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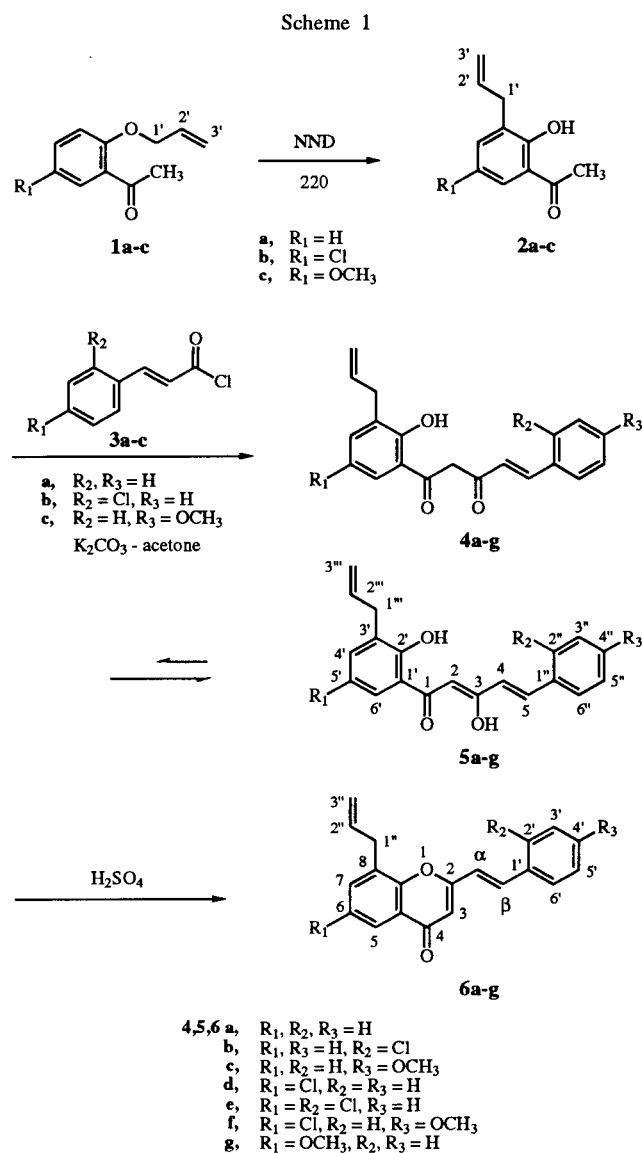
Substituted-2-hydroxy-3-allylacetophenones **2** react with cinnamoyl chlorides **3** in potassium carbonate-acetone to give good yields of polyfunctional 1-(2-hydroxy-3-allylaryl)-5-aryl-4-pentene-1,3-diones **4** which exist in their enol forms **5**. These on acid catalysed cyclodehydration gave 70-80% yields of substituted 8-allyl-2-styrylchromones **6**.

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Some substituted 2-styrylchromones have been reported to have antineoplastic action. 6-Methoxy-8-allyl-2-styrylchromone **6g** inhibits the growth of implanted colon C38 tumours in mice [1]. Zammattio *et al.* [2] reported the synthesis of two 8-allyl-2-styrylchromones **6a** and **6g** via the 1-[1-(2-hydroxybenzoyl)alkylidene]triphenylphosphoranes in 50 and 70% yields respectively. Earlier, 2-styrylchromones have been obtained by the condensation of aromatic aldehydes with 2-methylchromones in sodium ethoxide medium in generally very low yields [1,3] and by the conventional Baker-Venkataraman transformation which has several steps such as the reaction of 2-hydroxyacetophenones with cinnamoyl chlorides or acids to give 2-cinnamoyloxyacetophenones, their conversion by potassium hydroxide-pyridine to 1,5-diaryl-4-pentene-1,3-diones which were then cyclized in an acid medium to 2-styrylchromones [4-8].

In this paper we report a facile two-step modified Baker-Venkataraman synthesis of 8-allyl-2-styrylchromones **6a-g** via the polyfunctional 1-(2-hydroxy-3-allylaryl)-5-aryl-4-pentene-1,3-diones **4a-g** in 70-80% yields (Scheme 1). In this method **4a-g** are readily obtained in high yields on refluxing 2-hydroxy-3-allylacetophenones **2a-c** with cinnamoyl chlorides **3a-c** in potassium carbonate-acetone medium. In the conventional Baker-Venkataraman synthesis [4-8] diones of the type **4** are obtained in two steps, using potassium hydroxide-pyridine. Spectral data, ir, uv, ^1H and ^{13}C nmr of **4a-g** indicated that they exist exclusively in the tautomeric enol form **5a-g**. In their ir spectra **5a-g** showed the strongly chelated carbonyl peak at δ 1635 cm^{-1} . Compounds **5a-g** are bright yellow coloured and in their uv spectra showed the intense band in the region 384-400 nm indicating an extended conjugation. In their ^1H nmr, the phenolic hydroxyl group appeared at δ 12.20-12.60 while the enolic hydroxyl group appeared in the region δ 14.38-14.65. The three olefinic protons of the diene segment in **5a-g** appeared at $\sim\delta$ 6.20 as a singlet (H-2), $\sim\delta$ 6.50 as a doublet, $J = 16.0$ Hz (H-4) and $\sim\delta$ 8.00 as a doublet, $J = 16.0$ Hz (H-5). In the ^{13}C nmr of **5a** the five carbons of the pentadiene segment appeared at δ 196.1 (C=O), 115.8 (C-2), 174.0 (C-3), 97.1 (C-4) and 139.6 (C-5).

