

Organolead-mediated Arylation of Allyl β -Ketoesters: A Selective Synthesis of Isoflavanones and Isoflavones

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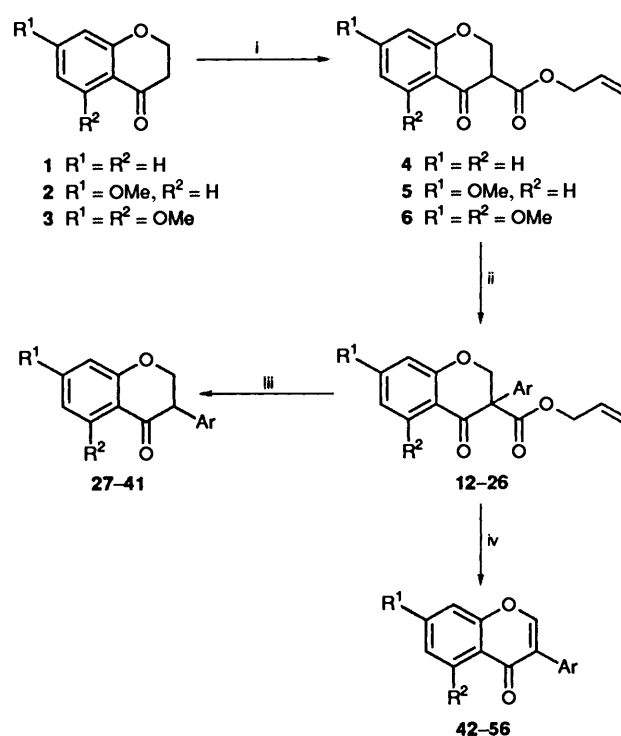
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Arylation of A-ring substituted and unsubstituted 3-allyloxycarbonylchroman-4-ones with aryllead(IV) triacetates followed by selective catalytic deallyloxycarbonylation affords isoflavanones or isoflavones in high overall yields. The highest yield in the arylation step was observed in the reaction of 5,7-dimethoxychroman-4-one with the more hindered 2,4,6-trimethoxyphenyllead triacetate.

Isoflavanones and isoflavones are biologically important natural products occurring mainly in species of the *Leguminosae* family. The isoflavonoids in general have shown a wide spectrum of biological activity, including oestrogenic, insecticidal, piscicidal and antifungal properties.^{1,2} In addition, isoflavanones and isoflavones are important intermediates in the total synthesis of, as well as in the metabolic pathways to, a number of more complex natural products such as coumestans, pterocarpanes and rotenoids.^{2,3} A number of synthetic routes have been reported for the synthesis of isoflavanones³⁻⁸ or isoflavones.⁹⁻¹⁵ Most of these rely on the synthesis of the carbon skeleton followed by cyclisation to form the pyran ring.

An ideal route would involve the coupling of the two preformed ring systems to give an intermediate which would then lead selectively to the isoflavanone or isoflavone systems. The coupling of two preformed rings was realised with the Heck-type palladium catalysed arylation.^{4,8,15} However this method could not lead to isoflavanones and isoflavones from a single intermediate and, moreover, was low yielding in the case of hindered aryl groups. The organobismuth-mediated ligand coupling route^{16,17} is high yielding but strongly limited by the lack of availability of suitably substituted arylbismuth(V) reagents. We now report that organolead-mediated arylation of chroman-4-one derivatives provides a general selective synthesis of isoflavanones and isoflavones, particularly the highly oxygenated species. The facile selective synthesis of appropriately substituted aryllead(IV) reagents led us to consider these as the most convenient reagents for a general synthesis of natural or non-natural isoflavonoid derivatives.

