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MODIFIED COUMARINS. 10. SYNTHESIS OF SUBSTITUTED 2-(7-OXOFURO[3,2-*g*]CHROMEN-6-YL) ACETIC ACIDS

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Substituted 2-(7-oxofuro[3,2-g]chromen-6-yl) acetic acids, modified psoralen analogs, were synthesized by linear fusion of a furan ring to the coumarin system.

Key words: coumarins, furocoumarins, psoralen, synthesis.

Furocoumarins are an important group of natural bioregulators. These compounds are mainly derivatives of the widely distributed natural linear furocoumarin psoralen. Its angular isomers, angelicin or allopsoralen and their derivatives are not nearly as common. Natural furocoumarins and their synthetic analogs possess a variety of physiological activities, depending on the chemical structure. In particular, they increase the sensitivity of humans and animals to sunlight by acting as photosensitizers. Furocoumarins in medicine are used to treat vitiligo (leucoderma), alopecia areata, and several skin diseases [1]. One type of blood cancer (T-cell lymphoma) is treated with 8-methoxypsoralen [2]. Derivatives of psoralen and angelicin typically have spasmolytic and angiotensive properties with a papaverin-like mechanism of action on smooth musculature of internal organs and coronary arteries [3]. The furocoumarins also comprise compounds with anticonvulsive, sedative (relieving hyperactivity caused by taking amphetamine), hypotensive, contraceptive, estrogenic, bactericidal, fungicidal [4], anti-tumor [5], antihepatitic [6], anti-infectional [7], and anti-HIV [8, 9] activities.

Our goal was to modify the psoralen core by introducing an additional pharmacophore as a carboxylic acid and substituents in the 2-, 3-, and 9-position of the 7*H*-furo[3,2-*g*]chromen-7-one ring. This could produce compounds with useful biological properties.

Methyl-2-(7-hydroxy-4-methyl-2-oxo-2*H*-3-chromenyl)acetate (**1**) and methyl-2-(7-hydroxy-4,8-dimethyl-2-oxo-2*H*-3-chromenyl)actate (**2**) that were necessary for further transformations were prepared by Pechmann condensation of dimethylacetylsuccinate with resorcinol or 2-methylresorcinol, respectively, in the presence of dry HCl as a condensing agent at 0°C.

Several approaches to fusing a furan ring to the coumarin core are known. In particular, psoralen and its isomers were prepared by the method of Spaeth [10] and methods based on Dieckmann condensation [11], Perkin reactions [12], and Claisen rearrangement [13]. The aforementioned methods involve many steps, low yields, and limited capabilities for modifying the coumarin and furan rings. Another method for forming the psoralen system and its angular isomers is the MacLeod method based on cyclization in alkaline medium of 7-(2-oxoethyl)coumarin derivatives [14]. The cyclization leads exclusively to linear furocoumarins (psoralen-type furocoumarins) because the 6-position of the coumarin ring is less strongly activated than the 8-position [15]. In our opinion, this method is more acceptable because the desired furocoumarins can be modified without limitation in high yields.

Williamson reaction of 7-hydroxycoumarins **1** and **2** with α-haloketones in the presence of potash as the base produces in high yields (68-96%) the corresponding substituted oxoethers **3-24**. The alkylating agents were chloroacetone (**3**, **4**), 1-chloropinacolone (**5**, **6**), 3-chloro-2-butanone (**7**, **8**), 2-bromopropiophenone (**9**, **10**), phenacylbromide (**11**, **12**), 2-chloro-4′-fluoroacetophenone (**13**, **14**), 2,4′-dichloroacetophenone (**15**, **16**), 4-bromophenacylbromide (**17**, **18**), 4-methoxyphenacylbromide

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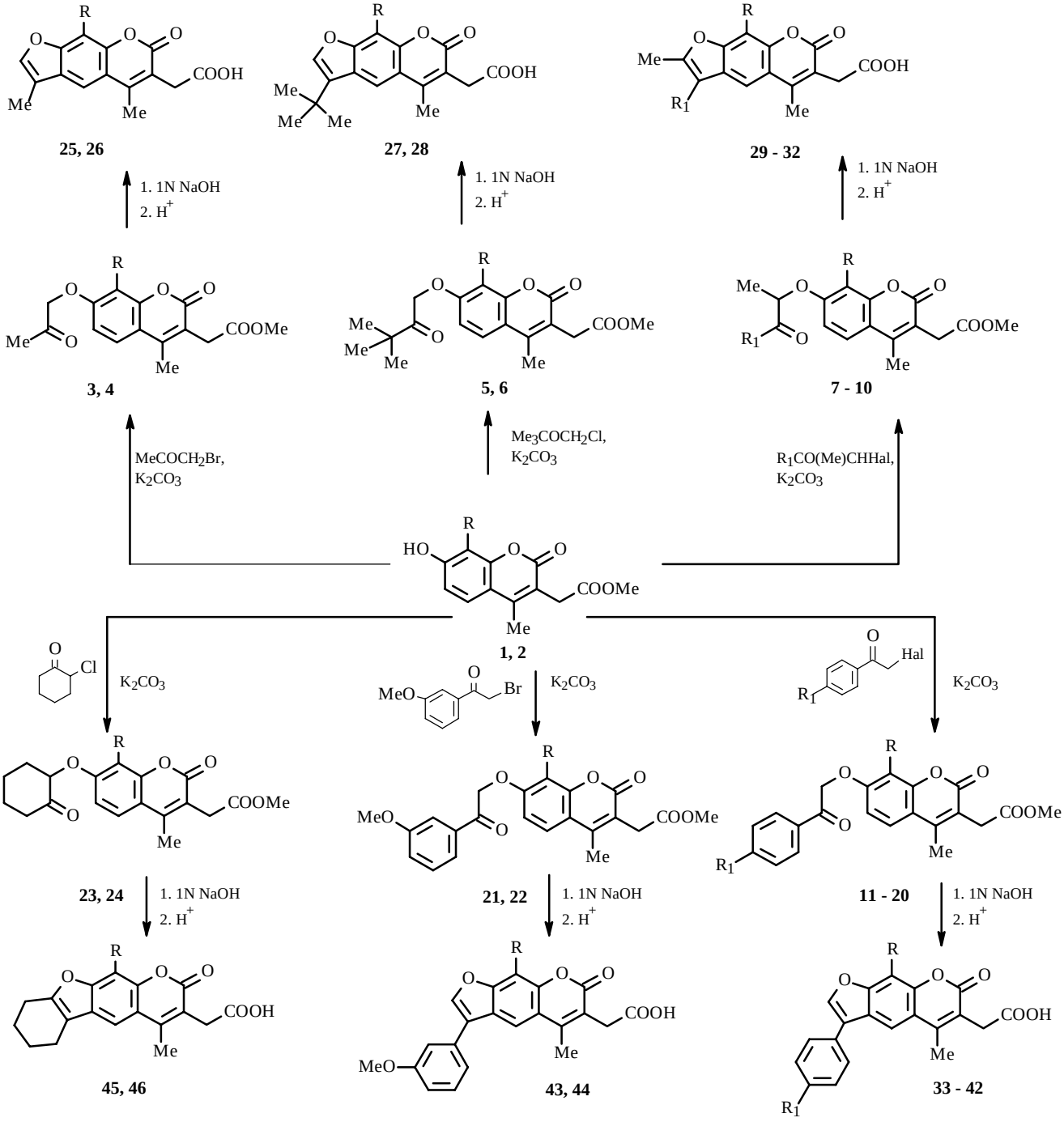
(**19**, **20**), 2-bromo-3′-methoxyacetophenone (**21**, **22**), and 2-chlorocyclohexanone (**23**, **24**). The PMR spectra of **3-24** contain signals characteristic of the coumarin ring and alkyl substituents. The UV spectra of these compounds have a main strong maximum at 202-206 nm, a maximum or shoulder at 219-224 nm, and a long-wavelength strong maximum at 318-325 nm [16]. For 7-(2-oxo-2-phenylethoxy)coumarins **9-22**, an additional maximum weaker than the long-wavelength band is observed in the range 243-286 nm. The IR spectra of **3-24** typically exhibit two bands in the range 1693-1738 cm^{-1} for C=O stretchings of the coumarin ring and the alkoxy carbonyl.



