SYNTHESIS OF N'-ALLYL-2-STYRYLCHROMONES BY A BAKER VENKATARAMAN TRANSFORMATION

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Abstract: n'-allyl-2-styrylchromones have been prepared by the Baker-Venkataraman method, by two different synthetic routes, both of them involving a Claisen rearrangement. The two synthetic routes were compared in terms of yields and practical execution. All compounds were fully characterized using 1D and 2D NMR techniques.

Introduction

Chromones are one of the most abundant groups of natural occurring heterocyclic compounds. Many pharmacological properties have been ascribed to various members of this family, including anti-inflammatory, anti-allergic and anti-tumour activities. (1) The majority of natural occurring chromones are 2- and 3-phenyl derivatives, also called flavones and isoflavones, respectively. However other types of chromones have been found in the plant kingdom, such as 3-methyl-, 2-hydroxymethyl- and 2-styrylchromones. (2)

Although only two 2-styrylchromones are known as natural compounds, (3,4) numerous synthetic analogues have been prepared in the last decades. (5) Both natural and synthetic derivatives have shown a remarkable variety of biological activities, such as important citoxicity against human leukaemia cells, (3,4) significant levels of anti-allergic (6) and anticancer (7) activities. Certain allyl-2-styrylchromones also shown important antineoplastic action. (7,8)

A classical approach has been recently used by us to assess the effects of 3'-allyl-4',5,7-trimethoxy-2-styrylchromone on rat liver mitochondria bioenergetic. (9) This study demonstrates that 2-styrylchromone strongly interacts with mitocondrial oxidative phosphorylation. The cancer chemopreventive activity observed for chromones and flavones (7,10), like possible, potencial anticancer activity of this 2-styrylchromone, may be attributed to the induction of mithocondrial cytochrome *c* release.

Taking into account the potential biological applications of chromones and especially those having 2-substituents, we decided to devote some of our attention to the synthesis of new 2-styrylchromones. In this paper we report the synthesis of several n'-allyloxy-2-styrylchromones by a Baker Venkataraman (11) transformation and the transposition of the allyl group to obtain n'-allyl-2-styrylchromones.

Experimental

Melting points were determined on a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. ^{1}H and ^{13}C nmr spectra were recorded in deuteriochloroform solutions, on a Bruker AMX 300 spectrometer, at 300.13 and 75.47 MHz, respectively; the chemical shifts are expressed in δ (ppm) values relative to TMS as internal reference. ^{1}H assignments were made by using 2D COSY spectra, while ^{13}C assignments were made using HETCOR and HMBC (delays for long-range *J* C/H couplings were optimised for 7 Hz) experiments. Electron impact mass spectra were obtained at 70 eV electron impact ionisation using a VG Autospec Q mass spectrometer. Elemental analyses were carried on a LECO 932 CHN analyser in Aveiro. Preparative thin layer chromatography was carried out on silica gel plates (Merck or Riedel silica gel 60 DGF_{254}). Column chromatography was also performed on silica gel (Merck silica gel 60, 70-230 mesh). All other chemicals and solvents used were obtained from commercial sources and used as received or dried using standard procedures.

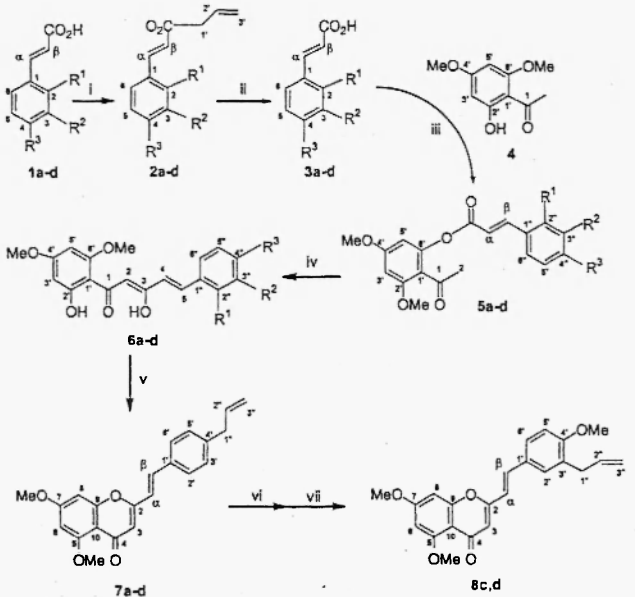
Results and Discussions

Chemistry

With the purpose of obtaining new derivatives of 2-styrylchromones, potentially bioactive, with allyl substituintes attached to the B ring, two synthetic routes were used. These were applied in the synthesis of 3'-allyl-4',5,7-trimethoxy-2-styrylchromone **8c**, with the purpose of verifying which of them was more adequate in terms of yields and practical execution, for the synthesis of the others 2-styrylchromones. n'-allyl-2-styrylchromones **8** were prepared according to the sequences shown in Scheme 1 and in Scheme 2.

These two different pathways studied, involved both of them a Claisen rearrangement. The first approach, Scheme 1, involves the *o*-acylation of 2'-hydroxy-4',6'-dimethoxyacetophenone **4** with the appropriate allyloxycinnamoyl chloride, prepared *in situ*, from allyloxycinnamic acids **3 a-d** and phosphorus oxychloride, to obtain the correspondent 2'-cinnamoyloxyacetophenones **5 a-d** in yields of 63-93 %. The improvements in the method described by Wadodkar and Ghiga (11) for this transformation, in terms of the temperature and the time reaction, significantly increase the yield of the reaction for the synthesis of 2'-(4-allyloxycinnamoyloxy)-4',6'-dimethoxyacetophenone **5c** (from 20% to 76%).The rearrangement of 2'-cinnamoyloxyacetophenones **5 a-d** into 5-aryl-3-hydroxy-1-(2-hydroxyphenyl)-2,4-penten-1-ones **6a-d** was performed upon treatment with KOH and dimethyl sulfoxide at room temperature (70-85 %). The treatment of **6 a,d** with DMSO/iodine and of **6b,c** with DMSO/*p*-toluenesulfonic acid, led to their cyclisation and dehydration giving the expected allyloxy-2-styrylchromones **7a-d** in good yields (70-83 %). n'-allyl-2-styrylchromones **8a-d** (38-54 %) were obtained by Claisen rearrangement of the correspondent n'-allyloxy-2-styrylchromones **7a-d**, followed by methylation (Scheme 1). In the other synthetic approach, Scheme 2, allylcinnamic acid derivative **10** was prepared from allyl 4-allyloxicinnamate **2c** by a Claisen rearrangement, followed by methylation. The synthesis of 3'-allyl-4',5,7-trimethoxy-2-styrylchromone **8c** has been carried out according to the sequence shown in Scheme 2.

Comparing the two synthetic approaches to obtain n'-allyl-2-styrylchromones, we can say that the pathway that involves the allyl group transposition from the 4'-allyloxy-5,7-dimethoxy-2-styrylchromone **7c**, gives better results in terms of yields and practical execution, scheme 1. We can say that the global yield of synthesis in this case, is about three times higher than the other one, scheme 2. For all these reasons, the transposition of the allyl group to obtain all the other n'-allyl-2-styrylchromones was done via n'-allyloxy-2-styrylchromones, scheme 1. The transposition of the allyl group from 2'-allyloxy-5,7-dimethoxy-2-styrylchromone **7a** and 3'-allyloxy-5,7-dimethoxy-2-styrylchromone **7b** was monitored by tic, but the purification of the corresponding allyl-2-styrylchromes was not possible, despite several attempts were performed. This fact was attributed to the degradation of these allyl-2-styrylchromes resulting in low amounts of product.