In general, arylation of ketonic substrates with aryllead reagents requires their activation as β -diketo compounds or as β -keto esters, although we recently reported the possible arylation of non-activated benzofuranones with these reagents. Activation of chroman-4-one with the previously reported groups (3-carbaldehyde or 3-oxalyl derivatives) seemed inappropriate. Indeed, in that report,¹⁶ monoarylation with arylbismuth(V) reagents was only observed in high yields at -23°C , a temperature at which arylation with aryllead derivatives generally does not occur. At higher temperatures, such as room temperature, removal of the activating group took place *in situ*, followed by a second arylation reaction to yield the 3,3-diarylchroman-4-one. More stable activated derivatives such as the 3-ethoxycarbonyl compounds were, therefore, desired. Unfortunately, our previous attempts to prepare such derivatives using classical carboxylation reagents proved unsuccessful. Eventually, these 3-carboxychroman-4-one derivatives were prepared by the method of Mander and Sethi.¹⁸ Our modification of that method, *i.e.* the use of an allyl ester,¹⁹ opened the way to the facile selective decarboxylation to iso-



Scheme 1 Reagents and conditions: i, LHMDs (1.1 equiv.), NCCO₂CH₂CHCH₂ (1.2 equiv.), THF, -78°C ; ii, ArPb(OAc)₃ 7-11 (1.1 equiv.), CHCl₃ (1.0 cm³ per 0.60 mmol substrate), pyridine (3.3 equiv.); iii, Pd(OAc)₂ (0.025 equiv.), PPh₃ (0.05 equiv.), HCO₂H (2.0 equiv.), Et₃N (2.0 equiv.), THF, room temp., 72 h; iv, Pd(OAc)₂ (0.05 equiv.), DPPE (0.05 equiv.), MeCN, reflux, 4 h

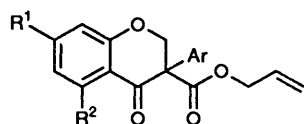
flavanones and isoflavones by Tsuji and co-workers methods.²⁰

3-Allyloxycarbonylchroman-4-ones **4-6** were prepared with 100% regioselectivity by reaction of allyl cyanofornate with the lithium enolate of chroman-4-ones **1-3** in good yields (62-80%). These enolates were preferably prepared with lithium bis(trimethylsilyl)amide (LHMDS) at -78°C in tetrahydrofuran (THF). A-Ring carboxylation *via ortho*-metallation of the *meta*-dimethoxyaryl system did not take place. In fact, in the case of 5,7-dimethoxychroman-4-one **3** the best yield for the synthesis of 3-allyloxycarbonyl derivatives was obtained (80% of **6** compared to 62% of **4**). In this case the lithium enolate of **3** was probably stabilised by the presence of the 5-methoxy substituent, thereby limiting undesirable reactions. The β -keto esters **4** and **5** were shown by their NMR spectra to consist of a mixture of keto and enol tautomers in CDCl₃ solution. No

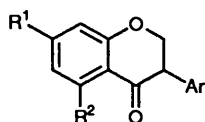
Table 1 Reaction of aryllead triacetates with β -keto esters 4–6

Substrate	ArPb(OAc) ₃	t/h	T/°C	Product (%)
4	7	10	R.t. ^a	12 (84)
4	8	2	R.t.	13 (75)
4	9	3	R.t.	14 (77)
4	10	12	40	15 (97)
4	11	3	R.t.	16 (86)
5	7	3	R.t.	17 (96)
5	8	3	R.t.	18 (92)
5	9	2	R.t.	19 (87)
5	10	6	R.t.	20 (95)
5	11	2	R.t.	21 (90)
6	7	2	40	22 (97)
6	8	3	40	23 (93)
6	9	3	40	24 (97)
6	10	3	40	25 (96)
6	11	2	R.t.	26 (99)

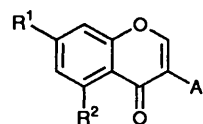
^a R.t. = room temperature. Those reactions which could not be readily monitored by TLC were carried out at 40 °C to ensure complete reaction.