1, 3, 5, 21, 23, 25, 27, 43, 45: R = H; **2, 4, 6, 22, 24, 26, 28, 44, 46:** R = Me;
7, 29: R = H, R_1 = Me; **8, 30:** R = R_1 = Me; **9, 31:** R = H, R_1 = Ph; **10, 32:** R = Me, R_1 = Ph;
11, 33: R = R_1 = H; **12, 34:** R = Me, R_1 = H; **13, 35:** R = H, R_1 = F; **14, 36:** R = Me, R_1 = F;
15, 37: R = H, R_1 = Cl; **16, 38:** R = Me, R_1 = Cl; **17, 39:** R = H, R_1 = Br;
18, 40: R = Me, R_1 = Br; **19, 41:** R = H, R_1 = OMe; **20, 42:** R = Me, R_1 = OMe

Ketones **3-24** cyclize smoothly upon heating with NaOH solution (1 N) and subsequent acidolysis with high yields (71-95%) and simultaneous saponification of the ester into the corresponding substituted 2-(5-methyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic acids **25-46**. Fusion of the furan ring to the 6,7-positions of the coumarin ring was confirmed by PMR spectroscopy. The PMR spectra of **25-46** exhibit a simpler splitting pattern for the aromatic protons than the starting ketones because H-6 of the coumarin is decoupled. For the 9-methyl derivatives of the furocoumarins, H-4′ is observed as a singlet at 7.55-7.99 ppm. Protons H-4′ and H-9′ in spectra of furocoumarins without a 9-methyl group resonate as singlets at 7.72-8.21 and 7.39-7.83 ppm, respectively. Furthermore, furocoumarins **25-28** and **33-44**, which have no substituent in the 2′-position, have a 1H singlet for H-2′, which is also a characteristic signature of formation of the furocoumarin ring. If the prepared furocoumamrins have alkyl substituents in the 3′-position (**25-28**), then the H-2′ singlet is located at 7.68-7.85 ppm. An aryl substituent in the 3′-position (**33-44**) causes the signal for H-2′ to shift to weaker field (8.22-8.54 ppm). A broad singlet for the free carboxylic acid occurs at 12.31-12.51 ppm. The UV spectra of the synthesized furocoumarins contain three strong absorption maxima at 202-217, 244-256, and 295-308 nm. It should be noted that the absorption at 244-256 nm is stronger than the long-wavelength band, which is also proof of the fusion of the furan ring.

EXPERIMENTAL

The course of reactions and purity of products were monitored by TLC on Merck 60 F254 plates using $CHCl_3$:CH_3OH (9:1 and 95:5). Melting points were measured on a Kofler block. IR and UV spectra were measured on a Nicolet FTIR Nexus 475 spectrometer and a Specord M40 spectrophotometer, respectively; PMR spectra, on Varian VXR-300 and Mercury-400 spectrometers at 300 and 400 MHz, respectively, vs. TMS (internal standard). Elemental analyses of all compounds agreed with those calculated.

Methyl-2-(7-hydroxy-4-methyl-2-oxo-2*H*-3-chromenyl)acetate (1). A cooled (0°C) solution of resorcinol (11.0 g, 0.1 mol) and dimetylacetylsuccinate (16.2 mL, 0.1 mol) in absolute CH_3OH (50 mL) was stirred vigorously. Dry HCl was passed through the solution for 3 h. The reaction mixture was stirred until thickened, left overnight at room temperature, and poured into ice water (500 mL). The resulting precipitate was filtered off and crystallized from CH_3OH (50%). Yield 60%, $C_{13}H_{12}O_5$, mp 203-205°C. IR spectrum (KBr, cm^{-1}): 3139, 1735, 1674, 1624, 1592, 1456, 1392, 1369, 1332, 1238, 1212, 1195, 1176, 1107, 988, 855, 787. UV spectrum (dioxane, λ_{max}, nm, log ε): 217 (4.33), 243 (3.85), 253 (3.83), 296 (4.05), 322 (4.27). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.36 (3H, s, Me-4′), 3.62 (2H, s, CH_2-2), 3.65 (3H, s, COOMe), 6.73 (1H, d, J = 2.4, H-8′), 6.83 (1H, dd, J = 2.4, J = 8.8, H-6′), 7.67 (1H, d, J = 8.8, H-5′), 10.54 (1H, s, OH-7′).

Methyl-2-(7-hydroxy-4,8-dimethyl-2-oxo-2*H*-3-chromenyl)acetate (2) was prepared analogously to **1** from 2-methylresorcinol (12.4 g, 0.1 mol) and dimethylacetylsuccinate (16.2 mL, 0.1 mol). Yield 67%, $C_{14}H_{14}O_5$, mp 197-198°C. IR spectrum (KBr, cm^{-1}): 3284, 1748, 1674, 1608, 1580, 1438, 1381, 1360, 1335, 1314, 1191, 1166, 1142, 1101, 815, 791. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.65), 223 (4.19), 322 (4.16). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.17 (3H, s, Me-8′), 2.33 (3H, s, Me-4′), 3.61 (2H, s, CH_2-2), 3.63 (3H, s, COOMe), 6.85 (1H, d, J = 9.0, H-6′), 7.41 (1H, d, J = 9.0, H-5′), 10.22 (1H, s, OH-7′).

Ketones 3-24. A hot solution of **1** or **2** (4 mmol) in absolute acetone (30 mL) was treated with freshly calcined potash (1.38 g, 10 mmol), stirred vigorously and heated (50-56°C), and treated with the appropriate α-haloketone (4.2 mmol). The reaction mixture was heated and stirred for 1-5 h (course of reaction monitored by TLC) and poured into H_2SO_4 solution (100 mL, 1 N). The resulting precipitate was filtered off and crystallized from aqueous CH_3OH.

