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Note

A facile synthesis of 2-(2′-vinylthiophene)chromones by the modified Baker-Venkataraman tansformation

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The modified Baker-Venkataraman transformation has been utilised for the synthesis of 2-(2′-vinylthiophene)-chromones **3a-e** which on methylation furnishes 7-methoxy- or 5,7-dimethoxy-2-(2′vinylthiophene)chromones **4a-e**

2-Styrylchromones have been synthesized earlier by (i) consensation of cinnamic anhydride and sodium cinnamate with 2,4-dihydroxyphenyl benzyl ketone[1], (ii) condensation of 2-methylchromones with benzaldehydes in the presence of sodium ethoxide[2], (iii) Baker-Venkataraman transformation involving the reaction of *o*-hydroxyacetophenones with cinnamoyl chlorride in acetone-K_2CO_3 medium[3,4], and (iv) modified Witting synthesis[5]. We have earlier reported the synthesis of 2-(2′-vinylfuryl)chromones, which are structurally similar to 2-strylchromones, by the Baker-Venkataraman transformation[6]. We now report a facile synthesis of 2-(2′-vinylthiophene)chromones (**3a-e**).

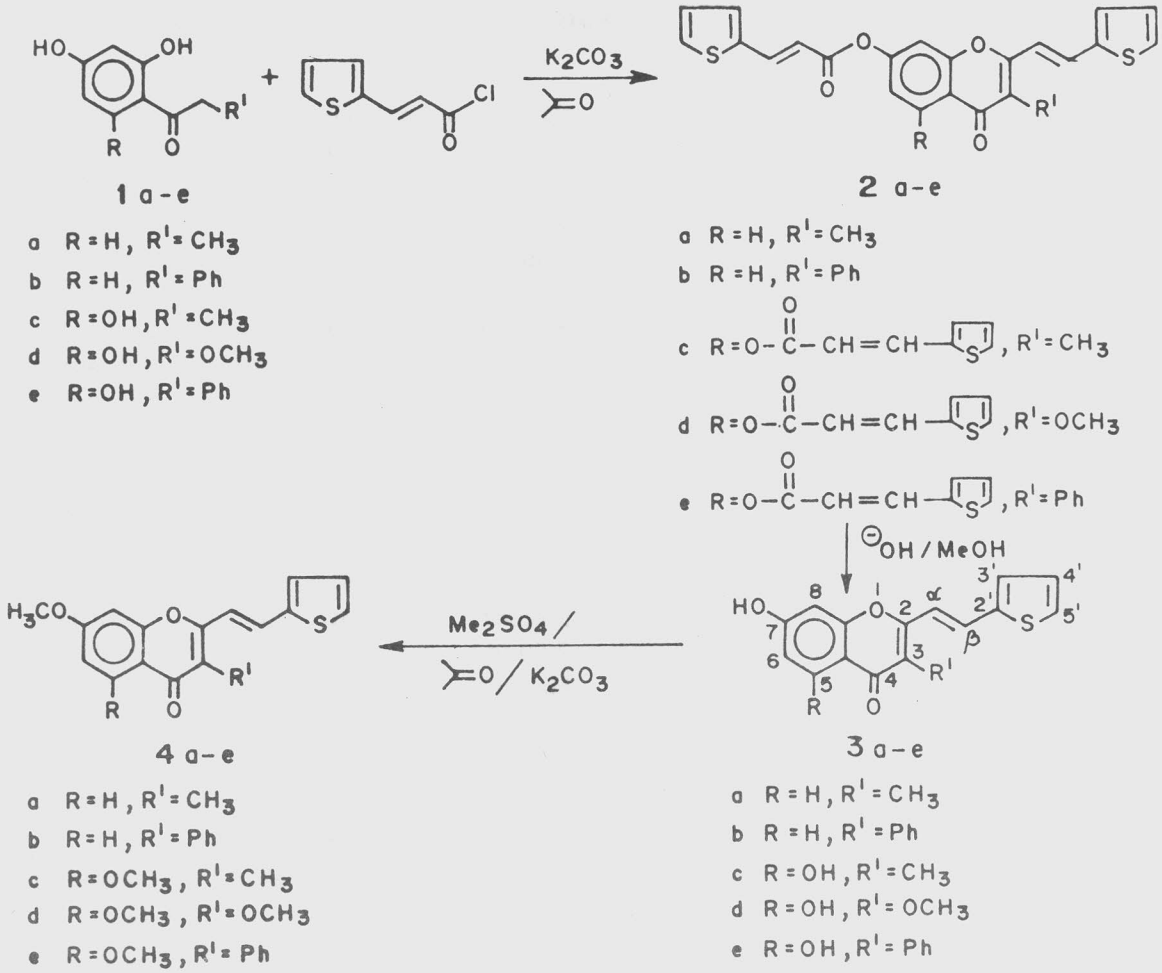
The modified Baker-Venkataraman transformation has now been applied for the synthesis of 7-hydroxy-3-methyl-(**3a**)-, 7-hydroxy-3-phenyl- (**3b**)-, 5,7-dihydroxy-3-methyl- (**3c**)-, 5,7-dihydroxy-3-methoxy- (**3d**)- and 5,7-dihyddoxy-3-phenyl-(**3e**)-2-(2′-vinylthiophene)chromones. Thus, condensation of respropiophenone **1a**[7], 2,4-dihydroxyphenyl benzyl ketone **1b**[8], phloropropiophenone **1c**[7], ω-methoxyphloracetophenone **1d**[9] and 2,4,6-trihydroxyphenyl benzyl ketone **1e**[10] with thiophene-2-acroyl chloride in acetone-K_2CO_3 afforded directly 7-(2′-thiopheneacroyloxy)-and 5,7-di(2′-thiopheneacroyloxy)-2-(2′-vinulthiophene) chromones (**2a,b** and **2c-e)** respectively. Chromones **2a-e** were hydrolysed with 5% methanolic potassium hydroxide to yield hydroxy-2-(2′-vinylthiophene)chromones **3a-e** in 50% yield (Scheme I). The structures of the compounds were assigned by the analysis of their spectral data. In **3a** the carbonyl peak appeared at 1618 cm^{-1} and UV peaks at 239, 272 and 376 nm indicating extended conjugation. In ^1H NMR of **3a**, the α- and β-protons appeared at δ 7.50 and 8.00 as doublets with J = 16.0 Hz indicating their *trans*-configuration. The three thiophene protons appared at δ 7.39-8.38 as a multiplet. Other chromone protons appeared at δ 7.80 (d, J = 10 Hz, H-5), 7.00 (dd, J = 10, 2.5 Hz, H-6), and 7.00 (d, J = 2.5 Hz, H-8). The C-3 methyl protons appeared as a singlet at δ 2.30. The MS of **3a** showed M^+ at m/z 284.

