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SYNTHESIS OF 3′,4′-DIMETHOXYISOFLAVONE DERIVATIVES

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2-(Un)substituted-3′,4′-dimethoxy-7-hydroxyisoflavones were synthesized. Their derivatives substituted at the phenolic hydroxyl were prepared by alkylation and acylation. Aminomethyl derivatives were also prepared.

Key words: isoflavonoids, alkylation, acylation, aminomethylation.

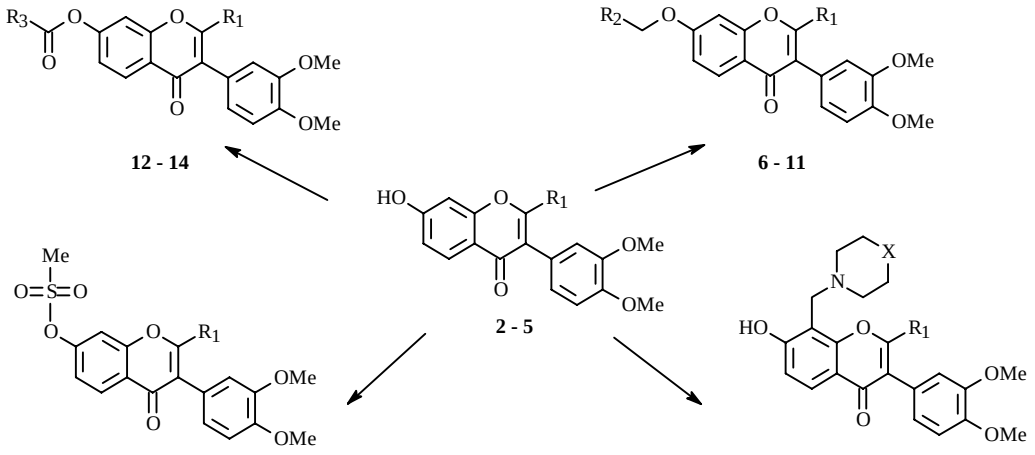
Isoflavonoids are a large and varied group of natural compounds with a wide spectrum of biological activity. Low toxicity in addition to selective pharmacologic activity enable them to be used for formulating new medicinal preparations.

Flavonoids occur in all plants, more often as hydroxylated, methoxylated, or glycosylated derivatives.

The isolation from seeds of *Calopogonium mucunoides* of 7-(3,3-dimethylallyloxy)-3′,4′-dimethoxyisoflavone [1] and the synthesis of its alkyl- and alkoxy-derivatives [2, 3], which exhibit high anti-inflammatory activity, have been previously reported.

It is known that 7-dimethylallyloxy- and 7-allyloxy-3′,4′-dimethoxyisoflavones are insecticides and are used as fish poisons [4].

Therefore, it seemed interesting to synthesize 2-(un)substituted-3′,4′-dimethoxy-7-hydroxyisoflavones (**2-5**) [4], study their reactivity, and prepare various derivatives.



2: R_1 = H; **3**: R_1 = Me;
4: R_1 = CF_3; **5**: R_1 = COOEt;
6: R_1 = Me, R_2 = CH_2CN;
7: R_1 = Me, R_2 = $CH_2C(=CH_2)CH_3$;
8: R_1 = Me, R_2 = CH_2COOPr-*i*;
9: R_1 = Me, R_2 = CH_2COOBu-*t*;
10: R_1 = COOEt, R_2 = CH(Ph)COOEt;
11: R_1 = Me, R_2 = CH(Ph)COOEt;
12: R_1 = Me, R_3 = Me;
13: R_1 = Me, R_3 = $(MeO)_2C_6H_3$;
14: R_1 = Me, R_3 = $(MeO)_3C_6H_2$;
15: R_1 = Me;
16: R_1 = COOEt;
17: R_1 = H, X = bond
18: R_1 = Me, X = bond
19: R_1 = H, X = CH_2;
20: R_1 = Me, X = CH_2;
21: R_1 = H, X = CH_2CH_2;
22: R_1 = Me, X = N-CH_3;
23: R_1 = COOEt, X = N-CH_3

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The starting compound for constructing the chromone was 1-(2,4-dihydroxyphenyl)-2-(3,4-dimethoxyphenyl)-ethanone (**1**). This was due to its availability and reactions ability to convert it preparatively into isoflavones.

