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Synthesis and structure elucidation of three series of nitro-2-styrylchromones using 1D and 2D NMR spectroscopy

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2-Styrylchromones, although scarce in nature, constitute a group of oxygen heterocyclic compounds which have shown significant biological activities. New nitro-2-styrylchromones have been synthesised by the Baker–Venkataraman method, and the structure elucidation was accomplished using extensive 1D (1H, 13C) and 2D NMR spectroscopic studies (COSY, HSQC and HMBC experiments). Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: ¹H NMR; ¹³C NMR; HMBC; nitro-2-styrylchromones

Introduction

Chromones are one of the most abundant groups of naturally 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] Almost all the natural occurring chromones are 2and 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 (hormothamnione and 6-desmethoxy-hormothamnione in the marine blue-green algae *Chrysophaem taylori*),^[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 cytotoxicity against human leukaemia cells,^[3,4] as well as significant levels of anti-allergic^[6] and anti-cancer^[7] activities. Some of the derivatives obtained by synthesis exhibited xanthine oxidase inhibitor properties.^[8] Taking into account the potential biological applications of chromones and especially those having 2-substituents, we decided to devote some attention to the synthesis of new 2-styrylchromones.

Experimental

The ¹H and ¹³C NMR spectra were recorded at 25 °C with *ca* 5-mg samples dissolved in 0.5 ml of CDCl₃ or DMSO-*d*₆ in 5-mm NMR tubes using a Bruker DRX 300 spectrometer (300.13 for ¹H and 75.47 for ¹³C). Chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. The internal standard was TMS. The Fourier-transform NMR measurement conditions were as follows: for ¹H NMR, pulse width 3.4 µs, pulse angle 30°, acquisition time 2.7 s and number of scans 80; for ¹³C NMR, pulse width 1.7 ms, pulse angle 30°, acquisition time 0.8 s, number of scans 6144 and number of data points 16 384. Unequivocal ¹³C assignments

were made with the aid of 2D *g*HSQC and *g*HMBC (delays for one-bond and long-range *J*(C,H) couplings were optimised for 147 and 7 Hz, respectively) experiments. Electron impact (EI, 70 eV) MS were recorded on VG Autospec Q and M spectrometers. Elemental analyses (CHN) were obtained with a Carlo Erba 1108 CHNS analyser and were in good agreement (0.4%) with the calculated values. Preparative thin-layer chromatography was performed with Merck silica gel 60 DGF254. Column chromatography was performed with 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.

Materials

The nitro-2-styrylchromones **5** were prepared in good overall yields according to the three-step sequence, shown in Scheme 1. For this purpose, the 2'-(nitrocinnamoyloxy)acetophenones **3a**–**j** were obtained from the reaction of the 2'-hydroxyacetophenone derivatives **1a**–**d** with the appropriate cinnamic acid **2a**–**c**. The rearrangement of the nitro-2'-cinnamoyloxy-acetophenones **3a**–**j** into 3-hydroxy-1-(2-hydroxyphenyl)-5-(nitrophenyl)-2,4-pentadien-1-ones **4a**–**j** was performed upon treatment with sodium hydride in dry tetrahydrofuran at reflux or with potassium hydroxide in dimethyl sulfoxide at room temperature. Cyclization of compounds **4a**–**j** into the desired nitro-2-styrylchromones **5a**–**j** was achieved by heating with *p*-toluenesulfonic acid in dimethyl sulfoxide at 80–90 °C or with iodine in dimethyl sulfoxide at 80–90 °C.

The nitro-2-styrylchromones bearing 7-methoxy substituents (5d-f) were obtained only in moderate yields (27–61%), while the others were obtained in better yields (67–79%); see Table 1.

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Table 1. Cor	mpounds	obtained a	nd yields			
Compound	R ¹	R ²	R ³	R ⁴	R⁵	Yield (%)
а	Н	Н	NO ₂	Н	Н	74
b	Н	Н	Н	NO_2	Н	73
c	Н	Н	Н	Н	NO_2	69
d	OCH ₃	Н	NO_2	Н	Н	27
e	OCH ₃	Н	Н	NO ₂	Н	61
f	OCH ₃	Н	Н	Н	NO ₂	31
g	Н	OCH_3	NO_2	Н	Н	67
h	Н	OCH_3	Н	NO ₂	Н	79
i	Н	OCH_3	Н	Н	NO_2	77
j	OCH ₃	OCH ₃	Н	NO_2	Н	74

General method for the synthesis of 2'-(nitrocinnamoyloxy)acetophenones 3a-j

Phosphorous oxychloride (15.6 mmol) was added to a solution of the appropriate 2'-hydroxyacethophenone 1a-d (12 mmol) and the appropriate nitrocinnamic acid 2a-c (15.6 mmol) in dry pyridine. The solution was stirred at 60–70 °C for 3 h, then poured into ice and water, and the reaction mixture acidified with hydrochloric acid (pH *ca* 3). The obtained solid was removed by filtration, taken in 100 ml CHCl₃ and purified by silica gel column chromatography using a 7:3 mixture of chloroform: *n*-hexane as the eluent. The solvent was evaporated to dryness and the residue recrystallised from ethanol, giving the expected compounds.

2'-(2-Nitrocynnamoyloxy)acetophenone (**3a**). Yield 55%; mp 118.7–119.9 °C. MS: (EI, 70 eV): m/z (%) = 311 (M^{+•}, 41), 296 (42), 279 (30), 265 (100), 250 (33), 238 (16), 220 (23), 190 (15); IR (KBr): ν = 1731, 1668, 1612, 1571, 1525, 1349, 1278, 1199, 1132, 1068, 970, 750 cm⁻¹.

2'-(3-Nitrocynnamoyloxy)acetophenone (**3b**). Yield 68%; mp 124.0–125.6 °C. MS: (EI, 70 eV): m/z (%) = 311 (M^{+•}, 3), 176 (100), 145 (5), 129 (11), 121 (6), 102 (26), 76 (7), 63 (3); IR (KBr): ν = 1713, 1683, 1637, 1600, 1527, 1471, 1436, 1349, 1303, 1261, 1199, 1072, 810, 750 cm⁻¹.

2'-(4-Nitrocynnamoyloxy)acetophenone (**3c**). Yield 60%; mp 130.6–132.0 °C. MS: (El, 70 eV): m/z (%) = 311 (M^{+•}, 2), 176 (100), 130 (16), 118 (3), 102 (18), 90 (6), 76 (5); IR (KBr): ν = 1731, 1695, 1635, 1602, 1523, 1346, 1305, 1147, 960, 844, 755 cm⁻¹.

