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MODIFIED COUMARINS. 14. SYNTHESIS OF 7-HYDROXY-[4,3′]DICHROMENYL-2,2′-DIONE DERIVATIVES

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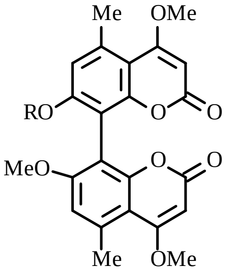
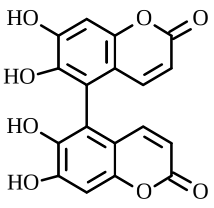
New derivatives of 3-(2-oxochromen-4-yl)chromen-2-one, modified analogs of natural dicoumarins, were prepared from substituted coumarin-4-acetic acids.

Key words: coumarins, dicoumarins, condensation, synthesis.

Dicoumarins are a group of natural compounds that occur as minor components from the biosynthesis of coumarins. In contrast with the monoanalogs, the activity of dicoumarins can be adjusted not only by adding substituents to the coumarin core but also by changing the fusion of the benzopyran rings. The first natural dicoumarins were cotanine (**1**) and its demethylcotanine analog (**2**), which were isolated from metabolic products of *Aspergillus glaucus* and were assigned as mycotoxins [1]. Their molecules contain 8,′8′-bonded coumarin rings. Euphorbetin (**3**) and isoeuphorbetin (**4**), which were isolated from seeds of *Euphorbia lathyris* [2], typically have 5,5′- and 5,8′-bonded benzopyran-2-one systems in the dicoumarin structure. Natural dicoumarins also occur with other types of bonding of coumarin fragments. Examples are toddasiatin (**5**), ipomopsin (**6**), and coumarin (**7**), which were isolated from *Toddalia asiatica* [3], *Ipomopsis aggregata* [4], and *Impatiens balsamina* [5], respecively.



1: R = Me
2: R = H



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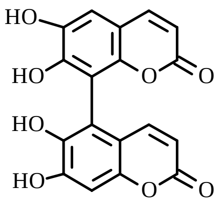

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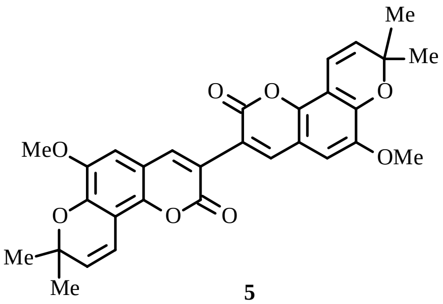

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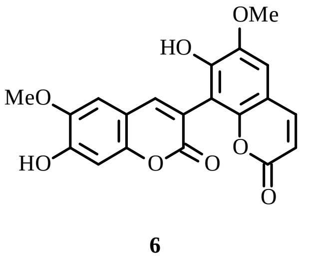

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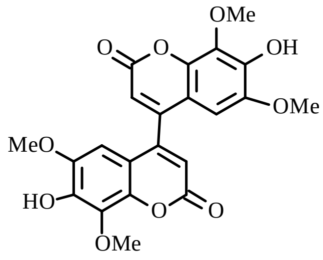

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Several approaches to the bonding of coumarin rings into dicoumarins are known, in particular, fusion of coumarin systems to substituted biphenyls [1, 6], bonding of coumarin rings using the Ulmann condensation [7] or ferrocyanide oxidation

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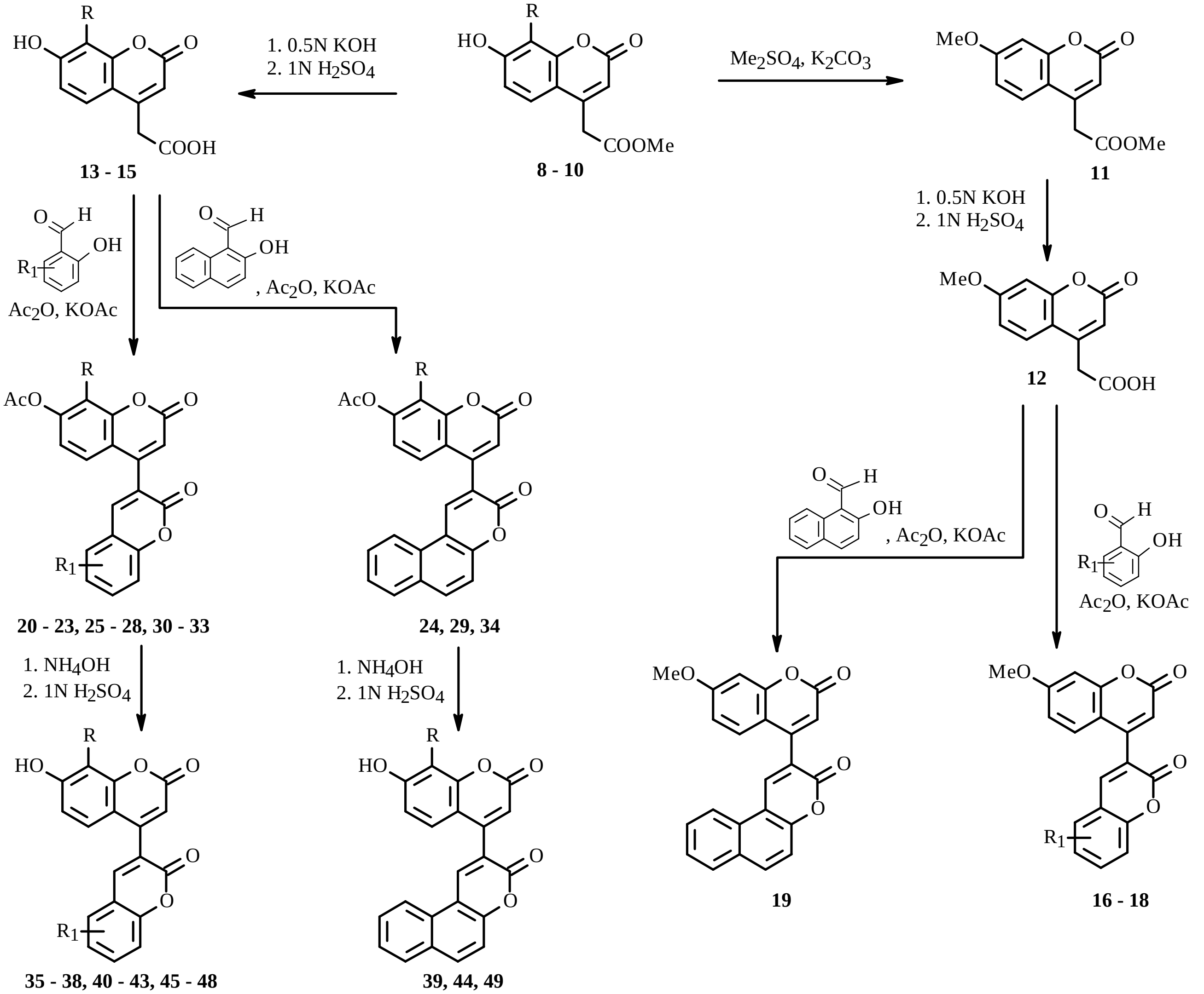
[7], and intermolecular condensation of 4-chloro- and 4-hydroxycoumarins [8]. In our opinion, the most convenient and effective method for bonding coumarin rings into dicoumarins is based on condensation of coumarin-4-acetic acid derivatives with substituted salicylaldehydes [9], which we used to synthesize 3,4′-dicoumarins.