The enol form of 1-(2-hydroxy-3-allylaryl)-5-aryl-4-pentene-1,3-diones **5a-g** on heating in ethanolic sulfuric acid underwent cyclodehydration to give the corresponding 8-allyl-2-styrylchromones **6a-g** in 70-80% yields.



Their structures are confirmed by the analytical and spectral data. In the ir spectra, the chromone carbonyl appeared at 1625-1635 cm^{-1} . The intense long wavelength band in the uv spectra appeared at 325-359 nm. In ^1H nmr of **6a-g** the styryl α and β protons appeared as doublets at δ 6.40-6.78 ($J = 16.0$ Hz) and δ 7.50-8.00 ($J = 16.0$ Hz) respectively.

Thus, adopting the procedure outlined here, the highly functionalized **5a-g** and **6a-g** can be readily synthesized starting from the easily available 2-hydroxy-3-allylacetophenones under mild reaction conditions in good yields. This method appears to be superior to the earlier reported procedure [2] for the synthesis of 8-allyl-2-styrylchromones.

EXPERIMENTAL

Melting points were measured using a Kofler hot stage apparatus and are uncorrected. The ir spectra were obtained on a FT-IR Perkin-Elmer 1710 spectrophotometer. The uv spectra were recorded on a Perkin Elmer Lambda UV-VIS spectrophotometer. The ^1H nmr (200 MHz) and ^{13}C nmr (50.3 MHz) were recorded on a Varian Gemini 200 spectrometer and the chemical shifts are given in δ ppm downfield from TMS. Elemental analysis were performed on a Calro Elba 1106 instrument. Thin layer chromatography was done on ACME silica gel G and column chromatography on ACME silica gel (finer than 200 mesh).

General Procedure for the Synthesis of 2-Hydroxy-3-allylacetophenones **2a-c**.

2-Allyloxyacetophenone **1a** [9], 2-allyloxy-5-methoxyacetophenone **1c** [10] and 2-hydroxy-3-allylacetophenone **2a** [9] are reported earlier.

A mixture of 2-hydroxyacetophenones (50 mmoles) and allyl bromide (50 mmoles) in dry acetone (150 ml) was refluxed for 8 hours. Acetone was removed under reduced pressure and the residue treated with cold water (100 ml) to give an oily product which was extracted into ether, dried and distilled to give liquids, 2-allyloxyacetophenones **1a-c**.

2-Allyloxyacetophenone **1a**.

This compound was obtained as a colourless liquid, bp 145° (0.1 mm) [lit bp 146°] 6.7 g; ir (chloroform): 1675, 1596, 1450, 1358, 1237, 999 cm^{-1} . ^1H nmr (deuteriochloroform): δ 2.56 (3H, s, COCH_3), 4.58 (2H, d, $J = 6.0$ Hz, H-1'), 5.30 (2H, m, H-3'), 6.00 (1H, m, H-2'), 6.90 (2H, m, H-4, 5), 7.40 (1H, m, H-3), 7.70 (1H, dd, $J = 10.0$ Hz, 2.0 Hz, H-6).

2-Allyloxy-5-chloroacetophenone **1b**.

This compound was obtained as a colourless liquid bp 155° (0.1 mm), 8.4 g; ir (chloroform): 1663, 1592, 1277, 1224, 1149, 1104, 1001, 928, 905, 849; ^1H nmr (deuteriochloroform): δ 2.62 (3H, s, COCH_3), 4.60 (2H, d, $J = 6.0$ Hz, H-1'), 5.38 (2H, m, H-3'), 6.05 (1H, m, H-2'), 6.89 (1H, d, $J = 10.0$ Hz, H-3), 7.37 (1H, dd, $J = 10.0$ Hz, 2.5 Hz, H-4), 7.70 (1H, d, $J = 2.5$ Hz, H-6).

2-Allyloxy-5-methoxyacetophenone **1c**.