4'-*Methoxy*-2'-(2-*nitrocynnamoyloxy*)*acetophenone* (**3***d*). Yield 52%; mp 95.7–96.9 °C. MS: (El, 70 eV): m/z (%) = 341 (M^{+•}, 7), 176 (100), 163 (11), 151 (26), 130 (98), 118 (4), 102 (29), 89 (6), 77 (16); IR (KBr): ν = 1732, 1665, 1609, 1569, 1524, 1349, 1277, 1229, 1198, 1065, 967 cm⁻¹.

4'-*Methoxy*-2'-(*3*-*nitrocynnamoyloxy*)*acetophenone* (**3e**). Yield 70%; mp 125.6–126.4 °C. MS: (EI, 70 eV): *m/z* (%) = 341 (M^{+•}, 15), 282 (21), 176 (100), 166 (11), 151 (19), 129 (17), 118 (9), 102 (32), 76 (12); IR (KBr): $\nu = 1737, 1677, 1639, 1608, 1525, 1349, 1259, 1141, 1068, 811, 740 cm⁻¹.$

4'-*Methoxy*-2'-(4-*nitrocynnamoyloxy*)*acetophenone* (**3f**). Yield 64%; mp 142.6–143.9 °C. MS: (EI, 70 eV): m/z (%) = 341 (M^{+•}, 6), 299 (15), 176 (100), 166 (3), 151 (13), 130 (22), 118 (5), 102 (25), 90 (10), 76 (8); IR (KBr): v = 1733, 1668, 1635, 1606, 1515, 1344, 1257, 1143, 979, 842 cm⁻¹.

6'-Methoxy-2'-(2-nitrocynnamoyloxy)acetophenone (**3g**). Yield 54%; mp 116.6–117.9 °C. MS: (EI, 70 eV): m/z (%) = 341 (M^{+•}, 100), 324 (22), 297 (14), 280 (67), 262 (54), 252 (26), 236 (15), 226 (22), 206 (54); IR (KBr): ν = 1735, 1708, 1641, 1606, 1521, 1469, 1440, 1351, 1141, 1081, 979 cm⁻¹.

6'-*Methoxy*-2'-(3-*nitrocynnamoyloxy*)*acetophenone* (**3***h*). Yield 78%; mp 121.6–122.4 °C. MS: (El, 70 eV): m/z (%) = 341 (M^{+•}, 17), 297 (18), 176 (100), 166 (16), 151 (24), 129 (23), 118 (11), 102 (45), 76 (14), 63 (7); IR (KBr): ν = 1725, 1689, 1643, 1604, 1531, 1469, 1353, 1276, 1228, 1151, 1076, 809, 744 cm⁻¹.

6'-*Methoxy*-2'-(4-*nitrocynnamoyloxy*)*acetophenone* (**3i**). Yield 70%; mp 193.4–195.0 °C. MS: (El, 70 eV): m/z (%) = 341 (M^{+•}, 7), 297 (10), 176 (100), 151 (12), 130 (22), 118 (6), 102 (24), 90 (9), 76 (8), 63 (4); IR (KBr): v = 1739, 1698, 1641, 1509, 1463, 1346, 1268, 1153, 1078, 983, 844 cm⁻¹.

4',6'-Dimethoxy-2'-(3-nitrocynnamoyloxy)acetophenone (3j). Yield 75%; mp 132.0–133.6 °C. MS: (EI, 70 eV): m/z (%) = 371 (M^{+•}, 10), 356 (3), 312 (54), 196 (22), 176 (100), 167 (7), 129 (22), 102 (46), 76 (14); IR (KBr): ν = 1733, 1675, 1641, 1608, 1533, 1349, 1253, 1226, 1151, 1095, 1074, 975, 813 cm⁻¹.

General method for the synthesis of 3-hydroxy-1-(2-hydroxyphenyl)-5-(nitrophenyl)-2,4-pentadien-1-ones 4a-j

Potassium hydroxide powder (0.05 mmol, 2.8 g) was added to a solution of 2'-(nitrocinnamoyloxy)acetophenones 3a - j (10 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 (*ca* 2 h). 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 purified by silica gel chromatography using chloroform: *n*-hexane (7:3) as eluent. The solvent was evaporated to dryness and the residue was recrystallised from ethanol, giving in each case, the expected compound.

3-Hydroxy-1-(2-hydroxyphenyl)-5-(2-nitrophenyl)-2,4-pentadien-1one (**4a**). Yield 60%; mp 186.6–187.1 °C. MS: (EI, 70 eV): m/z (%) = 311 (M^{+•}, 39), 294 (20), 264 (11), 176 (48), 163 (33), 145 (5), 130 (7), 121 (100), 102 (17), 93 (21), 77 (20), 65 (31); IR (KBr): ν = 1635, 1575, 1513, 1486, 1430, 1295, 1178, 955, 813, 750 cm⁻¹.

3-Hydroxy-1-(2-hydroxyphenyl)-5-(3-nitrophenyl)-2,4-pentadien-1one (**4b**). Yield 75%; mp 194.4–187.1 °C. MS: (EI, 70 eV): m/z (%) = 311 (M^{+•}, 53), 294 (7), 189 (10), 176 (100), 160 (15), 129 (16), 121 (81), 115 (13), 102 (29), 93 (14), 77 (9), 65 (18); IR (KBr): ν = 1639, 1575, 1490, 1434, 1353, 1295, 1243, 750 cm⁻¹. 3-Hydroxy-1-(2-hydroxyphenyl)-5-(4-nitrophenyl)-2,4-pentadien-1one (**4c**). Yield 84%; mp 198.2 – 199.7 °C. MS: (EI, 70 eV): m/z (%) = 311 (M^{+•}, 54), 294 (12), 189 (13), 176 (100), 163 (9), 144 (8), 130 (28), 121 (95), 115 (10), 102 (23), 93 (14), 65 (15); IR (KBr): v = 1600, 1571, 1515, 1486, 13380, 1295, 1168, 954, 836, 759 cm⁻¹.

3-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)-5-(2-nitrophenyl)-2,4pentadien-1-one (**4d**). Yield 16%; mp 190.2–191.8 °C. MS: (El, 70 eV): m/z (%) = 341 (M^{+•}, 100), 324 (26), 306 (17), 294 (14), 278 (18), 206 (64), 193 (73), 176 (42), 163 (51), 130 (28), 102 (9), 65 (8); IR (KBr): v = 1627, 1585, 1565, 1523, 1506, 1440, 1347, 1241, 1182, 1133, 962, 825 cm⁻¹.