2-Unsubstituted isoflavone **2** was synthesized by Vilsmeier formylation of 2-hydroxydeoxybenzoin and subsequent cyclization. 2-Substituted isoflavones were prepared using the Kostanetskii—Robinson reaction and acid anhydrides and chlorides as alkylating reagents.

We carried out reactions at the phenolic hydroxyl and electrophilic substitution reactions to synthesize new derivatives of 7-hydroxyisoflavones (**2-5**) and study their chemical properties.

Alkylation produced **6** and **7** and various ethers of 4-oxo-4*H*-chromenyl-7-hydroxyacetic and phenylacetic acids (**8-11**).

7-Hydroxyisoflavones are readily acylated at the phenolic hydroxyl. Reaction of the acid chlorides of veratric and 3,4,5-trimethoxybenzoic acids in pyridine at room temperature produced acyl derivatives (**12** and **13**). Use of methanesulfonylchloride as an acylating reagent produced the methanesulfonylisoflavones (**14** and **15**).

Considering the significant biological activity of N-substituted aminomethyl derivatives of isoflavones [5, 6], we synthesized this type of compounds based on 3′,4′-dimethoxyisoflavones. Use of various aminals led to the Mannich bases (**16**-**22**).

EXPERIMENTAL

The course of the reactions and the purity of the products were monitored by TLC on UV-254 Sorbfil (Russia) and Merck (Germany) plates. The eluent was $CHCl_3$:CH_3OH (95:5 and 9:1). PMR spectra were measured on VXR-300 and Mercury 400 instruments (Varian, 300 and 400 MHz, respectively) in DMSO-d_6 (Mannich bases in $CDCl_3$) relative to TMS (internal standard) on the δ scale. Elemental analyses corresponded to those calculated. Starting 2-hydroxydeoxybenzoin (**1**) and 7-hydroxyisoflavones (**2-3**) were prepared as before [4]: **1-(2,4-dihydroxyphenyl)-2-(3,4-dimethoxyphenyl)-ethanone (1)**, **3-(3,4-dimethoxyphenyl)-7-hydroxychromen-4-one (2)**, **3-(3,4-dimethoxyphenyl)-7-hydroxy-2-methylchromen-4-one (3)**.

Synthesis of 2-Trifluoromethyl- and 2-Ethoxycarbonylisoflavones (4, 5). A cooled (0°C) solution of **1** (2.72 g, 10 mmol) in absolute pyridine (10 mL) was treated dropwise with trifluoroacetic anhydride or ethoxycarbonylchloride (20 mmol), held for 1 d at room temperature, and poured into icewater (100 mL) containing HCl (1-3 mL, 1 N). The precipitate was filtered off and crystallized from the appropriate solvent.

3-(3,4-Dimethoxyphenyl)-7-hydroxy-2-trifluoromethylchromen-4-one (4), mp 232-233°C (methanol). PMR* (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.71 (3H, s, OMe-4′), 3.80 (3H, s, OMe-3′), 6.79 (1H, dd, ^3J = 8.4, ^4J = 2.0, H-6′), 6.88 (1H, d, ^4J = 2.0, H-2′), 7.01 (1H, d, ^3J = 8.4, H-5′), 7.02 (1H, dd, ^3J = 8.4, ^4J = 2.0, H-6), 6.94 (1H, d, ^4J = 2.0, H-8), 7.93 (1H, d, ^3J = 8.4, H-5), 11.13 (1H, s, 7-OH).

Ethyl 3-(3,4-dimethoxyphenyl)-7-hydroxy-4-oxo-4*H*-chromen-2-carboxylate (6), mp 212-213°C (ethanol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.97 (3H, t, ^3J = 6.8), 4.11 (2H, q, ^3J = 6.8, CH_3CH_2OOC-2), 3.72 (3H, s, OMe-4′), 3.78 (3H, s, OMe-3′), 6.75 (1H, dd, ^3J = 8.0, ^4J = 2.0, H-6′), 6.86 (1H, d, ^4J = 2.0, H-2′), 6.97 (1H, d, ^3J = 8.0, H-5′), 6.98 (1H, dd, ^3J = 8.8, ^4J = 2.0, H-6), 6.90 (1H, d, ^4J = 2.0, H-8), 7.93 (1H, d, ^3J = 8.8, H-5), 11.02 (1H, s, 7-OH).