Methyl-2-[4-methyl-7-(2-oxopropoxy)-2-oxo-2*H*-3-chromenyl]acetate (3). Yield 76%, $C_{16}H_{16}O_6$, mp 147-148°C. IR spectrum (KBr, cm^{-1}): 1723, 1611, 1436, 1394, 1335, 1290, 1272, 1198, 1173, 1104, 970, 873, 787. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.79), 221 (4.36), 292 (4.11), 319 (4.32). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.17 (3H, s, Me-3″), 2.38 (3H, s, Me-4′), 3.62 (2H, s, CH_2-2), 3.67 (3H, s, COOMe), 4.99 (2H, s, CH_2-1″), 6.98 (2H, m, H-6′, H-8′), 7.74 (1H, d, J = 8.8, H-5′).

Methyl-2-[4,8-dimethyl-7-(2-oxopropoxy)-2-oxo-2*H*-3-chromenyl]acetate (4). Yield 84%, $C_{16}H_{16}O_6$, mp 161-162°C. IR spectrum (KBr, cm^{-1}): 1728, 1693, 1603, 1379, 1346, 1304, 1219, 1201, 1182, 1131, 889, 803. UV spectrum (EtOH, λ_{max}, nm, log ε): 205 (4.73), 224 (4.27), 324 (4.31). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.20 (3H, s, Me-3″), 2.29 (3H, s, Me-8′), 2.37 (3H, s, Me-4′), 3.64 (5H, s, CH_2-2, COOMe), 4.91 (2H, s, CH_2-1″), 6.87 (1H, d, J = 9.0, H-6′), 7.54 (1H, d, J = 9.0, H-5′).

Metthyl-2-[7-(3,3-dimethyl-2-oxobutoxy)-4-methyl-2-oxo-2*H*-3-chromenyl]acetate (5). Yield 78%, $C_{19}H_{22}O_6$, mp 109-110°C. IR spectrum (KBr, cm^{-1}): 1738, 1720, 1703, 1607, 1509, 1391, 1288, 1253, 1229, 1160, 1083, 1042, 994, 974, 833. UV spectrum (EtOH, λ_{max}, nm, log ε): 203 (4.76), 222 (4.35), 322 (4.35). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.20 [9H, s, $(CH_3)_3$], 2.37 (3H, s, Me-4′), 3.64 (5H, s, CH_2-2, COOMe), 5.19 (2H, s, CH_2-1″), 6.88 (1H, d, J = 2.4, H-8′), 6.71 (1H, dd, J = 2.4, J = 8.7, H-6′), 7.66 (1H, d, J = 8.7, H-5′).

Methyl-2-[7-(3,3-dimethyl-2-oxobutoxy)-4,8-dimethyl-2-oxo-2*H*-3-chromenyl]acetate (6). Yield 81%, $C_{20}H_{24}O_6$, mp 145-146°C. IR spectrum (KBr, cm^{-1}): 1721, 1695, 1602, 1500, 1479, 1441, 1372, 1342, 1297, 1230, 1213, 1195, 1135, 1076, 997, 779. UV spectrum (EtOH, λ_{max}, nm, log ε): 205 (4.73), 225 (4.25), 322 (4.31). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.20 [9H, s, $(CH_3)_3$], 2.28 (3H, s, Me-8′), 2.36 (3H, s, Me-4′), 3.64 (5H, s, CH_2-2, COOMe), 5.24 (2H, s, CH_2-1″), 6.82 (1H, d, J = 9.0, H-6′), 7.52 (1H, d, J = 9.0, H-5′).

Methyl-2-[4-methyl-7-(1-methyl-2-oxopropoxy)-2-oxo-2*H*-3-chromenyl]acetate (7). Yield 84%, $C_{17}H_{18}O_6$, mp 108-109°C. IR spectrum (KBr, cm^{-1}): 1720, 1612, 1433, 1388, 1340, 1286, 1249, 1237, 1200, 1180, 1099, 876. UV spectrum (dioxane, λ_{max}, nm, log ε): 214 (4.39), 221 (4.35), 242 (3.80), 292 (4.09). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.50 (3H, d, J = 7.2, Me-1″), 2.10 (3H, s, Me-3″), 2.39 (3H, s, Me-4′), 3.63 (2H, s, CH_2-2), 3.66 (3H, s, COOMe), 5.07 (1H, q, H-1″), 6.87 (1H, d, J = 2.4, H-8′), 6.91 (1H, dd, J = 2.4, J = 8.8, H-6′), 7.71 (1H, d, J = 8.8, H-5′).

Methyl-2-[4,8-dimethyl-7-(1-methyl-2-oxopropoxy)-2-oxo-2*H*-3-chromenyl]acetate (8). Yield 96%, $C_{18}H_{20}O_6$, mp 98-99°C. IR spectrum (KBr, cm^{-1}): 1722, 1708, 1610, 1499, 1444, 1358, 1337, 1284, 1247, 1172, 1131, 1113, 997, 787. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 204 (4.62), 222 (4.18), 322 (4.20). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.51 (3H, d, J = 6.9, Me-1″), 2.18 (3H, s, Me-3″), 2.29 (3H, s, Me-8′), 2.36 (3H, s, Me-4′), 3.63 (5H, s, CH_2-2, COOMe), 5.04 (1H, q, H-1″), 6.81 (1H, d, J = 9.0, H-6′), 7.54 (1H, d, J = 9.0, H-5′).

Methyl-2-[4-methyl-7-(1-methyl-2-oxo-2-phenylethoxy)-2-oxo-2*H*-3-chromenyl]acetate (9). Yield 86%, $C_{22}H_{20}O_6$, mp 90-91°C. IR spectrum (KBr, cm^{-1}): 1736, 1703, 1698, 1617, 1424, 1330, 1301, 1256, 1232, 1171, 1097, 1004, 761. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 202 (4.91), 220 (4.39), 245 (4.33), 295 (4.15), 321 (4.33), 336 (4.11). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.61 (3H, d, J = 6.4, Me-2″), 2.36 (3H, s, Me-4′), 3.60 (2H, s, CH_2-2), 3.63 (3H, s, COOMe), 6.10 (1H, q, H-1″), 6.88 (1H, d, J = 2.4, H-8′), 6.90 (1H, dd, J = 2.4, J = 8.8, H-6′), 7.54 (2H, t, J = 7.6, H-3‴, H-5‴), 7.66 (2H, m, H-5′, H-4‴), 8.07 (2H, d, J = 8.0, H-2‴, H-6‴).