8, 13, 24, 39: R = H; **9, 14, 29, 44:** R = Me; **10, 15, 49:** R = OH; **16:** R_1= H; **17:** R_1 = 8-OMe

18: R_1 = 6-Br; **20, 35:** R = R_1= H; **21, 36:** R = H, R_1 = 8-OMe; **22, 37:** R = H, R_1 = 6-Br; **23:** R = H, R_1 = 7-OAc

25, 40: R = Me, R_1= H; **26, 41:** R = Me, R_1 = 8-OMe; **27, 41:** R = Me, R_1 = 6-Br; **28:** R = Me, R_1 = 7-OAc

30: R = OAc, R_1 = H; **31:** R = OAc, R_1 = 8-OMe; **32:** R = OAc, R_1 = 6-Br; **33:** R = OAc, R_1 = 7-OAc

34: R = OAc; **38:** R = H, R_1 = 7-OH; **43:** R = Me, R_1 = 7-OH; **45:** R = OH, R_1= H

46: R = OH, R_1 = 8-OMe; **47:** R = H, R_1= 6-Br; **48:** R = OH, R_1 = 7-OH

Methyl-2-(7-hydroxy-2-oxochromen-4-yl)acetate (**8**), methyl-2-(7-hydroxy-8-methyl-2-oxochromen-4-yl)acetate (**9**), and methyl-2-(7,8-dihydroxy-2-oxochromen-4-yl)acetate (**10**), which were necessary for further transformations, were prepared by Pechmann condensation of the appropriate dimetylacetonedicarboxylate with resorcinol, 2-methylresorcinol, and pyrogallol, respectively, in the presence of dry HCl as the condensing agent at 0°C.

Using methyl esters of coumarin-4-acetic acid in the condensation with salicylaldehydes gives the desired dicoumarins in small yields. Therefore, esters **8-10** were converted to the corresponding benzopyran-2-onyl-4-acetic acids **13-15** by treatment with KOH solution in the cold with subsequent acidolysis of the reaction mixture. 7-Hydroxycoumarinacetic acid and 2-(7-methoxy-2-oxochromen-4-yl)acetic acid (**12**) were also used in the condensation. These were prepared by alkylation of **8** in a Williamson reaction using dimethylsulfate with subsequent hydrolysis of **11** under alkaline conditions. The PMR spectra of **12-15** contain signals characteristic of the coumarin ring, a 2H singlet for the acetyl CH_2 at 3.73-3.80 ppm, and a broad signal for the carboxyl proton at 12.51-12.64 ppm.

Perkin condensation of **12-15** with substituted salicylaldehydes in the presenc of an equivalent of potassium acetate leads in 48-71% yield to bonding of the benzopyran system at the 4-position of the starting coumarin. We used salicylaldehyde (**16**, **20**, **25**, **30**), 2-hydroxy-3-methoxy-benzaldehyde (**17**, **21**, **26**, **31**), 5-bromo-2-hydroxybenzaldehyde (**18**, **22**, **27**, **32**), 2,4-dihydroxybenzaldehyde (**23**, **28**, **33**), and 2-hydroxy-1-naphthaldehyde (**19**, **24**, **29**, **34**) in this synthesis.

PMR spectra of **16-34**, in contrast with the starting acids, lack signals for the acetyl CH_2, carboxyl protons, and phenol hydroxyl (for **20-34**). The spectra of all dicoumarins contain in the range of aromatic protons signals for protons resulting from condensation of the coumarin ring. The most characteristic of these is the signal for H-4′ at 8.21-8.32 ppm. For **19**, **24**, **29**, and **34**, the signal for this proton is shifted to weak field (9.07-9.20 ppm) owing to the effect of the naphthalene π-system.

IR spectra of the acetates of the [4,3′]dichromenyl-2,2′-diones (**20-34**) typically have two bands near 1696-1784 cm^{-1}, characteristic of acetyl C=O stretching and coumarin-ring vibrations.

Acid and alkaline hydrolysis were used to synthesize hydroxy derivatives of the dicoumarins. The most acceptable results were obtained if the de-acetylation was performed in aqueous ammonia (25%). Treatment of **20-34** wth ammonia solution with subsequent acidification gave hydroxydicoumarins **35-49** in high yields (67-90%).

PMR spectra of the products typically had signals for phenol hydroxyls at 9.71-10.51 ppm and singlets for H-3 near 6.22-6.34 ppm and H-4′ near 8.11-8.25 ppm (for **39**, **44**, and **49**, at 9.05-9.10 ppm). This confirms that the dicoumarin structure was retained in the hydroxy derivatives. IR spectra of **35-49** contain absorption bands at 3104-3464 and 1700-1728 cm^{-1}, typical for stretching vibrations of phenol hydroxyl and coumarin carbonyl, respectively.

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 determined on a Kofler block. IR and UV spectra were measured on a Nicolet FTIR Nexus 475 spectrometer and Specord M40 spectrophotometer, respectively; PMR spectra, on a Varian VXR-300 spectrometer at 300 MHz relative to TMS (internal standard). Elemental analyses of all compounds agreed with those calculated.

Methyl-7-hydroxycoumarin-4-acetates (8-10). A cooled (0°C) solution of the appropriate polyphenol (0.2 mol) and dimethylacetonedicarboxylate (0.2 mol, 29.5 mL) in absolute CH_3OH (80 mL) was vigorously stirred and cooled. A stream of dry HCl was passed through the solution for 3 h. The reaction mixture was stirred until completely thickened, left overnight at room temperature, and poured into icewater (500 mL). The resulting solid was filtered off and crystallized from CH_3OH.

