Experimental part

1. General experimental procedure part

1.1. Chemicals

General chemicals were purchased from Merck or Aldrich, Fluka, Lancaster, Across, Riedel, Indofine, and were used without further purification. All solvents (Merck) were used without further purification. THF was freshly distilled under argon from sodium and benzophenone-ketyl as indicator. All nonaqueous reactions were performed in dry glassware and under argon atmosphere.

Preparative thin layer chromatography (TLC) was performed on precoated plates (5 x 10 cm), silica gel 60-F_{254} (Merck 1.16834, layer thickness 0.25 mm) using dichloromethane / methanol mixtures (9:1 or gradient) as developing system. The detection of the products on TLC was carried out with a UV-vis light at 254 nm and 365 nm. Column chromatography (CC) was also performed as flash chromatography (Merck, silica gel 60 1.09385, 70-230 mesh).

1.2. Melting point

Melting points are uncorrected and were determined on a Büchi 545 (Büchi Laboratoriums-Technik AG, Flavill Switzerland) instrument fitted with a microscope.

1.3. Nuclear Magnetic Resonance spectroscopy

^{1}H-NMR, ^{13}C-NMR and COSY spectra were recorded with a Fourier transform instrument at 250 MHz (Bruker AVANCE 250), at 300 MHz (BRUKER AC-300) or 500 MHz (Bruker AVANCE 500) for the ^{1}H-NMR and at 62.90 MHz (Bruker AVANCE 250) and 75.47 MHz (Bruker AC-300) for the ^{13}C-NMR. The chemical shifts are expressed in ppm values relative to tetramethylsilane (TMS, 0 ppm) or to dimethylsulfoxid (DMSO, 2.62 and 39.50 ppm, ^{1}H and ^{13}C respectively) as internal reference; the coupling constants (*J*) are expressed in Hertz (Hz). All deuteried solvents used for the preparation of the samples were chloroform ($CDCl_3$) and dimethylsulfoxid (CD_3SOCD_3, or DMSO-d^6). The data have been worked out on Spectra-Software (CLC InSpector 1.0, Creon Lab Control AG, Germany).

1.4. Mass spectroscopy

Samples were dissolved in acetonitrile / dichloromethane (85:15). Mass spectra were obtained at 70 eV, by electron impact ionisation (EI) using a VG Autospec spectrometer (Micromass, Manchester UK). The data have been worked out on Spectra-Software (CLC InSpector 1.0, Creon Lab Control AG, Germany).

1.5. UV-vis spectroscopy

UV-vis spectra were recorded on a Varian Cary 100 Bio spectrophotometer equipped with a thermostatted cuvette holder. The samples were dissolved in 2-propanol (1 mg / 100 mL). Data were worked out on a graphics Software (Origin 6.1, OriginLab corporation, Northampton USA).

1.6. Elementary analyses

Elementary analyses were performed by the elementary analyses department of Merck ZDA.

1.7. HPLC chromatography

The in process control and the purity determination of the synthesized products were carried out on a DAD-HPLC.

Apparatus:	Interface D7000 (LaChrom)
	UV-Detector L-7400 (LaChrom)
	Autosample L-7200 (LaChrom)
	Pump L-7100 (LaChrom)
	Column oven L-7350 (LaChrom)
Conditions:	
Column:	Chromolit RP-18e 100-4.6 (UM0015/043)
Flux:	0,5 mL/min
Column Temperature:	30°C
Wavelength:	260 nm

Eluent:

Eluent A: acetonitrile +2% distilled water (LiChrosolv)

Eluent B: 200 mL acetonitrile and 800 mL distilled water (LiChrosolv) were mixed with 12,7 g sodium dihydrogenphosphate monohydrate and brought with ortho-phosphorus acid to pH 2,6.

Time (min)	Eluent A (%)	Eluent B (%)
0	20	80
40	80	20
47	20	80
55	20	80

Table 16: Gradient program for Flavones determination

Samples preparation:

10 mg of the sample were dissolved in 2 mL ethanol and 10 µL of this solution were injected automatically with a syringe in the column.

Time of retention of the reactants

2-Hydroxyacetophenone R_f = 7.19 min

2,4-Dihydroxyacetophenone R_f = 8.19 min

2,5-Dihydroxyacetophenone R_f = 7.19 min

2,6-Dihydroxyacetophenone R_f = 10.52 min

2,3,4-Trihydroxyacetophenone R_f = 4.85 min

2,4,6-Trihydroxyacetophenone R_f = 6.92 min

The work up of the results is the quantification of the signal area (Area %).

1.8. Antioxidant activity (radical scavenger potential)

1.8.1. TEAC (Trolox Equivalent Antioxidant Activity)

Reagents:

2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS); Fluka Chemie Art.: 11557

Potassium peroxodisulfate, Merck Art.: 1.05092

6-Hydroxy-2,5,7,8-tetrametyl-chroman-2-carboxylic acid (Trolox); Fluka Chemie Art.: 56510

Principle:

ABTS decolourisation assay: the assay was carried out interacting the antioxidants with ABTS radical cation as described by Re et al[170]. A stock solution of 3.5 mM ABTS (96 mg)

was prepared in water (100 mL). To this solution potassium peroxodisulfate (4.3 mM, 116 mg for 100 mL - 2.45 mM final concentration) was added and the solutions allowed to react for a duration of 12-16 hours at room temperature in the dark. ABTS and potassium persulfate react stoichiometrically at 1:0.5 leading to an incomplete oxidation to generate $ABTS^{*+}$. The radical thus generated is stable in the dark at room temperature for two days. The ABTS radical cation solution was diluted in water or ethanol to obtain an absorbance of 0.70 ± 0.02 at 734 nm. The final concentration of the radical cation was calculated to be 80 µM (ε= 16000 $M^{-1} . cm^{-1}$, at λ_{734}).

The interaction between antioxidants and $ABTS^{*+}$ was carried out at 25°C, by measuring the absorbance of each antioxidant in comparison with the $ABTS^{*+}$ solution, in a spectrophotometer (Hewlett Packard 8453). One cuvette is filled with the antioxidant/ethanol solution (100µL Trolox or one of the antioxidant) and the other cuvette is filled with $ABTS^{*+}$ solution (2 mL). Measurement of the absorbance change is triggered as soon as the cuvette is filled which triggers a signal to the spectrophotometer. Absorbance changes are monitored every 0.1 s for a duration of 3 s at 734 nm and are recorded at 1, 4 and 6 minutes. Each measure is done 3 times.

Prior to the testing with the antioxidant, a baseline is obtained by monitoring the change of absorbance between $ABTS^{*+}$ and ethanol. The reading is used as the basal value for calculating the antioxidant activity of the compounds. Subsequently five concentrations of the antioxidants (0 to 12 µM, final concentration) are tested for their antioxidant activity. Stock solutions of the antioxidants (1 mM) are prepared in Ethanol and diluted subsequently with ethanol to give an initial concentration of 0 to 24 µM. As the antioxidants are mixed in the cuvette with $ABTS^{*+}$ solution, the final concentration are half the initial concentrations.

Results:

Results are expressed in terms of stoichiometric factor and Trolox equivalent antioxidant capacity (TEAC). Stoichiometric factor is calculated on the basis of extent of $ABTS^{*+}$ scavenged by the antioxidant. Results are calculated at 6 minutes. The extent of radical cation present at 6 minutes is calculated from the absorbance recorded and the extinction coefficient the concentration of the $ABTS^{*+}$ reacted is then plotted against the concentration of the antioxidant applied. The ratio of the concentration of the antioxidant to the concentration of the $ABTS^{*+}$ is expressed as the stoichiometric factor.

TEAC is calculated based on the percentage of the radical cation by the flavonoid relative to that by Trolox. Percentage scavenging of $ABTS^{*+}$ is calculated from the absorbance values at 6 minutes compared to the base value at 0 s. To calculated TEAC value, percentage

scavenging of the radical cation is plotted against the concentration of the flavonoid, which exhibits a linear relationship. A similar plot is also obtained with Trolox. The ratio of the slope obtained from the flavonoid percentage inhibition graph with the slope obtained from Trolox is the antioxidant activity expressed as TEAC.

1.8.2. DPPH – Assay: The free radical scavenging method

Reagents:

2,2 Diphenyl-1-picrylhydrazyl Hydrat (DPPH); Aldrich Art.: D21,140-0

Ethanol absolute for analysis; Merck Art.: 1.00983

Principle:

Determination of the antioxidant activity with the DPPH radical scavenging method was measured in terms of hydrogen donating or radical scavenging ability, using the stable radical DPPH (Brand et al).[171] An aliquot of ethanol (0.5 mL), solution containing different standard concentrations (1-400 µM) was added to 2.5 mL of $DPPH^*$ in ethanol (70µM) was prepared daily. Absorbances at 515 nm were measured at different time intervals (1 s, 2 min, 10 min and every 10 min) on a Varian Cary 50 UV-vis spectrophotometer with temperatable 18 - fold cell changer, until the reaction reached a plateau. The $DPPH^*$ concentration in the reaction medium was calculated from the following calibration curve, determination by linear regression:

$$A_{515\ nm} = 2935.68\ [DPPH^*]_T - 2.18 \times 10^{-3}$$

where $[DPPH^*]_T$ was expressed as g L^{-1} $r^2 \geq 0.96$.The percentage of remaining $DDPH^*$ (% $DPPH^*_{REM}$) was calculated as follows:

$$\%\ DPPH^*_{REM} = \frac{[DPPH^*]_T}{[DPPH^*]_{T=0}}$$

The percentage of remaining $DPPH^*$ against the standard concentration was then plotted to obtain the amount of antioxidant necessary to decrease the initial $DPPH^*$ concentration by 50%. The time needed to reach the steady state to EC_{50} concentration (T_{EC50}) was calculated graphically. Taking in account that both EC_{50} and T_{EC50}, affect the antiradical capacity, a new parameter: antiradical efficiency (AE), which combines these two factors, was defined:

$$AE = \frac{1}{EC_{50}\ T_{EC50}}$$

2. General procedures for the syntheses

2.1. General procedures for the syntheses of acetophenones

2.1.1. BF_3-Friedel-Crafts procedure

To a solution of the corresponding phenol (1 eq) in acetic acid anhydride (1 mL/mmol) was added under argon a solution of the complex boron trifluoride-etherate (1 eq) at 0°C. Then the cooling bath was removed and the resulting solution was heated at 80-90°C for one hour, cooled and the precipitated crystals were filtered. The mother liquor was poured into a saturated sodium acetate solution (1 mL/mmol). After extracting with diethyl ether, the ethereal solution was washed with 10% aqueous sodium hydrogen carbonate solution and water, and concentrated under reduced pressure. The residue was recrystallized from methanol affording the corresponding acetophenone.

2.1.2. Methyllithium procedure (Alkyl-de-oxido-substitution)

A stirred solution of the corresponding aroyl acid derivative (1 eq) in dry THF was cooled at 0°C and treated rapidly with methyl lithium (5% in Diethyl ether, 2.5 mL, 2.5 eq). After 2 hours at 0°C, the ice bath was removed and the reaction mixture was allowed to warm up at room temperature at which point HCl 1N was added. The resulting two-phase system was stirred at room temperature for 30 minutes. The mixture was extracted with diethyl ether and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and dried with Na_2SO_4. Filtration and removal of the solvent afforded the corresponding acetophenone.

2.1.3. Grignard procedure

The benzonitrile derivative (1 eq) dissolved in anhydrous ether was rapidly added to a solution of methyl magnesium iodide in diethyl ether (3.0 M, 1.5 eq) under argon atmosphere. No refluxing was observed and no precipitate formed for about one hour. The solution was therefore refluxed and stirred during 8 hours. The reaction was quenched with dilute HCl and extracted with diethyl ether. The combined organic phases were washed with water and dried

with Na_2SO_4 and the solvent was removed on a water bath to afford the corresponding acetophenone.

2.1.4. $AlCl_3$-Friedel-Crafts procedure

The Aluminium chloride (4 eq) was cooled at 0°C and ether was added to afford a light coloured solution. The stirring was continued for 30 minutes and the reaction mixture was allowed to warm up at room temperature. The corresponding phenol (1 eq) was dissolved in ether and added drop wise to the solution that became light white. The stirring was continued one hour and the methoxyacetyl chloride (1 eq) was dissolved in ether and added drop wise to the reaction mixture. The yellow reaction was stirred during one hour and was poured onto ice water. The product was extracted with ether and the combined extracts were washed with water and brine, dried with Na_2SO_4 and the solvent was evaporated. The crude product was recrystallized from methanol to afford the corresponding acetophenone.

2.1.5. Houben-Hoesch procedure

The corresponding phenol (1 eq) was dissolved in dry diethyl ether under argon. The methoxyacetonitrile (1 eq) was added and the reaction mixture was stirred for 10 minutes and HCl gas was bubbled through the solution. The reaction was slightly exothermic but did not need an ice bath. The bubbling was carried out 30 minutes and the precipitate was filtered off and washed with diethyl ether to afford the benzoimine hydrochloride intermediate. The benzoimine intermediate was dissolved in water and the reaction mixture was heated under reflux for one hour. The solution was cooled at room temperature and the precipitate filtered to afford the corresponding acetophenone derivative.

2.2. General procedures of deprotection

2.2.1. $AlCl_3$-deprotection procedure

The corresponding methylendioxy-derivative (1 eq) was dissolved into dichloromethane or tetrachloromethane and mixed with aluminium chloride (4 eq). The reaction mixture was heated for one hour under reflux. The reaction mixture was poured onto ice and acidified with concentrated acid chloride. The solvent was then removed and the hot solution was filtered

and cooled. The product was extracted with diethyl ether and the combined organic extracts were dried with Na_2SO_4 and the solvent was evaporated. The crude material was recrystallized from water to afford the corresponding hydroxy-derivative.

2.2.2. BBr_3-demethylation procedure (for acetophenone)

A solution of boron tribromide (1M in dichloromethane, 2.5 eq or 2.5 mL for each methoxy group) was slowly added to a cooled (-78°C) solution of methoxy-derivative (1 eq) in dichloromethane under argon. The cooling bath was removed and the resulting dark coloured solution was slowly warmed up to room temperature and stirred for 1.5 h. The dark coloured suspension was then poured into icy water and filtered to remove the dark coloured solid. The aqueous layer was separated out and extracted with chloroform twice. Then the combined organic extracts were washed with water and then saturated brine solution and dried (Na_2SO_4), thus giving the corresponding hydroxy-derivative.

2.2.3. BBr_3-demethylation procedure (for flavonoids)

A solution of boron tribromide (1M in dichloromethane, 2.5 eq or 2.5 mL for each methoxy group) was slowly added with a syringe to a stirred solution of methoxyflavone (1 eq) in dichloromethane under argon. After complete addition, the mixture was stirred for 24 hours at room temperature, and then poured into icy water. Filtration of the crude product gave a coloured residue, which was recrystallized from ethanol water (1:1) to afford the corresponding hydroxyflavone.

2.3. General procedures for the synthesis of flavonoids

2.3.1. Procedure A

A solution of LiHMDS in THF (Fluka or Lancaster, 1M, 1x(n+1) eq, n is the number of OH-substitutions on the acetophenone) was added to a well-stirred solution of the corresponding hydroxyacetophenone (1 eq) in THF under argon atmosphere at -78°C in 15 min. The reaction mixture was stirred at -78°C for 1 h and at -10°C for 2 h. It was cooled again at -78°C and a solution of the corresponding aroyl chloride (1.1 eq) in THF was added in 10 min. Stirring was continued for 30 min at -78°C and at room temperature for 4 h and the

reaction mixture was poured into a mixture of ice water and HCl. It was extracted with dichloromethane or chloroform and the combined extracts were dried (Na_2SO_4). Solvents were evaporated and the residue was mixed with glacial acetic acid and H_2SO_4 (0.5 %v) and heated at 95-100°C for 1 h. About 75% of the solvent was removed at reduced pressure and the residue was poured into water. The product was filtered, washed with water and dried overnight to afford the corresponding flavone.

2.3.2. Procedure B

Fine powdered anhydrous lithium hydroxide (1x(n+1) eq, n is the number of OH-substitutions on the acetophenone) was added in one portion to a well-stirred solution of the corresponding hydroxyacetophenone (1 eq) in THF under argon atmosphere at -78°C in 15 min. The reaction mixture was stirred at -78°C for 1 h and at -10°C for 2 h. It was cooled again at –78°C and a solution of the corresponding aroyl chloride (1.1 eq) in THF was added in 10 min. Stirring was continued for 30 min at -78°C and at room temperature for 4 h and the reaction mixture was poured into a mixture of ice water and HCl. It was extracted with dichloromethane or chloroform and the combined extracts were dried (Na_2SO_4). Solvents were evaporated and the residue was mixed with glacial acetic acid and H_2SO_4 (0.5 %v) and heated at 95-100°C for 1 h. About 75% of the solvent was removed at reduced pressure and the residue was poured into water. The product was filtered, washed with water and dried overnight to afford the corresponding flavone.

2.3.3. Procedure C

To a well-stirred solution of the corresponding hydroxyacetophenone (1 eq) in THF fine powdered lithium hydroxide (1x n eq, n is the number of OH-substitution on the acetophenone) was added under argon atmosphere at room temperature and the stirring was continued for 30 min, and a solution of the corresponding aroyl chloride (1.1 n eq) in THF was added and the stirring was continued at room temperature for 1 h 30. A second portion of Lithium hydroxide (5 eq) was added and the reaction mixture was refluxed under argon atmosphere for 5 h. The reaction mixture was poured into a mixture of ice water and HCl. It was filtered, when the product precipitated, or extracted with dichloromethane or chloroform and the combined extracts were dried (Na_2SO_4). Solvents were evaporated and the residue was mixed with glacial acetic acid and H_2SO_4 (0.5 %v) and heated at 95-100°C for 1 h. About

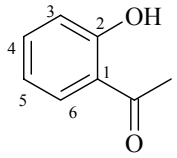
75% of the solvent was removed at reduced pressure and the residue was poured into water (500 mL). The product was filtered, washed with water and dried overnight to afford the corresponding flavone.

3. Compounds

3.1. Precursors of flavonoids (Chapter 2)

3.1.1. Precursors of flavones

3.1.1.1. 1-(2-Hydroxyphenyl)-ethanone (12a)



According to BF_3-Friedel-Crafts procedure, the phenol (**55a**) (2 g, 21.251 mmol) was mixed with boron trifluoride (2.7 mL, 21.25 mmol) and glacial acetic acid (7 mL) to afford the 2-hydroxyacetophenone (**12a**) as colourless oil (2.66 g, Yield 92%). B.p.: 34-37°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.04 (s, 1H, exchanges with D_2O, OH on C-2), 7.88 (dd, 1H, $^3J_{6,5}$ = 8.82, $^4J_{6,4}$ = 2.21, H-6), 7.54 (td, 1H, $^3J_{4,3}$ = $^3J_{4,5}$ = 8.33, $^4J_{4,6}$ = 2.21, H-4), 6.97 (d, 1H, $^3J_{3,4}$ = 8.82, H-3), 6.96 (td, 1H, $^3J_{5,6}$ = $^3J_{5,4}$ = 8.33, $^4J_{5,3}$ = 2.21, H-5), 2.64 (s, 3H, $COCH_3$).

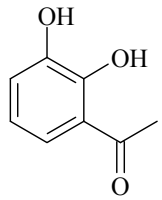
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 204.49 (CO), 160.91 (C-2), 136.14 (C-4), 131.28 (C-6), 119.40 (C-1), 119.00 (C-5), 117.50 (C-3), 27.23 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 136.0524 (70) $[C_8H_8O_2]^{+\cdot}$, 121 (100) $[C_7H_5O]^+$, 107 (1) $[C_7H_7O]^+$, 94 (4) $[C_6H_6O]^{+\cdot}$, 93 (25) $[C_6H_5O]^+$, 92 (2) $[C_6H_4O]^{+\cdot}$, 77 (3) $[C_6H_5]^+$, 68 (1) $[C_4H_4O]^{+\cdot}$, 66 (3) $[C_5H_6]^{+\cdot}$, 65 (24) $[C_5H_5]^+$, 53 (4) $[C_3HO]^+$, 52 (1) $[C_4H_4]^{+\cdot}$, 51 (4) $[C_4H_3]^+$, 43 (12) $[C_2H_3O]^+$, 41 (52) $[C_3H_5]^+$, 40 (28) $[C_3H_4]^{+\cdot}$, 39 (22) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm.

Anal. Calcd for $C_8H_8O_2$: C, 70.57%; H, 5.92%; O, 23.50%. Found: C, 70.5%; H, 5.9%; O, 24.4%.

3.1.1.2. 1-(2,3-Dihydroxyphenyl)-ethanone (12b)



According to the BBr_3-demethylation procedure, the solution of boron tribromide (1M in dichloromethane, 7 mL, 7 mmol) was added to 2,3-dimethoxyacetophenone (**59a**) (500 mg, 2.775 mmol) in dichloromethane (10 mL) to afford the 2,3-dihydroxyacetophenone (**12b**) as light brown crystals (273 mg, Yield 65%).

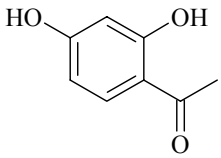
^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.07 (s, 1H, exchanges with D_2O, OH on C-2), 9.43 (br s, 1H, exchanges with D_2O, OH on C-3), 7.35 (dd, 1H, $^3J_{4,5}$ = 9.26, $^4J_{4,6}$ = 1.32, H-4), 7.07 (d, 1H, $^3J_{6,5}$ = 9.26, $^4J_{6,4}$ = 1.32, H-6), 6.79 (t, 1H, $^3J_{5,4}$ = $^3J_{5,6}$ = 9.26, H-5), 2.64 (s, 3H, CH_3).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 205.21 (CO), 152.60 (C-2), 146.01 (C-3), 121.16 (C-6), 121.12 (C-5) 120.18 (C-1), 118.52 (C-4), 54.78 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 152.0473 (75) $[C_8H_8O_3]^{+\cdot}$, 137 (100) $[C_7H_5O_3]^+$, 134 (10) $[C_8H_6O_2]^{+\cdot}$, 110 (2) $[C_6H_6O_2]^{+\cdot}$, 109 (8) $[C_6H_5O_2]^+$, 107 (4) $[C_6H_3O_2]^+$, 105 (2) $[C_7H_6O]^+$, 91 (1) $[C_6H_3O]^+$, 81 (18) $[C_5H_5O]^+$, 80 (1) $[C_5H_4O]^{+\cdot}$, 79 (3) $[C_5H_3O]^+$, 78 (4) $[C_6H_6]^{+\cdot}$, 77 (6) $[C_6H_5]^+$, 69 (1) $[C_4H_5O]^+$, 63 (6) $[C_5H_3]^+$, 62 (2) $[C_5H_2]^{+\cdot}$, 55 (6) $[C_4H_7]^+$, 53 (11) $[C_4H_5]^+$, 52 (8) $[C_4H_4]^{+\cdot}$, 51 (10) $[C_4H_3]^+$, 50 (2) $[C_4H_2]^{+\cdot}$, 43 (23) $[C_2H_3O]^+$, 41 (1) $[C_3H_5]^+$, 39 (7) $[C_3H_3]^+$.

Anal. Calcd for $C_8H_8O_3$: C, 63.15%; H, 5.30%; O, 31.55%. Found: C, 63.0%; H, 5.4%; O, 30.9%.

3.1.1.3. 1-(2,4-Dihydroxyphenyl)-ethanone (12c)



According to the BF_3-Friedel-Crafts procedure, the resorcinol (**55b**) (2 g, 18.16 mmol) was mixed with boron trifluoride (2.3 mL, 18.16 mmol) and glacial acetic acid (6 mL) to afford the 2,4-dihydroxyacetophenone (**12c**) as orange crystals (2.23 g, Yield 91%). M.p.: 140-143°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.60 (s, 1H, exchanges with D_2O, OH on C-2), 10.59 (s, 1H, exchanges with D_2O, OH on C-4), 7.76 (d, 1H, $^3J_{6,5}$ = 8.82, H-6), 6.38 (dd, 1H, $^3J_{5,6}$ = 8.82, $^4J_{5,3}$ = 2.21, H-5), 6.15 (d, 1H, $^4J_{3,5}$ = 2.21, H-3), 2.5 (s, 3H, CH_3).

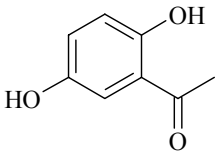
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 202.56 (CO), 164.83 (C-4), 164.17 (C-2), 133.61 (C-6), 112.84 (C-1), 108.06 (C-5), 102.26 (C-3), 26.26 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 152.0473 (65) $[C_8H_8O_3]^{+\cdot}$, 137 (100) $[C_7H_5O_3]^+$, 123 (3) $[C_7H_7O_2]^+$, 109 (5) $[C_6H_5O_2]^+$, 108 (5) $[C_6H_4O_2]^{+\cdot}$, 105 (2) $[C_7H_5O]^+$, 95 (2) $[C_6H_7O]^+$, 81 (28) $[C_5H_5O]^+$, 80 (3) $[C_5H_4O]^{+\cdot}$, 79 (3) $[C_5H_3O]^+$, 78 (1) $[C_6H_6]^{+\cdot}$, 77 (4) $[C_6H_5]^+$, 69 (24) $[C_5H_9]^+$, 68 (2) $[C_5H_8]^{+\cdot}$, 67 (2) $[C_5H_7]^+$, 65 (2) $[C_5H_5]^+$, 63 (8) $[C_5H_3]^+$, 62 (7) $[C_5H_2]^{+\cdot}$, 55 (10) $[C_4H_7]^+$, 53 (26) $[C_4H_5]^+$, 52 (10) $[C_4H_4]^{+\cdot}$, 51 (17) $[C_4H_3]^+$, 50 (6) $[C_4H_2]^{+\cdot}$, 43 (42) $[C_2H_3O]^+$, 41 (6) $[C_3H_5]^+$, 39 (19) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 277 (10442), 314.5 (5691).

Anal. Calcd for $C_8H_8O_3$: C, 63.15%; H, 5.30%; O, 31.55%. Found: C, 63.0%; H, 5.3%; O, 32.1%.

3.1.1.4. 1-(2,5-Dihydroxyphenyl)-ethanone (12d)



According to the BF_3-Friedel-Crafts procedure, the hydroquinone (55c) (2 g, 18.16 mmol) was mixed with boronn trifluoride (2.3 mL, 18.16 mmol) in glacial acetic acid (6 mL) to afford the 2,5-dihydroxyacetophenone (**12d**) as yellow needles (2.13 g, Yield 87%). M.p.: 200-203°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 11.30 (very br s, 1H, exchanges with D_2O, OH on C-2), 9.21 (br s, 1H, exchanges with D_2O, OH on C-4), 7.17 (d, 1H, $^4J_{6,4}$ = 2.21, H-6), 7.00 (dd, 1H, $^3J_{4,3}$ = 8.82, $^4J_{4,6}$ = 2.21, H-4), 6.99 (d, 1H, $^3J_{3,4}$ = 8.81, H-3), 2.58 (s, 3H, CH_3).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 204.00 (CO), 153.74 (C-5), 149.30 (C-2), 124.40 (C-4), 120.12 (C-1), 118.20 (C-3), 115.35 (C-6), 27.35 (CH_3).

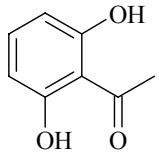
EI-MS *m/z* (% relative abundance) composition: 152.0473 (81) $[C_8H_8O_3]^{+\cdot}$, 137 (100) $[C_7H_5O_3]^+$, 123 (1) $[C_7H_7O_2]^+$, 110 (4) $[C_6H_6O_2]^{+\cdot}$, 109 (18) $[C_6H_5O_2]^+$, 105 (2) $[C_7H_5O]^+$, 95 (1) $[C_6H_7O]^+$, 82 (3) $[C_5H_6O]^{+\cdot}$, 81 (20) $[C_5H_5O]^+$, 78 (3) $[C_6H_6]^{+\cdot}$, 77 (7) $[C_6H_5]^+$, 69 (7) $[C_4H_5O]^+$, 67 (1) $[C_4H_3O]^+$, 63 (4) $[C_5H_3]^+$, 55 (5) $[C_3H_3O]^+$, 54 (4) $[C_4H_6]^{+\cdot}$, 53 (15) $[C_4H_5]^+$,

52 (7) $[C_4H_4]^{+\cdot}$, 51 (6) $[C_4H_3]^+$, 50 (3) $[C_4H_2]^{+\cdot}$, 43 (19) $[C_8H_3O]^+$, 41 (7) $[C_3H_5]^+$, 39 (6) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 256.5 (8222), 364.5 (4431).

Anal. Calcd for $C_8H_8O_3$: C, 63.15%; H, 5.30%; O, 31.55%. Found: C, 63.1%; H, 5.3%; O, 32.1%.

3.1.1.5. 1-(2,6-Dihydroxyphenyl)-ethanone (12e)



Purchased by Merck: Art. 820472. M.p.: 155-158°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ (br s, 2H, exchanges with D_2O, OH on C-2 and C-6), (d, 2H, $^3J_{3,4} = {}^3J_{5,4}$ =, H-3 and H-5), (t, 1H, $^3J_{4,3} = {}^3J_{4,5}$ =, H-4), (s, 3H, CH_3).

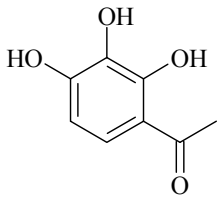
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 205.14 (CO), 161.56 (C-2 and C-6), 135.96 (C-4), 110.49 (C-1), 107.02 (C-3 and C-5), 33.12 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 152.0473 (54) $[C_8H_8O_3]^{+\cdot}$, 137 (100) $[C_7H_5O_3]^+$, 123 (2) $[C_7H_7O_2]^+$, 110 (2) $[C_6H_6O_2]^{+\cdot}$, 108 (5) $[C_6H_4O_2]^{+\cdot}$, 105 (4) $[C_7H_5O]^+$, 95 (1) $[C_6H_7O]^+$, 91 (3), 82 (5) $[C_5H_6O]^{+\cdot}$, 81 (32) $[C_5H_5O]^+$, 78 (9) $[C_6H_6]^{+\cdot}$, 76 (1) $[C_6H_6]^{+\cdot}$, 69 (13) $[C_4H_5O]^+$, 67 (4) $[C_4H_3O]^+$, 63 (11) $[C_5H_3]^+$, 53 (25) $[C_4H_5]^+$, 51 (13) $[C_4H_3]^+$, 43 (27) $[C_8H_3O]^+$, 39 (20) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 269.5 (11826), 344.5 (3346).

Anal. Calcd for $C_8H_8O_3$: C, 63.15%; H, 5.30%; O, 31.55%. Found: C, 63.1%; H, 5.2%; O, 32.3%.

3.1.1.6. 1-(2,3,4-Trihydroxyphenyl)-ethanone (12f)



According to the BF_3-Friedel-Crafts procedure, the pyrogallol (**55d**) (2 g, 15.859 mmol) was mixed with boron trifluoride (2 mL, 15.859 mmol) in glacial acetic acid (5 mL) to afford the 2,3,4-trihydroxyacetophenone (**12f**) as white powder (1.93 g, Yield 89%). M.p.: 169-172°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.59 (br s, 1H, exchanges with D_2O, OH on C-3), 9.91 (very br s, 1H, exchanges with D_2O, OH on C-3), 8.68 (very br s, 1H, exchanges with D_2O, OH on C-4), 6.85 (AB, 2H, δ_A = 7.30 (H-5), δ_B = 6.40 (H-6), $^3J_{AB}$ = 8.82), 2.5 (s, 3H, CH_3).

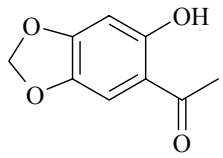
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 203.43 (CO), 152.48 (C-4), 152.14 (C-2), 132.16 (C-3), 123.03 (C-6), 113.12 (C-1), 107.60 (C-5), 26.63 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 168.0422 (67) $[C_8H_8O_4]^{+\cdot}$, 153 (100) $[C_7H_5O_4]^+$, 150 (5) $[C_8H_6O_3]^{+\cdot}$, 139 (3) $[C_7H_7O_3]^+$, 135 (1) $[C_7H_3O_3]^+$, 125 (4) $[C_6H_5O_3]^+$, 124 (2) $[C_6H_4O_3]^{+\cdot}$, 122 (1) $[C_7H_6O_2]^{+\cdot}$, 108 (1) $[C_6H_4O_2]^{+\cdot}$, 107 (7) $[C_6H_3O_2]^+$, 97 (2) $[C_5H_5O_2]^+$, 93 (4) $[C_6H_6O]^+$, 84 (1) $[C_4H_4O]^{+\cdot}$, 79 (14) $[C_5H_3O]^+$, 76 (2) $[C_6H_4]^{+\cdot}$, 71 (1) $[C_3H_3O_2]^+$, 65 (3) $[C_5H_5]^+$, 63 (2) $[C_5H_3]^+$, 55 (2) $[C_4H_3O]^+$, 53 (4) $[C_4H_5]^+$, 51 (7) $[C_4H_3]^+$, 43 (9) $[C_2H_3O]^+$, 41 (23) $[C_3H_5]^+$, 40 (12) $[C_3H_4]^{+\cdot}$, 39 (10) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 293 (14694).

Anal. Calcd for $C_8H_8O_4$: C, 57.14%; H, 4.80%; O, 38.06%. Found: C, 57.1%; H, 4.8%; O, 39.0%.

3.1.1.7. 1-(6-Hydroxybenzo[1,3]dioxol-5-yl)-ethanone (12g)



According to the BF_3-Friedel-Crafts procedure, the sesamol (**55f**)(10 g, 71 mmol) was mixed with acetic acid anhydride (72 mL) and a solution of the complex boron trifluoride-etherate (18 mL, 72 mmol). The crude product was recrystallized from methanol to afford the 2-hydroxy-4,5-methylendioxyacetophenone (**12g**) as beige crystals (11.3 g, 86%). M.p.: 114-116°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.95 (s, 1H, exchanges with D_2O, OH on C-2), 7.39 (s, 1H, H-6), 6.56 (s, 1H, H-3), 6.07 (s, 2H, OCH_2O), 2.54 (s, 3H, CH_3).

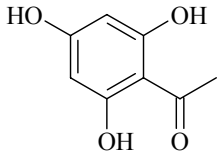
^{13}C NMR (DMSO-d^6, 75.46 MHz) δ 202.66 (CO), 160.74 (C-4), 154.05 (C-2), 140.15 (C-5), 112.01 (C-1), 107.99 (C-6), 102.04 (CH_2), 97.83 (C-3), 26.78 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 180.0422 (67) $[C_9H_8O_4]^{+\cdot}$, 165 (100) $[C_8H_5O_4]^+$, 162 (3) $[C_9H_6O_3]^{+\cdot}$, 137 (4) $[C_7H_5O_3]^+$, 135 (2) $[C_7H_3O_3]^+$, 121 (1) $[C_7H_5O_2]^+$, 109 (1) $[C_6H_5O_2]^+$, 108 (2) $[C_6H_4O_2]^{+\cdot}$, 107 (19) $[C_6H_3O_2]^+$, 93 (1) $[C_6H_5O]^+$, 82 (4) $[C_4H_2O_2]^{+\cdot}$, 79 (9) $[C_5H_3O]^+$, 69 (5) $[C_4H_5O]^+$, 66 (2) $[C_4H_2O_2]^{+\cdot}$, 55 (1) $[C_5H_5O_2]^+$, 53 (12) $[C_4H_5]^+$, 51 (4) $[C_4H_3]^+$, 43 (13) $[C_2H_3O]^+$, 41 (1) $[C_3H_5]^+$, 39 (1) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 276 (8080), 346.5 (9355).

Anal. Calcd for $C_9H_8O_4$: C, 60.00%; H, 4.48%; O, 35.52%. Found: C, 59.7%; H, 4.4%; O, 35.6%.

3.1.1.8. 1-(2,4,6-Trihydroxyphenyl)-ethanone (12h)



According to the BF_3-Friedel-Crafts procedure, the phloroglucinol (**55e**) (2 g, 15.859 mmol) was mixed with boron trifluoride (2 mL, 15.859 mmol) in glacial acetic acid (5 mL) to afford the 2,4,6-trihydroxyacetophenone (**12h**) as white powder (1.84 g, Yield 85%). M.p.: 169-172°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.18 (s, 2H, exchanges with D_2O, OH on C-2 and C-6), 10.31 (s, 1H, exchanges with D_2O, OH on C-4), 5.81 (s, 2H, H-3 and H-5), 3.32 (s, 3H, CH3).

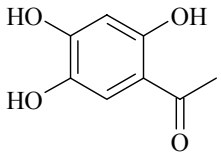
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 203.65 (CO), 164.71 (C-4), 164.23 (C-2 and C-6), 103.99 (C-1), 94.48 (C-3 and C-5), 32.27 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 168.0422 (58) $[C_8H_8O_4]^{+\cdot}$, 153 (100) $[C_7H_5O_4]^+$, 139 (3) $[C_7H_7O_3]^+$, 126 (2) $[C_6H_6O_3]^{+\cdot}$, 125 (1) $[C_6H_5O_3]^+$, 124 (2) $[C_6H_4O_3]^{+\cdot}$, 98 (5) $[C_5H_6O_2]^{+\cdot}$, 97 (4) $[C_5H_5O_2]^+$, 96 (3) $[C_5H_4O_2]^{+\cdot}$, 84 (5) $[C_4H_4O_2]^{+\cdot}$, 83 (3) $[C_4H_3O_2]^+$, 82 (1) $[C_4H_2O_2]^{+\cdot}$, 76 (2) $[C_6H_4]^{+\cdot}$, 70 (4) $[C_4H_6O]^{+\cdot}$, 69 (18) $[C_4H_5O]^+$, 55 (7) $[C_3H_3O]^+$, 53 (5) $[C_4H_5]^+$, 51 (5) $[C_4H_3]^+$, 50 (3) $[C_4H_2]^{+\cdot}$, 43 (23) $[C_2H_3O]^+$, 41 (30) $[C_3H_5]^+$, 40 (13) $[C_3H_4]^{+\cdot}$, 39 (11) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 287.5 (16629).

Anal. Calcd for $C_8H_8O_4$: C, 57.14%; H, 4.80%; O, 38.06%. Found: C, 51.4%; H, 5.5%; O, 44.0%.

3.1.1.9. 1-(2,4,5-Trihydroxyphenyl)-ethanone (12i)



According to the $AlCl_3$-Deprotection procedure, the 2-hydroxy-4,5-methylendioxy-acetophenone (**12g**) (1.2 g, 6.7 mmol) was mixed with aluminium chloride (3.5 g, 26.24

mmol) in 80 mL dichloromethane. The crude material was recrystallized from water to afford the 2,4,5-trihydroxyacetophenone (**12i**) as beige crystals (896 mg, Yield 88%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.19 (s, 1H, exchanges with D_2O, OH on C-2), 10.31 (s, 1H, exchanges with D_2O, OH on C-5), 8.75 (s, 1H, exchanges with D_2O, OH on C-4), 7.15 (s, 1H, H-3), 6.27 (s, 1H, H-6), 2.47 (s, 3H, CH_3).

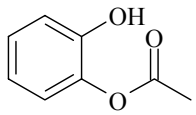
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 202.00 (CO), 157.42 (C-2), 154.49 (C-4), 138.14 (C-5), 115.74 (C-6), 111.26 (C-1), 102.77 (C-3), 26.37 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 168.0422 (59) $[C_8H_8O_4]^{+\cdot}$, 153 (100) $[C_7H_5O_4]^+$, 139 (1) $[C_7H_7O_3]^+$, 125 (3) $[C_6H_5O_3]^+$, 121 (5) $[C_7H_5O_2]^+$, 108 (1) $[C_6H_4O_2]^{+\cdot}$, 107 (12) $[C_6H_3O_2]^+$, 97 (5) $[C_5H_5O_2]^+$, 96 (1) $[C_5H_4O_2]^+$, 79 (7) $[C_5H_3O]^+$, 76 (2) $[C_6H_4]^{+\cdot}$, 69 (9) $[C_4H_5O]^+$, 67 (2) $[C_4H_3O]^+$, 57 (2) $[C_3H_5O]^+$, 53 (9) $[C_4H_5]^+$, 51 (7) $[C_4H_3]^+$, 50 (5) $[C_4H_2]^{+\cdot}$, 45 (1) $[C_3H_5O]^+$, 43 (17) $[C_2H_3O]^+$, 41 (5) $[C_3H_5]^+$, 39 (7) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 281 (13453), 349 (9048).

Anal. Calcd for $C_8H_8O_4$: C, 57.14%; H, 4.80%; O, 38.06%. Found: C, 56.9%; H, 5.0%; O, 38.3%.

3.1.1.10. Acetic acid 2-hydroxyphenyl ester (57)

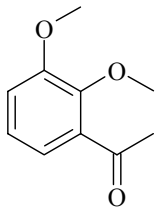


To a stirred solution of catechol (**55g**) (15.3 mg, 137 mmol) in pyridine (150 mL), was added the acetyl chloride (10 mL, 137 mmol) at room temperature in a very exothermic reaction. The reaction mixture was stirred for 30 minutes, and poured into a 3% aqueous HCl ice mixture with a vigorous stirring. The precipitate was filtered and washed with water. The crude material was distilled (4.3 mbar at 132°C) to afford the 2-acetoxyphenol (**57**) as a colourless oil (19.5 g, 94%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ 9.55 (br s, 1H, exchanges with D_2O, OH on C-2), 7.28 (m, 1H, H-5), 6.95 (m, 2H, H-4 and H-6), 6.75 (m, 1H, H-3), 2.23 (s, 3H, CH_3).

EI-MS *m/z* (% relative abundance) composition: 152.0473 (15) $[C_8H_8O_3]^{+\cdot}$, 110 (100) $[C_6H_6O_2]^{+\cdot}$, 109 (3) $[C_6H_5O_2]^+$, 92 (3) $[C_6H_4O]^{+\cdot}$, 82 (2) $[C_5H_6O]^{+\cdot}$, 81 (6) $[C_5H_5O]^+$, 80 (3) $[C_5H_4O]^{+\cdot}$, 79 (15) $[C_5H_3O]^+$, 78 (2) $[C_6H_6]^{+\cdot}$, 77 (2) $[C_6H_5]^+$, 64 (7) $[C_5H_4]^{+\cdot}$, 63 (2) $[C_5H_3]^+$, 55 (2) $[C_4H_7]^+$, 54 (1) $[C_4H_6]^{+\cdot}$, 53 (5) $[C_4H_5]^+$, 52 (13) $[C_4H_4]^{+\cdot}$, 51 (6) $[C_4H_3]^+$, 50 (3) $[C_4H_2]^{+\cdot}$, 43 (37) $[C_2H_3O]^+$, 39 (4) $[C_3H_3]^+$.

3.1.1.11. 1-(2,3-Dimethoxyphenyl)-ethanone (59a)



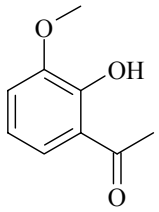
According to the Lithium salt procedure, the 2,3-dimethoxybenzoyl acid (**60**) (5.83 g, 32 mmol) in dry THF (15 mL) was mixed methyl lithium (5% in Diethyl ether, 80 mL, 8 mmol) and afforded the 2,3-dimethoxyacetophenone (**59a**) as a yellow oil (5.551 g, Yield 96%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ 7.34 (d, 1H, $^3J_{6,5}$ = 7.93, H-6), 7.05 (d, 1H, $^3J_{4,5}$ = 7.93, H-4), 6.85 (t, 1H, $^3J_{5,6}$ = $^3J_{5,4}$ = 7.93, H-5), 3.91 (s, 6H, OCH_3 on C-2 and C-3), 2.64 (s, 3H, CH_3CO).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 204.95 (CO), 152.80 (C-3), 149.99 (C-2), 121.97 (C-6), 119.99 (C-1), 119.00 (C-4), 116.90 (C-5), 56.18 (OCH_3 on C-2 and C-3), 27.05 (CH_3 on CO).

EI-MS *m/z* (% relative abundance) composition: 180.0786 (46) $[C_{10}H_{12}O_3]^{+\cdot}$, 165 (74) $[C_9H_9O_3]^+$, 151 (100) $[C_9H_{11}O_2]^+$, 150 (7) $[C_9H_{10}O_2]^{+\cdot}$, 149 (14), 148 (7), 147 (4), 137 (5) $[C_8H_9O_2]^{+\cdot}$, 136 (15), 135 (3) $[C_8H_7O_2]^{+\cdot}$, 134 (2) $[C_8H_6O_3]^{+\cdot}$, 133 (9) $[C_8H_5O_3]^+$, 132 (2), 123 (7) $[C_7H_7O_2]^+$, 122 (21) $[C_7H_6O_2]^{+\cdot}$, 121 (9) $[C_7H_5O_2]^{+\cdot}$, 120 (6) $[C_8H_8O]^{+\cdot}$, 119 (4) $[C_8H_7O]^+$, 118 (2) $[C_8H_6O]^{+\cdot}$, 109 (8) $[C_6H_5O_2]^{+\cdot}$, 108 (21) $[C_7H_8O]^{+\cdot}$, 107 (13) $[C_7H_7O]^+$, 106 (4) $[C_7H_6O]^{+\cdot}$, 105 (15) $[C_7H_5O]^+$, 95 (3) $[C_6H_7O]^+$, 94 (4) $[C_6H_6O]^{+\cdot}$, 93 (11) $[C_6H_5O]^+$, 92 (10) $[C_6H_4O]^{+\cdot}$, 91 (10) $[C_6H_3O]^+$, 81 (3) $[C_5H_5O]^+$, 80 (5) $[C_5H_4O]^{+\cdot}$, 79 (10) $[C_6H_7]^+$, 78 (6) $[C_6H_6]^{+\cdot}$, 77 (33) $[C_6H_5]^+$, 69 (2) $[C_5H_3O]^+$, 67 (7) $[C_4H_3O]^+$, 65 (13) $[C_5H_5]^+$, 64 (4) $[C_5H_4]^{+\cdot}$, 63 (10) $[C_5H_3]^+$, 53 (8) $[C_4H_5]^+$, 52 (12) $[C_4H_4]^{+\cdot}$, 51 (17) $[C_4H_3]^+$, 43 (45) $[C_2H_3O]^+$, 41 (4) $[C_3H_5]^+$, 39 (9) $[C_3H_3]^+$.

3.1.1.12. 1-(2-Hydroxy-3-methoxyphenyl)-ethanone (59b)



According to the Grignard procedure, the dimethoxybenzonitrile (**58**) (3.497 g, 21 mmol) dissolved in anhydrous ether (25 mL), was added to a solution of methyl magnesium iodide in diethyl ether (3.0 M, 35 mL, 35 mmol) to afford the 2,3-dimethoxyacetophenone (**59a**) as a

yellow oil (2.747 g, Yield 73%) and the 2-hydroxy-3-methoxyacetophenone (**59b**) as white crystals (1.497 g, 10%).

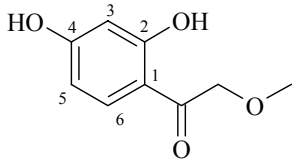
^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.57 (s, 1H, exchanges with D_2O, OH on C-2), 7.34 (dd, 1H, $^3J_{6,5}$ = 8.23, $^4J_{6,4}$ = 1.45, H-6), 7.05 (d, 1H, $^3J_{4,5}$ = 7.93, $^4J_{4,6}$ = 1.45, H-4), 6.85 (t, $^3J_{5,6}$ =8.23, $^3J_{5,4}$ = 8.23, H-5), 3.91 (s, 3H, OCH_3), 2.64 (s, 3H, CH_3CO).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 204.98 (CO), 152.81 (C-3), 148.88 (C-2), 121.87 (C-6), 119.71 (C-1), 118.27 (C-4), 116.98 (C-5), 56.18 (OCH_3), 27.10 (CH_3 on CO).

EI-MS *m/z* (% relative abundance) composition: 166.0630 (63) $[C_9H_{10}O_3]^{+\cdot}$, 151 (100) $[C_8H_7O_3]^+$, 148 (2) $[C_9H_8O_2]^{+\cdot}$, 136 (10) $[C_7H_4O_3]^{+\cdot}$, 133 (5) $[C_8H_5O_2]^+$, 123 (4) $[C_7H_7O_2]^+$, 121 (2) $[C_7H_5O_2]^+$, 120 (1) $[C_7H_4O_2]^{+\cdot}$, 108 (14) $[C_6H_4O_2]^{+\cdot}$, 105 (8) $[C_7H_5O]^+$, 93 (7) $[C_6H_5O]^+$, 92 (2) $[C_6H_4O]^{+\cdot}$, 80 (3) $[C_5H_4O]^{+\cdot}$, 79 (4) $[C_5H_3O]^+$, 77 (10) $[C_6H_5]^+$, 65 (5) $[C_5H_5]^+$, 64 (1) $[C_5H_4]^{+\cdot}$, 63 (3) $[C_5H_3]^+$, 55 (1) $[C_3H_3O]^+$, 53 (4) $[C_4H_5]^+$, 52 (5) $[C_4H_4]^{+\cdot}$, 51 (8) $[C_4H_3]^+$, 50 (3) $[C_4H_2]^{+\cdot}$, 43 (21) $[C_2H_3O]^+$, 39 (6) $[C_3H_3]^+$.

3.1.2. Precursors of flavonols

3.1.2.1. 1-(2,4-Dihydroxyphenyl)-2-methoxyethanone (63a)



According to the $AlCl_3$-Friedel-Crafts procedure, aluminium chloride (5.47 g, 41 mmol) was mixed with the resorcinol (**55c**) (1.29 g, 10 mmol) and the methoxyacetyl chloride (**61**) (1.03 mL, 11 mmol). The crude product was recrystallized from methanol to afford the 2,4-dihydroxymethoxyacetophenone (**63a**) as white pellets (1.25 g, Yield 63%).

According to the Houben-Hoesch procedure, the resorcinol (**55c**) (10 g, 90 mmol) was mixed with the methoxyacetonitrile (**64**) (6.85 mL, 90 mmol) under HCl bubbling to afford the benzoimine hydrochloride intermediate (**65a**) as yellow powder (16,1 g, Yield 83 %), which was hydrolysed to afford the 2,4-dihydroxymethoxyacetophenone (**63a**) as white pellets (9.2 g, Yield 54%). M.p.: 242.7°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 11.90 (very br s, 1H, exchanges with D_2O, OH on C-2), 10.60 (very br s, 1H, exchanges with D_2O, OH on C-4), 7.68 (d, 1H, $^3J_{6,5}$ = 8.82, H-6), 6.36 (dd, 1H, $^3J_{5,6}$ = 8.82, $^4J_{5,3}$ = 2.21, H-5), 6.28 (d, 1H, $^4J_{3,5}$ = 2.21, H-3), 4.69 (s, 2H, CH_2), 3.35 (s, 3H, CH_3).

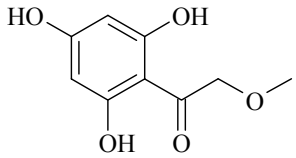
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 195.15 (CO), 164.61 (C-4), 163.41 (C-2), 131.89 (C-6), 111.61 (C-1), 108.18 (C-5), 102.43 (C-3), 74.31 (CH_2), 58.52 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 182.0579 (14) $[C_9H_{10}O_4]^{+\cdot}$, 152 (3) $[C_8H_8O_3]^{+\cdot}$, 137 (100) $[C_7H_5O_3]^+$, 123 (2) $[C_7H_7O_2]^+$, 109 (2) $[C_6H_5O_2]^+$, 108 (2) $[C_6H_4O_2]^{+\cdot}$, 95 (1) $[C_6H_7O]^+$, 81 (7) $[C_5H_5O]^+$, 79 (1) $[C_5H_6O]^+$, 69 (5) $[C_4H_5O]^+$, 63 (2) $[C_5H_3]^+$, 55 (2) $[C_3H_3O]^+$, 53 (5) $[C_4H_5]^+$, 51 (2) $[C_4H_3]^+$, 45 (10) $[C_2H_5O]^+$, 43 (2) $[C_2H_3O]^+$, 39 (4) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 281.5 (38470); 317.5 (24275).

Anal. Calcd for $C_9H_{10}O_4$: C, 70.99%; H, 4.61%; O, 24.40%. Found: C, 59.0%; H, 6.1%; O, 35.6%.

3.1.2.2. 1-(2,4,6-Trihydroxyphenyl)-2-methoxyethanone (63b)



According to the $AlCl_3$-Friedel-Crafts procedure, the phloroglucinol (**55e**) (1.3 g, 10 mmol) was mixed with the methoxyacetyl chloride (**61**) (1 mL, 11 mmol) and aluminium chloride (5.5 g, 41 mmol) to afford the 2,4,6-trihydroxymethoxyacetophenone (**63b**) as yellow needles (1.25 g, Yield 63%).

