Synthesis of 3-amino-1-aryl-9-methoxy-5,6-dihydro-1*H*- benzo[*f*] chromene-2-carbonitriles in aqueous media

Da-Qing Shi[a,b]*, Chen-Xia Yu[a], Qi-Ya Zhuang[a,b] and Xiang-Shan Wang[a,b]

[a]*Department of Chemistry, Xuzhou Normal University, Xuzhou 221116, P. R. China*

[b]*The Key Laboratory of Biotechnology on Medical Plants of Jiangsu Province, Xuzhou, 221116, P. R. China*

3-Amino-1-aryl-9-methoxy-5,6-dihydro-1*H*-benzo[*f*]chromene-2-carbonitriles were synthesised by the reaction of substituted cinnamonitriles with 7-methoxy-2-tetralone using triethylbenzylammonium chloride (TEBA) as catalyst in aqueous media. The synthetic method has the advantages of good yields, less pollution, simple operation and being environment friendly.The structures of the products were identified by IR, ^{1}H NMR and elemental analysis and confirmed by X-ray analysis.

Keywords: 1*H*-benzo[*f*]chromene, synthesis, aqueous media, green chemistry

The need to reduce the amount of toxic waste and byproducts arising from chemical processes requires increasing emphasis on the use of less toxic and environmentally compatible materials in the design of new synthetic methods.[1] One of the most promising approaches uses water as a reaction medium.[2] Breslow,[3] who showed that hydrophobic effects could strongly enhance the rate of several organic reactions, rediscovered the use of water as a solvent in organic reactions in 1980s. In recent years, there has been increasing recognition that water is an attractive medium for many organic reactions.[4] The aqueous medium is less expensive, dangerous and environment-unfriendly in comparison with organic solvents. Generally, the low solubility[5] of most reagents in water is not an obstacle to the reactivity, which, on the contrary, is reduced by the use of cosolvents.

In recent years, the synthesis of benzopyran (chromene) derivatives has attracted great interest. Since the discovery of cromakalim as a typical ATP-sensitive potassium channel opener (PCO), a large number of benzopyran derivatives have been synthesised and demonstrated to possess potent relaxant activity on blood vessels, cardiac muscle, and other smooth muscles.[6] These agents may find use in the treatment of a variety of diseases such as hypertension, asthma, ischemia, and urinary.

The pyran pharmacophore is an important core structure of many natural products showing antibacterial, antitumor, antiallergic, antibiotic, hypolipidemic and immunomodulating activities.[7,8] When the hydrogen atom of pyran ring is substituted by amino or cyano, they become synthons[9] of some natural products.

General, the conventional synthesis of benzopyran derivatives involves acid as well as base (*e.g.* piperdine or triethylamine) catalysed condensation of appropriate active methylene carbonyl compounds with substituted cinnamonitriles refluxing in organic solvents (*e.g.* ethanol or DMF) and are plagued by the limitation of prolonged reaction times, poor yields, and additionally by back of convincing structural proofs and environmental unfriendliness.[10,11]

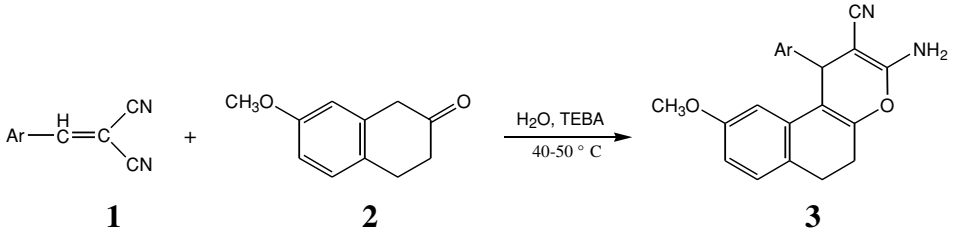
In the course of our search for new methods for construction of benzopyran nuclei, we became interested in the preparation of substituted 2-amino-3-cyano-5,6- dihydro-1*H*-benzo[*f*] chromenes with various aryl group substituents. Based on our previous studies on the use of water as a solvent for carrying out carbon–carbon forming reactions under phase transfer catalyst such as triethylbenzylammonium chloride,[12] here, we would like to report the synthesis of 3-amino-9-methoxy-1-aryl-5,6-dihydro-1*H*-benzo[*f*]chromenes-2- carbonitriles in aqueous media.