Table 2 3-Allyloxycarbonyl-3-arylchroman-4-ones

Compound	R ¹	R ²	Ar
12	H	H	C ₆ H ₅
13	H	H	4-MeC ₆ H ₄
14	H	H	4-MeOC ₆ H ₄
15	H	H	2,4-(MeO) ₂ C ₆ H ₃
16	H	H	2,4,6-(MeO) ₃ C ₆ H ₂
17	MeO	H	C ₆ H ₅
18	MeO	H	4-MeC ₆ H ₄
19	MeO	H	4-MeOC ₆ H ₄
20	MeO	H	2,4-(MeO) ₂ C ₆ H ₃
21	MeO	H	2,4,6-(MeO) ₃ C ₆ H ₂
22	MeO	MeO	C ₆ H ₅
23	MeO	MeO	4-MeC ₆ H ₄
24	MeO	MeO	4-MeOC ₆ H ₄
25	MeO	MeO	2,4-(MeO) ₂ C ₆ H ₃
26	MeO	MeO	2,4,6-(MeO) ₃ C ₆ H ₂

Table 3 Isoflavanones prepared by reductive decarboxylation of 12–26

Compound	R ¹	R ²	Ar	Yield (%)
27	H	H	C ₆ H ₅	91
28	H	H	4-MeC ₆ H ₄	87
29	H	H	4-MeOC ₆ H ₄	94
30	H	H	2,4-(MeO) ₂ C ₆ H ₃	79
31	H	H	2,4,6-(MeO) ₃ C ₆ H ₂	83
32	MeO	H	C ₆ H ₅	92
33	MeO	H	4-MeC ₆ H ₄	97
34	MeO	H	4-MeOC ₆ H ₄	91
35	MeO	H	2,4-(MeO) ₂ C ₆ H ₃	89
36	MeO	H	2,4,6-(MeO) ₃ C ₆ H ₂	87
37	MeO	MeO	C ₆ H ₅	90
38	MeO	MeO	4-MeC ₆ H ₄	97
39	MeO	MeO	4-MeOC ₆ H ₄	87
40	MeO	MeO	2,4-(MeO) ₂ C ₆ H ₃	92
41	MeO	MeO	2,4,6-(MeO) ₃ C ₆ H ₂	89

Table 4 Isoflavones prepared by oxidative decarboxylation of 12–26

Compound	R ¹	R ²	Ar	Yield (%)
42	H	H	C ₆ H ₅	72
43	H	H	4-MeC ₆ H ₄	82
44	H	H	4-MeOC ₆ H ₄	74
45	H	H	2,4-(MeO) ₂ C ₆ H ₃	83
46	H	H	2,4,6-(MeO) ₃ C ₆ H ₂	83
47	MeO	H	C ₆ H ₅	74
48	MeO	H	4-MeC ₆ H ₄	90
49	MeO	H	4-MeOC ₆ H ₄	73
50	MeO	H	2,4-(MeO) ₂ C ₆ H ₃	82
51	MeO	H	2,4,6-(MeO) ₃ C ₆ H ₂	81
52	MeO	MeO	C ₆ H ₅	84
53	MeO	MeO	4-MeC ₆ H ₄	77
54	MeO	MeO	4-MeOC ₆ H ₄	83
55	MeO	MeO	2,4-(MeO) ₂ C ₆ H ₃	68
56	MeO	MeO	2,4,6-(MeO) ₃ C ₆ H ₂	72

enolisation of β -keto ester 6 was observed at the NMR sample concentration used (20 mg cm⁻³).

Subsequently, the β -keto esters 4–6 proved to be excellent substrates for organolead arylation. Reaction with a range of aryllead triacetates 7–11 proceeded in good to excellent yields to furnish the 3-allyloxycarbonyl-3-arylchroman-4-ones 12–26 (75–99%). It is noteworthy that no recognisable variation in yield was observed in proceeding from the phenylation reaction to the introduction of the bulky, electron rich, 2,4,6-trimethoxyphenyl group (Tables 1 and 2). Moreover, the presence of a 5-methoxy group in the chroman-4-one moiety was beneficial in spite of the steric hindrance. Indeed a quantitative yield (99%) was observed in the reaction of the β -keto ester 6 with the most hindered 2,4,6-trimethoxyphenyllead reagent 11.