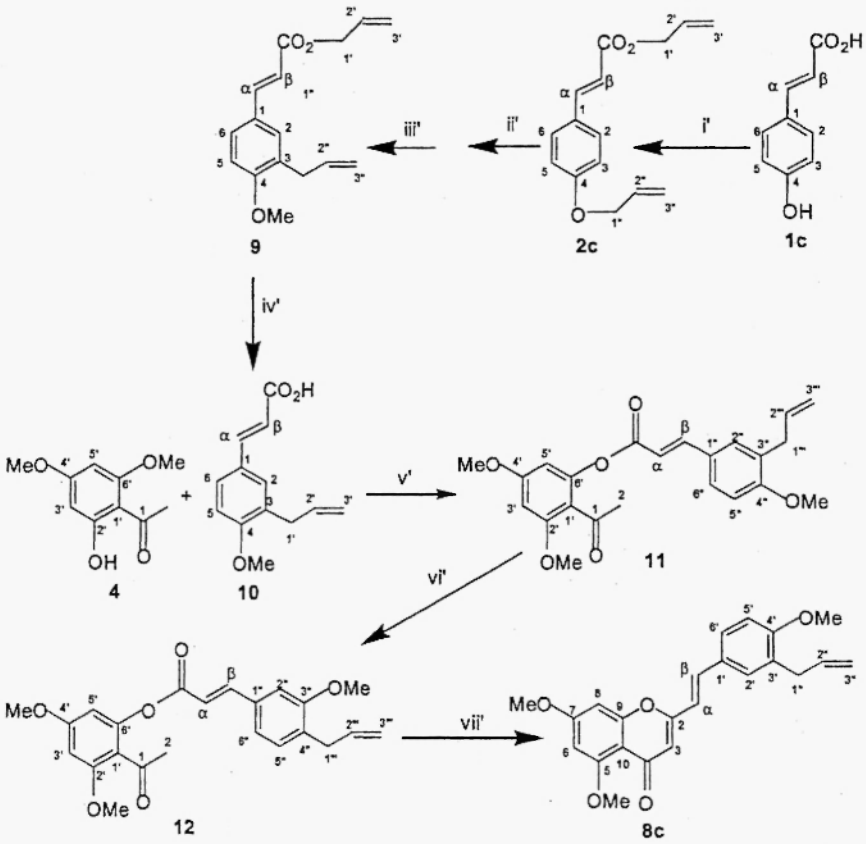


1 a) R^1=OH, R^2=R^3=H
b) R^2=OH, R^1=R^3=H
a) R^3=OH, R^1=R^2=H
a) R^2=R^3=OH, R^1=H

2, 3, 5, 6, 7 a) R^1=OCH_2CH=CH_2, R^2=R^3=H
b) R^2=OCH_2CH=CH_2, R^1=R^3=H
c) R^3=OCH_2CH=CH_2, R^1=R^2=H
d) R^2=R^3=OCH_2CH=CH_2, R^1=H

8 c) R^3=OCH_3, R^2=CH_2CH=CH_2, R^1=R^4=H
d) R^2=R^3=OCH_3, R^1=R^4=CH_2CH=CH_2

Scheme-1 - Synthesis of n'-allyl-2-styrylchromones **8a-d**



i) Allylbromide, K_2CO_3, Acetone ii') Dimethyl sulfate, K_2CO_3, acetone
iii') 250° C, 1,2,4-trichlorobenzene iv') MeOH, NaOH
v') $POCl_3$, py vi') DMSO, KOH
vii') DMSO, I_2

Scheme-2 - Synthesis of 3'-allyl-4'-methoxy-5,7-dimethoxy-2-styrylchromone **8c**

Synthesis

Synthesis of allyl n'-allyloxycinnamates 2a-d

To a solution of the appropriate hydroxycinnamic acid **1a-d** (60 mmol) in acetone (40 ml), K_2CO_3 (50.52 g, 0.36 mol for the mono hydroxylated acids and 69.04 g, 0.55 mol for the di-hydroxylated acid) and allyl bromide (31.6 ml, 0.36 mol for the mono hydroxylated acids and 43.2 ml, 0.55 mol for the di-hydroxylated acid) were added. The reaction mixture was refluxed under nitrogen for 48 hours; then the inorganic salts were filtered off and the acetone evaporated to dryness. The residue was dissolved in chloroform (80 ml) and washed with water; the organic layer was dried with anhydrous sodium sulphate. After solvent evaporation, all the allyl n'-allyloxycinnamates **2a-d** were obtained in very good yields.

Allyl 2-allyloxycinnamate 2a. Yield 96 %; orange oil; ^{1}H nmr: δ = 4.54-4.56 (m, 2H, H-1''), 4.69 (d, 2H, H-1', *J* 5.6 Hz), 5.22-5.43 (m, 2H, H-3', H-3''), 5.92-6.08 (m, 2H, H-2', H-2''), 6.55 (d, 1H, H-α, *J* 16.2 Hz), 6.85 (d, 1H, H-3, *J* 8.4 Hz), 6.92 (d, 1H, H-5, *J* 7.5 Hz), 7.28 (t, 1H, H-4, *J* 7.9 Hz), 7.48 (d, 1H, H-6, *J* 7.7 Hz), 8.08 (d, 1H, H-β, *J* 16.2 Hz); ^{13}C nmr: δ = 64.7 (C-1'), 68.8 (C-1''), 112.2 (C-3), 117.4 (C-3'), 117.7 (C-α), 118.0 (C-3''), 120.6 (C-5), 123.2 (C-1), 128.5 (C-6), 131.2 (C-4), 132.2 (C-2'), 132.6 (C-2''), 140.1 (C-β), 157.0 (C-2), 166.7 (C=O); ms: (EI) m/z (rel. int.) 244 ($M^{+\bullet}$, 37), 187 (29), 146 (25), 131 (42), 118 (100), 91 (40), 77 (11), 55 (6).

Allyl 3-allyloxycinnamate 2b. Yield 97 %; orange oil; ^{1}H nmr: δ = 4.51 (dt, 2H, H-1'', *J* 1.4 and 5.2 Hz), 4.69 (dt, 2H, H-1', *J* 1.3 and 5.7 Hz), 5.23-5.44 (m, 4H, H-3', H-3''), 5.91-6.07 (m, 2H, H-2', H-2''), 6.42

(d, 1H, H-α, *J* 16.0 Hz), 6.91 (dd, 1H, H-6, *J* 2.2 and 8.3 Hz), 7.03 (s, 1H, H-2), 7.08 (d, 1H, H-4, *J* 7.8 Hz), 7.25 (t, 1H, H-5, J 7.5 Hz), 7.65 (d, 1H, H-β, *J* 16.0 Hz); ^{13}C nmr: δ = 64.9 (C-1'), 68.5 (C-1''), 113.6 (C-2), 116.6 (C-6), 117.5 (C-3'), 117.8 (C-α), 117.9 (C-3''), 120.7 (C-4), 129.6 (C-5), 132.1 (C-2'), 132.8 (C-2''), 135.4 (C-1), 144.6 (C-β), 158.6 (C-3), 166.1 (C=O); ms: (EI) m/z (rel. int.) 244 ($M^{+\bullet}$, 100), 203 (36), 187 (60), 159 (89), 147 (62), 131 (55), 118 (62), 91 (63), 77 (21), 63 (33).

Allyl 4-allyloxycinnamate 2c. Yield 91 %; orange oil; ^{1}H nmr: δ = 4.56 (dt, 2H, H-1'', *J* 1.4 and 5.6 Hz), 4.70 (dt, 2H, H-1', *J* 1.4 and 5.6 Hz), 5.25-5.45 (m, 4H, H-3', H-3''), 5.93-6.10 (m, 2H, H-2', H-2''), 6.33 (d, 1H, H-α, *J* 16.1 Hz), 6.92 (d, 2H, H-3, H-5, *J* 9.0 Hz), 7.47 (d, 2H, H-2, H-6, *J* 9.0 Hz), 7.67 (d, 1H, H-β, *J* 16.1 Hz); ^{13}C nmr: δ = 65.0 (C-1'), 68.8 (C-1''), 115.0 (C-3, C-5), 115.3 (C-α), 118.0 and 118.1 (C-3' and C-3''), 127.2 (C-1), 129.7 (C-2, C-6), 132.4 and 132.7 (C-2' and C-2''), 144.7 (C-β), 160.4 (C-4), 166.9 (C=O); ms: (EI) m/z (rel. int.) 244 ($M^{+\bullet}$, 44), 187 (100), 161 (46), 160 (58), 147 (40), 131 (35), 119 (35), 91 (52).