According to the Houben-Hoesch procedure, the benzoimine chloride (**65b**) (3 g, 12.8 mmol) was hydrolysed to afford the 2,4,6-trihydroxymethoxyacetophenone (**63b**) as yellow needles (2.38 g, Yield 78%). M.p.: 196°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.13 (br s, 2H, exchanges with D_2O, OH on C-2 and C-6), 10.40 (very br s, 1H, exchanges with D_2O, OH on C-4), 5.82 (s, 2H, H-3 and H-5), 4.58 (s, 2H, CH_2), 3.33 (s, 3H, CH_3).

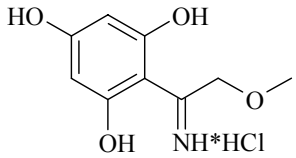
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 201.23 (CO), 164.88 (C-4), 163.97 (C-2 and C-6), 102.41 (C-1), 94.52 (C-3 and C-5), 77.00 (CH_2), 58.44 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 198.0528 (20) $[C_9H_{10}O_5]^{+\cdot}$, 166 (2) $[C_8H_8O_4]^{+\cdot}$, 153 (100) $[C_7H_5O_4]^+$, 139 (1) $[C_7H_7O_3]^+$, 137 (3) $[C_7H_5O_3]^+$, 136 (1) $[C_7H_4O_3]^+$, 124 (2) $[C_6H_6O_3]^{+\cdot}$, 111 (2) $[C_5H_3O_3]^+$, 108 (2) $[C_6H_4O_2]^{+\cdot}$, 97 (2) $[C_5H_5O_2]^+$, 83 (1) $[C_4H_3O_2]^+$, 69 (11) $[C_4H_5O]^+$, 67 (4) $[C_4H_3O]^+$, 55 (3) $[C_3H_3O]^+$, 53 (2) $[C_4H_5]^+$, 51 (2) $[C_4H_3]^+$, 50 (1) $[C_4H_2]^{+\cdot}$, 45 (9) $[C_2H_5O]^+$, 43 (3) $[C_2H_3O]^+$, 41 (6) $[C_3H_5]^+$, 39 (4) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 288.5 (60846); 332.5 sh (11685).

Anal. Calcd for $C_9H_{10}O_5$: C, 54.55%; H, 5.09%; O, 40.37%. Found: C, 47.5%; H, 5.6%; O, 46.7%.

3.1.2.3. 2-(1-Imino-2-methoxyethyl)-benzene-1,3,5-triol hydrochloride (65b)



According to the Houben-Hoesch procedure, the phloroglucinol (**55e**) (2 g, 15.8 mmol) was mixed with the methoxyacetonitrile (**64**) (1.2 mL, 15.8 mmol) under HCl bubbling to afford the benzoimine hydrochloride (**65b**) as white powder (3.18 g, Yield 88 %).

^{1}H NMR (DMSO-d^6, 250 MHz) δ ~11.60 (very br s, 2H, exchanges with D_2O, OH on C-2 and C-6), 10.97 (s, 1H, exchanges with D_2O, C=NH), 10.41 (br s, 1H, exchanges with D_2O, OH on C-4), 6.36 (s, 2H, H-3 and H-5), 4.83 (s, 2H, CH_2), 3.47 (s, 3H, CH_3).

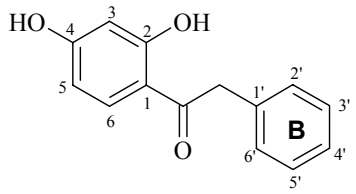
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 177.37 (C=NH), 166.61 (C-4), 163.33 (C-2), 134.54 (C-6), 98.61 (C-1), 96.38 (C-5), 95.39 (C-3), 72.43 (CH_2), 58.84 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 197. (100) $[C_9H_{11}NO_4]^{+\cdot}$, 182 (54) $[C_8H_8NO_4]^+$, 165 (2) $[C_8H_7NO_3]^{+\cdot}$, 155(3) $[C_7H_9NO_3]^{+\cdot}$, 154 (4) $[C_7H_8NO_3]^+$, 152 (2) $[C_7H_6NO_3]^+$, 141 (3), 140 (52), 136 (1), 127 (7), 126 (5), 125 (4) $[C_6H_5O_3]^+$, 122 (3), 113 (1), 112 (13), 110 (6), 99 (3), 98 (35) $[C_5H_6O_2]^{+\cdot}$, 96 (4) $[C_5H_3O_2]^+$, 94 (2) $[C_5H_2O_2]^{+\cdot}$, 85 (3) $[C_4H_5O_2]^+$, 84 (4) $[C_4H_4O_2]^{+\cdot}$, 83 (33) $[C_4H_3O_2]^+$, 82 (5) $[C_4H_2O_2]^{+\cdot}$, 72 (2), 70 (7) $[C_4H_6O_2]^{+\cdot}$, 69 (14) $[C_4H_5O_2]^+$, 68 (27) $[C_4H_4O_2]^+$, 66 (7) $[C_4H_2O_2]^{+\cdot}$, 62 (7), 55 (15) $[C_3H_3O]^+$, 53 (7) $[C_4H_5]^+$, 51 (3) $[C_4H_3]^+$, 45 (16) $[C_3H_5O]^+$, 43 (19) $[C_2H_3O]^+$, 41 (66) $[C_3H_5]^+$, 40 (36) $[C_3H_4]^{+\cdot}$, 39 (18) $[C_3H_3]^+$, 36 (23) $[HCl]^+$.

Anal. Calcd for $C_9H_{12}ClNO_4$: C, 46.27%; H, 5.18%; Cl, 15.17%; N, 5.99%; O, 27.39%. Found: C, 36.9%; H, 5.2%; Cl, 17.5%; N, 4.5%; O, 32.7%.

3.1.3. Precursors of isoflavonoids

3.1.3.1. 1-(2,4-Dihydroxyphenyl)-2-phenylethanone (67a)



According to the BF_3-Friedel-Crafts procedure, the resorcinol (**55b**) (1.12 g, 10 mmol), phenyl acetyl chloride (**66a**) (1.34 mL, 10 mmol) and boronn trifluoride etherate (12.6 mL, 50 mmol) were mixed to afford the deoxybenzoin (**67a**) as orange needles (1.87 g, Yield 82%). M.p.: 272.8°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.54 (br s, 1H, exchanges with D_2O, OH on C-2), 10.68 (very br s, 1H, exchanges with D_2O, OH on C-4), 7.96 (d, 1H, $^3J_{6,5}$ = 9.52, H-6), 7.26 (m, 5H, H_{Ar} B-ring), 6.40 (dd, 1H, $^3J_{5,6}$ = 9.52, $^4J_{5,3}$ = 2.11, H-5), 6.26 (d, 1H, $^4J_{3,5}$ = 2.11, H-3), 4.28 (s, 2H, CH_2).

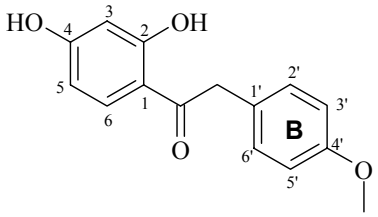
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 202.00 (CO), 164.89 (C-4), 164.53 (C-2), 135.11 (C-1′), 133.48 (C-6), 129.45 (C-2′ and C-6′), 128.25 (C-3′ and C-5′), 126.48 (C-4′), 112.11 (C-1), 108.20 (C-5), 102.38 (C-3), 44.01 (CH_2).

EI-MS *m/z* (% relative abundance) composition: 228.0786 (9) $[C_{14}H_{12}O_3]^{+\cdot}$, 165 (12) $[C_9H_9O_3]^+$, 137 (100) $[C_7H_5O_3]^+$, 123 (2) $[C_7H_7O_2]^+$,109 (2) $[C_6H_5O_2]^+$, 105 (6) $[C_7H_5O]^+$,91 (8) $[C_7H_7]^+$, 81 (5) $[C_5H_5O]^+$, 77 (3) $[C_7H_5]^+$, 69 (4) $[C_4H_5O]^+$, 65 (4) $[C_5H_5]^+$, 63 (2) $[C_5H_3]^+$, 55 (2) $[C_3H_3O]^+$, 53 (3) $[C_4H_5]^+$, 51 (2) $[C_4H_3]^+$, 43 (1) $[C_2H_3O]^+$, 41 (1) $[C_3H_5]^+$, 39 (3) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 281.5 (25120); 323 (16083).

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67%; H, 5.30%; O, 21.03%. Found: C, 73.7%; H, 5.3%; O, 20.9%.

3.1.3.2. 1-(2,4-Dihydroxyphenyl)-2-(4-methoxyphenyl)-ethanone (67b)



According to the BF_3-Friedel-Crafts procedure, the resorcinol (**55b**) (2.89 g, 26 mmol), 4-methoxyphenylacetyl chloride (**66b**) (4 mL, 25.6 mmol) and boronn trifluoride etherate (6.28 mL, 25 mmol) were mixed to afford the 4′-methoxydeoxybenzoin (**67b**) as pale yellow needles (5.51 g, Yield 82%). M.p.: 153.1°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.51 (br s, 1H, exchanges with D_2O, OH on C-2), 10.64 (very br s, 1H, exchanges with D_2O, OH on C-4), 7.93 (d, 1H, $^3J_{6,5}$ = 9.52, H-6), 7.21-6.66 (dm, AA′XX′, 4H, H_{Ar} B-ring), 6.38 (dd, 1H, $^3J_{5,6}$ = 9.52, $^4J_{5,3}$ = 2.11, H-5), 6.25 (d, 1H, $^4J_{3,5}$ = 2.11, H-3), 4.20 (s, 2H, CH_2), 3.72 (s, 3H, CH_3 on C-4′).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 208.29 (CO), 164.83 (C-4), 164.57 (C-2), 157.93 (C-4′), 133.47 (C-6), 130.40 (C-2′ and C-6′), 126.88 (C-1′), 113.74 (C-3′ and C-5′), 111.99 (C-1), 108.14 (C-5), 102.37 (C-3), 54.91 (CH_3 on C-4′), 43.12 (CH_2).

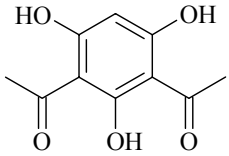
EI-MS *m/z* (% relative abundance) composition: 258.0892 (8) $[C_{15}H_{14}O_4]^{+\cdot}$, 167 (3) $[C_9H_9O_3]^+$, 149 (10) $[C_9H_9O_2]^+$, 137 (100) $[C_7H_5O_3]^+$, 122 (6) $[C_7H_6O_2]^+$, 121 (19) $[C_7H_5O_2]^+$,109 (2) $[C_6H_5O_2]^+$, 108 (4) $[C_6H_4O_2]^{+\cdot}$, 105 (6) $[C_7H_5O]^+$, 91 (11) $[C_7H_7]^+$, 81 (27) $[C_5H_5O]^+$, 77 (21) $[C_7H_5]^+$, 69 (14) $[C_4H_5O]^+$, 65 (8) $[C_5H_5]^+$, 63 (4) $[C_5H_3]^+$, 55 (15) $[C_3H_3O]^+$, 53 (20) $[C_4H_5]^+$, 51 (9) $[C_4H_3]^+$, 43 (16) $[C_2H_3O]^+$, 41 (19) $[C_3H_5]^+$, 39 (14) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 279 (35710); 321.5 (22923).

Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76%; H, 5.46%; O, 24.78%. Found: C, 69.5%; H, 5.6%; O, 24.9%.

3.1.4. Polyacetophenones

3.1.4.1. 1-(3-Acetyl-2,4,6-trihydroxyphenyl)-ethanone (68)



According to the $AlCl_3$-Friedel-Crafts procedure, the phloroglucinol (**55c**) (1.3 g, 10 mmol) was mixed with acetyl chloride (1.6 g, 20 mmol) and aluminium chloride (5.5 g, 41 mmol) to afford the 3-acetyl-2,4,6-trihydroxyacetophenone (**68**) as a yellow powder (1.424 g, Yield 68%). M.p.: 167.9°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 16.28 (s, 1H, exchanges with D_2O, OH on C-6), 13.19 (s, 2H, exchanges with D_2O, OH on C-2 and C-4), 5.86 (s, 1H, H-3), 2.60 (s, 6H, CH_3).

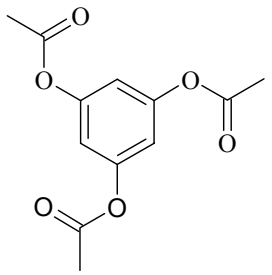
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 203.13 (CO), 171.07 (C-6), 168.55 (C-2 and C-4), 103.52 (C-1 and C-5), 94.57 (C-3), 32.37 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 210.0528 (66) $[C_{10}H_{10}O_5]^{+\cdot}$, 195 (100) $[C_9H_7O_5]^+$, 177 (56) $[C_9H_5O_4]^+$, 167 (2) $[C_8H_7O_4]^+$, 153 (5) $[C_7H_5O_4]^+$, 149 (4) $[C_8H_5O_3]^+$, 135 (2) $[C_7H_3O_3]^+$, 124 (2) $[C_6H_4O_3]^{+\cdot}$, 121 (5) $[C_7H_5O_2]^+$, 111 (2) $[C_5H_3O_3]^+$, 97 (2) $[C_5H_5O_2]^+$, 93 (4) $[C_6H_5O]^+$, 83 (3) $[C_4H_3O_2]^+$, 81 (3) $[C_5H_5O]^{+\cdot}$, 79 (3) $[C_5H_3O]^+$, 77 (3) $[C_6H_5]^+$, 69 (26) $[C_4H_5O]^+$, 67 (24) $[C_4H_3O]^+$, 65 (6) $[C_5H_5]^+$, 63 (3) $[C_5H_3]^+$, 55 (8) $[C_3H_3O]^+$, 53 (11) $[C_4H_5]^+$, 51 (7) $[C_4H_3]^+$, 43 (57) $[C_2H_3O]^+$, 41 (6) $[C_3H_5]^+$, 39 (12) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 270 (59396); 326 sh (8687); 375.5 (3670).

Anal. Calcd for $C_{10}H_{10}O_5$: C, 57.14%; H, 4.80%; O, 38.06%. Found: C, 53.7%; H, 5.1%; O, 40.6%.

3.1.4.2. Acetic acid 3,5-diacetoxyphenyl ester (69)



According to the $AlCl_3$-Friedel-Crafts procedure, the phloroglucinol (**55e**) (1.287 g, 10 mmol) was mixed with aluminium chloride (5.467 g, 41 mmol) and acetyl chloride (0.8 mL, 11 mmol) in diethyl ether (50 mL) to afford the acetic acid 3,5-diacetoxyphenyl ester (**69**) as white powder (131 mg, Yield 5%). M.p.: 103.6°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 6.92 (s, 3H, H-2, H-4 and H-6), 2.25 (s, 9H, CH_3).

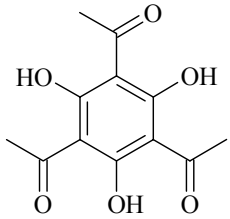
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 168.85 (CO), 150.93 (C-1, C-3 and C-5), 113.46 (C-2, C-4 and C-6), 20.71 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 252.0633 (6) $[C_{12}H_{12}O_6]^{+\cdot}$, 210 (16) $[C_{10}H_{10}O_5]^{+\cdot}$, 168 (30) $[C_8H_8O_4]^{+\cdot}$, 126 (100) $[C_6H_6O_3]^{+\cdot}$, 98 (1) $[C_5H_6O_2]^{+\cdot}$, 97 (7) $[C_5H_5O_2]^{+}$, 79 (1) $[C_5H_3O]^{+}$, 69 (5) $[C_4H_5O]^{+}$, 55 (2) $[C_3H_3O]^{+}$, 43 (83) $[C_2H_2O]^{+\cdot}$, 42 (4) $[C_3H_6]^{+\cdot}$, 41 (2) $[C_3H_5]^{+}$, 39 (2) $[C_3H_3]^{+}$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 270 (945).

Anal. Calcd for $C_{12}H_{12}O_6$: C, 57.14%; H, 4.80%; O, 38.06%. Found: C, 57.1%; H, 4.7%; O, 39.2%.

3.1.4.3. 1-(3,5-diacetyl-2,4,6-trihydroxyphenyl)-ethanone (70)



According to the BF_3-Friedel-Crafts procedure, the phloroglucinol (**55e**) (2 g, 15.7 mmol) was mixed acetic acid (2.5 mL), acetic acid anhydride (4.3 mL) and a solution of the complex boron trifluoride-etherate (50% in ether, 5 mL, 20 mmol). The precipitated product was filtered and washed with methanol to afford the 3,5-diacetyl-2,4,6-trihydroxyacetophenone (**70**) as white crystals (3.190 g, Yield 81%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ ~13.25 (very br s, 3H, exchanges with D_2O, OH on C-2, C-4 and C-6), 2.68 (s, 9H, CH_3).

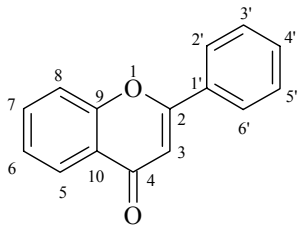
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 202.75 (CO), 173.05 (C-2, C-4 and C-6), 103.34 (C-1, C-3 and C-5), 32.43 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 252.0633 (71) $[C_{12}H_{12}O_6]^{+\cdot}$, 237 (100) $[C_{11}H_9O_6]^+$, 219 (32) $[C_{11}H_7O_5]^+$, 210 (2) $[C_{10}H_{10}O_5]^{+\cdot}$, 201 (7) $[C_{11}H_5O_4]^+$, 195 (3) $[C_9H_7O_5]^+$, 191 (2) $[C_{10}H_7O_4]^+$, 177 (10) $[C_9H_5O_4]^+$, 173 (2) $[C_9H_5O_3]^+$, 167 (1) $[C_8H_7O_3]^+$, 163 (3) $[C_9H_7O_3]^+$, 153 (2) $[C_7H_5O_4]^+$, 151 (3) $[C_8H_3O_4]^+$, 149 (1) $[C_8H_5O_3]^+$, 145 (2) $[C_9H_5O_2]^+$, 135 (2) $[C_8H_7O_2]^+$, 121 (3) $[C_7H_5O_2]^+$, 117 (1) $[C_8H_5O]^+$, 111 (2) $[C_5H_3O_3]^+$,109 (3) $[C_6H_5O_2]^+$, 107 (2) $[C_6H_3O_2]^+$, 93 (3) $[C_6H_5O]^+$, 91 (2) $[C_6H_3O]^+$, 79 (4) $[C_6H_7]^+$, 77 (3) $[C_6H_5]^+$, 69 (10) $[C_4H_5O]^+$, 67 (17) $[C_5H_7O]^+$, 65 (3) $[C_5H_5O]^+$, 55 (4) $[C_3H_3O]^+$, 53 (4) $[C_4H_5]^+$, 52 (1) $[C_4H_4]^{+\cdot}$, 51 (3) $[C_4H_3]^+$, 43 (50) $[C_2H_3O]^+$, 41 (13) $[C_3H_5]^+$, 39 (7) $[C_3H_3]^+$.

Anal. Calcd for $C_{12}H_{12}O_6$: C, 57.14%; H, 4.80%; O, 38.06%. Found: C, 57.0%; H, 4.9%; O, 38.8%.

3.2. Flavones (Chapter 3)

3.2.1. 2-Phenyl-4-oxo-4*H*-1-benzopyran (24)



The 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione (**132a**) (2.0 g, 8 mmol) was mixed with glacial acetic acid (100 mL) and H_2SO_4 (0.5 mL) and heated at 95-100°C for 1 h. About 75% of the solvent was removed at reduced pressure and the residue was poured into water (500 mL). The product was filtered, washed with water and dried overnight and the residue was recrystallized from ethanol to afford the flavone (**24**) as white needles (1,76 g, Yield 85%). M.p.: 341-342°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 8.22 (dd, 2H, $^3J_{2',3'} = {}^3J_{6',5'} = 7.32$, $^4J_{2',4'} = {}^4J_{6',4'} = 1.14$, H-2′ and H-6′), 8.17 (d, 1H, $^3J_{5,6} = 8.81$, H-5), 7.95 (m, 1H, H-7), 7.90 (m, 1H, H-8), 7.73 (dd, 1H, $^3J_{4',3'} = {}^3J_{4',5'} = 7.32$, $^4J_{4',2'} = {}^4J_{4',6'} = 1.14$, H-4′), 7.71 (m, 2H, H-3′ and H-5′), 7.62 (m, 1H, H-6), 7.14 (s, 1H, H-3).

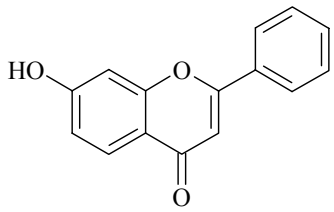
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.97 (C-4), 162.41 (C-2), 155.55 (C-9), 134.13 (C-7), 131.67 (C-4′), 131.02 (C-1′), 128.97 (C-3′ and C-5′), 126.22 (C-2′ and C-6′), 125.36 (C-6), 124.67 (C-5), 123.32 (C-10), 118.39 (C-8), 106.84 (C-3).

EI-MS *m/z* (% relative abundance) composition: 222.0678 (100) $[C_{15}H_{10}O_2]^+$, 221.0574 (29) $[C_{15}H_9O_2]^+$, 205.0672 (1) $[C_{15}H_9O]^+$, 194.0723 (40) $[C_{14}H_{10}O]^+$, 193.060723 (1) $[C_{14}H_9O]^+$, 181.0651 (1) $[C_{13}H_9O]^+$, 165.0687 (11) $[C_{13}H_9O]^+$, 152.0599 (1) $[C_{12}H_8]^+$, 139.0552 (3) $[C_{11}H_7]^+$, 129.0723 (2) $[C_{10}H_9]^+$, 120.0218 (64) $[C_7H_4O_2]^+$, 115.0538 (1) $[C_9H_7]^+$, 102.0466 (11) $[C_8H_6]^+$, 92.0264 (35) $[C_6H_4O]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 251 (28050), 293.5 (34035); (Figure 19, side 221).

Anal. Calcd for $C_{15}H_{10}O_2$: C, 81.06%; H, 4.54%; O, 14.40%. Found: C, 81.1%; H, 4.4%; O, 14.3%.

3.2.2. 7-Hydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran (73)



According to the procedure A, the 2,4-dihydroxyacetophenone (**12c**) (1 g, 6.4 mmol) was mixed with LiHMDS (18 mL, 18 mmol) and benzoyl chloride (**17a**) (982 mg, 6.6 mmol). The crude product was recrystallized from ethanol to afford the 7-hydroxyflavone (**73**) as white needles (172 mg, Yield 12%). M.p.: 245-246°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 10.87 (br s, 1H, exchanges with D_2O, OH on C-7), 8.04 (dd, 2H, $^3J_{2',3'} = {}^3J_{6',5'} = 7.57$, $^4J_{2',4'}, = {}^4J_{2',4'} = 2.32$, H-2′ and H-6′), 7.90 (d, 1H, $^3J_{5,6} = 8.73$, H-5), 7.56 (m, 3H, H-3′, H-4′ and H-5′), 7.00 (d, 1H, $^4J_{8,6} = 2.33$, H-8), 6.93 (dd, 1H, $^3J_{6,5} = 8.51$, $^4J_{6,8} = 2.36$, H-6), 6.92 (s, 1H, H-3).

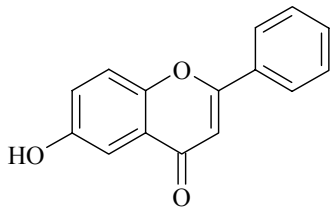
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.32 (C-4), 162.70 (C-7), 161.82 (C-2), 157.40 (C-9), 131.42 (C-4′), 131.20 (C-1′), 128.96 (C-3′ and C-5′), 126.45 (C-5), 126.06 (C-2′ and C-6′), 116.06 (C-10), 114.98 (C-6), 106.53 (C-8), 102.46 (C-3).

EI-MS *m/z* (% relative abundance) composition: 238.0629 (100), 237.0557 (19), 210.0680 (63), 181 (4), 152 (6), 136 (41), 129 (2), 108 (23), 105 (33), 102 (11), 95 (6).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 247 (16643), 308 (18663); (Figure 20, side 221).

Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62%; H, 4.23%; O, 20.15%. Found: C, 72.8%; H, 4.4%; O, 21.9%.

3.2.3. 6-Hydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran (74)



According to the procedure A, the 2,5-dihydroxyacetophenone (**12d**) (1 g, 6.4 mmol) was mixed with LiHMDS (20 mL, 20 mmol) and benzoyl chloride (**17a**) (1 g, 7 mmol). The crude product was recrystallized from ethanol to afford the 6-hydroxyflavone (**74**) as pale yellow crystals (325 mg, Yield 25%). M.p.: 236-237°C.

^{1}H NMR (DMSO-d^6, 500 MHz) δ 10.01 (s, 1H, exchanges with D_2O, OH on C-6), 8.08 (dd, 2H, $^3J_{2',3'} = {}^3J_{6',5'}$ = 7.76, $^4J_{2',4'} = {}^4J_{6',4'}$= 1.21, H-2′ and H-6′), 7.66 (d, 1H, $^4J_{8,7}$ = 8.92, H-8), 7.59 (m, 3H, H-3′, H-4′ and H-5′), 7.34 (d, 1H, $^4J_{5,7}$ = 2.59, H-5), 7.27 (dd, 1H, $^3J_{7,8}$ = 8.63, $^4J_{7,5}$ = 2.83, H-7), 6.90 (s, 1H, H-3).

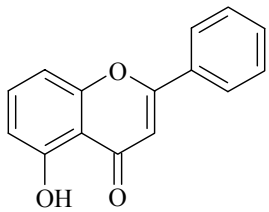
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.93 (C-4), 162.10 (C-2), 154.87 (C-6), 149.34 (C-9), 131.47 (C-4′), 131.34 (C-1′), 128.96 (C-3′ and C-5′), 126.13 (C-2′ and C-6′), 124.22 (C-10), 123.00 (C-7), 119.71 (C-8), 107.52 (C-5), 105.88 (C-3).

EI-MS *m/z* (% relative abundance) composition: 238.0629 (100), 237 (8), 210 (8), 181 (2), 165 (1), 152 (3), 136 (99), 129 (3), 108 (17), 105 (14), 102 (9).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 272 (32299), 302.5 (19353), 341.5 (7421); (Figure 21, side 222).

Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62%; H, 4.23%; O, 20.15%. Found: C, 75.4%; H, 4.3%; O, 20.3%.

3.2.4. 5-Hydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran (75)



According to the procedure A, the 2,6-dihydroxyacetophenone (**12e**) (1 g, 6.4 mmol) was mixed with LiHMDS (20 mL, 20 mmol) and benzoyl chloride (**17a**) (1 g, 7.2 mmol). The

crude product was recrystallized from ethanol to afford the 5-hydroxyflavone (**75**) as pale yellow crystals (764 mg, Yield 49%). M.p.: 156-157°C.

^{1}H NMR (DMSO-d^6, 500 MHz) δ 12.71 (s, 1H, exchanges with D_2O, OH on C-5), 8.12 (d, 2H, $^3J_{2',3'} = {}^3J_{6',5'} = 7.29$, $^4J_{2',4'} = {}^4J_{6',4'} = 1.58$, H-2′ and H-6′), 7.69 (t, 1H, $^3J_{7,8} = {}^3J_{7,6} = 8.32$, H-7), 7.55 (m, 3H, H-3′, H-4′ and H-5′), 7.21 (d, 1H, $^3J_{6,7} = 8.32$, H-6), 7.11 (s, 1H, H-3), 6.84 (d, 1H, $^3J_{8,7} = 8.32$, H-8).

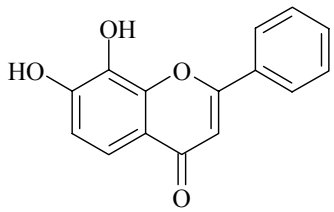
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 183.18 (C-4), 164.07 (C-2), 159.82 (C-5), 155.88 (C-9), 135.92 (C-7), 132.26 (C-4′), 130.52 (C-1′), 129.12 (C-3′ and C-5′), 126.57 (C-2′ and C-6′), 110.95 (C-6 or C-8), 110.11 (C-10), 107.48 (C-8 or C-6), 105.63 (C-3).

EI-MS *m/z* (% relative abundance) composition: 238.0629 (100), 237 (8), 210 (11), 181 (2), 165 (1), 152 (5), 136 (42), 108 (37), 105 (15), 102 (7).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 270.5 (30095), 338 (7046); (Figure 22, side 222).

Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62%; H, 4.23%; O, 20.15%. Found: C, 75.3%, H, 4.4%, O, 19.9%.

3.2.5. 7,8-Dihydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran (76)



According to the procedure A, the 2,3,4-trihydroxyacetophenone (**12f**) (2 g, 11.5 mmol) was mixed with LiHMDS (60 mL, 60 mmol) and the benzoyl chloride (**17a**) (1.8 g, 12.7 mmol). The crude product was recrystallized from ethanol to afford 7,8-dihydroxyflavone (**76**) as yellow crystals (1.135 g, Yield 39%). M.p.: 310-311°C.

^{1}H NMR (DMSO-d^6, 500 MHz) δ 10.10 (br s, 1H, exchanges with D_2O, OH on C-7), 9.53 (br s, 1H, exchanges with D_2O, OH on C-8), 8.16 (dd, 2H, $^3J_{2',3'} = {}^3J_{6',5'} = 7.85$, $^4J_{2',4'} = {}^4J_{6',4'} = 1.62$, H-2′ and H-6′), 7.6 (m, 3H, H-3′, H-4′ and H-5′), 7.1921 (AB, 2H, $\delta_A = 6.9669$ (H-6), $\delta_B = 7.4179$ (H-5), $^3J_{AB} = 8.567$), 6.90 (s, 1H, H-3).

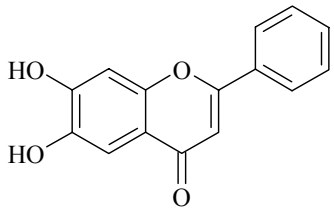
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.90 (C-4), 161.76 (C-2), 150.56 (C-7), 146.68 (C-9), 133.10 (C-1′), 131.46 (C-4′), 131.39 (C-8), 128.92 (C-3′ and C-5′), 126.30 (C-2′ and C-6′), 116.95 (C-10), 115.16 (C-5), 114.07 (C-6), 106.03 (C-3).

EI-MS *m/z* (% relative abundance) composition: 254.0579 (100), 226 (4), 197 (4), 169 (3), 152 (99), 124 (10), 117 (8), 106 (9), 102 (8).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 268.5 (42883), 318.5 (13000); (Figure 23, side 223).

Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86%; H, 3.96%; O, 25.17%. Found: C, 66.2%, H, 4.6%, O, 29.1%.

3.2.6. 6,7-Dihydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran (77)



According to the procedure B, the 2,4,5-trihydroxyacetophenone (**12i**) (1 g, 5.7 mmol) was mixed with LiOH (560 mg, 23 mmol) and benzoyl chloride (**17a**) (886 mg, 6.3 mmol). The crude product was recrystallized from ethanol to afford the 6,7-dihydroxyflavone (**77**) as yellow crystals (536 mg, Yield 37%). M.p.: 254-255°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 10.48 (br s, 1H, exchanges with D_2O, OH on C-7), 9.81 (br s, 1H, exchanges with D_2O, OH on C-6), 8.00 (dd, 2H, $^3J_{2',3'} = {}^3J_{6',5'} = 7.60$, $^4J_{2',4'} = {}^4J_{6',4'} = 3.16$, H-2′ and H-6′), 7.50 (m, 3H, H-3′, H-4′ and H-5′), 7.28 (s, 1H, H-5), 7.02 (s, 1H, H-3), 6.82 (s, 1H, H-8).

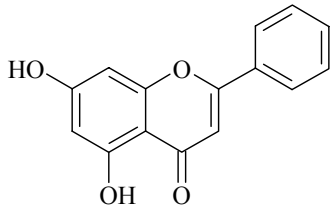
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.16 (C-4), 161.33 (C-2), 152.32 (C-7), 150.76 (C-9), 144.61 (C-6), 131.46 (C-1′), 131.21 (C-4′), 128.96 (C-3′ and C-5′), 125.92 (C-2′ and C-6′), 116.03 (C-10), 107.48 (C-5), 105.85 (C-8), 103.10 (C-3).

EI-MS *m/z* (% relative abundance) composition: 254.0579 (100), 239 (1), 226 (14), 225 (3), 208 (1), 166 (1), 153 (7), 152 (74), 151 (2), 124 (5), 123 (3), 113 (12), 105 (2), 103 (6), 96 (7), 82 (14), 76 (5), 69 (12), 64 (3), 54 (4), 51 (5), 39 (3).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 267 (18953), 311 (15415); (Figure 24, side 223).

Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86%; H, 3.96%; O, 25.17%. Found: C, 65.9%; H, 4.6%; O, 29.5%.

3.2.7. 5,7-Dihydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran / Chrysin (78)



According to the procedure C, the 2,4,6-trihydroxyacetophenone (**12h**) (1 g, 5.3 mmol) was mixed with LiOH (1.03 g, 42 mmol) and benzoyl chloride (**17a**) (2.04 mL, 17.3 mmol). The crude product was isolated in two fractions to afford the 5,7-dihydroxyflavone (**78**) as a yellow powder (577 mg, yield 43%). M.p.: 289-290°C.

^{1}H NMR (DMSO-d^6, 500 MHz) δ 12.80 (br s, 1H, exchanges with D_2O, OH on C-5), 10.91 (br s, 1H, exchanges with D_2O, OH on C-7), 8.07 (d, 2H, $^3J_{2',3'} = {}^3J_{6',5'}$ = 7.34, H-2′ and H-6′), 7.59 (m, 3H, H-3′, H-4′ and H-5′), 6.98 (s, 1H, H-3), 6.38 (AX, 2H, δ_A = 6.54 (H-6) and δ_X = 6.23 (H-8), J_{AX} = 2.22).

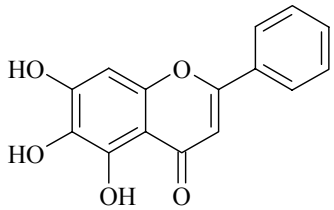
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ181.73 (C-4), 164.36 (C-7 or C-2), 163.03 (C-2 or C-7), 161.43 (C-5), 157.37 (C-9), 131.81 (C-4′), 130.67 (C-1′), 128.97 (C-3′ and C-5′), 126.25 (C-2′ and C-6′), 105.08 (C-6), 103.93 (C-10), 98.96 (C-8), 94.03 (C-3).

EI-MS *m/z* (% relative abundance) composition: 254.0579 (100), 253 (5), 226 (20), 197 (1), 164 (1), 152 (21), 141 (2), 124 (15), 122 (2), 113 (10), 105 (7), 102 (5).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 269.5 (37121), 315.5 (14246); (Figure 25, side 224).

Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86%; H, 3.96%; O, 25.17%. Found: C, 70.7%, H, 4.1%, O, 25.0%.

3.2.8. 5,6,7-Trihydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran / Baicalein (79)



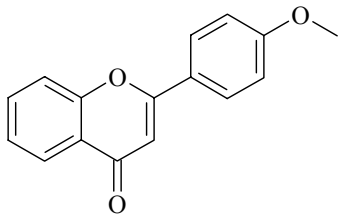
Purchased by Aldrich (Art-Nr.: 46,511-9) 98%. M.p: 256-271°C.

^{1}H NMR (DMSO-d^6, 500 MHz) δ 12.67 (s, 1H, exchanges with D_2O, OH on C-5), 10.54 (br s, 1H, exchanges with D_2O, OH on C-7), 8.80 (br s, 1H, exchanges with D_2O, OH on C-6), 8.05 (d, 2H, $^3J_{2',3'} = {}^3J_{6',5'}$ = 7.93, H-2′ and H-6′), 7.57 (m, 3H, H-3′, H-4′ and H-5′), 6.92 (s, 1H, H-8), 6.64 (s, 1H, H-3).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 182.05 (C-4), 162.85 (C-2), 153.59 (C-7), 149.81 (C-9), 146.97 (C-5), 131.70 (C-4′), 130.92 (C-1′), 129.29 (C-6), 129.00 (C3′ and C-5′), 126.21 (C-2′ and C-6′), 104.43 (C-8), 104.26 (C-10), 93.98 (C-3).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 276.5 (26649), 325.5 (15388); (Figure 26, side 224).

3.2.9. 2-(4-Methoxyphenyl)-4-oxo-4*H*-1-benzopyran (80)



According to the procedure A, the 2-hydroxyacetophenone (**12a**) (2 g, 14.7 mmol) was mixed with LiHMDS (30 mL, 30 mmol) and the 4-methoxybenzoyl chloride (**17b**) (2.8 g, 16.2 mmol). The crude product was recrystallized from ethanol to afford the 4′-methoxyflavone (**80**) as white crystals (1.768 g, Yield 48%). M.p.: 157-158°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 8.07-7.81 (m, 5H, H_{Ar} B-ring and H-5), 7.49 (m, 1H, H-7), 7.13 (m, 2H, H-8 and H-6), 6.93 (s, 1H, H-3), 3.87 (s, 3H, OCH_3 on C-4′).

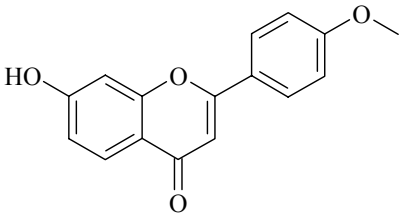
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.85 (C-4), 162.65 (C-2), 162.14 (C-4′), 155.59 (C-9), 134.06 (C-7), 128.18 (C-2′ and C-6′), 125.34 (C-5), 124.70 (C-6), 123.28 (C-1′), 123.22 (C-10), 118.38 (C-8), 114.55 (C-3′ and C-5′), 105.42 (C-3), 55.43 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 252.0786 (100), 252 (14), 237 (3), 224 (6), 221 (5), 209 (8), 195 (1), 181 (6), 159 (2), 152 (4), 132 (60), 120 (6), 117 (12), 112 (6) 102 (2).

UV-vis (2-propanol, 1 mg / 100 mL) $\lambda_{max.}$ (ε) nm: 252 (15310), 316.5 (23549); (Figure 27, side 225).

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.17%; H, 4.80%; O, 19.03%. Found: C, 75.0%; H, 4.6%; O, 19.6%.

3.2.10. 7-Hydroxy-2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran / Pratol (82)



According to the procedure B, the 2,4-dihydroxyacetophenone (**12c**) (2 g, 12.9 mmol) was mixed with LiOH (1.23 g, 51.5 mmol) and the 4-methoxybenzoyl chloride (**17b**) (2.42 g, 14.2 mmol). The crude product was recrystallized from ethanol to afford the 7-hydroxy-4′-methoxyflavone (**82**) as white crystals (2.11 g, Yield 61%). M.p.: 263-264°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 10.90 (br s, 1H, exchanges with D_2O, OH on C-7), 8.01-7.11 (dm, 4H, H_{Ar} B-ring), 7.87 (d, 1H, $^3J_{5,6}$ = 8.97, H-5), 7.00 (d, 1H, $^4J_{8,6}$ = 2.18, H-8), 6.93 (dd, 1H, $^3J_{6,5}$ = 8.97, $^4J_{6,8}$ = 2.18, H-6), 6.81 (s, 1H, H-3), 3.86 (s, 3H, OCH_3 on C-4′).

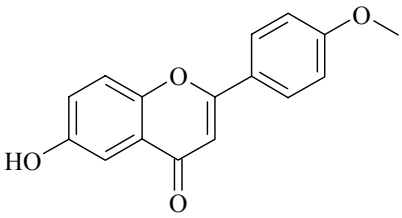
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.24 (C-4), 162.58 (C-7), 162.00 (C-2), 161.87 (C-4′), 157.37 (C-9), 127.93 (C-2′ and C-6′), 126.41 (C-5), 123.42 (C-1′), 116.07 (C-10), 114.83 (C-6), 114.48 (C-3′ and C-5′), 105.07 (C-8), 102.48 (C-3), 55.46 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 268.07356 (100), 267 (17), 253 (4), 240 (12), 225 (13), 197 (4), 168 (2), 152 (2), 139 (2), 132 (58), 120 (10), 117 (10), 108 (4), 102 (2).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 256 (9414), 323 (21766); (Figure 28, side 225).

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64%; H, 4.51%; O, 23.86%. Found: C, 67.8%, H, 5.1%, O, 27.5%.

3.2.11. 6-Hydroxy-2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran (83)



According to the Procedure A, the 2,5-dihydroxyacetophenone (**12d**) (2 g, 13.2 mmol) was mixed with LiHMDS (50 mL, 50 mmol) and the 4-methoxybenzoyl chloride (**17b**) (2.5 g, 14.5 mmol). The crude product was recrystallized from ethanol to afford the 6-hydroxy-4′-methoxyflavone (**83**) as a yellow powder (253 mg, Yield 7%). M.p.: 248-249°C.

^{1}H NMR (DMSO-d^6, 500 MHz) δ 10.08 (br s, 1H, exchanges with D_2O, OH on C-6), 8.02-7.11 (dm, 4H, H_{Ar} B-ring), 7.63 (d, 1H, $^{3}J_{8,7}$ = 8.72, H-8), 7.35 (d, 1H, $^{4}J_{5,7}$ = 2.81, H-5), 7.26 (d, 1H, $^{3}J_{7,8}$ = 8.72, $^{4}J_{7,5}$ = 2.81, H-7), 6.86 (s, 1H, H-3), 3.88 (s, 3H, OCH_3 on C-4′).

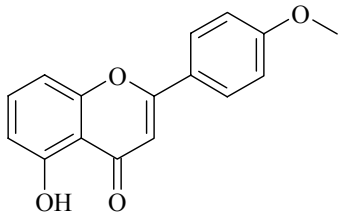
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.78 (C-4), 162.23 (C-2), 161.93 (C-4′), 154.73 (C-6), 149.24 (C-9), 127.97 (C-2′ and C-6′), 124.14 (C-1′), 123.44 (C-10), 122.77(C-7), 119.61 (C-8), 114.46 (C-3′ and C-5′), 107.52 (C-5), 104.44 (C-3), 55.43 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 268.0735 (100), 267 (12), 252 (3), 240 (2), 238 (3), 225 (6), 198 (2), 181 (1), 168 (1), 165 (1), 147 (2), 139 (3), 137 (6), 136 (66), 135 (14), 125 (1), 120 (9), 117 (10), 108 (13), 107 (6), 105 (2), 102 (1).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 278 (15096), 322 (24915); (Figure 29, side 226).

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64%; H, 4.51%; O, 23.86%. Found: C, 71.5%; H, 4.4%; O, 24.1%.

3.2.12. 5-Hydroxy-2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran (84)



According to the procedure B, the 2,6-dihydroxyacetophenone (**12e**) (1 g, 6.6 mmol) was mixed with LiOH (463 mg, 19 mmol) and the 4-methoxybenzoyl chloride (**17b**) (1.21 g, 7 mmol). The crude product was recrystallized from ethanol to afford the 5-hydroxy-4′-methoxyflavone (**84**) as a yellow powder (982 mg, Yield 57%). M.p.: 142-143°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 8.06-7.11 (dm, 4H, H_{Ar} B-ring), 7.64 (t, 1H, $^{3}J_{7,8}$ = $^{3}J_{7,6}$ = 8.64, H-7), 7.16 (d, 1H, $^{3}J_{6,7}$ = 8.64, H-6), 6.99 (s, 1H, H-3), 6.79 (d, 1H, $^{3}J_{8,7}$ = 8.64, H-8), 3.86 (s, 3H, OCH_3 on C-4′).

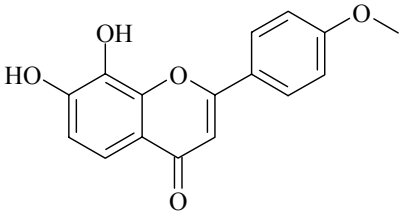
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 182.99 (C-4), 164.22 (C-2), 162.56 (C-4′), 159.87 (C-5), 155.86 (C-9), 135.72 (C-7), 128.61 (C-2′ and C-6′), 122.62 (C-1′), 114.57 (C-3′ and C-5′), 110.86 (C-6 or C-8), 109.92 (C-10), 107.45 (C-8 or C-6), 104.04 (C-3), 55.60 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 268.07355 (100), 267 (5), 253 (3), 240 (3), 238 (2), 225 (8), 197 (5), 181 (1) 167 (1), 168 (1), 152 (1), 141 (1), 136 (15), 132 (32), 127 (1), 120 (6), 117 (7), 115 (3), 108 (12), 102 (2).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 271 (15308), 321.5 (22321); (Figure 30, side 226).

Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64%; H, 4.51%; O, 23.86%. Found: C, 71.5%; H, 4.4%; O, 23.7%.

3.2.13. 7,8-Dihydroxy-2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran (85)



According to the procedure A, the 2,3,4-trihydroxyacetophenone (**12f**) (1 g, 6 mmol) was mixed with LiHMDS (24 mL, 24 mmol) and the 4-methoxybenzoyl chloride (**17b**) (1.13 g, 6.6 mmol). The crude product was recrystallized from ethanol to afford the 7,8-dihydroxy-4′-methoxyflavone (**85**) as brown crystals (94 mg, Yield 6%). M.p.: 310-312°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ ~10.3 (br s, 1H, exchanges with D_2O, OH on C-7), ~9.2 (br s, 1H, exchanges with D_2O, OH on C-8), 8.12 (d, 2H, $^3J_{2',3'} = {}^3J_{6',5'}$ = 8.81, H-2′ and H-6′), 7.1774 (AB, 2H, δ_A = 6.9495 (H-6), δ_B = 7.4054 (H-5), $^3J_{AB}$ = 8.567), 7.13 (d, 2H, $^3J_{3',2'} = {}^3J_{5',6'}$ = 8.81, H-3′ and H-5′), 6.79 (s, 1H, H-3), 3.86 (s, 3H, OCH_3 on C-4′).

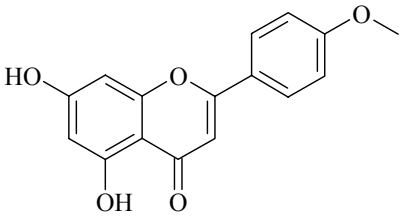
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.75 (C-4), 164.84 (C-2), 161.84 (C-4′), 150.37 (C-7), 146.52 (C-9), 132.98 (C-8), 128.12 (C-2′ and C-6′), 123.16 (C-1′), 116.86 (C-10), 115.04 (C-5), 114.38 (C-3′ and C-5′), 113.83 (C-6), 104.51 (C-3), 55.44 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 284.0685 (100), 283 (2), 256 (4), 255 (5), 241 (5), 213 (2), 153 (8), 152 (99), 134 (12), 133 (17), 132 (32), 128 (12), 124 (7), 123 (6), 118 (2), 117 (7), 106 (5), 102 (2).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 268.5 (27538), 309 (27275); (Figure 31, side 227).

Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60%, H, 4.26%, O, 28.14%. Found: C, 63.9%, H, 4.8%, O, 30.7%.

3.2.14. 5,7-Dihydroxy-2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran/Acacetin (87)



According to the procedure C, the 2,4,6-trihydroxyacetophenone (**12h**) (1 g, 5.4 mmol) was mixed with LiOH (1.03 g, 43 mmol) and the 4-methoxybenzoyl chloride (**17b**) (3.02 g, 17.7 mmol). The crude product was recrystallized from ethanol to afford the 5,7-dihydroxy-4′-methoxyflavone (**87**) as a beige powder (845 mg, Yield 55%). M.p.: 268°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.94 (s, 1H, exchanges with D_2O, OH on C-5), 10.88 (br s, 1H, exchanges with D_2O, OH on C-7), 8.02-7.09 (dm, 4H, H_{Ar} B-ring), 6.86 (s, 1H, H-3), 6.35 (AX, 2H, δ_A = 6.50 (H-6) and δ_X = 6.21 (H-8), J_{AX} = 2.06), 3.87 (s, 3H, OCH_3 on C-4′).

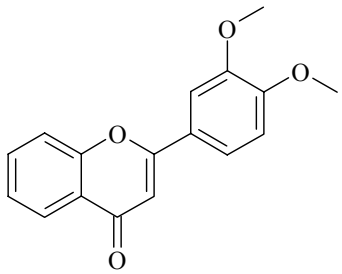
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 181.67 (C-4), 164.11 (C-7 or C-2), 163.13 (C-2 or C-7), 162.18 (C-4′), 161.35 (C-5), 157.22 (C-9), 128.18 (C-2′ and C-6′), 122.70 (C-1′), 114.44 (C-3′ and C-5′), 103.66 (C-10), 103.40 (C-6), 98.78 (C-8), 93.92 (C-3), 55.43 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 284.0685 (100), 283 (8), 269 (2), 256 (4), 255 (4), 241 (12), 213 (4), 153 (2), 152 (10), 139 (1), 135 (4), 132 (28), 128 (12), 124 (8), 117 (7), 115 (1), 111 (2), 107 (1), 102 (1).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 270 (28235), 327 (26472); (Figure 32, side 227).

Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60%; H, 4.26%; O, 28.14%. Found: C, 63.7%; H, 5.3%; O, 30.7%.

3.2.15. 2-(3,4-Dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (88)



According to the procedure A, using the 2-hydroxyacetophenone (**12a**) (2 g, 14.7 mmol) was mixed with LiHMDS (44 mL, 44 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**)

(3.24 g, 16.2 mmol). The crude product was recrystallized from ethanol to afford the 3′,4′-dimethoxyflavone (**88**) as a white powder (3.897 g, Yield 94%). M.p.: 154°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 8.04 (dd, 1H, H-5), 7.82 (d, 1H, H-7), 7.79 (d, 1H, H-8), 7.71 (dd, 1H, $^3J_{6',5'}$ = 8.81, $^4J_{6',2'}$ = 2.21, H-6′), 7.61 (d, 1H, $^4J_{2',6'}$ = 2.21, H-2′), 7.49 (m, 1H, H-6), 7.14 (d, 1H, $^3J_{5',6'}$ = 8.82, H-5′), 7.04 (s, 1H, H-3), 3.90 (s, 3H, OCH_3 on C-3′), 3.87 (s, 3H, OCH_3 on C-4′).

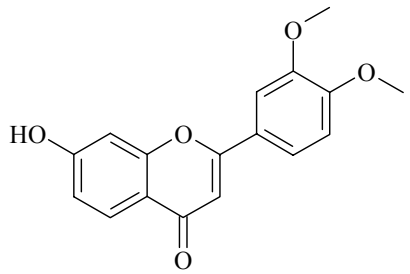
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.93 (C-4), 162.64 (C-2), 155.59 (C-9), 151.96 (C-4′), 149.02 (C-3′), 134.00 (C-7), 125.31 (C-5), 124.67 (C-6), 123.30 (C-1′ and C-10), 119.87 (C-6′), 118.43 (C-8), 111.72 (C-5′), 109.46 (C-2′), 105.71 (C-3), 55.84 (OCH_3 on C-3′), 55.70 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 282.0892 (100), 268 (1), 267 (6), 251 (2), 240 (1), 239 (6), 221 (2), 211 (4), 209 (1), 196 (3), 181 (2), 168 (4), 165 (2), 162 (14), 152 (1), 147 (6), 139 (2), 127 (6), 121 (14), 119 (5), 116 (1), 104 (1), 92 (5).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 242.5 (21693), 333.5 (23105); (Figure 33, side 228).

Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33%; H, 5.00%; O, 22.67%. Found: C, 69.6%; H, 4.7%; O, 24.7%.

3.2.16. 7-Hydroxy-2-(3,4-dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (90)



According to the procedure A, the 2,4-dihydroxyacetophenone (**12c**) (2 g, 13 mmol) was mixed with LiHMDS (40 mL, 40 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**) (2.6 g, 13 mmol). The crude product was recrystallized from ethanol to afford the 7-hydroxy-3′,4′-dimethoxyflavone (**90**) as a yellow powder (1.941 g, Yield 51 %). M.p.: 266-267°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 10.76 (br s, 1H, exchanges with D_2O, OH on C-7), 7.87 (d, 1H, $^3J_{5,6}$ = 8.82, H-5), 7.66 (dd, 1H, $^3J_{6',5'}$ = 8.82, $^4J_{6',2'}$ = 2.21, H-6′), 7.55 (d, 1H, $^4J_{2',6'}$ = 2.21, H-2′), 7.12 (d, 1H, $^3J_{5',6'}$ = 8.82, H-5′), 7.03 (d, 1H, $^4J_{8,6}$ = 2.21, H-8), 6.93 (dd, 1H, $^3J_{6,5}$ = 8.82, $^4J_{6,8}$ = 2.21, H-6), 6.88 (s, 1H, H-3), 3.84 (s, 3H, OCH_3 on C-3′), 3.81 (s, 3H, OCH_3 on C-4′).