Methyl-2-(7-hydroxy-2-oxochromen-4-yl)acetate (8). Yield 60%, empirical formula $C_{12}H_{10}O_5$, mp 215-217°C (lit. 220°C [10, 11], 221-223°C [12]).

IR spectrum (KBr, cm^{-1}): 1726, 1716, 1706, 1700, 1690, 1680, 1604, 1400, 1342, 1204, 1140. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 202 (4.78), 218 (4.34), 322 (4.25).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.66 (3H, s, $COOCH_3$), 3.95 (2H, s, CH_2-4), 6.24 (1H, s, H-3), 6.74 (1H, d, J = 2.1, H-8), 6.81 (1H, dd, J = 2.1, J = 8.7, H-6), 7.52 (1H, d, J = 8.7, H-5), 10.56 (1H, br.s, OH-7).

Methyl-2-(7-hydroxy-8-methyl-2-oxochromen-4-yl)acetate (9). Yield 64%, empirical formula $C_{13}H_{12}O_5$, mp 190-193°C.

IR spectrum (KBr, cm^{-1}): 3228, 2956, 1724, 1692, 1602, 1576, 1320, 1258, 1090, 874, 850, 726. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.67), 220 (4.21), 322 (4.14).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.18 (3H, s, CH_3-8), 3.65 (3H, s, $COOCH_3$), 3.86 (2H, s, CH_2-4), 6.16 (1H, s, H-3), 6.82 (1H, d, J = 8.7, H-6), 7.27 (1H, d, J = 8.7, H-5), 10.33 (1H, br.s, OH-7).

Methyl-2-(7,8-dihydroxy-2-oxochromen-4-yl)acetate (10). Yield 56%, empirical formula $C_{13}H_{10}O_6$, mp 185-187°C (lit. 182-185°C [13]).

IR spectrum (KBr, cm^{-1}): 1714, 1612, 1584, 1454, 1286, 1196, 1136, 1040. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 204 (4.63), 227 (4.06), 319 (4.12).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.64 (3H, s, $COOCH_3$), 3.92 (2H, s, CH_2-4), 6.24 (1H, s, H-3), 6.81 (1H, d, J = 8.7, H-6), 7.01 (1H, d, J = 8.7, H-5), 9.35 and 10.33 (2H, two br.s, OH-7, OH-8).

Methyl-2-(7-methoxy-2-oxochromen-4-yl)acetate (11). A hot solution of **8** (4.96 g, 20 mmol) in absolute acetone (100 mL) was treated with freshly calcined potash (6.90 g, 50 mmol). The reaction mixture was vigorously stirred, heated (50-56°C), treated with dimethylsulfate (1.9 mL, 21 mmol), and heated for 1 h with vigorous stirring (course of reaction monitored using TLC). After the reaction was complete, the mixture was poured in portions into cooled H_2SO_4 (1 N, 200 mL). The resulting solid was filtered off and crystallized from aqueous CH_3OH. Yield 88%, empirical formula $C_{14}H_{14}O_5$, mp 120-121°C (lit 122°C [10, 14]).

IR spectrum (KBr, cm^{-1}): 3932, 3440, 2920, 2852, 1734, 1612, 1404, 1340, 1266, 1236, 1200, 1180, 836. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.74), 224 (3.65), 322 (4.22).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.66 (3H, s, OCH_3-7), 3.86 (3H, s, $COOCH_3$), 3.92 (3H, s, CH_2-4), 6.26 (1H, s, H-3), 6.95 (2H, m, H-6, H-8), 7.55 (1H, d, J = 8.7, H-5).

Coumarin-4-acetic Acids (12-15). A cooled solution of KOH (3.36 g, 60 mmol) in water (100 mL) was vigorously stirred and treated with the appropriate coumarin (**8-11**, 15 mmol). The reaction mixture was stirred until the starting coumarin was completely dissolved, held at room temperature, stirred for 0.5-1 h, and acidified to pH 4. The resulting solid was filtered off and crystallized from aqueous propan-2-ol.

2-(7-Methoxy-2-oxochromen-4-yl)acetic Acid (12). Yield 74%, empirical formula $C_{12}H_{10}O_5$, mp 139-140°C (lit. 167-170°C [15], 175-176°C [16], 186°C [10], 187°C [14]).

IR spectrum (KBr, cm^{-1}): 3008, 1722, 1698, 1680, 1618, 1552, 1392, 1304, 1242, 1222, 1156, 856, 612. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.77), 220 (4.35), 321 (4.19).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.80 (2H, s, CH_2-4), 3.86 (3H, s, OCH_3-7), 6.25 (1H, s, H-3), 6.91 (1H, dd, J = 2.4, J = 9.0, H-6), 6.94 (1H, d, J = 2.4, H-8), 7.59 (1H, d, J = 9.0, H-5), 12.60 (1H, br.s, COOH).

2-(7-Hydroxy-2-oxochromen-4-yl)acetic Acid (13). Yield 69%, empirical formula $C_{11}H_8O_5$, mp 218-219°C (lit. 175-176°C [17], 201-202°C [16, 18], 203°C [19, 20], 209-210°C [14], 210°C [10, 11]).

IR spectrum (KBr, cm^{-1}): 3264, 1710, 1698, 1692, 1680, 1612, 1586, 1562, 1438, 1402, 1372, 1328, 1252, 1214, 1064. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 201 (4.72), 217 (4.28), 322 (4.19).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.75 (2H, s, CH_2-4), 6.16 (1H, s, H-3), 6.68 (1H, d, J = 2.1, H-8), 6.76 (1H, dd, J = 2.1, J = 9.0, H-6), 7.49 (1H, d, J = 9.0, H-5), 10.41 (1H, s, OH-7), 12.51 (1H, br.s, COOH).

2-(7-Hydroxy-8-methyl-2-oxochromen-4-yl)acetic Acid (14). Yield 72%, empirical formula $C_{12}H_{10}O_5$, mp 223-225°C (lit. 250°C [21]).

IR spectrum (KBr, cm^{-1}): 3276, 1704, 1696, 1690, 1684, 1680, 1602, 1590, 1572, 1316, 1248, 1090. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.98), 222 (4.22), 321 (4.15).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.18 (3H, s, CH_3-8), 3.74 (2H, s, CH_2-4), 6.14 (1H, s, H-3), 6.83 (1H, d, J = 9.0, H-6), 7.33 (1H, d, J = 9.0, H-5), 10.28 (1H, s, OH-7), 12.64 (1H, br.s, COOH).

