Heterocycl. Commun., Vol. 17(5-6), pp. 173–176, 2011 • Copyright © by Walter de Gruyter • Berlin • Boston. DOI 10.1515/HC.2011.037

Synthesis of novel-9-cyano/acetylpyrano[2,3-*f*]chromones *via* Baylis-Hillman reaction

Rao Y. Jayaprakash[1,*], K. Niranjan[1], Y. Hemasri[2] and Krupadanam G.L. David[3]

[1] Postgraduate College of Science, Saifabad, Osmania University, Hyderabad 500004, India
[2] A.V.P.G. Centre Gaganmahal (affiliated to Osmania University), Hyderabad 500029, India
[3] University College of Science, Osmania University, Hyderabad 500007, India

*Corresponding author
e-mail: yjpr_19@yahoo.com

Abstract

Condensation of 8-formyl-7-hydroxy chromones **2a–e** with methyl vinyl ketone and acrylonitrile in the presence of diazabicyclo[2.2.2]octane (DABCO) under Baylis-Hillman reaction conditions afforded 9-cyano/acetyl-substituted pyrano[2,3-*f*]chromones **3a–e** and **4a–e**.

Keywords: acrylonitrile; DABCO; 8-formyl-7-hydroxy-chromones; methyl vinyl ketone.

Introduction

Chromones, the 1,4-benzopyrones, constitute a class of naturally occurring compounds that show recognized pharmacological properties, antimicrobial, antiallergic, anti-inflammatory, antispasmodic and antitumor activities (Foroumadi et al., 2007). The chromone scaffold is therefore a promising tool for the design of new and effective therapeutic agents. Recently, a group of natural products with a tricyclic benzopyranone core structure was reported as a new class of inhibitors for bacterial metallo-β-lactamases. This promising class of inhibitors was proposed for the potential combination treatment of clinically relevant pathogens, multidrug-resistant strains in particular (Payne et al., 2002). The pyrano-benzopyrone core also occurs in other natural products, for example in the fungus metabolite fulvic acid (Dean et al., 1963; Yamauchi et al., 1984). Herein we describe the synthesis of new chromones with a pyran ring fused at 7,8 positions from 8-formyl-7-hydroxy chromones by application of the Baylis-Hillman reaction. The C–C bond formation and the functional group transformation are the most fundamental reactions for the construction of a molecular framework and are hence at the forefront of organic chemistry research. In recent years, the Baylis-Hillman reaction has become a powerful synthetic reaction for the atom-economic construction of a C–C bond involving coupling of the α-position of activated olefins with aldehyde or imine electrophiles under the influence of catalysts providing multifunctionalized molecules whose applications in various organic transformations and their methodologies have been well documented in the literature (Ciganek, 1997; Basavaiah et al., 2003; Deb et al., 2006; Srivardhana Rao et al., 2006). A detailed synthetic route to the desired products **3a–e** and **4a–e** is presented (Scheme 1).

Results and discussion

8-Formyl-7-hydroxychromones **2a–e** (Jayaprakash Rao and Krupadanam, 2000) were synthesized from 7-hydroxychromones **1a–e** (Jayaprakash Rao and Krupadanam, 1994) by Duff reaction with hexamethylenetetramine (HMTA). 8-Formyl-7-hydroxychromones **2a–e** on reaction with acrylonitrile in the presence of 1,4-diazabicyclo[2.2.2] octane (DABCO) as the catalyst in chloroform under nitrogen atmosphere at room temperature underwent smooth cyclization to afford new 9-cyano-pyrano[2,3-*f*]chromones in quantitative yields (Scheme 1) without any side-product formation being observed. Similar to acrylonitrile, the other electron-deficient olefin, methyl vinyl ketone underwent a reaction with 8-formyl-7-hydroxychromones **2a–e** under the Baylis-Hillman reaction conditions, as described above, to give 9-acetylpyrano[2,3-*f*]-chromones. The newly synthesized compounds **2a–e**, **3a–e** and **4a–e** were characterized by infrared (IR), nuclear magnetic resonance (NMR) and mass spectrometry.