This compound was obtained as a colourless liquid bp 100° (0.1 mm) [lit bp 102°] [10] 8.0 g, ir (chloroform): 1675, 1609,

1416, 1282, 1042, 994, 812; ^1H nmr (deuteriochloroform): δ 2.60 (3H, s, COCH_3), 3.75 (3H, s, OCH_3 -5), 4.55 (2H, d, $J = 6.0$ Hz, H-1'), 5.30 (2H, m, H-3'), 6.00 (1H, m, H-2'), 6.85 (1H, d, $J = 10.0$ Hz, H-3), 6.95 (1H, dd, $J = 10.0$ Hz, 2.5 Hz, H-4), 7.25 (1H, d, $J = 2.5$ Hz, H-6).

2-Allyloxyacetophenones **1a-c** (30 mmoles) were taken in *N,N*-diethylaniline (50 ml) and refluxed at 220° for 4 hours. The reaction mixture was cooled and poured in cold dilute hydrochloric acid and extracted with ether (100 ml), dried and distilled to afford 2-hydroxy-3-allylacetophenones **2a-c** as colourless liquids.

2-Hydroxy-3-allylacetophenone (**2a**).

This compound had bp 135-138° (0.1 mm) [lit bp 138°] [9] 4.2 g; ir (chloroform): 1636 ($\text{C}=\text{O}$), 1435, 1365, 1315, 1245, 984, 916, 752 cm^{-1} ; ^1H nmr (deuteriochloroform): δ 2.58 (3H, s, COCH_3), 3.40 (2H, d, $J = 6.0$ Hz, H-1'), 5.02 (2H, m, H-3'), 5.98 (1H, m, H-2'), 6.80 (1H, t, $J = 8.0$ Hz, H-5), 7.34 (1H, dd, $J = 8.0$ Hz, 1.0 Hz, H-4), 7.60 (1H, dd, $J = 8.0$ Hz, 1.0 Hz, H-6), 12.60 (1H, s, OH-2).

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_2$: C, 75.00; H, 6.81. Found: C, 74.95; H, 6.80.

2-Hydroxy-3-allyl-5-chloroacetophenone (**2b**).

This compound had bp 140° (0.1 mm) 5.0 g; ir (chloroform): 1643 ($\text{C}=\text{O}$), 1436, 1364, 1315, 1236, 920, 795, 748; ^1H nmr (deuteriochloroform): δ 2.60 (3H, s, COCH_3), 3.40 (2H, d, $J = 6.0$ Hz, H-1'), 5.15 (2H, m, H-3'), 5.95 (1H, m, H-2'), 7.35 (1H, d, $J = 2.5$ Hz, H-4), 7.60 (1H, d, $J = 2.5$ Hz, H-6), 12.50 (1H, s, OH-2).

Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{Cl}$: C, 62.70; H, 5.22. Found: C, 62.60; H, 5.20.

2-Hydroxy-3-allyl-5-methoxyacetophenone (**2c**).

This compound had bp 145° (0.1 mm) 4.8 g, ir (chloroform): 1638 ($\text{C}=\text{O}$), 1612, 1460, 1432, 1368, 1324, 1204, 988, 916, 783; ^1H nmr (deuteriochloroform): δ 2.55 (3H, s, COCH_3), 3.35 (2H, d, $J = 6.0$ Hz, H-1'), 3.75 (3H, s, OCH_3 -5), 5.05 (2H, m, H-3'), 5.98 (1H, m, H-2'), 6.96 (1H, d, $J = 2.5$ Hz, H-4), 7.02 (1H, d, $J = 2.5$ Hz, H-6), 12.20 (1H, s, OH-2).

Anal. Calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.90; H, 6.79. Found: C, 69.81; H, 6.76.

General Procedure for the Synthesis of 1-(2-Hydroxy-3-allyl-aryl)-5-aryl-4-pentene-1,3-diones **4a-g**.

2-Hydroxy-3-allylacetophenones **2a-c** (10.0 mmoles), cinnamoyl chlorides **3a-c** (10.0 mmoles) and anhydrous potassium carbonate (10 g) were taken in dry acetone (100 ml) and refluxed for 12 hours. Acetone was removed under reduced pressure and crushed ice (100 g) was added to the residue and macerated. A bright yellow coloured solid separated out. These solids were purified by column chromatography on silica gel by eluting with petroleum ether:chloroform to give **4a-g**. From analysis of the spectral data the diketones **4a-g** were found to exist exclusively in the enolic forms, 1-(2-hydroxy-3-allylaryl)-5-aryl-pent-3-hydroxy-2,4-diene-1-ones **5a-g**.

1-(2-hydroxy-3-allylphenyl)-5-phenylpent-3-hydroxy-2,4-dien-1-one (**5a**).