Methyl-2-[4,8-dimethyl-7-(1-methyl-2-oxo-2-phenylethoxy)-2-oxo-2*H*-3-chromenyl]acetate (10). Yield 93%, $C_{23}H_{22}O_6$, mp 142-143°C. IR spectrum (KBr, cm^{-1}): 1731, 1700, 1607, 1439, 1344, 1289, 1232, 1202, 1176, 1141, 112, 990, 964, 710. UV spectrum (EtOH, λ_{max}, nm, log ε): 204 (4.87), 247 (4.32), 324 (4.33). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.64 (3H, d, J = 6.3, Me-2″), 2.28 (3H, s, Me-8′), 2.32 (3H, s, Me-4′), 3.62 (5H, s, CH_2-2, COOMe), 6.15 (1H, q, H-1″), 6.82 (1H, d, J = 9.0, H-6′), 7.51 (1H, d, J = 9.0, H-5′), 7.54 (2H, m, H-3‴, H-5‴), 7.67 (1H, m, H-4‴), 8.05 (2H, d, J = 8.7, H-2‴, H-6‴).

Methyl-2-[4-methyl-7-(2-oxo-2-phenylethoxy)-2-oxo-2*H*-3-chromenyl]acetate (11). Yield 90%, $C_{21}H_{18}O_6$, mp 215-216°C. IR spectrum (KBr, cm^{-1}): 1736, 1709, 1698, 1617, 1450, 1425, 1330, 1301, 1256, 1232, 1172, 1097, 1004, 817, 761. UV spectrum (EtOH, λ_{max}, nm, log ε): 203 (5.01), 221 (4.67), 243 (4.44), 295 (4.21), 322 (4.46). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.39 (3H, s, Me-4′), 3.62 (2H, s, CH_2-2), 3.65 (3H, s, COOMe), 5.65 (2H, s, CH_2-1″), 7.00 (1H, dd, J = 2.4, J = 8.8, H-6′), 7.04 (1H, d, J = 2.4, H-8′), 7.55 (2H, t, J = 7.6, H-3‴, H-5‴), 7.66 (1H, m, H-4‴), 7.70 (1H, d, J = 8.8, H-5′), 8.03 (2H, d, J = 8.0, H-2‴, H-6‴).

Methyl-2-[4,8-dimethyl-7-(2-oxo-2-phenylethoxy)-2-oxo-2*H*-3-chromenyl]acetate (12). Yield 95%, $C_{22}H_{20}O_6$, mp 170-171°C. IR spectrum (KBr, cm^{-1}): 1734, 1708, 1603, 1436, 1336, 1288, 1225, 1135, 1068, 1000, 972, 764. UV spectrum (EtOH, λ_{max}, nm, log ε): 204 (4.92), 245 (4.38), 322 (4.35). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, Me-8′), 2.35 (3H, s, Me-4′), 3.63 (3H, s, COOMe), 3.65 (2H, s, CH_2-2), 5.70 (2H, s, CH_2-1″), 6.96 (1H, d, J = 9.0, H-6′), 7.55 (3H, m, H-5′, H-3‴, H-5‴), 7.67 (1H, m, H-4‴), 8.05 (2H, d, J = 8.4, H-2‴, H-6‴).

Methyl-2-[7-[2-(4-fluorophenyl)-2-oxoethoxy]-4-methyl-2-oxo-2*H*-3-chromenyl]acetate (13). Yield 75%, $C_{21}H_{17}FO_6$, mp 153-154°C. IR spectrum (KBr, cm^{-1}): 1730, 1696, 1615, 1598, 1509, 1425, 1330, 1298, 1232, 1161, 1098, 997, 841. UV spectrum (dioxane, λ_{max}, nm, log ε): 214 (4.45), 231 (4.19), 293 (4.03), 321 (4.26), 334 (4.06). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.39 (3H, s, Me-4′), 3.62 (2H, s, CH_2-2), 3.65 (3H, s, COOMe), 5.62 (2H, s, CH_2-1″), 6.99 (1H, dd, J = 2.4, J = 8.8, H-6′), 7.05 (1H, d, J = 2.4, H-8′), 7.31 (2H, m, H-3‴, H-5‴), 7.69 (1H, d, J = 8.8, H-5′), 8.12 (2H, m, H-2‴, H-6‴).

Methyl-2-[7-[2-(4-fluorophenyl)-2-oxoethoxy]-4,8-dimethyl-2-oxo-2*H*-3-chromenyl]acetate (14). Yield 69%, $C_{22}H_{19}FO_6$, mp 164-165°C. IR spectrum (KBr, cm^{-1}): 1736, 1708, 1600, 1505, 1434, 1337, 1290, 1235, 1177, 1140, 992, 842, 799. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 205 (4.79), 222 (4.21), 245 (4.23), 319 (4.24). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, Me-8′), 2.36 (3H, s, Me-4′), 3.63 (3H, s, COOMe), 3.67 (2H, s, CH_2-2), 5.69 (2H, s, CH_2-1″), 6.95 (1H, d, J = 9.0, H-6′), 7.35 (2H, m, H-3‴, H-5‴), 7.54 (1H, d, J = 9.0, H-5′), 8.11 (2H, m, H-2‴, H-6‴).

Methyl-2-[7-[2-(4-chlorophenyl)-2-oxoethoxy]-4-methyl-2-oxo-2*H*-3-chromenyl]acetate (15). Yield 82%, $C_{21}H_{17}ClO_6$, mp 169-170°C. IR spectrum (KBr, cm^{-1}): 1728, 1700, 1615, 1590, 1432, 1393, 1336, 1288, 1229, 1205, 1178, 1094, 995, 972, 832. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.86), 220 (4.38), 252 (4.37), 290 (4.11), 319 (4.28). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.40 (3H, s, Me-4′), 3.63 (2H, s, CH_2-2), 3.67 (3H, s, COOMe), 5.75 (2H, s, CH_2-1″), 7.07 (1H, dd, J = 2.4, J = 8.8, H-6′), 7.13 (1H, d, J = 2.4, H-8′), 7.68 (2H, d, J = 8.0, H-3‴, H-5‴), 7.77 (1H, d, J = 8.8, H-5′), 8.06 (2H, d, J = 8.0, H-2‴, H-6‴).

Methyl-2-[7-[2-(4-chlorophenyl)-2-oxoethoxy]-4,8-dimethyl-2-oxo-2*H*-3-chromenyl]acetate (16). Yield 74%, $C_{22}H_{19}ClO_6$, mp 189-190°C. IR spectrum (KBr, cm^{-1}): 1736, 1708, 1607, 1586, 1432, 1338, 1290, 1229, 1219, 1177, 1142, 1092, 976, 804. UV spectrum (dioxane, λ_{max}, nm, log ε): 211 (4.72), 254 (4.37), 320 (4.30), 336 (4.05). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.32 (3H, s, Me-8′), 2.36 (3H, s, Me-4′), 3.64 (5H, s, CH_2-2, COOMe), 5.67 (2H, s, CH_2-1″), 6.98 (1H, d, J = 9.0, H-6′), 7.53 (1H, d, J = 9.0, H-5′), 7.57 (2H, d, J = 8.7, H-3‴, H-5‴), 8.02 (2H, d, J = 8.7, H-2‴, H-6‴).