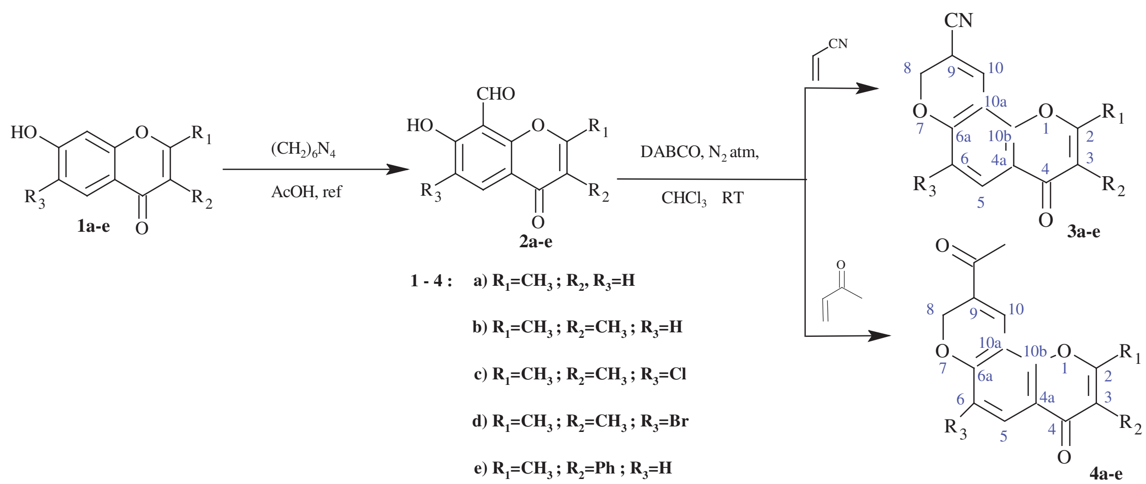
Conclusion

We have developed a facile and convenient method by which to synthesize novel 9-cyano/acetyl-pyrano[2,3-*f*]chromones containing a pyranobenzopyrone moiety, thus demonstrating that the Baylis-Hillman reaction is a valuable tool in the synthesis of these important heterocycles.

Experimental

General

All melting points were measured on a Polmon digital melting point apparatus (Model No MP-96) and were uncorrected. IR spectra were recorded in KBr on a Shimadzu-435 spectrophotometer. The ^{1}H (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Varian Gemini Unity Spectrometer in $CDCl_3$ with tetra methyl silane as the internal standard. The mass spectra were recorded on a Perkin-Elmer Hitachi RDO-62 instrument. 7-Hydroxychromones



Scheme 1 Synthesis of 9-cyano/acetyl-pyrano[2,3-*f*]chromones.

1a–e were prepared using methods reported by Jayaprakash Rao and Krupadanam (1994).

General procedure for synthesis of 8-formyl-7-hydroxychromones 2a–e

A solution of 7-hydroxychromone **1a–e** (10 mmol) and hexamethylenetetramine (10 mmol) in glacial acetic acid (80 ml) was heated over steam bath for 6 h and then treated with hot hydrochloric acid (20%, 40 ml). The mixture was further heated for 30 min, then treated with cold water (200 ml) and extracted with ether. The ether extract was washed with $NaHCO_3$ solution and water. Concentration of ether solution yielded crude product **2a–e** with about 95% yield. Crude product was crystallized from benzene to give pale yellow crystals.

8-Formyl-7-hydroxy-2-methylchromone (2a) Mp 171–173°C; IR: ν 1648 (CO), 1698 (CHO) and 3345 cm^{-1} (OH); ^{1}H NMR: δ 2.38 (s, 3H, 2-CH_3), 6.78 (s, 1H, H-3), 6.84 (d, 1H, *J*=10 Hz, H-6), 8.26 (d, 1H, *J*=10 Hz, H-5), 10.50 (s, 1H, 8-CHO), 12.10 (OH, D_2O exchangeable); ^{13}C NMR: δ 20.1 (C-2-CH_3), 108.5 (C-8), 115.6 (C-3), 115.9 (C-6), 121.0 (C-4a), 135.0 (C-5), 158.0 (C-2), 162.4 (C-8a), 167.5 (C-7), 176.1 (C-4), 192.2 (8-CHO); MS: *m/z* 204 $[M]^+$.

