Baker–Venkataraman Rearrangement Under Microwave Irradiation: A New Strategy for the Synthesis of 3-Aroyl-5-hydroxyflavones

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Abstract: Microwave irradiation selectively induces the Baker–Venkataraman rearrangement of 2′,6′-diaroyloxyacetophenones to give 3-aroyl-5-hydroxyflavones, in a very short reaction time. Under classical heating conditions these reactions afforded 5-hydroxyflavones as byproducts.

Key words: 3-aroyl-5-hydroxyflavones, Baker–Venkataraman rearrangement, microwave irradiation, antioxidant activity

The flavone nucleus seems to be an important scaffold to prepare pharmaceutical agents, since both natural and synthetic derivatives are responsible for a great variety of biological and pharmacological activities, including antitumour, anti-inflammatory, antiviral, and antioxidant properties.[1] The presence of hydroxyl groups in the flavone skeleton is very important for their capacity to act as antioxidants,[2] as exemplified by quercetin (3,3′,4′,5,7-pentahydroxyflavone), a well-known antioxidant agent and a very important compound with numerous biological activities such as inhibitory effect on tumour growth.[3] Another important structural feature of flavones is the presence of a 3-aroyl group, in fact it has been reported that flavones bearing this substituent possess antibacterial and antifungal activities.[4] More recently, it was also reported that some 3-aroylflavones present antitubulin activity.[5] As part of our continuing work on the synthesis and antioxidant evaluation of polyhydroxy-2-styrylchromones,[6] we have considered the synthesis of polyhydroxy-3-aroylflavones **7a**,**b**, which are new chromone-type compounds with essential features of good antioxidant and anti-inflammatory agents.

The most direct method to form 3-aroyl-5-hydroxyflavones is the Baker–Venkataraman rearrangement of 2′,6′-diaroyloxyacetophenones (as shown in Scheme 1). The classical method for the synthesis of 2′,6′-diaroyloxyacetophenones[7] was efficient for the synthesis of 2′,6′-di(3,4-dibenzyloxybenzoyloxy)acetophenone (**3c**), but gave several problems in the synthesis of 2′,4′,6′-tri(3,4-dibenzyloxybenzoyloxy)acetophenone (**4c**); there was contamination by the diester 2′,4′-tri(3,4-dibenzyloxybenzoyloxy)-6′-hydroxyacetophenone which was identifiable by the singlet at δ = 13.04 ppm in the ^{1}H NMR spectrum, due to the 6′-hydroxy proton involved in a hydrogen bond with the carbonyl group. The formation of this compound decreases the yield and it is difficult to remove, since it has a similar chromatographic behaviour to the expected product **4c**. Consequently we tested another methodology,[8] and were able to optimise the procedure[9] to obtain the desired triester **4c** in very good yield (79%). As a consequence of the simplicity in execution and in the purification when using this methodology, we applied it to the synthesis of other 2′,6′-diaroyloxyacetophenones **3a**–**c** and **4a**,**b**.[9] These were also obtained in good yields (78–85%; Scheme 1). The main NMR features of 2′,4′,6′-triaroyloxyacetophenones **4a**–**c**[10] are the singlets at δ = 7.12–7.34 and 2.37–2.51 ppm, assigned to the resonances of the equivalent protons H-3′,5′, due to the symmetry of the molecule, and of the protons of the 2-methyl group. In the ^{13}C NMR it is worth mentioning the resonance of the ester and ketone carbonyl groups, appearing at δ = 162.4–164.2 and 196.6–197.6 ppm, respectively.