When substituted cinnamonitriles (**1**), 7-methoxy-2-tetralone (**2**) were stirred for 15–20 h at 40–50 °C in aqueous suspension in the presence of triethylbenzylammonium chloride, 3-amino-1-aryl-9-methoxy-5,6-dihydro-1*H*-benzo[*f*]chromene-2-carbonitriles (**3**) were obtained in excellent yields (Scheme 1). The results are shown in Table 1.

Table 1 shows the results using a series of substituted cinnamonitriles that undergo the reaction to give excellent yields (86–92 %) of the products. This procedure does not require the use of any organic solvent. In fact the target

Table 1 3-Amino-1-aryl-9-methoxy-5,6-dihydro-1*H*-benzo[*f*] chromene-2-carbonitriles (**3**)

Entry	Ar	Time/h	Isolated yield/%
3a	4-FC_6H_4	17	92
3b	4-$CH_3OC_6H_4$	20	86
3c	3-$NO_2C_6H_4$	20	92
3d	4-$CH_3C_6H_4$	16	80
3e	2,4-$Cl_2C_6H_3$	18	89
3f	2-ClC_6H_4	20	91
3g	3,4-$OCH_2OC_6H_3$	20	87
3h	3,4-$(CH_3O)_2C_6H_3$	20	86
3i	2-$NO_2C_6H_4$	20	89
3j	3-ClC_6H_4	19	90



1 **2** **3**

Scheme 1

* Correspondent. E-mail: dqshi@263.net

compounds **3** were isolated in a practically pure form by simple Buchner filtration of the final aqueous mixture.

All the products were characterised by IR and ^{1}H NMR analysis. The IR spectra of compound **3** show the NH stretching in the region 3500–3300 cm^{-1}, the CN group at around 2190 cm^{-1}. The ^{1}H NMR spectra of compounds **3** show the NH proton absorption as a broad singlet at around δ 4.4 ppm. The one proton on C-1 gives a singlet at 4.4–5.6 ppm. In order to confirm the structures of the products, the X-ray crystal structure analysis **3g** was carried out (Fig. 1). In the structure, the pyran ring can be regard as having a boat conformation: atoms C1, C10, C12 and C13 are coplanar, while atoms O1 and C11 deviate from the plane by 0.098(2) and 0.188(3) Å, respectively. The fused six-membered ring adopts a screw-boat conformation: atoms C2, C10, C1 and C9 are coplanar, while atoms C3 and C4 deviate from the plane by 0.681(2) and 0.240(3) Å, respectively. In the crystal intermolecular hydrogen bonds are formed between the amine group and atom O2 of the methylenedioxy group, and between the amine group and atom N1 of the cyano group.

As earlier proposed,[14] we consider the reaction to proceed via addition, enolisation, cyclodehydration and tautomerisation. (Scheme 2)

In conclusion: we have developed a facile and effective procedure for carrying out the synthesis of 3-amino-1-aryl-9-methoxy-5,6-dihydro-1*H*-benzo[*f*]chromene-2-carbonitriles from substituted cinnamonitriles and 7-methoxy-2-tetralone in water in the presence of TEBA. Compared to the classical synthetic method, this method has the advantages of excellent yields, inexpensive operation and environmental friendliness.

Experimental

IR spectra were recorded on an FT IR-8101 spectrometer in KBr with absorptions in cm^{-1}. ^{1}H NMR spectra were determined on a Bruker-400 MHz spectrometer using $CDCl_3$ or DMSO-d_6 solution. Chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane. Microanalyses were carried out on a Perkin-Elmer 2400 II elemental analyser. X-ray diffraction was recorded using a Siemens P4 diffactometer.

General procedure for the synthesis of 3-amino-1-aryl-9-methoxy-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3**): A mixture of the substituted cinnamonitriles **1** (2 mmol), 7-methoxy-2-tetralone **2** (2 mmol) and TEBA (0.15 g) in H_2O (10 ml) was stirred for 15–20 h at 40–50 °C, then cooled to room temperature. The solid material formed was collected by filtration, washed with water and recrystallised from ethanol to give pure **3**.