General Method of Preparing 7-Alkyloxyisoflavones (6-11). A hot solution of the appropriate 7-hydroxyisoflavone (10 mmol) in absolute acetone (30 mL) was treated with freshly calcined potash (2.1 g, 15 mmol), stirred, boiled, and treated with the corresponding alkylhalide (12 mmol). The reaction mixture was stored for 1-4 h (completion of the reaction determined by TLC) and poured into acidified icewater (100 mL). The resulting precipitate was filtered off and crystallized from a suitable solvent.

[3-(3,4-Dimethoxyphenyl)-2-methyl-4-oxo-4*H*-chromen-7-yloxy]-acetonitrile (6), mp 177-178.5°C (ethanol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, Me-2), 3.75 (3H, s, OMe-4′), 3.81 (3H, s, OMe-3′), 5.37 (2H, s, CH_2O-7), 6.82 (1H, dd, ^3J = 8.4, ^4J = 2.0, H-6′), 6.88 (1H, d, ^4J = 2.0, H-2′), 7.01 (1H, d, ^3J = 8.4, H-5′), 7.17 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-6), 7.37 (1H, d, ^4J = 2.4, H-8), 8.02 (1H, d, ^3J = 8.4, H-5).

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*Primed chemical shifts refer to the 3-phenyl substituent.

3-(3,4-Dimethoxyphenyl)-2-methyl-7-(2-methylallyloxy)-4*H*-chromen-4-one (7), mp 118.5-119.5°C (methanol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.81 (3H, s, Me-2), 4.65 (2H, s, CH_2O-7), 5.02 (1H, s, CH_2), 5.11 (1H, s, CH_2) (2-methylallyl protons), 2.28 (3H, s, Me-2), 3.75 (3H, s, OMe-4′), 3.81 (3H, s, OMe-3′), 5.37 (2H, s, CH_2O-7), 6.80 (1H, dd, ^3J = 8.8, ^4J = 2.4, H-6′), 6.87 (1H, d, ^4J = 2.4, H-2′), 7.00 (1H, d, ^3J = 8.8, H-5′), 7.07 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-6), 7.13 (1H, d, ^4J = 2.4, H-8), 7.94 (1H, d, ^3J = 8.4, H-5).

Isopropyl [3-(3,4-dimethoxyphenyl)-2-methyl-4-oxo-4*H*-chromen-7-yloxy]acetate (8), mp 131-132°C (propan-2-ol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.29 (3H, s, Me-2), 1.24 (6H, d, J = 5.6, 2Me), 5.03 (1H, m, J = 6.4, CH), 4.96 (2H, s, CH_2) $CH_3CH(CH_3)OCOCH_2O$-7, 3.75 (3H, s, OMe-4′), 3.80 (3H, s, OMe-3′), 6.81 (1H, dd, ^3J = 8.4, ^4J = 2.0, H-6′), 6.87 (1H, d, ^4J = 2.0, H-2′), 7.01 (1H, d, ^3J = 8.4, H-5′), 7.08 (1H, dd, ^3J = 8.8, ^4J = 2.4, H-6), 7.14 (1H, d, ^4J = 2.4, H-8), 7.96 (1H, d, ^3J = 8.8, H-5).

***t*-Butyl [3-(3,4-dimethoxyphenyl)-2-methyl-4-oxo-4*H*-chromen-7-yloxy]acetate (9)**, mp 134-135°C (propan-2-ol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.29 (3H, s, Me-2), 1.45 (9H, s, 3Me), 4.88 (2H, s, CH_2) $(CH_3)_3COOCH_2O$-7, 3.75 (3H, s, OMe-4′), 3.80 (3H, s, Ome-3′), 6.81 (1H, dd, ^3J = 8.4, ^4J = 2.0, H-6′), 6.87 (1H, d, ^4J = 2.0, H-2′), 7.01 (1H, d, ^3J = 8.4, H-5′), 7.07 (1H, dd, ^3J = 8.8, ^4J = 2.4, H-6), 7.11 (1H, d, ^4J = 2.4, H-8), 7.95 (1H, d, ^3J = 8.8, H-5).