2-(7,8-Dihydroxy-2-oxochromen-4-yl)acetic Acid (15). Yield 66%, empirical formula $C_{11}H_8O_6$, mp 204-205°C.

IR spectrum (KBr, cm^{-1}): 3368, 1688, 1680, 1620, 1596, 1588, 1392, 1318, 1276, 1042. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.71), 253 (3.94), 262 (3.98), 319 (4.22).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.73 (2H, s, CH_2-4), 6.15 (1H, s, H-3), 6.78 (1H, d, J = 8.7, H-6), 6.97 (1H, d, J = 8.7, H-5), 9.22 and 9.88 (2H, two s, OH-7, OH-8), 12.63 (1H, br.s, COOH).

[4,3′]Dichromenyl-2,2′-diones (16-34). A mixture of the appropriate coumarin-4-acetic acid (**12-15**, 10 mmol), substituted salicylaldehyde (10 mmol), potassium acetate (0.98 g, 10 mmol), and freshly distilled acetic anhydride (25 mL) was heated (130-140°C) with vigorous stirring for 3 h (course of reaction monitored by TLC). After the reaction was complete, the mixture was cooled to room temperature and poured into icewater (200 mL). The resulting solid was filtered off and crystallized from CH_3CN.

7-Methoxy-4-(2-oxochromen-3-yl)chromen-2-one (16). Yield 57%, empirical formula $C_{19}H_{12}O_5$, mp 259°C (lit. 241°C [9]).

IR spectrum (KBr, cm^{-1}): 1725, 1617, 1560, 1476, 1374, 1270, 1205, 1060. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 208 (4.72), 285 (4.39), 328 (4.21).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.88 (3H, s, OCH_3-7), 6.37 (1H, s, H-3), 6.86 (1H, dd, J = 2.7, J = 8.7, H-6), 7.02 (1H, d, J = 2.7, H-8), 7.40 (1H, t, J = 7.5, H-7′), 7.46 (2H, d, J = 9.0, H-5, H-8′), 7.70 (1H, t, J = 7.5, H-6′), 7.78 (1H, d, J = 7.5, H-5′), 8.27 (1H, s, H-4′).

7-Methoxy-4-(8-methoxy-2-oxochromen-3-yl)chromen-2-one (17). Yield 61%, empirical formula $C_{20}H_{14}O_6$, mp 238-239°C.

IR spectrum (KBr, cm^{-1}): 1723, 1620, 1576, 1555, 1480, 1454, 1350, 1290, 1220, 1060. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 204 (4.81), 252 (4.25), 285 (4.30), 321 (4.26).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.89 (3H, s, OCH_3-7), 3.99 (3H, s, OCH_3-8′), 6.34 (1H, s, H-3), 6.84 (1H, dd, J = 2.7, J = 8.7, H-6), 7.00 (1H, d, J = 2.7, H-8), 7.32 (3H, m, H-5′, H-6′, H-7′), 7.41 (1H, d, J = 8.7, H-5), 8.22 (1H, s, H-4′).

7-Methoxy-4-(6-bromo-2-oxochromen-3-yl)chromen-2-one (18). Yield 58%, empirical formula $C_{19}H_{11}BrO_5$, mp 245-246°C.

IR spectrum (KBr, cm^{-1}): 1730, 1612, 1550, 1476, 1372, 1278, 1200, 1054. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 202 (4.83), 220 (4.59), 288 (4.34), 329 (4.27).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.88 (3H, s, OCH_3-7), 6.35 (1H, s, H-3), 6.84 (1H, dd, J = 2.4, J = 8.7, H-6), 7.01 (1H, d, J = 2.4, H-8), 7.43 (1H, d, J = 8.1, H-8′), 7.47 (1H, d, J = 8.7, H-5), 7.80 (1H, dd, J = 2.1, J = 8.1, H-7′), 8.01 (1H, d, J = 2.1, H-5′), 8.21 (1H, s, H-4′).

2-(7-Methoxy-2-oxochromen-4-yl)benzo[*f*]chromen-3-one (19). Yield 64%, empirical formula $C_{23}H_{14}O_5$, mp 310°C.

IR spectrum (KBr, cm^{-1}): 1724, 1618, 1592, 1572, 1552, 1400, 1296, 1214, 1158. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.90), 227 (4.88), 232 (4.87), 255 (4.35), 326 (4.45), 358 (4.41).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.89 (3H, s, OCH_3-7′), 6.77 (1H, s, H-3′), 6.85 (1H, dd, J = 2.4, J = 8.7, H-6′), 7.01 (1H, d, J = 2.4, H-8′), 7.46 (1H, d, J = 8.7, H-5′), 7.62 (2H, m, H-5, H-8), 7.72 (1H, t, J = 7.8, H-9), 8.04 (1H, d, J = 8.1, H-6), 8.23 (1H, d, J = 9.0, H-7), 8.56 (1H, d, J = 8.4, H-10), 9.07 (1H, s, H-1).

7-Acetoxy-4-(2-oxochromen-3-yl)chromen-2-one (20). Yield 59%, empirical formula $C_{20}H_{12}O_6$, mp 238-240°C (lit. 253°C [9]).

IR spectrum (KBr, cm^{-1}): 1764, 1726, 1610, 1374, 1264, 1210, 1174, 1144. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.69), 283 (4.37), 324 (4.27).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, OAc-7), 6.56 (1H, s, H-3), 7.06 (1H, dd, J = 2.1, J = 8.4, H-6), 7.27 (1H, d, J = 2.1, H-8), 7.41 (1H, t, J = 7.5, H-7′), 7.47 (1H, d, J = 8.7, H-8′), 7.63 (1H, d, J = 8.4, H-5), 7.70 (1H, t, J = 7.5, H-6′), 7.80 (1H, d, J = 8.4, H-5′), 8.30 (1H, s, H-4′).

7-Acetoxy-4-(8-methoxy-2-oxochromen-3-yl)chromen-2-one (21). Yield 60%, empirical formula $C_{21}H_{14}O_7$, mp 303-306°C.

IR spectrum (KBr, cm^{-1}): 1734, 1706, 1608, 1484, 1444, 1352, 1292, 1220. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 201 (4.89), 254 (4.17), 284 (4.35), 316 (4.36).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, OAc-7), 3.97 (3H, s, OCH_3-8′), 6.56 (1H, s, H-3), 7.06 (1H, dd, J = 2.1, J = 8.7, H-6), 7.28 (1H, d, J = 2.1, H-8), 7.34 (3H, m, H-5′, H-6′, H-7′), 7.62 (1H, d, J = 8.7, H-5), 8.27 (1H, s, H-4′).

