An Efficient Synthesis of Pyrrolocoumarins and Pyrroloquinolones by Acid-Catalysed Cyclisation of Acetylenic Amines in Water

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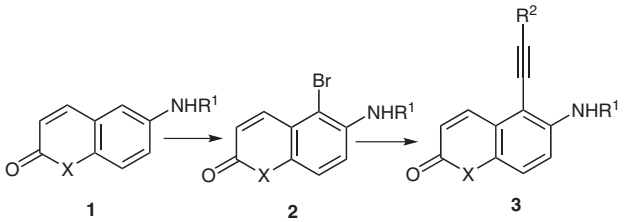
Abstract: A simple H^+-catalysed cyclisation of acetylenic amines for the synthesis of pyrrolocoumarins and pyrroloquinolones under conventional heating or microwave irradiation has been achieved. The reaction requires inexpensive catalyst and simple yet clean reaction conditions and offers potentially bioactive heterocycles in 82–95% yields.

Key words: pyrrolocoumarin, pyrroloquinolone, Brønsted acid catalysis, intramolecular cyclisation, microwave irradiation

Recently there has been a flurry of activity surrounding the development of green organic syntheses, sustainable and environmentally benign protocols. In this respect, use of water as a versatile solvent in place of hazardous organic reaction media is particularly relevant. Water is nontoxic, inexpensive, harmless and environmentally benign.[1,2] Water as solvent also eliminates some tedious protection and deprotection processes for certain acidic hydrogen containing functional groups, which contribute to the overall synthetic efficiency. Due to hydrophobic effects water not only accelerates the reaction rates but also enhances reaction selectivities. Water has been used for metal-mediated organic synthesis[3] and reactions involving water sensitive compounds.[4] Solubility of the substances and the metal catalyst are the main problems with the use of water and this problem can be overcome by performing the reaction at high temperature in a homogeneous medium. At high temperature water behaves like a pseudo organic solvent.[5,6] Because of its high dielectric constant water is also potentially a very useful solvent for microwave-mediated synthesis.[7,8] When water is heated well above its boiling point in a sealed vessel, or under microwave-mediated condition organic substrate may be more soluble.[9] This has prompted the development of new synthetic protocols[10–12] involving both water and microwaves.

Among the fundamental heterocycles, the pyrrole ring is one, which is widely distributed as structural unit in a variety of naturally and biologically important molecules such as porphyrins, bile pigments, co-enzymes, and alkaloids.[13] In recent years, there has been a continuous quest to synthesise pyrrole and its oligomer with different substituents efficiently from readily available starting materials.[14] Due to their potential application as conducting materials[15] coumarins and quinolones are subunits of many natural products possessing broad-spectrum biological activity and exhibit, for example, antifungal, antibacterial, antiviral, and antimicrobial properties.[16–20] In particular, pyrano-indole tethered heterocycles have been used for their antibacterial, monoamine oxidase (MAO) inhibitory, and anthelmintic activities.[21] We became interested to develop an efficient protocol for synthesising substituted pyrano[3,2-*e*]indolone and pyrrolo[3,2-*f*]quinolone derivatives. So far we have succeeded in synthesising pyrano[3,2-*e*]indolone and pyrrolo[3,2-*f*]quinolone derivatives through palladium(0)-mediated cross-coupling followed by copper(I)-catalysed or gold(III)-catalysed heteroannulations and palladium-catalysed Heck reaction or IBX-induced intramolecular oxidative amination of alkenes.[22] Herein we report the results of our investigation on the synthesis of biologically important substituted pyranoindoles and pyranoquinolones in water medium[23] via Brønsted acid catalysed cyclisation of acetylenic amines possessing an electron-donating group on the nitrogen atom.