2,3 Dimethyl-8-formyl-7-hydroxychromone (2b) Mp 182–185°C; IR: ν 1650 (CO), 1695 (CHO) and 3350 cm^{-1} (OH); ^{1}H NMR: δ 2.00 (s, 3H, 3-CH_3), 2.38 (s, 3H, 2-CH_3), 6.85 (d, 1H, *J*=10 Hz, H-6), 8.25 (d, 1H, *J*=10 Hz, H-5), 10.48 (s, 1H, 8-CHO) and 12.00 (OH, D_2O exchangeable); ^{13}C NMR: δ 11.1 (C-3-CH_3), 20.5 (C-2-CH_3), 109.0 (C-8), 115.8 (C-3), 116.5 (C-6), 122.0 (C-4a), 135.5 (C-5), 159.0 (C-2), 163.0 (C-8a), 168.0 (C-7), 179.0 (C-4), 195.0 (8-CHO); MS: *m/z* 218 $[M]^{+\cdot}$.

6-Chloro-2,3-dimethyl-8-formyl-7-hydroxychromone (2c) Mp 231–233°C, IR: ν 1655 (CO), 1690 (CHO) and 3355 cm^{-1} (OH); ^{1}H NMR: δ 2.02 (s, 3H, 3-CH_3), 2.38 (s, 3H, 2-CH_3), 7.98 (s, 1H, H-5), 10.35 (s, 1H, 8-CHO) and 12.50 (OH, D_2O exchangeable); ^{13}C NMR: δ 11.5 (C-3-CH_3), 20.7 (C-2-CH_3), 108.7 (C-8), 115.7 (C-3), 116.0 (C-6), 121.5 (C-4a), 136.0 (C-5), 158.5 (C-2), 162.8 (C-8a), 167.8 (C-7), 178.0 (C-4), 193.0 (8-CHO). MS: *m/z* 252 $[M]^+$.

6-Bromo-2,3-dimethyl-8-formyl-7-hydroxychromone (2d) Mp 240–242°C, IR: ν 1645 (CO), 1695 (CHO) and 3360 cm^{-1} (OH); ^{1}H NMR: δ 2.02 (s, 3H, 3-CH_3), 2.39 (s, 3H, 2-CH_3), 7.98 (s, 1H, H-5), 10.42 (s, 1H, 8-CHO) and 12.35 (OH, D_2O exchangeable); ^{13}C NMR: δ 11.3 (C-3-CH_3), 20.0 (C-2-CH_3), 108.4 (C-8), 116.5 (C-6), 119.9 (C-4a), 126.0 (C-3), 135.8 (C-5) 151.1 (C-2), 157.8 (C-8a), 167.3 (C-7), 176.5 (C-4), 192.0 (8-CHO); MS: *m/z* 296 $[M]^{+\cdot}$.

8-Formyl-7-hydroxy-2-methyl-3-phenyl chromone (2e) Mp 262–265°C, IR: ν 1644 (CO), 1695 (CHO) and 3365 cm^{-1} (OH); ^{1}H NMR: δ 2.45 (s, 3H, 2-CH_3), 6.91 (d, 1H, *J*=9 Hz, H-6), 7.42 (m, 3H, H-3′,4′,5′), 7.54 (m, 2H, H-2′,6′), 8.05 (d, 1H, *J*=9 Hz, H-5), 10.45 (s, 1H, 8-CHO) and 12.55 (OH, D_2O exchangeable); ^{13}C NMR: δ 20.0 (C-2-CH_3), 108.5 (C-8), 112.4 (C-3′,5′), 116.3 (C-6), 120.8 (C-4a), 126.0 (C-3), 123.5 (C-1′), 135.2 (C-5), 148.8 (C-4′), 149.4 (C-2′, 6′), 157.8 (C-8a), 158.1 (C-2), 167.2 (C-7), 174.4 (C-4), 191.9 (8-CHO); MS: *m/z* 280 $[M]^{+\cdot}$.