2-(2′-Vinylthophene)chromones **3a-e** on methylation with dimethyl sulphate in acetone-K_2CO_3 medium furnhised the corresponding 7-*O*-methyl- and 5,7-di-*O*-methyl ethers **4a-e**.

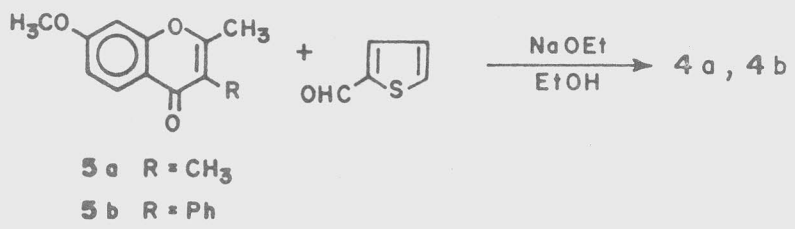
With a view to confirm the structures of the products obtained from Baker-Venkataraman transformation, **4a** and **4b** were synthesised by another route (Scheme II). 7-Methoxy-2,3-dimethylchromone **5a**[11] and 7-methoxy-3-phenyl-2-methylchromone **5b**[1] on condensation with thiophene-2-carboxyaldehyde in NaOEt/EtOH gave **4a** and **4b** respectively in 40% yield.