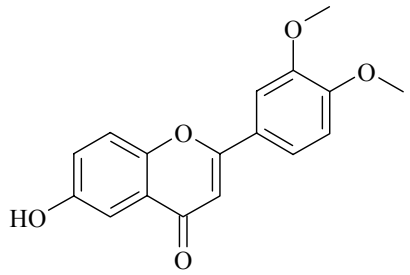
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.32 (C-4), 162.58 (C-7), 162.03 (C-2), 157.40 (C-9), 151.70 (C-4′), 148.99 (C-3′), 126.39 (C-5), 123.55 (C-1′), 119.59 (C-6′), 116.08 (C-10), 114.82 (C-6), 111.70 (C-5′), 109.33 (C-2′), 105.39 (C-8), 102.57 (C-3), 55.82 (OCH_3 on C-3′), 55.68 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 298.0841 (100), 283 (5), 269 (5), 255 (6), 253 (2), 227 (4), 226 (4), 212 (4), 199 (3), 197 (2), 184 (3), 182 (1), 165 (4), 162 (13), 158 (1), 155 (1), 147 (6), 137 (12), 135 (11), 127 (2), 119 (4), 116 (1), 112 (3), 108 (3), 105 (2), 104 (2), 101 (2).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 236.5 (27181), 332 (26809); (Figure 34, side 228).

Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.44%; H, 4.74%; O, 26.82%. Found: C, 67.4%; H, 4.9%; O, 27.9%.

3.2.17. 6-Hydroxy-2-(3,4-dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (91)



According to the procedure A, the 2,5-dihydroxyacetophenone (**12d**) (2 g, 13.2 mmol) was mixed with LiHMDS (50 mL, 50 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**) (2.9 g, 14.5 mmol). The crude product was recrystallized from ethanol to afford the 6-hydroxy-3′,4′-dimethoxyflavone (**90**) as yellow crystals (1.84 g, Yield 47%). M.p.: 226-227°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 9.92 (br s, 1H, exchanges with D_2O, OH on C-6), 7.70 (dd, 1H, $^3J_{6',5'}$ = 8.82, $^4J_{6',2'}$ = 2.21, H-6′), 7.65 (d, 1H, $^3J_{8,7}$ = 8.82, H-8), 7.57 (d, 1H, $^4J_{2',6'}$ = 2.21, H-2′), 7.32 (d, 1H, $^4J_{5,7}$ = 2.21, H-5), 7.25 (dd, 1H, $^3J_{7,8}$ = 8.82, $^4J_{7,5}$ = 2.21, H-7), 7.12 (d, 1H, $^3J_{5',6'}$ = 8.82, H-5′), 6.95 (s, 1H, H-3), 3.89 (s, 3H, OCH_3 on C-3′), 3.85 (s, 3H, OCH_3 on C-4′).

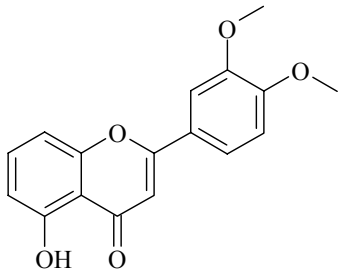
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.81 (C-4), 162.20 (C-2), 154.68 (C-6), 151.68 (C-4′), 149.21 (C-9), 148.90 (C-3′), 124.11 (C-1′), 123.50 (C-10), 122.70 (C-7), 119.69 (C-6′), 119.62 (C-8), 111.59 (C-5′), 109.23 (C-2′), 107.42 (C-5), 104.72 (C-3), 55.73 (OCH_3 on C-3′), 55.61 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 298.0841 (100), 297 (5), 284 (2), 283 (7), 267 (2), 255 (7), 240 (1), 238 (2), 227 (1), 225 (1), 212 (4), 198 (1), 184 (3), 165 (3), 163 (6), 162 (45), 149 (4), 147 (11), 137 (12), 136 (13), 135 (10), 128 (1), 119 (7), 116 (1), 108 (4), 107 (3), 103 (1), 101 (2).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 249.5 (17000), 277 (13454), 331 (26065); (Figure 35, side 229).

Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45%; H, 4.73%; O, 26.82%. Found: C, 67.2%; H, 4.8%; O, 27.8%.

3.2.18. 5-Hydroxy-2-(3,4-dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (92)



According to the procedure B, the 2,6-dihydroxyacetophenone (**12e**) (1 g, 6.4 mmol) was mixed with LiOH (463 mg, 19 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**) (1.45 g, 7.2 mmol). The crude product was recrystallized from ethanol to afford the 5-hydroxy-3′,4′-dimethoxyflavone (**92**) as a beige powder (1.74 g, Yield 89%). M.p.: 163-164°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.77 (s, 1H, exchanges with D_2O, OH on C-5), 7.71 (dd, 1H, $^3J_{6',5'}$ = 9.26, $^4J_{6',2'}$ = 2.65, H-6′), 7.66 (t, 1H, $^3J_{7,6}$ = $^3J_{7,8}$ = 9.26, H-7), 7.59 (d, 1H, $^4J_{2',6'}$ = 2.65, H-2′), 7.18 (d, 1H, $^3J_{6,7}$ = 9.26, H-6), 7.12 (d, 1H, $^3J_{5',6'}$ = 9.26, H-5′), 7.10 (s, 1H, H-3), 6.78 (d, 1H, $^3J_{8,7}$ = 9.26), 3.89 (s, 3H, OCH_3 on C-3′), 3.83 (s, 3H, OCH_3 on C-4′).

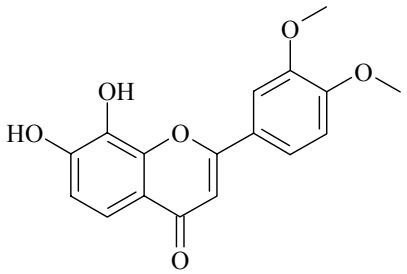
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 182.99 (C-4), 164.13 (C-2), 159.76 (C-9), 155.73 (C-5), 152.31 (C-4′), 148.93 (C-3′), 135.61 (C-7), 122.56 (C-1′), 120.26 (C-6′), 111.57 (C-5′), 110.77 (C-6 or C-8), 109.88 (C-10), 109.43 (C-2′), 107.39 (C-8 or C-6), 104.23 (C-3), 55.77 (OCH_3 on C-3′), 55.66 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 298.0841 (100), 297 (2), 283 (2), 282 (3), 268 (1), 255 (5), 253 (3), 240 (4), 237 (3), 227 (2), 225 (2), 212 (2), 197 (1), 184 (1), 163 (2), 162 (11), 149 (3), 147 (5), 137 (20), 136 (4), 135 (4), 128 (2), 119 (4), 114 (1), 108 (5), 105 (1), 101 (1).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 248 (23348), 269 (12768), 342 (26585); (Figure 36, side 229).

Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45%; H, 4.73%; O, 26.82%. Found: C, 68.0%; H, 4.6%; O, 26.7%.

3.2.19. 7,8-Dihydroxy-2-(3,4-dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (93)



According to the procedure A, the 2,3,4-trihydroxyacetophenone (**12f**) (1 g, 5.94 mmol) was mixed with LiHMDS (24 mL, 24 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**) (1.42 g, 6.6 mmol). The crude product was recrystallized from ethanol to afford the 7,8-dihydroxy-3′,4′-dimethoxyflavone (**93**) as a brown powder (377 mg, Yield 20%). M.p.: 266-267°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 10.19 (br s, 1H, exchanges with D_2O, OH on C-7), 9.42 (br s, 1H, exchanges with D_2O, OH on C-8), 7.84 (dd, 1H, $^{3}J_{6',5'}$ = 8.82, $^{4}J_{6',2'}$ = 2.21, H-6′), 7.64 (d, 1H, $^{4}J_{2',6'}$ = 2.21, H-2′), 7.171 (AB, 2H, δ_A = 6.9399 (H-6), δ_B = 7.4020 (H-5), $^{3}J_{AB}$ = 8.254), 7.17 (d, 1H, $^{3}J_{5',6'}$ = 8.82, H-5′), 6.87 (s, 1H, H-3), 3.88 (s, 3H, OCH_3 on C-3′), 3.85 (s, 3H, OCH_3 on C-4′).

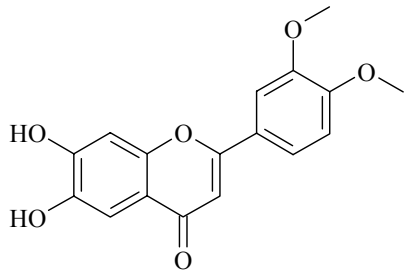
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.78 (C-4), 161.84 (C-2), 151.69 (C-4′), 150.47 (C-7), 148.92 (C-3′), 146.63 (C-9), 132.90 (C-8), 123.77 (C1′), 119.90 (C-6′), 116.86 (C-10), 115.10 (C-5), 113.84 (C-6), 111.67 (C-5′), 109.59 (C-2′), 104.89 (C-3), 55.84 (OCH_3 on C-3′), 55.67 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 314.0790 (100), 313 (2), 299 (3), 285 (7), 284 (1), 271 (2), 257 (1), 243 (2), 228 (3), 215 (1), 208 (3), 200 (1), 172 (1), 165 (4), 163 (11), 162 (65), 153 (7), 152 (43), 148 (3), 147 (11), 143 (10), 133 (2), 124 (4), 123 (6), 121 (2), 120 (2), 119 (5), 118 (1), 117 (1), 112 (2), 106 (4), 101 (3).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 269 (24816), 331 (24959); (Figure 37, side 230).

Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.96%; H, 4.50%; O, 30.54%. Found: C, 64.1%; H, 4.90%; O, 29.9%.

3.2.20. 6,7-Dihydroxy-2-(3,4-dimethoxyphenyl)- 4-oxo-4*H*-1-benzopyran (94)



According to the procedure A, using the 2,4,5-trihydroxyacetophenone (**12i**) (1 g, 5.7 mmol) was mixed with LiHMDS (22.6 mL, 22.6 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**) (1.27 g, 6.22 mmol). The product was separated by flash chromatography eluted with dichloromethane / methanol (39:1, 29:1 and 19:1) to afford the 6,7-dihydroxy-3′,4′-dimethoxyflavone (**94**) as white crystals (430 mg, Yield 24%). M.p.: 185-186°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ~10.50 (very br s, 2H, exchanges with D_2O, OH on C-6 and C-7), 7.54 (d, 1H, $^{3}J_{5',6'}$ = 9.54, H-5′), 7.31 (d, 1H, $^{4}J_{2',6'}$ = 2.14, H-2′), 7.23 (dd, $^{3}J_{6',5'}$ = 9.54, $^{4}J_{6',2'}$ = 2.14, H-6′), 7.14 (s, 1H, H-5), 7.00 (s, 1H, H-3), 6.86 (s, 1H, H-8), 3.90 (s, 3H, OCH_3 on C-3′), 3.86 (s, 3H, OCH_3 on C-4′).

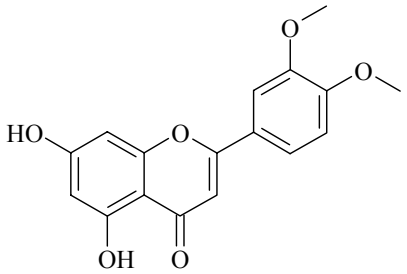
^{13}C NMR (DMSO-d^6, 75.46 MHz) δ176.86 (C-4), 162.63 (C-2), 157.59 (C-7), 151.83 (C-4′), 148.80 (C-3′), 146.17 (C-9), 144.19 (C-6), 127.98 (C-1′), 122.86 (C-10), 120.01 (C-6′), 119.66 (C-5), 116.80 (C-5′), 114.24 (C-2′), 107.44 (C-8), 104.93 (C-3), 55.61 (OCH_3 on C-3′), 55.48 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 314.0790 (100), 313 (5), 299 (8), 286 (2), 285 (6), 284 (2), 267 (6), 255 (1), 253 (1), 243 (3), 241 (2), 228 (4), 215 (2), 200 (2), 174 (1), 165 (4), 163 (6) 162 (46), 158 (2), 153 (8), 152 (11), 147 (11), 144 (3), 143 (10), 135 (2), 126 (2), 124 (2), 123 (2), 122 (2), 121 (2), 120 (2), 119 (6), 118 (1), 117 (1), 113 (1), 107 (2), 104 (1), 101 (2).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 259 (21312), 309 (12592); (Figure 38, side 230).

Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.97%; H, 4.49%; O, 30.54%. Found: C, 58.3%; H, 5.2%; O, 35.9%.

3.2.21. 5,7-Dihydroxy-2-(3,4-dimethoxyphenyl)- 4-oxo-4*H*-1-benzopyran/Luteolin 3′,4′-dimethyl ether (95)



According to the procedure B, the 2,4,6-trihydroxyacetophenone (**12h**) (2 g, 10.5 mmol) was mixed with LiOH (1.27 g, 53 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**) (2.2 g, 11 mmol). The crude product was recrystallized from ethanol to afford the 5,7-dihydroxy-3′,4′-dimethoxyflavone (**95**) as a beige powder (960 mg, Yield 29%). M.p.: 269-270°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.90 (s, 1H, exchanges with D_2O, OH on C-5), ~10.8 (s, 1H, exchanges with D_2O, OH on C-7), 7.68 (dd, 1H, $^3J_{6',5'}$ = 8.82, $^4J_{6',2'}$ = 2.21, H-6′), 7.57 (d, 1H, $^4J_{2',6'}$ = 2.21, H-2′), 7.12 (d, 1H, $^3J_{5',6'}$ = 8.82, H-5′), 6.90 (s, 1H, H-3), 6.33 (AX, 2H, δ_A = 6.4935 (H-6) and δ_X = 6.1675 (H-8), $^4J_{AX}$ = 1.32), 3.77 (s, 6H, OCH_3 on C-3′ and C-4′).

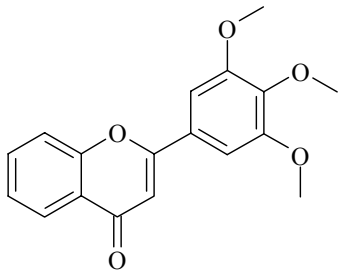
^{13}C NMR (DMSO-d^6, MHz) δ 181.75 (C-4), 164.15 (C-7 or C-2), 163.24 (C-2 or C-7), 161.35 (C-5), 157.05 (C-9), 152.05 (C-4′), 148.93 (C-3′), 122.82 (C-1′), 119.96 (C-6′), 111.60 (C-5′), 109.35 (C-2′), 103.77 (C-3), 94.03 (C-8), 55.77 (OCH_3 on C-3′), 55.66 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 314.0790 (100), 299 (1), 285 (4), 271 (5), 269 (2), 262 (1), 256 (2), 254 (1), 243 (1), 241 (1), 228 (3), 207 (2), 195 (2), 182 (5), 163 (3), 162 (8), 153 (17), 147 (5), 143 (5), 124 (5), 123 (4), 119 (5), 115 (2), 111 (2), 101 (1).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 270 (17492), 341 (18622); (Figure 39, side 231).

Anal. Calcd for $C_{17}H_{14}O_6$: C, 64.96%; H, 4.50%; O, 30.54%. Found: C, 64.3%; H, 4.8%; O, 30.9%.

3.2.22. 2-(3,4,5-Trimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (96)



According to the procedure C, the 2-hydroxyacetophenone (**12a**) (2 mL, 16.3 mmol) was mixed with LiOH (2.39 g, 98 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (4.21 g, 18 mmol). The crude product was recrystallized from ethanol to afford the 3′,4′,5′-trimethoxyflavone (**96**) as a white powder (1.182 g, Yield 23%). M.p.: 177-178°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 8.0 (d, 1H, *J*= 9, H-5), 7.78 (m, 2H, H-7 and H-8), 7.45 (m, 1H, H-6), 7.34 (s, 2H, H-2′ and H-6′), 7.1 (s, 1H, H-3), 3.88 (s, 6H, OCH_3 on C-3′ and C-5′), 3.72 (s, 3H, OCH_3 on C-4′).

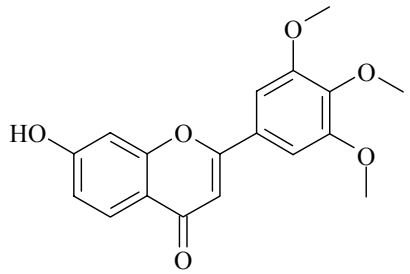
^{13}C NMR (DMSO-d^6, 75,47 MHz) δ 177.04 (C-4), 162.27 (C-2), 155.54 (C-9), 153.14 (C-3′ and C-5′), 140.44 (C-4′), 134.05 (C-7), 126.32 (C-1′), 125.38 (C-5), 124.62 (C-6), 123.17 (C-10), 118.56 (C-8), 106.73 (C-2′ and C-6′), 103.92 (C-3), 60.11 (OCH_3 on C-4′), 56.16 (OCH_3 on C-3′ and C-5′).

EI-MS *m/z* (% relative abundance) composition: 312.0998 (100), 298 (7), 297 (28), 296 (3), 282 (2), 270 (3), 269 (13), 254 (3), 252 (4), 241 (4), 239 (7), 237 (2), 226 (4), 211 (4), 209 (5), 198 (2), 197 (2), 195 (2), 193 (2), 183 (6), 181 (2), 177 (4), 168 (2), 165 (2), 156 (1), 155 (8), 149 (5), 142 (10), 134 (5), 127 (7), 121 (12), 119 (5), 112 (2), 106 (2), 101 (2).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 240 (17050), 357 (19871); (Figure 40, side 231).

Anal. Calcd for $C_{18}H_{16}O_5$: C, 67.60%; H, 4.26%; O, 28.14%. Found: C, 66.5%; H, 4.9%; O, 27.1%.

3.2.23. 7-Hydroxy-2-(3,4,5-trimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (98)



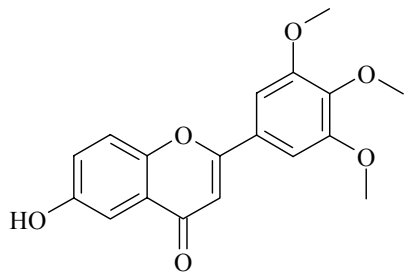
According to the procedure A, the 2,4-dihydroxyacetophenone (**12c**) (1 g, 6.4 mmol) was mixed with LiHMDS (20 mL, 20 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.7 g, 7.1 mmol). The crude product was recrystallized from ethanol to afford the 7-hydroxy-3′,4′,5′-trimethoxyflavone (**98**) as yellow crystals (300 mg, Yield 14%).

^{1}H NMR (DMSO-d^6, 500 MHz) δ 10.75 (s, 1H, exchanges with D_2O, OH on C-7), 7.88 (d, 1H, $^{3}J_{5,6}$ = 8.70, H-5), 7.33 (s, 2H, H-2′ and H-6′), 7.08 (d, 1H, $^{4}J_{8,6}$ = 2.25, H-8), 6.99 (s, 1H, H-3), 6.94 (dd, 1H, $^{3}J_{6,5}$ = 8.69, $^{4}J_{6,8}$ = 2.28, H-6), 3.91 (s, 6H, OCH_3 on C-3′ and C-5′), 3.76 (s, 3H, OCH_3 on C-4′).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.40 (C-4), 162.64 (C-2), 161.76 (C-7), 157.43 (C-9), 153.21 (C-3′ and C-5′), 140.44 (C-4′), 126.42 (C-5), 126.16 (C-1′), 114.76 (C-10), 107.30 (C-6), 106.52 (C-8), 103.53 (C-2′ and C-6′), 102.72 (C-3), 60.16 (OCH_3 on C-4′), 56.26 (OCH_3 on C-3′ and C-5′).

EI-MS *m/z* (% relative abundance) composition: 328.0946 (100), 313 (28), 299 (5), 285 (8), 266 (2), 264 (2), 257 (6), 255 (3), 243 (2), 226 (3), 225 (4), 214 (2), 199 (2), 196 (4), 195 (34), 177 (3), 171 (6), 170 (1), 165 (3), 151 (9), 149 (3), 137 (11), 135 (8), 134 (3), 120 (5), 119 (4), 114 (2), 107 (3), 101 (1).

3.2.24. 6-Hydroxy-2-(3,4,5-trimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (99)



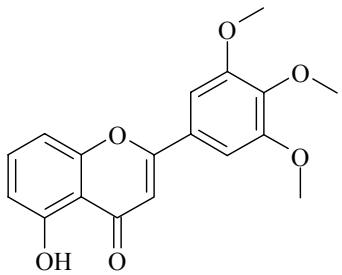
According to the procedure A, the 2,5-dihydroxyacetophenone (**12d**) (1 g, 6.4 mmol) was mixed with LiHMDS (20 mL, 20 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.7 g, 7.1 mmol). The crude product was recrystallized from ethanol to afford the 6-hydroxy-3′,4′,5′-trimethoxyflavone (**99**) as brown crystals (263 mg, Yield 13%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ 9.98 (br s, 1H, exchanges with D_2O, OH on C-6), 7.69 (d, 1H, $^{3}J_{8,7}$ = 8.96, H-8), 7.35 (s, 2H, H-2′ and H-6′), 7.32 (d, 1H, $^{4}J_{5,7}$ = 2.90, H-5), 7.25 (dd, 1H, $^{3}J_{7,8}$ = 8.95, $^{4}J_{7,5}$ = 3.03, H-7), 7.04 (s, 1H, H-3), 3.91 (s, 6H, OCH_3 on C-3′ and C-5′), 3.76 (s, 3H, OCH_3 on C-4′).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.96 (C-4), 161.98 (C-2), 154.82 (C-6), 153.21 (C-3′ and C-5′), 149.30 (C-9), 140.44 (C-4′), 126.67 (C-1′), 124.15 (C-10), 122.88 (C-7), 119.89 (C-8), 107.44 (C-5), 105.82 (C-2′ and C-6′), 103.99 (C-3), 60.16 (OCH_3 on C-4′), 56.25 (OCH_3 on C-3′ and C-5′).

EI-MS *m/z* (% relative abundance) composition: 328.0946 (100), 327 (2), 314 (9), 313 (38), 286 (3), 285 (15), 270 (3), 268 (3), 257 (3), 255 (5), 242 (3), 239 (1), 226 (3), 225 (4), 213 (1), 199 (3), 195 (1), 192 (8), 178 (1), 177 (10), 171 (4), 164 (5), 150 (4), 149 (6), 142 (2), 137 (12), 135 (6), 134 (4), 127 (2), 121 (2), 120 (2), 119 (4), 117 (2), 115 (1), 107 (3), 106 (2), 101 (1).

3.2.25. 5-Hydroxy-2-(3,4,5-trimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (100)



According to the procedure A and procedure C, the 2,6-dihydroxyacetophenone (**12e**) (1 g, 6.4 mmol) was mixed respectively with LiHMDS (20 mL, 20 mmol) and LiOH (944 mg, 39 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.7 g, 7.1 mmol). The crude product was recrystallized from ethanol to afford the 5-hydroxy-3′,4′,5′-trimethoxyflavone (**100**) as yellow crystals (A: 1.23 g, Yield 58%; C: 762 mg, Yield 36%). M.p.: 197-198°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.69 (s, 1H, exchanges with D_2O, OH on C-5), 7.69 (t, 1H, $^{3}J_{7,6}$ = $^{3}J_{7,8}$ = 8.38, H-7), 7.41 (s, 2H, H-2′ and H-6′), 7.25 (d, 1H, $^{3}J_{6,7}$ = 8.82, H-6), 7.22 (s, 1H, H-3), 6.82 (d, 1H, $^{3}J_{8,7}$ = 8.82, H-8), 3.92 (s, 6H, OCH_3 on C-3′ and C-5′), 3.78 (s, 3H, OCH_3 on C-4′).

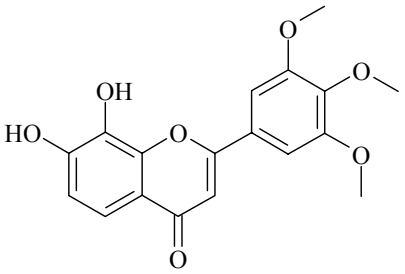
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 183.19 (C-4), 163.91 (C-2), 159.79 (C-9), 155.84 (C-5), 153.25 (C-3′ and C-5′), 141.10 (C-4′), 135.80 (C-7), 125.72 (C-1′), 110.92 (C-8 or C-6), 110.03 (C-10), 107.64 (C-6 or C-8), 105.49 (C-2′ and C-6′), 104.42 (C-3), 60.20 (OCH_3 on C-4′), 56.33 (OCH_3 on C-3′ and C-5′).

EI-MS *m/z* (% relative abundance) composition: 328.0946 (100), 313 (11), 314 (2), 315 (1), 299 (3), 298 (1), 285 (7), 271 (1), 270 (7), 268 (3), 255 (5), 253 (3), 242 (3), 240 (1), 227 (2), 225 (4), 213 (1), 199 (4), 197 (2), 195 (1), 178 (1), 177 (3), 171 (6), 164 (4), 155 (1), 150 (3), 149 (4), 142 (1), 137 (17), 135 (5), 127 (4), 119 (4), 115 (2), 108 (4), 105 (1), 100 (1).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 273.5 (12648), 329 (17750); (Figure 41, side 232).

Anal. Calcd for $C_{18}H_{16}O_6$: C, 67.60%; H, 4.26%; O, 28.14%. Found: C, 65.4%; H, 4.9%; O, 29.6%.

3.2.26. 7,8-Dihydroxy-2-(3,4,5-trimethoxyphenyl)-4-oxo-*4H*-1-benzopyran (101)



According to the procedure A, the 2,3,4-trihydroxyacetophenone (**12f**) (1 g, 6 mmol) was mixed with LiHMDS (24 mL, 24 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.51 g, 6.6 mmol). The crude product was recrystallized from ethanol to afford the 7,8-dihydroxy-3′,4′,5′-trimethoxyflavone (**101**) as yellow crystals (202 mg, Yield 10%). M.p.: 277-278°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 10.48 (br s, 1H, exchanges with D_2O, OH on C-7), 9.55 (br s, 1H, exchanges with D_2O, OH on C-8), 7.42 (s, 2H, H-2′ and H-6′), 7.15 (AB, 2H, δ_A = 7.41 (H-5) and δ_B = 6;95 (H-6), $^3J_{AB}$ = 8.65), 6.97 (s, 1H, H-3), 3.90 (s, 6H, OCH_3 on C-3′ and C-5′), 3.75 (s, 3H, OCH_3 on C-4′).

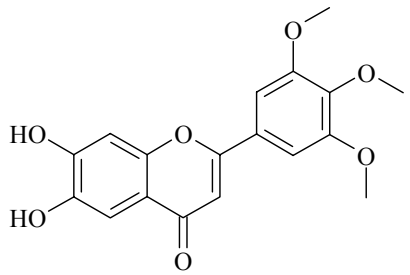
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.85 (C-4), 161.59 (C-2), 153.13 (C-3′ and C-5′), 150.74 (C-7), 146.71 (C-9), 140.39 (C-4′), 132.84 (C-8), 126.83 (C-1′), 116.80 (C-5), 115.19 (C-10), 114.03 (C-6), 106.05 (C-2′ and C-6′), 104.27 (C-3), 60.16 (OCH_3 on C-4′), 56.28 (OCH_3 on C-3′ and C-5′).

EI-MS *m/z* (% relative abundance) composition: 344.0896 (100), 343 (2), 330 (7), 329 (27), 315 (5), 301 (4), 286 (1), 284 (1), 273 (3), 271 (2) 269 (1), 258 (1), 243 (2), 241 (2), 215 (1), 195 (2), 193 (4), 192 (18), 187 (2), 178 (3), 177 (10), 172 (1), 162 (1), 159 (1), 158 (6), 153 (6), 152 (11), 149 (4), 143 (4), 137 (2), 135 (1), 134 (2), 128 (3), 123 (3), 119 (3), 117 (1), 115 (2), 106 (2), 100 (1).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 270.5 (22834), 309.5 (22395); (Figure 42, side 232).

Anal. Calcd for $C_{18}H_{16}O_7$: C, 62.79 %; H, 4.68 %; O, 32.53 %. Found: C, 62.3%; H, 5.0%; O, 31.8%.

3.2.27. 6,7-Dihydroxy-2-(3,4,5-trimethoxyphenyl)-4-oxo-*4H*-1-benzopyran / Prosogerin E (102)



According to the procedure A, the 2,4,5-trihydroxyacetophenone (**12i**) (1 g, 6 mmol) was mixed with LiHMDS (24 mL, 24 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.55 g, 6.6 mmol). The crude product was recrystallized from ethanol to afford the 6,7-dihydroxy-3′,4′,5′-trimethoxyflavone (**102**) as yellow crystals (361 mg, Yield 18%). M.p.: 253-254°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 7.29 (s, 1H, H-5), 7.27 (s, 2H, H-2′ and H-6′), 7.07(s, 1H, H-8), 6.90 (s, 1H, H-3), 3.88 (s, 6H, OCH_3 on C-3′ and C-5′), 3.73 (s, 3H, OCH_3 on C-4′).

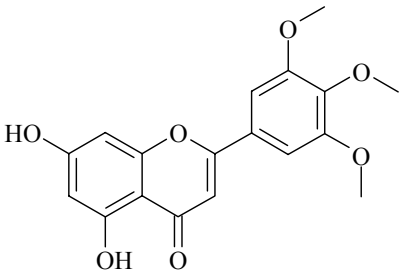
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.18 (C-4), 161.21 (C-2), 153.14 (C-3′ and C-5′), 152.19 (C-7), 150.72 (C-9), 144.52 (C-6), 140.05 (C-4′), 126.90 (C-1′), 115.99 (C-10), 107.46 (C-5), 105.82 (C-8), 103.66 (C-2′ and C-6′), 103.29 (C-3), 60.12 (OCH_3 on C-4′), 56.18 (OCH_3 on C-3′ and C-5′).

EI-MS *m/z* (% relative abundance) composition: 344.0896 (100), 343 (1), 330 (8), 329 (31), 328 (1), 315 (7), 314 (6), 302 (2), 301 (8), 286 (2), 284 (2), 273 (5), 271 (4), 269 (3), 258 (2), 255 (1), 243 (3), 242 (2), 241 (4), 215 (2), 213 (1), 195 (1), 193 (1), 192 (8), 187 (4), 177 (11), 162 (2), 158 (8), 153 (9), 152 (4), 149 (6), 143 (7) 137 (2), 135 (3), 134 (4), 132 (2), 128 (4), 121 (2), 119 (5), 117 (2), 115 (3), 107 (3), 106 (2), 101 (1), 100 (1).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 281 (8267), 324 (16036); (Figure 43, side 233).

Anal. Calcd for $C_{18}H_{16}O_7$: C, 62.79 %; H, 4.68 %; O, 32.53 %. Found: C, 51.0%; H, 4.9%; O, 37.6%.

3.2.28. 5,7-Dihydroxy-2-(3,4,5-trimethoxyphenyl)-4-oxo-4*H*-1-benzopyran (103)



According to the procedure C, the 2,4,6-trihydroxyacetophenone (**12h**) (1 g, 5.3 mmol) was mixed with LiOH (1.03 g, 42 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (4.13 g, 17.4 mmol). The crude product was recrystallized from ethanol to afford the 5,7-dihydroxy-3′,4′,5′-trimethoxyflavone (**103**) as a white powder (808 mg, Yield 45%). M.p.: 272-273°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.83 (s, 1H, exchanges with D_2O, OH on C-5), 10.87 (br s, 1H, exchanges with D_2O, OH on C-7), 7.30 (s, 2H, H-2′ and H-6′), 7.04 (s, 1H, H-3), (AX, 2H, δ_A = 6.54 (H-6), δ_X = 6.19 (H-8), J_{AX} = 2.65), 3.85 (s, 6H, OCH_3 on C-3′ and C-5′), 3.71 (s, 3H, OCH_3 on C-4′).

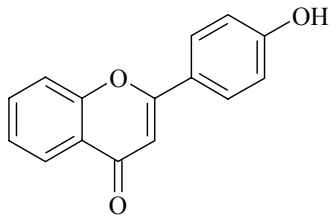
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 181.80 (C-4), 164.28 (C-7 or C-2), 162.90 (C-2 or C-7), 161.30 (C-5), 157.30 (C-9), 153.13 (C-3′ and C-5′), 140.58 (C-4′), 125.29 (C-1′), 104.92 (C-3), 103.97 (C-2′ and C-6′), 103.73 (C-10), 98.87 (C-6), 94.22 (C-8), 60.12 (OCH_3 on C-4′), 56.18 (OCH_3 on C-3′ and C-5′).

EI-MS *m/z* (% relative abundance) composition: 344.0896 (100), 330 (3), 329 (17), 316 (1), 315 (5), 314 (2), 301 (6), 300 (1), 286 (4), 285 (1), 284 (4), 273 (4), 271 (3), 269 (2), 258 (2), 255 (1), 243 (5), 241 (6), 230 (1), 215 (2), 213 (1), 187 (5), 178 (2), 172 (3), 158 (8), 153 (14), 149 (3), 143 (7), 135 (4), 134 (2), 128 (4), 124 (4), 119 (3), 115 (3), 108 (1), 100 (1).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 272 (15405), 328.5 (14858); (Figure 44, side 233).

Anal. Calcd for $C_{18}H_{16}O_7$: C, 62.78%; H, 4.69%; O, 32.53%. Found: C, 62.5%; H, 4.7%; O, 32.1%.

3.2.29. 2-(4-Hydroxyphenyl)-4-oxo-4*H*-1-benzopyran (104)



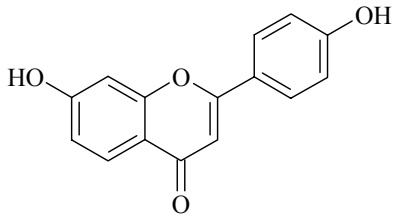
According to the procedure of demethylation for flavonoids, the 4′-methoxyflavone (**80**) (73 mg, 0.281 mmol) was mixed with boron tribromide (1 mL, 1 mmol) to afford the 4′-hydroxyflavone (**104**) as light yellow powder (454 mg, Yield 99%).

^{1}H NMR (DMSO-d^6, 300 MHz) δ ~9.70 (br s, 1H, exchanges with D_2O, OH on C-4′), 8.04 (dd, 1H, $^3J_{5,\,6}$ = 7.94, $^4J_{5,\,7}$ = 1.59, H-5), 7.95-6.95 (dm, 4H, supposed as a AA′XX′ system, H_{Ar} of B-ring), 7.76 (m, 2H, H-6 and H-8), 7.47 (td, 1H, $^3J_{7,\,6}$ = $^3J_{7,\,8}$ = 6.87, $^4J_{7,\,5}$ = 1.59, H-7), 6.86 (s, 1H, H-3).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.78 (C-4), 167.05 (C-2), 160.89 (C-4′), 155.53 (C-9), 135.89 (C-1′), 133.90 (C-7), 131.41 (C-5), 128.26 (C-2′ and C-6′), 124.65 (C-6), 123.25 (C-10), 118.24 (C-8), 115.89 (C-3′ and C-5′), 104.76 (C-3).

EI-MS *m/z* (% relative abundance) composition: 238.06 $[C_{15}H_{10}O_3]^{+\cdot}$ (100), 237 (26), 224 (1), 221 (20), 211 (1), 210 (20), 209 (5), 182 (1), 181 (8), 165 (1), 153 (1), 152 (6), 132 (10), 127 (1), 122 (4), 121 (51), 118 (21), 112 (1), 105 (15), 92 (20), 89 (11), 87 (1), 82 (3), 76 (5), 74 (2), 65 (6), 63 (14), 51 (3), 44 (1), 39 (4).

3.2.30. 7-Hydroxy-2-(4-hydroxyphenyl)-4-oxo-4*H*-1-benzopyran (106)



According to the procedure of demethylation for flavonoids, the 7-hydroxy-4′-methoxyflavone (**82**) (500 mg, 1.553 mmol) was mixed with boron tribromide (5 mL, 5 mmol) to afford the 7,4′-dihydroxyflavone (**106**) as beige crystals (400 mg, Yield 99%). M.p.: 324-325°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 10.78 (br s, 1H, exchanges with D_2O, OH on C-7), 10.28 (br s, 1H, exchanges with D_2O, OH on C-4′), 7.4251 (AB, 4H, δ_A = 7.91183 (H-3′ and H-5′) and δ_B = 6.9318 (H-2′ and H-6′), J_{AB} = 9.5229), 7.87 (d, 1H, $^3J_{5,\,6}$ = 9.25, H-5), 6.98 (d, 1H, $^4J_{8,\,6}$ = 2.21, H-8), 6.72 (s, 1H, H-3).

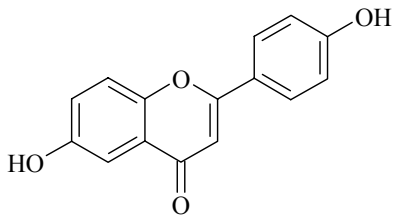
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.19 (C-4), 162.43 (C-7), 162.33 (C-2), 160.58 (C-4′), 157.27 (C-9), 128.02 (C-2′ and C-6′), 126.36 (C-5), 121.68 (C-1′), 116.01 (C-10), 115.78 (C-3′ and C-5′), 114.67 (C-6), 104.37 (C-3), 102.37 (C-8).

EI-MS *m/z* (% relative abundance) composition: 254.0579 (100), 253 (27), 237 (3), 227 (4), 226 (35), 225 (9), 197 (4), 168 (2), 151 (2), 139 (2), 138 (4), 137 (44), 136 (7), 121 (3), 118 (24), 113 (16), 108 (9), 98 (2), 95 (3), 89 (6), 84 (2), 80 (4), 72 (1), 69 (4), 63 (6), 53 (3), 51 (5), 39 (5).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 231 (24326), 254 (13137), 313 sh (28121), 329 (32096); (Figure 46, side 234).

Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86%; H, 3.96%; O, 25.17%. Found: C, 69.1%; H, 3.8%; O, 24.5%.

3.2.31. 6-Hydroxy-2-(4-hydroxyphenyl)-4-oxo-4*H*-1-benzopyran (107)



According to the procedure of demethylation for flavonoids, the 6-hydroxy-4′-methoxyflavone (**83**) (300 mg, 1.12 mmol) was mixed with boron tribromide (3 mL, 3 mmol) to afford the 6,4′-dihydroxyflavone (**107**) as white powder (216 mg, Yield 76%). M.p.: 340°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 10.17 (br s, 2H, exchanges with D_2O, OH on C-6 and C-4′), 7.4251 (AB, 4H, δ_A = 7.91183 (H-3′ and H-5′) and δ_B = 6.9318 (H-2′ and H-6′), J_{AB} = 9.5229), 7.61 (d, 1H, $^3J_{8,7}$ = 9.52, H-8), 7.34 (d, 1H, $^4J_{5,7}$ = 2.21, H-5), 7.18 (dd, 1H, $^3J_{7,8}$ = 9.52, $^4J_{7,5}$ = 2.21, H-7), 6.79 (s, 1H, H-3).

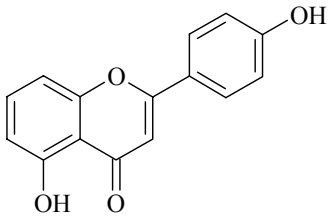
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.70 (C-4), 162.59 (C-2), 160.68 (C-4′), 154.62 (C-6), 149.14 (C-9), 128.10 (C-2′ and C-6′), 124.10 (C-10), 122.62 (C-7), 121.74 (C-1′), 119.53 (C-8), 115.81 (C-3′ and C-5′), 107.45 (C-5), 103.80 (C-3).

EI-MS *m/z* (% relative abundance) composition: 254.0579 (100), 253 (13), 237 (2), 226 (5), 225 (3), 197 (3), 139 (2), 137 (35), 136 (78), 135 (4), 121 (2), 119 (4), 118 (14), 113 (9), 108 (12), 107 (3), 99 (1), 89 (5), 86 (1), 82 (4), 80 (10), 76 (1), 65 (2), 63 (6), 54 (2), 52 (11), 39 (3).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 228 (23068), 277 (14805), 328 (30971); (Figure 47, side 235).

Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86%; H, 3.96%; O, 25.17%. Found: C, 70.4%; H, 4.0%; O, 25.4%.

3.2.32. 5-Hydroxy-2-(4-hydroxyphenyl)-4-oxo-4*H*-1-benzopyran (108)



According to the procedure of demethylation for flavonoids, the 5-hydroxy-4′-methoxyflavone (**84**) (500 mg, 1.86 mmol) was mixed with boron tribromide (5 mL, 5 mmol) to afford the 5,4′-dihydroxyflavone (**108**) as yellow powder (388 mg, Yield 82%).M.p.: 239-240°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.83 (s, 1H, exchanges with D_2O, OH on C-5), 10.45 (s, 1H, exchanges with D_2O, OH on C-4′), 7.4565 (AB, 4H, δ_A = 7.9275 (H-3′ and H-5′) and δ_B = 6.9538 (H-2′ and H-6′), $^3J_{AB}$ = 9.5229), 7.64 (t, 1H, $^3J_{7,6} = {}^3J_{7,8}$ = 9.52, H-7), 7.14 (d, 1H, $^3J_{6,7}$ = 9.52, H-6), 6.93 (s, 1H, H-3), 6.78 (d, 1H, $^3J_{8,7}$ = 9.52, H-8).

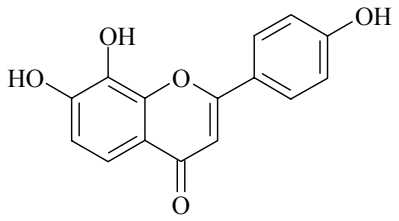
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 182.85 (C-4), 163.54 (C-2), 161.40 (C-5), 159.78 (C-4′), 155.67 (C-9), 135.51 (C-7), 128.67 (C-2′ and C-6′), 120.85 (C-1′), 115.91 (C-3′ and C-5′), 110.72 (C-8 or C-6), 109.82 (C-10), 107.22 (C-6 or C-8), 103.24 (C-3).

EI-MS *m/z* (% relative abundance) composition: 254.0579 (100), 253 (10), 237 (1), 226 (6), 225 (3), 197 (3), 138 (2), 137 (19), 136 (18), 121 (3), 119 (5), 118 (11), 103 (10), 109 (2), 108 (17), 91 (2), 89 (4), 80 (3), 77 (2), 65 (2), 63 (4), 52 (4), 50 (1), 41 (2), 39 (5).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 271 (10935), 334 (18456); (Figure 48, side 235).

Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86%; H, 3.96%; O, 25.17%. Found: C, 68.4%; H, 3.9%; O, 28.4%.

3.2.33. 7,8-Dihydroxy-2-(4-hydroxyphenyl)-4-oxo-4*H*-1-benzopyran (109)



According to the procedure of demethylation for flavonoids, the 7,8-dihydroxy-4′-methoxyflavone (**85**) (30 mg, 0.1 mmol) was mixed with boron tribromide (1 mL, 1 mmol) to afford the 7,8,4′-trihydroxyflavone (**109**) as pale yellow fine crystals (25 mg, Yield 93%). M.p.: 310-312°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 10.04 (br s, 1H, exchanges with D_2O, OH on C-4′), 7.5143 (AB, 4H, δ_A = 8.0881 (H-3′ and H-5′) and δ_B = 6.9406 (H-2′ and H-6′), $^3J_{AB}$ = 9.52), 7.1686 (AB, 2H, δ_A = 7.3966 (H-6) and δ_B = 6.9406 (H-5), $^3J_{AB}$ = 9.52), 6.72 (s, 1H, H-3).

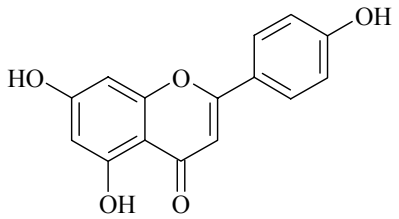
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.69 (C-4), 162.15 (C-2), 160.55 (C-4′), 150.22 (C-7), 146.42 (C-9), 132.94 (C-8), 128.20 (C-2′ and C-6′), 121.93 (C-1′), 116.80 (C-10), 115.71 (C-3′ and C-5′), 114.94 (C-5), 113.68 (C-6), 103.88 (C-3).

EI-MS *m/z* (% relative abundance) composition: 270.0528 (100), 269 (4), 254 (2), 242 (4), 241 (7), 213 (2), 153 (2), 152 (14), 151 (3), 139 (2), 128 (2), 124 (8), 123 (6), 121 (12), 119 (6), 118 (11), 107 (2), 106 (6), 96 (3), 91 (3), 89 (5), 79 (3), 70 (2), 68 (6), 63 (4), 55 (2), 53 (3), 39 (6).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 270.5 (24535), 325 (26847); (Figure 49, side 236).

Anal. Calcd for $C_{15}H_{10}O_5$: C, 66.67%; H, 3.73%; O, 29.60%. Found: C, 64.5%; H, 3.8%; O, 29.1%.

3.2.34. 5,7-Dihydroxy-2-(4-hydroxyphenyl)-4-oxo-4*H*-1-benzopyran (111)



According to the procedure of demethylation for flavonoids, the 5,7-dihydroxy-4′-methoxyflavone (**87**) (500 mg, 1.76 mmol) was mixed with boron tribromide (5 mL, 5 mmol) to afford the 5,7,4′-trihydroxyflavone (**111**) as beige yellow powder (427 mg, Yield 90%). M.p.: 340-341°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.94 (s, 1H, exchanges with D_2O, OH on C-5), 10.78 (br s, 1H, exchanges with D_2O, OH on C-7), 10.33 (br s, 1H, exchanges with D_2O, OH on C-4′), 7.4565 (AB, 4H, δ_A = 7.9275 (H-3′ and H-5′) and δ_B = 6.9538 (H-2′ and H-6′), $^3J_{AB}$ = 9.5229), 6.72 (s, 1H, H-3), 6.2820 (AX, 2H, δ_A = 6.4229 (H-6) and δ_X = 6.1411 (H-8), $^4J_{AX}$ = 1.5871).

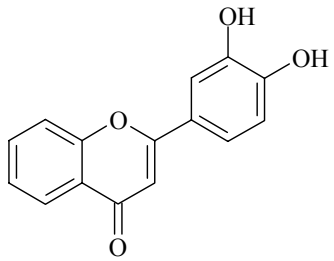
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 181.64 (C-4), 164.01 (C-7 or C-2), 163.61 (C-2 or C-7), 161.35 (C-5), 161.05 (C-4′), 157.19 (C-9), 128.35 (C-2′ and C-5′), 121.07 (C-1′), 115.84 (C-3′ and C-5′), 103.60 (C-10), 102.72 (C-3), 98.73 (C-6), 93.85 (C-8).

EI-MS *m/z* (% relative abundance) composition: 270.0528 (100), 269 (10), 243 (3), 242 (14), 241 (6), 213 (3), 154 (2), 153 (20), 152 (14), 128 (1), 124 (12), 123 (4), 121 (13), 118 (12), 111 (3), 107 (1), 96 (5), 93 (1), 89 (4), 84 (2), 78 (3), 69 (9), 63 (3), 51 (3), 42 (2), 39 (4).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 269 (23603), 339 (26605); (Figure 50, side 236).

Anal. Calcd for $C_{15}H_{10}O_5$: C, 66.67%; H, 3.73%; O, 29.60%. Found: C, 66.3%; H, 3.8%; O, 29.6%.

3.2.35. 2-(3,4-Dihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (112)



According to the procedure of demethylation for flavonoids, the 3′,4′-dimethoxyflavone (**88**) (474 mg, 1.595 mmol) was mixed with boron tribromide (8 mL, 8 mmol) to afford the 3′,4′-dihydroxyflavone (**112**) as yellow powder (320 mg, Yield 76%).

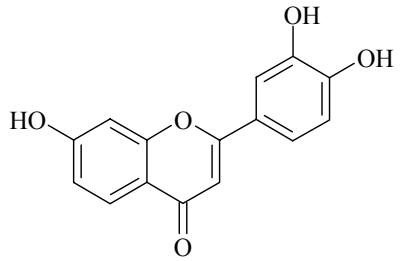
^{1}H NMR (DMSO-d^6, 300 MHz) δ 9.28 (br s, 2H, exchanges with D_2O, OH on C-3′ and C-4′), 8.04 (dd, 1H, $^3J_{5,6}$ = 9.25, $^4J_{5,7}$ = 2.64, H-5), 7.78 (m, 1H, H-7), 7.69 (m, 1H, H-8), 7.42 (m, 3H, H-2′, H-6′ and H-6), 6.91 (d, 1H, $^3J_{5',6'}$ = 9.52, H-5′), 6.69 (s, 1H, H-3).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.68 (C-4), 163.19 (C-2), 155.51 (C-9), 149.40 (C-4′), 145.68 (C-3′), 135.67 (C-7), 133.92 (C-5), 125.19 (C-6), 124.67 (C-1′), 123.38 (C-10), 121.90 (C-6′), 118.74 (C-8), 115.95 (C-5′), 113.34 (C-2′), 104.80 (C-3).

EI-MS *m/z* (% relative abundance) composition: 254.0579 [C15H10O4]+. (100), 253 (1), 238 (3), 237 (10), 227 (4), 226 (28), 210 (2), 198 (3), 197 (14), 181 (2), 168 (2), 152 (6), 151 (3), 150 (2), 137 (3), 135 (5), 134 (48), 126 (2), 121 (73), 113 (17), 105 (4), 104 (2), 92 (27), 88 (15), 86 (2), 78 (3), 76 (16), 69 (2), 64 (15), 62 (26), 55 (2), 51 (9), 49 (5), 41 (24), 39 (10).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 244.5 (31786), 309 (24904), 353 (39283); (Figure 51, side 237).

3.2.36. 7-Hydroxy-2-(3,4-dihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (114)



According to the procedure of demethylation for flavonoids, the 7-hydroxy-3′,4′-dimethoxyflavone (**90**) (700 mg, 2.35 mmol) was mixed with boron tribromide (12 mL, 12 mmol) to afford the 7,3′,4′-trihydroxyflavone (**114**) as yellow powder (599 mg, Yield 94%). M.p.: 326-327°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ ~10.0 (very br s, 3H, exchanges with D_2O, OH on C-7, C-3′ and C-4′), 7.87 (d, 1H, $^3J_{5,6}$ = 8.81, H-5), 7.40 (d, 1H, $^4J_{2',6'}$ = 2.21, H-2′), 7.39 (dd, 1H, $^3J_{6',5'}$ = 8.81, $^4J_{6',2'}$ = 2.21, H-6′), 6.93 (d, 1H, $^4J_{8,6}$ = 2.21, H-8), 6.91 (d, 1H, $^3J_{5',6'}$ = 8.81, H-5′), 6.90 (dd, 1H, $^3J_{6,5}$ = 8.81, $^4J_{6,8}$ = 2.21, H-6), 6.62 (s, 1H, H-3).

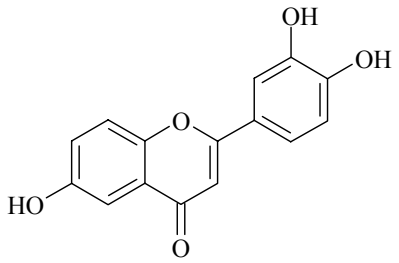
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.16 (C-4), 162.50 (C-2), 162.45 (C-7), 157.24 (C-9), 149.04 (C-4′), 145.48 (C-3′), 126.39 (C-5), 122.05 (C-1′), 118.44 (C-6′), 115.99 (C-10), 115.88 (C-5′), 114.68 (C-6), 113.06 (C-2′), 104.39 (C-8), 102.26 (C-3).

EI-MS *m/z* (% relative abundance) composition: 270.0528 (100), 269 (15), 254 (3), 253 (5), 214 (2), 213 (8), 190 (2), 168 (2), 153 (8), 152 (29), 151 (2), 139 (4), 137 (42), 134 (20), 128 (2), 121 (15), 118 (4), 108 (6), 106 (2), 95 (4), 88 (5), 84 (3), 81 (4), 74 (1), 70 (3), 69 (5), 63 (5), 55 (2), 51 (7), 39 (5).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 237 (29475), 311 sh (22399), 342 (31426); (Figure 52, side 237).

Anal. Calcd for $C_{15}H_{10}O_5$: C, 66.67%; H, 3.73%; O, 29.60%. Found: C, 62.3%; H, 4.3%; O, 33.9%.