Methyl-2-[7-[2-(4-bromophenyl)-2-oxoethoxy]-4-methyl-2-oxo-2*H*-3-chromenyl]acetate (17). Yield 96%, $C_{21}H_{17}BrO_6$, mp 162-163°C. IR spectrum (KBr, cm^{-1}): 1728, 1701, 1614, 1586, 1432, 1392, 1335, 1288, 1228, 1204, 1178, 1099, 1072, 994, 972, 828. UV spectrum (dioxane, λ_{max}, nm, log ε): 214 (4.64), 259 (4.47), 291 (4.20), 321 (4.36), 334 (4.18). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.40 (3H, s, Me-4′), 3.63 (2H, s, CH_2-2), 3.69 (3H, s, COOMe), 5.75 (2H, s, CH_2-1″), 7.07 (1H, dd, J = 2.4, J = 8.8, H-6′), 7.14 (1H, d, J = 2.4, H-8′), 7.77 (1H, d, J = 8.8, H-5′), 7.82 (2H, d, J = 8.0, H-3‴, H-5‴), 7.98 (2H, d, J = 8.0, H-2‴, H-6‴).

Methyl-2-[7-[2-(4-bromophenyl)-2-oxoethoxy]-4,8-dimethyl-2-oxo-2*H*-3-chromenyl]acetate (18). Yield 94%, $C_{22}H_{19}BrO_6$, mp 200-201°C. IR spectrum (KBr, cm^{-1}): 1737, 1709, 1606, 1584, 1432, 1331, 1289, 1224, 1142, 1069, 989, 799. UV spectrum (EtOH, λ_{max}, nm, log ε): 204 (4.72), 256 (4.21), 321 (4.14). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.30 (3H, s, Me-8′), 2.36 (3H, s, Me-4′), 3.63 (3H, s, COOMe), 3.66 (2H, s, CH_2-2), 5.69 (2H, s, CH_2-1″), 6.95 (1H, d, J = 9.0, H-6′), 7.54 (1H, d, J = 9.0, H-5′), 7.76 (2H, d, J = 8.4, H-3‴, H-5‴), 7.94 (2H, d, J = 8.4, H-2‴, H-6‴).

Methyl-2-[7-[2-(4-methoxyphenyl)-2-oxoethoxy]-4-methyl-2-oxo-2*H*-3-chromenyl]acetate (19). Yield 95%, $C_{22}H_{20}O_6$, mp 146-148°C. IR spectrum (KBr, cm^{-1}): 1728, 1700, 1613, 1600, 1512, 1430, 1388, 1336, 1290, 1264, 1238, 1205, 1173, 1099, 995, 973, 833. UV spectrum (EtOH, λ_{max}, nm, log ε): 203 (4.78), 221 (4.50), 286 (4.46), 322 (4.36). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.39 (3H, s, Me-4′), 3.62 (2H, s, CH_2-2), 3.68 (3H, s, COOMe), 3.87 (3H, s, OMe-4‴), 5.69 (2H, s, CH_2-1″), 7.04 (1H, dd, J = 2.4, J = 8.8, H-6′), 7.08 (1H, d, J = 2.4, H-8′), 7.11 (2H, d, J = 8.8, H-3‴, H-5‴), 7.76 (1H, d, J = 8.8, H-5′), 8.02 (2H, d, J = 8.8, H-2‴, H-6‴).

Methyl-2-[7-[2-(4-methoxyphenyl)-2-oxoethoxy]-4,8-dimethyl-2-oxo-2*H*-3-chromenyl]acetate (20). Yield 80%, $C_{23}H_{22}O_6$, mp 195-196°C. IR spectrum (KBr, cm^{-1}): 1728, 1705, 1613, 1583, 1430, 1336, 1290, 1265, 1204, 1180, 1096, 978, 811, 788. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 204 (4.90), 222 (4.56), 284 (4.51), 324 (4.40), 335 (4.24). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, Me-8′), 2.35 (3H, s, Me-4′), 3.64 (5H, s, CH_2-2, COOMe), 3.87 (3H, s, OMe-4‴), 5.60 (2H, s, CH_2-1″), 6.93 (1H, d, J = 9.0, H-6′), 7.05 (2H, d, J = 8.7, H-3‴, H-5‴), 7.52 (1H, d, J = 9.0, H-5′), 7.97 (2H, d, J = 8.7, H-2‴, H-6‴).

Methyl-2-[7-[2-(3-methoxyphenyl)-2-oxoethoxy]-4-methyl-2-oxo-2*H*-3-chromenyl]acetate (21). Yield 88%, $C_{22}H_{20}O_6$, mp 136-137°C. IR spectrum (KBr, cm^{-1}): 1729, 1706, 1614, 1583, 1456, 1430, 1336, 1291, 1265, 1201, 1185, 1101, 1006, 979, 814, 787. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 204 (4.73), 219 (4.62), 250 (4.06), 319 (4.30). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.38 (3H, s, Me-4′), 3.63 (5H, s, CH_2-2, COOMe), 3.85 (3H, s, OMe-3‴), 5.65 (2H, s, CH_2-1″), 7.01 (1H, dd, J = 2.4, J = 8.7, H-6′), 7.04 (1H, d, J = 2.4, H-8′), 7.23 (1H, dd, J = 2.7, J = 8.4, H-4‴), 7.48 (1H, t, J = 8.4, H-5‴), 7.53 (1H, dd, J = 2.7, J = 2.7, H-2‴), 7.61 (1H, J = 8.4, H-6‴), 7.71 (1H, d, J = 8.7, H-5′).

Methyl-2-[7-[2-(3-methoxyphenyl)-2-oxoethoxy]-4,8-dimethyl-2-oxo-2*H*-3-chromenyl]acetate (22). Yield 91%, $C_{23}H_{22}O_6$, mp 176-177°C. IR spectrum (KBr, cm^{-1}): 1737, 1704, 1604, 1467, 1433, 1336, 1291, 1267, 1175, 1139, 1012, 805, 790. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 204 (4.73), 220 (4.60), 249 (4.07), 318 (4.29). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, Me-8′), 2.38 (3H, s, Me-4′), 3.63 (3H, s, COOMe), 3.65 (2H, s, CH_2-2), 3.85 (3H, s,

OMe-3‴), 5.69 (2H, s, CH_2-1″), 6.96 (1H, d, J = 9.0, H-6′), 7.23 (1H, dd, J = 2.7, J = 8.4, H-4‴), 7.45 (1H, t, J = 8.4, H-5‴), 7.49 (1H, dd, J = 2.7, J = 2.7, H-2‴), 7.53 (1H, d, J = 9.0, H-5′), 7.61 (1H, d, J = 8.4, H-6‴).