This compound was obtained in the reaction of **2a** with **3a**. It was recrystallized from methanol, mp 100-102°, 2.75 g; ir (potassium bromide): 1635, 1561, 1478, 1437, 1290, 1236, 960, 766 cm^{-1} ; uv (dioxane): 390, 265 (sh), 215 nm; ^1H nmr

(deuteriochloroform): δ 3.35 (2H, d, $J = 6.0$ Hz, H-1'''), 5.00 (2H, m, H-3'''), 5.95 (1H, m, H-2'''), 6.20 (1H, s, H-2), 6.50 (1H, d, $J = 9.0$ Hz, H-4'), 6.75 (1H, t, $J = 9.0$ Hz, H-5'), 7.30 (4H, m, H-4, H-3'',4'',5''), 7.50 (4H, m, H-5, H-6', H-2'',6''), 12.46 (1H, s, OH-2'), 14.50 (1H, s, OH-3); ^{13}C nmr (deuteriochloroform): δ 33.5 (C-1'''), 97.1 (C-4), 115.8 (C-2), 118.4 (C-3'''), 122.1 (C-5'), 126.5 (C-6'), 127.9 (C-3'',5''), 128.5 (C-1'), 128.8 (C-2'',6''), 129.5 (C-3'), 129.9 (C-4'), 134.9 (C-1''), 135.7 (C-2''), 136.1 (C-4''), 139.6 (C-5), 160.5 (C-2'), 174.0 (C-3), 196.1 (C-1).

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_3$: C, 78.43; H, 5.88. Found: C, 78.35; H, 5.85.

1-(2-Hydroxy-3-allylphenyl)-5-(2-chlorophenyl)pent-3-hydroxy-2,4-dien-1-one (**5b**).

This compound was obtained in the reaction of **2a** with **3b**. It was recrystallized from methanol, mp 90-92°, 3.05 g; ir (potassium bromide): 1632, 1575, 1475, 1426, 1236, 1157, 963, 740 cm^{-1} ; uv (methanol) 400, 275 (sh), 205 nm; ^1H nmr (deuteriochloroform): δ 3.38 (2H, d, $J = 6.0$ Hz, H-1'''), 5.00 (2H, m, H-3'''), 6.00 (1H, m, H-2'''), 6.28 (1H, s, H-2), 6.50 (1H, d, $J = 16.0$ Hz, H-4), 6.80-7.60 (7H, m, H-3'',4'',5'',6'',4',5',6'), 8.00 (1H, d, $J = 16.0$ Hz, H-5), 12.50 (1H, s, OH-2'), 14.50 (1H, s, OH-3); ^{13}C nmr (deuteriochloroform): δ 33.5 (C-1'''), 97.6 (C-4), 115.9 (C-2), 118.4 (C-3'''), 124.5 (C-5'), 126.6 (C-6'), 127.0 (C-4'), 127.2 (C-4'',6''), 129.5 (C-3'), 130.1 (C-3''), 130.6 (C-5''), 133.1 (C-1''), 134.8 (C-2''), 135.1 (C-5), 135.8 (C-2''), 136.1 (C-1'), 160.6 (C-2'), 173.3 (C-3), 196.3 (C-1).

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{O}_3\text{Cl}$: C, 70.48; H, 4.99. Found: C, 70.38; H, 4.95.

1-(2-Hydroxy-3-allylphenyl)-5-(4-methoxyphenyl)-pent-3-hydroxy-2,4-dien-1-one (**5c**).

This compound was obtained in the reaction of **2a** with **3c**. It was recrystallized from methanol, mp 110-112°, 3.0 g; ir (potassium bromide): 1632, 1557, 1474, 1417, 1246, 1172, 832 cm^{-1} ; uv (dioxane): 385, 265 (sh), 220 nm; ^1H nmr (deuteriochloroform): δ 3.38 (2H, d, $J = 6.0$ Hz, H-1'''), 3.75 (3H, s, OCH_3 -4''), 5.00 (2H, m, H-3'''), 5.95 (1H, m, H-2'''), 6.25 (1H, s, H-2), 6.38 (1H, d, $J = 16.0$ Hz, H-4), 6.85 (3H, m, H-3'',5'',5'), 7.25-7.60 (5H, m, H-4',5',6',2'',6''), 12.50 (1H, s, OH-2'), 14.65 (1H, s, OH-3); ^{13}C nmr (deuteriochloroform): δ 33.5 (C-1'''), 55.2 (OCH_3 -4''), 91.0 (C-4), 113.9 (C-3'''), 115.8 (C-2), 118.4 (C-3'''), 125.6 (C-5'), 126.4 (C-6'), 128.6 (C-2'',6''), 129.0 (C-3'), 129.4 (C-4'), 131.0 (C-1'), 135.3 (C-2'''), 136.2 (C-5), 136.8 (C-1'), 160.2 (C-2'), 163.0 (C-4''), 177.2 (C-3), 194.9 (C-1).

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_4$: C, 75.00; H, 5.95. Found: C, 74.95; H, 5.92.

1-(2-Hydroxy-3-allyl-5-chlorophenyl)-5-phenylpent-3-hydroxy-2,4-dien-1-one (**5d**).

