60%; m.p. 83°C; IR: 1674 cm^{-1}; ^{1}H NMR: δ 2.81 (t, *J* = 8.0 Hz, 2H), 3.22 (t, *J* = 8.0 Hz, 2H), 3.77 (s, 3H), 3.86 (s, 3H), 6.20 (d, *J* = 2.4 Hz, 1H), 6.31 (d, *J* = 2.4 Hz, 1H), 7.25 (m, 5H), 10.5 (s, 1H); Anal. calcd. for $C_{17}H_{18}O_3$: C, 75.55; H, 6.66. Found: C, 75.9; H, 6.4.

2-Hydroxy-4-methoxy-6-(2-phenylethyl)benzaldehyde (**8**): A suspension of finely powered anhydrous $AlCl_3$ (0.3 g, 2.25 mmol) in dry DCM (10 ml) was stirred at room temperature for 20 min. To this mixture, a solution of 2,4-dimethoxy-6-(2-phenylethyl)benzaldehyde **(7)** (0.37 g, 1.37 mmol) in dry DCM (5 ml) was added under vigorous stirring over a period of 10 min. The resultant dark green coloured mixture was stirred at room temperature for an additional 1 h. The excess solvent was removed under reduced pressure and the residue was decomposed using ice cold 1 : 1 HCl/H_2O (20 ml) and extracted with ethyl acetate (2 × 25 ml). The organic layer was washed successively with water (2 × 20 ml), satd. $NaHCO_3$ solution (2 × 20 ml) and again with water (2 × 20 ml) and dried over anhydrous Na_2SO_4. Removal of organic solvent under reduced pressure followed by column chromatographic purification of the crude product over silica gel using hexane as eluent provided the required compound **(8)** (0.3 g) as pale yellow solid.

Yield: 87%; m.p. 50°C; IR: 1626 cm^{-1}; ^{1}H NMR: δ 2.94 (m, 2H), 3.12 (m, 2H), 3.8 (s, 3H), 6.24 (d, *J* = 2.44 Hz, 1H), 6.26 (d, *J* = 2.44 Hz, 1H), 7.17 (m, 5H), 9.94 (s, 1H) 12.45 (s, 1H); Anal. calcd. for $C_{16}H_{16}O_3$: C, 75.00; H, 6.25. Found: C, 74.8; H, 6.5.

Ethyl 2-formyl-5-methoxy-3-(2-phenylethyl)phenoxyethanoate (**9**): To a solution of 2-hydroxy-4-methoxy-6-(2-phenylethyl)benzaldehyde **(8)** (1 g, 3.9 mmol) in dry DMF (10 ml), anhydrous K_2CO_3 (0.8 g, 5.86 mmol) was added, followed by ethyl bromoacetate (0.65 g, 3.9 mmol). This mixture was stirred at room temperature for 1 h. After completion of reaction, the reaction mixture was poured onto crushed ice (50 g) and the resultant oil was extracted with ethyl acetate (2 × 20 ml). The organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the crude product by column chromatography over silica gel using hexane-ethyl acetate (3:1) as eluent provided the required ester **(9)** as pale yellow crystalline solid (1.14 g).

Yield: 86%; m.p. 71°C; IR: 1753.2 cm^{-1}, 1674 cm^{-1}; ^{1}H NMR: δ 1.29 (t, *J* = 7.3 Hz, 3H), 2.84 (t, *J* = 8.0 Hz, 2H), 3.23 (t, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 4.30 (q, *J* = 7.3 Hz, 2H), 4.70 (s, 2H), 6.21 (d, *J* = 2 Hz, 1H) 6.25 (d, *J* = 2 Hz, 1H), 7.26 (m, 5H), 10.62 (s, 1H); Anal. calcd. for $C_{20}H_{22}O_5$: C, 70.17; H, 6.43. Found: C, 70.4; H, 6.3.

2-Formyl-5-methoxy-3-(2-phenylethyl)phenoxyethanoic acid (**10**): A 5% aqueous NaOH solution (5 ml) was added to ethyl 2-formyl-5-methoxy-3-(2-phenylethyl)phenoxyethanoate **(9)** (1 g, 2.92 mmol) and the mixture was heated on a steam bath for 30 min. The solution was filtered over a pad of celite and the filtrate was acidified to pH 1–2 with conc. HCl. The precipitated solid was filtered and washed with water. The solid was further purified by dissolving in aqueous $NaHCO_3$ solution (5%, 10 ml), removing the insoluble matter by filtration and acidifying the filtrate to pH 1–2 with conc. HCl to obtain the required acid **(10)** (0.83 g) as off-white solid which was sufficiently pure to be subjected to the next reaction.