The Baker–Venkataraman rearrangement of aroyloxyacetophenones **3c** and **4c** under thermal heating conditions (K_2CO_3 in anhyd pyridine at 120 °C) afforded the expected 3-aroyl-5-hydroxyflavones **5c** and **6c** contaminated with flavones **5d**[11] and **6d**, respectively, as byproducts (Scheme 1). All attempts to eliminate these byproducts were unsuccessful. With shorter reaction times the starting 2′,6′-diaroyloxyacetophenones were recovered and/or mixtures of intermediates were obtained (these compounds were not characterised but seemed to be the tautomeric forms of the intermediate diketones).[12] Therefore, longer reaction times caused degradation[7,13] and consequently worse yields of the desired 3-aroylflavones. The purification of each one of the referred 3-aroyl-5-hydroxyflavones **5c** and **6c** are very tedious and complicated, since they have similar chromatographic behaviour to byproducts **5d** and **6d**.

As a result of these unsuccessful attempts and following our recent successes in microwave-assisted organic synthesis,[14] we decided to explore this technique to enhance the efficiency of the Baker–Venkataraman rearrangement of 2′,6′-diaroyloxyacetophenones (Scheme 1). After several attempts we found that the use of a constant power of 400 W for 10 minutes was sufficient to perform the rearrangement and also provided the best experimental conditions[15] to selectively obtain the expected 3-aroyl-5-hydroxyflavones **5c** and **6c** in good overall yields and without byproducts. Our results indicate that it is necessary to achieve the refluxing temperature of pyridine and

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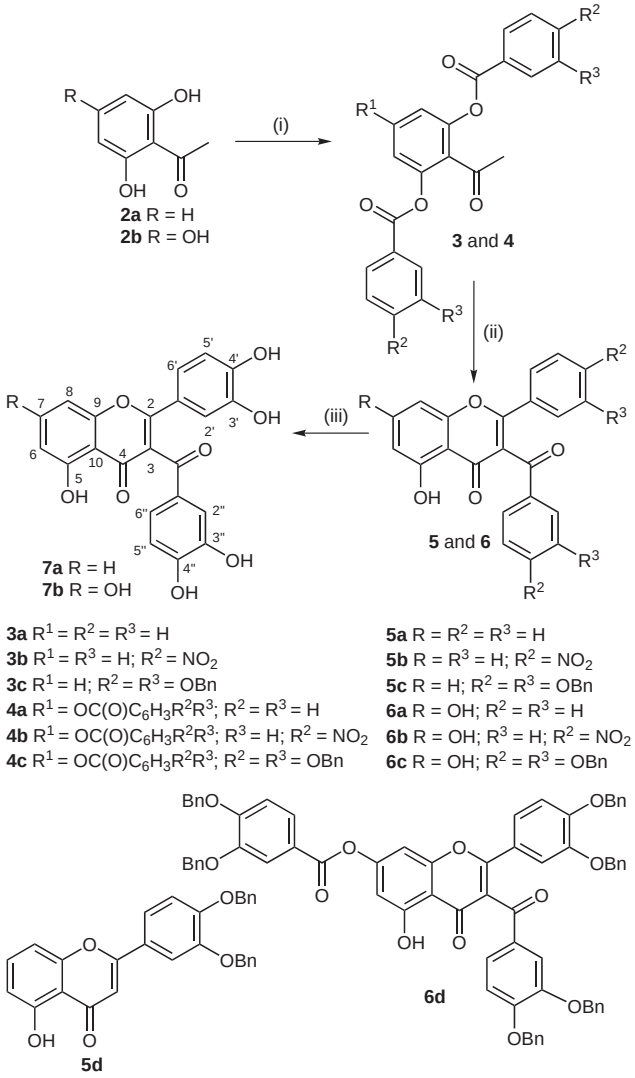

3a $R^1 = R^2 = R^3 = H$
3b $R^1 = R^3 = H$; $R^2 = NO_2$
3c $R^1 = H$; $R^2 = R^3 = OBn$
4a $R^1 = OC(O)C_6H_3R^2R^3$; $R^2 = R^3 = H$
4b $R^1 = OC(O)C_6H_3R^2R^3$; $R^3 = H$; $R^2 = NO_2$
4c $R^1 = OC(O)C_6H_3R^2R^3$; $R^2 = R^3 = OBn$