3-Amino-9-methoxy-1-(4-fluorophenyl)-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3a**): M.p. 177–178 °C. IR, ν/cm^{-1}: 3411, 3325, 2945, 2846, 2189, 1686, 1647, 1607, 1502, 842, 806, 774. ^{1}H NMR ($CDCl_3$): δ 2.56–2.63 (2H, m, CH_2), 2.88–2.92 (2H, m, CH_2), 3.63 (3H, s, CH_3O), 4.42 (2H, s, NH_2), 4.52 (1H, s, CH), 6.49 (1H, s, ArH), 6.57 (1H, d, *J* = 8.0 Hz, ArH), 6.96–7.01 (3H, m, ArH), 7.27–7.29 (2H, m, ArH). Anal. calcd for $C_{21}H_{17}FN_2O_2$: C 72.40, H 4.92, N 8.04; found C 72.62, H 4.75, N 8.28 %.

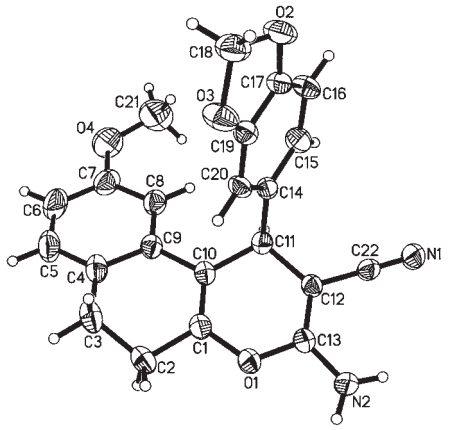


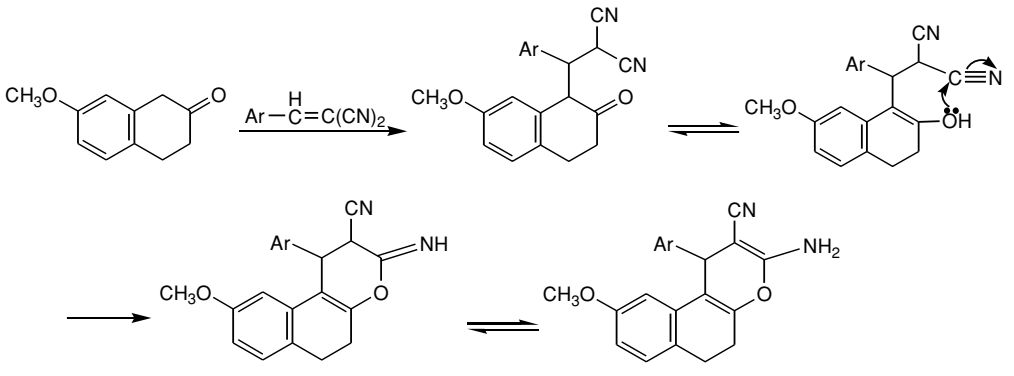
Fig. 1 The X-ray crystal structure of compound **3g**.

3-Amino-9-methoxy-1-(4-methoxyphenyl)-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3b**): M.p. 196–198 °C. IR, ν/cm^{-1}: 3407, 3315, 2948, 2891, 2190, 1684, 1643, 1603, 1503, 1455, 840, 769. ^{1}H NMR ($CDCl_3$): δ 2.56–2.63 (2H, m, CH_2), 2.85–2.96 (2H, m, CH_2), 3.63 (3H, s, CH_3O), 3.76 (3H, s, CH_3O), 4.39 (2H, s, NH_2), 4.47 (1H, s, CH), 6.55–6.58 (2H, m, ArH), 6.82 (2H, d, *J* = 8.4 Hz, ArH), 6.98 (1H, d, *J* = 8.0 Hz, ArH), 7.21–7.27 (2H, m, ArH). Anal. calcd for $C_{22}H_{20}N_2O_3$: C 73.32, H 5.59, N 7.77; found C 73.56, H 5.55, N 7.81 %.

3-Amino-9-methoxy-1-(3-nitrophenyl)-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3c**): M.p. 209–210 °C. IR, ν/cm^{-1}: 3434, 3325, 2940, 2853, 2193, 1685, 1641, 1605, 1532, 1409, 995, 857, 806, 719, 690. ^{1}H NMR ($CDCl_3$): δ 2.60–2.66 (2H, m, CH_2), 2.87–2.99 (2H, m, CH_2), 3.64 (3H, s, CH_3O), 4.54 (2H, s, NH_2), 4.68 (1H, s, CH), 6.46 (1H, s, ArH), 6.58 (1H, d, *J* = 8.0 Hz, ArH), 7.02 (1H, d, *J* = 8.0 Hz, ArH), 7.51 (1H, t, *J* = 8.0 Hz, ArH), 7.72 (1H, d, *J* = 8.0 Hz, ArH), 8.08 (1H, d, *J* = 8.0 Hz, ArH), 8.12 (1H, s, ArH). Anal. calcd for $C_{21}H_{17}N_3O_4$: C 67.19, H 4.56, N 11.19; found C 67.32, H 4.51, N 11.37 %.