Yield: 90%; m.p. 115°C.

6-Methoxy-4-(2-phenylethyl) benzofuran (**1**): A mixture of 2-formyl-5-methoxy-3-(2-phenylethyl)phenoxyethanoic acid **(10)** (0.5 g, 1.6 mmol) and freshly fused NaOAc (0.4 g, 4.88 mmol) in acetic acid (2.5 ml) and acetic anhydride (2.5 ml) was heated in an oil bath at 140°C for 1 h. The reaction mixture was poured onto ice (25 g). The resultant oil was extracted with ether (2 × 20 ml). The ether layer was washed successively with water (2 × 10 ml), satd. $NaHCO_3$ solution (2 × 10 ml), brine (2 × 10 ml) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure provided the crude product which was purified by column chromatography over silica gel using hexane as eluent to obtain the required natural product 6-methoxy-4-(2-phenylethyl)benzofuran **(1)** (0.25 g) as colourless viscous oil.

Yield: 63%; m.p. oil, (lit[1]. m.p. oil); ^{1}H NMR: δ 2.96 (m, 2H), 3.06 (m, 2H), 3.83 (s,3H), 6.67 (dd, *J* = 1.0, 2.2 Hz, 1H), 6.70 (d, *J* = 2.2 Hz, 1H), 6.90 (brs, 1H), 7.20 (m, 5H) 7.51 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR: δ 35.8, 38.0, 55.9, 93.6, 105.2, 110.9, 120.1, 126.0, 128.0, 128.6, 135.2, 141.5, 143.5, 156.0, 157.8; Anal. calcd. for $C_{17}H_{16}O_2$: C, 80.95; H, 6.34. Found: C, 81.2; H, 6.1.

2-Acetyl-1,5-dimethoxy-3(-2-phenylethyl)benzene (**11**): To a solution of 1,3-dimethoxy-5-(2-phenylethyl)benzene **(6)** (0.3 g, 1.24 mmol) in dry DCM (6 ml), a mixture of glacial acetic acid (0.1 ml) and trifluoroacetic anhydride (0.3 ml) was added. The reaction mixture was stirred for 3 h at room temperature. The excess solvent was removed under reduced pressure and the resultant residue was extracted in ether (25 ml). The organic layer was washed with water (2 × 10 ml), satd. $NaHCO_3$ solution (2 × 10 ml) and brine (10 ml), dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel using hexane:ethyl acetate (9:1) as eluent to provide the required compound **(11)** (0.23 g) as a light yellow oil.

Yield: 73%; m.p. oil; IR: 1680 cm^{-1}; ^{1}H NMR: δ 2.43 (s, 3H), 2.76 (brs, 2H), 2.89 (brs, 2H), 3.73 (s, 3H), 3.86 (s, 3H), 6.30 (brs, 2H), 7.04–7.37 (m, 5H). Anal. calcd. for $C_{18}H_{20}O_3$: C, 76.05; H, 7.04. Found: C, 76.35; H, 7.2.

2-Acetyl-1-hydroxy-5-methoxy-3-(2-phenylethyl)benzene (**12**): A suspension of finely powered anhydrous $AlCl_3$ (0.3 g, 2.25 mmol) in dry DCM (10 ml) was stirred at room temperature for 20 min. To this mixture, a solution of **(11)** (0.4 g, 1.41 mmol) in dry DCM (5 ml) was added under vigorous stirring over a period of 10 min. The resultant dark green coloured mixture was stirred at room temperature for an additional 1 h. Excess solvent was removed under reduced pressure and the residue was treated with ice-cold 1 : 1 HCl/H_2O (20 ml) and extracted with ethyl acetate (2 × 25 ml). The organic layer was washed successively with water (2 × 15 ml), satd. $NaHCO_3$ solution (2 × 15 ml), brine (20 ml) and dried over anhydrous Na_2SO_4. Removal of the organic solvent under reduced pressure followed by column chromatographic purification of the crude product over silica gel using hexane as eluent provided **(12)** (0.31 g) as light yellow viscous oil.

Yield: 82%; m.p. oil; IR: 1670 cm^{-1}; ^{1}H NMR: δ 2.69 (s, 3H), 2.93 (m, 2H), 3.20 (m, 2H), 3.82 (s, 3H), 6.30 (m, 2H), 7.04–7.37 (m, 5H), 13.2 (s, 1H). Anal. calcd. for $C_{17}H_{18}O_3$: C, 75.55; H, 6.66. Found: C, 75.8; H, 6.9.