This compound was obtained in the reaction of **2b** with **3a**. It was recrystallized from methanol, mp 97°, 3.0 g; ir (potassium bromide): 1635, 1575, 1475, 1420, 1250, 1140, 960, 765 cm^{-1} ; uv (methanol): 394, 250 (sh), 215 nm; ^1H nmr (deuteriochloroform): δ 3.38 (2H, d, $J = 6.0$ Hz, H-1'''), 5.10 (2H, m, H-3'''), 6.00 (1H, m, H-2'''), 6.25 (1H, s, H-2), 6.38 (1H, d, $J = 16.0$ Hz, H-4), 6.60 (1H, d, $J = 2.5$ Hz, H-4'), 7.20-7.80 (7H, m, H-6',5',2'',3'',4'',5'',6''), 12.60 (1H, s, OH-2'), 14.50 (1H, s, OH-3); ^{13}C nmr (deuteriochloroform): δ 32.5 (C-1'''), 96.5 (C-4), 115.8 (C-3'''), 122.3 (C-2), 123.5 (C-6'), 124.9 (C-4'), 127.1 (C-3'',5''), 128.8 (C-2'',6''), 130.7 (C-3'), 133.7 (C-1'), 134.0

(C-5), 134.8 (C-1''), 135.2 (C-2'''), 136.1 (C-5'), 136.2 (C-4''), 158.0 (C-2'), 172.5 (C-3), 185.0 (C-1).

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{O}_3\text{Cl}$: C, 70.48; H, 4.99. Found: C, 70.38; H, 4.96.

1-(2-Hydroxy-3-allyl-5-chlorophenyl)-5-(2-chlorophenyl)pent-3-hydroxy-2,4-dien-1-one (**5e**).

This compound was obtained in the reaction of **2b** with **3b**. It was recrystallized from methanol, mp 150-152°, 3.3 g; ir (potassium bromide): 1635, 1576, 1452, 1409, 1273, 969, 798, 746 cm^{-1} ; uv (methanol): 399, 275 (sh), 206 nm; ^1H nmr (deuteriochloroform): δ 3.40 (2H, d, $J = 6.0$ Hz, H-1'''), 5.10 (2H, m, H-3'''), 5.95 (1H, m, H-2'''), 6.25 (1H, s, H-2), 6.55 (1H, d, $J = 16.0$ Hz, H-4), 7.20-7.70 (6H, m, H-3'',4'',5'',6'',4',6'), 8.05 (1H, d, $J = 16.0$ Hz, H-5), 12.40 (1H, s, OH-2'), 14.38 (1H, s, OH-3); ^{13}C nmr (deuteriochloroform + $\text{DMSO}-d_6$): δ 32.6 (C-1'''), 97.0 (C-4), 115.9 (C-3'''), 122.3 (C-2), 123.7 (C-6'), 125.0 (C-4'), 126.4 (C-5''), 126.6 (C-6''), 129.2 (C-4''), 130.1 (C-3''), 130.7 (C-3'), 131.9 (C-1''), 133.8 (C-1'), 134.3 (C-5), 134.3 (C-2''), 134.5 (C-2'), 134.6 (C-5'), 158.1 (C-2'), 173.3 (C-3), 184.2 (C-1).

Anal. Calcd. for $\text{C}_{20}\text{H}_{16}\text{O}_3\text{Cl}_2$: C, 64.00; H, 4.26. Found: C, 63.95; H, 4.23.

1-(2-Hydroxy-3-allyl-5-chlorophenyl)-5-(4-methoxyphenyl)-pent-3-hydroxy-2,4-dien-1 one (**5f**).

This compound was obtained in the reaction of **2b** with **3c**. It was recrystallized from methanol, mp 120-122°, 3.3 g; ir (potassium bromide): 1634, 1603, 1566, 1507, 1437, 1260, 1169, 919, 838, 801, 768 cm^{-1} ; uv (dioxane): 384, 250 (sh), 215 nm; ^1H nmr (deuteriochloroform): δ 3.38 (2H, d, $J = 6.0$ Hz, H-1'''), 3.82 (3H, s, OCH_3 -4''), 5.10 (2H, m, H-3'''), 5.95 (1H, m, H-2'''), 6.65 (1H, s, H-2), 6.92 (2H, m, H-4, 5), 7.25 (1H, d, $J = 2.5$ Hz, H-4'), 7.55 (1H, d, $J = 2.5$ Hz, H-6'), 7.90 (2H, d, $J = 9.0$ Hz, H-3'',5''), 8.06 (2H, d, $J = 9.0$ Hz, H-2'',6''), 12.40 (1H, s, OH-2'), 14.50 (1H, s, OH-3); ^{13}C nmr (deuteriochloroform + $\text{DMSO}-d_6$): δ 32.8 (C-1'''), 55.3 (OCH_3 -4''), 91.7 (C-4), 113.4 (C-2), 113.9 (C-3'',5''), 116.4 (C-3'''), 119.2 (C-1''), 122.7 (C-4'), 124.7 (C-3'), 126.3 (C-6'), 129.3 (C-2'',6''), 130.9 (C-5'), 131.1 (C-5), 135.2 (C-2''), 135.7 (C-1'), 158.0 (C-2'), 163.2 (C-4''), 178.1 (C-3), 193.1 (C-1).

Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{O}_4\text{Cl}$: C, 68.01; H, 5.12. Found: C, 68.00; H, 5.11.

1-(2-Hydroxy-3-allyl-5-methoxyphenyl)-5-phenylpent-3-hydroxy-2,4-dien-1-one (**5g**).

This compound was obtained in the reaction of **2c** with **3a**. It was recrystallized from methanol, mp 138°, 3.0 g; ir (potassium bromide): 1635, 1570, 1475, 1430, 1280, 1230, 965, 760 cm^{-1} ; uv (methanol): 390, 245 (sh), 210 nm; ^1H nmr (deuteriochloroform): δ 3.35 (2H, d, $J = 6.0$ Hz, H-1'''), 3.75 (3H, s, OCH_3 -5'), 5.05 (2H, m, H-3'''), 5.95 (1H, m, H-2'''), 6.20 (1H, s, H-2), 6.50 (1H, d, $J = 16.0$ Hz, H-4), 6.90 (1H, d, $J = 2.5$ Hz, H-4'), 7.10 (1H, d, $J = 2.5$ Hz, H-6'), 7.30 (3H, m, H-3'',4'',5''), 7.50 (2H, m, H-2'',6''), 7.58 (1H, d, $J = 16.0$ Hz, H-5), 12.20 (1H, s, OH-2'), 14.50 (1H, s, OH-3); ^{13}C nmr (deuteriochloroform): δ 32.8 (C-1'''), 55.5 (OCH_3 -5'), 96.1 (C-4), 116.1 (C-3'''), 122.5 (C-2), 122.6 (C-6'), 124.0 (C-4'), 127.1 (C-3'',5''), 128.5 (C-2'',6''), 130.5 (C-3'), 133.5 (C-1'), 134.1 (C-5), 134.8 (C-1''), 136.0 (C-2''), 136.5 (C-4''), 157.2 (C-5'), 158.3 (C-2'), 173.2 (C-3), 186.2 (C-1).

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_4$: C, 75.00; H, 5.95. Found: C, 74.94; H, 5.92.

General Procedure for the Synthesis of Substituted 8-Allyl-2-styrylchromones **6a-g**.

1-(2-Hydroxy-3-allylaryl)-5-arylpent-3-hydroxy-2,4-dien-1-ones **5a-g** (5 mmoles) were dissolved in absolute ethanol (75 ml) and concentrated sulfuric acid (1 ml) added and the reaction mixture refluxed for 3 hours. It was cooled, ethanol distilled off and ice cold water (100 ml) was added. Pale yellow coloured solids **6a-g** were obtained.

8-Allyl-2-styrylchromone (**6a**).

This compound was obtained on cyclodehydration of **5a**, recrystallized from ethanol, mp 138-140° [ref [2], mp 142°], 1.1 g; ir (potassium bromide): 1625, 1568, 1480, 1393, 1207, 993, 751 cm^{-1} ; uv (dioxane): 325, 260, 215 nm; ^1H nmr (deuteriochloroform): δ 3.70 (2H, d, $J = 6.0$ Hz, H-1"), 5.15 (2H, m, H-3"), 6.00 (1H, m, H-2"), 6.30 (1H, s, H-3), 6.75 (1H, d, $J = 16.0$ Hz, α -H), 7.15-7.60 (8H, m, H-6,7, β ,2',3',4',5',6'), 8.04 (1H, dd, $J = 9.0$ Hz, 2.5 Hz, H-5); ^{13}C nmr (deuteriochloroform): δ 34.0 (C-1"), 110.4 (C-3), 116.8 (C-3"), 120.4 (C- α), 123.9 (C-6), 124.0 (C-4a), 124.6 (C-5), 127.6 (C-3',5'), 128.9 (C-2',6'), 129.2 (C-8), 129.8 (C-7), 134.0 (C- β), 134.9 (C-1'), 135.4 (C-4'), 136.8 (C-2"), 153.9 (C-8a), 161.3 (C-2), 178.6 (C-4).

Anal. Calcd. for $\text{C}_{20}\text{H}_{16}\text{O}_2$: C, 83.33; H, 5.55. Found: C, 83.28; H, 5.52.

8-Allyl-2'-chloro-2-styrylchromone (**6b**).