Allyl 3,4-diallyloxycinnamate 2d. Yield 76%, mp 160-161°C. ^{1}H nmr: δ = 4.62-4.72 (m, 4H, H-1'', H-1'''), 4.70 (dt, 2H, H-1', *J* 1.3 Hz and 5.7 Hz), 5.25-5.47 (m, 6H, H-3', H-3'', H-3'''), 5.93-6.15 (m, 3H, H-2', H-2'', H-2'''), 6.30 (d, 1H, H-α, *J* 15.9 Hz), 6.87 (d, 1H, H-5, *J* 8.9 Hz), 7.08 (d, 1H, H-2, *J* 2.1 Hz), 7.10 (d, 1H, H-6, *J* 2.1 Hz), 7.63 (d, 1H, H-β, *J* 15.9 Hz); ^{13}C nmr: δ = 65.1 (C-1'), 69.6 (C-1''), 69.9 (C-1'''), 112.5 (C-2), 113.3 (C-5), 115.5 (C-α), 117.9 e 118.0 e 118.2 (C-3' and C-3'' and C-3'''), 122.7 (C-6), 127.4 (C-1), 132.3 (C-2'), 132.8 and 133.0 (C-2'' and C-2'''), 144.9 (C-β), 148.5 (C-3), 150.6 (C-4), 166.8 (C=O); ms: (EI) m/z (rel. int.) 300 ($M^{+\bullet}$, 100), 259 (45), 229 (39), 173 (22), 133 (40), 105 (25), 91 (23), 77 (28).

Synthesis of allyl-3-allyl-4-methoxycinnamate 9

A solution of allyl 4-allyloxycinnamate **2c** (10 g, 41 mmol) was heated at 250°C, under nitrogen, for 3 hours. The reaction was left to reach room temperature, then acetone (20 ml), K_2CO_3 (17.0 g, 0.123 mol) and dimethyl sulfate (41 mmol) were added. The solution was refluxed at 70° C for 5 hours; the inorganic salts were filtered off, and the acetone evaporated to dryness. The residue was dissolved in chloroform (80 ml) and washed with water. The organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated to dryness giving the expected allyl-3-allyl-4-methoxycinnamate **9**.

Allyl-3-allyl-4-methoxycinnamate 9. Yield 84 %; orange oil. ^{1}H nmr: δ = 3.37 (d, 2H, H-1'', *J* 6.6 Hz), 3.83 (s, 3H, OCH_3), 4.69 (dt, 2H, H-1', *J* 1.3 and 5.6 Hz), 5.01-5.10 (m, 2H, H-3''), 5.23-5.39 (m, 2H, H-3'), 5.90-6.03 (m, 2H, H-2', H-2''), 6.33 (d, 1H, H-α, *J* 16.0 Hz), 6.83 (d, 1H, H-5, *J* 8.7 Hz), 7.36 (d, 1H, H-2, *J* 2.2 Hz), 7.38 (dd, 1H, H-6, *J* 2.2 and 8.7 Hz), 7.66 (d, 1H, H-β, *J* 16.0 Hz); ^{13}C nmr: δ = 33.9 (C-1''), 55.4 (OCH_3), 64.9 (C-1'), 110.2 (C-5), 114.9 (C-3''), 115.9 (C-α), 118.0 (C-3'), 126.6 (C-1), 128.2 (C-6), 129.1 (C-2), 129.2 (C-3), 132.3 (C-2''), 136.1 (C-2'), 144.9 (C-β), 159.0 (C-4), 166.8 (C=O); ms: (EI) m/z (rel. int.) 258 ($M^{+\bullet}$, 79), 244(16), 201 (47), 174 (100), 160 (45), 128 (30), 115 (40), 77 (20).

Synthesis of n'-allyloxycinnamic acids 3a-d and of 3-allyl-4-methoxycinnamic acid 10

An aqueous solution of sodium hydroxide (6.9 g NaOH / 24 ml H_2O) was added to a solution of the appropriate allyl n'-allyloxycinnamate **2a-d** and of allyl 3-allyl-4-methoxycinnamate **9** (41 mmol) in methanol (40 ml). The reaction mixture was stirred at 60-70°C, for 3 hours. After that period, the solution was poured into ice, water and hydrochloric acid (pH adjusted to 3). The obtained solid was removed by filtration, dissolved in chloroform (100 ml) and washed with water. The solvent was evaporated to dryness and the residue was recrystallized from ethanol, giving the expected n'-allyloxycinnamic acids **3a-d** and 3-allyl-4-methoxycinnamic acid **9**.

2-Allyloxycinnamic acid 3a. Yield 81, mp 101-102°C. ^{1}H nmr: δ = 4.64 (d, 2H, H-1', *J* 5.2 Hz), 5.29 (dq, 1H, H-3' *cis*, *J* 1.7 and 10.5 Hz), 5.41 (dq, 1H, H-3' *trans*, *J* 1.7 and 17.3 Hz), 6.01-6.12 (m, 1H, H-2'), 6.53 (d, H-α, *J* 16.2 Hz), 6.97 (t, 1H, H-5, *J* 7.5 Hz), 7.06 (d, 1H, H-3, *J* 7.9 Hz), 7.37 (dt, 1H, H-4, *J* 1.5 and 7.9 Hz), 7.68 (dd, 1H, H-6, *J* 1.5 and 7.7 Hz), 7.88 (d, 1H, H-β, *J* 16.2 Hz); ^{13}C nmr: δ = 68.7 (C-1'), 113.0 (C-3), 118.0 (C-3'), 119.4 (C-α), 121.0 (C-5), 122.7 (C-1), 128.6 (C-6), 131.8 (C-4), 133.5 (C-2'),

138.8 (C-β), 156.7 (C-2), 168.0 (C=O); ms: (EI) m/z (rel.int.) 204 ($M^{+\bullet}$, 56), 185 (6), 158 (18), 146 (100), 131 (25), 118 (96), 91 (90), 77 (18), 65 (24).

3-Allyloxycinnamic acid 3b. Yield 79 %, mp 100-102 °C. ^{1}H nmr: δ = 4.60 (dt, 2H, H-1', *J* 1.5 and 5.2 Hz), 5.26 (dq, 1H, H-3' *cis*, *J* 1.6 and 10.6 Hz), 5.40 (dq, 1H, H-3' *trans*, *J* 1.6 and 17.2 Hz), 5.98-6.11 (m, 1H, H-2'), 6.55 (d, 1H, H-α, *J* 16.0 Hz), 6.97-7.00 (m, 1H, H-4), 7.23-7.29 (m, 2H, H-2, H-6), 7.31 (t, 1H, H-5 *J* 7.9 Hz), 7.55 (d, 1H, H-β, *J* 16.0 Hz); ^{13}C nmr: δ = 68.3 (C-1'), 113.7 (C-6), 117.0 (C-4), 117.6 (C-3'), 119.6 (C-α), 121.0 (C-2), 130.0 (C-5), 133.7 (C-2'), 135.7 (C-1), 143.9 (C-β), 158.6 (C-3), 167.7 (C=O); ms: (EI) m/z (rel. int.) 204 ($M^{+\bullet}$, 100), 187 (7), 163 (23), 159 (73), 147 (20), 131 (38), 118 (27), 91 (36), 77 (26), 65 (19).

4-Allyloxycinnamic acid 3c. Yield 88 %, mp 160-161°C. ^{1}H nmr: δ = 4.61 (d, 2H, H-1', *J* 5.1 Hz), 5.27 (dq, 1H, H-3'*cis*, *J* 1.2 and 10.5 Hz), 5.40 (dq, 1H, H-3'*trans*, *J* 1.2 and 17.4 Hz), 5.98-6.10 (m, 1H, H-2'), 6.37 (d, 1H, H-α, *J* 15.9 Hz), 6.98 (d, 2H, H-3,5, *J* 8.6 Hz), 7.52 (d, 1H, H-β, *J* 15.9 Hz), 7.62 (d, 2H, H-2,6, *J* 8.6 Hz), 12.25 (s br, 1H, CO_2H); ^{13}C nmr: δ = 68.3 (C-1'), 115.0 (C-3,5), 116.9 (C-α), 117.7 (C-3'), 127.0 (C-1), 129.9 (C-2,6), 133.4 (C-2'), 143.5 (C-β), 159.8 (C-4), 168.2 (C=O); ms: (EI) m/z (rel. int.) 204 ($M^{+\bullet}$, 100), 163 (32), 159 (23), 147 (17), 145 (22), 131 (17), 118 (16), 107 (19), 91 (27), 89 (25).