The starting materials for this study **3a–j** were prepared according to our earlier published procedure[22a] (Scheme 1). We have conducted an optimisation study to explore the influence of acids, temperature, and solvents on the outcome of the cycloisomerisation of 5-(6-aminocoumarin)ylacetylenic amines **3a–g** and 5-(6-aminoquinolone)ylacetylenic amines **3h–j** to pyrrolocoumarins **4a–g** and pyrroloquinolones **4h–j**, both under conventional heating and microwave irradiation.



a X = O, R^1 = Et, R^2 = C_5H_{11}
b X = O, R^1 = Me, R^2 = Ph
c X = O, R^1 = Et, R^2 = Ph
d X = O, R^1 = H, R^2 = Ph
e X = O, R^1 = Me, R^2 = Bu
f X = O, R^1 = Et, R^2 = Bu
g X = O, R^1 = H, R^2 = Bu
h X = NMe, R^1 = H, R^2 = Ph
i X = NMe, R^1 = Me, R^2 = Ph
j X = NMe, R^1 = Et; R^2 = Ph

Scheme 1 Preparation of the starting materials **3a–j**

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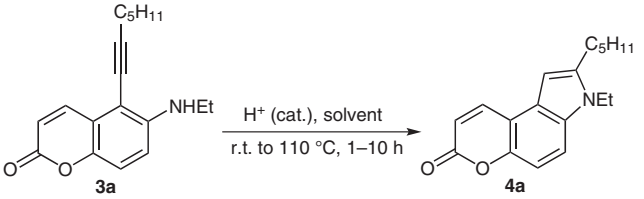
No change was detected on TLC when the cycloisomerisation reaction of the alkyne **3a** was carried out in the absence of any acid as a catalyst in ethanol at 80 °C or water at 100 °C (Table 1, entries 1 and 2). In the presence of one equivalent of acid (TsOH), the reaction proceeds smoothly when refluxed in ethanol at 80 °C and gives 80% yield of the product **4a** (Table 1, entry 3). For optimisation of the reaction conditions we have carried out a series of experiments, in which the solvent, temperature, and the Brønsted acid were changed sequentially. It was found that at 100 °C water is the best solvent and 1 equivalent of the acid is sufficient to bring about the highest yield of the product (entry 9).

Table 1 Optimisation of the Cycloisomerisation Reaction of **3a** to **4a**

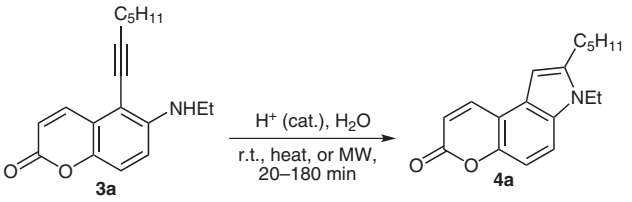


Entry	H^+ (cat.)	Solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	–	EtOH	80	10	n.r.
2	–	H_2O	100	10	n.r.
3	TsOH	EtOH	80	3	80
4	TsOH	toluene	110	3	85
5	TsOH	MeCN	80	3	83
6	TsOH	DMF	110	3	81
7	TsOH	H_2O	r.t.	10	n.r.
8	TsOH	H_2O	100	1	50
9[b]	TsOH	H_2O	100	3	95
10	TsOH	–	100	3	n.r.
11	H_2SO_4	H_2O	100	3	95
12	HNO_3	H_2O	100	3	94
13	HCl	H_2O	100	3	92
14	AcOH	H_2O	100	3	93

[a] Isolated yield; n.r. = no reaction.
[b] Optimised reaction conditions.

The reaction was also carried out without any solvent and the result was unsatisfactory (Table 1, entry 10). We subsequently found that TsOH affords slightly higher or similar yields in comparison to other acids (Table 1, entries 11–14). The reaction failed completely at room temperature (Table 1, entry 7). Therefore, the optimised reaction conditions consist of TsOH (1 equiv), H_2O, reflux at 100 °C for three hours. The optimisation experiments are summarised in Table 1. Various 2-substituted indoles were synthesised in excellent yields both under conventional heating and microwave irradiation on an ordinary kitchen microwave oven using a power level of 150 W. Almost similar yields were also obtained under microwave heating (Table 2); the most important advantage being the significant reduction of the reaction time, from several hours to typically 20–30 minutes.