General procedure for synthesis of 9-cyanopyrano [2,3-*f*]chromones 3a–e

A solution of 8-formyl-7-hydroxychromone **2a–e** (10 mmol), acrylonitrile (15 mmol) and DABCO (7.7 mmol) in chloroform (50 ml) was stirred at room temperature under nitrogen atmosphere for 60 h. The chloroform was removed by distillation and the crude product subjected to column chromatography, eluting with petroleum ether/ethyl acetate (9:1) to give 9-cyanopyrano[2,3-*f*]chromones **3a–e**.

9-Cyano-2-methylpyrano[2,3-*f*]chromone (3a) Mp 187–189°C; IR: ν 1626 (CO, chromone), 2213 cm^{-1} (CN); ^{1}H NMR: δ 2.50 (s, 3H, C-2-CH_3), 5.05 (s, 2H, 8-OCH_2), 6.91 (s, 3H, H-3), 7.51 (s, 1H, H-10), 7.92 (d, 1H, *J*=9 Hz, H-6), 8.19 (d, 1H, *J*=9 Hz, H-5); ^{13}C NMR: δ 21.8 (C-2, CH_3), 65.5 (8-OCH_2), 107.5 (C-3), 114 (C-10a), 117.5 (CN), 119.8 (C-4a), 122.5 (C-6), 126.0 (C-5), 130.1 (C-10), 131.0 (C-9), 151.2 (C-2), 153.1 (C-10b), 156.5 (C-6a), 170.9 (C-4); MS: *m/z* 239 $[M]^{+\cdot}$. Anal. calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.76; N, 5.85. Found: C, 70.08; H, 3.48; N, 5.68.

9-Cyano-2,3-dimethylpyrano[2,3-*f*]chromone (3b) Mp 189–191°C, IR: ν 1628 (CO, chromone), 2215 cm^{-1} (CN); ^{1}H NMR: δ 2.00 (s, 3H, C-3-CH_3), 2.40 (s, 3H, C-2-CH_3), 5.04 (s, 2H, 8-OCH_2), 7.51 (s, 1H, H-10), 7.92 (d, 1H, *J*=9 Hz, H-6), 8.19 (d, 1H, *J*=9 Hz, H-5); ^{13}C NMR: δ 10.1 (C-3-CH$_3$), 21.9 (C-2-CH$_3$), 65.5 (8-OCH$_2$), 107.4 (C-3), 114.5 (C-10a), 117.7 (CN), 120.0 (C-4a), 122.5 (C-6), 126.8 (C-5), 130.2 (C-10), 131.7 (C-9), 151.2 (C-2), 153.6 (C-10b), 157.0 (C-6a), 171.0 (C-4); MS: *m/z* 253 [M]$^{+\cdot}$. Anal. calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.34; N, 5.53. Found: C, 70.89; H, 4.02; N, 5.46.

6-Chloro-9-cyano-2,3-dimethylpyrano[2,3-*f*]chromone (3c) Mp 195–197°C, IR: ν 1630 (CO, chromone), 2220 cm^{-1} (CN); ^{1}H NMR: δ 2.00 (s, 3H, C-3-CH$_3$), 2.54 (s, 3H, C-2-CH$_3$), 5.10 (s, 2H, 8-OCH$_2$), 7.70 (s, 1H, H-10), 7.95 (d, 1H, *J*=9 Hz, H-6), 8.25 (s, 1H, H-5); ^{13}C NMR: δ 10.9 (C-3-CH$_3$), 22.0 (C-2-CH$_3$), 66.0 (8-OCH$_2$), 107.8 (C-3), 115.0 (C-10a), 118.0 (CN), 121.0 (C-4a), 123.0 (C-6), 128.0 (C-5), 130.6 (C-10), 132.0 (C-9), 152.0 (C-2), 154.0 (C-10b), 157.6 (C-6a), 171.5 (C-4); MS: *m/z* 287 [M]$^{+\cdot}$, 289 [M+2]. Anal. calcd for $C_{15}H_{10}ClNO_3$: C, 62.60; H, 3.47; N, 4.86. Found: C, 62.36; H, 3.38; N, 4.78.