Experimental Section

General. Melting points were determined in a sulphuruc acid-bath and are uncorrected. ^1H NMR spectra were recorded on a Varian-Gemini instrument at 200 MHz in DMSO-d_6. ^{13}C NMR spectra were recorded on a Varian-Gemini 200 spectrometer at 50.3 MHz. IR spectra were recorded on FT-IR Perkin-Elmer 1710 spectrophotometer and UV spectra on a Perkin-Elmer Lambda UV-Vis spectrophotometer. MS



Scheme I



Scheme II

were recorded on a VG Micromass 7070 H spectrometer.

General methods for synthesis of 7-hydroxy- and 5,7-dihydroxy-2-(2′-vinylthiophene)chromones 3a-e. A solution of *o*-hydroxyacetophenones **1a-e** (10 mmoles) and thiophene-2-acroyl chloride (20 mmoles for **1a, 1b**; 30 mmoles for **1c-e**) was refluxed with anhydrous K_2CO_3 (10 g) in acetone (200 mL) for 15 hr on a water-bath. Acetone was removed and the residue treated with cold water to give yellow solids **2a-e** which were hydrolysed with 5% methanolic potassium hydroxide (100 mL) by refluxing for 1 hr. Thereafter, MeOH was removed under reduced pressure and the residue treated with water and neutralized with dil. HCl. The product was washed with 5% aqueous $NaHCO_3$ and the remaining yellow solid purified by chromatography over silica gel (using eluent; chloroform-acetone,

8:2 v/v) to give **3a-e** in 50% yield.

7-Hydroxy-3-methyl-2-(2′-vinylthiophene) chromone 3a: It crystallised from methanol as yellow needles, m.p. 292°; IR (KBr): 1618 cm^{-1} (C=O); UV(nm, log ε): 208 (4.77), 239 (4.82), 272 (4.88), 376 (5.02); ^1H NMR: δ 7.80 (d, 1H, J =10 Hz, C_5-H), 7.00 (dd, J = 10, 2.4 Hz, C_6-H), 7.39 (s, C_7-OH), 7.00 (d, J = 2.4 Hz, C_8-H), 7.50 (d, J = 16 Hz, α-H), 8.00 (d, J =16 Hz, β-H), 7.39-8.38 (m, C_3', C_4', C_5'-H), 2.30 (s, C_3-CH_3); MS: m/z 284 (M^+); Anal. Calcd for $C_{16}H_{12}O_3S$: C, 67.59; H, 4. 25. Found : C, 67.60; H, 4.22%.

7-Hydroxy-3-phenyl-2-(2′-vinylthiophene) chromone 3b: It crystallised from methanol as bright yellow needles, m.p. 225°; IR (KBr): 1635 cm^{-1} (C=O); UV (nm, log ε): 208 (4.85), 232 (4.94), 266 (4.96), 366 (5.10); ^1H NMR: δ 7.90 (d, J = 9 Hz, C_5-H), 6.80 (m, C_6-H), 7.39 (C_7-OH), 6.90 (bs, C_8-H), 6.50 (d, J = 16 Hz, α-H), 7.70 (d, J =16 Hz, β-H), 7.20-7.50 (m, 3′-H, 4′-H, 5′-H and 3-Ph); MS: m/z 194 (M^+); Anal. Calcd for $C_{21}H_{14}O_3S$: C, 72.81; H, 4.07. Found: C, 72.83; H, 4.04%.

5,7-Dihydroxy-3-methyl-2-(2′-vinylthiophene) chromone 3c: It crystallised from methanol as yellow crystals, m.p. 295°; IR (KBr): 1645 cm^{-1} (C=O); UV (nm, log ε): 205 (4.78), 235 (4.84), 262 (4.89), 380 (5.05); ^1H NMR: δ 12.50 (s, C_5-OH), 6.80 (d, J = 2 Hz, C_6-H), 7.90 (s, C_7-OH), 6.85 (d, J = 2 Hz, C_8-H), 6.90 (d, J = 16 Hz, α-H), 7.60 (d, J = 16 Hz, β-H), 7.10-7.50 (m, C_3', C_4', C_5'-H), 2.15 (s, C_3-CH_3); MS: m/z 300 (M^+) 300; Anal. Calcd for $C_{16}H_{12}O_4S$: C, 69.98; H, 4.02. Found: C, 64.00; H, 4.00%.