This compound was obtained on cyclodehydration of **5b**, recrystallized from ethanol, mp 166-167°, 1.2 g; ir (potassium bromide): 1625, 1589, 1571, 1395, 1205, 996, 750 cm^{-1} ; uv (dioxane): 325, 215 nm; ^1H nmr (deuteriochloroform): δ 3.72 (2H, d, $J = 6.0$ Hz, H-1"), 5.15 (2H, m, H-3"), 6.10 (1H, m, H-2"), 6.32 (1H, s, H-3), 6.78 (1H, d, $J = 16.0$ Hz, α -H), 7.20-7.80 (6H, m, H-6,7,3',4',5',6'), 8.05 (1H, d, $J = 16.0$ Hz, β -H), 8.10 (1H, dd, $J = 9.0$ Hz, 2.5 Hz, H-5); ^{13}C nmr (deuteriochloroform): δ 34.0 (C-1"), 110.9 (C-3), 116.8 (C-3"), 122.5 (C- α), 123.7 (C-6), 123.9 (C-4a), 124.7 (C-5), 126.9 (C-4'), 127.1 (C-7), 129.3 (C-8), 130.0 (C-6'), 130.5 (C-5'), 132.4 (C-3'), 132.8 (C-2'), 134.2 (C- β), 134.6 (C-1'), 135.2 (C-2"), 153.8 (C-8a), 160.7 (C-2), 178.5 (C-4).

Anal. Calcd. for $\text{C}_{20}\text{H}_{15}\text{O}_2\text{Cl}$: C, 74.41; H, 4.65. Found: C, 74.35; H, 4.63.

8-Allyl-4'-methoxy-2-styrylchromone (**6c**).

This compound was obtained on cyclodehydration of **5c**, recrystallized from methanol, mp 118°, 1.3 g; ir (potassium bromide): 1633, 1603, 1575, 1510, 1453, 1277, 1022, 925, 839, 751 cm^{-1} ; uv (methanol): 359, 248, 208 nm; ^1H nmr (deuteriochloroform): δ 3.65 (2H, d, $J = 6.0$ Hz, H-1"), 5.10 (2H, m, H-3"), 6.00 (1H, m, H-2"), 6.16 (1H, s, H-3), 6.55 (1H, d, $J = 16.0$ Hz, H- α), 6.80 (2H, d, $J = 9.0$ Hz, H-3",5"), 7.20 (1H, m, H-6), 7.30-7.45 (4H, m, H-2',6",7, β), 7.95 (1H, dd, $J = 9.0$ Hz, 2.5 Hz, H-5); ^{13}C nmr (deuteriochloroform): δ 33.7 (C-1"), 55.0 (OCH₃-4'), 109.3 (C-3), 114.1 (C-3',5'), 116.6 (C-3"), 117.5 (C- α), 123.4 (C-6), 123.7 (C-4a), 124.1 (C-5), 127.3 (C-1'), 128.9 (C-2',6'), 128.9 (C-8), 133.5 (C-7), 135.2 (C- β), 136.1 (C-2"), 153.5 (C-8a), 160.7 (C-4'), 161.4 (C-2), 178.1 (C-4).

Anal. Calcd. for $\text{C}_{21}\text{H}_{18}\text{O}_3$: C, 79.29; H, 5.66. Found: C, 79.20; H, 5.67.

8-Allyl-6-chloro-2-styrylchromone (**6d**).

This compound was obtained by the cyclodehydration of **5d**, recrystallized from methanol, mp 150°, 1.3 g; ir (potassium

bromide): 1635, 1603, 1570, 1475, 1440, 1390, 1170, 920, 750 cm^{-1} ; uv (methanol): 330, 260, 215 nm; ^1H nmr (deuteriochloroform): δ 3.62 (2H, d, $J = 6.0$ Hz, H-1"), 5.15 (2H, m, H-3"), 6.00 (1H, m, H-2"), 6.20 (1H, s, H-3), 6.70 (1H, d, $J = 16.0$ Hz, H- α), 7.20-7.70 (7H, m, H- β ,7,2',3',4', 5',6'), 7.90 (1H, d, $J = 2.5$ Hz, H-5); ^{13}C nmr (deuteriochloroform): δ 33.5 (C-1"), 110.0 (C-3), 117.5 (C-3"), 121.8 (C- α), 123.2 (C-5), 124.5 (C-4a), 127.1 (C-3',5'), 128.9 (C-2',6'), 130.5 (C-8), 132.8 (C- β), 133.5 (C-7), 134.6 (C-2"), 134.8 (C-6), 134.9 (C-1'), 135.3 (C-4'), 152.0 (C-8a), 162.1 (C-2), 178.1 (C-4).

Anal. Calcd. for $\text{C}_{20}\text{H}_{15}\text{O}_2\text{Cl}$: C, 74.41; H, 4.65. Found: C, 74.36; H, 4.66.