7-Acetoxy-4-(6-bromo-2-oxochromen-3-yl)chromen-2-one (22). Yield 55%, empirical formula $C_{20}H_{11}BrO_6$, mp 235-236°C (lit. 247-248°C [9]).

IR spectrum (KBr, cm^{-1}): 1726, 1620, 1562, 1370, 1264, 1202, 1128, 1064. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 202 (4.81), 280 (4.40), 321 (4.21).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, OAc-7), 6.55 (1H, s, H-3), 7.06 (1H, dd, J = 2.1, J = 8.7, H-6), 7.28 (1H, d, J = 2.1, H-8), 7.46 (1H, d, J = 8.4, H-8′), 7.64 (1H, d, J = 8.7, H-5), 7.82 (1H, dd, J = 2.1, J = 8.4, H-7′), 8.03 (1H, d, J = 2.1, H-5′), 8.24 (1H, s, H-4′).

7-Acetoxy-4-(7-acetoxy-2-oxochromen-3-yl)chromen-2-one (23). Yield 62%, empirical formula $C_{22}H_{14}O_8$, mp 239-240°C.

IR spectrum (KBr, cm^{-1}): 1764, 1752, 1728, 1620, 1370, 1266, 1200, 1144, 1014, 908, 648. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 214 (4.54), 286 (4.35), 321 (4.38), 338 (4.19).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 and 2.34 (6H, two s, OAc-7, OAc-7′), 6.55 (1H, s, H-3), 7.07 (1H, dd, J = 2.1, J = 8.7, H-6), 7.19 (1H, dd, J = 2.1, J = 8.7, H-6′), 7.28 (1H, d, J = 2.1, H-8), 7.33 (1H, d, J = 2.1, H-8′), 7.66 (1H, d, J = 8.7, H-5), 7.84 (1H, d, J = 8.7, H-5′), 8.30 (1H, s, H-4′).

2-(7-Acetoxy-2-oxochromen-4-yl)benzo[*f*]chromen-3-one (24). Yield 63%, empirical formula $C_{24}H_{14}O_6$, mp 253-256°C.

IR spectrum (KBr, cm^{-1}): 1720, 1690, 1620, 1572, 1368, 1206, 1144, 1128, 820, 784. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 212 (4.81), 228 (4.80), 232 (4.81), 257 (4.34), 324 (4.28), 362 (4.22).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s OAc-7′), 6.66 (1H, s, H-3′), 7.08 (1H, dd, J = 2.1, J = 8.7, H-6′), 7.31 (1H, d, J = 2.1, H-8′), 7.65 (3H, m, H-5, H-8, H-5′), 7.74 (1H, t, J = 8.1, H-9), 8.07 (1H, d, J = 8.1, H-6), 8.26 (1H, d, J = 9.0, H-7), 8.58 (1H, d, J = 8.4, H-10), 9.16 (1H, s, H-1).

8-Methyl-7-acetoxy-4-(2-oxochromen-3-yl)chromen-2-one (25). Yield 65%, empirical formula $C_{21}H_{14}O_6$, mp 222-224°C.

IR spectrum (KBr, cm^{-1}): 1760, 1752, 1730, 1610, 1384, 1218, 1084. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.71), 286 (4.42), 292 (4.41), 326 (4.25).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.25 (3H, s, CH_3-8), 2.34 (3H, s, OAc-7), 6.54 (1H, s, H-3), 7.03 (1H, d, J = 8.7, H-6), 7.35-7.48 (3H, m, H-5, H-7′, H-8′), 7.69 (1H, t, J = 7.5, H-6′), 7.78 (1H, d, J = 7.5, H-5′), 8.25 (1H, s, H-4′).

8-Methyl-7-acetoxy-4-(8-methoxy-2-oxochromen-3-yl)chromen-2-one (26). Yield 67%, empirical formula $C_{22}H_{16}O_7$, mp 256-259°C.

IR spectrum (KBr, cm^{-1}): 1728, 1608, 1480, 1372, 1280, 1262, 1224, 1214, 1192, 1086. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 201 (4.81), 254 (4.13), 299 (4.38).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.24 (3H, s, CH_3-8), 2.35 (3H, s, OAc-7), 3.97 (3H, s, OCH_3-8′), 6.55 (1H, s, H-3), 7.03 (1H, d, J = 8.7, H-6), 7.33 (3H, m, H-5′, H-6′, H-7′), 7.44 (1H, d, J = 8.7, H-5), 8.23 (1H, s, H-4′).

8-Methyl-7-acetoxy-4-(6-bromo-2-oxochromen-3-yl)chromen-2-one (27). Yield 60%, empirical formula $C_{21}H_{13}BrO_6$, mp 242-244°C.

IR spectrum (KBr, cm^{-1}): 1728, 1700, 1692, 1602, 1368, 1260, 1244, 1194, 1084, 888. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.81), 221 (4.62), 283 (4.42), 324 (4.17).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.24 (3H, s, CH_3-8), 2.35 (3H, s, OAc-7), 6.54 (1H, s, H-3), 7.04 (1H, d, J = 8.7, H-6), 7.44 (1H, d, J = 9.0, H-8′), 7.47 (1H, d, J = 9.0, H-5), 7.81 (1H, dd, J = 2.1, J = 9.0, H-7′), 8.03 (1H, d, J = 2.1, H-5′), 8.22 (1H, s, H-4′).

8-Methyl-7-acetoxy-4-(7-acetoxy-2-oxochromen-3-yl)chromen-2-one (28). Yield 65%, empirical formula $C_{23}H_{16}O_8$, mp 228-230°C.

IR spectrum (KBr, cm^{-1}): 1766, 1748, 1728, 1604, 1372, 1194, 1146, 1124, 1084. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 215 (4.67), 291 (4.43), 321 (4.41), 336 (4.28).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.24 (3H, s, CH_3-8), 2.33 and 2.35 (6H, two s, OAc-7, OAc-7′), 6.55 (1H, s, H-3), 7.04 (1H, d, J = 8.7, H-6), 7.18 (1H, dd, J = 2.1, J = 8.7, H-6′), 7.33 (1H, d, J = 2.1, H-8′), 7.49 (1H, d, J = 8.7, H-5), 7.84 (1H, d, J = 8.7, H-5′), 8.27 (1H, s, H-4′).

2-(8-Methyl-7-acetoxy-2-oxochromen-4-yl)benzo[*f*]chromen-3-one (29). Yield 63%, empirical formula $C_{25}H_{16}O_6$, mp 283-286°C.