The excellent catalytic deallyloxycarbonylation and deallyloxycarbonylation–dehydrogenation reactions of Tsuji and co-workers²⁰ were employed for the conversion of 3-aryl- β -keto esters 12–26 into isoflavanones and isoflavones respectively. Thus, 3-aryl- β -keto esters 12–26 were stirred at room temperature for 72 h under nitrogen with catalytic amounts of palladium(II) acetate (0.025 equiv.), triphenylphosphine (0.05 equiv.) and triethylammonium formate (2 equiv.) in THF. Chromatography on silica afforded the isoflavanones 27–41 in high yields (79–97%) (Table 3).

Isoflavones 42–56 were obtained in good to excellent yields after chromatography on silica (62–90%) by refluxing the 3-aryl- β -keto esters 12–26 under nitrogen for 4 h in acetonitrile containing catalytic amounts of palladium(II) acetate (0.05 equiv.) and 1,2-bis(diphenylphosphino)ethane [DPPE (0.05 equiv.)] (Table 4).

As a large number of aryllead(IV) triacetates can be selectively prepared in high yields by tin–lead exchange between aryltrialkyltin and lead tetraacetate,^{21,22} this procedure opens the way to the synthesis of a wide range of isoflavanones and isoflavones, including such highly hindered systems as the 2',4',6'-trisubstituted phenyl derivative which, as we have herein reported, can be easily obtained in high yield.

Experimental

M.p.s were determined on a Reichert-Jung Thermovar apparatus and are uncorrected. ¹H NMR spectra were recorded at either 60 MHz (JEOL JNM-PMX 60), 100 MHz (Bruker AC 100), 270 MHz (JEOL JNM-GX 270), 400 MHz (Bruker AM

400X) or 500 MHz (Varian Unity 500). ^{13}C NMR spectra were recorded at either 67.8 MHz (JEOL JNM-PMX270), 100.6 MHz (Bruker AM 400X) or 125.7 MHz (Varian Unity 500). The assignment of ^{13}C NMR signals for 3-allyloxycarbonylchroman-4-one **4** was aided by a ^{13}C , ^1H -COSY spectrum recorded on the Varian Unity 500. J Values are given in Hz. IR spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer. Mass spectra were recorded on a VG Analytical 770 mass spectrometer. Separations by column chromatography (CC) and flash chromatography (FC) were performed using Merck Kieselgel 60 (70–230 mesh ASTM) and 60 (230–400 mesh ASTM) respectively. Lead tetraacetate was dried prior to use over potassium hydroxide pellets at 0.1 mmHg for 3 h. Ether refers to diethyl ether. Light petroleum refers to the fraction boiling in the range 40–60 °C. All solvents were purified by standard techniques. Chroman-4-one **1** is commercially available (Janssen Chimica) as is phenyllead triacetate **52** (Alfa).

Preparation of Allyl Cyanofornate.^{18,23}—To a stirred mixture of allyl chloroformate (24.1 g, 0.2 mol) and anhydrous potassium cyanide (14.42 g, 0.22 mol) in dry dichloromethane (200 cm³) under nitrogen, was added, in one portion, 18-crown-6 (200 mg). Stirring was continued under nitrogen at room temp. for 18 h and then the reaction mixture was filtered and washed through with dichloromethane. The filtrate was fractionally distilled to give allyl cyanofornate (18.69 g, 84%) as a liquid; b.p. 132–133 °C; ν_{max} (neat)/cm⁻¹ 2247, 1752, 1230 and 1159; δ_{H} (60 MHz; CDCl₃) 4.76 (2 H, br s, J 10, OCH₂) and 5.24–6.4 (3 H, m, CH=CH₂).

Preparation of Chroman-4-ones.—7-Methoxychroman-4-one **2** [53%, m.p. 53 °C, (lit.,²⁴ m.p. 52–54 °C)] and 5,7-dimethoxychroman-4-one **3** [55%, m.p. 100–101 °C (lit.,²⁵ m.p. 99 °C)] were each prepared in two steps by the method of Naylor *et al.*²⁶ from resorcinol and phloroglucinol dihydrate respectively.