3.2.37. 6-Hydroxy-2-(3,4-dihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (115)



According to the procedure of demethylation for flavonoids, the 6-hydroxy-3′,4′-dimethoxyflavone (**91**) (700 mg, 2.35 mmol) was mixed with boron tribromide (12 mL, 12 mmol) to afford the 6,3′,4′-trihydroxyflavone (**115**) as beige yellow powder (548 mg, Yield 86%). M.p.: 326-328°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 9.76 (very br s, 3H, exchanges with D_2O, OH on C-6, C-3′ and C-4′), 7.58 (d, 1H, $^{3}J_{8,7}$ = 8.88, H-8), 7.42 (d, 1H, $^{4}J_{2',6'}$ = 2.21, H-2′), 7.41 (dd, 1H, $^{3}J_{6',5'}$ = 8.88, $^{4}J_{6',2'}$ = 2.21, H-6′), 7.31 (d, 1H, $^{4}J_{5,7}$ =2.21, H-5), 7.23 (dd, 1H, $^{3}J_{7,8}$ = 8.88, $^{4}J_{7,5}$ =2.21, H-7), 6.91 (d, 1H, $^{3}J_{5',6'}$ = 8.88, H-5′), 6.68 (s, 1H, H-3).

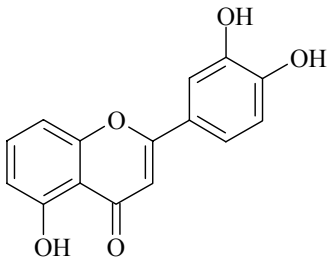
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.63 (C-4), 162.76 (C-2), 154.61 (C-6), 149.14 (C-9 and C-4′), 145.61 (C-3′), 124.10 (C-10), 122.63 (C-7), 122.10 (C-1′), 119.46 (C-6′), 118.55 (C-8), 115.88 (C-5′), 113.16 (C-2′), 107.47 (C-5), 103.84 (C-3).

EI-MS *m/z* (% relative abundance) composition: 270.0528 (100), 269 (10), 254 (2), 253 (4), 242 (6), 241 (3), 214 (1), 213 (5), 161 (1), 152 (4), 139 (3), 138 (4), 137 (61), 136 (39), 134 (21), 121 (10), 109 (4), 108 (10), 105 (2), 88 (6), 82 (3), 80 (9), 77 (2), 64 (1), 62 (4), 52 (11), 50 (3), 39 (2).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 251 (22789), 277 (16157), 339 (34254); (Figure 53, side 238).

Anal. Calcd for $C_{15}H_{10}O_5$: C, 66.67%; H, 3.73%; O, 29.60%. Found: C, 65.4%; H, 3.9%; O, 30.1%.

3.2.38. 5-Hydroxy-2-(3,4-dihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (116)



According to the procedure of demethylation for flavonoids, the 5-hydroxy-3′,4′-dimethoxyflavone (**92**) (700 mg, 1.35 mmol) was mixed with boron tribromide (12 mL, 12 mmol) to afford the 5,3′,4′-trihydroxyflavone (**116**) as green beige fine crystals (612 mg, Yield 96%). M.p.: 317-318°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.82 (s, 1H, exchanges with D_2O, OH on C-5), 10.00 (br s, 1H, exchanges with D_2O, OH on C-3′), 9.44 (br s, 1H, exchanges with D_2O, OH on C-4′), 7.59 (t, 1H, $^{3}J_{7,6} = {}^{3}J_{7,8} = 8.55$, H-7), 7.45 (d, 1H, $^{4}J_{2',6'} = 2.21$, H-2′), 7.44 (dd, 1H, $^{3}J_{6',5'} = 8.55$, $^{4}J_{6',2'} = 2.21$, H-6′), 7.07 (d, 1H, $^{3}J_{6,7} = 8.55$, H-6), 6.88 (d, 1H, $^{3}J_{5',6'} = 8.55$, H-5′), 6.78 (s, 1H, H-3), 6.75 (d, 1H, $^{3}J_{8,7} = 8.55$, H-8).

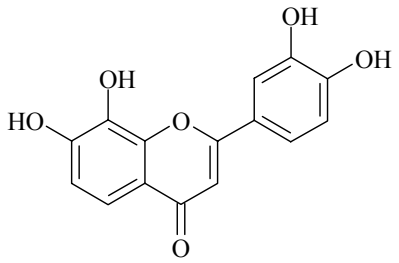
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 182.73 (C-4), 164.71 (C-2), 159.79 (C-5), 155.66 (C-9), 149.96 (C-4′), 145.70 (C-3′), 135.50 (C-7), 121.21 (C-1′), 119.24 (C-6′), 115.93 (C-5′), 113.48 (C-2′), 110.71 (C-8 or C-6), 109.81 (C-10), 107.13 (C-6 or C-8), 103.29 (C-3).

EI-MS *m/z* (% relative abundance) composition: 270.0528 (100), 269 (12),, 253 (3), 242 (8), 241 (3), 214 (1), 213 (8), 138 (4), 137 (46), 136 (15), 134 (20), 128 (2), 121 (14), 109 (2), 108 21), 89 (2), 88 (5), 87 (2), 84 (2), 80 (4), 74 (2), 70 (6), 69 (4), 62 (5), 55 (2), 51 (6), 39 (4).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 252 (16616), 355 (20727); (Figure 54, side 238).

Anal. Calcd for $C_{15}H_{10}O_5$: C, 66.67%; H, 3.73%; O, 29.60%. Found: C, 66.5%; H, 3.9%; O, 29.8%.

3.2.39. 7,8-Dihydroxy-2-(3,4-dihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (117)



According to the procedure of demethylation for flavonoids, the 7,8-dihydroxy-3′,4′-dimethoxyflavone (**93**) (77 mg, 0.25 mmol) was mixed with boron tribromide (2 mL, 2 mmol) to afford the 7,8,3′,4′-tetrahydroxyflavone (**117**) as pale yellow crystals (55 mg, Yield 77%). M.p.: 309-310°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 9.67 (br s, 4H, exchanges with D_2O, OH on C-7, C-8, C-3′ and C-4′), 7.59 (d, 1H, $^4J_{2',6'}$ = 2.21, H-2′), 7.47 (dd, 1H, $^3J_{6',5'}$ = 8.64, $^4J_{6',2'}$ = 2.21, H-6′), 7.16 (AB, 2H, δ_A = 7.39 (H-6)and δ_B = 6.93 (H-5), $^3J_{AB}$ = 8.64), 6.90 (d, 1H, $^3J_{5',6'}$ = 8.64, H-5′), 6.61 (S, 1H, H-3).

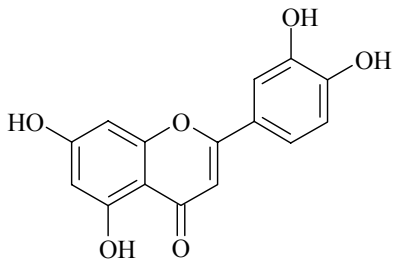
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.64 (C-4), 162.34 (C-2), 150.09 (C-7), 149.00 (C-4′), 146.61 (C-9), 145.52 (C-3′), 133.04 (C-8), 122.30 (C-1′), 118.61 (C-6′), 116.87 (C-10), 115.80 (C-5′), 114.87 (C-5), 113.59 (C-2′), 113.33 (C-6), 103.82 (C-3).

EI-MS *m/z* (% relative abundance) composition: 286.0477 (100), 285 (3), 272 (3), 271 (12), 270 (66), 269 (7), 258 (6), 257 (8), 254 (2), 242 (7), 241 (2), 230 (1), 229 (6), 213 (4), 161 (1), 154 (1), 153 (2), 152 (8), 151 (1), 138 (4), 137 (31), 134 (29), 129 (12), 124 (9), 121 (7), 118 (2), 108 (7), 107 (3), 95 (7), 88 (9), 81 (3), 79 (5), 68 (7), 66 (2), 55 (3), 53 (6), 51 (9), 44 (1), 39 (7).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 255 (18125), 343 (17865); (Figure 55, side 239).

Anal. Calcd for $C_{15}H_{10}O_6$: C, 62.94%; H, 3.52%; O, 33.54%. Found: C, 61.0%; H, 3.0%; O, 28.7%.

3.2.40. 5,7-Dihydroxy-2-(3,4-dihydroxyphenyl)-4-oxo-4*H*-1-benzopyran / Luteolin (119)



According to the procedure of demethylation for flavonoids, the 5,7-dihydroxy-3′,4′-dimethoxyflavone (**95**) (500 mg, 1.5 mmol) was mixed with boron tribromide (10 mL, 10 mmol) to afford the 5,7,3′,4′-Tetrahydroxyflavone (**119**) as yellow powder (388 mg, Yield 85%). M.p.: 160-161°C.

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.99 (s, 1H, exchanges with D_2O, OH on C-5), ~10.00 (very br s, exchanges with D_2O, OH on C-7, C-3′ and C-4′), 7.42 (dd, 1H, $^{3}J_{6',5'}$ = 8.81, $^{4}J_{6',2'}$ = 2.21, H-6′), 7.41 (d, 1H, $^{4}J_{2',6'}$ = 2.21, H-2′), 6.90 (d, 1H, $^{3}J_{5',6'}$ = 8.81, H-5′), 6.69 (s, 1H, H-3), 6.30 (AX, 2H, δ_A = 6.4319 (H-6), δ_X = 6.1681 (H-8), $^{4}J_{AX}$ = 1.32).

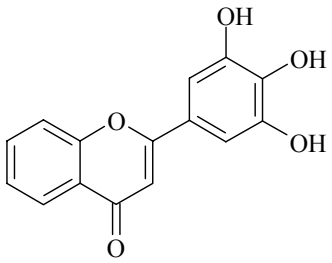
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 181.56 (C-4), 164.06 (C-7 or C-2), 163.78 (C-2 or C-7), 161.37 (C-5), 157.18 (C-9), 149.61 (C-4′), 145.64 (C-3′), 121.37 (C-1′), 118.90 (C-6′), 115.90 (C-5′), 113.24 (C-2′), 103.57 (C-10), 102.75 (C-3), 98.73 (C-6), 93.74 (C-8).

EI-MS *m/z* (% relative abundance) composition: 286.0477 (100), 285 (7), 270 (11), 269 (3), 258 (16), 257 (5), 242 (2), 229 (7), 213 (1), 154 (2), 153 (28), 152 (8), 137 (5), 134 (13), 129 (11), 124 (11), 123 (5), 111 (3), 96 (5), 95 (1), 88 (5), 78 (3), 75 (2), 69 (11), 62 (5), 55 (3), 51 (6), 43 (2), 39 (4).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 256 (27631), 268 sh (24295), 354 (30681); (Figure 56, side 239).

Anal. Calcd for $C_{15}H_{10}O_6$: C, 62.94%; H, 3.52%; O, 33.54%. Found: C, 60.0%; H, 3.9%; O, 36.3%.

3.2.41. 2-(3,4,5-Trihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (120)



According to the procedure of demethylation for flavonoids, the 3′,4′,5′-trimethoxyflavone (**96**) (79 mg, 0.25 mmol) was mixed with boron tribromide (2 mL, 2 mmol) to afford the 3′,4′,5′-trihydroxyflavone (**120**) as light brown powder (55 mg, Yield 81%).

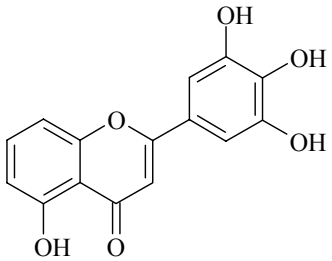
^{1}H NMR (DMSO-d^6, 300 MHz) δ ~9.12 (s, 3H, exchanges with D_2O, OH on C-3′, C-4′ and C-5′), 8.09 (m, 1H, H-5), 7.76 (m, 1H, H-7), 7.66 (m, 1H, H-8), 7.44 (m, 1H, H-6), 7.29 (s, 2H, H-2′ and H-6′), 6.42 (s, 1H, H-3).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.67 (C-4), 163.62 (C-2), 154.25 (C-9), 145.67 (C-3′ and C-5′), 137.90 (C-7 and C-4′), 135.72 (C-6), 124.63 (C-1′), 124.26 (C-5), 121.06 (C-10), 117.95 (C-8), 107.28 (C-2′ and C-6′), 102.09 (C-3).

EI-MS *m/z* (% relative abundance) composition: 270.05 [C15H10O5]+. (100), 269 (10), 255 (2), 254 (12), 242 (27), 241 (4), 237 (1), 226 (3), 224 (1), 196 (4), 185 (3), 171 (3), 168 (5), 153 (1), 151 (5), 150 (39), 139 (14), 134 (6), 128 (4), 122 (8), 121 (98), 120 (10), 113 (4), 104 (8), 94 (2), 92 (29), 84 (6), 79 (3), 76 (22), 69 (6), 65 (12), 63 (17), 55 (2), 53 (7), 50 (11), 42 (2), 39 (7).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 255 (18125), 343 (17865); (Figure 57, side 240).

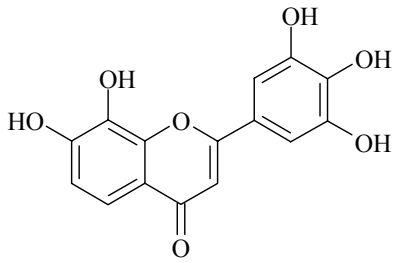
3.2.42. 5-Hydroxy-2-(3,4,5-trihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (124)



According to the procedure of demethylation for flavonoids, the 5-hydroxy-3′,4′,5′-trimethoxyflavone (**100**) (100 mg, 0.298 mmol) was mixed with boron tribromide (5 mL, 5 mmol) to afford the 5,3′,4′,5′-tetrahydroxyflavone (**124**) as dark powder (90 mg, Yield 100%).

HPLC-APCI-MS *m/z* composition: 286.0477 $[C_{15}H_{10}O_6]^{+\cdot}$, 287 $[M+H]^+$.

3.2.43. 7,8-Dihydroxy-2-(3,4,5-trihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (125)



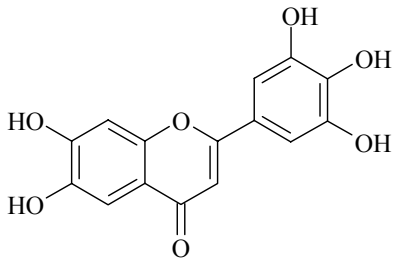
According to the procedure of demethylation for flavonoids, the 7,8-dihydroxy-3′,4′,5′-trimethoxyflavone (**101**) (80 mg, 0.232 mmol) was mixed with boron tribromide (5 mL, 5 mmol) to afford the 7,8,3′,4′,5′-pentahydroxyflavone (**125**) as light brown powder (63 mg, Yield 89%).

^{1}H NMR (DMSO-d^6, 300 MHz) δ ~10.27 (br s, 2H, exchanges with D_2O, OH on C-7 and C-8), ~9.26 (br s, 3H, exchanges with D_2O, OH on C-3′, C-4′ and C-5′), 7.13 (AB, 2H, δ_A = 7.35 (H-6) and δ_B = 6.91 (H-5, $^3J_{AB}$ = 7.94), 7.03 (s, 2H, H-2′ and H-6′), 6.43 (s, 1H, H-3).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.48 (C-4), 162.60 (C-2), 150.02 (C-7), 146.48 (C-9), 146.16 (C-3′ and C-5′), 137.13 (C-4′), 133.13 (C-8), 121.31 (C-1′), 116.96 (C-10), 114.82 (C-5), 113.55 (C-6), 105.56 (C-2′ and C-6′), 103.85 (C-3).

EI-MS *m/z* (% relative abundance) composition: 302.0427 $[C_{15}H_{10}O_7]^{+\cdot}$ (100), 286 (3), 274 (6), 273 (11), 256 (1), 255 (6), 254 (32), 245 (9), 237 (2), 226 (8), 225 (2), 208 (1), 197 (4), 171 (3), 155 (3), 154 (9), 153 (98), 152 (93), 150 (20), 138 (2), 137 (21), 125 (3), 124 (12), 121 (22), 113 (6), 106 (9), 103 (3), 96 (4), 92 (8), 89 (3), 82 (4), 79 (9), 76 (15), 69 (5), 63 (11), 58 (1), 55 (4), 51 (11), 43 (2), 39 (12).

3.2.44. 6,7-Dihydroxy-2-(3,4,5-trihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (126)

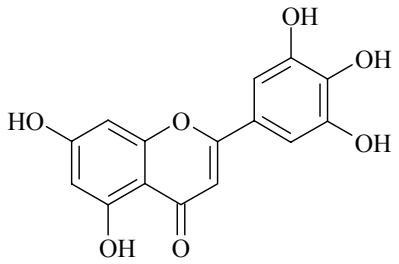


According to the procedure of demethylation for flavonoids, the 6,7-dihydroxy-3′,4′,5′-trimethoxyflavone (**102**) (80 mg, 0.232 mmol) was mixed with boron tribromide (5 mL, 5 mmol) to afford the 6,7,3′,4′,5′-pentahydroxyflavone (**126**) as light brown powder (26.4 mg, Yield 37%).

^{1}H NMR (DMSO-d^6, 300 MHz) δ ~9.17 (br s, exchanges with D_2O, OH on C-3′, C-4′ and C-5′), 7.26 (s, 1H, H-5), 6.91 (s, 3H, H-2′, H-6′ and H-8), 6.38 (s, 1H, H-3).

EI-MS *m/z* (% relative abundance) composition: $[C_{15}H_{10}O_7]^{+\cdot}$ (100), 301 (8), 286 (4), 274 (12), 273 (10), 254 (4), 245 (9), 223 (2), 208 (4), 206 (5), 191 (2), 177 (2), 154 (6), 153 (72), 152 (29), 150 (15), 149 (4), 147 (1), 137 (15), 125 (3), 124 (5), 107 (4), 105 (2), 96 (6), 91 (2), 82 (23), 80 (13), 76 (9), 69 (14), 65 (3), 60 (1), 55 ‘6), 50 (8), 44 (24).

3.2.45. 5,7-Dihydroxy-2-(3,4,5-trihydroxyphenyl)-4-oxo-4*H*-1-benzopyran (127)



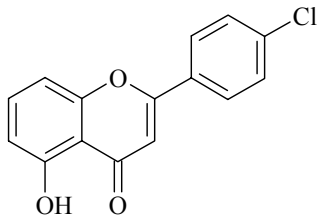
According to the procedure of demethylation for flavonoids, the 5,7-dihydroxy-3′,4′,5′-trimethoxyflavone (**103**) (80 mg, 0.232 mmol) was mixed with boron tribromide (5 mL, 5 mmol) to afford the 5,7,3′,4′,5′-pentahydroxyflavone (**127**) as light yellow powder (15 mg, Yield 17%).

^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.93 (s, 1H, exchanges with D_2O, OH on C-5), 10.80 (s, 1H, exchanges with D_2O, OH on C-7), 9.31 (s, 2H, exchanges with D_2O, OH on C-3′ and C-5′), 9.02 (s, 1H, exchanges with D_2O, OH on C-4′), 7.97 (s, 2H, H-2′ and H-6′), 6.52 (s, 1H, H-3), 6.29 (AX, 2H, δ_A = 6.40 (H-6) and δ_X = 6.17 (H-8) $^4J_{AX}$ = 2.64).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 181.78 (C-4), 164.04 (C-7 or C-2), 162.78 (C-2 or C-7), 161.42 (C-5), 157.25 (C-9), 146.26 (C-3′ and C-5′), 137.77 (C-4′), 121.56 (C-1′), 105.61 (C-2′ and C-6′), 103.81 (C-10), 102.82 (C-3), 98.74 (C-6), 93.66 (C-8).

EI-MS *m/z* (% relative abundance) composition: $[C_{15}H_{10}O_7]^{+\cdot}$ (100), 301 (4), 275 (2), 274 (10), 273 (6), 254 (2), 245 (6), 231 (1), 177 (1), 154 (2), 153 (24), 150 (8), 137 (10), 124 (4), 122 (2), 100 (3), 79 (1), 73 (4), 69 (6), 55 (2), 42 (2), 39 (2).

3.2.46. 5-Hydroxy-2-(4-chlorophenyl)-4-oxo-4*H*-1-benzopyran (128)



According to the Procedure B, the 2,6-dihydroxyacetophenone (**12e**) (2 g, 13 mmol) was mixed with LiOH (1.24 g, 51 mmol) and the 4-chlorobenzoyl chloride (**17e**) (2.44 g, 14 mmol) to afford the 5-hydroxy-4′-chloroflavone (**128**) as yellow powder (3.16 g, Yield 90%). M.p.: 185-186°C.

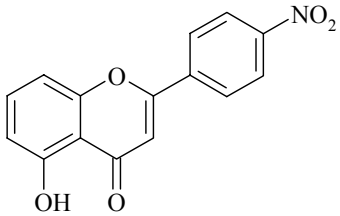
^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.58 (s, 1H, exchanges with D_2O, OH on C-5), 8.14-7.65 (dm supposed as a AA′XX′ system, 4H, H_{Ar} B-ring), 7.69 (t, 1H, $^3J_{7,5} = {}^3J_{7,6} = 8.82$, H-7), 7.20 (d, 1H, $^3J_{6,7} = 8.82$, H-6), 7.14 (S, 1H, H-3), 6.84 (d, 1H, $^3J_{8,7} = 8.82$, H-8).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 183.16 (C-4), 162.89 (C-2), 159.79 (C-5), 155.83 (C-9), 137.12 (C-4′), 136.04 (C-7), 129.43 (C-1′), 129.22 (C-3′ and C-5′), 128.41 (C-2′ and C-6′), 111.05 (C-8 or C-6), 110.11 (C-10), 107.52 (C-6 or C-8), 105.98 (C-3).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 275 (28249), 337.5 (7401); (Figure 58, side 240).

Anal. Calcd for $C_{15}H_9ClO_3$: C, 67.60%; H, 4.26%; Cl, 13.00%; O, 28.14%. Found: C, 65.7%; H, 3.3%; Cl, 12.8%; O, 18.0%.

3.2.47. 5-Hydroxy-2-(4-nitrophenyl)-4-oxo-4*H*-1-benzopyran (129)

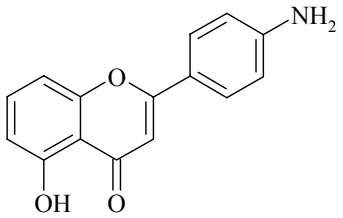


According to the procedure B, the 2,6-dihydroxyacetophenone (**12e**) (1 g, 6.4 mmol) was mixed with LiOH (463 mg, 19 mmol) and the 4-nitrobenzoyl chloride (**17f**) (1.13 g, 6.6 mmol). The product was recrystallized from ethanol to afford the 5-hydroxy-4′-nitroflavone (**129**) as a yellow powder (508 mg, Yield 27%).

^{1}H NMR ($CDCl_3$, 250 MHz) δ 12.32 (s, 1H, exchanges with D_2O, OH on C-5), 8.39-8.15 (dm supposed as a AA′XX′ system, 4H, H_{Ar} B-ring), 7.61 (t, 1H, $^3J_{7,6} = {}^3J_{7,8} = 8.81$, H-7), 7.04 (d, 1H, $^3J_{6,7} = 8.81$, H-6), 6.87 (d, 1H, $^3J_{8,7} = 8.81$, H-8), 6.82 (s, 1H, H-3).

EI-MS *m/z* (% relative abundance) composition: 283.048072 (100), 253 (2), 238(5), 237 (28), 236 (1), 225 (4), 209 (3), 208 (2), 207 (1), 197 (3), 182 (1), 181 (6), 163 (2), 153 (2), 152 (8), 137 (2), 136 (7), 126 (2), 125 (1), 119 (3), 117 (2), 115 (1), 113 (1), 109 (1), 108 (17), 102 (1), 101 (2).

3.2.48. 5-Hydroxy-2-(4-aminophenyl)-4-oxo-4*H*-1-benzopyran (130)



The 5-hydroxy-4′-nitroflavone (**129**) (300 mg, 1.1 mmol) was dissolved in THF and hydrogenated in presence of Palladium/charcoal (Merck 275175, Pd/C 5% H_2O free) under H_2 pressure during 5h. The solution was filtered to separate the catalyst and the solvent was removed under reduced pressure. The product was recrystallized from ethanol to afford the 5-hydroxy-4′-aminoflavone (**130**) as a yellow powder (275 mg, Yield 99%). M.p.: 245°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 13.01 (s, 1H, exchanges with D_2O, OH on C-5), 7.83-6.69 (dm supposed as a AA′XX′ system, 4H, H_{Ar} B-ring), 7.61 (t, 1H, $^3J_{7,6} = {}^3J_{7,8} = 8.38$, H-7), 7.14 (d, 1H, $^3J_{6,7} = 8.37$, H-6), 6.77 (s, 1H, H-3), 6.76 (d, 1H, $^3J_{8,7} = 8.22$, H-8), 6.14 (s, 2H, exchanges with D_2O, NH_2).

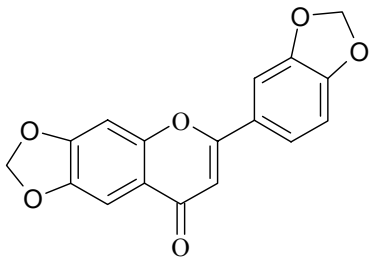
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 182.48 (C-4), 165.48 (C-2), 159.90 (C-5), 155.67 (C-9), 153.28 (C-4′), 135.22 (C-7), 128.46 (C-2′ and C-6′), 116.15 (C-1′), 113.46 (C-3′ and C-5′), 110.61 (C-8 or C-6), 109.61 (C-10), 107.09 (C-6 or C-8), 101.21 (C-3).

EI-MS *m/z* (% relative abundance) composition: 253.0738 (100), 252 (9), 237 (1), 225 (5), 224 (3), 197 (1), 196 (1), 168 (1), 167 (1), 137 (2), 136 (1), 126 (2), 120 (2), 118 (8), 117 (57), 116 (2), 112 (9), 108 (5).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 267.5 (10530), 381 (31985); (Figure 59, side 241).

Anal. Calcd for $C_{15}H_9NO_5$: C, 71.14%; H, 4.38%; N, 5.53%; O, 18.95%. Found: C, 70.4%; H, 4.3%; N, 5.5%.

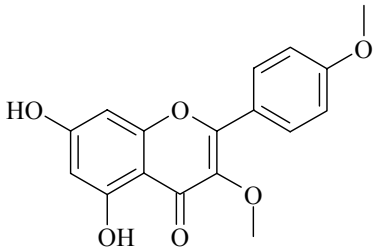
3.2.49. 2-Benzo[1,3]dioxol-5-yl-[1,3]dioxolo[6,7]-4-oxo-4*H*-1-benzopyran (131)



According to the procedure B, the 2,6-dihydroxyacetophenone (**12g**) (1 g, 6.4 mmol) was mixed with LiOH (463 mg, 19 mmol) and the piperonyl chloride (**17g**) (1.13 g, 6.6 mmol). The product was recrystallized from ethanol to afford the 6,7,3′,4′-bis[1,3]dioxoloflavone (**131**) as a yellow powder (508 mg, Yield 27%).

EI-MS *m/z* (% relative abundance) composition: 310.04 $[C_{17}H_{10}O_6]^{+\cdot}$ (100), 309 (23), 282 (18), 253 (2), 180 (2), 166 (2), 164 (51), 154 (7), 149 (19), 146 (70), 145 (26), 141 (14), 140 (10), 136 (7), 125 (3), 123 (2), 111 (5), 108 (2), 95 (2), 88 (7), 83 (5), 80 (3), 75 (2), 69 (10), 66 (6), 63 (4), 57 (8), 51 (2), 43 (5), 39 (2).

3.2.50. 5,7-Dihydroxy-3-methoxy-2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran / Kaempherol 3,4′-dimethyl ether (138)



According to the procedure A, the 2,4,6-trihydroxymethoxyacetophenone (**65b**) (1 g, 5 mmol) was mixed with LiHMDS (25 mL, 25 mmol) and the 4-methoxybenzoyl chloride (**17b**) (966 mg, 5.5 mmol). The product was recrystallized from ethanol to afford the 5,7-dihydroxy-3,4′-dimethoxyflavone (**138**) as a light pink powder (mg, Yield 27%).

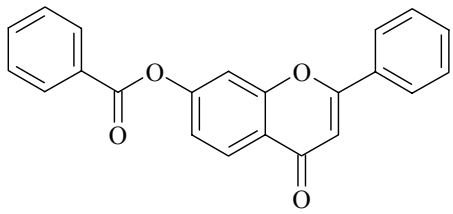
^{1}H NMR ($CDCl_3$, 250 MHz) δ 12.62 (s, 1H, exchanges with D_2O, OH on C-5), 10.79 (s, 1H, exchanges with D_2O, OH on C-7), 8.01-7.13 (m, supposed as AA′XX′ system, 4H, H_{Ar} of B-ring), 6.34 (AX, 2H, δ_A = 6.45 (H-6) and δ_X = 6.22 (H-8), $^4J_{AX}$ = 2.64), 3.87 (s, 3H, OCH_3 on C-4′), 3.79 (s, 3H, OCH_3 on C-3).

EI-MS *m/z* (% relative abundance) composition: 314.07 $[C_{17}H_{14}O_6]^{+\cdot}$ (100), 313 (74), 299 (9), 296 (12), 285 (15), 271 (55), 269 (4), 257 (3), 228 (8), 227 (3), 202 (1), 201 (4), 179 (16),

178 (1), 156 (1), 152 (4), 149 (7), 143 (13), 135 (33), 132 (9), 119 (12), 108 (7), 97 (9), 93 (3), 90 (1), 81 (8), 77 (14), 69 (22), 65 (4), 57 (16), 53 (2), 43 (12), 39 (5).

3.3. Flavonoid esters (Chapter 3)

3.3.1. Benzoic acid 2-phenyl-4-oxo-4*H*-1-benzopyran-7-yl ester (139)



According to the procedure A, the 2,4-dihydroxyacetophenone (**12c**) (1 g, 6.4 mmol) was mixed with LiHMDS (18 mL, 18 mmol) and the benzoyl chloride (**17a**) (928 mg, 6.6 mmol) to afford the flavone ester (**139**) as white needles (42 mg, Yield 4%). M.p.: 159.7°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 8.23-8.09 (m, 5H, H-2″ to H-6″), 8.13 (d, 1H, $^3J_{5,\,6}$ = 8.82, H-5), 7.89 (d, 1H, $^4J_{8,\,6}$ = 2.21, H-8), 7.71-7.58 (m, 5H, H_{Ar} B-ring), 7.49 (dd, 1H, $^3J_{6,\,5}$ = 2.21, $^4J_{6,\,8}$ = 8.82, H-6), 7.07 (s, 1H, H-3).

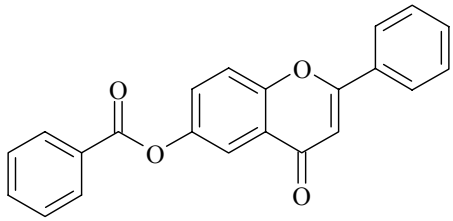
^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.46 (C-4), 164.02 (C-2), 162.86 (C-11), 156.20 (C-7), 154.63 (C-9), 134.57 (C-4″), 131.88 (C-5), 130.96 (C-1′), 129.95 (C-2″ and C-6″), 129.11 (C-3″ and C-5″), 129.05 (C-3′ and C-5′), 128.39 (C-1″), 126.35 (C-2′ and C-6′), 126.29 (C-4′), 121.37 (C-10), 120.13 (C-6), 111.94 (C-8), 107.06 (C-3).

EI-MS *m/z* (% relative abundance) composition: 342.0892 (9) $[C_{22}H_{14}O_4]^{+\cdot}$, 238 (1) $[C_{15}H_{10}O_3]^{+\cdot}$, 210 (1) $[C_{14}H_{10}O_2]^{+\cdot}$, 209 (3) $[C_{14}H_9O_2]^+$, 181 (1) $[C_{13}H_9O]^+$, 153 (2) $[C_{12}H_9]^+$, 127 (1) $[C_{10}H_7]^+$, 105 (100) $[C_7H_5O]^+$, 103 (3) $[C_8H_7]^+$, 77 (53) $[C_6H_5]^+$, 69 (2) $[C_4H_5O]^+$, 63 (3) $[C_5H_3]^+$, 51 (9) $[C_4H_3]^+$, 39 (1) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 245 (28606), 296 (26869); (Figure 60, side 241).

Anal. Calcd for $C_{22}H_{14}O_4$: C, 77.18%; H, 4.12%; O, 18.69%. Found: C, 77.1%; H, 4.1%; O, 18.9%.

3.3.2. Benzoic acid 2-phenyl-4-oxo-4*H*-1-benzopyran-6-yl ester (140)



According to the procedure A, the 2,5-dihydroxyacetophenone (**12d**) (1 g, 6.4 mmol) was mixed with LiHMDS (18 mL, 18 mmol) and the benzoyl chloride (**17a**) (928 mg, 6.6 mmol) to afford the flavone ester (**140**) as brown silver pellets (367 mg, Yield 33%). M.p.: 188.0°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 8.27-8.11 (m, 5H, H-2″ to H-6″), 8.08 (dd, 2H, $^3J_{2',3'}$ = $^3J_{6',5'}$ = 7.76, $^4J_{2',4'}$ = $^4J_{6',4'}$ = 1.21, H-2′ and H-6′), 7.66 (d, 1H, $^4J_{8,7}$ = 8.92, H-8), 7.59 (m, 3H, H-3′, H-4′ and H-5′), 7.34 (d, 1H, $^4J_{5,7}$ = 2.57, H-5), 7.27 (dd, 1H, $^3J_{7,8}$ = 8.92, $^4J_{7,5}$ = 2.57, H-7), 6.90 (s, 1H, H-3).

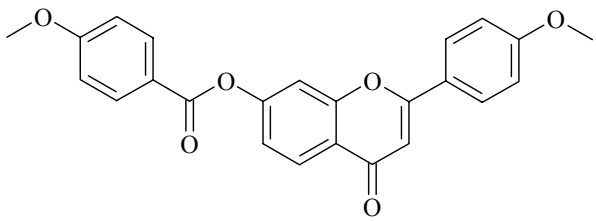
^{13}C NMR (DMSO-d^6, 62.80 MHz) δ 176.56 (C-4), 164.52 (C-2), 162.87 (C-11), 153.31 (C-9), 147.57 (C-6), 134.16 (C-4″), 131.92 (C-7), 131.01 (C-1′), 129.89 (C-2″ and C-6″), 129.19 (C-3″ and C-5″), 128.95 (C-3′ and C-5′), 128.49 (C-1″), 128.57 (C-4′), 126.43 (C-2′ and C-6′), 124.00 (C-10), 120.24 (C-5), 116.92 (C-8), 106.53 (C-3).

EI-MS *m/z* (% relative abundance) composition: 342.0892 (32) $[C_{22}H_{14}O_4]^{+\cdot}$, 238 (3) $[C_{15}H_{10}O_3]^{+\cdot}$, 237 (2) $[C_{15}H_9O_3]^+$, 210 (1) $[C_{14}H_{10}O_2]^{+\cdot}$, 209 (1) $[C_{14}H_9O_2]^+$, 181 (1) $[C_{13}H_9O]^+$, 152 (2) $[C_{12}H_8]^+$, 126 (1) $[C_{10}H_6]^+$, 105 (100) $[C_7H_5O]^+$, 102 (3) $[C_8H_7]^{+\cdot}$, 79 (5) $[C_5H_3O]^+$, 77 (38) $[C_6H_5]^+$, 69 (1) $[C_4H_5O]^+$, 63 (3) $[C_5H_3]^+$, 53 (2) $[C_4H_5]^+$, 51 (8) $[C_4H_3]^+$, 39 (1) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 254 (37210), 296 (31892); (Figure 61, side 242).

Anal. Calcd for $C_{22}H_{14}O_4$: C, 77.18%; H, 4.12%; O, 18.69%. Found: C, 77.0%; H, 4.2%; O, 19.0%.

3.3.3. 4-Methoxy-benzoic acid 2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran-7-yl ester (141)



According to the procedure A, the 2,4-dihydroxyacetophenone (**12c**) (2 g, 13 mmol) was mixed with LiHMDS (40 mL, 40 mmol) and the 4-methoxybenzoyl chloride (**17b**) (2.42 g, 14.2 mmol) to afford the flavone ester (**141**) as light purple powder (213 mg, Yield 4%). M.p.: 158.2°C.

^{1}H NMR (DMSO-d^6, 250 MHz) δ 8.16-7.78 (dm, 4H, H_{Ar} B-ring), 8.13 (d, 1H, $^3J_{5,\,6}$ = 8.97, H-5), 7.89 (d, 1H, $^4J_{8,\,6}$ = 2.18, H-8), 7.47 (dd, 1H, $^3J_{6,\,5}$ = 8.97, $^4J_{6,\,8}$ = 2.18, H-6), 7.35 (dm, 2H, H-2″ and H-6″), 7.11 (dm, 2H, H-3″ and H-5″), 7.03 (s, 1H, H-3), 3.86 (s, 3H, OCH_3 on C-4′ and C-4″).

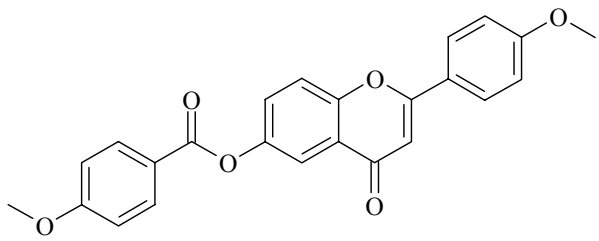
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.44 (C-4), 163.11 (C-11), 162.53 (C-2), 162.22 (C-4″), 162.11 (C-7), 161.52 (C-4′), 158.83 (C-9), 132.19 (C-2″ and C-6″), 131.68 (C-5), 130.01 (C-1′), 129.53 (C-1″), 128.17 (C-2′ and C-6′), 126.08 (C-6), 116.24 (C-10), 114.53 (C-5″ and C-3″), 114.34 (C-5′ and C-3′), 111.81 (C-8), 105.33 (C-3), 55.64 (OCH_3 on C-4′ and C-4″).

EI-MS *m/z* (% relative abundance) composition: 402.1103 (26) $[C_{24}H_{18}O_6]^{+\cdot}$, 268 (17) $[C_{16}H_{12}O_4]^{+\cdot}$, 267 (4) $[C_{16}H_{11}O_4]^{+}$, 240 (4) $[C_{15}H_{12}O_3]^{+\cdot}$, 239 (8) $[C_{15}H_{11}O_3]^{+}$, 225 (3), 196 (2) $[C_{13}H_8O_2]^{+\cdot}$, 168 (2) $[C_{12}H_8O]^{+\cdot}$,152 (1) $[C_8H_8O_3]^{+\cdot}$,140 (1) $[C_{11}H_8]^{+\cdot}$, 135 (100) $[C_8H_7O_2]^{+}$, 132 (10), 117 (4), 107 (7) $[C_7H_7O]^{+}$, 104 (1) $[C_7H_4O]^{+\cdot}$, 92 (10) $[C_6H_4O]^{+\cdot}$, 89 (4) $[C_7H_5]^{+}$, 77 (15) $[C_6H_5]^{+}$, 64 (4) $[C_5H_4]^{+\cdot}$, 51 (2) $[C_4H_3]^{+}$, 39 (1) $[C_3H_3]^{+}$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 262 (47487), 274.5 (46494), 305.5 (49185); (Figure 62, side 242).

Anal. Calcd for $C_{24}H_{18}O_6$: C, 71.64%; H, 4.51%; O, 23.86%. Found: C, 70.8%; H, 4.7%; O, 24.6%.

3.3.4. 4-Methoxybenzoic acid 2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran-6-yl ester (142)



According to the procedure A, the 2,5-dihydroxyacetophenone (**12d**) (2 g, 13.2 mmol) was mixed with LiHMDS (50 mL, 50 mmol) and the 4-methoxybenzoyl chloride (**17b**) (2.42 g, 14.2 mmol) to afford the flavone ester (**141**) as a yellow powder (318 mg, Yield 11%). M.p.: 214.5°C.

^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.17 (dm, 2H, H-2′ and H-6′), 8.04 (d, 1H, $^{4}J_{5,7}$ = 2.21, H-8), 7.80 (dm, 2H, H-3′ and H-5′), 7.59 (m, 2H, H-7 and H-5), 7.03 (dm, 2H, H-2″ and H-6″), 7.01 (dm, 2H, H-3″ and H-5″), 6.75 (s, 1H, H-3), 3.91 (s, 6H, OCH_3 on C-4′ and C-4″).

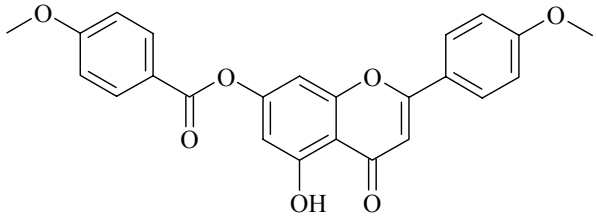
^{13}C NMR ($CDCl_3$, 75.47 MHz) δ 178.38 (C-4), 165.44 (C-2), 164.86 (C-11), 164.34 (C-6), 163.24 (C-4″), 154.37 (C-9), 148.71 (C-4′), 133.11 (C-2″ and C-6″), 128.78 (C-2′ and C-6′), 128.67 (C-7), 125.48 (C-1′), 124.64 (C-1″), 122.05 (C-10), 119.91 (C-5), 118.56 (C-8), 115.24 (C-3″ and C-5″), 114.68 (C-3′ and C-5′), 106.52 (C-3), 56.24 (OCH_3 on C-4′ and C-4″).

EI-MS *m/z* (% relative abundance) composition: 402.1103 (3) $[C_{24}H_{18}O_6]^{+\cdot}$, 268 (3) $[C_{16}H_{12}O_4]^{+\cdot}$, 239 (1) $[C_{15}H_{11}O_3]^{+}$, 211 (1) $[C_{11}H_{14}O_2]^{+}$, 152 (1) $[C_8H_8O_3]^{+\cdot}$, 135 (100) $[C_8H_7O_2]^{+}$, 132 (5) $[C_9H_8O]^{+\cdot}$, 107 (7) $[C_7H_7O]^{+}$, 92 (6) $[C_6H_4O]^{+\cdot}$, 89 (3) $[C_7H_5]^{+\cdot}$, 79 (3) $[C_5H_3O]^{+}$, 77 (8) $[C_6H_5]^{+}$, 63 (3) $[C_5H_3]^{+}$, 62 (2) $[C_5H_2]^{+\cdot}$, 55 (2) $[C_3H_3O]^{+}$, 51 (2) $[C_4H_3]^{+}$, 43 (2) $[C_2H_3O]^{+}$, 41 (2) $[C_3H_5]^{+}$, 39 (1) $[C_3H_3]^{+}$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 265.5 (33637), 320 (31501); (Figure 63, side 243).

Anal. Calcd for $C_{24}H_{18}O_6$: C, 71.64%; H, 4.51%; O, 23.86%. Found: C, 70.3%; H, 5.1%; O, 24.3%.

3.3.5. 4-Methoxybenzoic acid 5-hydroxy-2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran-7-yl ester (143)



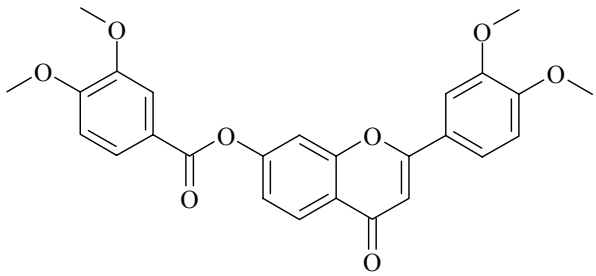
According to the procedure C, the 2,4,6-trihydroxyacetophenone (**12h**) (1 g, 5.3 mmol) was mixed to LiOH (1.29 g, 42.11 mmol) and the 4-methoxybenzoyl chloride (**17b**) (2.69 g, 16 mmol) to afford the flavone ester (**143**) as brown powder (347 mg, Yield 16%).

EI-MS *m/z* (% relative abundance) composition: 418.1853 (12) $[C_{24}H_{18}O_7]^{+\cdot}$, 403 (1) $[C_{23}H_{15}O_7]^+$, 389 (2) $[C_{23}H_{17}O_6]^+$, 326 (1), 311 (1), 284 (12) $[C_{16}H_{12}O_5]^{+\cdot}$, 269 (3) $[C_{15}H_9O_5]^+$, 256 (4) $[C_{15}H_{12}O_5]^{+\cdot}$, 255 (4) $[C_{15}H_{11}O_5]^+$, 241 (7) $[C_{14}H_9O_4]^+$, 213 (2) $[C_{13}H_9O_3]^+$, 152 (1) $[C_8H_8O_3]^{+\cdot}$, 135 (100) $[C_8H_7O_2]^+$, 128 (6) $[C_6H_8O_3]^{+\cdot}$, 126 (8) $[C_6H_6O_3]^{+\cdot}$, 124 (4) $[C_7H_8O_2]^{+\cdot}$, 123 (3) $[C_7H_7O_2]^+$, 118 (1) $[C_8H_6O]^{+\cdot}$, 117 (4) $[C_8H_5O]^+$, 107 (6) $[C_7H_7O]^+$, 97 (2) $[C_5H_5O_2]^+$, 92 (9) $[C_6H_4O]^{+\cdot}$, 89 (4), 83 (1) $[C_5H_7O]^+$, 77 (13) $[C_6H_5]^+$, 69 (6) $[C_4H_5O]^+$, 65 (3) $[C_5H_5]^+$, 63 (6) $[C_5H_3]^+$, 62 (1) $[C_5H_2]^{+\cdot}$, 51 (3) $[C_4H_3]^+$, 41 (3) $[C_3H_5]^+$, 39 (3) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm:

Anal. Calcd for $C_{24}H_{18}O_7$: C, 68.90%; H, 4.34%; O, 26.77%. Found: C, 63.7%; H, 5.3%; O, 30.7%.

3.3.6. 3,4-Dimethoxybenzoic acid 2-(3,4-dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran-7-yl ester (144)



According to the procedure A, the 2,4-dihydroxyacetophenone (**12c**) (2 g, 13 mmol) was mixed with LiHMDS (40 mL, 40 mmol) and the 3,4-dimethoxybenzoyl chloride (**17b**) (2.58 g, 13 mmol) to afford the flavone ester (**144**) as white powder (253 mg, Yield 4%).

^{1}H NMR (DMSO-d^6, 300 MHz) δ 8.15 (d, 1H, $^3J_{5,6}$ = 9.26, H-5), 7.87 (m, 2H, H-2″ and H-6″), 7.76 (dd, 1H, $^3J_{6,5}$ = 9.26, $^4J_{6,8}$ = 1.32, H-8), 7.67 (s, 2H, H-6 and H-2′), 7.45 (dd, 1H, $^3J_{6',5'}$ = 9.52, $^4J_{6',2'}$ = 1.05, H-6′), 7.20 (d, 1H, $^3J_{5'',6''}$ = 9.52, H-5″), 7.18 (d, 1H, $^3J_{5',6'}$ = 9.52,

H-5′), 7.11 (s, 1H, H-3), 3.92 (s, 6H, OCH_3 on C-3″ and C-4″), 3.90 (s, 6H, OCH_3 on C-3′ and C-4′).

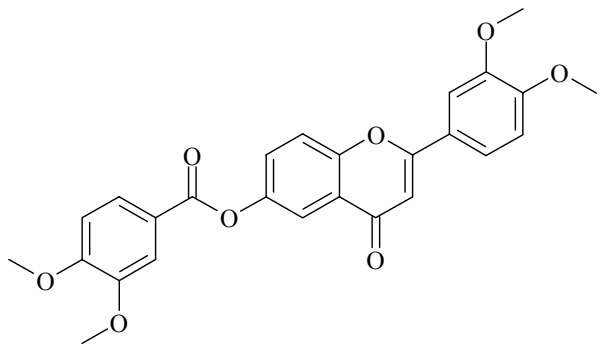
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.03 (C-4), 163.97 (C-2), 163.24 (C-11), 162.44 (C-7), 154.56 (C-9), 153.47 (C-4″), 148.91 (C-3″), 139.75 (C-3′), 136.78 (C-4′), 126.06 (C-5), 124.34 (C-6″), 123.84 (C-1′), 121.55 (C-1″), 119.97 (C-6′), 116.44 (C-10), 112.08 (C-6), 111.91 (C-5″), 111.66 (C-2″), 111.31 (C-5′), 109.26 (C-2′), 105.65 (C-8), 102.83 (C-3), 55.80 (OCH_3 on C-3″), 55.73 (OCH_3 on C-4″ and C-3′), 55.60 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 462.1314 (15) $[C_{26}H_{22}O_8]^{+\cdot}$, 298 (6) $[C_{17}H_{14}O_5]^{+\cdot}$, 283 (1) $[C_{16}H_{11}O_5]^+$, 269 (4) $[C_{16}H_{13}O_4]^+$, 253 (1) $[C_{15}H_9O_4]^+$, 225 (2) $[C_{14}H_9O_3]^+$, 165 (100) $[C_9H_9O_3]^+$, 137 (4) $[C_8H_9O_2]^+$, 122 (2) $[C_7H_6O_2]^{+\cdot}$, 107 (2) $[C_7H_7O]^+$, 92 (2) $[C_6H_4O]^{+\cdot}$, 79 (3) $[C_5H_3O]^+$, 77 (4) $[C_6H_5]^+$, 51 (1) $[C_4H_3]^+$, 41 (1) $[C_3H_5]^+$, 39 (1) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 306 (25343), 338 (24848); (Figure 64, side 243).

Anal. Calcd for $C_{26}H_{24}O_8$: C, 67.53%; H, 4.80%; O, 27.68%. Found: C, 66.9%; H, 4.9%; O, 27.9%.

3.3.7. 3,4-Dimethoxy-benzoic acid 2-(3,4-dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran-6-yl ester (145)



According to the procedure A, the 2,5-dihydroxyacetophenone (**12d**) (2 g, 13.2 mmol) was mixed with LiHMDS (50 mL, 50 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**) (2.9 g, 14.5 mmol) to afford the flavone ester (**145**) as silver pellets (1.84 g, Yield 55%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ 7.91 (m, 2H, H-2″ and H-8), 7.85 (dd, 1H, $^3J_{6'',5''}$ = 7.93, $^4J_{6'',2''}$ = 1.58, H-6″), 7.79 (dd, 2H, $^3J_{7,8}$ = $^3J_{6',5'}$ = 9.25, $^4J_{7,5}$ = $^4J_{6',2'}$ = 2.65, H-7 and H-6′), 7.67 (m, 2H, H-2′ and H-5), 7.19 (d, 1H, $^3J_{5'',6''}$ = 9.52, H-5″), 7.17 (d, 1H, $^3J_{5',6'}$ = 9.52, H-5′), 7.11 (s, 1H, H-3), 3.93 (s, 3H, OCH_3 on C-3″), 3.91 (s, 3H, OCH_3 on C-4″), 3.89 (s, 6H, OCH_3 on C-3′ and C-4′).

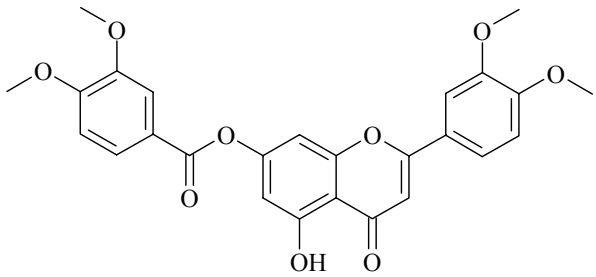
^{13}C NMR ($CDCl_3$, 62.89 MHz) δ 178.04 (C-4), 164.61 (C-11), 164.06 (C-2), 157.37 (C-9), 155.37(C-6), 154.46 (C-4″), 152.57 (C-3″), 149.74 (C-4′), 149.37 (C-3′), 127.47 (C-7), 125.13 (C-6″), 124.43 (C-1″), 122.12 (C-1′), 121.45 (C-10), 120.42 (C-6′), 119.90 (C-8), 112.81 (C-5″), 111.65 (C-2″ and C-2′), 110.92 (C-5′), 109.19 (C-5), 106.93 (C-3), 56.49 (OCH_3 on C-4″, C-4′, C-3″ and C-3′).