IR spectrum (KBr, cm^{-1}): 1766, 1728, 1604, 1586, 1572, 1210, 1084, 820. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 205 (4.77), 211 (4.78), 228 (4.78), 232 (4.79), 257 (4.31), 324 (4.24), 360 (4.24).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.24 (3H, s, CH_3-8′), 2.31 (3H, s, OAc-7′), 6.66 (1H, s, H-3), 7.05 (1H, d, J = 8.7, H-6v), 7.51 (1H, d, J = 8.7, H-5′), 7.65 (2H, m, H-5, H-8), 7.73 (1H, t, J = 8.1, H-9), 8.07 (1H, d, J = 7.8, H-6), 8.26 (1H, d, J = 9.0, H-7), 8.58 (1H, d, J = 9.0, H-10), 9.15 (1H, s, H-1).

7,8-Diacetoxy-4-(2-oxochromen-3-yl)chromen-2-one (30). Yield 56%, empirical formula $C_{22}H_{14}O_8$, mp 178-180°C.

IR spectrum (KBr, cm^{-1}): 1778, 1754, 1730, 1696, 1608, 1442, 1372, 1274, 1180, 1108, 1058. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 212 (4.61), 284 (4.33), 322 (4.19).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.33 and 2.43 (6H, two s, OAc-7, OAc-8), 6.60 (1H, s, H-3), 7.19 (1H, d, J = 8.7, H-6), 7.40 (1H, t, J = 7.5, H-7′), 7.45 (1H, d, J = 7.5, H-8′), 7.54 (1H, d, J = 8.7, H-5), 7.70 (1H, t, J = 7.5, H-6′), 7.78 (1H, d, J = 7.5, H-5′), 8.32 (1H, s, H-4′).

7,8-Diacetoxy-4-(8-methoxy-2-oxochromen-3-yl)chromen-2-one (31). Yield 61%, empirical formula $C_{23}H_{16}O_9$, mp 142-145°C.

IR spectrum (KBr, cm^{-1}): 1744, 1612, 1580, 1480, 1454, 1442, 1374, 1276, 1178, 1102, 1056, 880, 778. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 202 (4.82), 218 (4.53), 254 (4.15), 301 (4.38).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.33 and 2.43 (6H, two s, OAc-7, OAc-8), 3.97 (3H, s, OCH_3-8′), 6.62 (1H, s, H-3), 7.19 (1H, d, J = 8.7, H-6), 7.34 (3H, m, H-5′, H-6′, H-7′), 7.55 (1H, d, J = 8.7, H-5), 8.30 (1H, s, H-4′).

7,8-Diacetoxy-4-(6-bromo-2-oxochromen-3-yl)chromen-2-one (32). Yield 55%, empirical formula $C_{22}H_{13}BrO_8$, mp 194-196°C.

IR spectrum (KBr, cm^{-1}): 1784, 1772, 1724, 1612, 1572, 1368, 1202, 1176, 1060. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.82), 220 (4.62), 282 (4.42), 329 (4.18).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.33 and 2.43 (6H, two s, OAc-7, OAc-8), 6.62 (1H, s, H-3), 7.21 (1H, d, J = 8.7, H-6), 7.46 (1H, d, J = 9.0, H-8′), 7.60 (1H, d, J = 8.7, H-5), 7.83 (1H, dd, J = 2.4, J = 9.0, H-7′), 8.03 (1H, d, J = 2.4, H-5′), 8.27 (1H, s, H-4′).

7,8-Diacetoxy-4-(7-acetoxy-2-oxochromen-3-yl)chromen-2-one (33). Yield 48%, empirical formula $C_{24}H_{16}O_{10}$, mp 247-251°C.

IR spectrum (KBr, cm^{-1}): 1776, 1754, 1728, 1618, 1372, 1196, 1152, 1144, 1120, 1058. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 216 (4.63), 233 (4.17), 288 (4.42), 321 (4.41).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.33 and 2.42 (9H, two s, OAc-7, OAc-8, OAc-7′), 6.61 (1H, s, H-3), 7.18 (1H, dd, J = 2.1, J = 8.7, H-6′), 7.20 (1H, d, J = 8.7, H-6), 7.33 (1H, d, J = 2.1, H-8′), 7.60 (1H, d, J = 8.7, H-5), 7.83 (1H, d, J = 2.4, H-5′), 8.32 (1H, s, H-4′).

2-(7,8-Diacetoxy-2-oxochromen-4-yl)benzo[*f*]chromen-3-one (34). Yield 59%, empirical formula $C_{26}H_{16}O_8$, mp 252-254°C.

IR spectrum (KBr, cm^{-1}): 1780, 1754, 1728, 1612, 1572, 1440, 1370, 1274, 1208, 1060. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 211 (4.89), 228 (4.89), 258 (4.40), 324 (4.29), 362 (4.30).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.34 and 2.44 (6H, two s, OAc-7′, OAc-8′), 6.71 (1H, s, H-3), 7.18 (1H, d, J = 8.7, H-6′), 7.65 (2H, m, H-5, H-8, H-5′), 7.73 (1H, t, J = 8.1, H-9), 8.06 (1H, d, J = 7.8, H-6), 8.27 (1H, d, J = 9.0, H-7), 8.58 (1H, d, J = 9.0, H-10), 9.20 (1H, s, H-1).

Hydroxy[4,3′]dichromenyl-2,2′-diones (35-49). The appropriate acetyldicoumarin (**20-34**, 2 mmol) was dissolved in aqueous ammonia (25-30 mL, 25%) at room temperature with vigorous stirring (15-18 h). The mixture was cooled and acidified with H_2SO_4 solution (1 N) until the pH was 4. The resulting solid was filtered off and crystallized from aqueous propan-2-ol.

7-Hydroxy-4-(2-oxochromen-3-yl)chromen-2-one (35). Yield 82%, empirical formula $C_{18}H_{10}O_5$, mp 303-305°C (lit. 311°C [9]).

IR spectrum (KBr, cm^{-1}): 3356, 1710, 1700, 1692, 1610, 1572, 1394, 1324, 1268, 1132, 760. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 216 (4.60), 291 (4.40), 324 (4.39).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.27 (1H, s, H-3), 6.70 (1H, dd, J = 2.1, J = 8.7, H-6), 6.75 (1H, d, J = 2.1, H-8), 7.34 (1H, d, J = 8.7, H-5), 7.40 (1H, t, J = 7.5, H-7′), 7.46 (1H, d, J = 8.1, H-8′), 7.69 (1H, t, J = 7.5, H-6′), 7.78 (1H, d, J = 8.4, H-5′), 8.25 (1H, s, H-4′), 10.44 (1H, br.s, OH-7).