Ethyl 3-(3,4-dimethoxyphenyl)-7-(ethoxycarbonylphenylmethoxy)-4-oxo-4*H*-chromen-2-carboxylate (10), mp 126-127°C (ethanol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.98 (3H, t, ^3J = 6.8), 4.13 (2H, q, ^3J = 6.8, CH_3CH_2COO-2), 1.14 (3H, t, ^3J = 6.8), 4.18 (2H, q, ^3J = 6.8), 6.39 (1H, s), 7.41-7.60 (5H of phenyl) $CH_3CH_2OCOC(Ph)O$-7, 3.73 (3H, s, OMe-4′), 3.79 (3H, s, OMe-3′), 6.77 (1H, dd, ^3J = 8.0, ^4J = 2.0, H-6′), 6.87 (1H, d, ^4J = 2.0, H-2′), 6.99 (1H, d, ^3J = 8.0, H-5′), 7.24 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-6), 7.25 (1H, d, ^4J = 2.4, H-8), 8.02 (1H, d, ^3J = 8.4, H-5).

Ethyl [3-(3,4-dimethoxyphenyl)-2-methyl-4-oxo-4*H*-chromen-7-yloxy]phenylacetate (11), mp 127-128.5°C (propan-2-ol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.14 (3H, t, ^3J = 6.8), 4.17 (2H, m, ^3J = 6.8), 6.32 (1H, s), 7.40-7.60 (5H of phenyl) $CH_3CH_2OCOC(Ph)O$-7, 3.74 (3H, s, OMe-4′), 3.79 (3H, s, OMe-3′), 6.79 (1H, dd, ^3J = 8.4, ^4J = 2.0, H-6′), 6.86 (1H, d, ^4J = 2.0, H-2′), 7.01 (1H, d, ^3J = 8.4, H-5′), 7.16 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-6), 7.17 (1H, d, ^4J = 2.4, H-8), 7.97 (1H, d, ^3J = 8.4, H-5).

General Method for Preparing 7-Acyloxyisoflavones (12-15). A solution of the appropriate 7-hydroxyisoflavone (10 mmol) in the minimum amount of absolute pyridine was treated with acid chloride (12 mmol). The reaction mixture was stored for 1 d at room temperature and then poured into icewater. The resulting precipitate was filtered off and crystallized from a suitable solvent.

3-(3,4-Dimethoxyphenyl)-2-methyl-4-oxo-4*H*-chromen-7-yl 3,4-dimethoxybenzoate (12), mp 187-188.5°C (propan-2-ol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.32 (3H, s, Me-2), 3.75 (3H, s, OMe-4′), 3.80 (3H, s, OMe-3′), 3.87-3.89 (6H, 2s, OMe-3,4), 6.84 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-6′), 6.90 (1H, d, ^4J = 2.4, H-2′), 7.18 (1H, d, ^3J = 8.4, H-5′), 7.42 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-6), 7.68 (1H, d, ^4J = 2.4, H-8), 8.13 (1H, d, ^3J = 8.4, H-5), acyl protons: 7.04 (1H, d, ^3J = 8.4, H-5), 7.61 (1H, d, ^4J = 1.6, H-2), 7.83 (1H, dd, ^3J = 8.4, ^4J = 1.6, H-6).

3-(3,4-Dimethoxyphenyl)-2-methyl-4-oxo-4*H*-chromen-7-yl 3,4,5-trimethoxybenzoate (13), mp 178-179°C (propan-2-ol:DMF). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, Me-2), 3.74 (3H, s, OMe-4′), 3.80 (3H, s, OMe-3′), 3.79-3.88 (9H, 2s, OMe-3,4,5), 6.83 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-6′), 7.00 (1H, d, ^4J = 2.4, H-2′), 7.02 (1H, d, ^3J = 8.4, H-5′), 7.43 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-6), 7.68 (1H, d, ^4J = 2.4, H-8), 8.13 (1H, d, ^3J = 8.4, H-5), acyl protons: 7.44 (2H, s, H-2,6).