3-Amino-9-methoxy-1-(4-methylphenyl)-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3d**): M.p. 179–181 °C. IR, ν/cm^{-1}: 3430, 3344, 2948, 2898, 2834, 2188, 1687, 1644, 1606, 1570, 1498, 989, 862, 813, 756. ^{1}H NMR ($CDCl_3$): δ 2.28 (3H, s, CH_3), 2.56–2.60 (2H, m, CH_2), 2.87–2.94 (2H, m, CH_2), 3.62 (3H, s, CH_3O), 4.38 (2H, s, NH_2), 4.47 (1H, s, CH), 6.55–6.57 (2H, m, ArH), 6.98 (1H, d, *J* = 8.4 Hz, ArH), 7.09–7.10 (2H, m, ArH), 7.18–7.21 (2H, m, ArH). Anal. calcd for $C_{22}H_{20}N_2O_2$: C 76.72, H 5.85, N 8.13; found C 76.85, H 5.73, N 8.31 %.

3-Amino-1-(2,4-dichlorophenyl)-9-methoxy-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3e**): M.p. 223–225 °C. IR, ν/cm^{-1}: 3463, 3334, 2986, 2937, 2898, 2834, 2189, 1690, 1637, 1577, 1499, 1463, 990, 868, 834, 769. ^{1}H NMR ($CDCl_3$): δ 2.51–2.61 (2H, m, CH_2), 2.83–2.95 (2H, m, CH_2), 3.68 (3H, s, CH_3O), 4.48 (2H, s, NH_2), 5.17 (1H, s, CH), 6.52 (1H, s, ArH), 6.60 (1H, d, *J* = 8.0 Hz, ArH), 6.98 (1H, d, *J* = 8.0 Hz, ArH), 7.15 (1H, d, *J* = 8.0 Hz, ArH), 7.22 (1H, d, *J* = 8.0 Hz, ArH), 7.39 (1H, s, ArH). Anal. calcd for $C_{21}H_{16}Cl_2N_2O_2$: C 63.17, H 4.04, N 7.02; found C 63.32, H 3.97, N 7.18 %.



Scheme 1

3-Amino-1-(2-chlorophenyl)-9-methoxy-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3f**)*:* M.p. 227–229 °C. IR, ν/cm^{-1}: 3456, 3307, 2943, 2901, 2834, 2192, 1687, 1645, 1606, 1570, 1498, 989, 860, 813, 747. ^{1}H NMR ($CDCl_3$): δ 2.55–2.63 (2H, m, CH_2), 2.84–2.95 (2H, m, CH_2), 3.66 (3H, s, CH_3O), 4.45 (2H, s, NH_2), 5.22 (1H, s, CH), 6.57–6.59 (2H, m, ArH), 6.97 (1H, d, *J* = 8.4 Hz, ArH), 7.13–7.20 (2H, m, ArH), 7.27–7.28 (1H, m, ArH), 7.36 (1H, d, *J* = 7.2 Hz, ArH). Anal. calcd for $C_{21}H_{17}ClN_2O_2$: C 69.14, H 4.70, N 7.68; found C 69.29, H 4.58, N 7.49 %.

3-Amino-9-methoxy-1-(3,4-methylenedioxyphenyl)-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3g**)*:* M.p. 239–241 °C. IR, ν/cm^{-1}: 3434, 3325, 2940, 2890, 2185, 1692, 1634, 1605, 1489, 923, 814, 763. ^{1}H NMR ($CDCl_3$): δ 2.55–2.60 (2H, m, CH_2), 2.87–2.94 (2H, m, CH_2), 3.65 (3H, s, CH_3O), 4.40 (2H, s, NH_2), 4.44 (1H, s, CH), 5.90 (2H, d, *J* = 8.4 Hz, OCH_2O), 6.57–6.59 (2H, m, ArH), 6.72–6.74 (2H, m, ArH), 6.83 (1H, d, *J* = 8.4 Hz, ArH), 6.99 (1H, d, *J* = 8.0 Hz, ArH). Anal. calcd for $C_{22}H_{18}N_2O_4$: C 70.58, H 4.85, N 7.48; found C 70.73, H 4.71, N 7.59 %.