3-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)-5-(3-nitrophenyl)-2,4pentadien-1-one (**4e**). Yield 42%; mp 204.2–205.0 °C. MS: (El, 70 eV): m/z (%) = 341 (M^{+•}, 49), 324 (9), 271 (5), 176 (51), 151 (100), 137 (13), 124 (31), 102 (24), 69 (8); IR (KBr): ν = 1729, 1643, 1606, 1581, 1515, 1463, 1347, 1263, 1155, 1106, 1025, 954, 840, 784 cm⁻¹.

3-Hydroxy-1-(2-hydroxy-4-methoxyphenyl)-5-(4-nitrophenyl)-2,4pentadien-1-one (**4f**). Yield 24%; mp 200.9–201.6 °C. MS: (El, 70 eV): m/z (%) = 341 (M^{+•}, 37), 326 (6), 311 (8), 279 (22), 252 (12), 167 (39), 149 (100), 124 (14), 105 (48), 91 (23), 71 (39); IR (KBr): ν = 1731, 1645, 1581, 1523, 1463, 1347, 1266, 1159, 1110, 1025, 956, 840, 784 cm⁻¹.

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-5-(2-nitrophenyl)-2,4pentadien-1-one (**4g**). Yield 54%; mp 199.9–200.6 °C. MS: (El, 70 eV): m/z (%) = 341 (M^{+•}, 78), 324 (35), 310 (65), 292 (8), 271 (16), 176 (74), 151 (100), 124 (38), 115 (15), 102 (42), 95 (10), 65 (17); IR (KBr): ν = 1738, 1640, 1567, 1525, 1460, 1344, 1264, 1159, 1106, 1014, 936, 870, 745 cm⁻¹.

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-5-(3-nitrophenyl)-2,4pentadien-1-one (**4h**). Yield 60%; mp 201.4–202.6 °C. MS: (El, 70 eV): m/z (%) = 341 (M^{+•}, 78), 324 (35), 310 (65), 292 (8), 271 (16), 176 (74), 151 (100), 124 (38), 115 (15), 102 (42), 95 (10), 65 (17); IR (KBr): ν = 1736, 1643, 1564, 1520, 1456, 1340, 1262, 1149, 1110, 1023, 954, 864, 730 cm⁻¹.

3-Hydroxy-1-(2-hydroxy-6-methoxyphenyl)-5-(4-nitrophenyl)-2,4pentadien-1-one (**4i**). Yield 72%; mp 193.6–194.3 °C. MS: (El, 70 eV): m/z (%) = 341 (M^{+•}, 100), 324 (38), 310 (98), 306 (8), 292 (30), 271 (22), 264 (6), 193 (13), 102 (35), 65 (16); IR (KBr): ν = 1708, 1627, 1592, 1569, 1511, 1428, 1336, 1238, 1083, 838, 690 cm⁻¹.

General method for the synthesis of nitro-2-styrylchromones

Method A

p-Toluenesulfonic acid (3.42 mmol) was added to a solution of the appropriate 3-hydroxy-1-(2-hydroxyphenyl)-5-(nitrophenyl)-2,4-pentadien-1-ones $4\mathbf{a} - \mathbf{c}$ and $4\mathbf{g} - \mathbf{j}$ (6.5 mmol) in dimethyl sulfoxide (20 ml). The reaction mixture was heated at 90 °C for 2 h, then poured into ice and water and stirred for 10 min. The obtained solid was removed by filtration, dissolved in chloroform (100 ml) and washed with a 20% aqueous solution of sodium thiosulfate. The solvent was evaporated to dryness and the residue was purified by silica gel chromatography, using chloroform: *n*-hexane (7:3) as eluent.

Method B

A catalytic amount of iodine (1.3 mmol, 0.33 g) was added to a solution of the appropriate 3-hydroxy-1-(2-hydroxyphenyl)-5-(nitrophenyl)-2,4-pentadien-1-ones 4d-f (6.5 mmol) in dimethyl sulfoxide (20 ml). The solution was heated at 80–90 °C for 3 h 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 dissolved in chloroform (150 ml) and purified by silica gel chromatography, using chloroform : *n*-hexane (7 : 3) as eluent.

The obtained solid was removed by filtration, dissolved in chloroform (150 ml) and purified by silica gel chromatography, using chloroform:*n*-hexane (6:4) as eluent. The solvent was evaporated to dryness, and the residue was recrystallised from ethanol.

2'-*Nitro-2-styrylchromone* (**5***a*). Yield 74%; mp 210.6–211.4 °C. MS: (El, 70 eV): *m/z* (%) = 293 (M⁺•, 67), 292 (43), 273 (74), 264 (11), 247 (100), 236 (4), 218 (15), 189 (23), 165 (8), 145 (6), 132 (13), 119 (40), 104 (19), 92 (90), 76 (18), 64 (27); IR (KBr): ν = 1641, 1604, 1527, 1467, 1378, 1135, 777 cm⁻¹. Anal. calcd for C₁₇H₁₁NO₄: C, 69.62; H, 3.75; N, 4.78. Found: C, 69.55; H, 3.63; N, 4.78.

3'-*Nitro-2-styrylchromone* (**5b**). Yield 73%; mp 221.2–222.7 °C. MS: (El, 70 eV): *m/z* (%) = 293 (M^{+•}, 100), 292 (34), 276 (18), 245 (77), 230 (6), 218 (21), 189 (20), 165 (5), 126 (13), 120 (33), 92 (61), 77 (13), 64 (18); IR (KBr): ν = 1652, 1621, 1517, 1463, 1394, 1351, 1126, 975, 769 cm⁻¹. Anal. calcd for C₁₇H₁₁NO₄: C, 69.62; H, 3.75; N, 4.78. Found: C, 69.79; H, 3.81; N, 4.89.

4'-*Nitro-2-styrylchromone* (**5***c*). Yield 69%; mp 282.6–283.0 °C. MS: (EI, 70 eV): *m/z* (%) = 293 (M^{+•}, 100), 292 (64), 276 (43), 263 (4), 246 (32), 230 (10), 218 (17), 200 (9), 189 (16), 165 (4), 121 (32), 92 (51), 77 (11), 64 (15); IR (KBr): ν = 1648, 1511, 1463, 1396, 1338, 1220, 973, 771 cm⁻¹. Anal. calcd for C₁₇H₁₁NO₄: C, 69.62; H, 3.75; N, 4.78. Found: C, 69.58; H, 3.79; N, 4.73.