Methyl-2-[4-methyl-2-oxo-7-(2-oxocyclohexyloxy)-2*H*-3-chromenyl]acetate (23). Yield 68%, $C_{19}H_{20}O_6$, mp 168-169°C. IR spectrum (KBr, cm^{-1}): 1744, 1720, 1698, 1611, 1450, 1435, 1389, 1339, 1295, 1266, 1215, 1200, 1184, 1102, 1070, 1001, 790. UV spectrum (EtOH, λ_{max}, nm, log ε): 206 (4.79), 223 (4.45), 325 (4.38). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.63-2.62 (8H, m, CH_2-3″, CH_2-4″, CH_2-5″, CH_2-6″), 2.36 (3H, s, Me-4′), 3.63 (5H, s, CH_2-2, COOMe), 5.15 (1H, m, H-2″), 6.88 (2H, m, H-6′, H-8′), 7.64 (1H, d, J = 8.8, H-5′).

Methyl-2-[4,8-dimethyl-2-oxo-7-(2-oxocyclohexyloxy)-2*H*-3-chromenyl]acetate (24). Yield 76%, $C_{20}H_{22}O_6$, mp 189-190°C. IR spectrum (KBr, cm^{-1}): 2930, 1730, 1706, 1602, 1500, 1432, 1344, 1287, 1209, 1198, 1177, 1130, 1106, 995, 803. UV spectrum (EtOH, λ_{max}, nm, log ε): 204 (4.74), 231 (4.29), 318 (4.23). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.65-2.62 (8H, m, CH_2-3″, CH_2-4″, CH_2-5″, CH_2-6″), 2.25 (3H, s, Me-8′), 2.35 (3H, s, Me-4′), 3.63 (5H, s, CH_2-2, COOMe), 5.15 (1H, m, H-2″), 6.83 (1H, d, J = 9.0, H-6′), 7.48 (1H, d, J = 9.0, H-5′).

2-(5-Methyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acids 25-46. A solution or suspension of ketone **3-24** (2 mmol) in propan-2-ol (10 mL) was treated with NaOH solution (10 mL, 1 N). The reaction mixture was heated for 3-4 h (course of reaction monitored by TLC) and poured into H_2SO_4 solution (100 mL, 1 N). The resulting precipitate was filtered off and crystallized from propan-2-ol.

2-(3,5-Dimethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (25). Yield 85%, $C_{15}H_{12}O_5$, mp 259-261°C. IR spectrum (KBr, cm^{-1}): 3219, 1743, 1675, 1628, 1579, 1461, 1382, 1347, 1174, 1149, 1112, 1064, 870. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 206 (4.59), 249 (4.52), 294 (4.22), 329 (4.03). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 2.31 (3H, s, Me-3′), 2.52 (3H, s, Me-5′), 3.60 (2H, s, CH_2-2), 7.49 (1H, s, H-9′), 7.72 (1H, s, H-2′), 7.95 (1H, s, H-4′), 12.29 (1H, br.s, COOH).

2-(2,5,9-Trimethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (26). Yield 93%, $C_{16}H_{14}O_5$, mp 274-275°C. IR spectrum (KBr, cm^{-1}): 2927, 1733, 1658, 1620, 1594, 1396, 1359, 1313, 1182, 1161, 1134, 1070, 875, 795. UV spectrum (EtOH, λ_{max}, nm, log ε): 211 (4.58), 252 (4.46), 299 (4.20), 335 (3.95). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 2.29 (3H, s, Me-3′), 2.48 (3H, s, Me-9′), 2.52 (3H, s, Me-5′), 3.61 (2H, s, CH_2-2), 7.76 (1H, s, H-2′), 7.81 (1H, s, H-4′), 12.31 (1H, br.s, COOH).

2-[3-*t*-Butyl)-5-methyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (27). Yield 82%, $C_{18}H_{18}O_5$, mp 269-270°C. IR spectrum (KBr, cm^{-1}): 1734, 1670, 1626, 1576, 1390, 1343, 1173, 1140, 1081, 842. UV spectrum (EtOH, λ_{max}, nm, log ε): 210 (4.32), 248 (4.19), 296 (3.93), 337 (3.75). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 1.45 [9H, s, $(CH_3)_3$], 2.52 (3H, s, Me-5′), 3.62 (2H, s, CH_2-2), 7.54 (1H, s, H-9′), 7.68 (1H, s, H-2′), 8.01 (1H, s, H-4′), 12.36 (1H, br.s, COOH).

2-[3-*t*-Butyl)-5,9-dimethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (28). Yield 84%, $C_{19}H_{20}O_5$, mp 218-219°C. IR spectrum (KBr, cm^{-1}): 1704, 1631, 1596, 1449, 1423, 1395, 1353, 1302, 1207, 1127, 1080, 799. UV spectrum (EtOH, λ_{max}, nm, log ε): 211 (4.83), 244 (4.68), 251 (4.70), 265 (4.38), 303 (4.46), 340 (4.17). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 1.44 [9H, s, $(CH_3)_3$], 2.51 (6H, s, Me-5′, Me-9′), 3.61 (2H, s, CH_2-2), 7.68 (1H, s , H-4′), 7.85 (1H, s, H-2′), 12.36 (1H, br.s, COOH).

2-(2,3,5-Trimethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (29). Yield 87%, $C_{16}H_{14}O_5$, mp 255-256°C. IR spectrum (KBr, cm^{-1}): 2920, 1710, 1693, 1641, 1625, 1582, 1399, 1348, 1322, 1271, 1155, 1101, 897. UV spectrum (dioxane, λ_{max}, nm, log ε): 215 (4.51), 254 (4.69), 293 (4.27), 301 (4.23), 338 (4.09). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 2.21 (3H, s, Me-3′), 2.42 (3H, s, Me-2′), 2.51 (3H, s, Me-5′), 3.59 (2H, s, CH_2-2), 7.39 (1H, s, H-9′), 7.79 (1H, s, H-4′), 12.33 (1H, br.s, COOH).

2-(2,3,5,9-Tetramethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (30). Yield 71%, $C_{17}H_{16}O_5$, mp 273-274° C. IR spectrum (KBr, cm^{-1}): 2915, 1712, 1694, 1646, 1594, 1434, 1410, 1393, 1270, 1179, 1153, 1130, 1101, 898. UV spectrum (dioxane, λ_{max}, nm, log ε): 217 (4.45), 254 (4.64), 296 (4.27), 303 (4.24), 338 (3.98). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 2.17 (3H, s, Me-3′), 2.40 (3H, s, Me-9′), 2.42 (6H, s, Me-2′, Me-5′), 3.57 (2H, s, CH_2-2), 7.53 (1H, s, H-4′), 12.34 (1H, br.s, COOH).

2-(2,5-Dimethyl-3-phenyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (31). Yield 76%, $C_{21}H_{16}O_5$, mp 202-204°C. IR spectrum (KBr, cm^{-1}): 3423, 2920, 1719, 1627, 1582, 1437, 1394, 1327, 1197, 1149, 1096, 937. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 226 (4.43), 254 (4.57), 295 (4.25), 338 (3.93). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 2.46 (3H, s, Me-2′), 2.50 (3H, s, Me-5′), 3.60 (2H, s, CH_2-2), 7.41 (1H, m, H-4″), 7.55 (5H, m, H-9′, H-2″, H-3″, H-5″, H-6″), 7.82 (1H, s, H-4′), 12.32 (1H, br.s, COOH).