3,4-Diallyloxycinnamic acid 3d. Yield 43 %, mp 104-105°C. ^{1}H nmr: δ = 4.59-4.64 (m, 4H, H-1', H-1''), 5.24-5.28 (m, 2H, H-3'), 5.37-5.46 (m, 2H, H-3''), 5.98-6.10 (m, 2H, H-2', H-2''), 6.43 (d, 1H, H-α, *J* 15.9 Hz), 6.98 (d, 1H, H-5, *J* 8.4 Hz), 7.19 (dd, 1H, H-6, *J* 1.9 and 8.4 Hz), 7.34 (d, 1H, H-2, *J* 1.9 Hz), 7.50 (d, 1H, H-β, *J* 15.9 Hz); ^{13}C nmr: δ = 68.8 (C-1'), 68.9 (C-1''), 112.3 (C-2), 113.3 (C-5), 116.9 (C-α), 117.5 (C-3'), 117.6 (C-3''), 122.8 (C-6), 127.2 (C-1), 133.6 (C-2'), 133.8 (C-2''), 144.1 (C-β), 148.0 (C-3), 149.9 (C-4), 167.9 (C=O); ms: (EI) m/z (rel. int.) 260 ($M^{+\bullet}$, 100), 219 (28), 189 (19), 147 (11), 105 (15), 91 (71), 83 (36), 77 (17), 65 (14), 55 (11).

3-Ally-4-methoxycinnamic acid 10. Yield 86 %, mp 140-143 °C. ^{1}H nmr: δ = 3.31 (d, 2H, H-1', *J* 6.6 Hz), 3.82 (s, 3H, OCH_3), 4.50-5.07 (m, 2H, H-3'), 5.89-6.00 (m, 1H, H-2'), 6.35 (d, 1H, H-α, *J* 15.9 Hz), 7.00 (d, 1H, H-5, *J* 8.4 Hz), 7.47 (d, 1H, H-2, *J* 2.1 Hz), 7.51 (d, 1H, H-β, *J* 15.9 Hz), 7.53 (dd, 1H, H-6, *J* 2.1 and 8.4 Hz); ^{13}C nmr: δ = 33.7 (C-1'), 55.6 (OCH_3), 111.0 (C-5), 115.8 (C-3'), 116.4 (C-α), 126.5 (C-1), 128.4 (C-3), 128.6 (C-6), 129.2 (C-2), 136.5 (C-2'), 143.9 (C-β), 158.7 (C-4), 167.8 (C=O); ms: (EI) m/z (rel. int.) 218 ($M^{+\bullet}$, 100), 204 (13), 191 (21), 177 (9), 161 (18), 128 (23), 115 (26), 103 (15), 91 (17)

Synthesis of 2'-cinnamoyloxyacetophenones 5a-d and 11

Phosphorous oxychloride (2.90 ml, 32 mmol) was added to a solution of 2'-hydroxy-4',6'-dimethoxyacetophenone **4** (2.5 g, 12..8 mmol) and allyloxycinnamic acids **3a-d** or allylcinnamic acid **10** (15.3 mmol) in dry pyridine (10 ml). The solution was stirred at room temperature for 24 hours for the allyloxycinnamic acids **3a-d** and at 70°C for 18 hours for the allylcinnamic acid **10**; then poured into ice, water and hydrochloric acid (pH adjusted to 5). The obtained solid was removed by filtration, dissolved in chloroform (150 ml) and purified by silica gel column chromatography, using chloroform as eluent. The solvent was evaporated to dryness and the residue recrystallized from ethanol, giving in each case, the expected compound.

2'-(2-Allyloxycinnamoyloxy)-4',6'-dimethoxyacetophenone 5a. Yield 68 %; yellow oil. ^{1}H nmr: δ = 2.49 (s, 3H, CH_3), 3.79 (s, 3H, 6'-OCH_3), 3.82 (s, 3H, 4'-OCH_3), 4.61 (dt, 2H, H-1''', *J* 1.4 and 5.1 Hz), 5.29 (dq, 1H, H-3'''*cis*, *J* 1.5 and 10.5 Hz), 5.42 (dq, 1H, H-3'''*trans*, *J* 1.5 and 15.8 Hz), 6.00-6.13 (m, 1H, H-2'''), 6.32 (d, 1H, H-3', *J* 2.2 Hz), 6.37 (d, 1H, H-5', *J* 2.2 Hz), 6.69 (d, 1H, H-α, *J* 16.1 Hz), 6.90 (d, 1H, H-3'', *J* 8.3 Hz), 6.96 (d, 1H, H-5'', *J* 7.6 Hz), 7.33 (dt, 1H, H-4'', *J* 1.6 and 7.9 Hz), 7.55 (dd, 1H, H-6'', *J* 1.6 and 7.6 Hz), 8.18 (d, 1H, H-β, *J* 16.1 Hz); ^{13}C nmr: δ = 31.7 (CH_3,), 55.4 (4'-OCH_3), 55.7 (6'-OCH_3), 69.0 (C-1'''), 96.2 (C-5'), 99.9 (C-3'), 112.3 (C-3''), 116.9 (C-α), 117.2 (C-1'), 117.7 (C-3'''), 120.7 (C-5''), 123.0 (C-1''), 129.1 (C-6''), 131.8 (C-4''), 132.6 (C-2'''), 142.4 (C-β), 149.5 (C-2'), 157.3 (C-6'), 158.8 (C-2''), 161.9 (C-4'), 165.4 (C=O), 199.4 (C-1); ms: (EI) m/z (rel. int.) 382 ($M^{+\bullet}$, 15), 354 (28), 299 (24), 244 (44), 236 (41), 196 (48), 187 (100), 159 (24), 147 (45), 118 (38), 90 (16), 83 (39), 63 (7).

2'-(3-Allyloxycinnamoyloxy)-4',6'-dimethoxyacetophenone 5b. Yield 63 %, mp 70-72°C. ^{1}H nmr: δ = 2.49 (s, 3H, CH_3), 3.82 (s, 3H, 6'-OCH_3), 3.85 (s, 3H, 4'-OCH_3), 4.57 (dt, 2H, H-1''', *J* 1.4 and 5.3 Hz), 5.32 (dq, 1H, H-3'''*cis*, *J* 1.4 and 10.6 Hz), 5.43 (dq, 1H, H-3'''*trans*, dq, *J* 1.4 and 17.2 Hz), 6.00-6.13 (m, 1H, H-2'''), 6.31 (d, 1H, H-3', *J* 2.2 Hz), 6.39 (d, 1H, H-5', *J* 2.2 Hz), 6.56 (d, 1H, H-α, *J* 16.0 Hz), 6.96-7.00 (m, 1H, H-4''), 7.10 (t, 1H, H-2'', *J* 1.4 and 3.6 Hz), 7.16 (d, 1H, H-6'', *J* 7.8 Hz), 7.31 (t, 1H, H-5'', *J* 7.8 Hz), 7.79 (d, 1H, H-β, *J* 16.0 Hz); ^{13}C nmr: δ = 31.9 (*C*H$_3$), 55.6 (4'-O*C*H$_3$), 55.9 (6'-O*C*H$_3$), 68.8 (C-1'''), 96.5 (C-5'), 99.9 (C-3'), 113.9 (C-2''), 117.0 (C-α), 117.3 (C-1'), 117.5 (C-4''), 117.9 (C-3'''), 121.3 (C-6''), 129.9 (C-5''), 132.9 (C-2'''), 135.4 (C-1''), 147.0 (C-β), 149.5 (C-2')158.8 (C-6'), 159.1 (C-3''), 162.2 (C-4'), 165.1 (C=O), 199.5 (C-1); ms: (EI) m/z (rel. int.) 382 ($M^{+\bullet}$, 17), 339 (36), 299 (15), 244 (14), 207 (9), 187 (100), 147 (16), 131 (11), 118 (20), 91 (13).