EI-MS *m/z* (% relative abundance) composition: 462.1314 (22) $[C_{26}H_{22}O_8]^{+\cdot}$, 298 (4) $[C_{17}H_{14}O_5]^{+\cdot}$, 297 (3) $[C_{17}H_{13}O_5]^{+}$, 269 (1) $[C_{16}H_{13}O_4]^{+}$, 241 (1) $[C_{15}H_{13}O_3]^{+}$, 181 (1) $[C_{13}H_9O]^{+}$, 165 (100) $[C_9H_9O_3]^{+}$, 162 (5) $[C_{10}H_{10}O_2]^{+\cdot}$, 147 (2) $[C_9H_7O_2]^{+}$, 137 (7) $[C_8H_9O_2]^{+}$, 135 (6) $[C_8H_7O_2]^{+}$, 122 (5) $[C_7H_6O_2]^{+\cdot}$, 119 (2), 107 (7) $[C_7H_7O]^{+}$, 94 (3) $[C_6H_6O]^{+\cdot}$, 92 (4) $[C_6H_4O]^{+\cdot}$, 91 (3) $[C_6H_3O]^{+}$, 79 (7) $[C_5H_3O]^{+}$, 77 (9) $[C_6H_5]^{+}$, 76 (2) $[C_6H_4]^{+\cdot}$, 66 (2) $[C_5H_6]^{+\cdot}$, 53 (1) $[C_4H_5]^{+}$, 51 (2) $[C_4H_3]^{+}$, 44 (2) $[C_2H_4O]^{+\cdot}$, 41 (1) $[C_3H_5]^{+}$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 266 (21123), 304.5 (20284), 334 (20930); (Figure 65, side 244).

Anal. Calcd for $C_{26}H_{22}O_8$: C, 67.53%; H, 4.80%; O, 27.68%. Found: C, 67.2%; H, 4.8%; O, 27.8%.

3.3.8. 3,4-Dimethoxybenzoic acid 5-hydroxy-2-(3,4-dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran-7-yl ester (146)



According to the procedure B, the 2,4,6-trihydroxyacetophenone (**12h**) (1 g, 5.3 mmol) was mixed with LiOH (463 mg, 19 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**) (1.19 g, 5.79 mmol) to afford the flavone ester (**146**) as pale yellow needles (78 mg, Yield 6%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.99 (s, 1H, exchanges with D_2O, OH on C-5), 7.81 (dd, 1H, $^3J_{6'',5''}$ = 8.82, $^4J_{6'',2''}$ = 2.22, H-6″), 7.76 (dd, 1H, $^3J_{6',5'}$ = 8.82, $^4J_{6',2'}$ = 2.22, H-6′), 7.65 (d, 1H, $^4J_{2'',6''}$ = 2.22, H-2″), 7.60 (d, 1H, $^4J_{2',6'}$ = 2.22, H-2′), 7.19 (d, 1H, $^3J_{5'',6''}$ = 8.82, H-5″), 7.17 (s, 1H, H-3), 7.16 (d, 1H, $^3J_{5',6'}$ = 8.82, H-5′), 7.05 (AX, 2H, δ_A = 7.29 (H-6) and δ_X = 6.81 (H-8), $^4J_{AX}$ = 2.21), 3.90 (s, 6H, OCH_3 on C-3″ and C-4″), 3.87 (s, 6H, OCH_3 on C-3′ and C-4′).

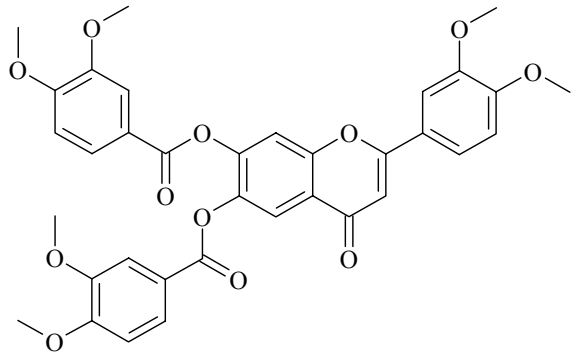
^{13}C NMR (DMSO-d^6, 62.89 MHz) δ 182.86 (C-4), 164.77 (C-2), 163.81 (C-11), 161.91 (C-7), 156.48 (C-5), 154.19 (C-9), 152.48 (C-4″), 149.53 (C-3″), 148.77 (C-3′), 144.01 (C-4′), 124.77 (C-6″), 123.43 (C-1′), 121.72 (C-1″), 121.14 (C-10), 120.35 (C-6′), 112.44 (C-2″), 111.26 (C-5″), 110.51 (C-5′), 108.83 (C-2′), 105.61 (C-6), 104.96 (C-8), 101.23 (C-3), 56.16 (OCH_3 on C-3′, C-3″, C-4′ and C-4″).

EI-MS *m/z* (% relative abundance) composition: 478.1264 (17) $[C_{26}H_{22}O_9]^{+\cdot}$, 314 (16) $[C_{17}H_{14}O_6]^{+\cdot}$, 299 (1) $[C_{16}H_{11}O_6]^{+}$, 285 (1) $[C_{16}H_{13}O_5]^{+}$, 271 (1) $[C_{15}H_{11}O_5]^{+}$, 239 (1) $[C_{15}H_{11}O_3]^{+}$, 182 (1) $[C_9H_8O_4]^{+\cdot}$, 165 (100) $[C_9H_9O_3]^{+}$, 153 (2) $[C_8H_9O_3]^{+}$, 148 (1) $[C_9H_8O_2]^{+\cdot}$, 137 (3) $[C_8H_9O_2]^{+}$, 123 (4) $[C_7H_7O_2]^{+}$, 122 (2) $[C_7H_6O_2]^{+\cdot}$, 107 (1) $[C_7H_7O]^{+}$, 92 (2) $[C_6H_4O]^{+\cdot}$, 79 (3) $[C_5H_3O]^{+}$, 77 (5) $[C_6H_5]^{+}$, 69 (1) $[C_4H_5O]^{+}$, 44 (1) $[C_2H_4O]^{+\cdot}$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 272 (7323), 346 (6727); (Figure 66, side 244).

Anal. Calcd for $C_{26}H_{22}O_9$: C, 65.27%; H, 4.63%; O, 30.10%. Found: C, 64.6%; H, 4.6%; O, 31.2%.

3.3.9. Bis 3,4-dimethoxybenzoic acid 2-(3,4-dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran-6,7-yl ester (147)



According to the procedure A, the 2,4,5-trihydroxyacetophenone (**12i**) (1 g, 5.7 mmol) was mixed with LiHMDS (22.6 mL, 22.6 mmol) and the 3,4-dimethoxybenzoyl chloride (**17c**) (1.27 g, 6.2 mmol) to afford the flavone ester (**147**) as a brown powder (110 mg, Yield 8%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ 7.82-7.05 (m, 9H, H_{Ar} of 3 phenyl rings), 7.75 (s, 1H, H-5), 7.26 (s, 1H, H-8), 6.95 (s, 1H, H-3), 3.91 (s, 3H, OCH_3 on C-3″), 3.89 (s, 3H, OCH_3 on C-3‴), 3.85 (s, 9H, OCH_3 on C-4′, C-4″, and C-4‴), 3.83 (s, 3H, OCH_3 on C-3′).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 175.92 (C-4), 163.78 (C-2), 163.09 (C-11), 162.71 (C-12), 162.28 (C-7), 154.77 (C-4″), 154.56 (C-4‴), 153.53 (C-9), 151.71 (C-6), 148.91 (C-

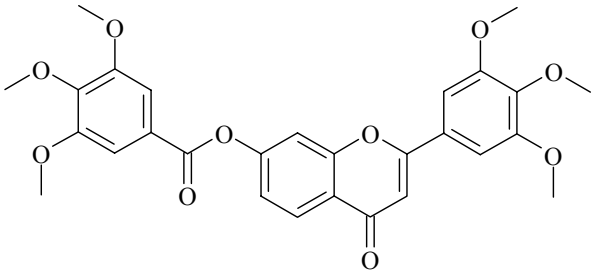
3″), 148.47 (C-3‴), 139.94 (C-3′), 137.56 (C-4′), 124.38 (C-6″), 124.18 (C-6‴), 123.35 (C-1′), 121.49 (C-1″), 120.48 (C-1‴), 119.96 (C-5), 119.65 (C-6′), 118.65 (C-2″), 118.24 (C-2‴), 115.70 (C-10), 114.06 (C-5′), 112.08 (C-2′), 111.59 (C-5″), 111.19 (C-5‴), 109.26 (C-8), 104.22 (C-3), 55.74 (OCH_3 on C-4′, C-4″ and C-4‴), 55.61 (OCH_3 on C-3″ and C-3‴), 55.26 (OCH_3 on C-3′).

EI-MS *m/z* (% relative abundance) composition: 642.1737 (5) $[C_{35}H_{30}O_{12}]^{+\cdot}$, 478 (2) $[C_{26}H_{22}O_9]^{+\cdot}$, 314 (3) $[C_{17}H_{14}O_6]^{+\cdot}$, 285 (1) $[C_{16}H_{13}O_5]^{+}$, 235 (1) $[C_{12}H_{11}O_5]^{+}$, 182 (9) $[C_9H_8O_4]^{+\cdot}$, 165 (100) $[C_9H_9O_3]^{+}$, 137 (3) $[C_8H_9O_2]^{+}$, 121 (2) $[C_{35}H_{30}O_{12}]^{+}$, 107 (1) $[C_7H_7O]^{+}$, 92 (1) $[C_6H_4O]^{+\cdot}$, 79 (3) $[C_5H_3O]^{+}$,77 (5) $[C_6H_5]^{+}$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 264 (30401), 331.5 (29642); (Figure 67, side 245).

Anal. Calcd for $C_{36}H_{32}O_{12}$: C, 65.85%; H, 4.91%; O, 29.24%. Found: C, 63.9%; H, 4.9%; O, 30.9%.

3.3.10. 3,4,5-Trimethoxybenzoic acid 2-(3,4,5-trimethoxyphenyl)-4-oxo-4*H*-1-benzopyran-7-yl ester (148)



According to the procedure A, the 2,4-dihydroxyacetophenone (**12c**) (1 g, 6.4 mmol) was mixed with LiHMDS (20 mL, 20 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.67 g, 7.1 mmol) to afford the flavone ester (**148**) as a white powder (170 mg, Yield 9%).

^{1}H NMR (DMSO-d^6, 300 MHz) δ 8.14 (d, 1H, $^3J_{5,6}$ = 7.94, H-5), 7.94 (d, 1H, $^4J_{8,7}$ = 2.65, H-8), 7.48 (dd, 1H, $^3J_{6,5}$ = 7.94, $^4J_{6,8}$ = 2.65, H-6), 7.46 (s, 2H, H-2″ and H-6″), 7.42 (s, 2H, H-2′ and H-6′), 7.21 (s, 1H, H-3), 3.91 (s, 6H, OCH_3 on C-3′ and C-5′), 3.88 (s, 6H, OCH_3-3″ and C-5″), 3.80 (s, 3H, OCH_3 on C-4″), 3.76 (s, 3H, OCH_3 on C-4′).

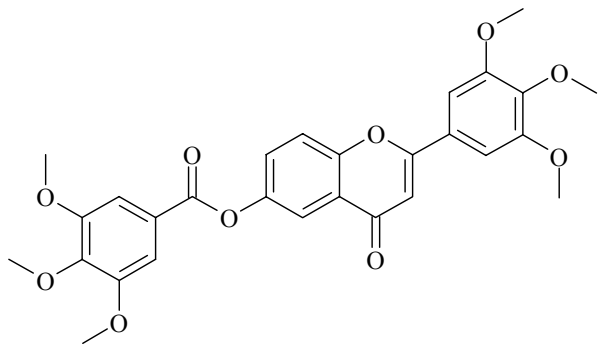
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.47 (C-4), 163.64 (C-2), 162.50 (C-11), 156.08 (C-7), 154.49 (C-9), 153.18 (C-3″ and C-5″), 152.87 (C-3′ and C-5′), 142.67 (C-4″), 140.53 (C-4′), 129.20 (C-1′), 126.13 (C-5), 124.91 (C-1″), 123.16 (C-10), 120.04 (C-6), 112.09 (C-8), 107.24 (C-2″ and C-6″), 106.74 (C-3), 103.95 (C-2′ and C-6′), 60.21 (OCH_3 on C-4″), 60.13 (OCH_3 on C-4″), 56.18 (OCH_3 on C-3″ and C-5″), 56.11 (OCH_3 on C-3′ and C-5′).

EI-MS *m/z* (% relative abundance) composition: 522.1526 (16) $[C_{28}H_{26}O_{10}]^{+\cdot}$, 328 (4) $[C_{18}H_{16}O_6]^{+\cdot}$, 313 (2) $[C_{17}H_{13}O_6]^{+}$, 299 (3) $[C_{17}H_{15}O_5]^{+}$, 238 (1) $[C_{15}H_{10}O_3]^{+\cdot}$, 195 (100) $[C_{10}H_{11}O_4]^{+}$, 167 (2) $[C_9H_{11}O_3]^{+}$, 165 (4) $[C_9H_9O_3]^{+}$, 152 (5) $[C_8H_8O_3]^{+\cdot}$, 137 (3) $[C_8H_9O_2]^{+}$, 135 (2) $[C_8H_7O_2]^{+}$, 122 (2) $[C_7H_6O_2]^{+\cdot}$, 107 (2) $[C_7H_7O]^{+}$, 105 (1) $[C_7H_5O]^{+}$, 92 (1) $[C_6H_4O]^{+\cdot}$, 81 (1) $[C_5H_5O]^{+}$, 77 (3) $[C_6H_5]^{+}$, 65 (1) $[C_5H_5]^{+}$, 53 (1) $[C_4H_5]^{+}$, 43 (2) $[C_2H_3O]^{+}$, 41 (4) $[C_3H_5]^{+}$, 39 (2) $[C_3H_3]^{+}$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 306 (24601), 331 sh (17347); (Figure 68, side 245).

Anal. Calcd for $C_{28}H_{26}O_{10}$: C, 64.36%; H, 5.02%; O, 30.62%. Found: C, 64.4%; H, 5.0%; O, 30.8%.

3.3.11. 3,4,5-Trimethoxybenzoic acid 2-(3,4,5-trimethoxyphenyl)-4-oxo-4*H*-1-benzopyran-6-yl ester (149)



According to the procedure A, the 2,5-dihydroxyacetophenone (**12d**) (1 g, 6.4 mmol) was mixed with LiHMDS (20 mL, 20 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.67 g, 7.1 mmol) to afford the flavone ester (**149**) as a pale yellow green powder (232 mg, Yield 13%).

^{1}H NMR (DMSO-d^6, 300 MHz) δ 8.35 (d, 1H, $^3J_{8,\,7}$ = 7.94, H-8), 7.79 (dd, 1H, $^3J_{7,\,8}$ = 7.94, $^4J_{7,\,5}$ = 2.65, H-7), 7.58 (d, 1H, $^4J_{5,\,7}$ = 2.65, H-5), 7.47 (s, 2H, H-2″ and H-6″), 7.44 (s, 2H, H-2′ and H-6′), 7.26 (s, 1H, H-3), 3.91 (s, 6H, OCH_3 on C-3′ and C-5′), 3.88 (s, 6H, OCH_3 on C-3″ and –5″), 3.80 (s, 3H, OCH_3 on C-4″), 3.76 (s, 3H, OCH_3 on C-4′).

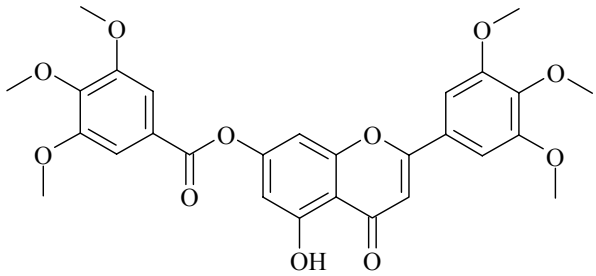
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.57 (C-4), 164.12 (C-2), 162.51 (C-11), 153.29 (C-9), 153.23 (C-3″ and C-5″), 152.65 (C-3′ and C-5′), 147.57 (C-6), 142.38 (C-4′), 141.98 (C-4″), 131.92 (C-7), 129.28 (C-1′), 125.79 (C-10), 125.14 (C-1″), 117.57 (C-8), 114.49 (C-5), 107.11 (C-2″ and C-6″), 106.21 (C-3), 103.89 (C-2′ and C-6′), 60.21 (OCH_3 on C-4″), 60.13 (OCH_3 on C-4″), 56.18 (OCH_3 on C-3″ and C-5″), 56.11 (OCH_3 on C-3′ and C-5′).

EI-MS *m/z* (% relative abundance) composition: 522.1526 (15) $[C_{28}H_{26}O_{10}]^{+\cdot}$, 328 (3) $[C_{18}H_{16}O_6]^{+\cdot}$, 327 (2) $[C_{18}H_{15}O_6]^{+}$, 313 (1) $[C_{17}H_{13}O_6]^{+}$, 195 (100) $[C_{10}H_{11}O_4]^{+}$, 192 (1) $[C_{10}H_9O_4]^{+\cdot}$, 177 (3) $[C_{10}H_9O_3]^{+}$, 167 (2) $[C_9H_{11}O_3]^{+}$, 152 (4) $[C_8H_8O_3]^{+\cdot}$, 137 (2) $[C_8H_9O_2]^{+}$, 135 (2) $[C_8H_7O_2]^{+}$, 122 (1) $[C_7H_6O_2]^{+\cdot}$, 109 (2) $[C_6H_5O_2]^{+}$, 107 (2) $[C_7H_7O]^{+}$, 92 (1) $[C_6H_4O]^{+\cdot}$, 81 (1) $[C_5H_5O]^{+}$, 77 (3) $[C_6H_5]^{+}$, 66 (1) $[C_5H_6]^{+}$, 53 (1) $[C_4H_5]^{+}$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 278 (9303), 317.5 (12382), 352 sh (8289); (Figure 69, side 246).

Anal. Calcd for $C_{28}H_{26}O_{10}$: C, 64.36%; H, 5.02%; O, 30.6%2. Found: C, 63.9%; H, 5.2%; O, 30.6%.

3.3.12. 3,4,5-Trimethoxybenzoic acid 5-hydroxy-2-(3,4,5-trimethoxyphenyl)-4-oxo-4*H*-1-benzopyran-7-yl ester (150)



According to the procedure B, the 2,4,6-trihydroxyacetophenone (**12h**) (1 g, 5.3 mmol) was mixed with LiOH (463 mg, 19 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.36 g, 5.8 mmol) to afford the flavone ester (**150**) as white needles (165 mg, Yield 11%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ 12.91 (s, 1H, exchanges with D_2O, OH on C-5), 7.42 (s, 4H, C-2″, C-2′, C-6″ and C-6’), 7.29 (s, 1H, H-3), 7.10 5AX, 2H, δ_A = 7.35 (H-6) and δ_X = 6.85 (H-8), $^4J_{AX}$ = 2.21), 3.91 (s, 6H, OCH_3 on C-3″ and C-5″), 3.87 (s, 6H, OCH_3 on C-3′ and C-5′), 3.79 (s, 3H, OCH_3 on C-4″), 3.76 (s, 3H, OCH_3 on C-4′).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 182.61 (C-4), 163.96 (C-2), 163.41 (C-11), 160.76 (C-7), 156.24 (C-5), 155.77 (C-9), 153.27 (C-3″ and C-5″), 152.92 (C-3′ and C-5′), 138.45 (C-4″), 132.54 (C-4′), 125.50 (C-1′), 123.22 (C-1″), 108.26 (C-10), 107.39 (C-2″ and C-6″), 105.51 (C-2′ and C-6′), 104.39 (C-6 and C-8), 101.96 (C-3), 60.22 (OCH_3 on C-4′ and C-4″), 56.31 (OCH_3 on C-3″ and C-5″), 56.20 (OCH_3 on C-3′ and C-5′).

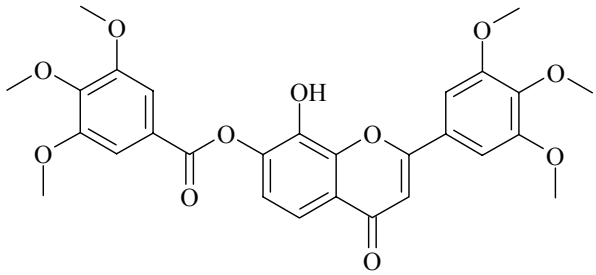
EI-MS *m/z* (% relative abundance) composition: 538.1475 (16) $[C_{28}H_{26}O_{11}]^{+\cdot}$, 344 (22) $[C_{18}H_{16}O_7]^{+\cdot}$, 329 (3) $[C_{17}H_{13}O_7]^{+}$, 315 (3) $[C_{17}H_{15}O_6]^{+}$, 301 (2) $[C_{16}H_{13}O_6]^{+}$, 241 (2) $[C_{14}H_9O_4]^{+}$, 212 (3) $[C_{13}H_8O_3]^{+\cdot}$, 195 (100) $[C_{10}H_{11}O_4]^{+}$, 177 (2) $[C_{11}H_9O_3]^{+}$, 165 (2) $[C_9H_9O_3]^{+}$, 153 (3) $[C_8H_9O_3]^{+}$, 152 (4) $[C_8H_8O_3]^{+\cdot}$, 143 (2), 139 (3) $[C_7H_7O_3]^{+\cdot}$, 123 (4)

$[C_7H_7O_2]^+$, 122 (2) $[C_7H_6O_2]^{+\cdot}$, 109 (2) $[C_6H_5O_2]^+$, 107 (2) $[C_7H_7O]^+$, 105 (1) $[C_7H_5O]^+$, 93 (1) $[C_6H_5O]^+$, 81 (1) $[C_5H_5O]^+$, 77 (1) $[C_6H_5]^+$, 69 (1) $[C_4H_5O]^+$, 66 (1) $[C_5H_6]^{+\cdot}$, 53 (1) $[C_4H_5]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 277 (12022), 333 (9814); (Figure 71, side 247).

Anal. Calcd for $C_{28}H_{26}O_{11}$: C, 62.45%; H, 4.87%; O, 32.68%. Found: C, 62.2%; H, 4.8%; O, 33.0%.

3.3.13. 3,4,5-Trimethoxybenzoic acid 8-hydroxy-2-(3,4,5-trimethoxyphenyl)- 4-oxo-4*H*-1-benzopyran-7-yl ester (151)



According to the procedure A, the 2,3,4-trihydroxyacetophenone (**12f**) (1 g, 6 mmol) was mixed with LiHMDS (20 mL, 20 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.5 g, 6.6 mmol) to afford the flavone ester (**151**) as a pale yellow powder (217 mg, Yield 14%).

^{1}H NMR (DMSO-d^6, 500 MHz) δ 11.20 (br s, 1H, exchanges with D_2O, OH on C-8), 7.57 (s, 2H, H-2″ and H-6″), 7.50 (AB, 2H, δ_A = 7.85 (H-6) and δ_B= 7.15 (H-5), $^3J_{AB}$ = 8.81), 7.12 (s, 1H, H-3), 7.09 (s, 2H, H-2′ and H-6′), 3.87 (s, 6H, OCH_3 on C-3″ and C-5″), 3.82 (s, 3H, OCH_3 on C-4″), 3.68 (s, 3H, OCH_3 on C-4′), 3.50 (s, 6H, OCH_3 on C-3′ and C-5′).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 176.11 (C-4), 163.16 (C-2), 160.94 (C-11), 154.69 (C-7), 153.05 (C-3″, C-5″, C-3′ and C-5′), 149.34 (C-9), 142.80 (C-4″), 140.37 (C-4′), 139.54 (C-8), 125.95 (C-1′), 125.61 (C-1″), 122.85 (C-5), 116.35 (C-10), 115.21 (C-6), 107.49 (C-2″ and C-6″), 106.41 (C-3), 103.24 (C-2′ and C-6′), 60.27 (OCH_3 on C-4″), 60.11 (OCH_3 on C-4′), 56.23 (OCH_3 on C-3″ and C-5″), 55.34 (OCH_3 on C-3′ and C-5′).

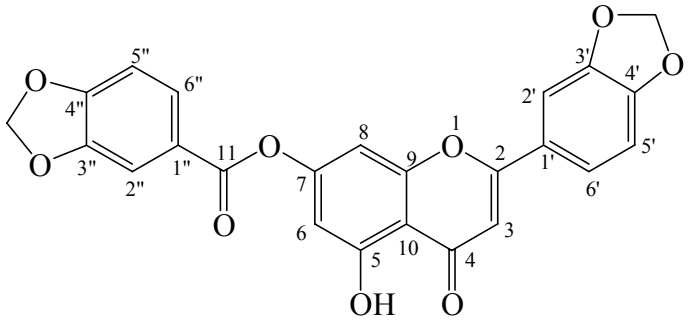
EI-MS *m/z* (% relative abundance) composition: 538.1475 (7) $[C_{28}H_{26}O_{11}]^{+\cdot}$, 344 (19) $[C_{18}H_{16}O_7]^{+\cdot}$, 329 (5) $[C_{17}H_{13}O_7]^+$, 315 (3) $[C_{17}H_{15}O_6]^+$, 301 (1) $[C_{16}H_{13}O_6]^+$, 241 (2) $[C_{14}H_9O_4]^+$, 212 (1) $[C_{13}H_8O_3]^{+\cdot}$, 195 (100) $[C_{10}H_{11}O_4]^+$, 192 (5) $[C_{10}H_8O_3]^{+\cdot}$, 181 (2) $[C_9H_7O_4]^+$, 178 (2) $[C_{10}H_{10}O_3]^{+\cdot}$, 177 (4) $[C_{10}H_9O_3]^+$, 167 (2) $[C_9H_{11}O_3]^+$, 158 (1) $[C_{10}H_6O_2]^{+\cdot}$, 153 (2) $[C_8H_9O_3]^+$, 152 (8) $[C_8H_8O_3]^{+\cdot}$, 151 (2) $[C_8H_7O_3]^+$, 150 (1) $[C_8H_6O_3]^{+\cdot}$, 149 (2) $[C_9H_9O_2]^+$, 137 (4) $[C_8H_9O_2]^+$, 133 (2) $[C_8H_5O_2]^+$, 124 (2) $[C_7H_8O_2]^{+\cdot}$, 123 (4) $[C_7H_7O_2]^+$, 122

(4) $[C_7H_6O_2]^{+\cdot}$, 119 (1) $[C_7H_3O_2]^+$, 109 (3) $[C_6H_5O_2]^+$, 108 (2) $[C_6H_4O_2]^{+\cdot}$, 107 (2) $[C_7H_7O]^+$, 97 (2) $[C_5H_5O_2]^+$, 92 (2) $[C_6H_4O]^{+\cdot}$, 81 (3) $[C_5H_5O]^+$, 77 (4) $[C_6H_5]^+$, 66 (3) $[C_5H_6]^{+\cdot}$, 63 (2) $[C_5H_3]^+$, 53 (2) $[C_4H_5]^+$, 39 (1) $[C_3H_3]^+$.

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 270 (17665), 304 (14360); (Figure 70, side 246).

Anal. Calcd for $C_{28}H_{26}O_{11}$: C, 62.45%; H, 4.87%; O, 32.68%. Found: C, 61.9%; H, 4.9%; O, 33.1%.

3.3.14. Benzo[1,3]dioxole-5-carboxylic acid 2-benzo[1,3]dioxol-5-yl-5-hydroxy-4-oxo-4*H*-1-benzopyran-7-yl ester (152)

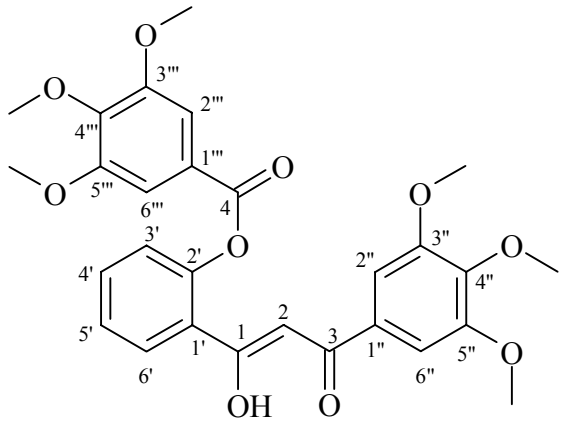


According to the procedure B, the 2,4,6-trihydroxyacetophenone (**12h**) (1 g, 5.3 mmol) was mixed with LiOH (508 mg, 21.2 mmol) and the piperonyloyl chloride (**17g**) (978 mg, 5.3 mmol) to afford the flavone ester (**152**) as yellow powder (863 mg, Yield 36%).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 12.73 (s, 1H, exchanges with D_2O, OH on C-5), 7.76 (d, 1H, $^3J_{6'', 5''}$ = 8.81, H-6″), 7.52 (s, 1H, H-2″), 7.43 (d, 1H, $^3J_{6', 5'}$ = 8.81, H-6′), 6.88 (s, 1H, H-3), 6.87 (m, 2H, H-5″ and H-2′), 6.60 (s, 1H, H-5′), 6.55 (s, 2H, H-6 and H-8), 6.05 (s, 2H, OCH_2O on C-3″ and C-4″), 6.02 (s, 2H, OCH_2O on C-3′ and C-4′).

Maldi-MS *m/z* (% relative abundance): $[M+H]^+$ 447.1 (100) $[C_{24}H_{14}O_9+H]$.

3.3.15. 3,4,5-Trimethoxybenzoic acid 2-[1-hydroxy-3-oxo-3-(3,4,5-trimethoxyphenyl)-propenyl]-phenyl ester (153)



According to the procedure A, the 2-hydroxyacetophenone (**12a**) (2 g, 14.67 mmol) was mixed with LiHMDS (30 mL, 30 mmol) and the 3,4,5-trimethoxybenzoyl chloride (**17d**) (3.8 g, 16.15 mmol) to afford the propanedione derivative (**153**) as beige crystals (2.04 g, Yield 27%).

^{1}H NMR (DMSO-d^6, 250 MHz) δ 16.87 (very br s, 1H, exchanges with D_2O, OH on C-1), 7.98 (dd, 1H, $^3J_{6',5'}$ =, $^4J_{6',4'}$ = 8.81, H-6′), 7.70 (td, 1H, $^3J_{4',5'}$ = $^3J_{4',3'}$ = 8.81, $^4J_{4',6'}$ = 2.21, H-4′), 7.5 (m, 2H, H-5′ and H-3′), 7.42 (s, 2H, H-2″ and H-6‴), 7.26 (s, 2H, H-2″ and H-6″), 7.04 (s, 1H, H-2), 3.82 (s, 6H, OCH_3 on C-3″ and C-5″), 3.78 (s, 6H, OCH_3 on C-3‴ and C-5‴), 3.76 (s, 3H, OCH_3 on C-4″), 3.75 (s, 3H, OCH_3 on C-4‴).

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 185.03 (C-3), 184.14 (C-1), 163.96 (C-4), 152.90 (C-3″ and C-5″), 152.86 (C-3‴ and C-5‴), 148.51 (C-2′), 142.55 (C-4″), 141.93 (C-4‴), 133.03 (C-4′), 129.78 (C-6′), 129.52 (C-1″), 129.09 (C-1″), 126.53 (C-5′), 123.85 (C-3′), 123.63 (C-1‴), 107.34 (C-2‴ and C-6‴), 104.92 (C-2″ and C-6″), 96.84 (C-2), 60.15 (C-6 and C-9), 56.09 (C-5 and C-7), 56.06 (C-8 and C-10).

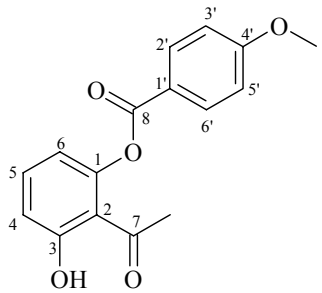
EI-MS *m/z* (% relative abundance) composition: 524.1683 (2) $[C_{28}H_{28}O_{10}]^{+\cdot}$, 406 (4), 405 (18), 404 (75), 389 (1), 373 (2), 361 (2), 330 (3) $[C_{18}H_{18}O_6]^{+\cdot}$, 319 (1), 312 (2), 236 (2), 202 (2), 196 (12) $[C_{10}H_{12}O_4]^{+\cdot}$, 195 (100) $[C_{10}H_{11}O_4]^+$, 193 (7) $[C_{10}H_{10}O_4]^+$, 186 (2), 181 (1) $[C_9H_9O_4]^+$, 169 (4), 168 (11), 154 (6), 153 (5), 151 (2), 137 (5), 124 (1), 122 (4), 121 (2), 119 (3), 117 (2), 92 (3).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 317.5 (18672); 365.5 (35661); (Figure 72, side 247).

Anal. Calcd for $C_{28}H_{26}O_{11}$: C, 64.12%; H, 5.38%; O, 30.50%. Found: C, 63.3%; H, 7.9%; O, 30.0%.

3.4. BK-VK intermediates (Chapter 3)

3.4.1. 4-Methoxybenzoic acid 2-acetyl-3-hydroxyphenyl ester (154a)



To a stirring solution of 2,6-dihydroxyacetophenone (**12e**) (500 mg, 3.25 mmol) in pyridine (5 mL), was added the 4-methoxybenzoyl chloride (**17b**) (833 mg, 4.88 mmol) at room temperature. It was stirred for 30 min, and poured into 3% aqueous HCl/ice solution with vigorous stirring. The precipitate, which was formed, was filtered and washed with water and dried overnight under reduced pressure. The crude product was recrystallized from methanol and led to the 2-(4-methoxybenzoyl)oxy-6-hydroxyacetophenone (**154a**) as white powder (856 mg, Yield 92%).

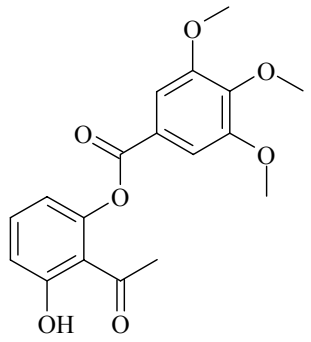
The 2,6-dihydroxyacetophenone (**12e**) (100 mg, 0.65 mmol) and lithium hydroxide (16 mg, 0.65 mmol) was mixed in THF (5 mL) at room temperature for 30 minutes. The 4-methoxybenzoyl chloride (**17b**) (120 mg, 0.7 mmol) in THF (2 mL) was then added dropwise to the reaction mixture. The stirring was continued for one hour and the reaction was quenched with HCl (3%). The product was extracted with CH_2Cl_2 and the organic phases were washed with water and brine, dried with Na_2SO_4 and the solvents evaporated under reduced pressure. The crude product was recrystallized from methanol to afford the 2-(4-methoxybenzoyl)oxy-6-hydroxyacetophenone (**154a**) as white powder (179 mg, Yield 96%).

^{1}H NMR (DMSO-d^6, 300 MHz) δ 10.65 (br s, 1H, exchanges with D_2O, OH on C-3), 8.02-7.12 (dm, 4H, supposed as a AA′XX′ system, H_{Ar} of benzoyl), 7.64 (t, 1H, $^3J_{5,4} = {}^3J_{5,6}$ = 7.94, H-5), 6.87 (d, 1H, $^3J_{6,5}$ = 7.94, H-6), 6.73 (D, 1H, $^3J_{4,5}$ = 7.94, H-4), 3.89 (s, 3H, OCH_3 on C-4′), 2.46 (s, 3H, $COCH_3$).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 200.00 (C-7), 64.03 (C-8), 163.09 (C-4′), 156.52 (C-3), 147.40 (C-1), 132.10 (C-2′ and C-6′), 131.53 (C-5), 121.51 (C-1′), 120.96 (C-2), 114.40 (C-3′ and C-5′), 113.90 (C-6), 113.35 (C-4), 55.63 (OCH_3 on C-4′), 31.47 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 286.08 $[C_{16}H_{14}O_5]^{+\cdot}$ (2), 152 (2), 135 (100), 108 (2), 107 (5), 92 (8), 79 (4), 77 (11), 64 (4), 52 (3), 39 (2).

3.4.2. 3,4,5-Trimethoxybenzoic acid 2-acetyl-3-hydroxy-phenyl ester (154b)



To a stirring solution of 2,6-dihydroxyacetophenone (**12e**) (500 mg, 3.25 mmol) in pyridine (5 mL), was added the 3,4,5-trimethoxybenzoyl chloride (**17d**) (1.15 g, 4.88 mmol) at room temperature. It was stirred for 30 min, and poured into 3% aqueous HCl/ice solution with vigorous stirring. The precipitate, which was formed, was filtered and washed with water and dried overnight under reduced pressure. The crude product was recrystallized from methanol and led to the 2-(3,4,5-trimethoxybenzoyl)oxy-6-hydroxyacetophenone (**154b**) as white powder (1.04 g, Yield 92%).

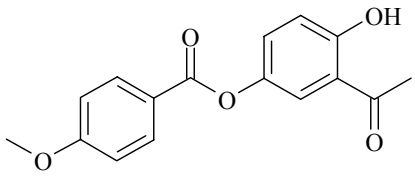
The 2,6-dihydroxyacetophenone (**12e**) (200 mg, 1.31 mmol) and lithium hydroxide (32 mg, 1.31 mmol) was mixed in THF (7 mL) at room temperature for 30 minutes. The 3,4,5-trimethoxybenzoyl chloride (**17d**) (332 mg, 1.44 mmol) in THF (4 mL) was then added dropwise to the reaction mixture. The stirring was continued for one hour and the reaction was quenched with HCl (3%). The product was extracted with CH_2Cl_2 and the organic phases were washed with water and brine, dried with Na_2SO_4 and the solvents evaporated under reduced pressure. The crude product was recrystallized from methanol to afford the 2-(4-methoxybenzoyl)oxy-6-hydroxyacetophenone (**154b**) as white powder (425 mg, Yield 94%)

^{1}H NMR (DMSO-d^6, 500 MHz) δ 10.64 (br s, 1H, exchanges with D_2O, OH on C-3), 7.68 (t, 1H, $^3J_{5,6} = {}^3J_{5,4}$ = 7.94, H-5), 7.32 (s, 2H, H-2′ and H-6′), 6.88 (d, 1H, $^3J_{6,5}$ = 7.94, H-6), 6.75 (d, 1H, $^3J_{4,5}$ = 7.94, H-4), 3.82 (s, 6H, OCH_3 on C-3′ and C-5′), 3.77 (s, 3H, OCH_3 on C-4′), 2.4 (s, 3H CH_3).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 200.01 (C-7), 163.72 (C-8), 163.60 (C-3), 156.57 (C-1), 152.92 (C-3′ and C-5′), 147.41 (C-4′), 142.87 (C-5), 128.03 (C-1′), 122.96 (C-2), 121.02 (C-6), 114.07 (C-4), 107.39 (C-2′ and C-6′), 60.19 (OCH_3 on C-4′), 56.15 (OCH_3 on C-3′ and C-5′), 31.16 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 346.11 $[C_{18}H_{18}O_7]^{+\cdot}$ (4), 212 (1), 195 (100), 181 (2), 179 (3), 165 (1), 152 (9), 150 (2), 137 (12), 134 (1), 122 (3), 107 (4), 105 (3), 92 (2), 81 (5), 73 (2), 66 (3), 57 (5), 53 (3), 43 (8), 39 (4).

3.4.3. 4-Methoxybenzoic acid 3-acetyl-4-hydroxyphenyl ester (155)



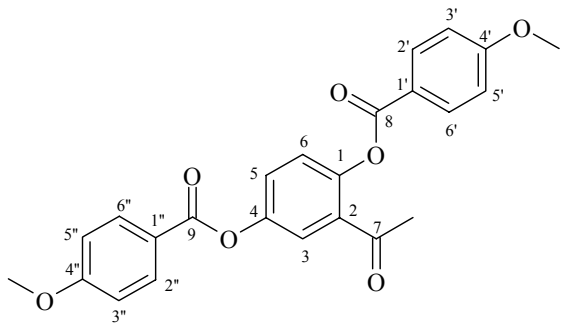
The 2,5-dihydroxyacetophenone (**12d**) (100 mg, 0.65 mmol) and lithium hydroxide (16 mg, 0.65 mmol) was mixed in THF (5 mL) at room temperature for 30 minutes. The 4-methoxybenzoyl chloride (**17b**) (120 mg, 0.7 mmol) in THF (2 mL) was then added dropwise to the reaction mixture. The stirring was continued for one hour and the reaction was quenched with HCl (3%). The product was extracted with CH_2Cl_2 and the organic phases were washed with water and brine, dried with Na_2SO_4 and the solvents evaporated under reduced pressure. The crude product was recrystallized from methanol to afford the 3-(4-methoxybenzoyl)oxy-6-hydroxyacetophenone (**155**) as white powder (167 mg, Yield 90%).

^{1}H NMR (DMSO-d^6, 300 MHz) δ 11.76 (br s, 1H, exchanges with D_2O, OH on C-5), 8.08-7.11 (dm, 4H, supposed as a AA′XX′ system, H_{Ar} of benzoyl), 7.76 (d, 1H, $^4J_{6,2}$ = 2.64, H-6), 7.44 (dd, 1H, $^3J_{2,3}$ = 7.94, $^4J_{2,6}$ = 2.64, H-2), 7.04 (d, 1H, $^3J_{3,2}$ = 7.94, H-3), 3.87 (s, 3H, OCH_3 on C-4′), 2.62 (s, 3H, $COCH_3$).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 203.05 (C-7), 170.38 (C-4′), 167.81 (C-8), 158.12 (C-4), 142.36 (C-1), 131.92 (C-2′ and C-6′), 130.04 (C-2), 127.25 (C-5), 123.50 (C-6), 120.87 (C-1′), 118.31 (C-3), 114.40 (C-3′ and C-5′), 55.58 (OCH_3 on C-4′), 27.88 (CH_3).

EI-MS *m/z* (% relative abundance) composition: 286.08 $[C_{16}H_{14}O_5]^{+\cdot}$ (26), 271 (1), 151 (4), 137 (4), 136 (35), 135 (100), 108 (2), 107 (15), 92 (22), 79 (1), 77 (25), 64 (7), 52 (1), 43 (4).

3.4.4. Bis 4-methoxybenzoic acid 2-acetylphenyl [1,4]ester (156)



To a stirring solution of 2,5-dihydroxyacetophenone (**12e**) (500 mg, 3.25 mmol) in pyridine (5 mL), was added the 4-methoxybenzoyl chloride (**17b**) (1.11 g, 6.51 mmol) at

room temperature. It was stirred for 30 min, and poured into 3% aqueous HCl/ice solution with vigorous stirring. The precipitate, which was formed, was filtered and washed with water and dried overnight under reduced pressure. The crude product was recrystallized from methanol and led to the 2,4-di(4-methoxybenzoyl)oxyacetophenone (**156**) as white powder (1.231 g, Yield 90%).

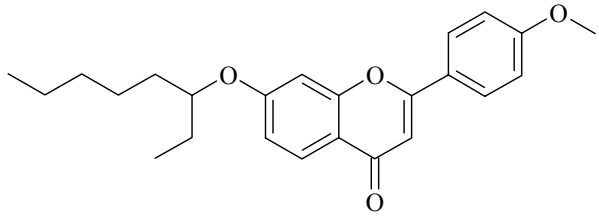
The 2,5-dihydroxyacetophenone (**12d**) (100 mg, 0.65 mmol) and lithium hydroxide (32 mg, 1.31 mmol) was mixed in THF (5 mL) at room temperature for 30 minutes. The 4-methoxybenzoyl chloride (**17b**) (240 mg, 1.5 mmol) in THF (4 mL) was then added dropwise to the reaction mixture. The stirring was continued for one hour and the reaction was quenched with HCl (3%). The product was extracted with CH_2Cl_2 and the organic phases were washed with water and brine, dried with Na_2SO_4 and the solvents evaporated under reduced pressure. The crude product was recrystallized from methanol to afford the 2,4-di(4-methoxybenzoyl)oxyacetophenone (**156**) as white powder (249 mg, Yield 91%).

^{1}H NMR (DMSO-d^6, 500 MHz) δ 8.09-7.12 (dm, 4H, supposed as a AA′XX′ system, H_{Ar} of benzoyl (B′), 7.90-7.02 (dm, 4H, supposed as a AA′XX′ system, H_{Ar} of benzoyl (B″)), 7.75 (d, 1H, $^4J_{3,\,5}$ = 2.2, H-3), 7.45 (dd, 1H, $^3J_{5,\,6}$ = 9.70, $^4J_{5,\,3}$ = 2.20, H-5), 7.04 (d, 1H, $^3J_{6,\,5}$ = 9.70, H-6), 3.88 (s, 3H, OCH3 on C-4′), 3.81 (s, 3H, OCH_3 on C-4″), 2.83 (s, 3H, CH_3).

EI-MS *m/z* (% relative abundance) composition: 420.12 $[C_{24}H_{20}O_7]^{+\cdot}$ (3), 135 (100), 107 (8), 92 (12), 77 (18), 64 (1).

3.5. Cosmetics derivatives (Chapter 3)

3.5.1. 7-Ethylhexyloxy-2-(4-methoxyphenyl)-4-oxo-4*H*-benzopyran (157a)



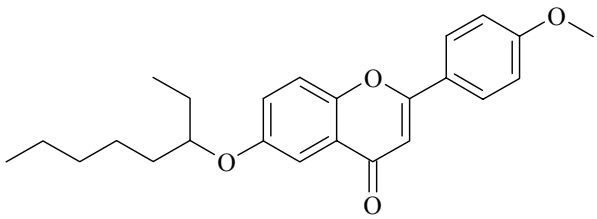
The 7-hydroxy-4′-methoxyflavone (**82**) (100 mg, 0.36 mmol), 2-ethylhexyl iodide (0.067 ml, 0.36 mmol), potassium carbonate (100 mg, 0.72 mmol) and acetonitrile (5 ml) were mixed together and heated at reflux 24h. Then the acetonitrile was removed under reduced pressure and the residue was pout into water. The crude product was extracted with ethyl acetate, and the organic phases were washed with sodium carbonate and water, dried with

sodium sulphate and the solvent was evaporated to afford the 7-ethylhexyloxy-4′-methoxyflavone (**157a**) as a light orange oil (130 mg, Yield 94%).

EI-MS *m/z* (% relative abundance) composition: 380.49 $[C_{24}H_{28}O_4]^{+\cdot}$ (44), 281 (2), 268 (100), 240 (12), 239 (10), 225 (3), 196 (2), 168 (2), 152 (2), 132 (19), 119 (3), 117 (4), 89 (4), 71 (11), 63 (2), 57 (19), 43 (21), 39 (1).

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 317.5 (18672); 365.5 (35661); (Figure 73, side 247).

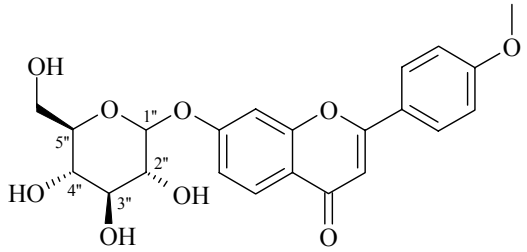
3.5.2. 6-Ethylhexyloxy-2-(4-methoxyphenyl)-4-oxo-4*H*-benzopyran (157b)



The 7-hydroxy-4′-methoxyflavone (**83**) (200 mg, 0.75 mmol), 2-ethylhexyl iodide (0.138 ml, 0.75 mmol), potassium carbonate (206 mg, 1.49 mmol) and acetonitrile (5 ml) were mixed together and heated at reflux 24h. Then the acetonitrile was removed under reduced pressure and the residue was pout into water. The crude product was extracted with ethyl acetate, and the organic phases were washed with sodium carbonate and water, dried with sodium sulphate and the solvent was evaporated to afford the 6-ethylhexyloxy-4′-methoxyflavone (**157a**) as a yellow oil (242 mg, Yield 85%).

EI-MS *m/z* (% relative abundance) composition: 380.19 $[C_{25}H_{30}O_4]^{+\cdot}$ (2), 361 (1), 351 (3), 323 (4), 305 (1), 281 (14), 268 (100), 253 (3), 239 (2), 225 (7), 197 (4), 168 (1), 152 (1), 136 (10), 132 (25), 120 (4), 117 (7), 108 (11), 92 (2), 89 (7), 69 (2), 57 (4), 52 (2), 43 (4), 41 (11), 39 (3).

3.5.3. 7-(3,4,5-Trihydroxy-6-hydroxymethyltetrahydropyran-2-yloxy)-2-(4-methoxyphenyl)-4-oxo-4*H*-benzopyran (158)



The 7-hydroxy-4′-methoxyflavone (**82**) (50 mg, 0.18 mmol) and the D-(+)-acetobromoglucose (80 mg, 0.19 mmol) were dissolved in pyridine (2 mL). The silver carbonate salts (50 mg, 0.18 mmol) cooled at 8°C, were slowly added to the reaction mixture. The reaction was weakly exothermic and was stirred 3 hours. The brown-green suspension was poured on acid solution (15 mL H_20, 5 g ice, 2.5 mL acetic acid), precipitated and was stirred 15 min, before being filtered and washed with water (5 x 1 mL). The product was dissolved in hot acetone (2 mL) to be separated from the insoluble silver salts. Potassium hydroxide (55 mg, 0.98 mmol) in 2 mL water was added to the filtrate, a clear yellow solution heated at 30-40°C. The reaction mixture was stirred one hour at room temperature and 2 mL water were again added before standing overnight. The precipitated was filtered and washed with water. The mother liquor was mixed with water (2 mL) and acetic acid (1 mL), which led to the precipitation of a white product. It was filtered and dried to afford the 7-*O*-glucosyl-4′-methoxyflavone as white powder (15 mg, 20 %).

The 7-hydroxy-4′-methoxyflavone (**82**) (1 g, 3.73 mmol) was dissolved in sodium hydroxide (1N, 50 mL) and stirred 15 min to lead to a yellow solution. The D-(+)-acetobromoglucose (4.6 g, 11.19 mmol) and the tetrabutyl ammonium (1.8 g, 5.58 mmol) in dichloromethane (50 mL) were added to the reaction mixture and stirred at room temperature for 5 hours. The reaction mixture was carefully quenched with H_2SO_4 (2.45 g, 25 mmol)/H_2O (47 mL) and extracted with ethyl acetate. A white product precipitated and was filtered (P1, 200 mg), the organic phases were washed with water and brine, dried with Na_2SO_4 and the solvents were evaporated under reduced pressure to afford yellow crystals (P2, 2.5 g). Products were separately added to a solution of sodium (P1: 100 mg, P2: 1g) methylate in methanol (P1: 15 mL, P2: 150 mL) and stirred over night. The solution was quenched glacial acetic acid (c.a. pH 5-6) and stirred one hour in an ice bath. The precipitated product was filtered, washed with methanol (30 min stirring at room temperature) and dried overnight (at 40°C, 200 mbar) twice to lead to the 7-*O*-Glucosyl-4′-methoxyflavone as a light yellow powder (1.017 g, 64%).

^{1}H NMR (DMSO-d^6, 500 MHz) δ 8.05 (d, 2H, $^{3}J_{2', 3'} = {}^{3}J_{6', 5'}$ = 8.82, H-2′ and H-6′), 7.95 (d, 1H, $^{3}J_{5, 6}$ = 8.82, H-5), 7.37 (d, 1H, $^{4}J_{8, 6}$ = 2.21, H-8), 7.12 (d, 3H, $^{3}J_{3', 2'} = {}^{3}J_{5', 6'} = {}^{3}J_{6, 5}$ = 8.81, H-3′, H-5′ and H-6), 6.88 (s, 1H, H-3), 5.41 (s, 1H, H-1″), 5.12 (m, 2H, CH_2), 5.05 (s, 1H, H-5″), 4.58 (m, 1H, H-2″), 3.86 (s, 3H, OCH_3 on C-4′), 3.74 (m, 1H, H-3″), 3.48 (m, 1H, H-4″), 3.30 (s, exchanges with D_2O, OH of the glucose moiety).

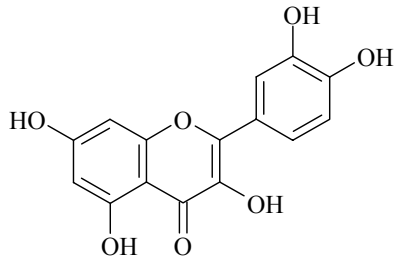
^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 176.561 (C-4), 162.37 (C-2), 162.05 (C-7), 161.84 (C-4′), 156.97 (C-9), 128.14 (C-2′ and C-6′), 126.56 (C-5), 122.28 (C-1′), 117.43 (C-10), 115.24 (C-6), 114.67 (C-3′ and C-5′), 106.55 (C-8), 103.08 (C-1″), 102.77 (C-3), 77.07 (C-2″), 76.30 (C-5″), 73.02 (C-3″), 69.43 (C-4″), 60.51 (CH_2OH).

EI-MS *m/z* (% relative abundance) composition: 430.12 $[C_{22}H_{22}O_9]^{+\cdot}$

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 322 (37157); (Figure 74, side 248).

3.6. Other compounds (chapters 4, 5, 6)

3.6.1. 3,5,7-Trihydroxy-2-(3,4-dihydroxyphenyl)-4-oxo-4H-benzopyran / Quercetin (159)



purchased by Merck KGaA (Art.-Nr.: 107542).