8-Allyl-6,2'-dichloro-2-styrylchromone (**6e**).

This compound was obtained by the cyclodehydration of **5e**, recrystallized from methanol, mp 158°, 1.5 g; ir (potassium bromide): 1635, 1570, 1451, 1376, 1305, 1193, 963, 749 cm^{-1} ; uv (methanol): 331, 245 (sh), 207 nm; ^1H nmr (deuteriochloroform): δ 3.65 (2H, d, $J = 6.0$ Hz, H-1"), 5.15 (2H, m, H-3"), 6.00 (1H, m, H-2"), 6.30 (1H, s, H-3), 6.72 (1H, d, $J = 16.0$ Hz, H- α), 7.20-7.70 (5H, m, H-3',4',5',6',7), 7.95 (1H, d, $J = 2.5$ Hz, H-5), 7.97 (1H, d, $J = 16.0$ Hz, H- β); ^{13}C nmr (deuteriochloroform): δ 33.7 (C-1"), 110.2 (C-3), 117.7 (C-3"), 122.1 (C- α), 123.1 (C-5), 124.9 (C-4a), 126.9 (C-6'), 127.2 (C-4'), 130.1 (C-3'), 130.7 (C-5'), 131.0 (C-8), 131.6 (C-2'), 132.9 (C- β), 134.0 (C-2"), 134.3 (C-6), 134.5 (C-7), 134.7 (C-1'), 152.5 (C-8a), 161.0 (C-2), 177.3 (C-4).

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{O}_2\text{Cl}_2$: C, 67.22; H, 3.92. Found: C, 67.00; H, 3.91.

8-Allyl-6-chloro-4'-methoxy-2-styrylchromone (**6f**).

This compound was obtained by the cyclodehydration of **5f**, recrystallized from methanol, mp 155°, 1.4 g; ir (potassium bromide): 1635, 1599, 1569, 1510, 1453, 1378, 1247, 1173, 967, 816 cm^{-1} ; uv (dioxane): 341, 250 (sh), 214 nm; ^1H nmr (deuteriochloroform): δ 3.70 (2H, d, $J = 6.0$ Hz, H-1"), 3.85 (3H, s, OCH₃-4'), 5.25 (2H, m, H-3"), 6.05 (1H, m, H-2"), 6.30 (1H, s, H-3), 6.65 (1H, d, $J = 16.0$ Hz, H- α), 6.95 (2H, d, $J = 9.0$ Hz, H-3',5'), 7.40-7.60 (4H, m, H-2',6',7, β), 8.05 (1H, d, $J = 2.5$ Hz, H-5); ^{13}C nmr (deuteriochloroform): δ 33.7 (C-1"), 55.3 (OCH₃-4'), 109.4 (C-3), 114.4 (C-3',5'), 117.5 (C-3"), 117.7 (C- α), 123.1 (C-5), 124.9 (C-4a), 127.4 (C-1'), 129.2 (C-2',6'), 130.4 (C-8), 131.4 (C-6), 133.5 (C-7), 134.4 (C- β), 136.8 (C-2"), 152.1 (C-8a), 161.2 (C-4'), 161.9 (C-2), 177.1 (C-4).

Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{O}_3\text{Cl}$: C, 71.48; H, 4.82. Found: C, 71.40; H, 4.84.

8-Allyl-6-methoxy-2-styrylchromone (**6g**).

This compound was obtained by the cyclodehydration of **5g**, recrystallized from methanol, mp 130° [ref 2, mp 132°] 1.3 g; ir (potassium bromide): 1630, 1600, 1575, 1510, 1479, 1450, 1270, 1250, 920, 840, 750 cm^{-1} ; uv (methanol): 341, 228 nm; ^1H nmr (deuteriochloroform): δ 3.75 (2H, d, $J = 6.0$ Hz, H-1"), 3.95 (3H, s, OCH₃-6), 5.20 (2H, m, H-3"), 6.00 (1H, m, H-2"), 6.30 (1H, s, H-3), 6.40 (1H, d, $J = 16.0$ Hz, H- α), 7.15-7.70 (8H, m, H-7,5, β ,2',3',4',5',6'); ^{13}C nmr (deuteriochloroform): δ 34.0 (C-1"), 55.7 (OCH₃-6), 103.8 (C-7), 109.5 (C-3), 119.4 (C-3"), 120.5 (C- α), 124.9 (C-4a), 127.6 (C-3',5'), 128.9 (C-2',6'), 129.4 (C-8), 129.7 (C-5), 130.1 (C-1'), 134.9 (C-4'), 136.6 (C- β), 137.0 (C-2"), 156.4 (C-8a), 158.0 (C-6), 161.1 (C-2), 178.3 (C-4).

Anal. Calcd. for $\text{C}_{21}\text{H}_{18}\text{O}_3$: C, 79.24; H, 5.66. Found: C, 79.18; H, 5.65.

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