2,2-Dimethyl-7-methoxy-5-(2-phenylethyl)chroman-4-one (**13**): To a solution of 2-acetyl-1-hydroxy-5-methoxy-3-(2-phenylethyl)benzene **(12)** (0.5 g, 1.85 mmol) in dry benzene (5 ml) was added freshly distilled pyrrolidine (0.2 ml, 1.85 mmol) and dry acetone (0.25 ml, 3.70 mmol). The resulting solution was allowed to stand for 15 min, with intermittent swirling at room temperature and subsequently refluxed using a Dean Stark separator for 48 h when TLC analysis indicated completion of the reaction. The reaction mixture was allowed to attain room temperature. Removal of excess solvent under vacuum provided a residue which was extracted into ethyl acetate (30 ml). The organic layer was washed successively with water (2 × 15 ml), dil. HCl (2 × 15 ml), satd. $NaHCO_3$ solution (2 × 15 ml), brine (20 ml) and dried over anhydrous Na_2SO_4. Removal of the organic solvent under reduced pressure followed by column chromatographic purification of the crude product over silica gel using hexane as eluent yielded the required compound **(13)** (0.37 g) as a colourless oil.

Yield: 65%; m.p. oil; IR: 1688 cm^{-1}; ^{1}H NMR: δ 1.40 (s, 3H), 1.60 (s, 3H), 2.6 (brs, 2H), 3.0 (t, *J* = 6.0 Hz, 2H), 3.5 (t, *J* = 6.0 Hz, 2H) 3.80 (s, 3H), 6.33 (s, 1H), 6.80 (s, 1H), 7.0–7.3 (m, 5H); Anal. calcd. for $C_{20}H_{22}O_3$: C, 77.41; H, 7.10. Found: C, 77.7; H, 6.8.

2,2-Dimethyl-7-methoxy-5-(2-phenylethyl)chroman (**2**): A mixture of 2,2-dimethyl-7-methoxy-5-(2-phenylethyl)chroman-4-one **(13)** (0.4 g, 1.29 mmol) and hydrazine hydrate (2 ml) was heated on water bath. To this ethylene glycol (40 ml) was added and refluxed until a homogenous solution resulted. KOH (3 g, 53.5 mmol) was carefully added into this refluxing solution in small portions over a period of 2 h. The reaction mixture was refluxed for an additional 1 h when TLC indicated completion of reaction. After cooling the reaction mixture to room temperature it was poured into a beaker containing ice-cold conc. HCl (5 ml) and extracted with ether (2 × 50 ml). The ether layer was washed thoroughly with water, dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the crude residue was purified by column chromatography over silica gel using hexane as eluent to obtain the desired natural product 2,2-dimethyl-7-methoxy-5-(2-phenylethyl)chroman **(2)** (0.3 g) as a colourless oil.

Yield: 79%; m.p. oil (lit.[1]. m.p. oil); ^{1}H NMR: δ 1.3 (s, 3H), 1.4 (s, 3H), 1.69 (brs, 2H), 2.52 (brs, 2H), 2.84 (brs, 4H), 3.80 (s, 3H), 6.32 (brs, 2H), 7.1 (m, 5H); ^{13}C NMR: δ 16.8, 27.4, 27.6, 32.2, 34.5, 37.8, 55.6, 75.8, 100.2, 105.8, 114.4, 126.0, 128.0, 128.5, 138.8, 140.8, 154.5, 159.9; Anal. calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.4; H, 8.33.

7-Methoxy-5-(2-phenylethyl)chromen-2-one (**3**): A solution of 2-hydroxy-4-methoxy-6-(2-phenylethyl)benzaldehyde **(8)** (0.3 g, 1.17 mmol) and (carbethoxymethylene)triphenylphosphorane (0.4 g, 1.17 mmol) in toluene (10 ml) was refluxed for 48 h. The excess solvent was removed under reduced pressure to yield a residue, which on purification by column chromatography over silica gel using hexane as eluent provided the required coumarin **(3)** (0.25 g) as light yellow oil.

Yield: 76%; m.p. oil; IR: 1730 cm^{-1}; ^{1}H NMR: δ 2.9 (m, 2H), 3.1 (m, 2H), 3.82 (s, 3H), 6.16 (d, J = 9.1 Hz, 1H), 6.64 (brs, 1H), 6.67 (brs, 1H), 7.1–7.3 (m, 5H), 7.7 (d, J = 9.1 Hz, 1H); ^{13}C NMR: δ 31.6, 35.8, 55.6, 102.8, 108.0, 112.0, 120.7, 126.0, 128.0, 128.6, 140.8, 141.2, 143.8, 151.5, 160.1, 160.7; Anal. calcd. for $C_{18}H_{16}O_3$: C, 77.14; H, 5.71. Found: C, 77.5; H, 5.9.

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