7-*Methoxy*-2'-*nitro*-2-*styrylchromone* (**5***d*). Yield 27%; mp 268.6–269.4 °C. MS: (EI, 70 eV): m/z (%) = 323 (M⁺•, 100), 322 (28), 306 (7), 151 (80), 122 (5), 79 (8); IR (KBr): v = 1654, 1623, 1567, 1513, 1438, 1386, 1347, 1253, 1087 cm⁻¹. Anal. calcd for C₁₈H₁₃NO₅: C, 63.15; H, 4.02; N, 4.33. Found: C, 63.53; H, 4.24; N, 4.48.

7-Methoxy-3'-nitro-2-styrylchromone (**5e**). Yield 61%; mp 149.9-150.4 °C. MS: (EI, 70 eV): m/z (%) = 323 (M⁺•, 100), 322 (38), 306 (12), 276 (51), 151 (40), 122 (14), 107 (13), 79 (8); IR (KBr): ν = 1654, 1619, 1587, 1513, 1438, 1388, 1347, 1253, 973 cm⁻¹; Anal. calcd for C₁₈H₁₃NO₅: C, 63.15; H, 4.02; N, 4.33. Found: C, 63.49; H, 4.22; N, 4.40.

7-Methoxy-4'-nitro-2-styrylchromone (**5f**). Yield 31%; mp 249.6–250.4 °C. MS: (EI, 70 eV): m/z (%) = 323 (M^{+•}, 100), 322 (35), 306 (11), 276 (49), 234 (9), 151 (40), 121 (15), 107 (14), 79 (8); IR (KBr): ν = 1652, 1623, 1580, 1510, 1380, 1347, 1253, 953 cm⁻¹. Anal. calcd for C₁₈H₁₃NO₅: C, 63.15; H, 4.02; N, 4.33. Found: C, 63.26; H, 4.09; N, 4.36.

5-Methoxy-2'*-nitro*-2-*styrylchromone* (*5g*). Yield 67%; mp 212.4–213.6 °C. MS (EI, 70 eV): *m/z* (%) = 323 (M^{+•}, 100), 322 (28), 306 (39), 294 (23), 276 (32), 247 (19), 202 (12), 149 (7), 121 (11), 107 (26), 92 (28), 77 (14), 63 (13); IR (KBr): ν = 1653, 1604, 1519, 1473, 1398, 1359, 1268, 1087, 829, 754 cm⁻¹. Anal. calcd for C₁₈H₁₃NO₅: C, 63.15; H, 4.02; N, 4.33. Found: C, 63.33; H, 4.14; N, 4.50.

5-Methoxy-3'*-nitro*-2-*styrylchromone* (*5h*). Yield 79%; mp 212.4–213.6 °C. MS: (EI, 70 eV): *m/z* (%) = 323 (M^{+•}, 100), 322 (19), 306 (52), 294 (18), 276 (88), 260 (7), 247 (24), 231 (12), 176 (7), 120 (17), 107 (41), 92 (34), 77 (20), 63 (17); IR (KBr): ν = 1644, 1604, 1525, 1471, 1390, 1347, 1263, 1083, 796 cm⁻¹. Anal. calcd for C₁₈H₁₃NO₅: C, 63.15; H, 4.02; N, 4.33. Found: C, 63.48; H, 4.16; N, 4.28.

5-Methoxy-4'*-nitro-2-styrylchromone* (*5i*). Yield 77%; mp 229.9–231.0 °C. MS: (EI, 70 eV): *m/z* (%) = 323 (M^{+•}, 100), 322 (29), 306 (50), 294 (25), 276 (86), 247 (16), 231 (19), 218 (13), 167 (31), 149 (70), 121 (15), 107 (28), 92 (21), 77 (11), 57 (21); IR (KBr): $\nu = 1727$, 1641, 1508, 1471, 1436, 1388, 1334, 1261, 1083, 971, 848, 744 cm⁻¹. Anal. calcd for C₁₈H₁₃NO₅: C, 63.15; H, 4.02; N, 4.33. Found: C, 63.43; H, 4.36; N, 4.31.

5,7-Dimethoxy-3'-*nitro*-2-*styrylchromone* (*5j*). Yield 642%; mp 229.9–231.0 °C. MS: (EI, 70 eV): *m/z* (%) = 353 (M⁺•, 100), 352 (25), 336 (29), 324 (20), 306 (25), 276 (19), 234 (6), 151 (17), 176 (7), 121 (9), 95 (7), 81 (12), 69 (22); IR (KBr): ν = 1617, 1590, 1525, 1486, 1455, 1394, 1347, 1205, 1159, 1093, 827 cm⁻¹. Anal. calcd for C₁₈H₁₃NO₅: C, 63.59; H, 4.25; N, 3.97. Found: C, 64.36; H, 4.16; N, 3.88.

Results and Discussion

The full characterisation of compounds **3**, **4** and **5** is presented in the Tables 2–6. The ¹H NMR spectra of the compounds were well resolved, and unambiguous chemical shift assignments were based on the multiplicity pattern of ¹H resonances and also on the use of homonuclear ¹H–¹H COSY spectra.

Some typical proton and carbon resonances can be found in the NMR spectra of the 2'-(nitrocinnamoyloxy)acetophenones **3a**-j: namely, it is possible in the ¹H NMR spectra of all 2'-(nitrocinnamoyloxy)acetophenones **3a**-j to identify the resonances of the vinylic protons H- α and H- β at $\delta = 6.51 - 7.12$ ppm and 7.86-8.28 ppm, respectively. These two signals appear in all spectra as a pair of doublets, and the determination of its coupling constants, $J(H-\alpha,H-\beta) = 15.8-16.2$ Hz, allowed identification of the trans configuration of this double bond. From the analysis of the ¹³C NMR spectra of the 2'-(nitrocinnamoyloxy)acetophenones **3a**-j and applying two-dimensional heteronuclear correlation experiments (HSQC, ¹H, ¹³C), the resonances of C- α at δ = 119.9–122.1 ppm and of C- β at δ = 141.7–144.9 ppm were identified. As expected, C- β is deshielded relative to C- α due to conjugation of the vinylic system with the carbonyl group. All other signals of protonated carbons have also been identified by this technique.