2'-(4-Allyloxycinnamoyloxy)-4',6'-dimethoxyacetophenone 5c. Yield 76%; yellow oil. ^{1}H nmr: δ = 2.49 (s, 3H, CH_3), 3.79 (s, 3H, 6'-OCH_3), 3.83 (s, 3H, 4'-OCH_3), 4.56 (d, 2H, H-1''', *J* 5.1 Hz), 5.30 (dq, 1H, H-3'''*cis*, *J* 1.2 and 10.5 Hz), 5.43 (dq, 1H, H-3'''*trans*, *J* 1.2 and 17.3 Hz), 5.98-6.09 (m, 1H, H-2'''), 6.30 (d, 1H, H-3', *J* 2.1 Hz), 6.37 (d, 1H, H-5', *J* 2.1 Hz), 6.44 (d, 1H, H-α, *J* 15.9 Hz), 6.92 (d, 2H, H-3'',5'', *J* 8.7 Hz), 7.49 (d, 2H, H-2'',6'', *J* 8.7 Hz), 7.78 (d, 1H, H-β, *J* 15.9 Hz); ^{13}C nmr: δ = 31.8 (*C*H$_3$), 55.6 (4'-O*C*H$_3$), 55.8 (6'-O*C*H$_3$), 68.8 (C-1'''), 96.4 (C-5'), 99.9 (C-3'), 114.1 (C-α), 115.0 (C-3'',5''), 117.2 (C-1'), 118.0 (C-3'''), 126.9 (C-1''), 130.1 (C-2'',6''), 132.6 (C-2'''), 146.8 (C-β), 149.6 (C-2'), 159.0 (C-6'), 160.7 (C-4''), 162.1 (C-4'), 165.4 (C=O), 199.6 (C-1); ms: (EI) m/z (rel. int.) 382 ($M^{+\bullet}$, 9), 367 (5), 339 (4), 299 (3), 248 (4), 196 (2), 193 (2), 187 (100), 147 (8), 146 (10), 131 (9), 118 (8), 91 (8).

2'-(3,4-Diallyloxycinnamoyloxy)-4',6'-dimethoxyacetophenone 5d Yield 93%; orange oil. ^{1}H nmr: δ = 2.48 (s, 3H, CH_3), 3.79 (s, 3H, 6'-OCH_3), 3.80 (s, 3H, 4'-OCH_3), 4.63-4.66 (m, 4H, H-1''', H-1''''), 5.30-5.33 (m, 2H, H-3'''), 5.40-5.48 (m, 2H, H-3''''), 6.02-6.14 (m, 2H, H-2''', H-2''''), 6.30 (d, 1H, H-3', *J* 2.5 Hz), 6.38 (d, 1H, H-5', *J* 2.5 Hz), 6.41 (d, 1H, H-α, *J* 16.0 Hz), 6.89 (d, 1H, H-5'', *J* 8.8 Hz), 7.08-7.14 (m, 2H, H-2'', H-6''), 7.75 (d, 1H, H-β, *J* 16.0 Hz); ^{13}C nmr: δ = 31.8 (*C*H$_3$), 55.6 (4'-O*C*H$_3$), 55.8 (6'-O*C*H$_3$), 69.6 (C-1'''), 69.8 (C-1''''), 96.4 (C-5'), 100.0 (C-3'), 112.6 (C-6''), 113.2 (C-5''), 114.3 (C-α), 117.3 (C-1'), 117.9 (C-3'''), 118.0 (C-3''''), 123.3 (C-1''), 127.1 (C-2''), 132.7 (C-2'''), 132.9 (C-2''''), 147.0 (C-β), 148.4 (C-2'), 149.6 (C-3''), 150.9 (C-4''), 159.0 (C-6'), 162.1 (C-4'), 165.4 (C=O), 199.7 (C-1); ms: (EI) m/z (rel. int.) 438 ($M^{+\bullet}$, 15), 395 (14), 355 (22), 314 (14), 260 (24), 243 (100), 181 (25), 173 (11), 133 (18), 105 (11), 91 (7), 77 (131), 69 (7).

2'-(3-Allyl-4-metoxycinnamoyloxy)-4',6'-dimethoxyacetophenone 11. Yield 56%; orange oil. ^{1}H nmr: δ = 2.49 (s, 3H, CH_3), 3.38 (d, 2H, H-1''', *J* 6.6 Hz), 3.79 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.00-5.10 (m, 2H, H-3'''), 5.91-6.02 (m, 1H, H-2'''), 6.30 (d, 1H, H-3', *J* 2.1 Hz), 6.37 (d, 1H, H-5', *J* 2.1 Hz), 6.45 (d, 1H, H-α, *J* 15.9 Hz), 6.85 (d, 1H, H-5'', *J* 8.7 Hz), 7.38 (s, 1H, H-2''), 7.41 (d, 1H, H-6'', *J* 8.7 Hz), 7.77 (d, 1H, H-β, *J* 15.9 Hz); ^{13}C nmr: δ = 31.7 (*C*H3), 33.8 (C-1'''), 55.3 (O*C*H$_3$), 55.4 (O*C*H$_3$), 55.7 (O*C*H$_3$), 96.2 (C-5'), 99.9 (C-3'), 110.2 (C-5''), 113.7 (C-α), 115.9 (C-3'''), 117.2 (C-1'), 126.3 (C1''), 128.6 (C-6''), 129.0 (C-3''), 129.4 (C-2''), 136.0 (C-2'''), 146.9 (C-β), 149.5 (C-2'), 158.8 (C-6'), 159.4 (C-4''), 162.0 (C-4'), 165.3 (C=O), 199.4 (C-1); ms: (EI) m/z (rel. int.) 396 ($M^{+\bullet}$, 71), 387 (6), 375 (14), 353 (28), 277 (15), 241 (29), 218 (16), 201 (100), 181 (26), 173 (22), 158 (23)

Synthesis of 5-aryl-3-hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-2,4-pentadien-1-ones 6a-d and 12

Potassium hydroxide in powder (1.96g, 35 mmol) was added to a solution of 2'-cinnamoyloxyacetophenone **5a-d and 11** (7 mmol) in dimethyl sulfoxide (15 ml). The solution was stirred at room temperature, until complete disappearance of the starting material, which was monitored by tlc (~ 2 hours). After that period, the solution was poured into ice, water and hydrochloric acid (pH adjusted to 5). The obtained solid was removed by filtration, dissolved in chloroform (150 ml) and washed with water; the organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated to dryness and the residue was recrystallized from ethanol.

5-(2-Allyloxyphenyl)-3-hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-2,4-pentadien-1-one 6a. Yield 70%, mp 104-105°C. ^{1}H nmr: δ = 3.82 (s, 3H, 6'-OCH_3,), 3.89 (s, 3H, 4'-OCH_3)), 4.63 (dt, 2H, H-1''', *J* 1.5 and 5.1 Hz), 5.33 (dq, 1H, H-3'''*cis*, *J* 1.5 and 10.6 Hz), 5.46 (dq, 1H, H-3'''*trans*, *J* 1.5 and 17.3 Hz), 5.96 (d, 1H, H-5', *J* 2.4 Hz), 6.05-6.16 (m, 1H, H-2'''), 6.10 (d, 1H, H-3', *J* 2.4 Hz), 6.67 (dd, 1H, H-α, *J*

1.1 and 15.8 Hz), 6.75 (s, 1H, H-2), 6.91 (d, 1H, H-3'', *J* 8.5 Hz), 6.97 (t, 1H, H-5'', *J* 7.4 Hz), 7.30 (ddd, 1H, H-4'', *J* 1.5 and 7.4 and 8.5 Hz), 7.57 (dd, 1H, H-6'', *J* 1.5 and 7.4 Hz), 7.95 (d, 1H, H-β, *J* 15.8 Hz), 13.67 (s, 1H, 2'-O*H*), 14.77 (d, 1H, 3-O*H*), *J* 1.0 Hz); ^{13}C nmr: δ = 55.5 (4'-OCH_3), 55.7 (6'-OCH_3), 69.1 (C-1'''), 91.3 (C-3'), 94.0 (C-5'), 102.7 (C-2), 104.6 (C-1'), 112.5 (C-3''), 117.6 (C-3'''), 120.9 (C-5''), 123.7 (C-α), 124.6 (C-1''), 128.2 (C-6''), 130.8 (C-4''), 133.0 (C-2'''), 133.7 (C-β), 157.1 (C-2''), 161.8 (C-6'), 165.4 (C-4'), 167.1 (C-2'), 174.1 (C-3), 193.7 (C-1); ms: (EI) m/z (rel. int.) 382 ($M^{+\bullet}$, 28), 341 (23), 299 (16), 235 (23), 207 (20), 181 (100), 167 (17), 147 (28), 118 (20), 91 (16), 77 (7), 69 (11).). *Anal.* Calcd. for $C_{22}H_{22}O_6$: C, 69.11; H, 5.76. Found: C, 69.26; H, 6.19