5,7-Dihydroxy-3-methoxy-2(2′-vinylthiophene)chromone 3d: It crystallised from methanol as pale yellow rods, m.p. 255°; IR (KBr): 1642 cm^{-1} (C=O); UV (nm, log ε): 298 (4.81), 245 (4.88), 304 (4.98), 386 (5.08); ^{1+}H NMR: δ 12.60 (s, C_5-OH), 6.20 (d, J = 2.5 Hz, C_6-H), 8.31 (s, C_7-OH), 6.45 (d, J = 2.5 Hz, C_8-H), 7.00 (d, J = 16 Hz, α-H), 7.80 (d, J = 16 Hz, β-H), 7.10-7.80 (m, C_3', C_4', C_5'-H), 3.95 (s, C_3-OCH_3); ^{13}C NMR (50.3 MHz, DMSO-d_6 + $CDCl_3$): δ 160.0 (C-2), 163.0 (C-3), 176.0 (C-4), 155.8 (C-5), 153.0 (C-8a), 139.0 (C-7), 136.0 (C-8), 129.5 (C-6a), 127.0 (C-4a), 127.0 (C-α), 126.9 (C-β), 59.5 (C-9), 113.0 (C-2′), 103.5 (C-3′), 97.1 (C-4′), 92.0 (C-5′); MS: m/z 316 (M^+); Anal. Calcd for $C_{16}H_{12}O_5S$: C, 60.75; H, 3.82. Found: C, 60.75; H, 3.79%.

5, 7-Dihydroxy-3-phenyl-2-(2′-vinylthioiphene)-chromone 3e. It crystallised from methanol as yellow flakes, m.p. 205°; IR (KBr): 1645 cm^{-1} (C=O); UV (nm, log ε): 208 (4.87), 238 (4.93), 265 (4.98), 376 (5.13); ^1H NMR: δ 12.58 (s, C_5-OH), 6.18 (d, J = 2.5 Hz, C_6-H). 8.28 (s, C_7-OH), 6.85 (d, J = 2.5 Hz, C_8-H), 7.20 (d, J = 16 Hz, α-H), 7.75 (d, J = 16 Hz, β-H), 7.30-7.90 (m, C_3', C_4', C_5'-H and C_3-Ph); Anal. Calcd for $C_{21}H_{14}O_4S$: C, 69.59; H, 3.89. Found: C, 64.74; H, 4.32%.

7-Methoxy- and 5,7-dimethoxy-2-(2′-vinylthiophene)chromones 4a-e. To a solution of **3a-e** (10 mmoles) in acetone (100 mL), anhydrous K_2CO_3 (5 g) and dimethyl sulphate (25 mmoles) were added and the mixture was refluxed for 6 hr in case of **3a, b** and for 20 hr in case of **3c-e**. The acetone was removed and the product treated with cold water. Yellow solids in 90% yield were obtained.

7-Methoxy-3-methyl-2-(2′-vinylthiiphene) chromone 4a. It crystallised from aqueous methanol as yellow solid, m.p. 192°; IR (KBr): 1635 cm^{-1} (C=O); UV (nm, log ε): 208 (4.79), 238 (4.85), 270 (4.90), 376 (5 04); ^1H NMR: δ 8.10 (d, J = 10 Hz, C_5-H), 6.50 (dd, J=10 Hz, 2.5 Hz, C_6-H), 3.90 (s, C_7-OCH_3), 6.70 (d, J=2.5 Hz, C_8-H), 7.00 (d, J=16 Hz, α-H), 7.60 (d, J=16 Hz, β-H), 7.10-7.50 (m, C_3', C_4', C_5'-H), 2.15 (s, C_3-CH_3); MS: m/z 298: M^+. Anal. Calcd for $C_{17}H_{14}O_3S$: C, 70.50; H, 4.87. Found: C, 68.45; H, 4.69%.