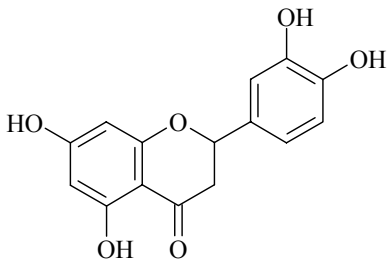
^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.52 (s, 1H, exchanges with D_2O, OH on C-5), 10.80 (br s, 1H, exchanges with D_2O, OH on C-7), 9.40 (br s, 3 H, exchanges with D_2O, OH on C-3, C-3′ and C-4′), 7.71 (d, 1H, $^{4}J_{2',5'}$ = 2.65, H-2′), 7.57 (dd, 1H, $^{3}J_{5', 6'}$ = 7.94, $^{4}J_{5', 2'}$ = 2.65, H-5′), 6.91 (d, 1H, $^{3}J_{6', 5'}$ = 7.94, H-6′), 6.44 (d, 1H, $^{4}J_{6, 8}$ = 2.65, H-6), 6.22 (d, 1H, $^{4}J_{8, 6}$ = 2.65, H-8).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 175.74 (C-4), 163.79 (C-7), 160.02 (C-5), 156.04 (C-9), 147.60 (C-3′), 146.69 (C-2), 144.95 (C-4′), 135.64 (C-1′), 121.87 (C-3), 119.89 (C-6′), 115.51 (C-5′), 114.96 (C-2′), 102.91 (C-10), 98.08 (C-6), 93.26 (C-8).

EI-MS *m/z* (% relative abundance) composition: 302.24 $[C_{15}H_{10}O_7]^{+\cdot}$

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 256 (20253), 302 (7145), 374 (21567); (Figure 75, side 249).

3.6.2. 5,7-Dihydroxy-2,3-dihydro-2-(3,4-dihydroxyphenyl)-4-oxo-*4H*-benzopyran / Eriodictyol (160)



Synthesized at the Pigments R&D Cosmetics Department (Merck KGaA).

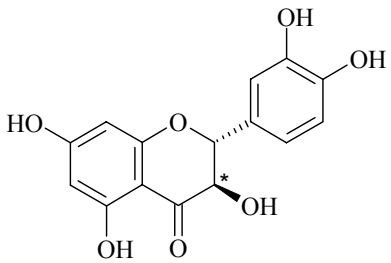
^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.15 (s, 1H, exchanges with D_2O, OH on C-5), 10.76 (br s, 1H, exchanges with D_2O, OH on C-7), 9.05 (br s, 1H, exchanges with D_2O, OH on C-3), 9.02 (br s, 2H, exchanges with D_2O, OH on C-3′ and C-4′), 6.87 (s, 1H, H-5′), 6.74 (s, 2H, H-2′ and C-6′), 5.89 (s, 2H, H-6 and H-8), 5.37 (m, 1H, H-2), 3.17 (m, 1H, H-3), 2.67 (m, 1H, H-3)

^{13}C NMR (DMSO-d^6, 62.90 MHz) δ 196.00 (C-4), 166.53 (C-7), 163.38 (C-5), 162.81 (C-9), 145.62 (C-3′), 145.10 (C-4′), 129.36 (C-1′), 117.86 (C-6′), 115.24 (C-5′), 114.25 (C-2′), 101.70 (C-10), 95.66 (C-6), 94.86 (C-8), 78.37 (C-2), 41.98 (C-3).

EI-MS *m/z* (% relative abundance) composition: 288.26 $[C_{15}H_{12}O_6]^{+\cdot}$

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 290 (23311), 335 (3970); (Figure 76, side 249).

3.6.3. 3,5,7-Trihydroxy-2,3-dihydro-2-(3,4-dihydroxyphenyl)-4-oxo-*4H*-benzopyran / Taxifolin (161)



Purchased by Indofine Inc. USA (Art.-Nr.: P-101).

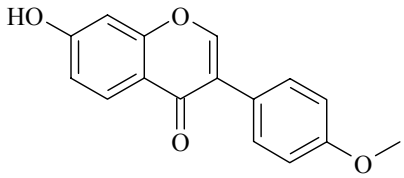
^{1}H NMR (DMSO-d^6, 300 MHz) δ 11.91 (s, 1H, exchanges with D_2O, OH on C-5), 10.85 (s, 1H, exchanges with D_2O, OH on C-7), 9.05 (s, 1H, exchanges with D_2O, OH on C-3), 8.99 (s, 2H, exchanges with D_2O, OH on C-3′ and C-4′), 6.87 (s, 1H, H-5′), 6.74 (s, 2H, H-2′ and H-6′), 5.91 (d, 1H, $^{4}J_{6,8}$ = 2.64, H-6), 5.86 (d, 1H, $^{4}J_{8,6}$ = 2.64, H-8), 5.77 (d, 1H, $^{3}J_{2,3}$ = 6.88, H-2), 4.98 (d, 1H, $^{3}J_{3,2}$ = 11.11, H-3).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 197.90 (C-4), 166.88 (C-7), 163.22 (C-5), 162.46 (C-9), 145.67 (C-3′), 144.83 (C-4′), 127.93 (C-1′), 119.31 (C-6′), 115.25 (C-5′), 115.00 (C-2′), 100.38 (C-10), 95.88 (C-6), 94.88 (C-8), 82.95 (C-3), 71.45 (C-2).

EI-MS *m/z* (% relative abundance) composition: 304.26 $[C_{15}H_{12}O_4]^{+\cdot}$

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 291 (16372), 335 (3298); (Figure 77, side 250).

3.6.4. 7-Hydroxy-3-(4-methoxyphenyl)-4-oxo-*4H*-benzopyran / Formononetin (162)



Purchased by Indofine Inc. USA (Art.-Nr.: F-103).

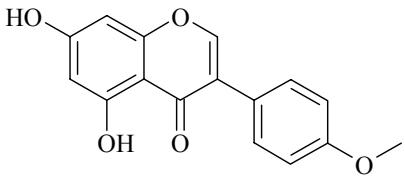
^{1}H NMR (DMSO-d^6, 300 MHz) δ 10.82 (s, 1H, exchanges with D_2O, OH on C-7), 8.35 (s, 1H, H-2), 7.98 (d, 1H, $^3J_{5,6}$ = 7.94, H-5), 7.52-7.48 (m, supposed as AA′XX′ system, 4H, H_{Ar} of B-ring), 6.95 (dd, 1H, $^3J_{6,5}$ = 7.94, $^4J_{6,8}$ = 2.65, H-6), 6.89 (d, 1H, $^4J_{8,6}$ = 2.65, H-8), 3.79 (s, 3H, OCH_3 on C-4′).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 174.52 (C-4), 162.48 (C-7), 158.86 (C-4′), 157.36 (C-9), 153.05 (C-2), 129.99 (C-2′ and C-6′), 127.21 (C-5), 124.15 (C-1′), 123.06 (C-3), 116.53 (C-10), 115.09 (C-6), 113.50 (C-3′ and C-5′), 102.04 (C-8), 55.05 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 268.27 $[C_{16}H_{12}O_4]^{+\cdot}$

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 250 (31034), 301 (12672); (Figure 78, side 250).

3.6.5. 5,7-Dihydroxy-3-(4-methoxyphenyl)-4-oxo-*4H*-benzopyran / Biochanin A (163)



Purchased by Indofine Inc. USA (Art.-Nr.: B-106).

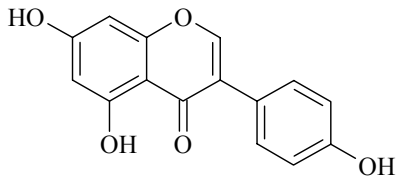
^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.94 (s, 1H, exchanges with D_2O, OH on C-5), 10.30 (br s, 1H, exchanges with D_2O, OH on C-7), 8.37 (s, 1H, H-2), 7.50-7.00 (m, supposed as AA′XX′ system, 4H, H_{Ar} of B-ring), 6.41 (d, 1H, 2.64, H-6), 6.24 (d, 1H, 2.64, H-8), 3.80 (s, 3H, OCH_3 on C-4′).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 180.02 (C-4), 164.26 (C-7), 161.91 (C-4′), 159.07 (C-9), 157.51 (C-5), 154.21 (C-2), 130.08 (C-2′ and C-6′), 122.84 (C-1′), 121.87 (C-3), 113.62 (C-3′ and C-5′), 104.37 (C-10), 98.93 (C-6), 93.63 (C-8), 55.08 (OCH_3 on C-4′).

EI-MS *m/z* (% relative abundance) composition: 284.27 $[C_{15}H_{12}O_5]^{+\cdot}$

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 263 (36418), 330 (4148); (Figure 79, side 251).

3.6.6. 5,7-Dihydroxy-3-(4-hydroxyphenyl)-4-oxo-*4H*-benzopyran / Genistein (164)



Purchased by Indofine Inc. USA (Art.-Nr.: G-103).

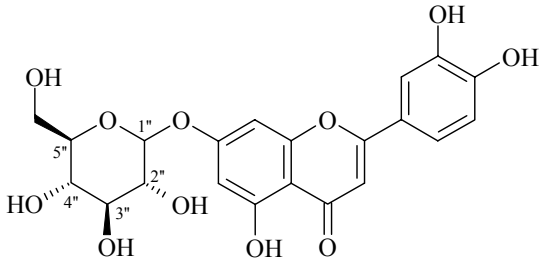
^{1}H NMR (DMSO-d^6, 300 MHz) δ 12.96 (s, 1H, exchanges with D_2O, OH on C-5), 10.89 (br s, 1H, exchanges with D_2O, OH on C-7), 9.60 (br s, 1H, exchanges with D_2O, OH on C-4′), 8.33 (s, 1H, H-2), 7.39-6.82 (m, supposed as AA′XX′ system, 4H, H_{Ar} of B-ring), 6.39 (d, 1H, $^{4}J_{6,8}$ = 2.65, H-6), 6.23 (d, 1H, $^{4}J_{8,6}$ = 2.65, H-8).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 182.12 (C-4), 164.19 (C-7), 161.91 (C-5), 157.49 (C-9), 157.33 (C-4′), 153.89 (C-2), 130.07 (C-2′ and C-6′), 122.19 (C-1′), 121.12 (C-3), 114.97 (C-3′ and C-5′), 104.38 (C-10), 98.87 (C-6), 93.57 (C-8).

EI-MS *m/z* (% relative abundance) composition: 270.24 $[C_{15}H_{10}O_5]^{+\cdot}$

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 263 (54832), 331 (6215); (Figure 80, side 251).

3.6.7. 5-Hydroxy-7-(3,4,5-trihydroxy-6-hydroxymethyltetrahydropyran-2-yloxy)-2-(3,4-dihydroxyphenyl)-4-oxo-*4H*-benzopyran / Luteolin 7-*O*-glucosyl (166)



Purchased by Indofine Inc. USA (Art.-Nr.: 020053).

^{1}H NMR (DMSO-d^6, 300 MHz) δ 13.00 (s, 1H, exchanges with D_2O, OH on C-5), ~9.67 (br s, 2H, exchanges with D_2O, OH on C-3′ and C-4′), 7.42 (m, 2H, H-2′ and H-6′), 6.91 (d, 1H, $^{3}J_{5', 6'}$ = 7.94, H-5′), 6.80 (d,1H, $^{3}J_{6, 8}$ = 2.64, H-6), 6.76 (s, 1H, H-3), 6.44 (d, 1H, $^{3}J_{8, 6}$ = 2.64, H-8), ~5.39 (br s), 5.10 (d, 1H, $^{3}J_{1'', 2''}$ =7.94, H-1″), ~4.63 (br s), 3.70 (m, 1H, H-2″), ~3.35 (m, glucose moiety).

^{13}C NMR (DMSO-d^6, 75.47 MHz) δ 181.81 (C-4), 164.37 (C-2), 162.85 (C-7), 161.04 (C-9), 156.85 (C-5), 149.83 (C-3′), 145.67 (C-4′), 121.28 (C-1′), 119.08 (C-6′), 115.88 (C-5′), 113.48 (C-2′), 105.24 (C-10), 103.08 (C-1″), 99.77 (C-6), 99.43 (C-8), 94.61 (C-3), 77.07 (C-2″), 76.30 (C-5″), 73.02 (C-3″), 69.43 (C-4″), 60.51 (CH_2OH).

EI-MS *m/z* (% relative abundance) composition: 448.39 $[C_{21}H_{20}O_{11}]^{+\cdot}$

UV-vis (2-propanol, 1 mg / 100 mL) λ_{max} (ε) nm: 255 (28460), 267sh (25916), 353 (30933); (Figure 81, side 252).

4. Absorption spectra of flavonoids

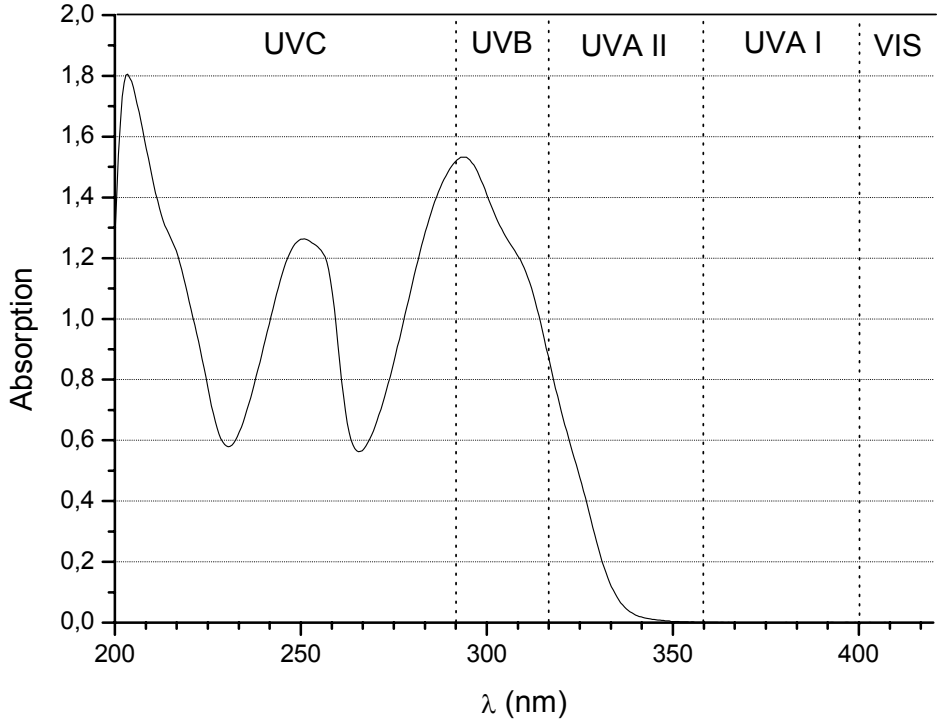


Figure 19: Absorption spectrum of the Flavone. 10 mM in isopropanol.

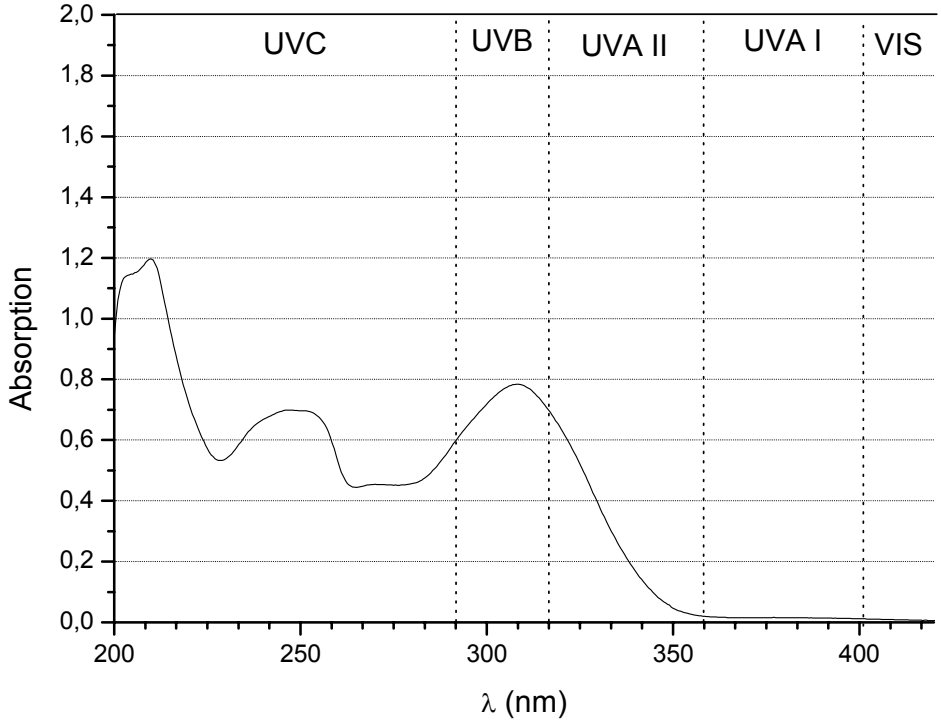


Figure 20: Absorption spectrum of the 7-Hydroxyflavone. 10 mM in isopropanol.

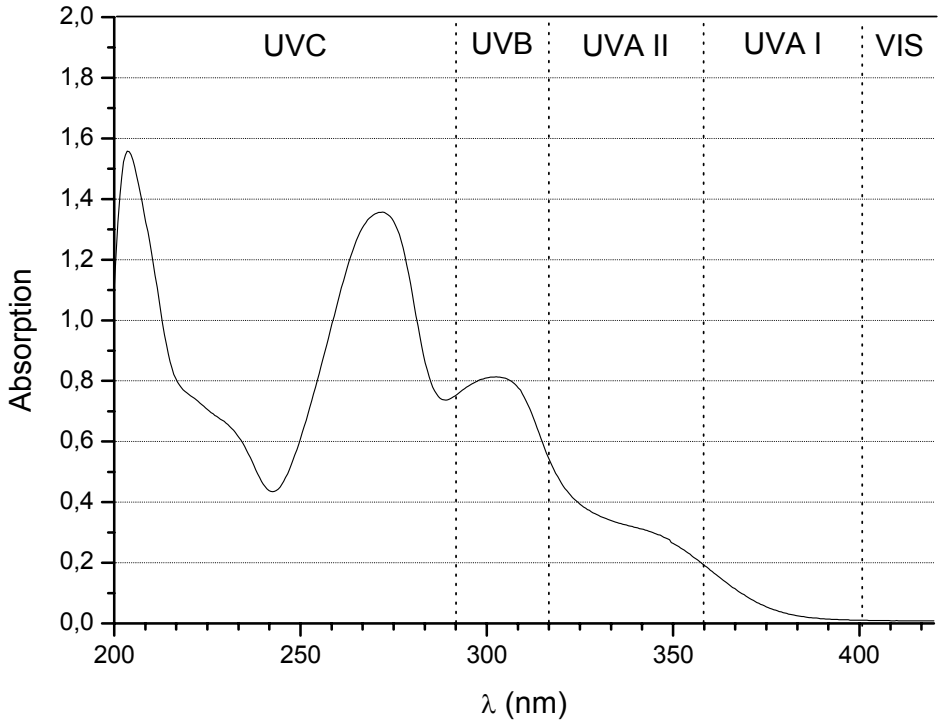


Figure 21: Absorption spectrum of the 6-Hydroxyflavone. 10 mM in isopropanol.

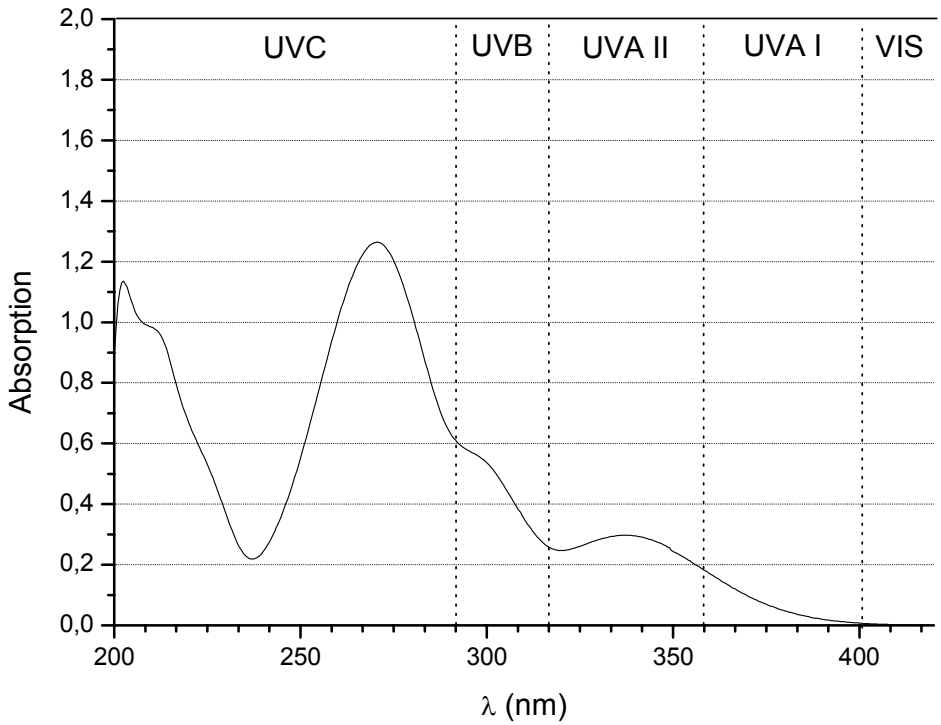


Figure 22: Absorption spectrum of the 5-Hydroxyflavone. 10 mM in isopropanol.

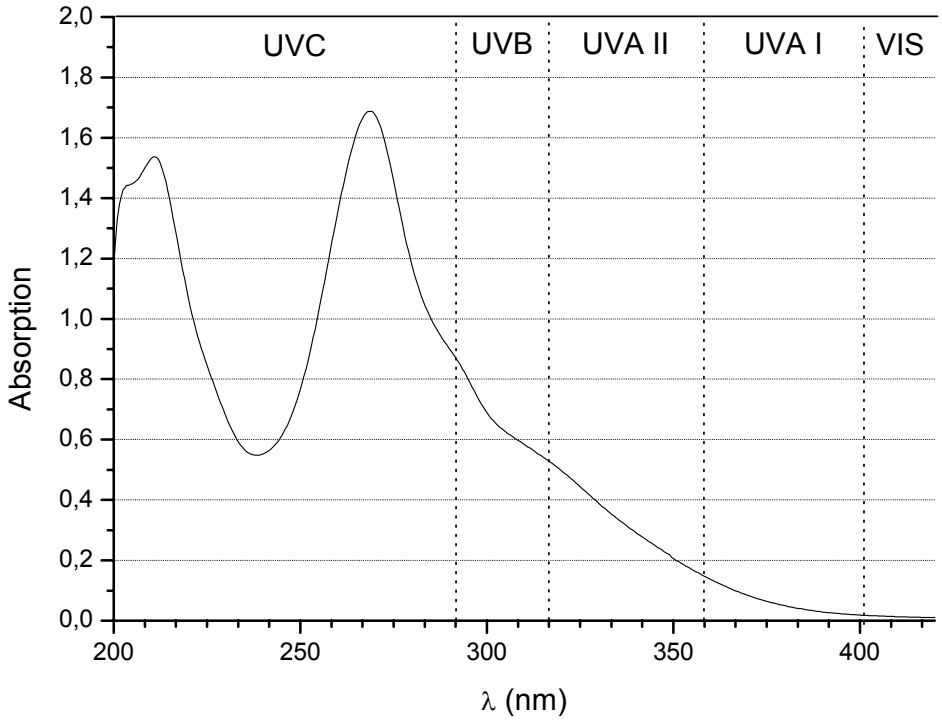


Figure 23: Absorption spectrum of the 7,8-Dihydroxyflavone. 10 mM in isopropanol.

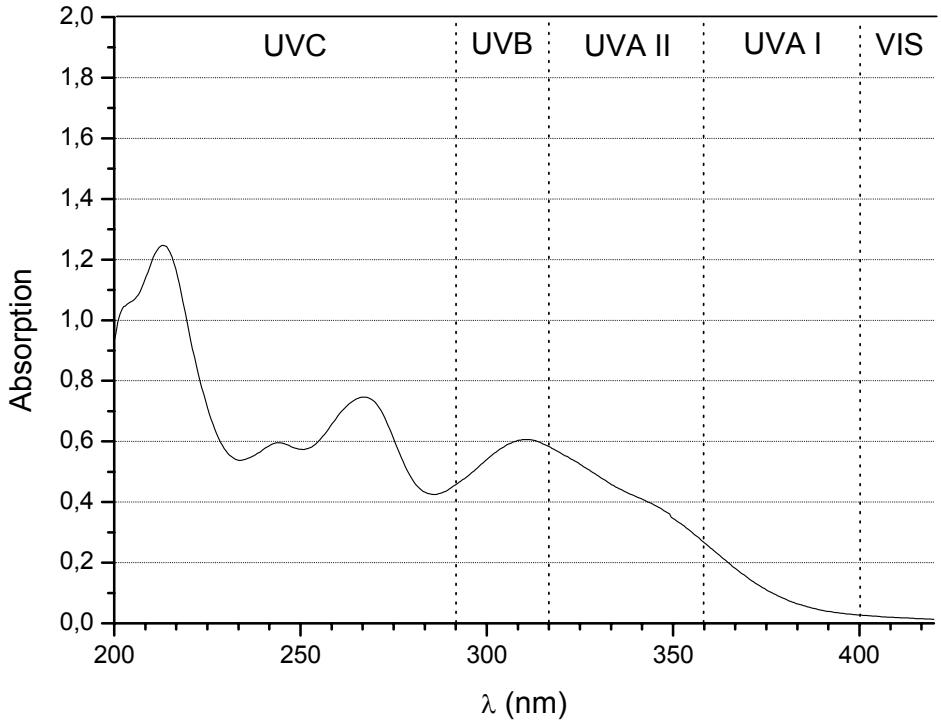


Figure 24: Absorption spectrum of the 6,7-Dihydroxyflavone. 10 mM in isopropanol.

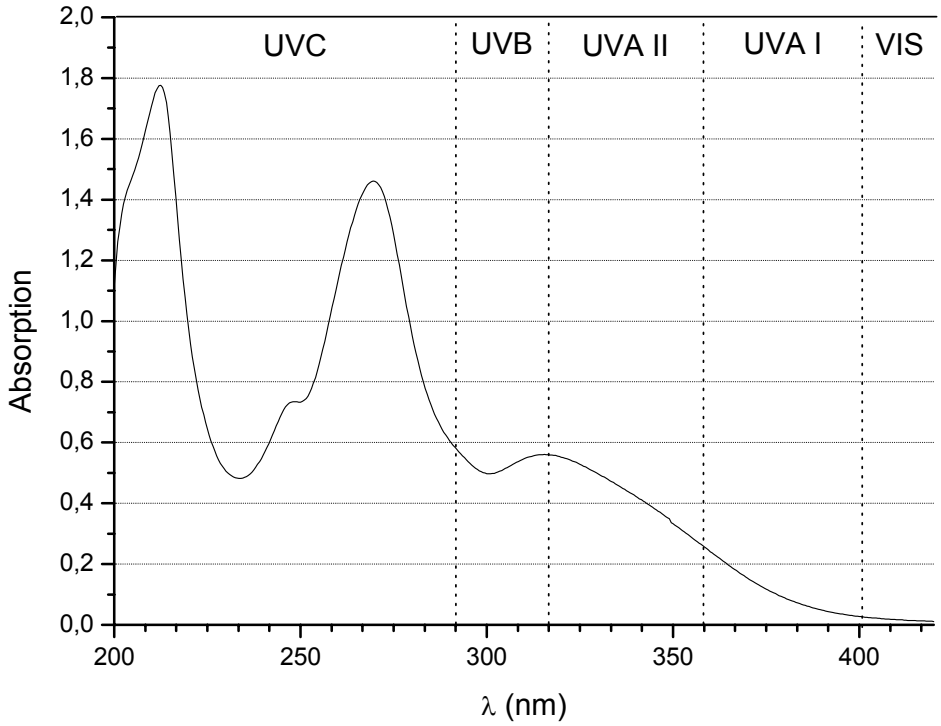


Figure 25: Absorption spectrum of the 5,7-Dihydroxyflavone (Chrysin). 10 mM in isopropanol

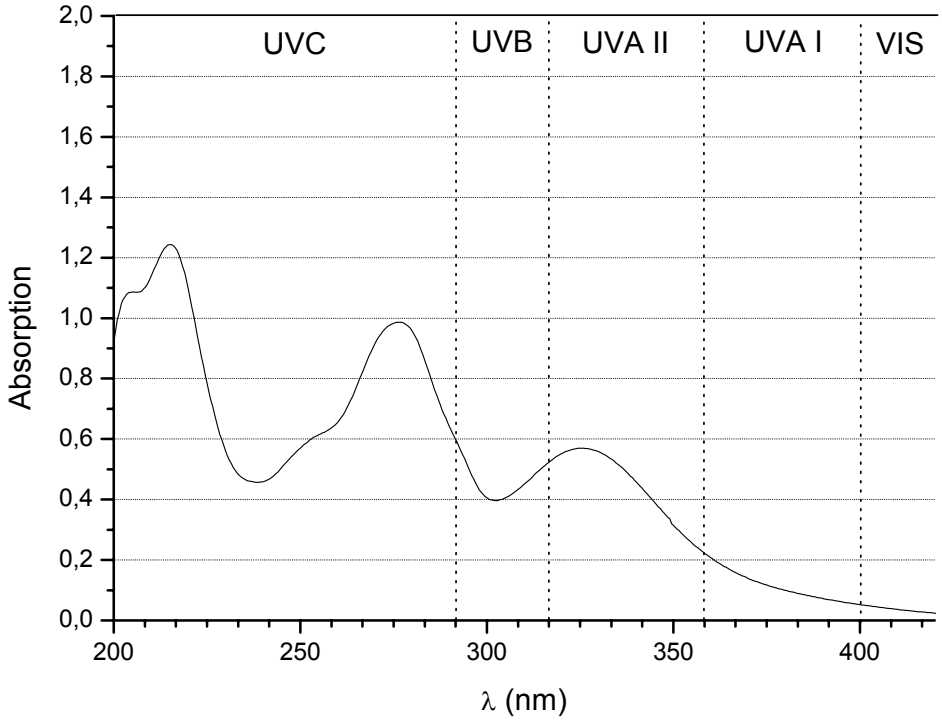


Figure 26: Absorption spectrum of the 5,6,7-Trihydroxyflavone (Bacalein). 10 mM in isopropanol

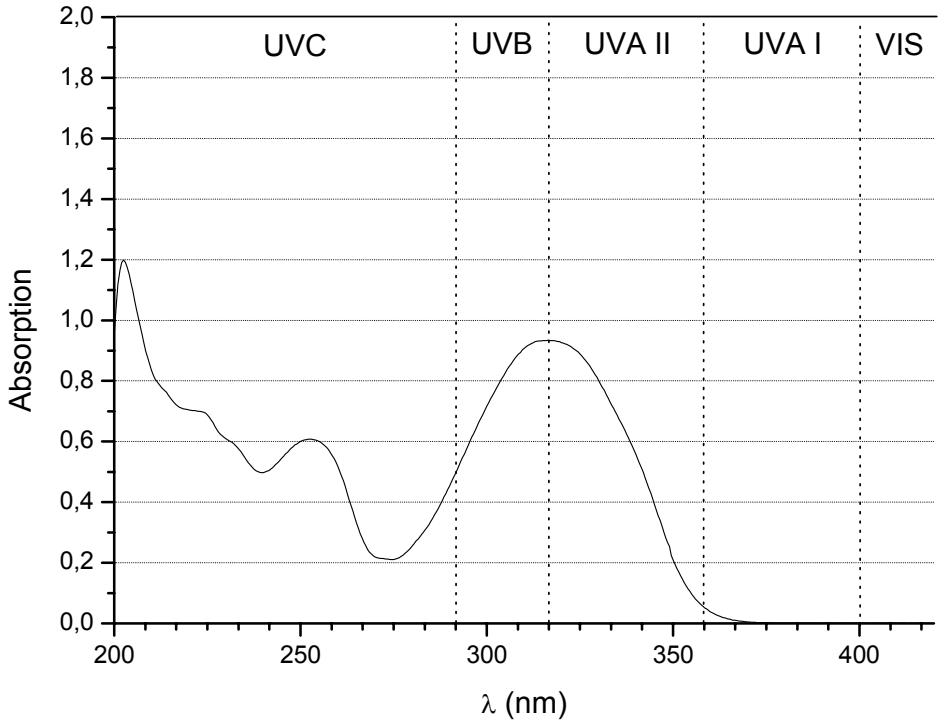


Figure 27: Absorption spectrum of the 4′-Methoxyflavone. 10 mM in isopropanol.

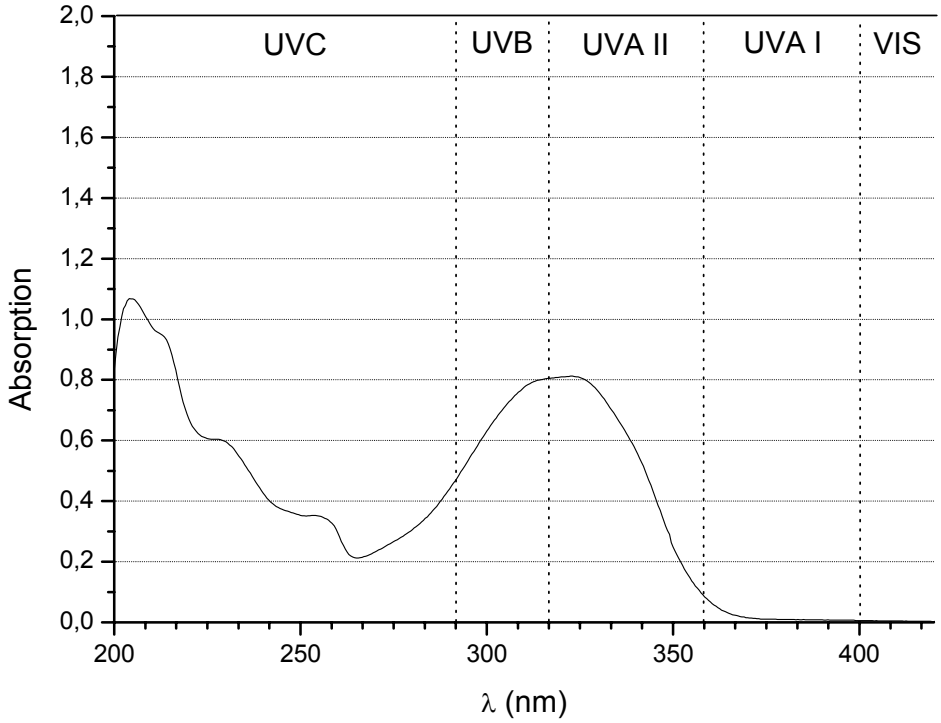


Figure 28: Absorption spectrum of the 7-Hydroxy-4′-methoxyflavone. 10 mM in isopropanol.

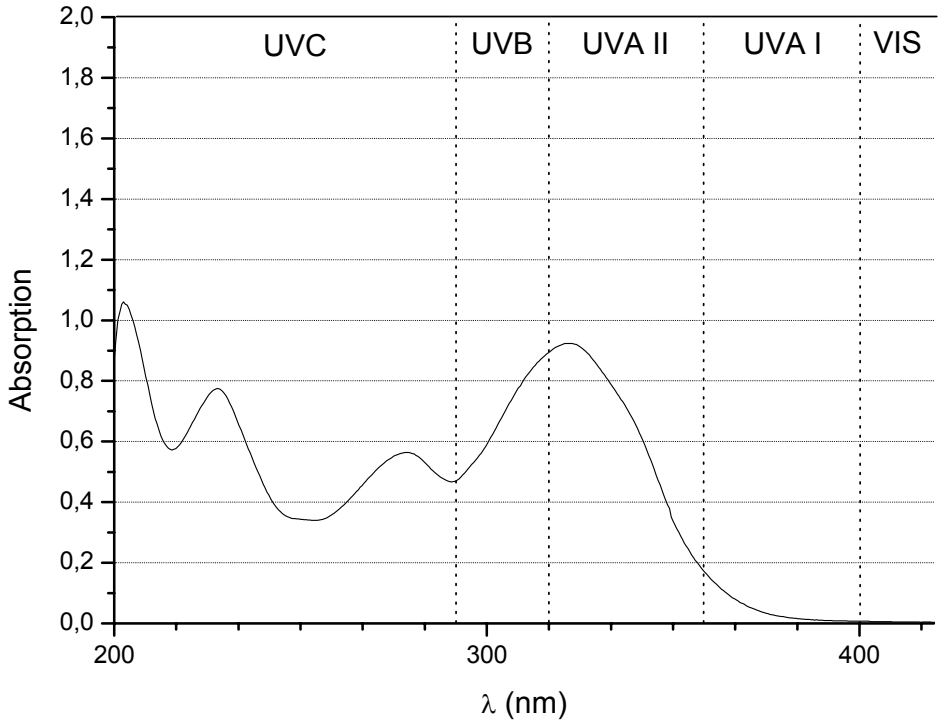


Figure 29: Absorption spectrum of the 6-Hydroxy-4′-methoxyflavone. 10 mM in isopropanol.

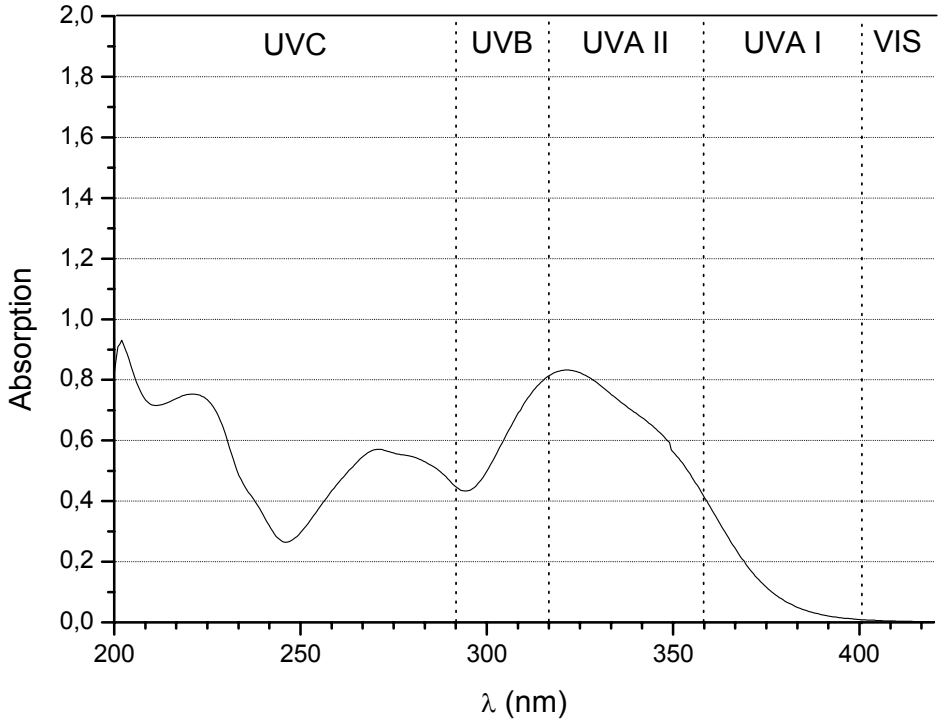


Figure 30: Absorption spectrum of the 5-Hydroxy-4′-methoxyflavone. 10 mM in isopropanol.

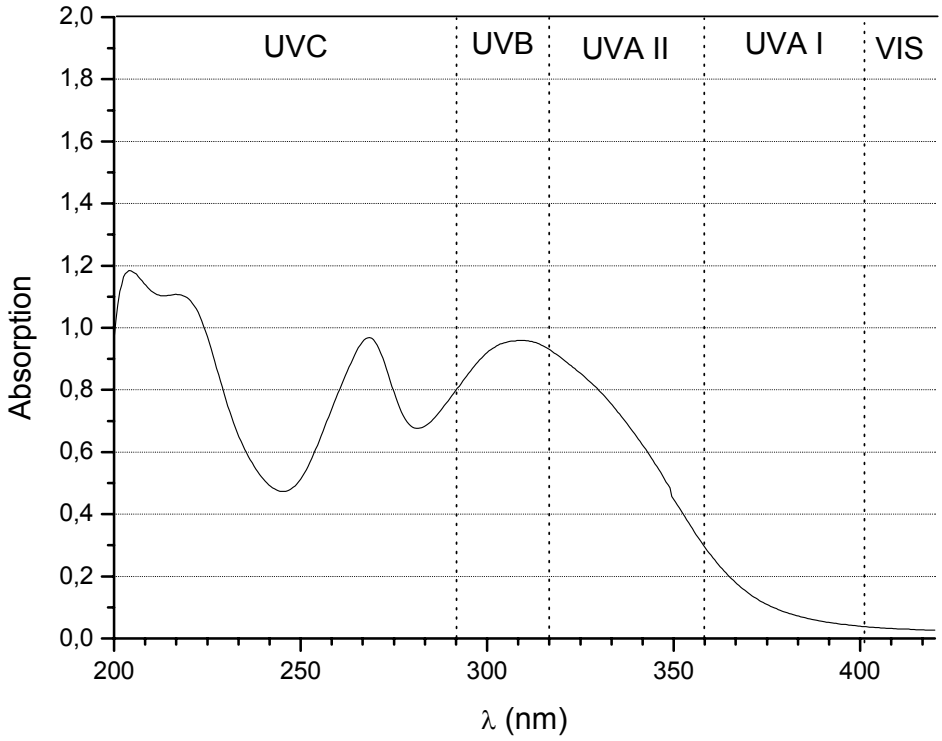


Figure 31: Absorption spectrum of the 7,8-Dihydroxy-4′-methoxyflavone. 10 mM in isopropanol.

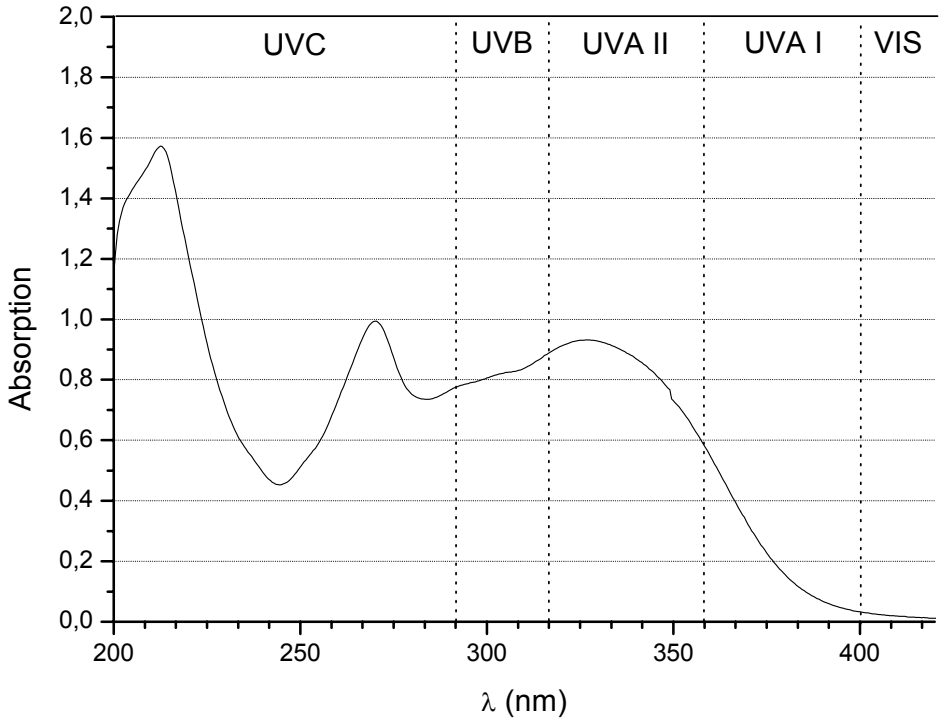


Figure 32: Absorption spectrum of the 5,7-Dihydroxy-4′-methoxyflavone. 10 mM in isopropanol.

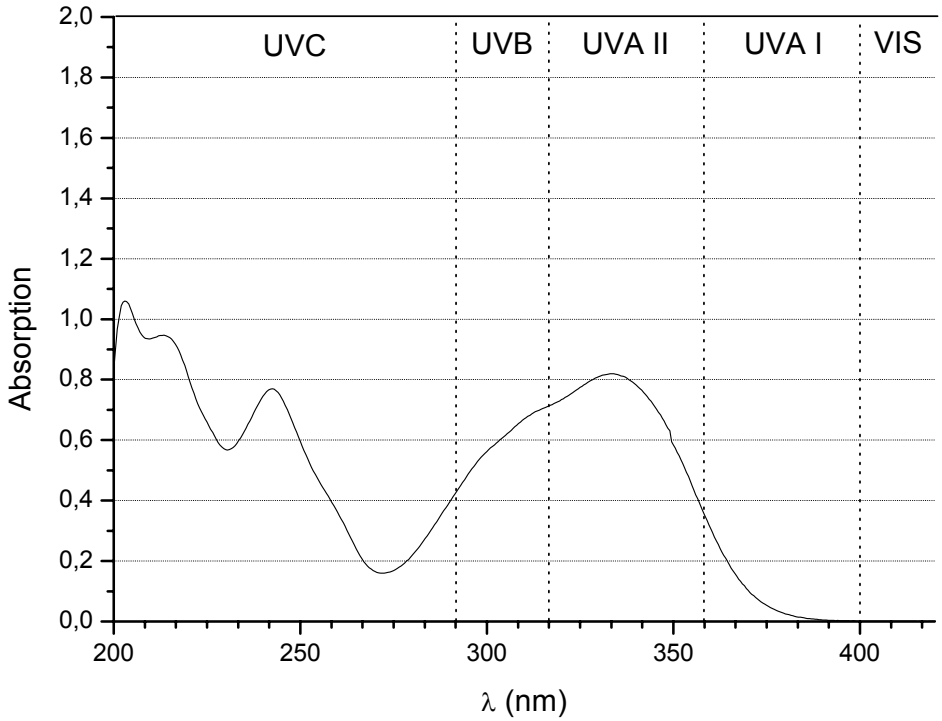


Figure 33: Absorption spectrum of the 3′,4′-Dimethoxyflavone. 10 mM in isopropanol.

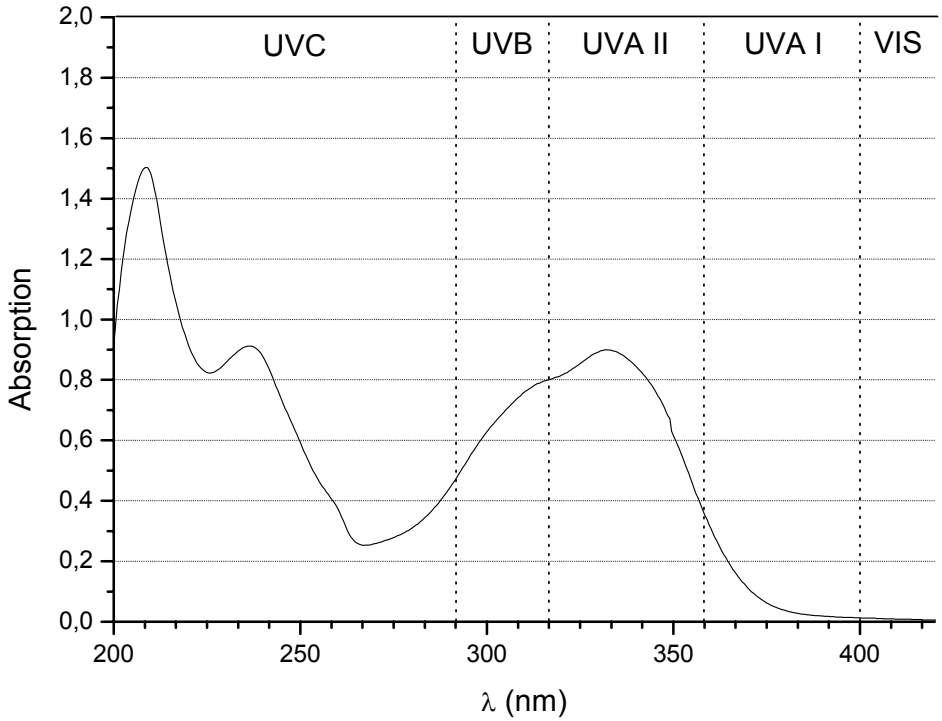


Figure 34: Absorption spectrum of the 7-Hydroxy-3′,4′-dimethoxyflavone. 10 mM in isopropanol.

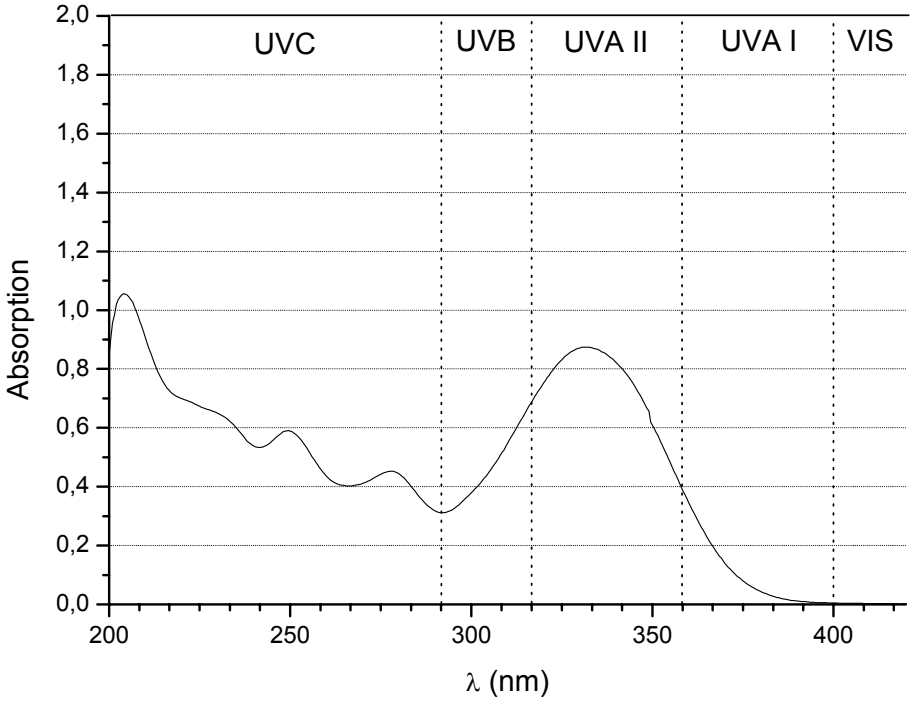


Figure 35: Absorption spectrum of the 6-Hydroxy-3′,4′-dimethoxyflavone. 10 mM in isopropanol.

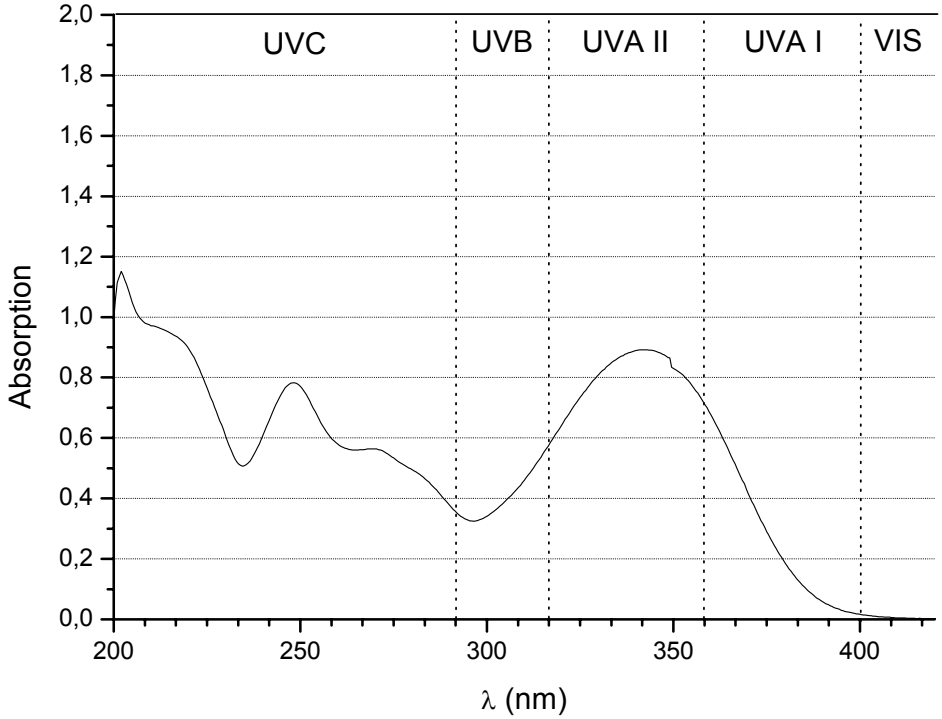


Figure 36: Absorption spectrum of the 5-Hydroxy-3′,4′-dimethoxyflavone. 10 mM in isopropanol.