5-(3-Allyloxyphenyl)-3-hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-2,4-pentadien-1-one 6b. Yield 73%, mp 114-115°C. ^{1}H nmr: δ = 3.82 (s, 3H, 6'-OCH_3), 3.89 (s, 3H, 4'-OCH_3), 4.58 (dd, 2H, H-1'''', *J* 1.3 and 4.5 Hz), 5.32 (dq, 1H, H-3''''*cis*, *J* 1.5 and 10.5 Hz), 5.44 (dq, 1H, H-3''''*trans*, *J* 1.5 and 17.3 Hz), 5.97 (d, 1H, H-5', *J* 2.4 Hz), 6.01-6.13 (m, 1H, H-2''''), 6.10 (d, 1H, H-3', *J* 2.4 Hz), 6.55 (d, 1H, H-α, *J* 15.8 Hz), 6.76 (s, 1H, H-2), 6.92 (dd, 1H, H-6'', *J* 2.1 and 7.9 Hz), 7.10 (s, 1H, H-2''), 7.16 (d, 1H, H-4'', *J* 7.9 Hz), 7.30 (t, 1H, H-5'', *J* 7.9 Hz), 7.54 (d, 1H, H-β, *J* 15.8 Hz), 13.61 (s, 1H, 2'-O*H*), 14.71 (d, 1H, 3-O*H*, *J* 1.0 Hz); ^{13}C nmr: δ = 55.5 (4'-OCH_3), 55.8 (6'-OCH_3), 68.9 (C-1''''), 91.4 (C-3'), 94.0 (C-5'), 103.1 (C-2), 104.7 (C-1'), 113,8 (C-2''), 116.0 (C-6''), 117.9 (C-3'''), 120.7 (C-4''), 123.6 (C-α), 129.8 (C-5''), 133.0 (C-1''), 136.7 (C-2'''), 138.2 (C-β), 158.9 (C-3''), 161.9 (C-6'), 165.6 (C-4'),167.2 (C-2'), 173.0 (C-3), 194.0 (C-1); ms: (EI) m/z (rel. int.) 382 ($M^{+\bullet}$, 36), 263 (9), 313 (8), 235 (6), 200 (14), 193 (11), 181 (100), 167 (16), 154 (45), 147 (16), 118 (14), 103 (6), 91 (13), 77 (8), 69 (12). *Anal.* Calcd. for $C_{22}H_{22}O_6$: C, 69.11; H, 5.76. Found: C, 69.27; H, 5.87.

5-(4-Allyloxyphenyl)-3-hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-2,4-pentadien-1-one 6c. Yield 85%, mp 143-144°C. ^{1}H nmr: δ = 3.82 (s, 3H, 6'-OCH_3), 3.89 (s, 3H, 4'-OCH_3), 4.58 (dt, 2H, H-1'''', *J* 1.3 and 5.4 Hz), 5.32 (dq, 1H, H-3''''*cis*, *J* 1.3 and 10.5 Hz), 5.43 (dq, 1H, H-3''''*trans*, *J* 1.3 and 17.1 Hz), 5.96 (d, 1H, H-5', *J* 2.4 Hz), 6.02-6.11 (m, 1H, H-2''''), 6.10 (d, 1H, H-3', *J* 2.4 Hz), 6.45 (dd, 1H, H-4, *J* 0.9 and 15.8 Hz), 6.72 (s, 1H, H-2), 6.93 (d, 2H, H-3'',5'', *J* 8.9 Hz), 7.50 (d, 2H, H-2'',6'', *J* 8.9 Hz), 7.54 (d, 1H, H-5, *J* 15.8 Hz), 13.65 (s, 1H, 2'-O*H*), 14.84 (d, 1H, 3-O*H*, *J* 0.9 Hz); ^{13}C nmr: δ = 55.5 (4'-OCH_3), 55.7 (6'-OCH_3), 68.8 (C-1''''), 91.3 (C-3'), 94.0 (C-5'), 102.5 (C-2), 104.6 (C-1'), 115.0 (C-3'',5''), 118.0 (C-3'''), 120.9 (C-4), 128.3 (C-1''), 129.4 (C-2'',6''), 132.8 (C-2'''), 138.2 (C-5), 159.9 (C-4''), 161.8 (C-6'), 165.4 (C-4'), 167.1 (C-2'), 173.9 (C-3), 193.6 (C-1); ms: (EI) m/z (rel. int.) 382 ($M^{+\bullet}$, 35), 365 (7), 351 (9), 313 (10), 271 (12), 230 (17), 228 (19), 201 (23), 200 (22), 194 (19), 193 (30), 187 (81), 181 (100), 167 (20), 159 (35), 147 (36), 131 (17), 119 (12), 91 (15). *Anal.* Calcd. for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80. Found: C, 69.10; H, 5.86.

5-(3,4-Diallyloxyphenyl)-3-hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-2,4-pentadien-1-one 6d. Yield 82%, mp 110-113°C; ^{1}H nmr: δ = 3.83 (s, 3H, 6'-OCH_3), 3.90 (s, 3H, 4'-OCH_3,), 4.64-4.67 (m, 4H, H-1''''', H-1''''''), 5.29-5.34 (m, 2H, H-3'''''), 5.40-5.48 (m, 2H, H-3''''''), 5.97 (d, 1H, H-3', *J* 2.4 Hz), 6.05-6.16 (m, 2H, H-2''''', H-2''''''), 6.10 (d, 1H, H-5', *J* 2.4 Hz), 6.41 (d, 1H, H-α, *J* 15.7 Hz), 6.73 (s, 1H, H-2), 6.89 (d, 1H, H-5'', *J* 9.5 Hz), 7.12 (dd, 1H, H-6'', *J* 1.8 and 9.5 Hz), 7.13 (d, 1H, H-2'', *J* 1.8 Hz), 7.50 (d, 1H, H-β, *J* 15.7 Hz), 13.63 (s, 1H, 2'-O*H*), 14.83 (d, 1H, 3-O*H*, *J* 1.2 Hz); ^{13}C nmr: δ = 55.5 (4'-OCH_3), 55.8 (6'-OCH_3), 69.7 (C-1'''), 70.0 (C-1''''), 91.3 (C-5'), 94.0 (C-3'), 102.5 (C-2), 104.6 (C-1'), 112.8 (C-2''), 113.5 (C-5''), 117.9 (C-3'''), 118.0 (C-3''''), 121.1 (C-α), 122.3 (C-6''), 128.6 (C-1''), 132.9 (C-2'''), 133.2 (C-2''''), 138.4 (C-β), 148.5 (C-3''), 150.2 (C-4''), 161.8 (C-6'), 165.4 (C-4'), 167.1 (C-2'), 173.7 (C-3), 193.6 (C=O); ms: (EI) m/z (rel. int.) 438 ($M^{+\bullet}$, 20), 397 (5), 327 (14), 257 (7), 243 (23), 203 (19), 181 (100), 167 (9), 105 (6), 81 (8), 69 (9). *Anal.* Calcd. for $C_{25}H_{26}O_7$: C, 68.48; H, 5.94. Found: C, 68.37; H, 5.99.

5-(3-Allyl-4-metoxyphenyl)-3-hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-2,4-pentadien-1-one 12. Yield 42%, mp 120-121°C. ^{1}H nmr: δ = 3.39 (d, 2H, H-1''''', *J* 6.3 Hz), 3.81 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 5.08 (d, 2H, H-3''''', *J* 12.6 Hz), 5.96 (d, 1H, H-5', *J* 2.3 Hz), 5.98-6.05 (m, 1H, H-2''''), 6.08 (d, 1H, H-3', *J* 2.3 Hz), 6.43 (d, 1H, H-α, *J* 15.8 Hz), 6.72 (s, 1H, H-2), 6.85 (d, 1H, H-5'', *J* 8.3 Hz), 7.37 (s, 1H, H-2''), 7.38 (d, 1H, H-6'', *J* 8.3 Hz), 7.55 (d, 1H, H-β, *J* 15.8 Hz), 13.65 (s, 1H, 2'-O*H*), 14.85 (s, 1H, 3-O*H*); ^{13}C nmr: δ = 34.2 (C-1'''''), 55.4 (OCH_3), 55.5 (OCH_3), 55.8 (OCH_3), 91.3 (C-3'), 94.0 (C-5'), 102.4 (C-2), 104.6 (C-1'), 110.4 (C-5''), 115.8 (C-3'''''), 120.5 (C-α), 127.8 (C-3''), 128.1 (C-1''), 129.2 (C-6''), 129.2 (C-2''), 136.4 (C-2'''''), 138.5 (C-β), 159.8 (C-4''), 161.8 (C-6'), 165.3 (C-4'),

167.1 (C-2'), 174.1 (C-3), 193.5 (C-1); ms: (EI) m/z (rel. int.) 396 ($M^{+\bullet}$, 39), 365 (16), 242 (29), 215 (30), 201 (65), 181 (100), 161 (38), 128 (15), 115 (20). *Anal.* Calcd. for $C_{23}H_{24}O_6$: C, 69.70; H, 6.06. Found: C, 69.32; H, 6.34.