General Procedure for Preparation of 3-Allyloxycarbonylchroman-4-ones 4–6.—A solution of the appropriate chroman-4-one **1**, **2** or **3** (30 mmol) in anhydrous THF (100 cm³) was added dropwise over 20 min *via* a double tipped needle to a stirred 1 mol dm⁻³ solution of LHMDS in THF (33 cm³, 33 mmol) at –78 °C under nitrogen. After 30 min a solution of allyl cyanofornate (4 g, 36 mmol) in anhydrous THF (5 cm³) was added. The suspension was stirred at –78 °C for 15 min and then poured onto 10% aqueous NH₄Cl (200 cm³). The mixture was extracted with ether (3 × 50 cm³) and the combined ethereal extracts were washed with water (2 × 50 cm³). The organic phase was dried (MgSO₄), filtered and the solvent removed under reduced pressure. The resultant oil was purified by chromatography on silica using the solvent system specified.

3-Allyloxycarbonylchroman-4-one 4. CC (light petroleum–ether, 3:1) gave **4** as an oil consisting of a mixture of keto and enol tautomers (62%); ν_{max} (Nujol)/cm⁻¹ 1742, 1693, 1661 and 1628; δ_{H} (500 MHz; CDCl₃; keto tautomer) 7.93 (0.7 H, ddd, J 7.9, 1.7 and 0.4, 5-H), 7.50 (0.7 H, ddd, J 8.4, 7.5 and 2, 7-H), 7.05 (0.7 H, ddd, J 7.9, 7.5 and 1, 6-H), 6.99 (0.7 H, distorted ddd, J 8.5, 1 and 0.5, 8-H), 5.90 (0.7 H, ddt, J 17.2, 10.4 and 5.6, 3'-H), 5.31 (0.7 H, ddt, J 17.2, 3 and 1.5, 4'-H *cis*), 5.24 (0.7 H, ddt, J 10.5, 2.5 and 1, 4'-H *trans*), 4.81 (0.7 H, dd, J 11.5 and 8.5, 2-H equatorial), 4.69 (1.4 H, m, 2'-H), 4.64 (0.7 H, dd, J 11.5 and 4.5, 2-H axial) and 3.77 (0.7 H, dd, J 8.0 and 4.5, 3-H); δ_{H} (enol tautomer) 11.92 (0.3 H, br s, OH), 7.66 (0.3 H, ddd, J 7.7, 1.7 and 0.4, 5-H), 7.32 (0.3 H, ddd, J 8.2, 7.4 and 1.7, 7-H), 6.99 (0.3 H, m, 6-H), 6.85 (0.3 H, m, 8-H), 5.97 (0.3 H, ddt, J 17.2, 10.4 and 5.7, 3'-H), 5.36 (0.3 H, ddt, J 17.2, 3 and 1.5, 4'-H *cis*), 5.29 (0.3 H, m, 4'-H *trans*), 4.98 (0.6 H, s, 2-H) and 4.73 (0.6 H, m, 2'-H); δ_{C} (125.7 MHz; CDCl₃; keto tautomer) 52.61 (C-3), 66.19

(C-2'), 68.18 (C-2), 118.68 (C-4'), 120.55 (C-10), 121.86 (C-6), 127.62 (C-5), 131.36 (C-3'), 136.38 (C-7), 161.40 (C-9), 166.92 (C-1') and 186.78 (C-4); δ_{C} (enol tautomer) 63.76 (C-2), 65.19 (C-2'), 91.72 (C-3), 116.48 (C-8), 118.27 (C-10), 118.56 (C-4'), 121.48 (C-6), 124.60 (C-5), 131.89 (C-3'), 133.14 (C-7), 157.77 (C-9), 166.92 (C-1') and 186.78 (C-4); m/z 232.1 (M⁺, 36%), 174 (26), 147 (55), 120 (100), 92 (36) and 41.1 (48) (Found: C, 67.5; H, 5.4. C₁₃H₁₂O₄ requires C, 67.2; H, 5.2%).