7-Hydroxy-4-(8-methoxy-2-oxochromen-3-yl)chromen-2-one (36). Yield 90%, empirical formula $C_{19}H_{12}O_6$, mp 315-317°C.

IR spectrum (KBr, cm^{-1}): 3304, 3064, 1722, 1700, 1690, 1684, 1680, 1606, 1558, 1480, 1326. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 201 (5.10), 220 (4.74), 253 (4.34), 305 (4.62).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.97 (3H, s, OCH_3-8′), 6.27 (1H, s, H-3), 6.70 (1H, dd, J = 2.1, J = 8.7, H-6), 6.74 (1H, d, J = 2.1, H-8), 7.34 (3H, m, H-5, H-5′, H-6′, H-7′), 8.21 (1H, s, H-4′), 10.51 (1H, br.s, OH-7).

7-Hydroxy-4-(6-bromo-2-oxochromen-3-yl)chromen-2-one (37). Yield 82%, empirical formula $C_{18}H_9BrO_5$, mp 319°C (lit. 308-310°C [9]).

IR spectrum (KBr, cm^{-1}): 3324, 1722, 1698, 1692, 1680, 1600, 1556, 1412, 1322. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 202 (5.02), 222 (4.80), 288 (4.55), 331 (4.49).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.26 (1H, s, H-3), 6.70 (1H, dd, J = 2.1, J = 8.7, H-6), 6.75 (1H, d, J = 2.1, H-8), 7.35 (1H, d, J = 8.7, H-5), 7.44 (1H, d, J = 9.0, H-8′), 7.80 (1H, dd, J = 2.4, J = 9.0, H-7′), 8.01 (1H, d, J = 2.4, H-5′), 8.20 (1H, s, H-4′), 10.13 (1H, br.s, OH-7).

7-Hydroxy-4-(7-hydroxy-2-oxochromen-3-yl)chromen-2-one (38). Yield 71%, empirical formula $C_{18}H_{10}O_6$, mp 300°C (dec.).

IR spectrum (KBr, cm^{-1}): 3248, 1718, 1622, 1586, 1572, 1506, 1392, 1324, 1276, 1220, 1152, 1130. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 201 (4.89), 218 (4.47), 333 (4.49).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.22 (1H, s, H-3), 6.70 (1H, dd, J = 2.1, J = 8.7, H-6), 6.73 (1H, d, J = 2.1, H-8), 6.77 (1H, d, J = 2.1, H-8′), 6.82 (1H, dd, J = 2.1, J = 8.7, H-6′), 7.30 (1H, d, J = 8.7, H-5), 7.58 (1H, d, J = 8.7, H-5′), 8.11 (1H, s, H-4′), 10.13 (2H, br.s, OH-7, OH-7′).

2-(7-Hydroxy-2-oxochromen-4-yl)benzo[*f*]chromen-3-one (39). Yield 88%, empirical formula $C_{22}H_{12}O_5$, mp > 350°C.

IR spectrum (KBr, cm^{-1}): 3268, 1724, 1688, 1620, 1572, 1512, 1400, 1344, 1322, 1220, 1132, 1074. UV spectrum (dioxane, λ_{max}, nm, log ε): 235 (4.67), 255 (4.18), 324 (4.25), 353 (4.21).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.36 (1H, s, H-3′), 6.71 (1H, dd, J = 2.1, J = 8.4, H-6′), 6.77 (1H, d, J = 2.1, H-8′), 7.36 (1H, d, J = 8.4, H-5′), 7.62 (2H, m, H-5, H-8), 7.72 (1H, t, J = 7.5, H-9), 8.05 (1H, d, J = 7.5, H-6), 8.24 (1H, d, J = 9.0, H-7), 8.57 (1H, d, J = 8.4, H-10), 9.08 (1H, s, H-1), 9.92 (1H, br.s, OH-7′).

8-Methyl-7-hydroxy-4-(2-oxochromen-3-yl)chromen-2-one (40). Yield 87%, empirical formula $C_{19}H_{12}O_5$, mp 286-289°C.

IR spectrum (KBr, cm^{-1}): 3104, 1726, 1684, 1678, 1608, 1576, 1566, 1556, 1298, 1096. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 225 (4.58), 294 (4.58), 324 (4.57).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.23 (3H, s, CH_3-8), 6.24 (1H, s, H-3), 6.78 (1H, d, J = 8.7, H-6), 7.14 (1H, d, J = 8.7, H-5), 7.39 (1H, t, J = 7.2, H-7′), 7.44 (1H, d, J = 8.1, H-8′), 7.68 (1H, t, J = 7.2, H-6′), 7.77 (1H, d, J = 8.1, H-5′), 8.20 (1H, s, H-4′), 10.27 (1H, br.s, OH-7).

8-Methyl-7-hydroxy-4-(8-methoxy-2-oxochromen-3-yl)chromen-2-one (41). Yield 85%, empirical formula $C_{20}H_{14}O_6$, mp 296-299°C.

IR spectrum (KBr, cm^{-1}): 3216, 1728, 1700, 1692, 1610, 1590, 1572, 1480, 1280, 1196, 1098. UV spectrum (EtOH, λ_{max}, nm, log ε): 203 (4.89), 220 (4.48), 253 (4.14), 310 (4.41).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.22 (3H, s, CH_3-8), 3.97 (3H, s, OCH_3-8′), 6.25 (1H, s, H-3), 6.77 (1H, d, J = 8.7, H-6), 7.15 (1H, d, J = 8.7, H-5), 7.32 (3H, m, H-5′, H-6′, H-7′), 8.19 (1H, s, H-4′), 9.71 (1H, br.s, OH-7).

8-Methyl-7-hydroxy-4-(6-bromo-2-oxochromen-3-yl)chromen-2-one (42). Yield 79%, empirical formula $C_{19}H_{11}BrO_5$, mp 339-340°C.

IR spectrum (KBr, cm^{-1}): 3412, 1712, 1610, 1574, 1478, 1388, 1310, 1252, 1196, 1090, 1068. UV spectrum (dioxane, λ_{max}, nm, log ε): 222 (4.61), 289 (4.34), 329 (4.27).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.21 (3H, s, CH_3-8), 6.25 (1H, s, H-3), 6.76 (1H, d, J = 8.7, H-6), 7.18 (1H, d, J = 8.7, H-5), 7.43 (1H, d, J = 9.0, H-8′), 7.80 (1H, dd, J = 2.1, J = 9.0, H-7′), 8.02 (1H, d, J = 2.1, H-5′), 8.17 (1H, s, H-4′), 10.25 (1H, br.s, OH-7).