5a $R = R^2 = R^3 = H$
5b $R = R^3 = H$; $R^2 = NO_2$
5c $R = H$; $R^2 = R^3 = OBn$
6a $R = OH$; $R^2 = R^3 = H$
6b $R = OH$; $R^3 = H$; $R^2 = NO_2$
6c $R = OH$; $R^2 = R^3 = OBn$

Scheme 1 *Reagents and conditions*: (i) DCC, 4-pyrrolidinopyridine, $HO_2CC_6H_3R^2R^3$, CH_2Cl_2, r.t.; (ii) classical heating conditions: K_2CO_3, anhyd pyridine, 120 °C, under nitrogen, 2 h; microwave conditions: K_2CO_3, anhyd pyridine, 400 W, 10 min; (iii) BBr_3, anhyd CH_2Cl_2, r.t.

maintain the temperature for at least seven minutes. Attempts to use higher power to reach the refluxing temperature more quickly resulted in more degradation, even when the reaction time was reduced. Furthermore, attempts to use less power combined with longer reaction times were also unsuccessful – the desired 3-aroyl-5-hydroxyflavones **5c** and **6c** were obtained, but contaminated with the intermediate diketones and/or the corresponding 5-hydroxyflavones **5d** and **6d**.

The target polyhydroxy-3-aroylflavones **7a**,**b** were successfully obtained by treatment of 3-aroyl-5-hydroxyflavones **5c** and **6c** with boron tribromide.[16]

In order to determine the scope of this reaction and its utility as a new synthetic methodology to obtain 3-aroyl-5-hydroxyflavones via Baker–Venkataraman rearrangement of 2′,6′-diaroyloxyacetophenones, we extended our study to other derivatives, including the use of 2′,6′-diaroyloxyacetophenones with strong electron-withdrawing substituents in the aromatic ring of the aroyl groups. The Baker–Venkataraman rearrangement of 2′,6′-diaroyloxyacetophenones **3a**,**b** and **4a**,**b** under the referred microwave experimental conditions[15] allowed for the synthesis of 3-aroyl-5-hydroxyflavones **5a**,**b** and **6a**,**b** in good yields (68–72%).

All the synthesised novel 3-aroyl-5-hydroxyflavones **5c**,[17] **6a**–**c**, and **7a**,**b** have been characterised by NMR spectroscopy.[18] The most noticeable features in their ^{1}H NMR spectra are: i) the singlet due to the resonance of the proton of the 5-OH, which is unaffected by solvent changes and appears at δ = 12.15–12.64 ppm; ii) the resonances of protons H-6 and H-8 of **6a**–**c** and **7a**, appearing as broad singlets or as doublets with a small coupling constant (^4J = 2.1 Hz) at δ = 6.16–6.40 and 6.29–6.65 ppm, respectively; iii) in the case of 3-aroyl-5-hydroxyflavones **5c** and **7a** the proton resonances of H-6 (δ = 6.83–6.86 ppm), H-8 (δ = 6.96–7.19 ppm) and H-7 (δ = 7.59–7.73 ppm), appear as double doublets (H-6 and H-8) and as a triplet (H-7). The most important signals in the ^{13}C NMR spectra **5c**,[17] **6a**–**c**, and **7a**,**b** are the resonances of the chromone and aroyl carbonyl groups, which appear at δ = 179.9–181.5 and 190.5–192.6 ppm, respectively. The carbonyl carbon resonances of the 3-aroyl substituents were unequivocally assigned by the connectivities with H-2″ and H-6″ in their HMBC spectra.

In conclusion, we established a new and successful methodology to perform the Baker–Venkataraman rearrangement of 2′,6′-diaroyloxyacetophenones into the corresponding 3-aroyl-5-hydroxyflavones. The beneficial effect of using microwave irradiation as source of energy was the shortening of the reaction time from two hours to 10 minutes and the fact that this new methodology allowed us to obtain selectively 3-aroyl-5-hydroxyflavones in good yields.