The signals corresponding to quaternary carbons have been assigned by applying HMBC spectroscopy. Thus, for example, one can find a correlation between the signal of H- α at $\delta = 6.51-7.12$ ppm and the signal corresponding to the resonance of C-1". The signal of this carbon appears at very

different frequencies depending on the substitution pattern: for the *ortho*-nitrated derivatives (**a**, **d** and **g**), C-1" appears at $\delta = 128.9-130.1$ ppm, for the *meta*-nitrated derivatives (**b**, **e**, **h** and **j**) its appears at $\delta = 135.7-136.7$ ppm and for the *para*nitrated derivatives (**c**, **f**, and **i**), it appears at $\delta = 140.0-140.2$ ppm. In addition, HMBC spectra allowed finding the correlations between the H- β signal at $\delta = 7.86-8.28$ ppm and the signals of C-2"/C-6" and the signal of the carbonyl group of the ester ($\delta = 163.9-164.8$ ppm).

In the ¹H NMR spectra of each 3-hydroxy-1-(2-hydroxyphenyl)-5-(nitrophenyl)-2,4-pentadien-1-one, 4a-j, the presence of two signals can be observed at $\delta~=~$ 10.73–12.63 ppm and δ 14.63-15.31 ppm, which are due to the protons involved in hydrogen bonds. The former signals correspond to resonances of the phenolic protons, whereas the latter are due to the 3-OH protons. From the ¹H NMR spectra, one can be also identify a singlet at $\delta = 6.38-6.96$ ppm corresponding to the resonance of H-2 and the presence of two signals at $\delta = \delta$ 6.99–7.55 ppm and δ = 7.61–7.85 which were attributed to H-4 and H-5. From the values of the coupling constants ³J(H-4, H-5), it was possible to establish the trans configuration of these two protons. On the basis of ¹³C NMR the following assignments were made: (i) the C-2 signal at $\delta = 99.8 - 105.6$ ppm, (ii) the C-4 and C-5 signals at $\delta = 126.2-128.3$ ppm and at $\delta = 133.0 - 137.2$ ppm, respectively, and (iii) the carbonyl (C-1) signal at $\delta = 186.1 - 194.7$ ppm.

The NMR spectra of nitro-2-styrylchromones **5a**-**j** show some further typical proton and carbon resonances, namely those of H-3 (singlet at $\delta = 6.22-6.56$ ppm), C-3 ($\delta = 160.9-167.0$ ppm) and C-4 ($\delta = 176.5-178.2$ ppm). The C-4 assignment is based on their high frequency value since it is the most deshielded carbon atom of 2-styrylchromones **5a**-**j** while that of C-3 is based on the correlation with H-3 in the HSQC of **5a**-**j**. The assignments of all carbon resonances of 2-styrylchromones **5a**-**j** are based on the analysis of the HSQC and HMBC spectra. Figure 1 shows some of the typical connectivities found in their HMBC spectra.

Taking 5,7-dimethoxy-3'-nitro-2-styrylchromone **(5j**, Fig. 2a) as an example, one can identify three singlets at $\delta = 3.93$, 3.96 and 6.22 ppm in the ¹H NMR spectra corresponding to the two OCH₃ and to H-3, respectively (Fig. 2b). In addition, one can assign a pair of doublets corresponding to the resonances of H- α and H- β protons at $\delta = 6.81$ and δ 7.51 ppm, respectively; the



Figure 1. Typical connectivities found in the 2-styrylchromones HMBC spectra.



iii) DMSO/I₂, 80-90 °C or DMSO/p-Toluenesulfonic acid, 80-90 °C

For compounds 3, 4 and 5

	а	b	с	d	е	f	g	h	i	j
R ¹	Н	н	н	OMe	OMe	OMe	н	н	н	OMe
R ²	Н	н	н	Н	н	н	OMe	OMe	OMe	OMe
R ³	NO ₂	Н	Н	NO ₂	н	н	NO_2	н	н	н
\mathbb{R}^4	н	NO_2	Н	Н	NO ₂	н	н	NO ₂	н	NO ₂
R⁵	Н	н	NO ₂	Н	н	NO_2	н	н	NO ₂	н

Scheme 1. Structures of compounds 1 to 5.

corresponding coupling constants $J(H-\alpha, H-\beta) = 16.1$ Hz indicate a trans configuration of this double bond (Fig. 3) and a triplet signal at a high frequency value of $\delta = 8.37$ ppm and a small coupling constant (J = 2.1 Hz). The latter signal corresponds to H-2' (adjacent to the nitro group) and its multiplicity results from the ⁴J couplings with the H-4' and H-6' protons.

Given the structure of the compound, the spectrum must also display two doublets corresponding to the resonances of H-6 and

H-8 with a small ⁴J coupling constant. Indeed, two doublets at $\delta = 6.37$ ppm and $\delta = 6.54$ ppm can be identified with a coupling of 2.3 Hz. The unambiguous assignment of these signals to H-6 and H-8 was verified by analysis of the HMBC spectrum. Further assignments are (i) the signals corresponding to methoxy carbons at $\delta = 55.8$ and 56.4 ppm; (ii) the C-3 signal at $\delta = 113.5$ ppm; (iii) the C- α and C- β at $\delta = 123.7$ and 132.8 ppm, respectively; (iv) the C-2' signal at $\delta = 122.2$ ppm.



Figure 2. ¹H NMR spectra of 5,7-dimethoxy-3'-nitro-2-styrylchromone (5j) in CDCl₃.



Figure 3. Expansion of the ¹H NMR spectra of 5,7-dimethoxy-3'-nitro-2-styrylchromone (5j) in CDCl₃.

In order to confirm the assignments based on HSQC and COSY spectra and to deduce more information about the structure of 2-styrylchromone **5***j*, a 2D HMBC spectrum was recorded, resulting in (i) H-3 signal at δ (H-3) = 6.36 ppm, which is correlated with the carbon resonances of C-10, C- α and C-2, at δ = 114.6, 123.7 and 157.7 ppm, respectively; (ii) the H- α signal at δ (H- α) = 6.81 ppm, which shows a long-range correlation with the carbon resonances

for C-3, C- β , C-1' and C-2, at $\delta = 114.6$, 123.7 and 157.7 ppm, respectively; (iii) the doublet signal at $\delta = 7.85$ ppm, which is correlated with the carbon resonances for C-2' at $\delta = 122.2$ ppm and C- β at $\delta = 132.8$ ppm. The signals of H-4' and H-5' were identified by their multiplicities and those of their attached carbons by HSQC.