6-Bromo-9-cyano-2,3-dimethylpyrano[2,3-*f*]chromone (3d) Mp 199–201°C, IR: ν 1638 (CO, chromone), 2218 cm^{-1} (CN); ^{1}H NMR: δ 2.00 (s, 3H, C-3-CH$_3$), 2.51 (s, 3H, C-2-CH$_3$), 5.08 (s, 2H, 8-OCH$_2$), 7.60 (s, 1H, H-10), 8.24 (s, 1H, H-5); ^{13}C NMR: δ 10.1 (C-3-CH$_3$), 21.5 (C-2-CH$_3$), 65.0 (8-OCH$_2$), 106.5 (C-3), 114.5 (C-10a), 117.5 (CN), 120.0 (C-4a), 122.5 (C-6), 127.5 (C-5), 129.6 (C-10), 130.5 (C-9), 150.0 (C-2), 153.5 (C-10b), 156.5 (C-6a), 170.0 (C-4); MS: *m/z* 331 [M]$^{+\cdot}$, 333 [M+2]. Anal. calcd for $C_{15}H_{10}BrNO_3$: C, 54.38; H, 3.02; N, 4.22. Found: C, 53.89; H, 2.81; N, 4.07.

9-Cyano-2-methyl-3-phenyl pyrano[2,3-*f*]chromone (3e) Mp 194–196°C, IR: ν 1625 (CO, chromone), 2220 cm^{-1} (CN); ^{1}H NMR: δ 2.40 (s, 3H, C-2-CH$_3$), 5.00 (s, 2H, 8-OCH$_2$), 6.90 (d, 1H, *J*=9 Hz, H-6), 7.46 (m, 3H, H-3′, 4′, 5′), 7.56 (m, 3H, H-2′, 6′, H-10), 8.06 (d, 1H, *J*=9 Hz, H-5); ^{13}C NMR: δ 21.4 (C-2-CH$_3$), 64.5 (C-8-OCH$_2$), 108.8 (C-10a), 114.9 (C-6), 117.0 (C-3), 118.0 (C-4a), 118.6 (CN), 126.4 (C-5), 129.0 (C-2′,6′), 129.2 (C-3′,5′), 129.5 (C-1′), 130.0 (C-10), 130.5 (C-4′), 133.2 (C-9), 154.0 (C-10b), 160.0 (C-2), 160.5 (C-6a), 177.5 (C-4); MS: *m/z* 315 [M]$^{+\cdot}$. Anal. calcd for $C_{20}H_{13}NO_3$: C, 76.19; H, 4.12; N, 4.44. Found: C, 76.03; H, 3.86; N, 4.18.

General procedure for synthesis of 9-acetylpyrano[2,3-*f*]chromones 4a–e

Substitution of methyl vinyl ketone for acrylonitrile in the procedure desribed above gave products **4a–e**.

9-Acetyl-2-methylpyrano[2,3-*f*]chromone (4a) Mp 179–182°C, IR: ν 1620 (CO, chromone), 1665 cm^{-1} (CO, 9-COCH$_3$); ^{1}H NMR: δ 2.34 (s, 3H, 9-COCH$_3$), 2.60 (s, 3H, 2-CH$_3$), 5.06 (d, 2H, *J*=1.4 Hz, 8-OCH$_2$), 6.78 (s, 1H, H-3), 6.82 (d, 1H, *J*=9 Hz, H-6), 7.58 (s, 1H, H-10), 8.06 (d, 1H, *J*=9 Hz, H-5); ^{13}C NMR: δ 21.4 (C-2-CH$_3$), 24.0 (C-9-COCH$_3$), 64.5 (C-8-OCH$_2$), 108.3 (C-10a), 114.4 (C-6), 116.0 (C-3), 117.9 (C-4a), 126.7 (C-5), 129.9 (C-10), 133.4 (C-9), 153.5 (C-10b), 160.0 (C-2), 160.4 (C-6a), 177.7 (C-4, CO), 195.9 (C-9-COCH$_3$); MS: *m/z* 256 [M]$^{+\cdot}$. Anal. calcd for $C_{15}H_{12}O_4$: C, 70.31; H, 4.68. Found: C, 70.25; H, 4.51.