2-(2,5,9-Trimethyl-3-phenyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (32). Yield 85%, $C_{22}H_{18}O_5$, mp 234-235°C. IR spectrum (KBr, cm^{-1}): 3312, 1723, 1708, 1596, 1399, 1361, 1332, 1306, 1176, 1130, 754. UV spectrum (EtOH, λ_{max}, nm, log ε): 202 (4.61), 217 (4.56), 256 (4.59), 302 (4.32). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 2.44 (3H, s, Me-9′), 2.55 (3H, s, Me-2′), 2.57 (3H, s, Me-5′), 3.60 (2H, s, CH_2-2), 7.41 (1H, m, H-4″), 7.55 (4H, m, H-2″, H-3″, H-5″, H-6″), 7.66 (1H, s, H-4′), 12.24 (1H, br.s, COOH).

2-(5-Methyl-3-phenyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (33). Yield 92%, $C_{20}H_{14}O_5$, mp 209-211°C. IR spectrum (KBr, cm^{-1}): 2923, 1710, 1696, 1631, 1580, 1396, 1335, 1226, 1161, 1114, 1091, 882, 844, 764. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 226 (4.44), 251 (4.47), 298 (4.25), 335 (3.89). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 2.55 (3H, s, Me-5′), 3.66 (2H, s, CH_2-2), 7.44 (1H, m, H-4″), 7.56 (2H, t, J = 8.0, H-2″, H-6″), 8.21 (1H, s, H-4′), 8.50 (1H, s, H-2′), 12.32 (1H, br.s, COOH).

2-(5,9-Dimethyl-3-phenyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (34). Yield 93%, $C_{21}H_{16}O_5$, mp 270-271°C. IR spectrum (KBr, cm^{-1}): 1737, 1706, 1677, 1591, 1390, 1358, 1304, 1178, 1164, 1134, 865, 796. UV spectrum (dioxane, λ_{max}, nm, log ε): 216 (4.33), 253 (4.39), 300 (4.19), 336 (3.76). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 2.48 (3H, s, Me-5′), 2.56 (3H, s, Me-9′), 3.62 (2H, s, CH_2-2), 7.40 (1H, m, H-4″), 7.52 (2H, m, H-3″, H-5″), 7.76 (2H, m, H-2″, H-6″), 7.99 (1H, s, H-4′), 8.36 (1H, s, H-2′), 12.36 (1H, br.s, COOH).

2-[3-(4-Fluorophenyl)-5-methyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (35). Yield 89%, $C_{20}H_{13}O_5$, mp 245-247°C. IR spectrum (KBr, cm^{-1}): 3106, 1744, 1704, 1668, 1628, 1575, 1508, 1398, 1348, 1327, 1229, 1165, 1122, 1092, 856, 827. UV spectrum (dioxane, λ_{max}, nm, log ε): 215 (4.47), 252 (4.50), 293 (4.25), 301 (4.23), 329 (4.00). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm): 2.54 (3H, s, Me-5′), 3.66 (2H, s, CH_2-2), 7.39 (2H, t, J = 8.8, H-3″, H-5″), 7.81 (1H, s, H-9′), 7.87 (2H, m, H-2″, H-6″), 8.18 (1H, s, H-4′), 8.48 (1H, s, H-2′), 12.51 (1H, br.s, COOH).

2-[3-(4-Fluorophenyl)-5,9-dimethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (36). Yield 90%, $C_{21}H_{15}FO_5$, mp 305-306°C. IR spectrum (KBr, cm^{-1}): 3105, 1715, 1675, 1571, 1508, 1398, 1348, 1327, 1291, 1165, 1130, 1095, 838, 812. UV spectrum (EtOH, λ_{max}, nm, log ε): 207 (4.37), 229 (4.25), 252 (4.29), 305 (4.08). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 2.49 (3H, s, Me-5′), 2.56 (3H, s, Me-9′), 3.61 (2H, s, CH_2-2), 7.28 (2H, m, H-3″, H-5″), 7.78 (2H, m, H-2″, H-6″), 7.93 (1H, s, H-4′), 8.30 (1H, s, H-2′), 12.32 (1H, br.s, COOH).

2-[3-(4-Chlorophenyl)-5-methyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (37). Yield 85%, $C_{20}H_{13}ClO_5$, mp 235-237°C. IR spectrum (KBr, cm^{-1}): 3140, 1756, 1706, 1665, 1627, 1578, 1493, 1396, 1367, 1347, 1296, 1189, 1166, 1124, 1097, 1075, 864, 805. UV spectrum (EtOH, λ_{max}, nm, log ε): 203 (4.79), 251 (4.73), 299 (4.51), 335 (4.15). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.51 (3H, s, Me-5′), 3.66 (2H, s, CH_2-2), 7.60 (2H, d, J = 8.0, H-3″, H-5″), 7.83 (1H, s, H-9′), 7.87 (2H, d, J = 8.0, H-2″, H-6″), 8.20 (1H, s, H-4′), 8.54 (1H, s, H-2′), 12.48 (1H, br.s, COOH).

2-[3-(4-Chlorophenyl)-5,9-dimethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (38). Yield 83%, $C_{21}H_{15}ClO_5$, mp 292-293°C. IR spectrum (KBr, cm^{-1}): 1718, 1673, 1589, 1494, 1389, 1357, 1291, 1165, 1132, 1099, 864, 838, 812. UV spectrum (dioxane, λ_{max}, nm, log ε): 212 (4.56), 251 (4.60), 296 (4.37), 308 (4.30), 338 (3.91). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.49 (3H, s, Me-5′), 2.56 (3H, s, Me-9′), 3.61 (2H, s, CH_2-2), 7.53 (2H, d, J = 8.4, H-3″, H-5″), 7.78 (2H, d, J = 8.4, H-2″, H-6″), 7.93 (1H, s, H-4′), 8.32 (1H, s, H-2′), 12.32 (1H, br.s, COOH).

2-[3-(4-Bromophenyl)-5-methyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (39). Yield 92%, $C_{20}H_{13}BrO_5$, mp 240-242°C. IR spectrum (KBr, cm^{-1}): 3298, 1743, 1710, 1682, 1629, 1581, 1392, 1348, 1157, 1116, 1090, 1071, 1006, 814. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 212 (4.55), 248 (4.56), 295 (4.31), 333 (3.92). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.54 (3H, s, Me-5′), 3.66 (2H, s, CH_2-2), 7.73 (2H, d, J = 8.0, H-3‴, H-5‴), 7.80 (2H, d, J = 8.0, H-2″, H-6″), 7.82 (1H, s, H-9′), 8.19 (1H, s, H-4′), 8.54 (1H, s, H-2′), 12.51 (1H, br.s, COOH).