3-Amino-1-(3,4-dimethoxyphenyl)-9-methoxy-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3h**): M.p. 173–175 °C. IR, ν/cm^{-1}: 3431, 3332, 2994, 2939, 2897, 2188, 1683, 1602, 1570, 1509, 1456, 858, 812, 762. ^{1}H NMR ($CDCl_3$): δ 2.56–2.61 (2H, m, CH_2), 2.88–2.92 (2H, m, CH_2), 3.63 (3H, s, CH_3O), 3.83 (3H, s, CH_3O), 3.85 (3H, s, CH_3O), 4.40 (2H, s, NH_2), 4.47 (1H, s, CH), 6.56–6.58 (2H, m, ArH), 6.77–6.85 (3H, m, ArH), 6.99–7.01 (1H, m, ArH). Anal. calcd for $C_{23}H_{22}N_2O_4$: C 70.75, H 5.68, N 7.17; found C 70.89, H 5.57, N 7.32 %.

3-Amino-9-methoxy-1-(2-nitrophenyl)-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3i**): M.p. 210–212 °C. IR, ν/cm^{-1}: 3440, 3361, 2946, 2838, 2191, 1686, 1642, 1604, 1526, 992, 906, 862, 812, 734. ^{1}H NMR ($CDCl_3$): δ 2.53–2.67 (2H, m, CH_2), 2.83–2.98 (2H, m, CH_2), 3.62 (3H, s, CH_3O), 4.50 (2H, s, NH_2), 5.59 (1H, s, CH), 6.58–6.62 (2H, m, ArH), 6.98 (1H, d, *J* = 8.0 Hz, ArH), 7.33–7.36 (1H, m, ArH), 7.47–7.51 (2H, m, ArH), 7.87 (1H, d, *J* = 8.0 Hz, ArH). Anal. calcd for $C_{21}H_{17}N_3O_4$: C 67.19, H 4.56, N 11.19; found C 67.31, H 4.49, N 11.07 %.

3-Amino-9-methoxy-1-(3-chlorophenyl)-5,6-dihydro-1H-benzo[f]chromene-2-carbonitrile (**3j**)*:* M.p. 208–210 °C. IR, ν/cm^{-1}: 3437, 3327, 3006, 2948, 2896, 2180, 1685, 1633, 1572, 1492, 1472, 996, 855, 806, 757, 704. ^{1}H NMR (DMSO-d_6): δ 2.50–2.54 (2H, m, CH_2), 2.80–2.83 (2H, m, CH_2), 3.61 (3H, s, CH_3O), 4.70 (1H, s, CH), 6.58 (1H, d, *J* = 8.4 Hz, ArH), 6.66 (1H, s, ArH), 6.85 (2H, s, NH_2), 7.01 (1H, d, *J* = 8.0 Hz, ArH), 7.23–7.26 (1H, m, ArH), 7.30–7.33 (2H, m, ArH), 7.38–7.39 (1H, m, ArH). Anal. calcd for $C_{21}H_{17}ClN_2O_2$: C 69.14, H 4.70, N 7.68; found C 69.38, H 4.76, N 7.55 %.

Crystal data of **3g**: $C_{22}H_{18}N_2O_4$, *Mr* = 374.83, Monoclinic, $P2_1/c$, *a* = 10.277(1)Å, *b* = 6.9852(5) Å, *c* = 25.695(3) Å, β = 92.512(9)°, *V* = 1842.8(3) Å^3, *Z* = 4, D_x = 1.349 Mg/m^3, μ = 0.09 mm^{-1}, T = 299(2) K. A single crystal of **3g** dimension of 0.56 × 0.38 × 0.24 mm was chosen for X-ray diffraction studies. Intensity data were collected on a Siemens P4 diffractometer with graphite monochromated *Mo*Kα radiation (λ = 0.71073 Å) using ω-2θ scan mode with 5.60°<θ<13.20°. 3336 unique reflections were measured and 2127 reflections with $I>2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and expanded using Fourier techniques. The fined refinement was converged to *R* = 0.035 and *wR* = 0.082. Full crystallographic data has been deposited at the Cambridge Crystallographic Data Centre, deposition number CCDC 262454. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1E2, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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