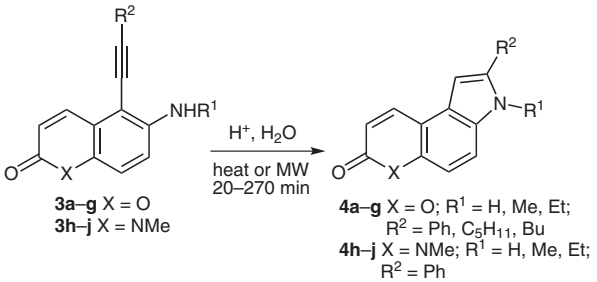
Table 2 Acid-Catalysed Cycloisomerisation Reaction of **3a** to **4a**



Entry	H^+ (equiv)	Heating	Time (min)	Yield (%)[a]
1	2	r.t.	180	–
2	1	100 °C[b]	180	95
3	2	MW[c]	20	80
4	1	MW[c]	20	94

[a] Isolated yields.
[b] Conventional heating.
[c] Microwave heating at 150 W.

Having established the optimised reaction conditions, the scope of this protocol was explored with different substrates **3a–g** and **3h–j** for the synthesis of various heterocycles (Scheme 2, Table 3). Few examples of the cycloisomerisation of acetylenic amines have been reported.[24–26] Cycloisomerisation of acetylenic amines with electron-donating substituents are very rare.[22a,b] Here we have been able to demonstrate that acetylenic amines with electron-donating as well as without electron-withdrawing groups readily undergo cycloisomerisation to give the pyrrolocoumarin and pyrroloquinoline derivatives.



Scheme 2 Acid-catalysed cycloisomerisation of **3** to **4**

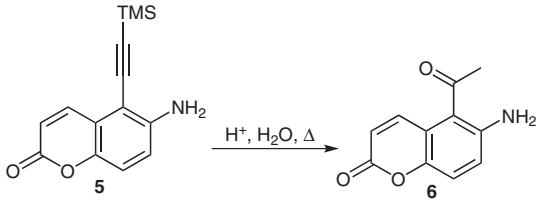
However, in the case of 6-amino-5-[(trimethylsilyl)ethynyl]-2*H*-chromen-2-one (**5**), exclusively the hydration product, 5-acetyl-6-aminochromen-2-one (**6**) was obtained instead of the desired pyrrolocoumarin derivative (Scheme 3).

Table 3 Pyrrolocoumarins **4a–g** and Pyrroloquinolines **4h–j**

Entry	Substrate	X	R^1	R^2	Heating[a]	Time (min)	Product	Yield (%)[b]
1	**3a**	O	Et	C_5H_{11}	100 °C	180	**4a**	95
2	**3a**	O	Et	C_5H_{11}	MW	20	**4a**	94
3	**3b**	O	Me	Ph	100 °C	180	**4b**	94
4	**3b**	O	Me	Ph	MW	20	**4b**	93
5	**3c**	O	Et	Ph	100 °C	180	**4c**	95
6	**3d**	O	H	Ph	100 °C	210	**4d**	89
7	**3d**	O	H	Ph	MW	25	**4d**	89
8	**3e**	O	Me	Bu	100 °C	180	**4e**	90
9	**3e**	O	Me	Bu	MW	20	**4e**	89
10	**3f**	O	Et	Bu	100 °C	180	**4f**	93
11	**3g**	O	H	Bu	100 °C	240	**4g**	89
12	**3g**	O	H	Bu	MW	25	**4g**	87
13	**3h**	NMe	H	Ph	100 °C	270	**4h**	85
14	**3i**	NMe	Me	Ph	100 °C	240	**4i**	87
15	**3i**	NMe	Me	Ph	MW	30	**4i**	86
16	**3j**	NMe	Et	Ph	100 °C	240	**4j**	82

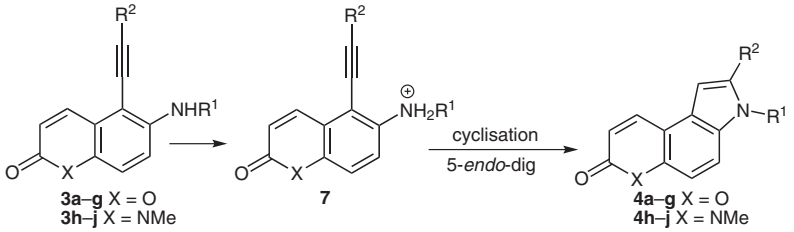
[a] Conventional heating at 100 °C or microwave heating at 150 W.
[b] Isolated yields.