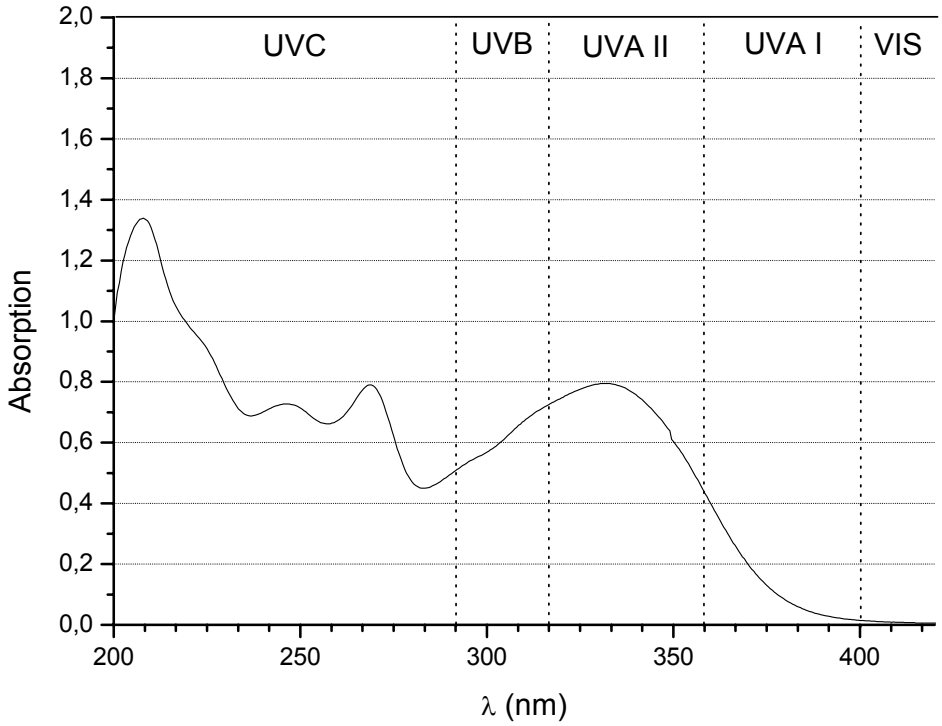


Figure 37: Absorption spectrum of the 7,8-Dihydroxy-3′,4′-dimethoxyflavone. 10 mM in isopropanol.

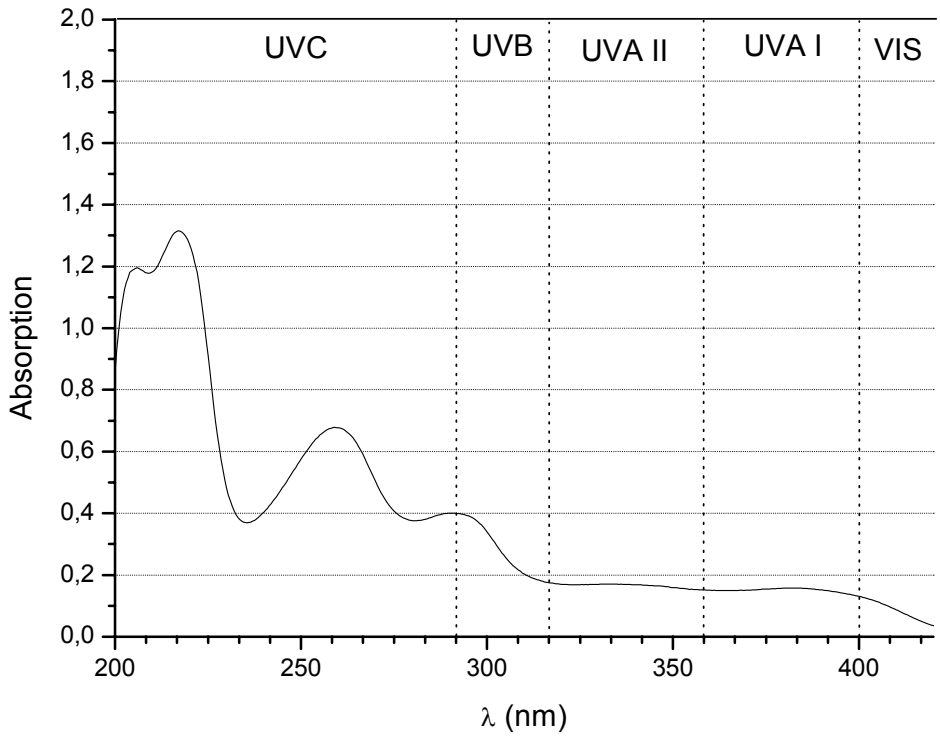


Figure 38: Absorption spectrum of the 6,7-Dihydroxy-3′,4′-dimethoxyflavone . 10 mM in isopropanol.

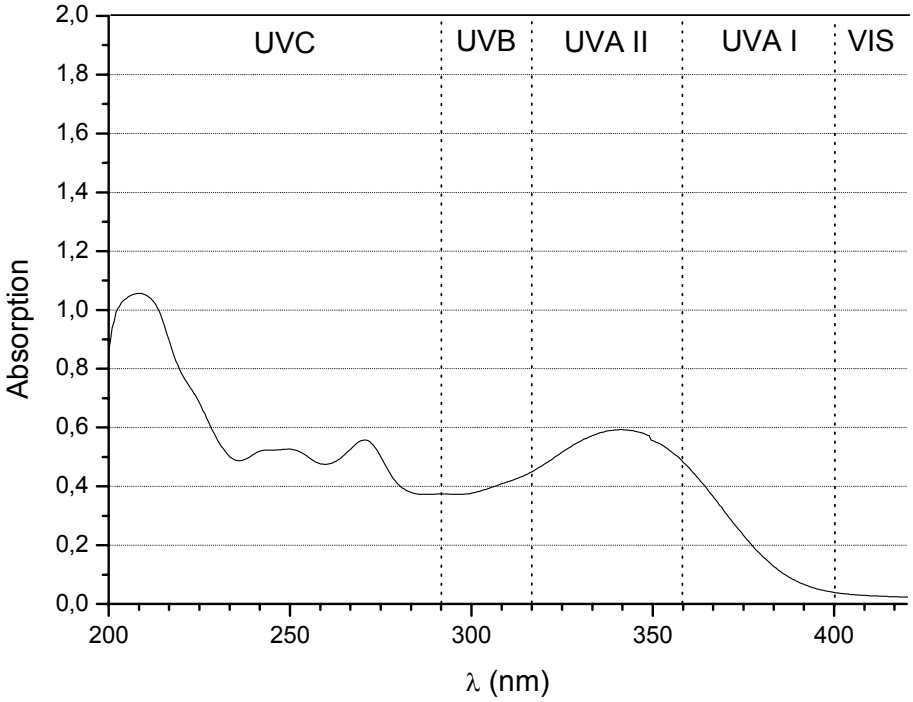


Figure 39: Absorption spectrum of the 5,7-Dihydroxy-3′,4′-dimethoxyflavone. 10 mM in isopropanol.

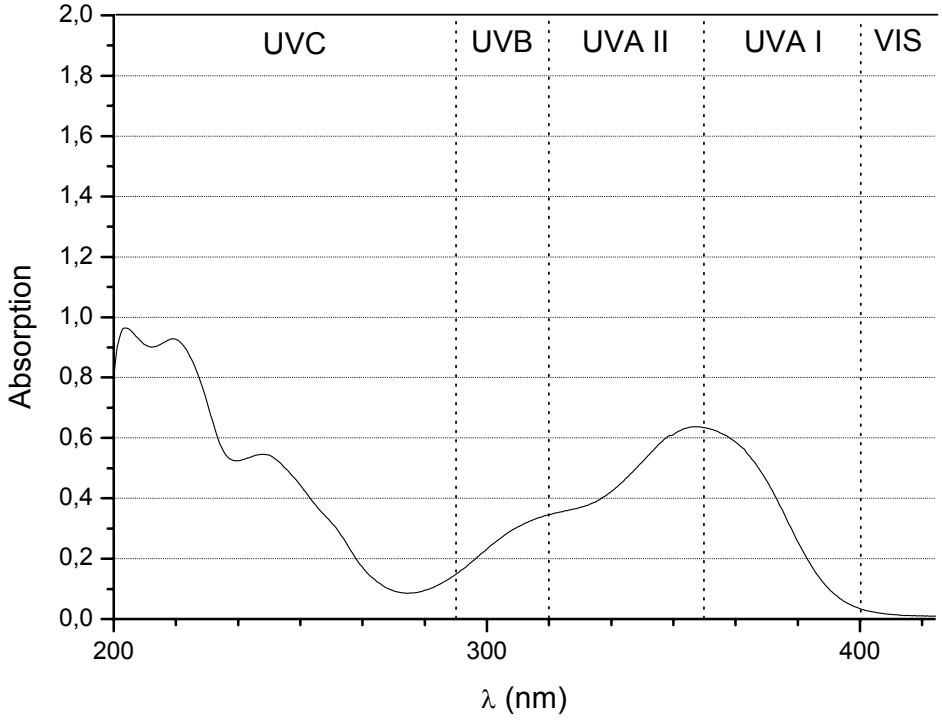


Figure 40: Absorption spectrum of the 3′,4′,5′-Trimethoxyflavone. 10 mM in isopropanol.

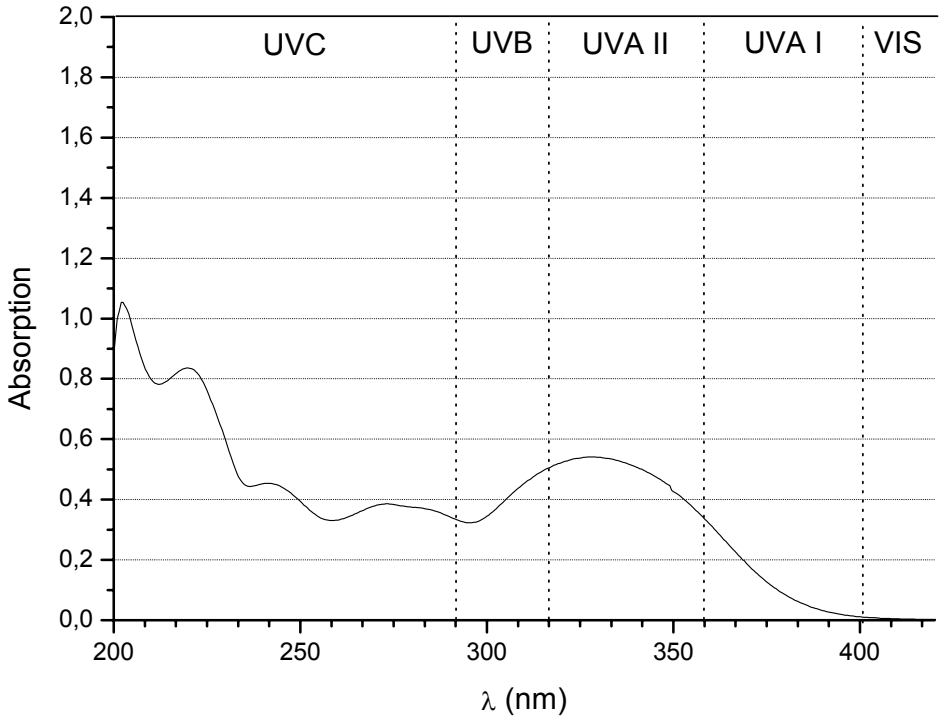


Figure 41: Absorption spectrum of the 5-Hydroxy-3′,4′,5′-trimethoxyflavone. 10 mM in isopropanol.

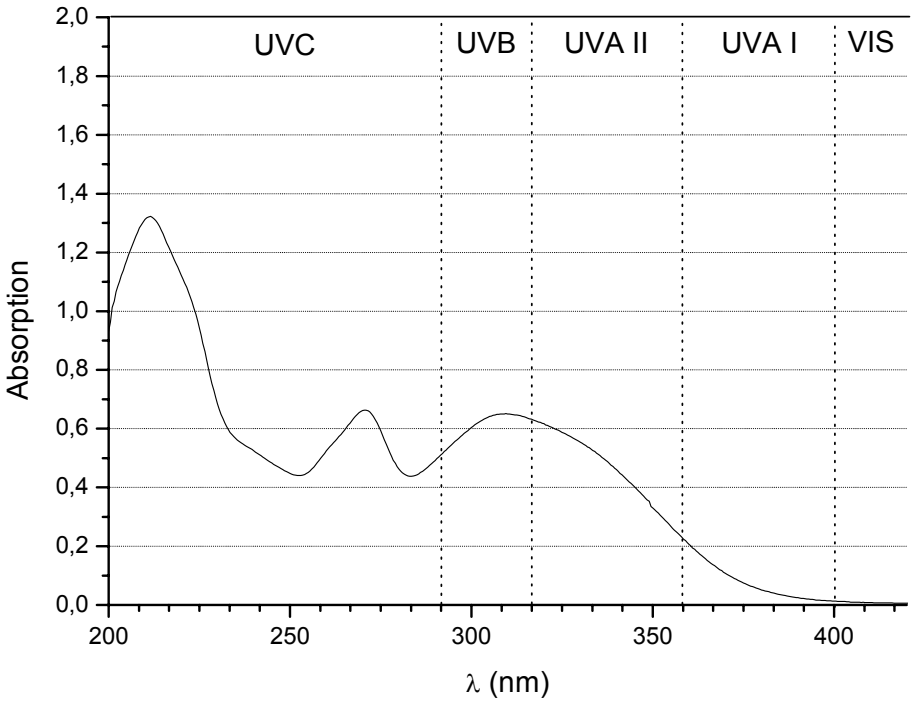


Figure 42: Absorption spectrum of the 7,8-Dihydroxy-3′,4′,5′-trimethoxyflavone. 10 mM in isopropanol.

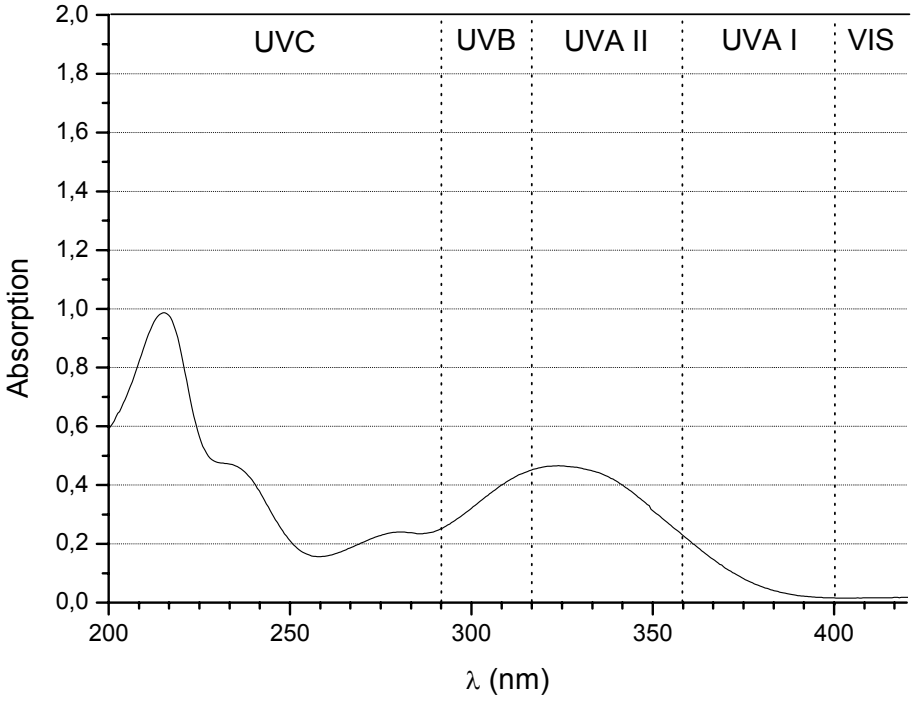


Figure 43: Absorption spectrum of the 6,7-Dihydroxy-3′,4′,5′-trimethoxyflavone. 10 mM in isopropanol.

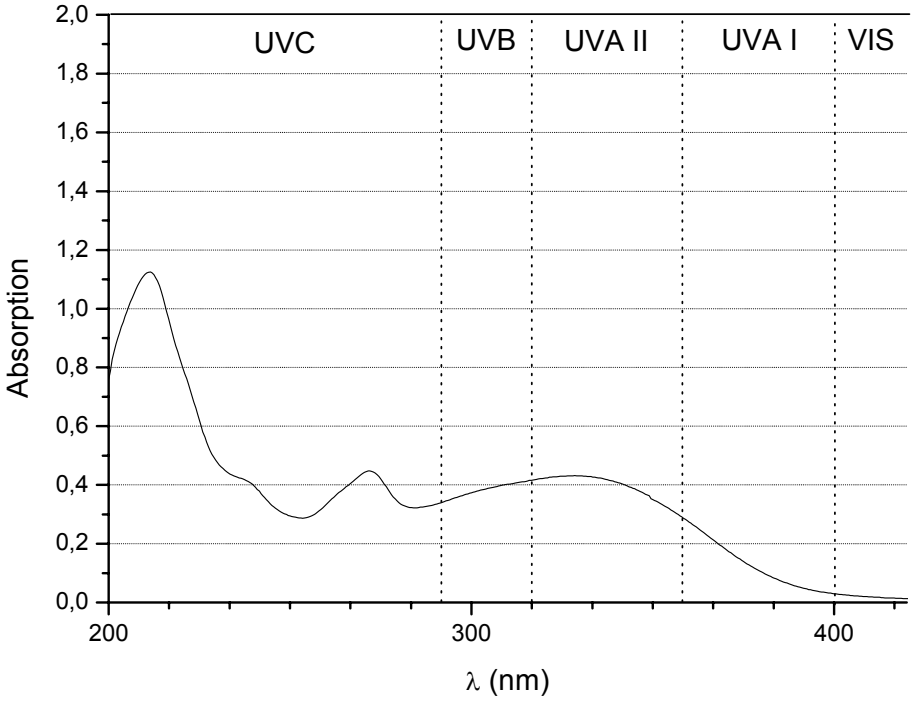


Figure 44: Absorption spectrum of the 5,7-Dihydroxy-3′,4′,5′-trimethoxyflavone. 10 mM in isopropanol.

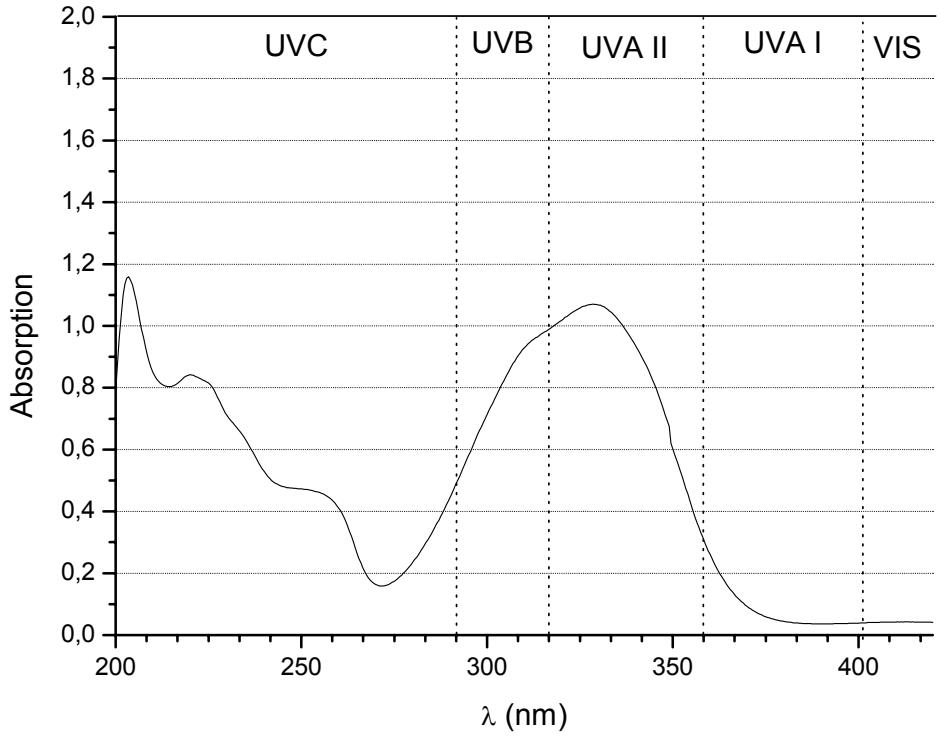


Figure 45: Absorption spectrum of the 4′-Hydroxyflavone. 10 mM in isopropanol.

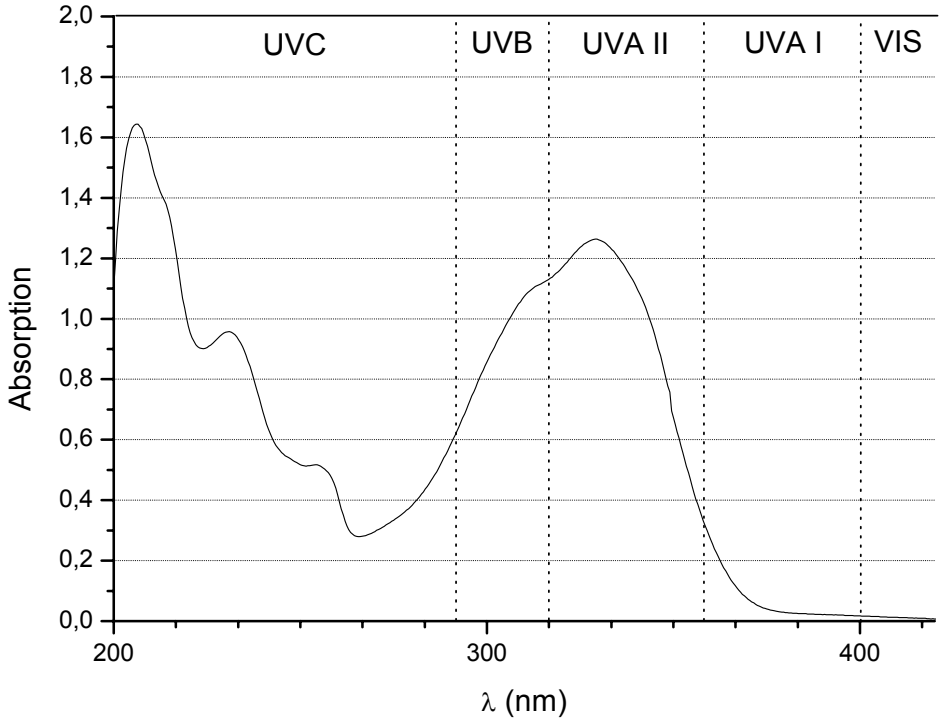


Figure 46: Absorption spectrum of the 7,4′-Dihydroxyflavone. 10 mM in isopropanol.

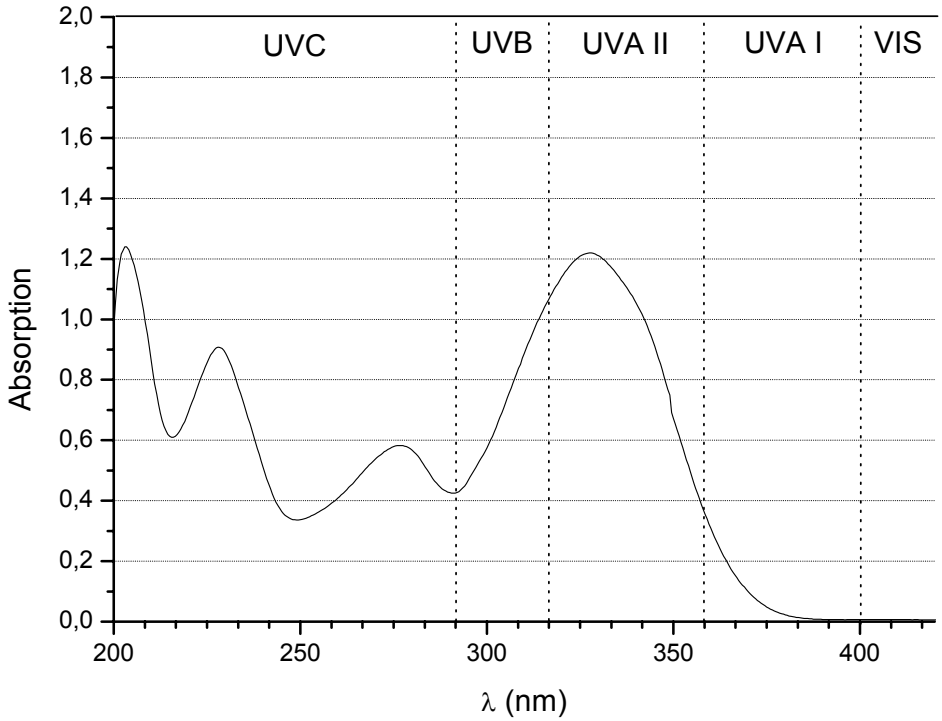


Figure 47: Absorption spectrum of the 6,4′-Dihydroxyflavone. 10 mM in isopropanol.

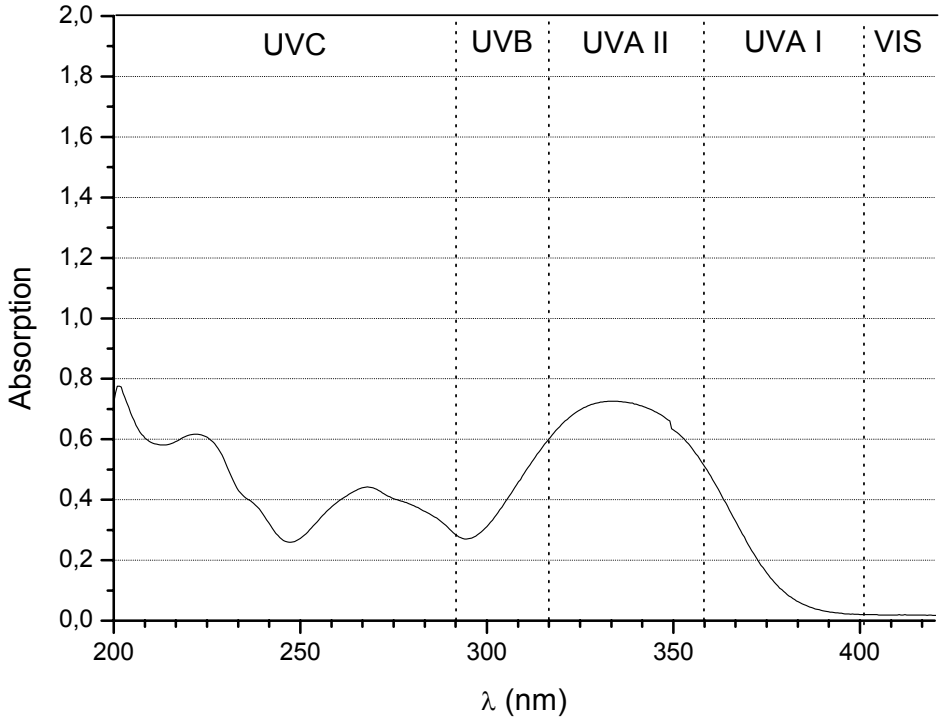


Figure 48: Absorption spectrum of the 5,4′-Dihydroxyflavone. 10 mM in isopropanol.

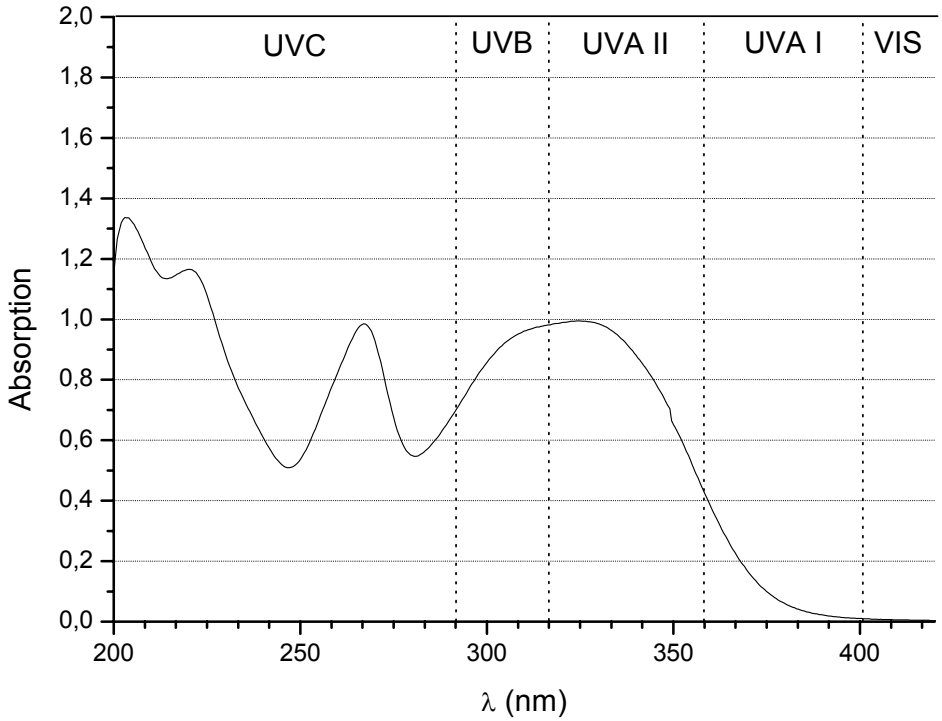


Figure 49: Absorption spectrum of the 7,8,4′-Trihydroxyflavone. 10 mM in isopropanol.

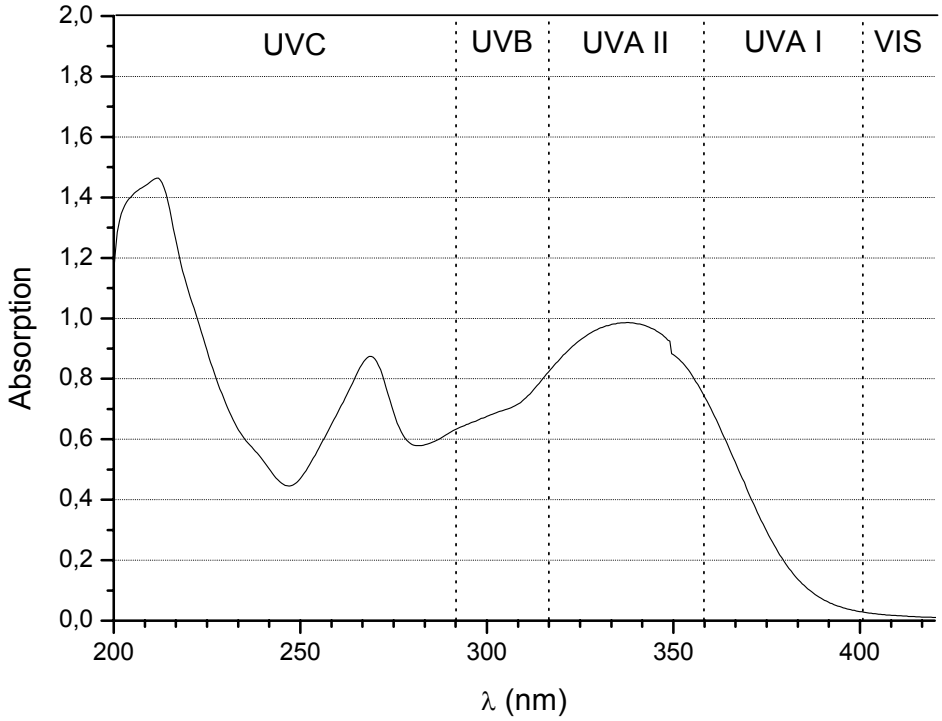


Figure 50: Absorption spectrum of the 5,7,4′-Trihydroxyflavone (Apigenin). 10 mM in isopropanol.

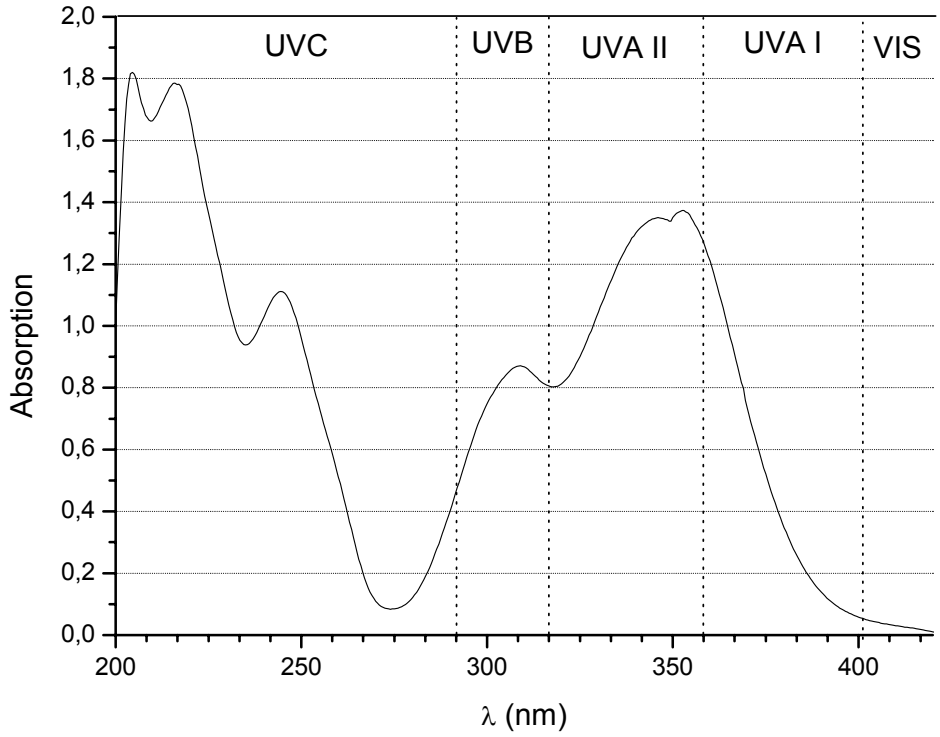


Figure 51: Absorption spectrum of the 3′,4′-Dihydroxyflavone. 10 mM in isopropanol.

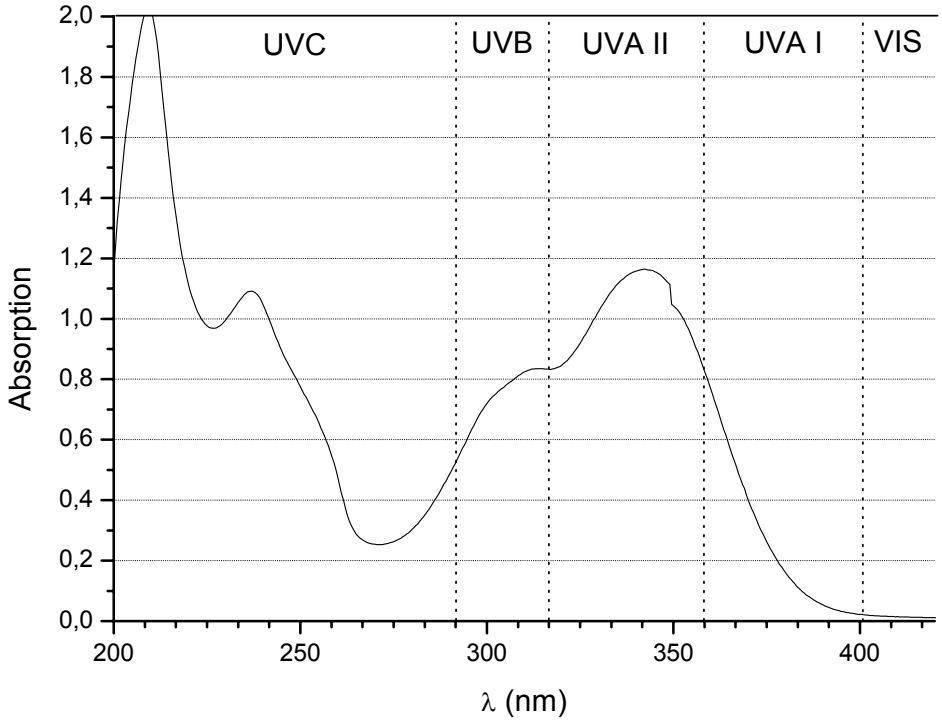


Figure 52: Absorption spectrum of the 7,3′,4′-Trihydroxyflavone. 10 mM in isopropanol.

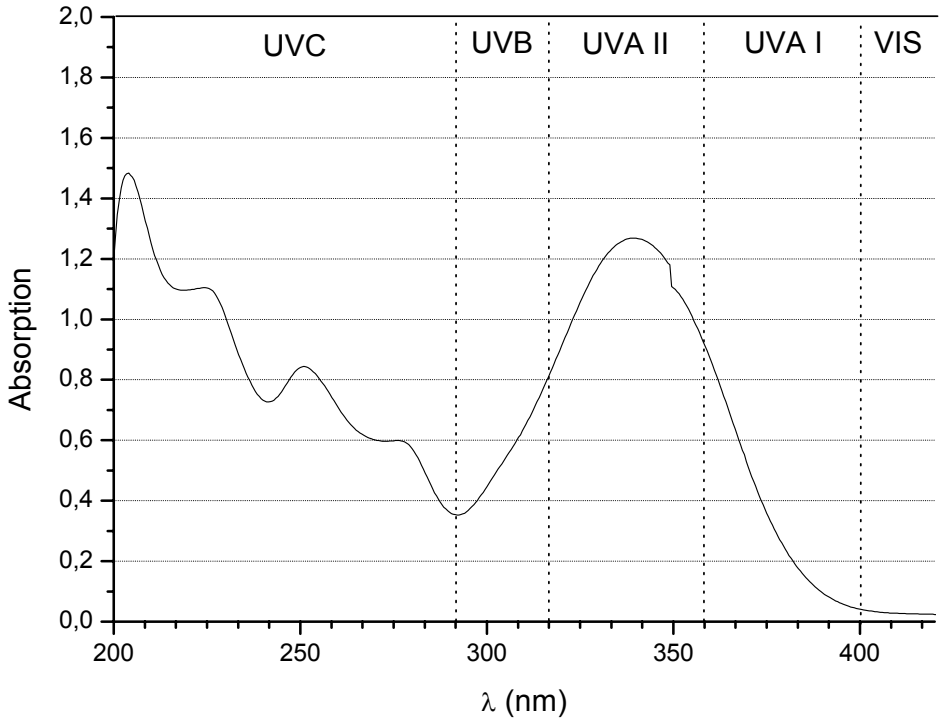


Figure 53 Absorption spectrum of the 6,3′,4′-Trihydroxyflavone. 10 mM in isopropanol.

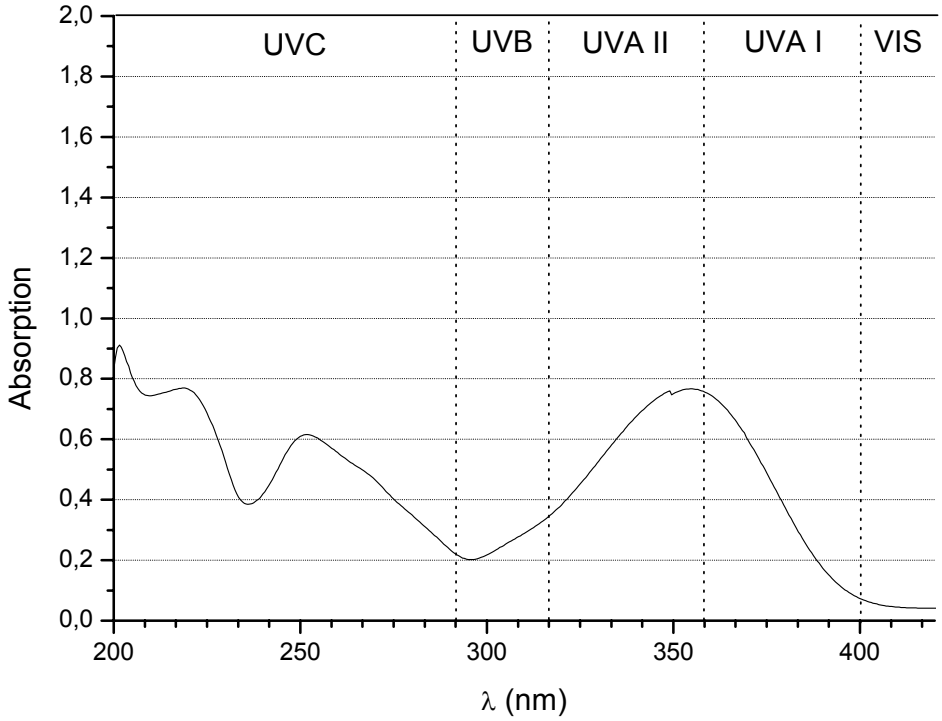


Figure 54: Absorption spectrum of the 5,3′,4′-Trihydroxyflavone. 10 mM in isopropanol.

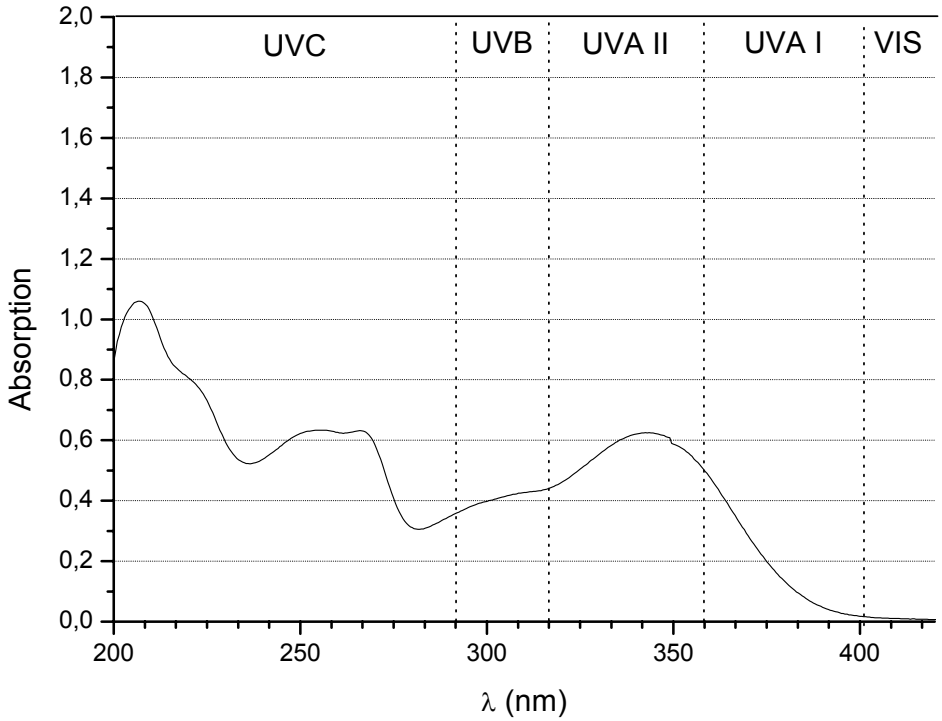


Figure 55: Absorption spectrum of the 7,8,3′,4′-Tetrahydroxyflavone. 10 mM in isopropanol.

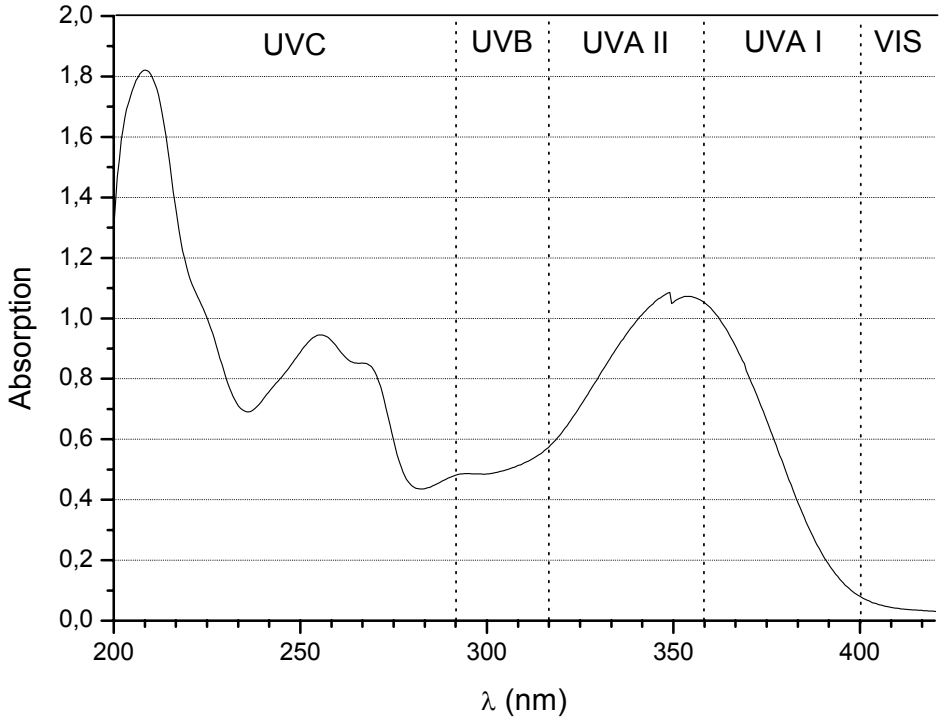


Figure 56: Absorption spectrum of the 5,7,3′,4′-Tetrahydroxyflavone (Luteolin). 10 mM in isopropanol.

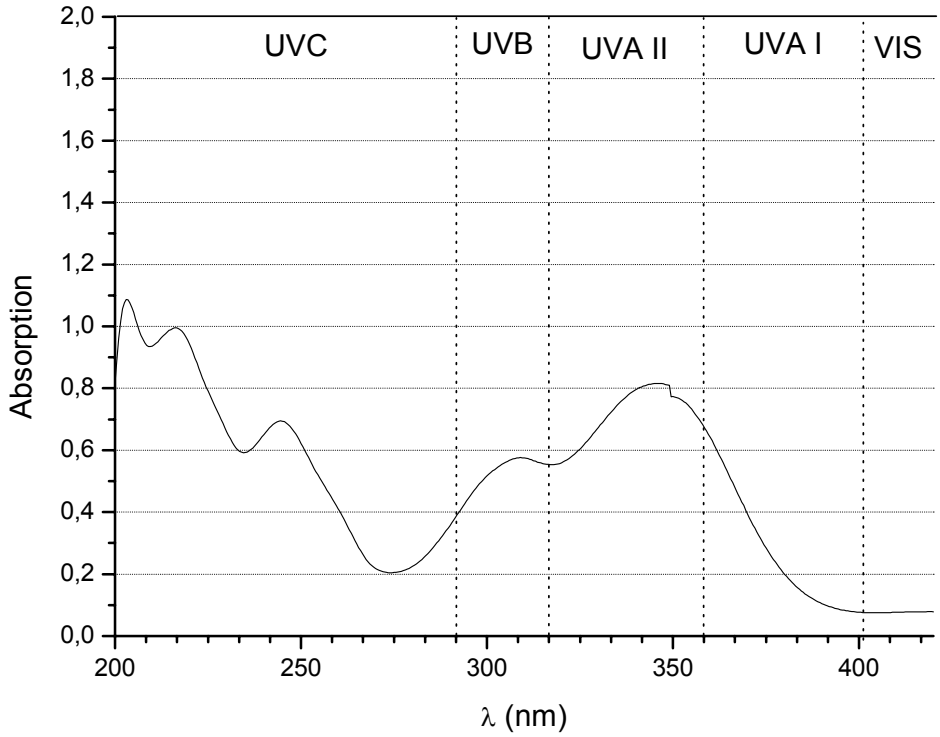


Figure 57: Absorption spectrum of the 3′,4′,5′-Trihydroxyflavone. 10 mM in isopropanol.

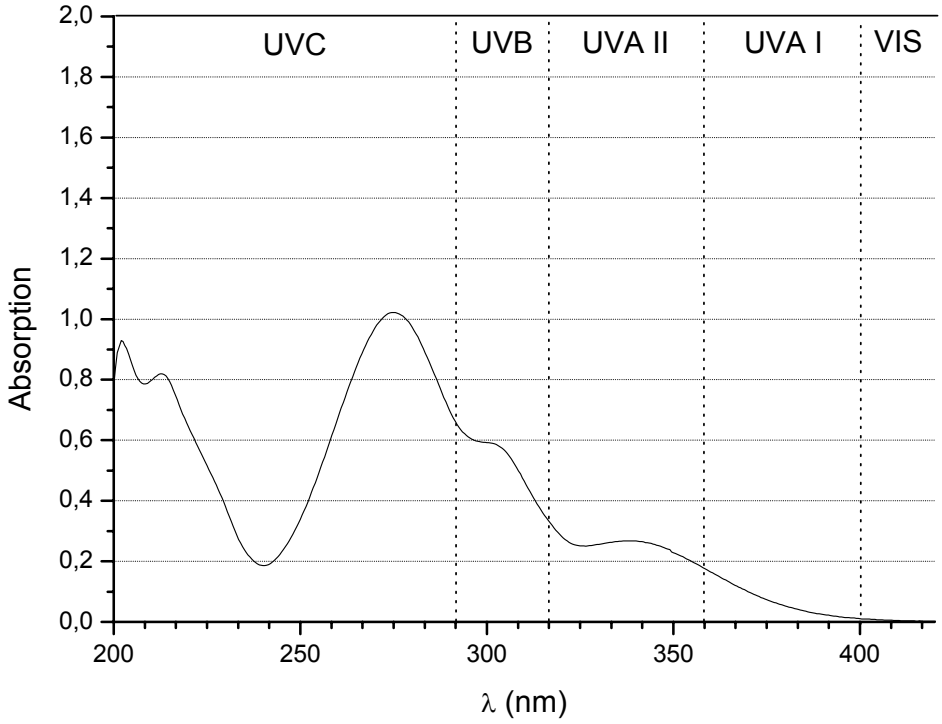


Figure 58: Absorption spectrum of the 5-Hydroxy-4′-chloroflavone **128**. 10 mM in isopropanol.

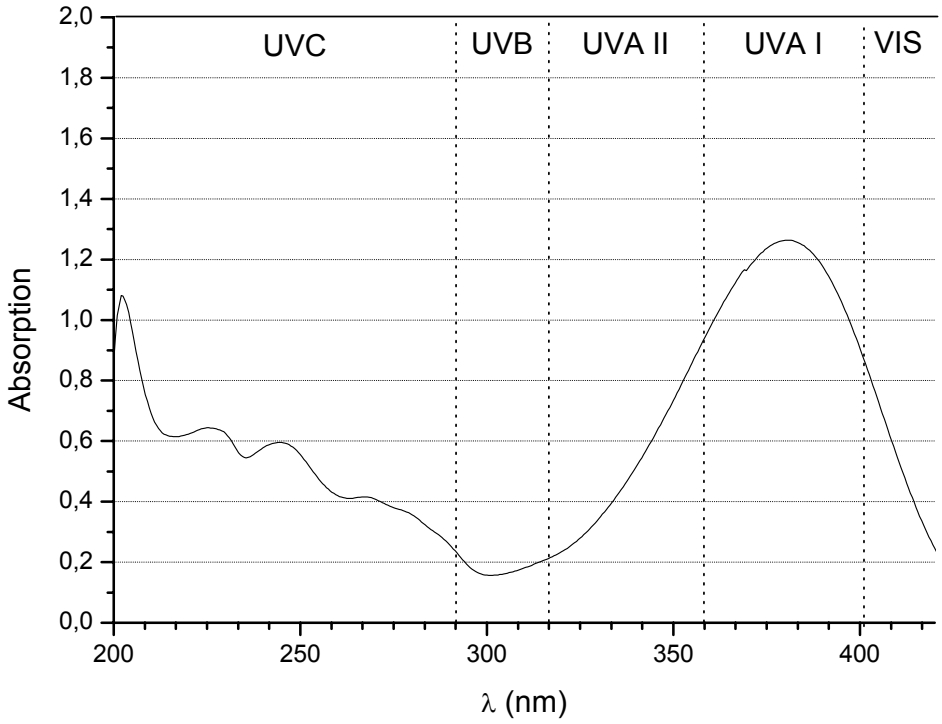


Figure 59: Absorption spectrum of the 5-Hydroxy-4′-aminoflavone **130**. 10 mM in isopropanol.