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(9) **Optimised Experimental Procedure**

A mixture of the 2′,6′-dihydroxyacetophenone (**2a**, 0.92 g, 6.05 mmol), the appropriate benzoic acid (13.31 mmol), 4-pyrrolidinopyridine (197 mg, 1.33 mmol), and *N*,*N*-dicyclohexylcarbodiimide (2.75 g, 13.33 mmol) in CH_2Cl_2 (50 mL) was stirred at r.t. for 12 h. The obtained dicyclohexylurea was filtered off and washed with CH_2Cl_2 (2 × 25 mL). The filtrate was evaporated to dryness and the residue recrystallised in from EtOH to provide the 2′,6′-diaroyloxyacetophenones **3a**–**c** (**3a**, 83%; **3b**, 78%; **3c**, 80%).

A mixture of the 2′,4′,6′-trihydroxyacetophenone (**2b**, 0.86 g, 5.11 mmol), the appropriate benzoic acid (16.88 mmol), 4-pyrrolidinopyridine (250 mg, 1.69 mmol), and *N*,*N*-dicyclohexylcarbodiimide (3.48 g, 16.87 mmol) in CH_2Cl_2 (100 mL) was stirred at r.t. for 20 h. The obtained dicyclohexylurea was filtered off and washed with CH_2Cl_2 (2 × 30 mL). The filtrate was evaporated to dryness and the residue recrystallised in from EtOH to provide the 2′,4′,6′-triaroyloxyacetophenones **4a**–**c** (**4a**, 80%; **4b**, 85%; **4c**, 79%).

(10) **Physical Data of 2′,4′,6′-Tribenzoyloxyacetophenone (4a)**

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.51 (s, 3 H, 2-CH_3), 7.25 (s, 2 H, H-3′,5′), 7.52 (dd, 6 H, *J* = 7.6, 6.4 Hz, H-3,5 of 2′,4′,6′-$OCOC_6H_5$), 7.66 (t, 3 H, *J* = 7.6 Hz, H-4 of 2′,4′,6′-$OCOC_6H_5$), 8.15–8.20 (m, 6 H, H-2,6 of 2′,4′,6′-$OCOC_6H_5$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 31.4 (2-CH_3), 114.6 (C-3′,5′), 125.8 (C-1′), 128.4 (C-1 of 2′,6′-$OCOC_6H_5$), 128.6 (C-1 of 4′-$OCOC_6H_5$), 128.7 (C-3,5 of 4′-$OCOC_6H_5$), 128.8 (C-3,5 of 2′,6′-$OCOC_6H_5$), 130.25 (C-2,6 of 4′-$OCOC_6H_5$), 130.31 (C-2,6 of 2′,6′-$OCOC_6H_5$), 134.0 (C-4 of 4′-$OCOC_6H_5$), 134.2 (C-4 of 2′,6′-$OCOC_6H_5$), 148.5 (C-2′,6′), 152.0 (C-4′), 164.1 (C=O of 4′-$OCOC_6H_5$), 164.2 (C=O of 2′,6′-$OCOC_6H_5$), 197.5 (C-1) ppm. MS (ES^+): *m/z* (%) = 503 (100) $[M + Na]^+$.