3-(3,4-Dimethoxyphenyl)-2-methyl-4-oxo-4*H*-chromen-7-yl methanesulfonate (14), mp 172-173°C (ethanol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.31 (3H, s, Me-2), 3.51 (3H, s, 7-CH_3SO_2O), 3.73 (3H, s, OMe-4′), 3.80 (3H, s, OMe-3′), 6.82 (1H, dd, ^3J = 8.4, ^4J = 2.0, H-6′), 6.87 (1H, d, ^4J = 2.0, H-2′), 7.01 (1H, d, ^3J = 8.4, H-5′), 7.45 (1H, dd, ^3J = 8.4, ^4J = 2.4, H-6), 7.72 (1H, d, ^4J = 2.4, H-8), 8.14 (1H, d, ^3J = 8.4, H-5).

Ethyl 3-(3,4-dimethoxyphenyl)-7-methanesulfonyloxy-4-oxo-4*H*-chromen-2-carboxylate (15), mp 126-127°C (propan-2-ol). PMR (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.99 (3H, t, ^3J = 7.2), 4.14 (2H, q, ^3J = 7.2), 2-CH_3CH_2COO, 3.53 (3H, s, 7-CH_3SO_2O), 3.72 (3H, s, OMe-4′), 3.79 (3H, s, OMe-3′), 6.79 (1H, dd, ^3J = 8.4, ^4J = 2.0, H-6′), 6.88 (1H, d, ^4J = 2.0, H-2′), 7.00 (1H, d, ^3J = 8.4, H-5′), 7.51 (1H, dd, ^3J = 8.0, ^4J = 2.4, H-6), 7.83 (1H, d, ^4J = 2.4, H-8), 8.19 (1H, d, ^3J = 8.0, H-5).

General Method for Preparing 8-Dialkylaminomethylisoflavones (16-22). A boiling solution of the appropriate isoflavone (10 mmol) in absolute dioxane (20 mL) was treated with the corresponding aminal (15 mmol). The reaction mixture was refluxed for 1 h (completion of the reaction monitored by TLC), cooled, and evaporated in vacuum. The solid was crystallized from a suitable solvent.

3-(3,4-Dimethoxyphenyl)-7-hydroxy-8-pyrrolidin-1-ylmethylchromen-4-one (16), mp 179-180°C (ethylacetate:hexane). PMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.84-2.00, 2.65-2.85 (4H, 2H, 2m, pyrrolidine protons), 3.90 (3H, s, OMe-4′), 3.92 (3H, s, OMe-3′), 4.15 (2H, s, CH_2-8), 6.91 (1H, dd, ^3J = 9.0, ^4J = 1.8, H-6′), 7.21 (1H, d, ^4J = 1.8, H-2′), 7.02 (1H, d, ^3J = 9.0, H-5′), 7.04 (1H, d, ^3J = 8.4, H-6), 8.11 (1H, d, ^3J = 8.4, H-5), 7.91 (1H, s, H-2).

3-(3,4-Dimethoxyphenyl)-7-hydroxy-2-methyl-8-pyrrolidin-1-ylmethylchromen-4-one (17), mp 164-165.5°C (ethylacetate:hexane). PMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.84-2.00, 2.65-2.85 (4H, 2H, 2m, pyrrolidine protons), 2.30 (3H, s, CH_3-2), 3.87 (3H, s, OMe-4′), 3.90 (3H, s, OMe-3′), 4.15 (2H, s, CH_2-8), 6.92 (1H, dd, ^3J = 8.1, ^4J = 1.8, H-6′), 6.82 (1H, d, ^4J = 1.8, H-2′), 6.85 (1H, d, ^3J = 8.1, H-5′), 6.81 (1H, d, ^3J = 8.6, H-6), 8.04 (1H, d, ^3J = 8.6, H-5).