2-[3-(4-Bromophenyl)-5,9-dimethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (40). Yield 95%, $C_{21}H_{15}BrO_5$, mp 298-299°C. IR spectrum (KBr, cm^{-1}): 3290, 1741, 1708, 1676, 1614, 1586, 1391, 1358, 1160, 1190, 1095, 1006, 836. UV spectrum (EtOH, λ_{max}, nm, log ε): 206 (4.65), 219 (4.52), 252 (4.55), 303 (4.32), 315 (4.21). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.56 (3H, s, Me-5′), 2.62 (3H, s, Me-9′), 3.62 (2H, s, CH_2-2), 7.63 (2H, d, J = 8.1, H-3″, H-5″), 7.70 (2H, d, J = 8.1, H-2″, H-6″), 7.96 (1H, s, H-4′), 8.37 (1H, s, H-2′), 12.38 (1H, br.s, COOH).

2-[3-(4-Methoxyphenyl)-5-methyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (41). Yield 80%, $C_{21}H_{16}O_6$, mp 224-226°C. IR spectrum (KBr, cm^{-1}): 2932, 1702, 1630, 1585, 1567, 1509, 1395, 1346, 1324, 1247, 1230, 1158, 1114, 1076, 1020, 833. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 231 (4.55), 251 (4.58), 304 (4.35). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.54 (3H, s, Me-5′), 3.66 (2H, s, CH_2-2), 3.83 (3H, s, OMe-4″), 7.11 (2H, d, J = 8.0, H-3″, H-5″), 7.75 (2H, d, J = 8.0, H-2″, H-6″), 7.80 (1H, s, H-9′), 8.17 (1H, s, H-4′), 8.40 (1H, s, H-2′), 12.50 (1H, br.s, COOH).

2-[3-(4-Methoxyphenyl)-5,9-dimethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (42). Yield 80%, $C_{22}H_{18}O_6$, mp 249-250°C. IR spectrum (KBr, cm^{-1}): 2965, 1722, 1659, 1614, 1586, 1568, 1512, 1386, 1358, 1295, 1259, 1166, 1135, 1107, 1032, 836, 803. UV spectrum (dioxane, λ_{max}, nm, log ε): 212 (4.51), 253 (4.54), 302 (4.29), 313 (4.22). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.48 (3H, s, Me-5′), 2.53 (3H, s, Me-9′), 3.61 (2H, s, CH_2-2), 7.05 (2H, d, J = 8.4, H-3″, H-5″), 7.75 (2H, d, J = 8.4, H-2″, H-6″), 7.91 (1H, s, H-4′), 8.22 (1H, s, H-2′), 12.35 (1H, br.s, COOH).

2-[3-(3-Methoxyphenyl)-5-methyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (43). Yield 84%, $C_{21}H_{16}O_6$, mp 211-212°C. IR spectrum (KBr, cm^{-1}): 3082, 1706, 1629, 1609, 1580, 1563, 1429, 1395, 1318, 1248, 1220, 1160, 1101, 1021, 889, 773. UV spectrum (dioxane, λ_{max}, nm, log ε): 212 (4.69), 251 (4.46), 296 (4.26), 305 (4.24). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.52 (3H, s, Me-5′), 3.62 (2H, s, CH_2-2), 3.86 (3H, s, OCH_3-3″), 6.95 (1H, dd, J = 2.7, J = 8.4, H-4″), 7.25 (1H, dd, J = 2.7, J = 2.7, H-2″), 7.33 (1H, d, J = 8.4, H-6″), 7.43 (1H, t, J = 8.4, H-5″), 7.66 (1H, s, H-9′), 8.13 (1H, s, H-4′), 8.35 (1H, s, H-2′), 12.37 (1H, br.s, COOH).

2-[3-(3-Methoxyphenyl)-5,9-dimethyl-7-oxo-7*H*-furo[3,2-*g*]chromen-6-yl)acetic Acid (44). Yield 89%, $C_{22}H_{18}O_6$, mp 236-237°C. IR spectrum (KBr, cm^{-1}): 3424, 1708, 1685, 1596, 1424, 1390, 1329, 1305, 1245, 1136, 1031, 838, 783. UV spectrum (dioxane, λ_{max}, nm, log ε): 214 (4.60), 251 (4.42), 299 (4.27), 308 (4.23). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.49 (3H, s, Me-5′), 2.55 (3H, s, Me-9′), 3.62 (2H, s, CH_2-2), 3.86 (3H, s, OCH_3-3″), 6.95 (1H, dd, J = 2.7, J = 8.4, H-4″), 7.24 (1H, dd, J = 2.7, J = 2.7, H-2″), 7.34 (1H, d, J = 8.4, H-6″), 7.42 (1H, t, J = 8.4, H-5″), 7.97 (1H, s, H-4′), 8.35 (1H, s, H-2′), 12.31 (1H, br.s, COOH).

2-(4-Methyl-2-oxo-6,7,8,9-tetrahydro-2*H*-benzo[4,5]furo[3,2-*g*]chroomen-3-yl)acetic Acid (45). Yield 79%, $C_{18}H_{16}O_5$, mp 285-286°C. IR spectrum (KBr, cm^{-1}): 1699, 1603, 1573, 1503, 1466, 1449, 1371, 1285, 1267, 1227, 1139, 1110, 965, 778. UV spectrum (EtOH, λ_{max}, nm, log ε): 210 (4.20), 256 (4.24), 298 (3.89), 340 (3.71). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 1.85 (2H, m, CH_2-7), 1.92 (2H, m, CH_2-8), 2.43 (3H, s, Me-4′), 2.55 (2H, m, CH_2-6), 2.73 (2H, m, CH_2-9), 3.57 (2H, s, CH_2-2), 7.39 (1H, s, H-11′), 7.72 (1H, s, H-5′), 12.33 (1H, br.s, COOH).

2-(4,11-Dimethyl-2-oxo-6,7,8,9-tetrahydro-2*H*-benzo[4,5]furo[3,2-*g*]chromen-3-yl)acetic Acid (46). Yield 86%, $C_{19}H_{18}O_5$, mp 202-203°C. IR spectrum (KBr, cm^{-1}): 2956, 1703, 1645, 1597, 1411, 1336, 1239, 1184, 1129, 1113, 1092, 898, 788. UV spectrum (EtOH, λ_{max}, nm, log ε): 210 (4.23), 256 (4.22), 301 (3.93), 344 (3.68). PMR spectrum (300 MHz, DMSO-d_6, δ, ppm): 1.84 (2H, m, CH_2-7), 1.93 (2H, m, CH_2-8), 2.42 (3H, s, Me-11′), 2.44 (3H, s, Me-4′), 2.55 (2H, m, CH_2-6), 2.74 (2H, m, CH_2-9), 3.57 (2H, s, CH_2-2), 7.55 (1H, s, H-5′), 12.31 (1H, br.s, COOH).

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