Synthesis of n'-allyloxy-2-styrylchromone 7c,d

p-Toluenesulfonic acid (0.50 g, 2.6 mmol) was added to a solution of the appropriate 5-aryl-3-hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-2,4-pentadien-1-ones **6c,d** (5.2 mmol) in dimethyl sulfoxide (20 ml). The reaction mixture was heated at 90° C for three hours; then was poured into ice and water. The obtained solid was removed by filtration, dissolved in chloroform (50 ml) and washed with a 20% aqueous solution of sodium thiosulfate. The solvent was evaporated to dryness and the residue recrystallized from ethanol.

4'-Allyloxy-5,7-dimethoxy-2-styrylchromone 7c. Yield 83%, mp 183-184°C. ^{1}H nmr: δ = 3.92 (s, 3H, 7-OC*H*$_3$), 3.95 (s, 3H, 5-OC*H*$_3$), 4.58 (dt, 2H, H-1'', *J* 1.5 and 5.1 Hz), 5.32 (dq, 1H, H-3''*cis*, *J* 1.2 and 10.5 Hz), 5.44 (dq, 1H, H-3''*trans*, *J* 1.2 and 17.3 Hz), 6.00-6.13 (m, 1H, H-2''), 6.14 (s, 1H, H-3), 6.35 (d, 1H, H-6, *J* 2.1 Hz), 6.54 (d, 1H, H-8, *J* 2.1 Hz), 6.56 (d, 1H, H-α, *J* 16.1 Hz), 6.94 (d, 2H, H-3',5', *J* 8.7 Hz), 7.44 (d, 1H, H-β, *J* 16.1 Hz), 7.50 (d, 2H, H-2',6', *J* 8.7 Hz); ^{13}C nmr: δ = 55.7 (7-O*C*H$_3$), 56.4 (5-O*C*H$_3$), 68.8 (C-1''), 92.7 (C-8), 95.9 (C-6), 109.3 (C-10), 111.5 (C-3), 115.1 (C-3',5'), 117.6 (C-α), 118.0 (C-3''), 128.0 (C-1'), 129.0 (C-2',6'), 132.8 (C-2''), 135.3 (C-β), 159.5 (C-4'), 159.6 and 159.8 (C-2 and C-9), 160.8 (C-5), 163.9 (C-7), 177.7 (C-4); ms: (EI) m/z (rel. int.) 364 ($M^{+\bullet}$, 100), 363 (33), 347 (5), 335 (9), 324 (25), 323 (50), 305 (11), 295 (25), 293 (23), 277 (11), 265 (13), 237 (6), 181 (10), 165 (10), 151 (14), 137 (13), 115 (25), 89 (8). *Anal.* Calcd. for $C_{22}H_{20}O_5$: C, 72.53; H, 5.50. Found: C, 72.15; H, 5.77.

3',4'-Diallyloxy-5,7-dimethoxy-2-styrylchromone 7d. Yield 73%, mp 180-182° C. ^{1}H nmr: δ = 3.91 (s, 3H, 7-OC*H*$_3$), 3.94 (s, 3H, 5-OC*H*$_3$), 4.59 (t, 4H, H-1'', H-1''', *J* 5.4 Hz), 5.30-5.34 (m, 2H, H-3''), 5.41-5.50 (m, 2H, H-3'''), 6.04-6.17 (m, 2H, H-2'', H-2'''), 6.15 (s, 1H, H-3), 6.34 (d, 1H, H-6, *J* 2.1 Hz), 6.52 (d, 1H, H-α, *J* 15.9 Hz), 6.53 (d, 1H, H-8, *J* 2.1 Hz), 6.90 (d, 1H, H-5', *J* 7.8 Hz), 7.10 (d, 2H, H-2', H-6', *J* 7.8 Hz), 7.40 (d, 1H, H-β, *J* 15.9 Hz); ^{13}C nmr: δ = 55.7 (7-O*C*H$_3$), 56.3 (5-O*C*H$_3$), 69.7 (C-1''), 70.0 (C-1'''), 92.7(C-8), 95.9 (C-6), 109.3 (C-10), 111.5 (C-3), 112.2 (C-2'), 113.5 (C-5'), 117.0 (C-α), 117.9 (C-3''), 118.0 (C-3'''), 121.8 (C-6'), 128.4 (C-1'), 132.8 (C-2''), 133.1 (C-2'''), 135.5 (C-β), 148.6 (C-3') 150.0 (C-4'), 159.4 (C-2), 159.6 (C-5), 160.8 (C-9), 163.9 (C-7), 177.7 (C-4); ms: (EI) m/z (rel. int.) 420 ($M^{+\bullet}$, 100), 403 (8), 379 (38), 361 (13), 351 (32), 338 (18), 321 (11), 310 (31), 293 (22), 281 (11), 267 (8), 226 (6), 181 (45), 151 (12), 137 (7), 91 (22). *Anal.* Calcd. for $C_{25}H_{24}O_6$: C, 71.43; H, 5.71. Found: C, 71.60; H, 5.54.

Synthesis of n'-allyloxy-2-styrylchromone 7a,b

A catalitical amount of iodine (0.20 g, 0.78 mmoles) was added to a solution of the appropriate 5-aryl-3-hydroxy-1-(2-hydroxy-4,6-dimethoxyphenyl)-2,4-pentadien-1-ones **6a,b** (3.9 mmoles) in dimethyl sulfoxide (20 ml). The solution was heated at 80-90° for four hours, and poured into ice and water. The solid obtained was removed by filtration, dissolved in chloroform (100 ml) and washed with water. the organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated in each case to dryness and the residue was crystallized from ethanol to give the expected products **7a,b.**

2'-Allyloxy-5,7-dimethoxy-2-styrylchromone 7a. Yield 70%, mp 180-181°C. ^{1}H nmr: δ = 3.89 (s, 3H, 7-OC*H*$_3$), 3.92 (s, 3H, 5-OC*H*$_3$), 4.62 (d, 2H, H-1'', *J* 5.3 Hz), 5.32 (dq, 1H, H-3''cis, *J* 1.3 and 10.6 Hz), 5.46 (dq, 1H, H-3''trans, *J* 1.3 and 17.3 Hz), 6.05-6.15 (m, 1H, H-2''), 6.35 (d, 1H, H-6, *J* 2.3 Hz), 6.54 (d, 1H, H-8, *J* 2.3 Hz), 6.57 (d, 1H, H-α, *J* 16.0 Hz), 6.91 (d, 1H, H-3', *J* 2.1 Hz), 6.96 (t,. 1H, H-5', *J* 7.4 Hz), 7.29 (ddd, H-4', *J* 1.5 and 7.4 and 8.3 Hz), 7.60 (dd, 1H, H-6', *J* 1.5 and 7.4 Hz), 7.83 (d, 1H, H-β, *J* 16.0 Hz); ^{13}C nmr: δ = 55.5 (7-O*C*H$_3$), 55.7 (5-O*C*H$_3$), 69.1(C-1''), 91.3 (C-8), 93.7 (C-6), 109.2 (C-10), 111.3 (C-3), 112.5 (C-3'), 114.3 (C-5'), 118.0 (C-α), 118.6 (C-3''), 127.8 (C-1'), 129.2 (C-5'), 131.0 (C-6'), 132.3 (C-2''), 133.8 (C-4'), 135.0 (C-β), 159.4 (C-2), 159.6 (C-2'), 160.0 (C-5), 160.4 (C-9), 163.8 (C-7), 177.7 (C-4); ms: (EI) m/z (rel. int.) 364 ($M^{+\bullet}$, 100), 347 (7), 333 (10), 324 (54), 295 (23), 277 (12), 263 (14), 237 (6), 181 (24), 115 (20). *Anal.* Calcd. for $C_{22}H_{20}O_5$: C, 72.53; H, 5.50. Found: C, 72.23; H, 5.55.