3-(3,4-Dimethoxyphenyl)-7-hydroxy-8-piperidin-7-ylmethylchromen-4-one (18), mp 183-184°C (toluene:hexane). PMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.25-3.36 (10H, m, piperidine protons), 3.90 (3H, s, OMe-4′), 3.93 (3H, s, OMe-3′), 3.99 (2H, s, CH_2-8), 6.92 (1H, dd, ^3J = 9.0, ^4J = 2.0, H-6′), 7.22 (1H, d, ^4J = 2.0, H-2′), 6.98 (1H, d, ^3J = 9.0, H-5′), 7.04 (1H, d, ^3J = 8.4, H-6), 8.11 (1H, d, ^3J = 8.4, H-5), 7.90 (1H, s, H-2).

3-(3,4-Dimethoxyphenyl)-7-hydroxy-2-methyl-8-piperidin-1-ylmethylchromen-4-one (19), mp 200-201.5°C (toluene:hexane). PMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.27-3.32 (10H, m, piperidine protons), 2.30 (3H, s, CH_3-2), 3.87 (3H, s, OMe-4′), 3.91 (3H, s, OMe-3′), 3.99 (2H, s, CH_2-8), 6.80 (1H, dd, ^3J = 8.6, ^4J = 2.0, H-6′), 6.82 (1H, d, ^4J = 2.0, H-2′), 6.84 (1H, d, ^3J = 8.6, H-5′), 6.93 (1H, d, ^3J = 8.0, H-6), 8.03 (1H, d, ^3J = 8.0, H-5).

8-Azepan-1-ylmethyl-3-(3,4-dimethoxyphenyl)-7-hydroxychromen-4-one (20), mp 158-159°C (propan-2-ol). PMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.63-1.86, 2.74-2.92 (8H, 4H, 2m, azepane protons), 3.91 (3H, s, OMe-4′), 3.92 (3H, s, OMe-3′), 4.11 (2H, s, CH_2-8), 7.03 (1H, dd, ^3J = 8.4, ^4J = 1.8, H-6′), 7.21 (1H, d, ^4J = 1.80, H-2′), 7.04 (1H, d, ^3J = 8.4, H-5′), 6.91 (1H, d, ^3J = 9.0, H-6), 8.12 (1H, d, ^3J = 9.0, H-5), 7.90 (1H, s, H-2).

3-(3,4-Dimethoxyphenyl)-7-hydroxy-2-methyl-8-(4-methylpiperazin-1-ylmethyl)chromen-4-one (21), mp 203-204.5°C (propan-2-ol). PMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.93-3.25 (8H, m, piperazine protons), 2.34 (3H, s, NCH_3), 2.31 (3H, s, CH_3-2), 3.87 (3H, s, OMe-4′), 3.91 (3H, s, OMe-3′), 4.03 (2H, s, CH_2-8), 6.80 (1H, dd, ^3J = 8.0, ^4J = 2.0, H-6′), 6.81 (1H, d, ^4J = 2.0, H-2′), 6.92 (1H, d, ^3J = 8.0, H-5′), 6.85 (1H, d, ^3J = 8.8, H-6), 8.05 (1H, d, ^3J = 8.8, H-5).

Ethyl 3-(3,4-dimethoxyphenyl)-7-hydroxy-8-(4-methylpiperazin-1-ylmethyl)-4-oxo-4*H*-chromen-2-carboxylate (22), mp 159-160°C (propan-2-ol). PMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.04 (3H, t, ^3J = 8.0), 4.16 (2H, q, ^3J = 8.0) CH_3CH_2COO-2, 1.80-3.28 (8H, m, piperazine protons), 2.34 (3H, s, NCH_3), 3.87 (3H, s, OMe-4′), 3.91 (3H, s, OMe-3′), 4.08 (2H, s, CH_2-8), 6.82 (1H, dd, ^3J = 8.4, ^4J = 2.0, H-6′), 6.86 (1H, d, ^4J = 2.0, H-2′), 6.90 (1H, d, ^3J = 8.4, H-5′), 6.90 (1H, d, ^3J = 8.8, H-6), 8.07 (1H, d, ^3J = 8.8, H-5).

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