The mechanistic rationalisation for the formation of products **4a–j** is depicted in Scheme 4. Initially the protonation of the amine **3** may give the intermediate cation **7**, which may then add to the triple bond in a concerted manner where a proton transfer and 5-*endo*-dig cyclisation may occur to give the products **4** because 4-*exo*-dig is energetically unfavourable. There is only one report[27]for the Brønsted acid-catalysed formation of pyrrole by a 5-*endo*-dig cyclisation. More over the substrate they used were activated ynamide derivatives.



Scheme 3 Hydration of compound **5**

In conclusion, to our knowledge the work reported here represents the first example of H^+-catalysed preparation of pyrrolocoumarins and pyrroloquinolones in excellent yields. The notable feature of the proposed methodology includes the use of water as a reaction medium under conventional heating. As expected considerable reduction of reaction time under microwave irradiation was observed. Moreover, the transformation proceeds well during the course of the reaction without requiring an inert atmosphere and the procedure offers several advantages including inexpensive catalyst, improved yields and simple yet clean reaction conditions, making it a useful and attractive strategy for the synthesis of bioactive heterocycles.



Scheme 4 Probable mechanistic pathway of acid-catalysed cycloisomerisation

Melting points were determined in open capillaries and are uncorrected. IR spectra (cm^{-1}) were recorded using samples as neat liquids and solid samples were recorded in KBr disks. ^1H NMR (400 MHz) spectra were recorded in $CDCl_3$ (chemical shifts in δ) with TMS as internal standard. Microwave irradiations were done on an ordinary kitchen microwave oven, Model No. BMO 800 TS. silica gel (60–120, 230–400 mesh, Rankem, India) was used for chromatographic separation. Silica gel G (Spectrochem, India) was used for TLC.

The starting acetylenic amines were prepared according to our earlier published procedure.[22a] Compounds **3b–d**,**g–j** are all known. The analytical and spectral data of the new acetylenic amines are given below.

3a
Yield: 79%; yellow gum.

IR (KBr): 1716, 2217, 3402 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.2 Hz, 3 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.35–1.42 (m, 2 H), 1.44–1.53 (m, 2 H), 1.65–1.72 (m, 2 H), 2.58 (t, *J* = 7.2 Hz, 2 H), 3.24 (t, *J* = 7.2 Hz, 2 H), 4.99 (s, 1 H), 6.42 (d, *J* = 10.0 Hz, 1 H), 6.79 (d, *J* = 10.0 Hz, 1 H), 7.15 (d, *J* = 8.8 Hz, 1 H), 8.05 (d, *J* = 10.0 Hz, 1 H).

MS: *m*/*z* = 283 [M^+].

Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.53; H, 7.54; N, 4.80.

3e
Yield: 74%; yellow solid; mp 76–78 °C.

IR (KBr): 1716, 2216, 3379 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, *J* = 7.2 Hz, 3 H), 1.53 (m, 2 H), 1.67 (m, 2 H), 2.57 (t, *J* = 7.2 Hz, 2 H), 2.94 (s, 3 H), 4.62 (s, 1 H), 6.42 (d, *J* = 9.6 Hz, 1 H), 6.79 (d, *J* = 8.8 Hz, 1 H), 7.18 (d, *J* = 9.2 Hz, 1 H), 8.05 (d, *J* = 9.6 Hz, 1 H).

MS: *m*/*z* = 255 [M^+].

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.31; H, 6.84; N, 5.41.

3f
Yield: 72%; yellow gum.

IR (KBr): 1732, 2212, 3400 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.2 Hz, 3 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.52 (m, 2 H), 1.67 (m, 2 H), 2.59 (t, *J* = 7.2 Hz, 2 H), 3.23 (q, *J* = 7.2 Hz, 2 H), 4.48 (s, 1 H), 6.41 (d, *J* = 9.6 Hz, 1 H), 6.78 (d, *J* = 9.2 Hz, 1 H), 7.14 (d, *J* = 9.2 Hz, 1 H), 8.04 (d, *J* = 9.6 Hz, 1 H).