3'-Allyloxy-5,7-dimethoxy-2-styrylchromone 7b. Yield 72%, mp 179-180°; ^{1}H nmr: δ = 3.92 (s, 3H, 7-OC*H*$_3$), 3.93 (s, 3H, 5-OC*H*$_3$), 4.59 (dd, 2H, H-1'', *J* 1.3 and 4.0 Hz), 5.33 (dq, 1H, H-3'' *cis*, *J* 1.3 and 10.6 Hz), 5.46 (dq, 1H, H-3'' *trans*, *J* 1.3 and 17.3 Hz), 6.03-6.16 (m, 1H, H-2''), 6.19 (s, 1H, H-3), 6.36 (d, 1H, H-6, *J* 2.1 Hz), 6.55 (d, 1H, H-8, *J* 2.1 Hz), 6.67 (d, 1H, H-α, *J* 16.0 Hz), 6.94 (dd, 1H, H-5', *J* 2.3 and 8.0 Hz), 7.10 (s, 1H, H-2'), 7.15 (d, 1H, H-6', *J* 8.0 Hz), 7.31 (d, 1H, H-4', *J* 8.0 Hz), 7.46 (d, 1H, H-β, *J* 16.0 Hz); ^{13}C nmr: δ = 55.7 (7-O*C*H$_3$), 56.3 (5-O*C*H$_3$), 68.8 (C-1''), 92.7 (C-8), 96.0 (C-6), 109.3 (C-10), 112.2 (C-3), 113.4 (C-2'), 116.0 (C-5'), 117.8 (C-3''), 120.1 (C-α), 120.3 (C-6'), 129.9 (C-4'), 133.0 (C-2''), 135.6 (C-β), 136.5 (C-2), 159.0 (C-3'), 159.6 (C-5), 160.8 (C-9), 164.0 (C-7), 171.7 (C-4); ms: (EI) m/z (rel. int.) 364 ($M^{+\bullet}$, 100), 347 (5), 335 (14), 322 (47), 295 (23), 277 (16), 263 (10), 237 (8), 181 (18), 115 (29), 89 (6). *Anal.* Calcd. for $C_{22}H_{20}O_5$: C, 72.53; H, 5.50. Found: C, 72.40; H, 5.35.

Synthesis of n'-ally-2-styrylchromone 8 a-d

A solution of the appropriate n'-allyloxy-2-styrylchromone **7a-d** (2.8 mmol) in 1,2,4-trichlorobenzene (10 ml) was heated at 250°C, under nitrogen, for 3 hours. The reaction was left to reach room temperature, then acetone (20 ml), K_2CO_3 (1.16 g, 8.4 mmol) and dimethyl sulfate (2.8 mmol) were added. The solution was refluxed at 70° C for 5 hours; the inorganic salts were filtered off, and the acetone evaporated to dryness. The residue was dissolved in chloroform (80 ml) and washed with water. The organic layer was dried over Na_2SO_4 and evaporated to dryness; the obtained crude material was purified over thin layer chromatography (eluent 3:7 mixture of chloroform-light petroleum), giving the expected n'-allyl-2-styrylchromones **8c** and **d.** The transposition of the allyl group from 2'-allyloxy-5,7-dimethoxy-2-styrylchromone **7a** and 3'-allyloxy-5,7-dimethoxy-2-styrylchromone **7b** was monitored by tlc, but the purification of the corresponding allyl-2-styrylchromes was not possible. Probably occurs the degradation of these allyl-2-styrylchromes resulting in low amounts of product.

3'-Allyl-4'-methoxy-5,7-dimethoxy-2-styrylchromone 8c. Yield 54%, mp 130-132°C. ^{1}H nmr δ = 3.41 (d, 2H, H-1'', J 6.5 Hz), 3.88 (s, 3H, 4'-OCH$_3$), 3.92 (s, 3H, 7-OCH$_3$), 3.94 (s, 3H, 5-OCH$_3$), 5.08-5.12 (m, 2H, H-3''), 5.97-6.08 (m, 1H, H-2''), 6.15 (s, 1H, H-3), 6.35 (d, 1H, H-6, J 2.2 Hz), 6.54 (d, 1H, H-8, J 2.2 Hz), 6.56 (d, 1H, H-α, J 15.9 Hz), 6.88 (d, 1H, H-5', J 8.2 Hz), 7.37 (s br, 1H, H-2'), 7.41 (d br, 1H, H-6', J 8.2 Hz), 7.45 (d, 1H, H-β, J 15.9 Hz); ^{13}C nmr: δ = 34.1 (C-1''), 55.5 (7-O*C*H$_3$), 55.7 (5-O*C*H$_3$), 56.4 (4'-O*C*H$_3$), 92.7 (C-8), 95.9 (C-6), 109.4 (C-10), 110.5 (C-5'), 111.4 (C-3), 115.9 (C-3''), 117.3 (C-α), 127.3 (C-6'), 127.7 (C-1'), 128.9 (C-2'), 129.2 (C-3'), 135.6 (C-β), 136.3 (C-2''), 158.6 (C-4'), 159.6 (C-2 and C-9), 160.9 (C-5), 163.9 (C-7), 177.7 (C-4); ms: (EI) m/z (rel. int.) 378 ($M^{+\bullet}$, 100), 361 (22), 347 (28), 307 (45), 291 (22), 264 (25), 248 (17), 225 (29), 201 (26), 175 (30), 115 (19), 91 (11), 77 (10), 69 (14). Anal. Calcd. for $C_{23}H_{22}O_5$.1/2 H_2O: C, 71.32; H ,5.94. Found: C, 71.58; H, 5.98

2',5'-Diallyl-3',4'-dimethoxy-5,7-dimethoxy-2-styrylchromone 8d. Yield 48%; orange oil. ^{1}H nmr δ = 3.62 (d, 2H, H-1'', *J* 6.4 Hz), 3.64 (d, 2H, H-1''', *J* 6.4 Hz), 3.77 (s, 3H, 7-OC*H*$_3$), 3.87 (s, 3H, 5-OC*H*$_3$), 3.89 (s, 3H, 4'-OCH$_3$ or3'-OC*H*$_3$), 3.90 (s, 3H, 4'-OCH$_3$ or3'-OC*H*$_3$), 5.09 (dq, 1H, H-3''*cis*, *J* 1.2 and 10.4 Hz), 5.13 (dq, 1H, H-3''*trans*, *J* 1.2 and 15.9 Hz), 5.64-5.88 (m, 2H, H-3'''), 5.99-6.12 (m, 2H, H-2'', H-2'''), 6.14 (s, 1H, H-3), 6.32 (d, 1H, H-6, *J* 2.2 Hz), 6.47 (d, 1H, H-8, *J* 2.2 Hz), 6.52 (d, 1H, H-α, *J* 15.9 Hz), 6.86 (s, 1H, H-6'), 7.38 (d, 1H, H-β, *J* 15.9 Hz),); ^{13}C nmr: δ = 34.7 (C-1''), 35.2 (C-1'''), 55.4 (7-O*C*H$_3$), 55.6 (5-O*C*H$_3$), 56.8 and 57.0 (3'-O*C*H$_3$ and 4'-O*C*H$_3$), 92.6 (C-8), 95.9 (C-6), 109.2 (C-10), 111.9 (C-3), 115.7 (C-3''), 117.4 (C-α), 127.8 (C-6'), 128.7 (C-1'), 129.2 or 129.8 (C-2' or C-5'), 135.4 (C-2''), 136.8 (C-β), 158.4 (C-2), 159.4 or 159.6 (C-3' or C-4'), 160.0 (C-5), 160.9 (C-9), 163.7 (C-7), 177.9 (C-4). ms: (EI) m/z (rel. int.) 448 ($M^{+\bullet}$, 100), 407 (35), 366 (202), 335 (28), 273 (15), 242 (8), 225 (12), 77 (29), 69 (32). *Anal.* Calcd. for $C_{27}H_{28}O_6$: C, 72.32; H ,6.25. Found: C, 71.93; H, 6.66.

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