Finally, a clear allocation of H-6 and H-8 is still missing. For the analysis of the HMBC spectrum, both doublet signals are correlated

Table	2. ¹ H NMR c	chemical shifts (8 in	ppm), multiplic	ities and coupli	ng constants	(/ in Hz) for	compound	s 3a -j						
	H-3′	H-4′	H-5′	,9-Н	H-α	heta-H	H-2″	H-3‴	H-4″	H-5″	H-6″	CH ₃	OCH ₃	OCH ₃
3a	7.34 d	7.69 ddd	7.46 t	7.94 dd	6.94 d	8.15 d	I	8.16 d	7.74 dd	7.85 t	8.08 d	2.52 s	I	I
	J = 8.0	J = 1.2; 7.5; 8.0	J = 7.5	J = 1.2; 7.5	J = 16.0	J = 16.0	I	J = 7.5	J = 0.7; 7.5	J = 7.5	J = 7.5	I	I	I
Зb	7.21 d	7.56-7.62 m	7.38 dt	7.64 d	6.82 d	7.93 d	8.46 t	I	8.28 dd	7.91 d	7.86 dd	2.59 s	I	I
	J = 1.1; 8.1	I	J = 1.1; 7.8	J = 7.8	<i>J</i> = 16.2	<i>J</i> = 16.2	J = 1.9	I	J = 1.9; 8.0	J = 8.0	J = 1.9; 8.0	I	I	I
ž	7.20 d	7.58 ddd	7.37 dt	7.86 dd	6.81 d	7.91 d	7.74 d	8.26 d	I	8.26 d	7.74 d	2.58 s	I	I
	J = 1.1; 8.2	J = 1.7; 7.8; 8.2	J = 1.1; 7.8	J = 1.7; 7.8	<i>J</i> = 16.0	<i>J</i> = 16.0	J = 8.8	J = 8.8	I	J = 8.8	J = 8.8	I	I	I
3d	6.92 d	I	7.00 dd	7.97 d	6.93 d	8.13 d	I	8.12 dd	7.73 ddd	7.85 dt	8.07 dd	2.51 s	3.86 s	I
	J = 2.6	I	J = 2.6; 8.8	J = 8.8	<i>J</i> = 15.8	<i>J</i> = 15.8	I	J = 1.3; 8.0	J = 1.2; 7.6; 8.0	J = 1.3; 7.6	J = 1.2; 7.6	I	I	I
Зe	6.87 d	I	6.96 dd	7.93 d	7.12 d	7.98 d	8.62 t	I	8.24–8.29 m	7.72 t	8.24-8.29 m	2.47 s	3.83 s	I
	J = 2.5	I	J = 2.5; 8.8	J = 8.8	J = 16.1	J = 16.1	J = 1.8	I	I	J = 8.0		I	I	I
зf	6.89 d	I	6.98 dd	7.96 d	7.12 d	7.95 d	8.09 d	8.27 d	I	8.27 d	8.09 d	2.48 s	3.84 s	I
	J = 2.6	I	J = 2.6; 8.8	J = 8.8	<i>J</i> = 16.1	<i>J</i> = 16.1	J = 8.8	J = 8.8	I	J = 8.8	J = 8.8	I	I	I
3g	6.84 dd	7.40 t	6.87 dd	I	6.51 d	8.28 d	I	8.08 dd	7.55–7.61 m	7.69-7.71 m	7.69-7.71 m	2.54 s	3.89 s	I
	J = 0.7; 8.3	J = 8.3	J = 0.7; 8.3	I	<i>J</i> = 15.8	<i>J</i> = 15.8	I	J = 0.9; 7.6	I	I	I	I	I	I
Зh	6.80 dd	7.40 t	6.87 d	I	6.70 d	7.86 d	8.42 t	I	8.26 ddd	7.61 t	7.84 d	2.53 s	3.89 s	I
	J = 0.5; 8.2	J = 8.2	J = 8.2	I	J = 16.0	<i>J</i> = 16.0	J = 1.9	I	J = 0.8; 1.9; 8.4	J = 8.4	J = 8.4	I	I	I
ä	6.89 dd	7.50 t	7.10 d	I	7.06 d	7.94 d	8.10 d	8.28 d	I	8.28 d	8.10 d	2.43 s	3.88 s	I
	J = 0.5; 8.3	J = 8.3	J = 8.3	I	J = 16.0	<i>J</i> = 16.0	J = 8.9	J = 8.9	I	J = 8.9	J = 8.9	I	I	I
3j	6.31 d	I	6.41 d	I	6.71 d	7.86 d	8.43 t	I	8.27 ddd	7.61 t	7.85 d	2.50 s	3.84 s	3.87 s
	J = 2.2	I	J = 2.2	I	<i>J</i> = 16.0	<i>J</i> = 16.0	<i>J</i> = 1.9	I	J = 0.9; 1.9; 8.1	J = 8.1	J = 8.1	I	I	I