(11) **Physical Data of 3′,4′-Dibenzyloxy-5-hydroxyflavone (5d)**

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 5.25 and 5.26 (2 s, 2 × 2 H, 3′,4′-$OCH_2C_6H_5$), 6.57 (s, 1 H, H-3), 6.80 (dd, 1 H, *J* = 8.3, 0.7 Hz, H-6), 6.94 (dd, 1 H, *J* = 8.3, 0.7 Hz, H-8), 7.02 (d, 1 H, *J* = 8.5 Hz, H-5′), 7.31–7.44 (m, 6 H, H-3,4,5 of 3′,4′-$OCH_2C_6H_5$), 7.45 (br s, 1 H, H-2′), 7.45–7.51 (m, 5 H, H-6′ and H-2,6 of 3′,4′-$OCH_2C_6H_5$), 7.52 (t, 1 H, *J* = 8.3 Hz, H-7), 12.64 (s, 1 H, 5-OH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 70.9 (3′-$OCH_2C_6H_5$), 71.5 (4′-$OCH_2C_6H_5$), 104.8 (C-3), 106.9 (C-8), 110.7 (C-10), 111.3 (C-6), 112. 8 (C-2′), 114.0 (C-5′), 120.7 (C-6′), 123.9 (C-1′), 127.1 and 127.4 (C-2,6 of 3′,4′-$OCH_2C_6H_5$), 128.11 and 128.13 (C-4 of 3′,4′-$OCH_2C_6H_5$), 128.7 (C-3,5 of 3′,4′-$OCH_2C_6H_5$), 135.2 (C-7), 136.3 and 136.6 (C-1 of 3′,4′-$OCH_2C_6H_5$), 148.8 (C-3′), 152.3 (C-4′), 156.3 (C-9), 160.7 (C-5), 164.3 (C-2), 183.4 (C-4) ppm. MS (EI): *m/z* (%) = 450 (8) [M^+]. HRMS (EI): *m/z* calcd for $C_{29}H_{22}O_5$: 450.1467; found: 450.1472.

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(15) **Optimised Experimental Procedure**

A mixture of the appropriate 2′,6′-diaroyloxyacetophenone **3a**–**c** and **4a**–**c** (0.5 mmol) with anhyd K_2CO_3 (152 mg, 1.1 mmol) in anhyd pyridine (6 mL), was poured in a two-necked glassware apparatus equipped with a magnetic stirring bar, fibre-optic temperature control and reflux condenser, and was then irradiated in an Ethos SYNTH microwave (Milestone Inc.) at constant power of 400 W for 10 min. After that period the reaction mixture was poured into a mixture of ice and water and the pH was adjusted to 3–4 with diluted HCl. The obtained solid was filtered off and recrystallised from EtOH to provide the 3-aroyl-5-hydroxyflavones **5a**–**c** and **6a**–**c**; in several cases a purification by column chromatography was necessary, using $CHCl_3$ as eluent (**5a**, 70%; **5b**, 69%; **5c**, 72%; **6a**, 72%; **6b**, 68%; **6c**, 73%).

(16) **Optimised Experimental Procedure**

BBr_3 (1.5 mol per benzyloxy group) was added to a solution of the appropriate 3-aroyl-5-hydroxyflavone **5c** and **6c** (0.3 mmol) in anhyd CH_2Cl_2 (25 mL) at low temperature (–70 °C). After the addition was complete, the cooling system was removed and the reaction mixture was stirred at r.t. for 24 h. Then, H_2O (50 mL) was added and the resulting reaction mixture was stirred at r.t. for 2–3 h. The obtained solid was filtered off and washed several times with H_2O and CH_2Cl_2; the expected 3-aroylflavones **7a**,**b** were obtained in good yields (**7a**, 62%; **7b**, 58%).

Physical Data of 3-(3,4-Dihydroxybenzoyl)-3′,4′,5,7-tetrahydroxyflavone (7b)