9-Acetyl-2,3-dimethyl-pyrano[2,3-*f*]chromone (4b) Mp 182–186°C, IR: ν 1615 (CO, chromone), 1664 cm^{-1} (CO, 9-COCH$_3$); ^{1}H NMR: δ 2.00 (s, 3H, 3-CH$_3$), 2.34 (s, 3H, 9-COCH$_3$), 2.50 (s, 3H, 2-CH$_3$), 5.04 (d, 1H, *J*=1.4 Hz, 8-OCH$_2$), 6.81 (d, 1H, *J*=9 Hz, H-6), 7.52 (s,1H, H-10), 8.05 (d, 1H, *J*=9 Hz, H-5); ^{13}C NMR: δ 12.3 (C-3-CH$_3$), 21.3 (C-2-CH$_3$), 24.0 (C-9-COCH$_3$), 64.5 (C-8-OCH$_2$), 108.3 (C-10a), 114.3 (C-6), 116.0 (C-3), 117.9 (C-4a), 126.5 (C-5), 129.8 (C-10), 133.1 (C-9), 153.2 (C-10b), 159.0 (C-2), 160.2 (C-6a), 177.5 (C-4), 195.6 (C-9-COCH$_3$); MS: *m/z* 270 [M]$^{+\cdot}$. Anal. calcd for $C_{16}H_{14}O_4$: C, 71.11; H, 5.18. Found: C, 70.85; H, 4.94.

9-Acetyl-6-chloro-2,3-dimethylpyrano[2,3-*f*]chromone (4c) Mp 188–191°C; IR: ν 1622 (CO, chromone), 1669 cm^{-1} (CO, 9-COCH$_3$); ^{1}H NMR: δ 2.10 (s, 3H, C-3-CH$_3$), 2.38 (s, 3H, 9-COCH$_3$), 2.60 (s, 1H, 2-CH$_3$), 5.10 (d, 2H, *J*=1.5 Hz, 8-OCH$_2$), 7.60 (s, 1H, H-10), 8.10 (s, 1H, H-5); ^{13}C NMR: δ 13.5 (C-3-CH$_3$), 21.4 (C-2-CH$_3$), 24.0 (C-9-COCH$_3$), 64.5 (C-8-OCH$_2$), 108.3 (C-10a), 114.4 (C-6), 116.0 (C-3), 117.9 (C-4a), 126.7 (C-5), 129.9 (C-10), 133.4 (C-9), 153.5 (C-10b), 160.0 (C-2), 160.4 (C-6a), 177.7 (C-4), 195.9 (C-9-COCH$_3$); MS: *m/z* 304 [M]$^{+\cdot}$, 306 [M+2]. Anal. calcd for $C_{16}H_{13}ClO_4$: C, 63.05; H, 4.26. Found: C, 62.90; H, 4.09.

9-Acetyl-6-bromo-2,3-dimethylpyrano[2,3-*f*]chromone (4d) Mp 191–194°C; IR: ν 1621 (CO, chromone), 1668 cm^{-1} (CO, 9-COCH$_3$); ^{1}H NMR: δ 2.10 (s, 3H, 3-CH$_3$), 2.37 (s, 3H, 9-COCH$_3$), 2.50 (s, 3H, 2-CH$_3$), 5.08 (d, 2H, *J*=1.4 Hz, 8-OCH$_2$), 7.50 (s, 1H, H-10), 8.00 (s, 1H, H-5); ^{13}C NMR: δ 13.0 (C-3-CH$_3$), 22.0 (C-2-CH$_3$), 25.0 (C-9-COCH$_3$), 64.9 (C-8-OCH$_2$), 108.8 (C-10a), 114.8 (C-6), 116.5 (C-3), 118.0 (C-4a), 126.8 (C-5), 130.0 (C-10), 133.3 (C-9), 153.6 (C-10b), 159.5 (C-2), 160.5 (C-6a), 177.8 (C-4), 195.8 (C-9-COCH$_3$); MS: *m/z* 348 [M]$^{+\cdot}$, 350 [M+2]. Anal. calcd for $C_{16}H_{13}BrO_4$: C, 55.17; H, 3.73. Found: C, 54.93; H, 3.47.