Table	3. ¹ H NMR ch	emical shifts (δ	in ppm), multipli	cities and coupl	ling constar	nts (J in Hz)	for compounds 4	ła−i							
	H-3′	H-4′	H-5′	,9-Н	H-2″	H-3″	H-4″	H-5″	H-6″	H-2	H-4	H-5	0H-2′	0H-3	OCH ₃
4a	6.96-7.04 m -	7.48 dd J = 1.2; 7.7	6.96-7.04 m _	7.87 dd J = 1.2; 7.0	1 1	8.06 d J = 7.6	7.65 t J = 7.6	7.78 d J = 7.6	7.99 d J = 7.6	6.94 s -	7.04 d J = 16.0	7.85 d J = 16.0	11.34 s _	15.31 s _	I I
4b	6.98-7.03 m -	7.50 dt J = 1.6; 7.8	6.98-7.03 m -	7.88 dd J = 1.6; 8.0	8.59 d J = 1.7	1 1	7.73 dt J = 1.7; 7.8	8.22–8.25 m -	8.18 d J = 7.8	6.96 s _	7.25 d J = 16.0	7.74 d J = 16.0	11.38 s _	15.26 s _	I I
4c	7.00 d J = 8.0	7.49 dt J = 1.4; 8.0	7.00 d J = 8.0	7.88 dt J = 1.4; 8.0	7.97 d J = 8.7	8.25 d J = 8.7	1 1	8.25 d J = 8.7	7.97 d J = 8.7	6.94 s -	7.19 d J = 16.0	7.68 d J = 16.0	11.18 s _	15.16 s _	I I
4d	6.52 d J = 2.3	1 1	6.59 dd J = 2.3; 9.1	7.87 d J = 9.1	1 1	7.97 d J = 8.0	7.64–7.72 m -	7.64–7.72 m –	8.07 d J = 8.0	6.86 s -	6.09 d J = 15.6	7.81 d J = 15.6	12.03 s _	14.84 s -	3.82 s -
4e	6.51 d J = 2.4	1 1	6.59 dd J = 2.4; 9.0	7.86 d J = 9.0	8.55 s -	1 1	8.23 dd J = 1.7; 7.9	7.73 t J = 7.9	8.15 d J = 7.9	6.86 s -	7.18 d J = 16.0	7.69 d J = 16.0	12.05 s _	14.87 s _	3.83 s -
4f	6.47 d J = 1.7	1 1	6.59 dd J = 1.7; 8.9	7.87 d J = 8.9	8.28 d J = 8.4	7.97 d J = 8.4	1 1	7.97 d J = 8.4	8.28 d J = 8.4	6.88 s -	7.18 d J = 15.7	7.67 d J = 15.7	12.00 s _	14.86 s _	3.82 s _
49	6.55 d J = 8.3	7.29 t J = 8.3	6.57 d J = 8.3	1 1	1 1	8.07 d J = 8.0	7.66 t J = 8.0	7.78–7.83 m -	7.98 d J = 8.0	6.38 s -	6.99 d J = 15.4	7.82 d J = 15.4	10.73 s _	14.88 s _	3.82 s _
4h	6.55 d J = 8.3	7.29 t J = 8.3	6.58 d J = 8.3	1 1	8.58 s -	1 1	8.23 dd J = 1.8; 8.0	7.78 t J = 8.0	8.17 d J = 8.0	6.40 s -	7.20 d J = 16.0	7.61 d J = 16.0	10.77 s _	15.02 s _	3.82 s _
4i	6.43 d J = 8.3	6.35 d J = 8.3	6.70 d J = 8.3	1 1	8.26 d J = 8.8	8.10 d J = 8.8	1 1	8.10 d J = 8.8	8.26 d J = 8.8	6.87 s _	7.55 d J = 15.8	7.63 d J = 15.8	12.63 s _	14.63 s _	3.94 s -

Table	4. ¹³ C N	MR chemi	cal shifts (δ	in ppm) fo	r compoun	ıds 3a – j anı	d 4a−i												
	C-1	C-2	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-1″	C-2″	C-3″	C-4′′	C-5″	C-6″	C=0	C-a	C-β	OCH ₃	OCH ₃
3a	197.6	29.6	130.8	148.2	123.9	133.7	126.5	130.4	129.0	148.4	124.9	131.5	134.1	129.5	164.2	121.5	141.8	I	I
Зb	197.6	29.4	130.8	148.8	123.7	133.5	126.3	130.0	136.7	122.7	148.6	124.9	130.3	133.9	164.5	120.1	144.1	I	I
ğ	197.5	29.3	130.7	148.7	123.6	133.4	126.2	130.2	140.0	128.9	124.1	148.6	124.1	128.9	164.3	121.1	143.9	I	I
зd	195.9	29.7	123.3	151.1	109.8	163.8	112.5	133.0	129.3	148.8	125.3	131.8	134.5	129.9	164.4	122.1	144.9	56.4	I
Зe	195.4	29.3	123.0	150.8	109.4	163.4	111.8	132.6	135.7	123.3	148.3	125.0	130.4	134.4	164.3	120.3	144.1	55.9	I
Зf	195.5	29.2	122.9	150.7	109.5	163.4	111.9	132.7	140.2	129.8	124.1	148.3	124.1	129.8	164.2	121.6	143.8	56.0	I
3g	200.6	31.7	124.2	147.4	115.1	131.0	108.8	157.4	130.1	148.2	125.0	130.7	133.6	129.2	163.8	121.7	142.3	56.0	I
Зh	200.5	31.7	124.2	147.5	115.0	131.2	108.9	157.5	135.7	122.7	148.6	124.9	130.0	133.8	164.3	119.9	144.0	56.0	I
3:	199.7	31.6	124.0	148.4	115.1	131.4	109.7	157.0	140.1	129.9	123.9	146.8	123.9	129.9	164.1	121.0	144.2	56.3	I
3j	193.3	32.0	116.9	149.5	100.0	162.4	96.7	159.4	135.8	122.7	148.6	124.9	130.0	133.8	164.4	120.1	143.9	55.6	56.0
	C-1	C-2	C-3	C-4	C-5	C-1′	C-2′	C-3/	٦ ل	4, 0	-5′	C-6′	C-1″	C-2″	C-3″	C-4″	C-5″	C-6″	OCH ₃
4a	192.8	101.8	175.5	128.3	133.8	121.0	160.1	1 118.2	135	5.8 11	9.9 1	30.0	130.2	148.8	125.2	131.0	134.2	129.3	I
4b	192.8	101.6	175.9	126.7	137.2	121.0	160.1	1 118.2	135	.8 11	9.9 1	30.0	137.0	122.7	148.8	130.9	124.6	134.8	I
4	192.8	101.6	174.9	127.7	136.3	120.7	159.7	7 117.8	135	5.5 11	9.9 1	29.8	141.4	129.1	124.1	147.7	124.1	129.1	I
4d	192.8	100.0	172.7	127.8	135.8	113.2	163.4	4 101.4	165	5.6 1C	17.7	31.6	130.5	148.3	128.8	132.6	131.4	124.8	55.7
4e	192.7	99.8	173.2	126.2	135.8	113.2	163.4	4 101.4	165	5.6 1C	1.7 1	31.3	136.9	122.1	148.4	124.1	130.5	134.3	55.7
4f	192.8	100.3	172.8	127.6	135.6	113.3	163.5	3 101.4	165	5.6 1G	17.7	31.6	141.5	129.0	124.2	147.6	124.2	129.0	55.7
4g	194.7	105.6	172.9	127.7	133.0	114.0	158.5	3 109.3	133	3.0 10	12.4 1	58.0	129.9	148.3	124.8	130.5	133.7	128.9	55.9
4h	194.4	105.4	173.6	126.2	136.8	113.9	158.4	4 109.4	133	3.0 1C	12.3 1	58.1	136.3	122.3	148.4	124.1	130.4	134.2	55.9
i4	186.1	104.6	172.1	128.0	135.8	115.2	160.₄	4 111.2	135	5.7 1C	18.4 1	64.2	140.4	124.2	123.6	151.6	123.6	124.2	55.9