^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 6.25 (d, 1 H, *J* = 1.9 Hz, H-6), 6.48 (d, 1 H, *J* = 1.9 Hz, H-8), 6.73 (d, 1 H, *J* = 8.4 Hz, H-5′), 6.74 (d, 1 H, *J* = 8.2 Hz, H-5″), 6.94 (dd, 1 H, *J* = 8.4, 2.2 Hz, H-6′), 7.06 (d, 1 H, *J* = 2.2 Hz, H-2′), 7.24 (dd, 1 H, *J* = 8.2, 2.0 Hz, H-6″), 7.29 (d, 1 H, *J* = 2.0 Hz, H-2″), 9.42, 9.86, and 10.06 (3 s, 4 H, 3′,4′,3″,4″-OH), 11.05 (s, 1 H, 7-OH), 12.48 (s, 1 H, 5-OH) ppm. ^{13}C NMR (75.47 MHz, DMSO-d_6): δ = 94.0 (C-8), 99.1 (C-6), 103.0 (C-10), 115.4 (C-2′,2″), 115.7 (C-5′ and C-5″), 118.7 (C-3), 120.7 (C-1′), 121.9 (C-6′), 123.2 (C-6″), 128.8 (C-1″), 145.4 (C-3′ and C-3″), 149.2 (C-4′), 151.7 (C-4″), 157.3 (C-9), 161.3 (C-2), 161.5 (C-5), 164.7 (C-7), 179.9 (C-4), 190.7 (C=O) ppm. MS (ES^+): *m/z* (%) = 445 (63) $[M + Na]^+$.

(17) **Physical Data of 3′,4′-Dibenzyloxy-3-(3,4-dibenzyloxybenzoyl)-5-hydroxyflavone (5c)**

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 4.89 (s, 2 H, 3′-$OCH_2C_6H_5$), 5.16 (s, 2 H, 4′-$OCH_2C_6H_5$), 5.14 (s, 2 H, 3″-$OCH_2C_6H_5$), 5.21 (s, 2 H, 4″-$OCH_2C_6H_5$), 6.83 (dd, 1 H, *J* = 8.4, 0.7 Hz, H-6), 6.85 (d, 1 H, *J* = 8.6 Hz, H-5′), 6.88 (d, 1 H, *J* = 8.5 Hz, H-5″), 6.96 (dd, 1 H, *J* = 8.4, 0.7 Hz, H-8), 7.16 (d, 1 H, *J* = 2.2 Hz, H-2′), 7.22 (dd, 1 H, *J* = 8.6, 2.2 Hz, H-6′), 7.23–7.43 (m, 20 H, H-2,3,4,5,6 of 3′,4′,3″,4″-$OCH_2C_6H_5$), 7.47 (dd, 1 H, *J* = 8.5, 2.0 Hz, H-6″), 7.59 (t, 1 H, *J* = 8.4 Hz, H-7), 7.59 (d, 1 H, *J* = 2.0 Hz, H-2″), 12.23 (s, 1 H, 5-OH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ =

70.75 (4′-O*C*H$_2$C$_6$H$_5$), 70.78 (4″-O*C*H$_2$C$_6$H$_5$), 71.0 (3′-O*C*H$_2$C$_6$H$_5$), 71.2 (3″-O*C*H$_2$C$_6$H$_5$), 106.9 (C-8), 110.0 (C-10), 111.7 (C-6), 112.9 (C-5″), 113.7 (C-5′), 114.1 (C-2″), 114. 4 (C-2′), 120.0 (C-3), 122.7 (C-6′), 123.7 (C-1′), 125.0 (C-6″), 127.0, 127.1, and 127.2 (C-2,6 of 3′,4′,3″,4″-OCH$_2$*C*$_6$H$_5$), 127.9, 128.0, and 128.1 (C-4 of 3′,4′,3″,4″-OCH$_2$*C*$_6$H$_5$), 128.49, 128.51, 128.60, and 128.64 (C-3,5 of 3′,4′,3″,4″-OCH$_2$*C*$_6$H$_5$), 130.3 (C1″), 135.9 (C-7), 136.16, 136.24, 136.4, and 136.6 (C-1 of 3′,4′,3″,4″-OCH$_2$*C*$_6$H$_5$), 148.4 (C-3′), 148.8 (C-3″), 151.8 (C-4′), 154.1 (C-4″), 156.0 (C-9), 160.8 (C-5), 162.5 (C-2), 181.5 (C-4), 191.2 (C=O) ppm. MALDI-MS: *m/z* (%) = 789 (100) [M + Na]$^+$.

(18) The structural characterisation of 3-aroyl-5-hydroxy-flavones **5a**,**b** is according to the literature (ref. 7).