MS: *m*/*z* = 269 [M^+].

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.68; H, 7.03; N, 5.11.

Pyrrolocoumarins 4a–g and Pyrroloquinolines 4h–j; General Procedure

A mixture of acetylenic amine **3** (1 equiv) and TsOH (1 equiv) was refluxed in H_2O (5 mL) for 3 h or charged in a 20 mL thick-walled glass sealed tube and irradiated for 20–30 min. After completion of the reaction as monitored by TLC, the reaction mixture was cooled, diluted with sat. aq $NaHCO_3$ (50 mL), and extracted with EtOAc (3 × 25 mL). The combined organic extracts were washed with brine (50 mL) and dried (Na_2SO_4). The solvent was distilled off and the resulting crude product was purified by column chromatography over silica gel (60–120 mesh) using hexane–EtOAc mixture (80:20) as eluent to give the products **4a–g** or **4h–j**.

The analytical and spectral data of the products **4b–d**,**g–j** were in agreement with the reported values.[22b,e] The new products are listed below.

4a
Yield: 95%; colourless solid; mp 72–74 °C.

IR (KBr): 2932, 1716 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 6.8 Hz, 3 H), 1.37 (t, *J* = 7.2 Hz, 3 H), 1.40–1.46 (m, 4 H), 1.75–1.83 (m, 2 H), 2.77 (t, *J* = 8.0 Hz, 2 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 6.44 (d, *J* = 9.6 Hz, 1 H), 6.49 (s, 1 H), 7.13 (d, *J* = 8.4 Hz, 1 H), 7.42 (d, *J* = 8.8 Hz, 1 H), 8.11 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 14.0, 15.5, 22.5, 26.8, 28.8, 31.7, 38.0, 96.7, 109.5, 110.1, 112.9, 114.3, 124.4, 132.2, 141.1, 143.5, 149.8, 162.1.

HRMS: *m*/*z* calcd for $C_{18}H_{21}NO_2$ + Na [M + Na]$^+$: 306.1470; found; 306.1468.

4e
Yield: 90%; colourless solid; mp 86–88 °C.

IR (KBr): 2930, 1704 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.2 Hz, 3 H), 1.49 (q, *J* = 7.2 Hz, 2 H), 1.74 (q, *J* = 7.6 Hz, 2 H), 2.79 (t, *J* = 7.2 Hz, 2 H), 3.72 (s, 3 H), 6.44 (d, *J* = 9.6 Hz, 1 H), 6.49 (s, 1 H), 7.13 (d, *J* = 8.8 Hz, 1 H), 7.41 (d, *J* = 8.8 Hz, 1 H), 8.10 (d, *J* = 9.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.5, 26.7, 19.8, 30.6, 96.6, 109.5, 110.0, 112.8, 114.4, 124.1, 133.4, 141.1, 144.1, 149.8, 162.1.

MS: *m*/*z* = 255 [M^+].

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 74.97; H, 6.68; N, 5.55.

4f
Yield: 93%; colourless solid; mp 78–80 °C.

IR (KBr): 2930, 1705 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.2 Hz, 3 H), 1.37 (t, *J* = 7.2 Hz, 3 H), 1.45–1.52 (m, 2 H), 1.73–1.81 (m, 2 H), 2.77 (t, *J* = 7.6 Hz, 2 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 6.44 (d, *J* = 9.2 Hz, 1 H), 6.49 (s, 1 H), 7.13 (d, *J* = 8.4 Hz, 1 H), 7.43 (d, *J* = 8.8 Hz, 1 H), 8.11 (d, *J* = 9.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 15.5, 22.6, 26.5, 30.6, 38.0, 96.6, 109.5, 110.1, 112.9, 114.4, 124.4, 132.2, 141.1, 143.4, 149.7, 162.2.

MS: *m*/*z* = 269 [M^+].

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.64; H, 7.20; N, 5.16.

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