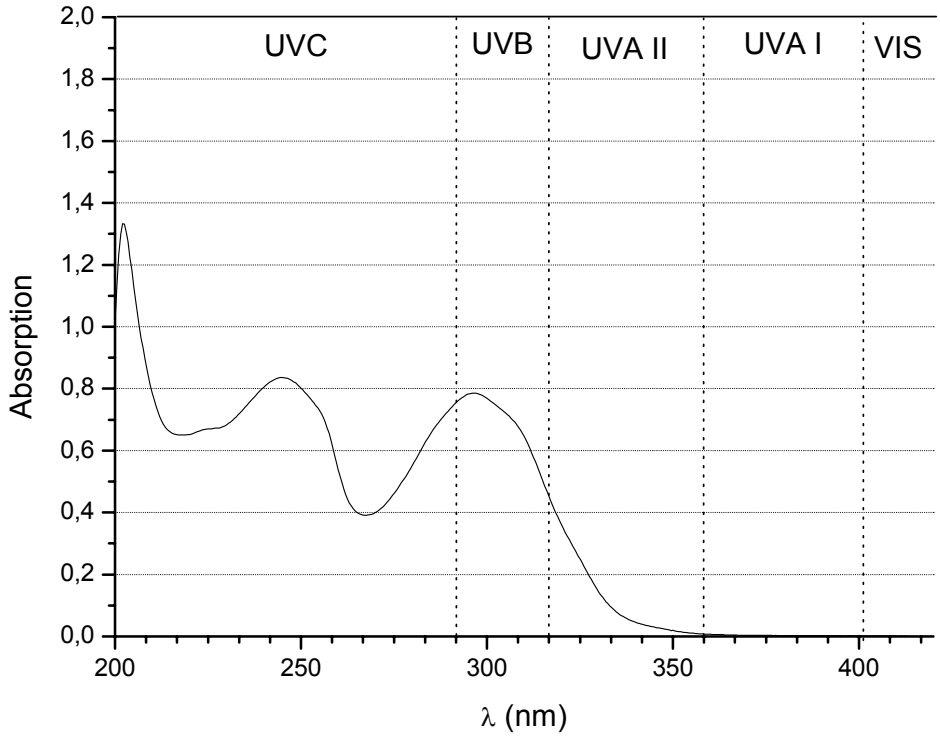


Figure 60: Absorption spectrum of the Benzoic acid 4-oxo-2-phenyl-4*H*-1-benzopyran-7-yl ester **139**. 10 mM in isopropanol.

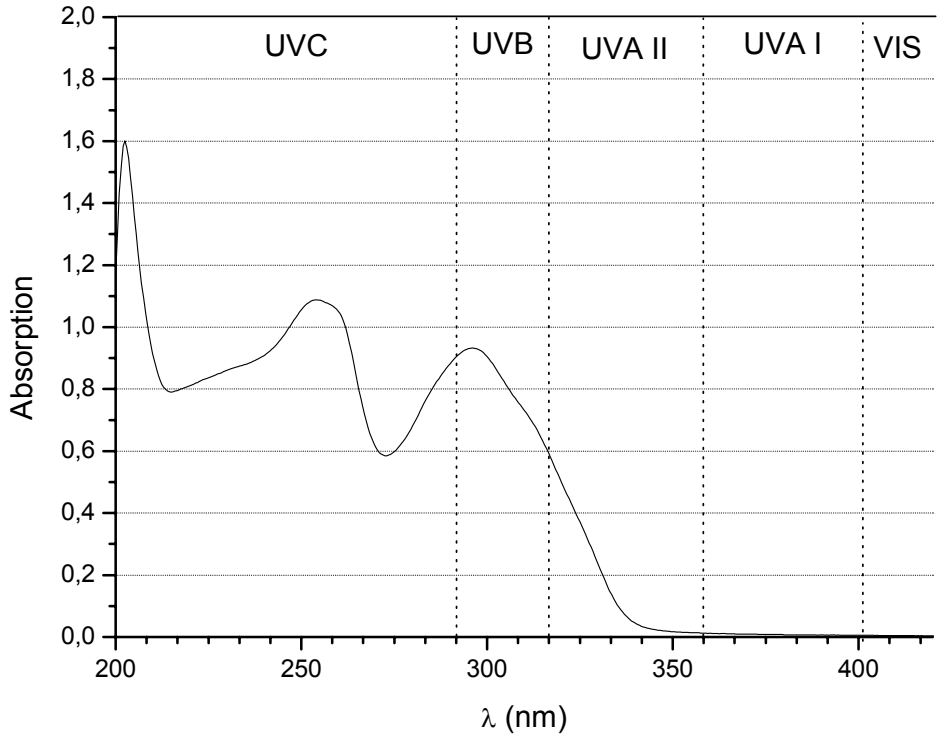


Figure 61: Absorption spectrum of the Benzoic acid 4-oxo-2-phenyl-4*H*-1-benzopyran-6-yl ester **140**. 10 mM in isopropanol.

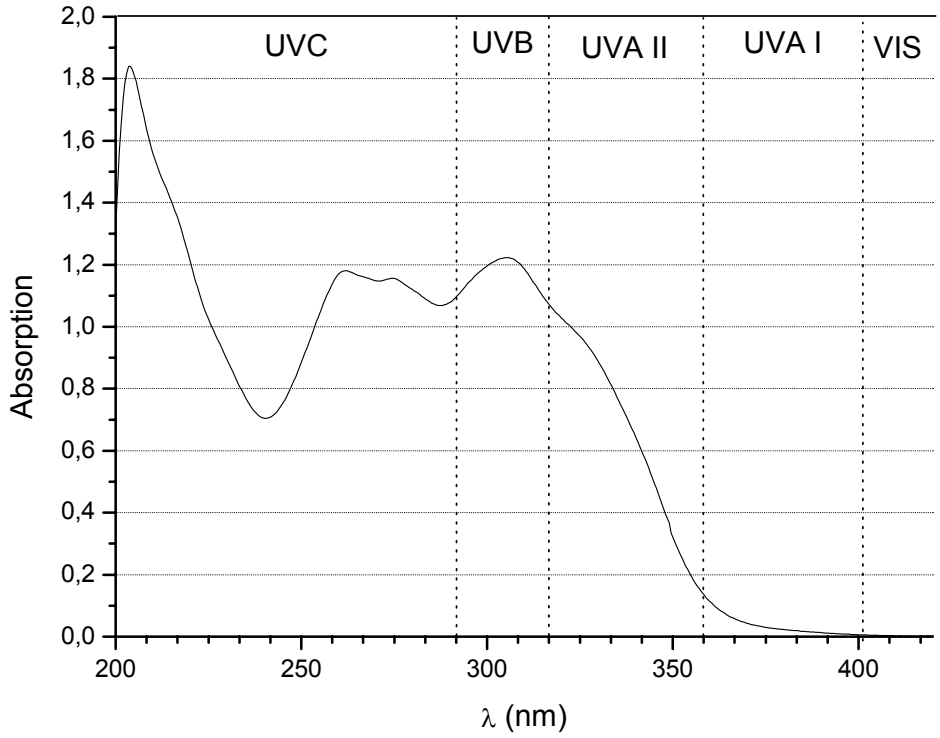


Figure 62: Absorption spectrum of the 4-Methoxy-benzoic acid 2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran-7-yl ester **141**. 10 mM in isopropanol.

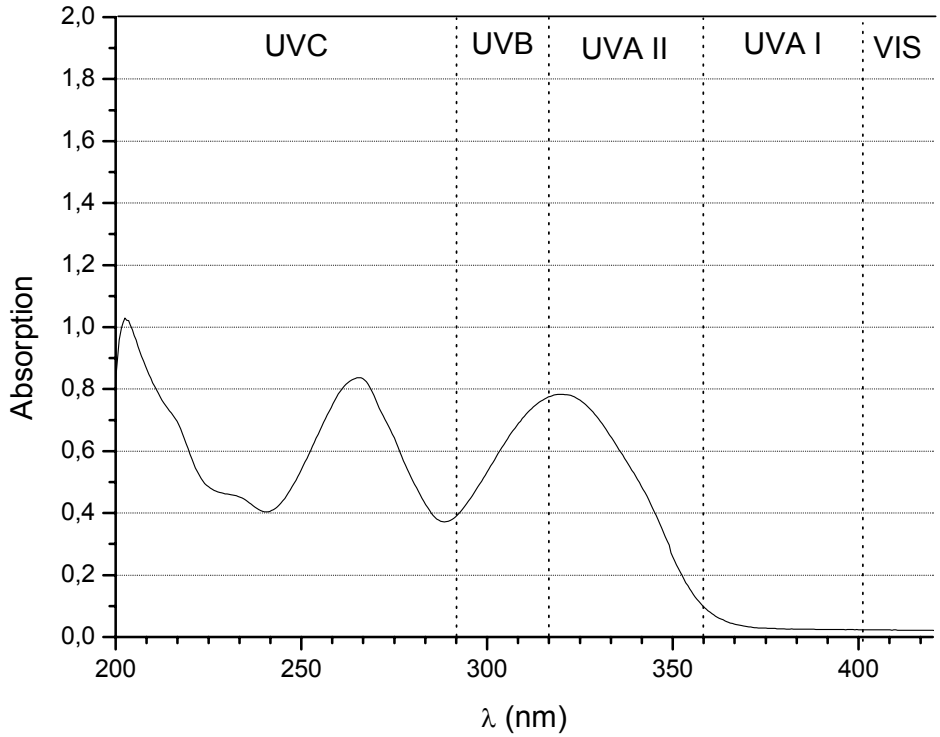


Figure 63: Absorption spectrum of the 4-Methoxybenzoic acid 2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran-6-yl ester **142**. 10 mM in isopropanol.

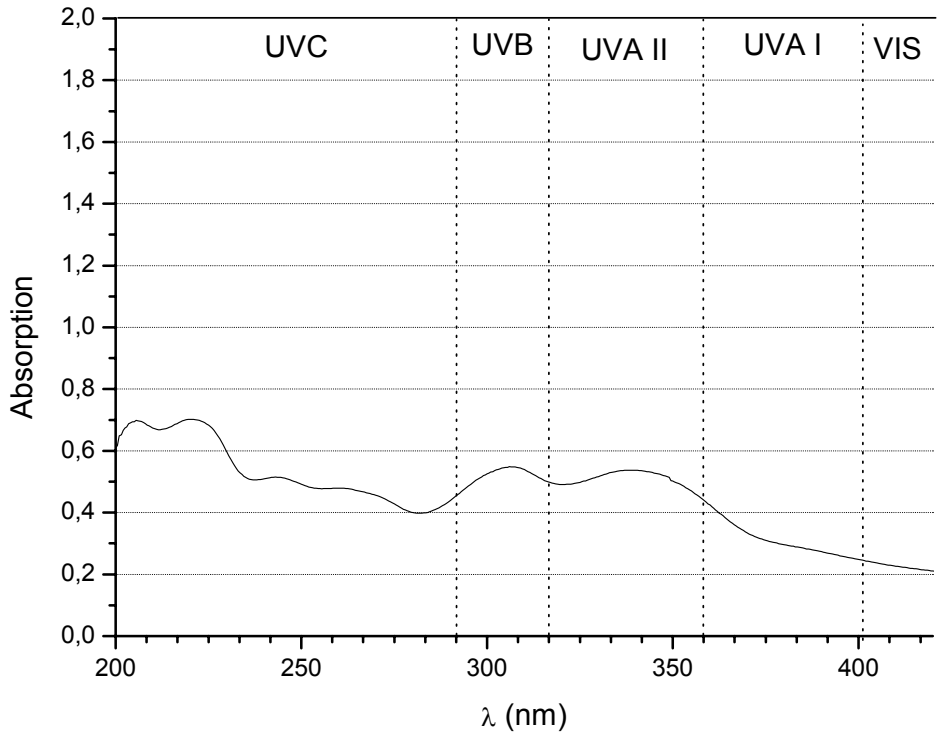


Figure 64: Absorption spectrum of the 3,4-Dimethoxybenzoic acid 2-(3,4-dimethoxyphenyl)-4-oxo-4*H*-1-benzopyran-7-yl ester **144**. 10 mM in isopropanol.

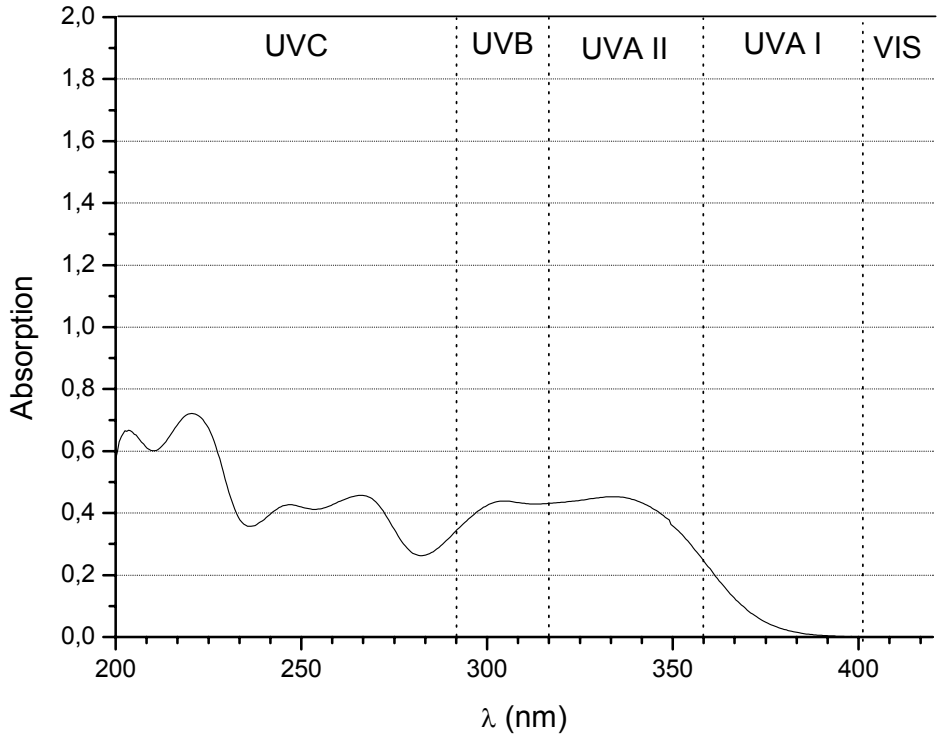


Figure 65: Absorption spectrum of the 3,4-Dimethoxy-benzoic acid 2-(3,4-dimethoxy-phenyl)-4-oxo-4*H*-1-benzopyran-6-yl ester **145**. 10 mM in isopropanol.

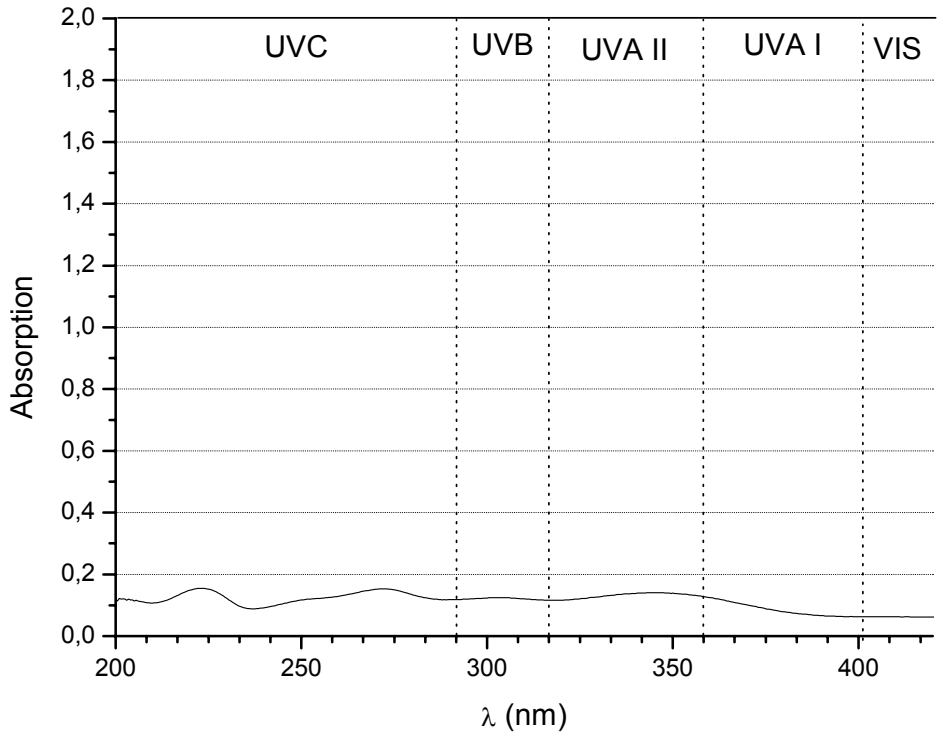


Figure 66: Absorption spectrum of the 3,4-Dimethoxy-benzoic acid 5-hydroxy-4-oxo-2-(3,4-dimethoxy-phenyl)-4*H*-1-benzopyran-7-yl ester **146**. 10 mM in isopropanol.

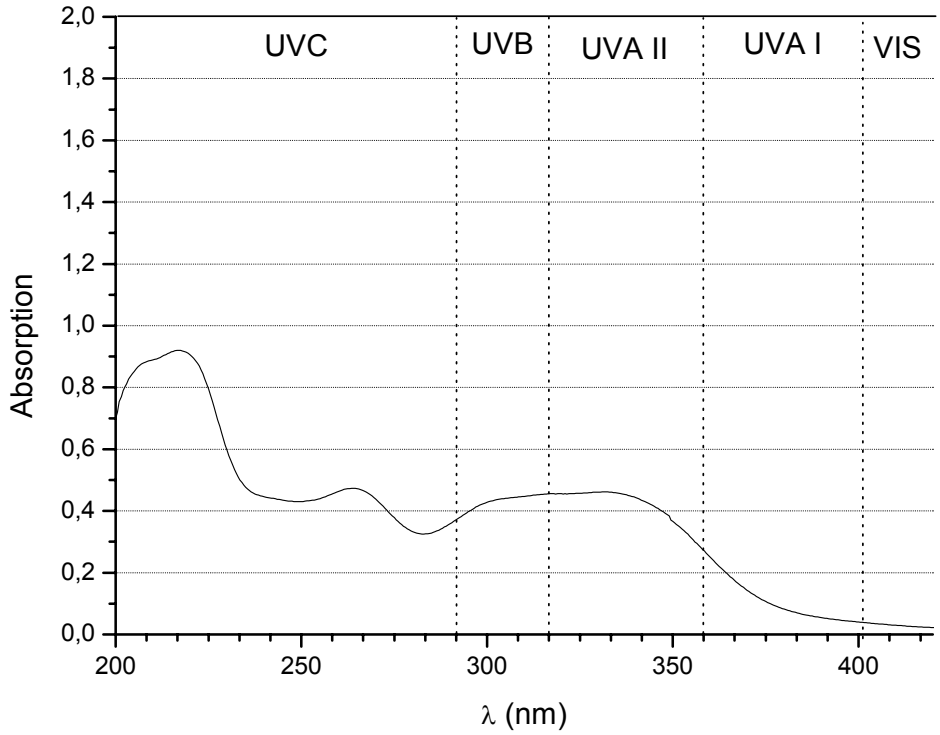


Figure 67: Absorption spectrum of the Bis 3,4-dimethoxy-benzoic acid 2-(3,4-dimethoxy-phenyl)-4-oxo-4*H*-1-benzopyran-6,7-yl ester **147**. 10 mM in isopropanol.

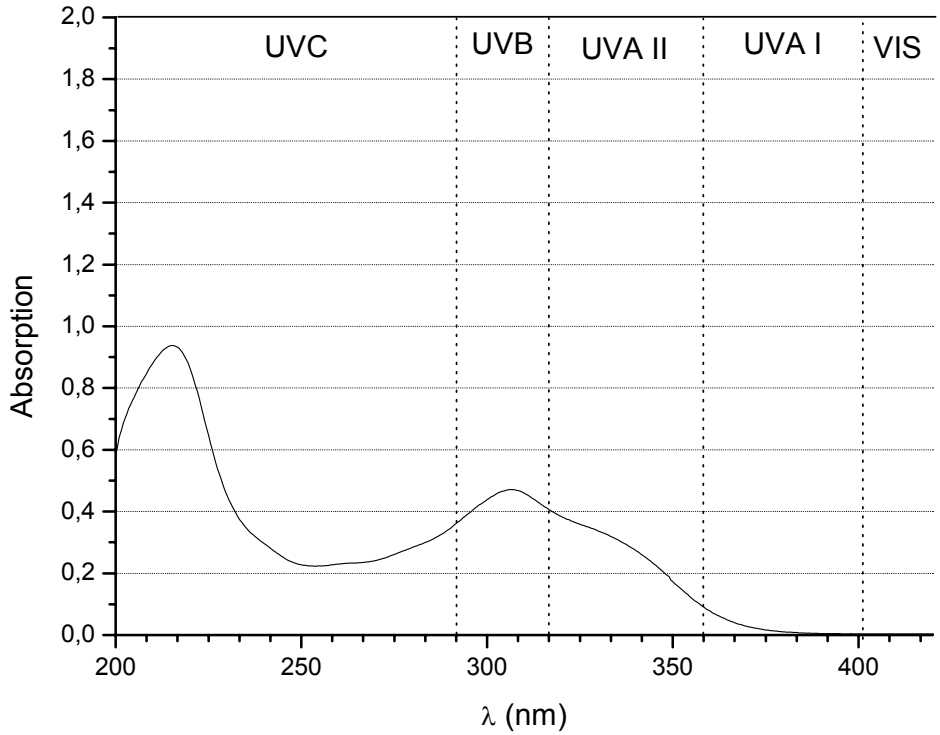


Figure 68: Absorption spectrum of the 3,4,5-Trimethoxy-benzoic acid 2-(3,4,5-trimethoxy-phenyl)-4-oxo-4*H*-1-benzopyran-7-yl ester **148**. 10 mM in isopropanol.

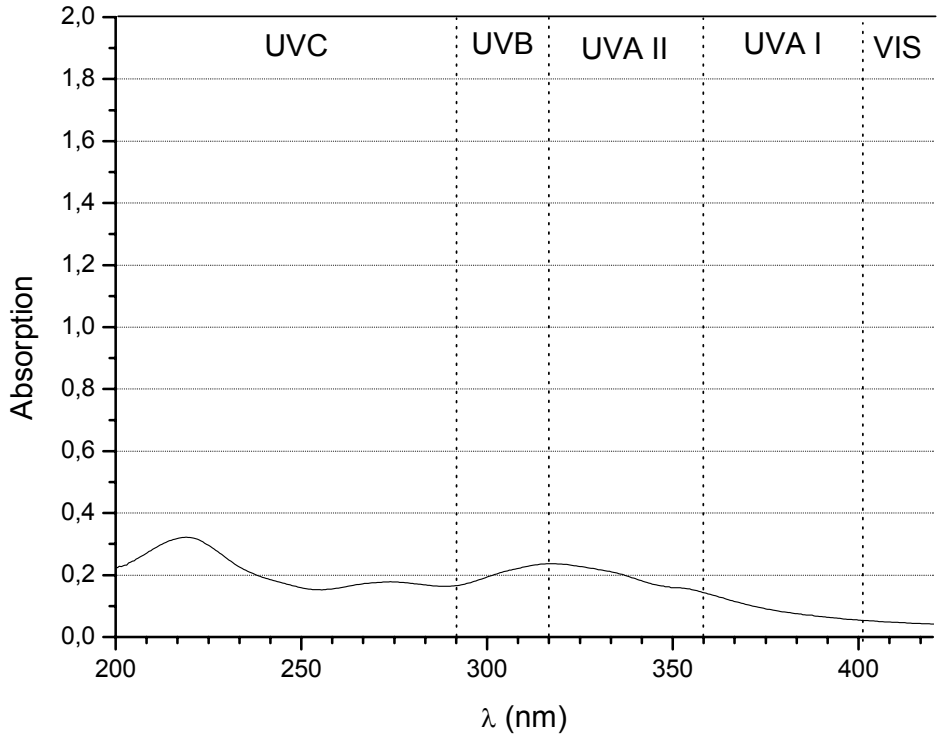


Figure 69: Absorption spectrum of the 3,4,5-Trimethoxy-benzoic acid 2-(3,4,5-trimethoxy-phenyl)-4-oxo-4*H*-1-benzopyran-6-yl ester **149**. 10 mM in isopropanol.

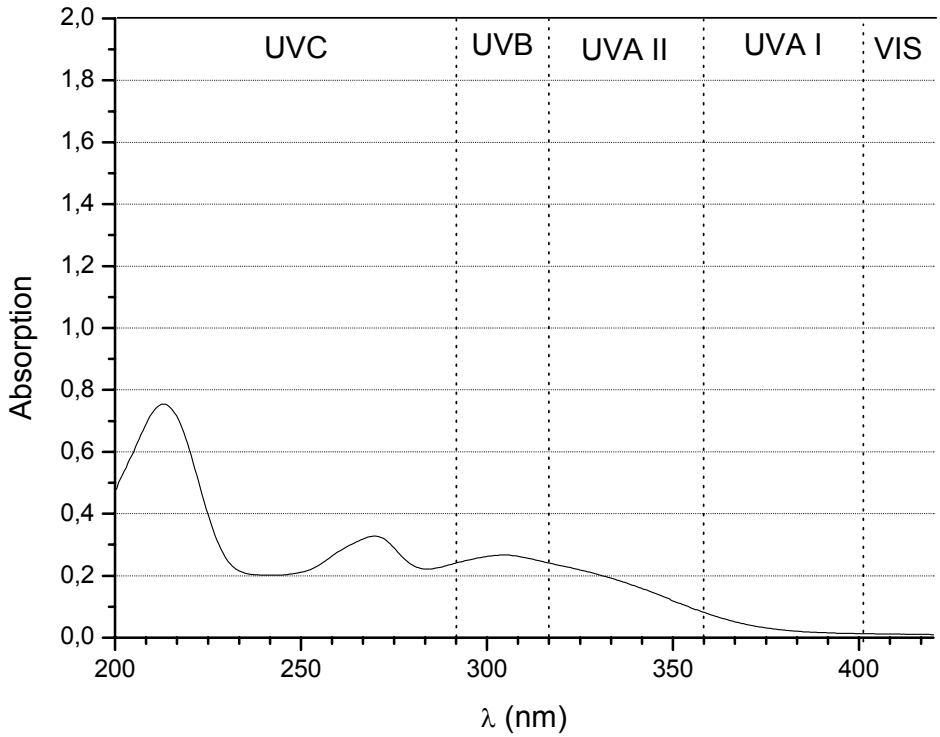


Figure 70: Absorption spectrum of the 3,4,5-trimethoxy-benzoic acid 2-(3,4,5-trimethoxyphenyl)-8-hydroxy-4-oxo-4*H*-1-benzopyran-7-yl ester **150**. 10 mM in isopropanol.

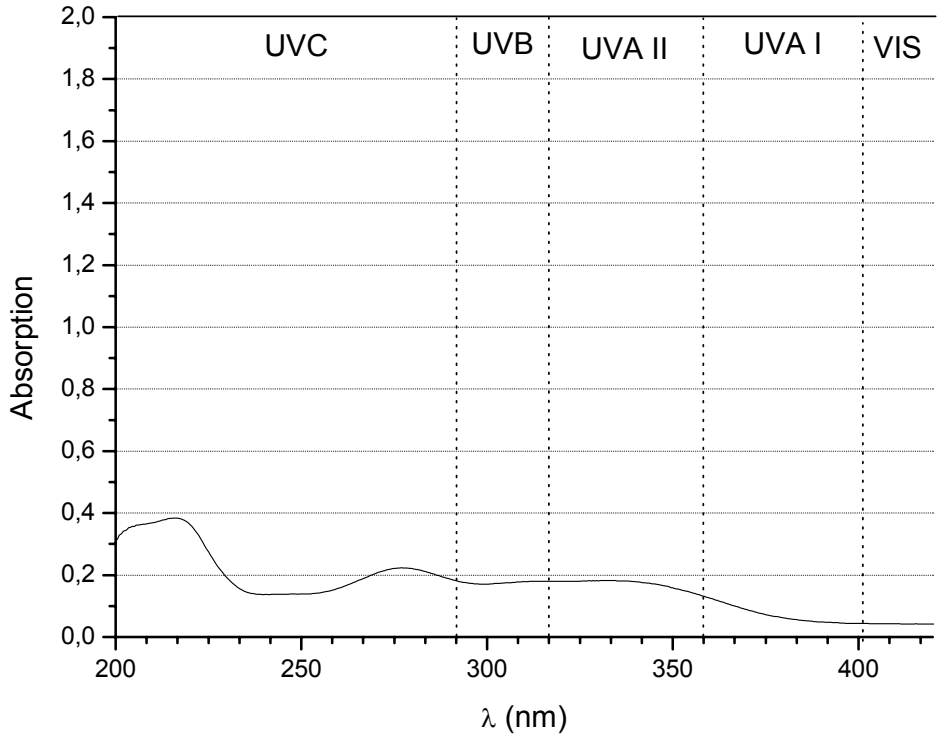


Figure 71: Absorption spectrum of the 3,4,5-Trimethoxy-benzoic acid 5-hydroxy-4-oxo-2-(3,4,5-trimethoxy-phenyl)-4*H*-1-benzopyran-7-yl ester **151**. 10 mM in isopropanol.

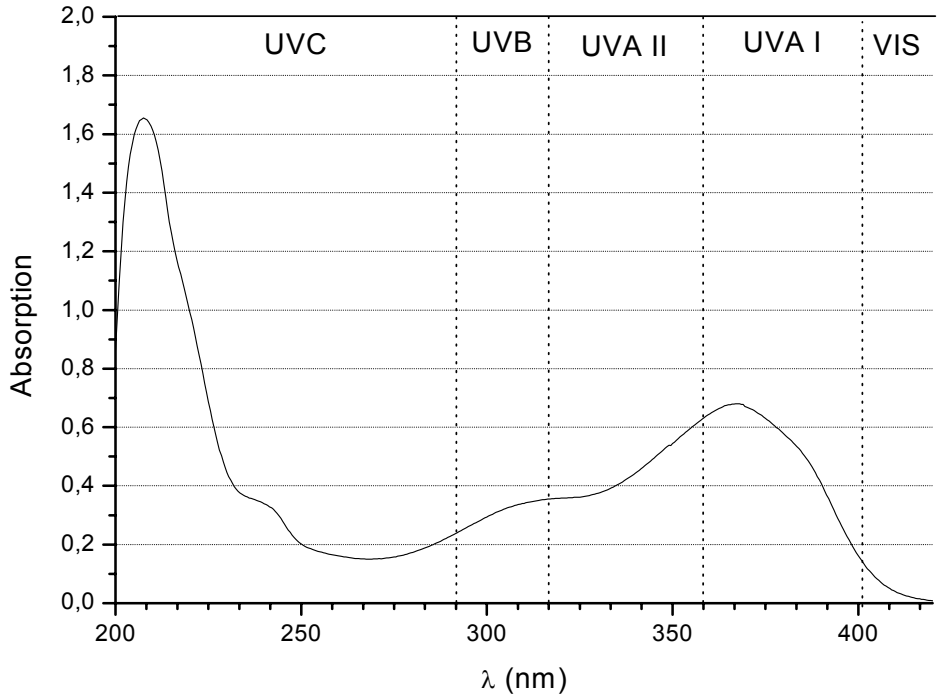


Figure 72: Absorption spectrum of the 3,4,5-Trimethoxybenzoic acid 2-[1-hydroxy-3-oxo-3-(3,4,5-trimethoxyphenyl)-propenyl]-phenyl ester **153**. 10 mM in isopropanol.

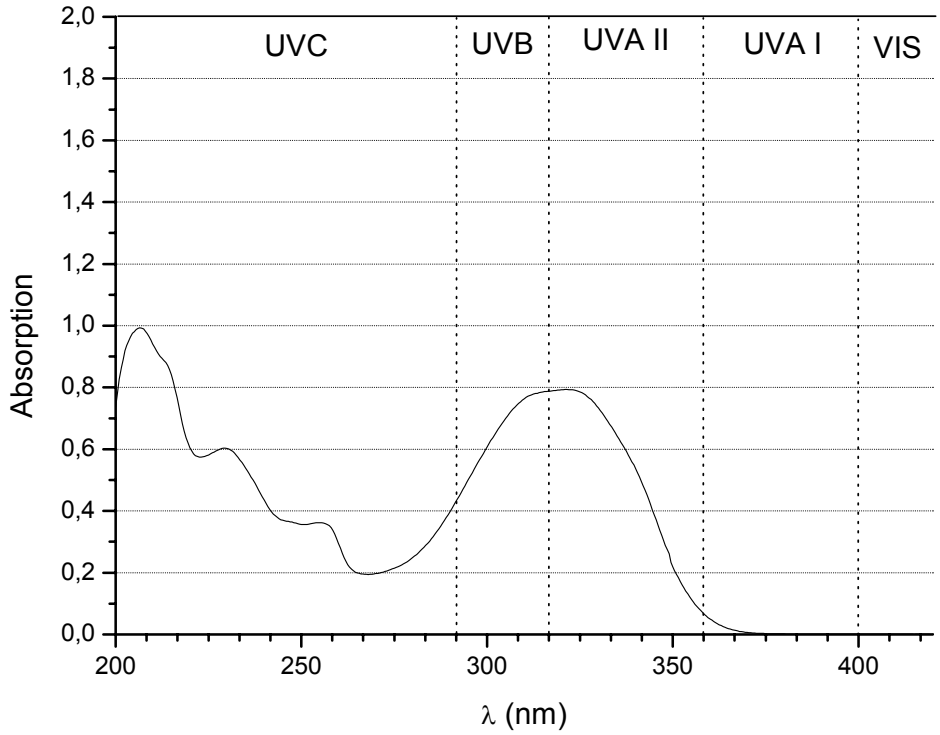


Figure 73: Absorption spectrum of the7-ethylhexyloxy-4′-methoxyflavone **157a**. 10 mM in isopropanol.

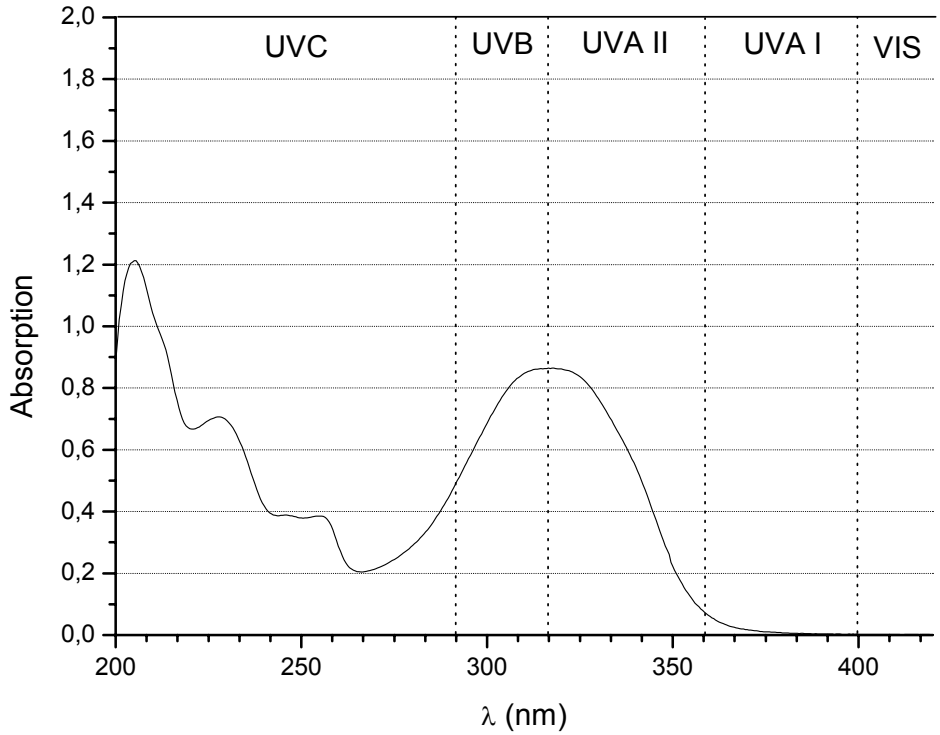


Figure 74: Absorption spectrum of the 7-*O*-Glucosyl-4′-methoxyflavone **158**. 10 mM in isopropanol.

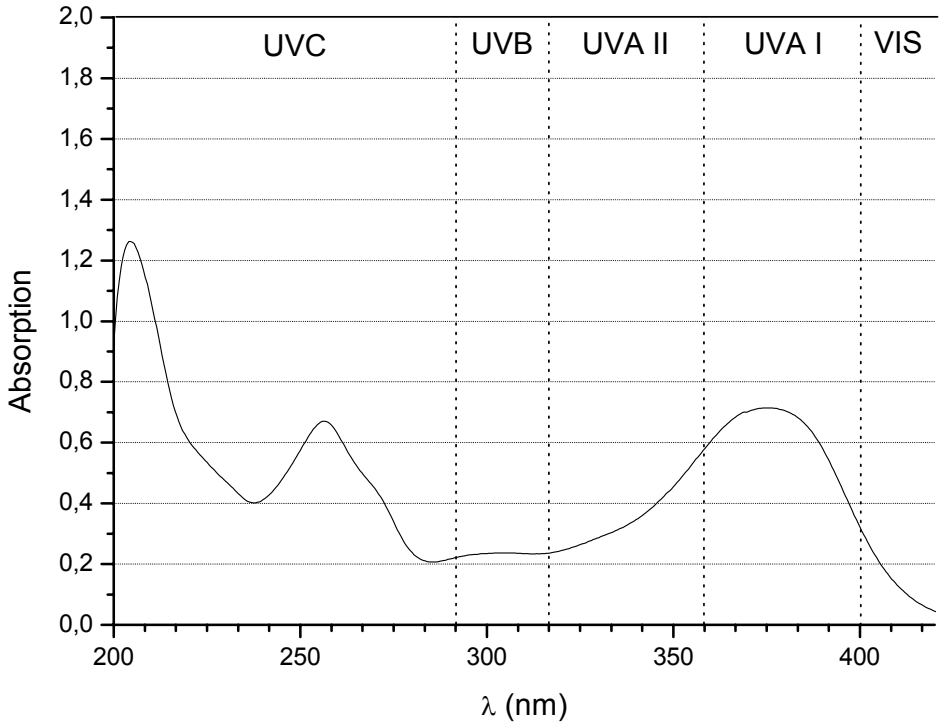


Figure 75: Absorption spectrum of the 3,5,7,3′,4′-Pentahydroxyflavone **159** (Quercetin). 10 mM in isopropanol.

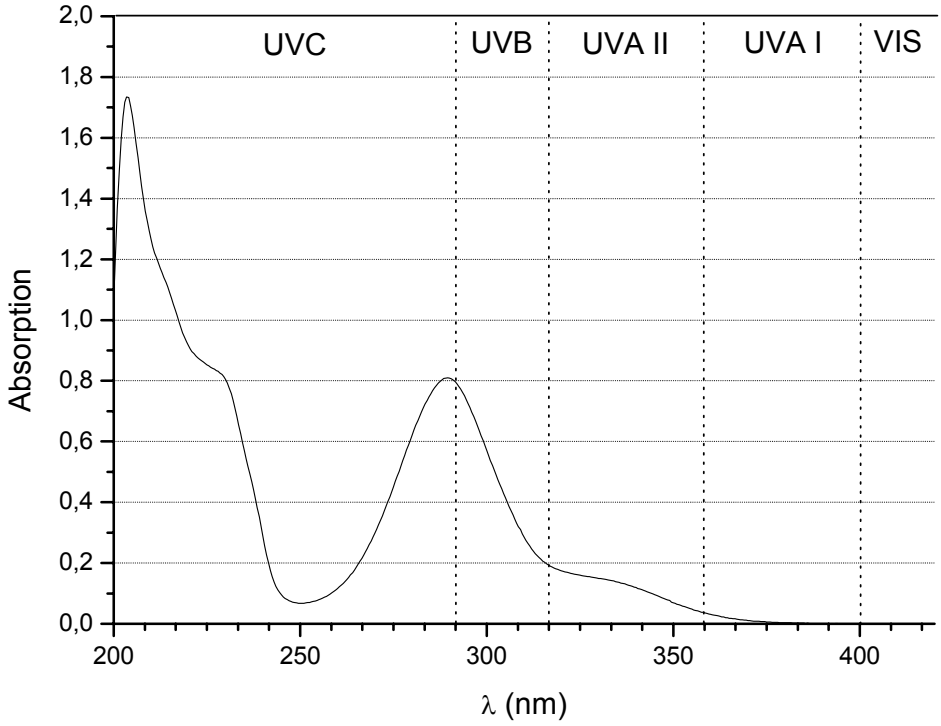


Figure 76: Absorption spectrum of the 5,7,3′,4′-tetrahydroxy-2,3-dihydroflavone **160** (Eriodictyol). 10 mM in isopropanol

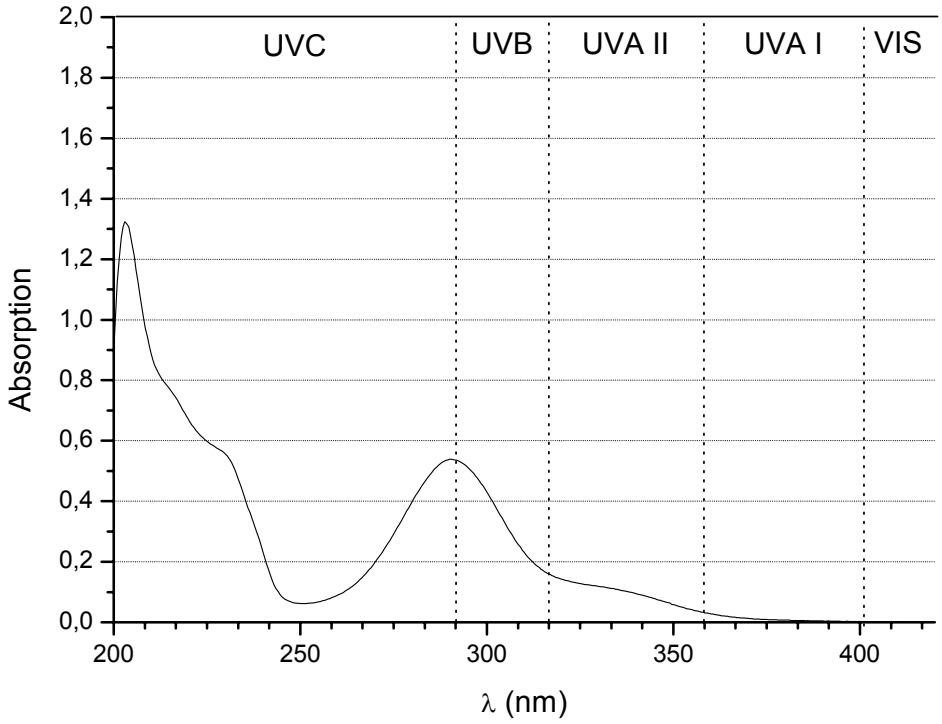


Figure 77: Absorption spectrum of the 3,5,7,3′,4′-Pentahydroxy-2,3-dihydroflavone **161** ((+)-Taxifolin). 10 mM in isopropanol.

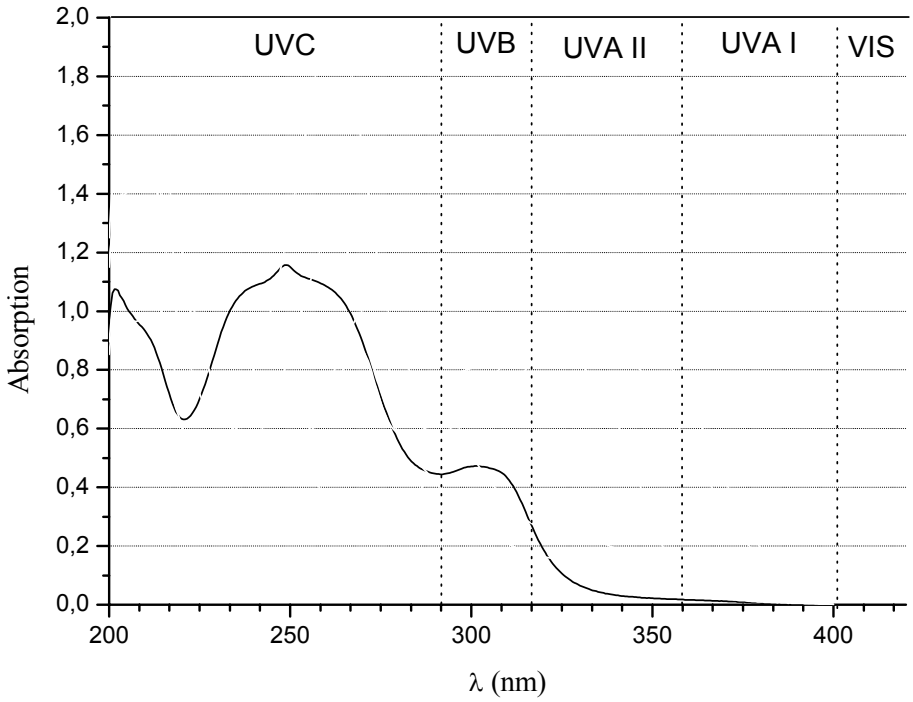


Figure 78: Absorption spectrum of the 7-Hydroxy-4′-methoxyisoflavone **162** (Formononetin). 10 mM in isopropanol.

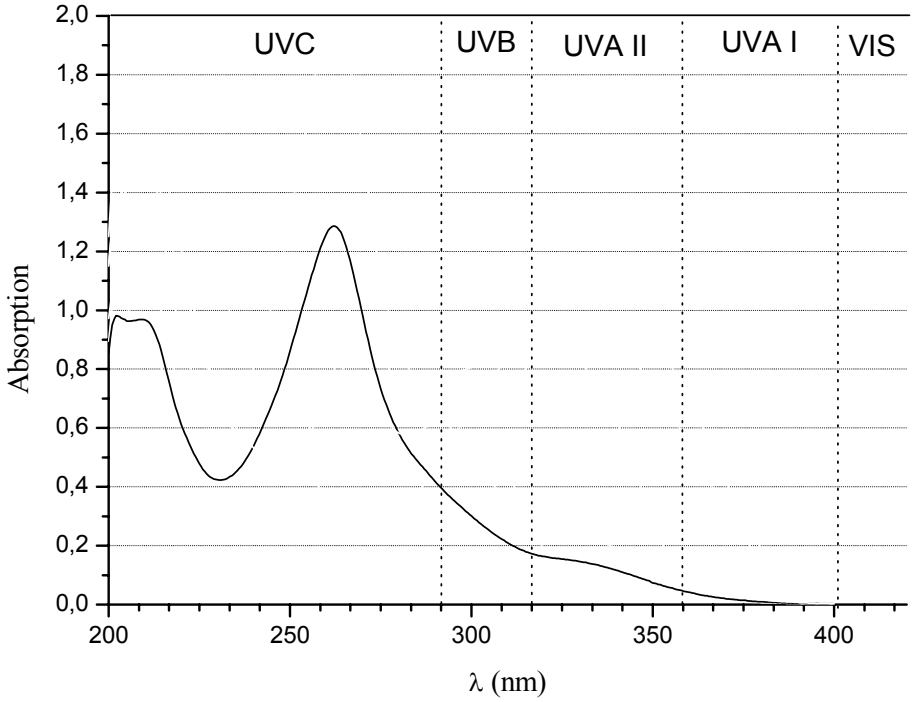


Figure 79:Absorption spectrum of the 5,7-Dihydroxy-4′-methoxyisoflavone **163** (Biochanin A). 10 mM in isopropanol.

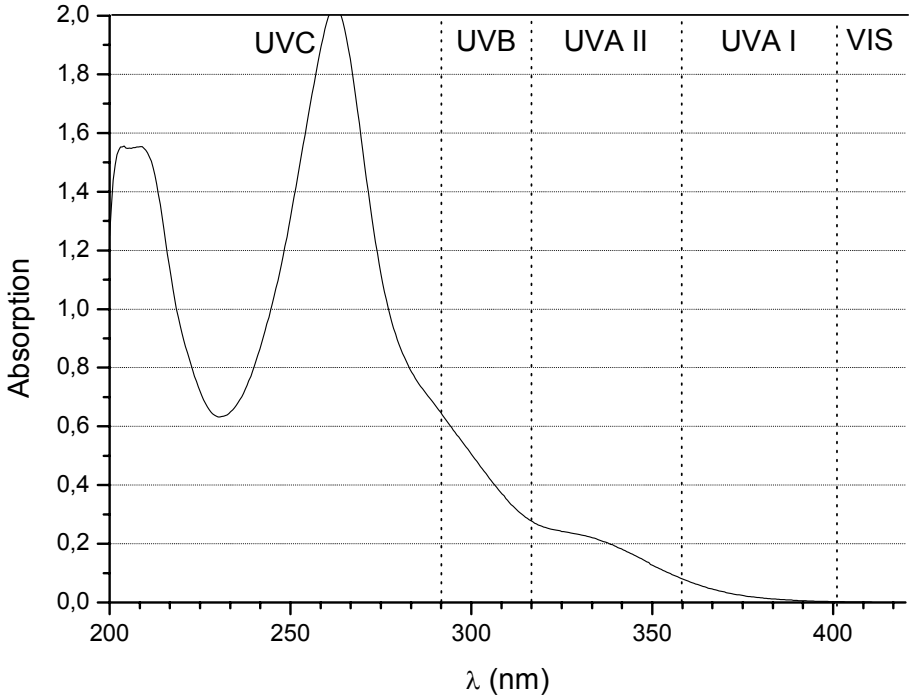


Figure 80: Absorption spectrum of the 5,7,4′-Trihydroxyisoflavone **164** (Genistein). 10 mM in isopropanol.

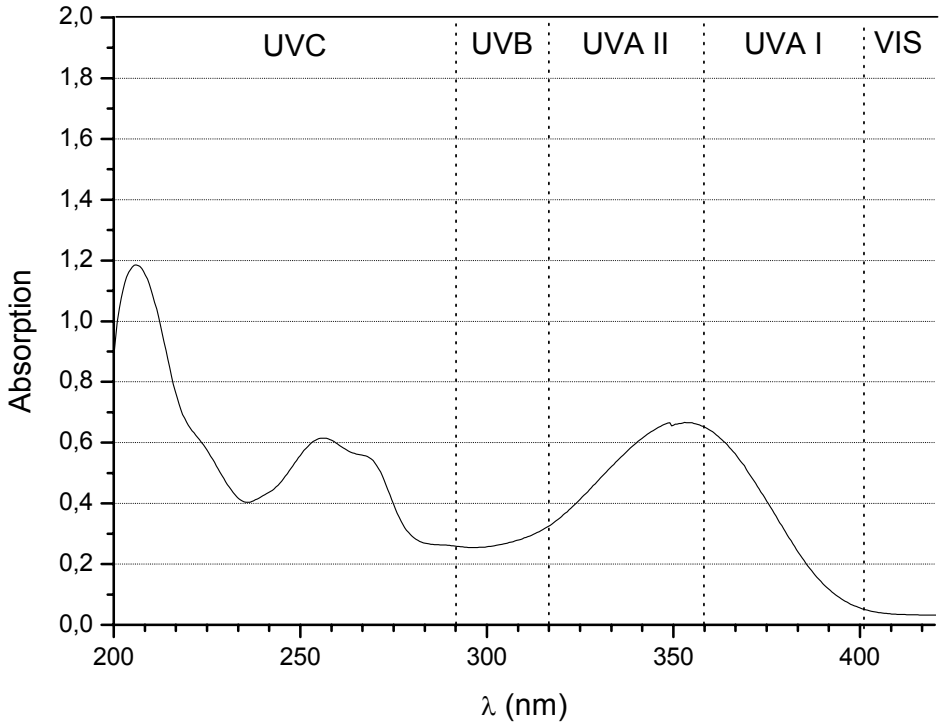


Figure 81: Absorption spectrum of the 7-*O*-Glucosyl-Luteolin 166. 10 mM in isopropanol.

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Curriculum Vitae

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Patents and Publications

I. Perruchon, S. and Buchholz, H. A. (Merck Patent GmbH), International Application *"New synthesis for flavones"*, **WO02/060889**.

II. Perruchon, S.; Carola, C. and Buchholz, H. A. (Merck Patent GmbH), International Application *"Flavones as UV-Filter"*, August **2002** (unpublished).

III. Perruchon, S.; Carola, C. and Buchholz, H. A. (Merck Patent GmbH), International Application *"Flavones as Antioxidants"*, September **2002** (unpublished).

IV. Perruchon, S.; Carola, C.; Moinet, C.; Fessner, W.-D. and Buchholz, H *"Studies of Flavonoids properties for Cosmetics via Structure-Function Relationship"* Proceedings oral papers at the 22nd IFSCC Congress, Edinburgh **2002**.

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Eidesstattliche Erklärung

Ich erkläre hiermit an Eides Statt, dass ich meine Dissertation selbständig und nur mit den angegebenen Hilfsmitteln angefertigt habe

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Erklärung

Ich erkläre hiermit, noch keinen Promotionsversuch unternommen zu haben.