7-Methoxy-3-phenyl-2-(2′-vinylthiophene)-chromone 4b: It crystallised from aqueous methanol as colourless needles, m.p. 203°; IR (KBr): 1640 cm^{-1} (C=O); UV (nm, log ε): 208 (4.85), 238 (4.92), 270 (4.96), 386 (5.12); ^1H NMR: δ 8.15 (d, J = 9 Hz, C_5-H), 3.90 (s, C_7-OCH_3), 6.80 (dd, J = 10, 2.5 Hz, C_6-H), 6.90 (d, J = 2.5 Hz, C_8-H), 6.60 (d, J = 16 Hz, α-H), 7.70 (d, J = 16 Hz, β-H), 7.10-7.60 (m, C_3', C_4', C_5'-H and phenyl); MS: m/z 360 (M^+); Anal. Calcd for $C_{22}H_{16}O_3S$: C, 73.31; H, 4.47. Found: C, 73.33; H, 4.44%.

5,7-Dimethoxy-3-methyl-2-(2′-vinylthiophene)-chromone 4c. It crystallised from the aqueous methanol as pale yellow needles, m.p. 190°; IR (KBr): 1626 cm^{-1} (C=O); UV (nm, log ε): 208 (4.83), 234 (4.88), 272 (4.95), 380 (5.09); ^1H NMR: δ 4.00 (s, C_5-OCH_3), 6.20 (d, J = 2.5 Hz, C_6-H). 4.05 (s, C_7-OCH_3), 6.40 (d, J = 2.5 Hz, C_8-H), 7.00 (d, J = 16 Hz, α-H), 7.60 (d, J = 16 Hz, β-H), 7.10-7.80 (m, C_3', C_4', C_5'-H), 2.25 (s, C_3-CH_3); MS: m/z 328 (M^+); Anal. Calcd for $C_{18}H_{16}O_4S$: C, 65.83; H, 4.91. Found: C, 65.85; H, 4.80%.

3-5,7-Trimethoxy-2-(2′-vinylthiophene)-chromone 4d. It crystallised from aqueous methanol as yellow needles, m.p. 183°; IR (KBr): 1638 cm^{-1} (C=O); UV (nm, log ε): 208 (4.85), 236 (4.91), 272 (4.97), 382 (5.11); ^1H NMR: δ 3.90 (s, C_5-OCH_3), 3.98 (s, C_3-OCH_3), 3.95 (s, C_7-OCH_3), 6.32 (bs, C_6-H), 6.50 (bs, C_8-H), 7.05 (d, J = 16 Hz, α-H), 7.58 (d, J = 16 Hz, β-H), 7.10-7.30 (m, C_3', C_4', C_5'-H),; MS: m/z 344 (M^+).

5,7-Dimethoxy-3-phenyl-2-(2′-vinylthiophene)-chromone 4e. It crystallised from aqueous methanol as yellow needles, m.p. 195°; IR (KBr): 1635 cm^{-1} (C=O); UV (nm, log ε): 208 (4.84), 234 (4.95), 270 (5.01), 382 (5.16); ^1H NMR: δ 3.95 (s, C_5-OCH_3), 3.90 (s, C_7-OCH_3), 6.80 (d, J = 2.5 Hz, C_6-H), 6.90 (d, J = 2.5 Hz, C_8-H), 6.60 (d, J = 16 Hz, α-H), 7.70 (d, J = 16 Hz, β-H), 7.10-7.60 (m, C_3', C_4', C_5'-H and C_3-Ph), MS: m/z 390 (M^+); Anal. Calcd for $C_{23}H_{16}O_4S$: C, 70.75; H, 4.64. Found: C, 70.76; H, 4.61%.

Synthesis of 4a and 4b by reaction of 5a and 5b with thiophene-2-carboxaldehyde. Chromone **5a** or **5b** (10 mmoles) was dissolved in dry ethanol (40 mL) and NaOEt (prepared by dissolving 0.5 g of Na in 25 mL of EtOH) added and the reaction mixture kept at room temperature for 25 hr. EtOH was distilled off and the product treated with water to give **4a** or **4b** as a yellow solid which was purified by column chromatography over silica gel using benzene as eluent, yield obtained 30%.

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