9-Acetyl-2,3-dimethyl-3-phenylpyrano[2,3-*f*]chromone (4e) Mp 196–200°C; IR: ν 1620 (CO, chromone), 1662 cm^{-1} (CO, 9-COCH$_3$); ^{1}H NMR: δ 2.36 (s, 3H, 9-COCH$_3$), 2.40 (s, 3H, 2-CH$_3$), 5.04 (d, 2H, *J*=1.5 Hz, 8-OCH$_2$), 6.84 (d, 1H, *J*=9 Hz, H-6), 7.57 (m, 3H, H-2′, 6′, H-10), 8.07 (d, 1H, *J*=9 Hz, H-5); ^{13}C NMR: δ 21.5 (C-2-CH$_3$), 25.1 (C-9-COCH$_3$), 65.0 (C-8-OCH$_2$), 109.0 (C-10a), 114.7 (C-6), 116.9 (C-3), 117.9 (C-4a), 126.3 (C-5), 128.6 (C-2′,6′), 128.8 (C-3′,5′), 129.3 (C-1′), 129.8 (C-10), 130.3 (C-4′), 133.1 (C-9), 153.3 (C-10b), 159.5 (C-2), 160.1 (C-6a), 177.5 (C-4), 195.4 (C-9-COCH$_3$). MS: *m/z* 332 [M]$^{+\cdot}$. Anal. calcd for $C_{21}H_{16}O_4$: C, 75.90; H, 4.81. Found: C, 75.78; H, 4.54.

Acknowledgments

This work was supported by the University Grants Commission, India, for minor research projects.

References

Basavaiah, D.; Rao, A. J.; Satayanarayana T. Recent advances in the Baylis-Hillman reaction and applications. *Chem. Rev.* **2003**, *103*, 811–891.

Ciganek, E. The catalyzed α-hydroxyalkylation and α-aminoalkylation of activated olefins (the Morita-Baylis-Hillman reaction). *Org. React.* **1997**, *51*, 201–350.

Dean, F. M. *Naturally Occurring Oxygen Ring Compounds*, Butterworth's: London, 1963.

Deb, I.; Dadwal, M.; Mobin, S. M.; Namboothri, I. N. N. Hydroxyalkylation of conjugated nitroalkenes with activated non-enolizable carbonyl compounds. *Org. Lett.* **2006**, *8*, 1201–1204.

Foroumadi, A.; Samzadeh-Kermani, A.; Emami, S.; Dehghan, G.; Sorkhi, M.; Arabsorkhi, F.; Heidari, M. R.; Abdollahi Mand Shafiee, A. Synthesis and antioxidant properties of substituted 3-benzylidene-7-alkoxychroman-4-ones. *Bioorg. Med. Chem. Lett*. **2007**, *17*, 6764–6769.

Jayaprakash Rao, Y.; Krupadanam, G. L. D. Facile synthesis of linear and angular 2-methyl furobenzopyranone. *Bull. Chem. Soc. Jpn*. **1994**, *67*, 1972–1975.

Jayaprakash Rao, Y.; Krupadanam, G. L. D. A facile synthesis of 7,8/6,7 fused pyranopyridochromones and evaluation of antibacterial activity. *Ind. J. Chem.* **2000**, *39B*, 610–613.

Payne, D. J.; Hueso-Rodriguez, J. A.; Boyd, H.; Concha, N. O.; Janson, C. A.; Gilpin, M. J.; Bateson, H.; Cheever, C.; Niconovich, N. L.; Pearson, S.; et al. Identification of a series of tricyclic natural products as potent broad-spectrum inhibitors of metallo-ß-lactamases. *Antimicrob. Agents Chemother*. **2002**, *46*, 1880–1886.

Srivardhana Rao, J.; Briere, J. F.; Metzer, P.; Basavaiah, D. An efficient and rapid chalcogenide-Morita–Baylis–Hillman process promoted by TBDMSOTf and a thiolane. *Tetrahed. Lett.* **2006**, *47*, 3553–3556.

Yamauchi, M.; Katayama, S.; Todoroki, T.; Watanabe, T. Total synthesis of fulvic acid. *J. Chem. Soc. Chem. Commun.* **1984**, *23*, 1565–1566.

Received July 27, 2011; accepted September 24, 2011; previously published online November 1, 2011