Table	<mark>е 5. ¹Н N</mark>	MR chemical s	shifts (δ in ppm), mul	ltiplicities and coup	ling constants (J	in Hz) for co	ompounds 5a –j							
	Н-3	H-5	H-6	Н-7	Н-8	H-2″	H-3′	H-4′	H-5′	H-6′	Η-α	θ-Н	OCH ₃	OCH ₃
5a	6.55 s _	9.05 dd J = 1.5; 7.7	7.49 t J = 0.8; 7.7	8.03 dt J = 1.5; 7.7	7.70 d J = 7.7	1 1	8.09 dd J = 1.0; 8.0	7.66 t J = 8.0	7.84 t J = 8.4	7.96-7.97 m -	7.26 d J = 16.0	7.93 J = 16.0	1 1	1 1
5b	6.50 s _	8.00 dd J = 1.6; 8.4	7.46 ddd J = 1.0; 7.0; 8.4	7.79–7.85 m -	7.68 d J = 8.7	8.54 t J = 1.7	1 1	8.20 dd J = 1.7; 8.0	7.73 t J = 8.0	8.14 d J = 8.0	7.44 d J = 16.0	7.81 d J = 16.0	1 1	1 1
50	6.56 s _	8.04 d J = 7.6	7.50 d J = 7.6	7.84 ddd J = 1.7; 7.6; 8.2	7.71 d J = 8.2	7.99 d J = 8.8	1 1	8.29 d J = 8.8	8.29 d J = 8.8	7.99 d J = 8.8	7.43 d J = 16.3	7.81 d J = 16.3	1 1	1 1
5d	6.33 s -	8.16 d J = 8.7	6.95–7.02 m _	1 1	7.20 d J = 2.2	1 1	8.13 d J = 8.0	7.60 t J = 8.0	7.80 t J = 8.0	7.99 d J = 8.0	6.94 d J = 15.9	7.89 d J = 15.9	3.90 s _	
5e	6.34 s -	8.11 d J = 8.8	6.95–7.01 m _	1 1	6.95-7.01 m -	8.643 t J = 2.0	1 1	8.23 dt J = 2.0; 7.9	7.61 t J = 7.9	7.90 d J = 7.9	6.91 d J = 16.0	7.62 d J = 16.0	3.95 s _	1 1
5f	6.33 s _	8.30 d J = 8.4	6.95 dd J = 2.2; 8.4	1 1	7.06 d J = 2.2	7.81 d J = 8.7	8.12 d J = 8.7	1 1	8.12 d J = 8.7	7.81 d J = 8.7	7.44 s J = 15.1	7.77 d J = 15.1	3.88 s -	1 1
59	6.42 s -	1 1	7.05 d J = 8.0	7.69–7.78 m -	7.22 d J = 7.2	1 1	8.15 dd J = 1.0; 8.0	7.69-7.78 m -	7.89 t J = 8.0	8.03 d J = 8.0	7.24 d J = 16.0	7.91 d J = 16.0	3.92 s _	1 1
5h	6.30 s -	1 1	6.83 d J = 8.1	7.61 d J = 8.1	7.11 dt J = 0.9; 8.1	8.41 t J = 2.0	1 1	8.22 ddd J = 0.9; 2.0; 8.0	7.62 d J = 8.0	7.90 d J = 8.0	6.86 d J = 16.0	7.55 d J = 16.0	4.00 s _	1 1
5i	6.31 s _	1 1	6.84 dd J = 0.7; 8.4	7.52-7.62 m -	7.11 dd J = 0.7; 8.4	7.70 d J = 8.8	8.28 d J = 8.8	1 1	8.28 d J = 8.8	7.70 d J = 8.8	6.87 d J = 16.0	7.58 d J = 16.0	4.00 s _	1 1
5j	6.22 s _	1 1	6.37 d J = 2.3	1 1	6.54 d J = 2.3	8.37 t J = 2.1	1 1	8.18 ddd J = 0.8; 2.1; 8.0	7.58 t J = 8.0	7.85 d J = 8.0	6.81 d J = 16.1	7.51 d J = 16.1	3.93 s _	3.96 s -

Tabl	e 6. ¹³ CI	NMR chemi	ical shifts (s in ppm) f	or compou	inds 5a-j													
	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-1,	C-2′	C-3′	C-4′	C-5′	C-6′	OCH ₃	OCH ₃	C-α	C-β
5a	160.7	111.5	177.1	125.0	125.5	135.6	118.4	155.4	123.5	130.1	148.2	124.9	130.5	133.9	128.8	I	I	125.2	131.0
5b	161.0	111.1	177.1	124.9	125.4	134.5	118.2	155.5	123.5	136.9	122.1	148.4	123.9	130.5	133.8	I	I	123.5	134.0
ñ	160.6	111.2	176.8	124.6	124.8	134.2	118.0	155.3	123.4	141.3	128.5	123.8	147.5	123.8	128.5	I	I	125.2	133.8
5d	161.0	111.6	177.6	125.0	114.4	163.5	100.3	157.2	117.4	130.3	148.2	124.9	130.5	133.7	128.8	56.2	I	124.7	130.9
5e	160.1	111.9	177.7	127.1	114.3	164.4	100.3	157.7	118.0	136.8	122.2	148.7	124.0	130.0	132.9	55.9	I	123.3	133.4
5f	165.6	111.6	176.5	125.1	114.7	163.7	100.4	157.4	116.6	141.6	128.4	124.3	146.3	124.3	128.4	56.2	I	126.4	133.4
59	158.3	113.1	176.5	157.3	107.3	134.6	109.8	159.2	113.9	130.2	148.2	124.9	130.2	133.9	128.8	56.1	I	124.9	130.4
5h	158.3	113.4	178.2	159.8	106.5	134.0	109.9	158.0	114.6	136.8	122.1	148.7	123.9	130.0	132.9	56.5	I	123.0	133.4
2	158.2	113.7	178.2	159.8	106.5	134.1	109.9	158.0	114.7	141.2	128.1	124.3	148.0	124.3	128.1	56.5	I	124.2	133.4
5j	157.9	113.5	177.1	161.3	96.3	164.4	93.0	159.7	114.6	137.2	122.2	149.1	123.3	129.9	132.6	55.8	56.4	123.7	132.8

with the carbon resonance for C-10 at $\delta = 114.6$ ppm and with the carbon resonance for C-7 at $\delta = 164.4$ ppm, but only one of them shows a long-range correlation with C-5. Thus, it was possible to assign unambiguously the signals of H-6 ($\delta = 6.37$ ppm) and H-8 ($\delta = 6.54$ ppm).

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