7-Hydroxy-4-(7-hydroxy-2-oxochromen-3-yl)-8-methylchromen-2-one (43). Yield 67%, empirical formula $C_{19}H_{12}O_6$, mp >350°C.

IR spectrum (KBr, cm^{-1}): 3276, 1704, 1700, 1690, 1678, 1608, 1572, 1316, 1268, 1090. UV spectrum (dioxane, λ_{max}, nm, log ε): 212 (4.59), 224 (4.41), 336 (4.52).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.19 (3H, s, CH_3-8), 6.31 (1H, s, H-3), 6.79 (1H, d, J = 8.7, H-6), 6.81 (1H, d, J = 2.1, H-8′), 6.85 (1H, dd, J = 2.1, J = 8.7, H-6′), 7.23 (1H, d, J = 8.7, H-5), 7.62 (1H, d, J = 8.7, H-5′), 8.15 (1H, s, H-4′), 10.13 (1H, br.s, OH), 10.13 (1H, br.s, OH).

2-(8-Methyl-7-hydroxy-2-oxochromen-4-yl)benzo[*f*]chromen-3-one (44). Yield 88%, empirical formula $C_{23}H_{14}O_5$, mp >350°C.

IR spectrum (KBr, cm^{-1}): 3332, 1724, 1688, 1610, 1570, 1400, 1362, 1316, 1092. UV spectrum (dioxane, λ_{max}, nm, log ε): 235 (4.83), 253 (4.37), 324 (4.40), 353 (4.37).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.24 (3H, s, CH_3-8′), 6.34 (1H, d, H-3′), 6.78 (1H, d, J = 8.7, H-6′), 7.19 (1H, d, J = 8.7, H-5′), 7.63 (2H, m, H-5, H-8), 7.72 (1H, t, J = 7.8, H-9), 8.05 (1H, d, J = 7.8, H-6), 8.24 (1H, d, J = 9.0, H-7), 8.57 (1H, d, J = 8.4, H-10), 9.07 (1H, s, H-1), 10.04 (1H, s, OH-7′).

7,8-Dihydroxy-4-(2-oxochromen-3-yl)chromen-2-one (45). Yield 70%, empirical formula $C_{18}H_{10}O_6$, mp 302-303°C.

IR spectrum (KBr, cm^{-1}): 3296, 2924, 1704, 1692, 1608, 1580, 1458, 1288, 1162. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 201 (4.85), 294 (4.37), 324 (4.34).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.26 (1H, s, H-3), 6.72 (1H, d, J = 8.7, H-6), 8.81 (1H, d, J = 8.7, H-5), 7.39 (1H, t, J = 7.2, H-7′), 7.47 (1H, d, J = 8.1, H-8′), 7.68 (1H, t, J = 7.2, H-6′), 7.77 (1H, d, J = 8.1, H-5′), 8.22 (1H, s, H-4′), 9.35 (1H, s, OH-8), 10.00 (1H, s, OH-7).

7,8-Dihydroxy-4-(8-methoxy-2-oxochromen-3-yl)chromen-2-one (46). Yield 77%, empirical formula $C_{19}H_{12}O_7$, mp 349-350°C.

IR spectrum (KBr, cm^{-1}): 3408, 1704, 1610, 1570, 1480, 1452, 1384, 1348, 1280, 1232, 1106. UV spectrum (dioxane, λ_{max}, nm, log ε): 224 (4.49), 254 (4.22), 305 (4.39), 347 (4.06).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.96 (3H, s, OCH_3-8′), 6.25 (1H, s, H-3), 6.71 (1H, d, J = 8.7, H-6), 6.81 (1H, d, J = 8.7, H-5), 7.32 (3H, m, H-5′, H-6′, H-7′), 8.19 (1H, s, H-4′).

7,8-Dihydroxy-4-(6-bromo-2-oxochromen-3-yl)chromen-2-one (47). Yield 82%, empirical formula $C_{18}H_9BrO_6$, mp 301-302°C.

IR spectrum (KBr, cm^{-1}): 3180, 1704, 1650, 1602, 1540, 1408, 1268, 1100. UV spectrum (dioxane, λ_{max}, nm, log ε): 225 (4.18), 289 (3.90), 333 (3.86).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.25 (1H, s, H-3), 6.72 (1H, d, J = 8.7, H-6), 6.81 (1H, d, J = 8.7, H-5), 7.43 (1H, d, J = 8.4, H-8′), 7.79 (1H, dd, J = 2.1, J = 8.4, H-7′), 8.00 (1H, d, J = 2.1, H-5′), 8.16 (1H, s, H-4′).

7,8-Dihydroxy-4-(7-hydroxy-2-oxochromen-3-yl)chromen-2-one (48). Yield 74%, empirical formula $C_{18}H_{10}O_7$, mp 344-345°C.

IR spectrum (KBr, cm^{-1}): 3464, 1712, 1624, 1580, 1512, 1446, 1386, 1328, 1260, 1216, 1172. UV spectrum (dioxane, λ_{max}, nm, log ε): 221 (4.53), 250 (4.15), 336 (4.56).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.21 (1H, s, H-3), 6.77 (4H, m, H-5, H-6, H-6′, H-8′), 7.56 (1H, d, J = 8.4, H-5′), 8.08 (1H, s, H-4′).

2-(7,8-Dihydroxy-2-oxochromen-4-yl)benzo[*f*]chromen-3-one (49). Yield 84%, empirical formula $C_{22}H_{12}O_6$, mp >350°C.

IR spectrum (KBr, cm^{-1}): 3384, 1722, 1652, 1570, 1518, 1400, 1376, 1332, 1312, 1246, 1214, 1180, 1056. UV spectrum (dioxane, λ_{max}, nm, log ε): 230 (4.84), 256 (4.46), 324 (4.41), 355 (4.42).

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.35 (1H, s, H-3′), 6.72 (1H, d, J = 8.7, H-6′), 6.85 (1H, d, J = 8.7, H-5′), 7.63 (2H, m, H-5, H-8), 7.72 (1H, t, J = 6.9, H-9), 8.05 (1H, d, J = 7.8, H-6), 8.24 (1H, d, J = 8.7, H-7), 8.57 (1H, d, J = 7.8, H-10), 9.06 (1H, s, H-1), 9.95 (1H, s, OH-7′).

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