3-Allyloxycarbonyl-7-methoxychroman-4-one 5. CC (light petroleum–ether, 2:1) (72%); m.p. 73.5–74.5 °C (from ether); ν_{max} (KBr)/cm⁻¹ 1726 and 1674; δ_{H} (400 MHz; CDCl₃; keto tautomer) 7.82 (0.9 H, d, J 8.8, 5-H), 6.57 (0.9 H, dd, J 8.8 and 2.4, 6-H), 6.38 (0.9 H, d, J 2.4, 8-H), 5.87 (0.9 H, ddt, J 17.2, 10.4 and 5.6, 3'-H), 5.28 (0.9 H, ddt, J 17.3, 3.0 and 1.5, 4'-H *cis*), 5.20 (0.9 H, ddt, J 10.5, 2.5 and 1.3, 4'-H *trans*), 4.76 (0.9 H, dd, J 11.6 and 8.2, 2-H equatorial), 4.65 (1.8 H, m, 2'-H), 4.58 (0.9 H, dd, J 11.6 and 4.5, 2-H axial), 3.80 (2.7 H, s, 7-OCH₃) and 3.68 (0.9 H, dd, J 8.1 and 4.5, 3-H); δ_{H} (enol tautomer) 7.54 (0.1 H, d, J 8.6, 5-H), 6.52 (0.1 H, dd, J 8.7 and 2.4, 6-H), 6.37 (0.1 H, d, J 2.4, 8-H), 4.94 (0.2 H, s, 2-H) and 3.77 (0.3 H, s, 7-OCH₃). The remaining enol ^1H signals merged almost completely with the baseline noise; δ_{C} (100.6 MHz; CDCl₃; keto tautomer) 52.30 (C-3), 55.74 (7-OCH₃), 66.22 (C-2'), 68.49 (C-2), 100.77 (C-8), 110.59 (C-6), 114.30 (C-10), 118.73 (C-4'), 129.39 (C-5), 131.40 (C-3'), 163.40 (C-9), 166.39 (C-7), 167.22 (C-1') and 185.43 (C-4); δ_{C} (enol tautomer) 55.74 (7-OCH₃), 64.23 (C-2), 65.04 (C-2'), 89.30 (C-3), 101.34 (C-8), 108.52 (C-6), 111.24 (C-10), 118.43 (C-4'), 126 (C-5), 132.05 (C-3'), 159.70 (C-9), 164 (C-7), 167.22 (C-1') and 185.43 (C-4); m/z 262 (M⁺, 25%), 177 (23), 150 (100), 122 (36), 107 (18) and 55 (18) (Found: C, 64.15; H, 5.4. C₁₄H₁₄O₅ requires C, 64.1; H, 5.4%).

3-Allyloxycarbonyl-5,7-dimethoxychroman-4-one 6. FC (ethyl acetate–light petroleum, 2:1) (80%); m.p. 75–77 °C (from ethanol); ν_{max} (KBr)/cm⁻¹ 1726 and 1668; δ_{H} (400 MHz; CDCl₃) 6.02 (1 H, distorted d, J 2.2, 6-H or 8-H), 6.01 (1 H, distorted d, J 2.3, 8-H or 6-H), 5.85 (1 H, ddt, J 17.2, 10.4 and 5.5, 3'-H), 5.26 (1 H, ddt, J 16, 3 and 1.4, 4'-H *cis*), 5.17 (1 H, ddt, J 8, 2.4 and 1.2, 4'-H *trans*), 4.68 (1 H, dd, J 11.4 and 8, 2-H equatorial), 4.62 (2 H, m, 2'-H), 4.50 (1 H, dd, J 11.3 and 4.4, 2-H axial), 3.82 (3 H, s, 5-OCH₃), 3.77 (3 H, s, 7-OCH₃) and 3.62 (1 H, dd, J 8.1 and 4.4, 3-H); δ_{C} (100.6 MHz; CDCl₃) 53.34 (C-3), 55.64 (7-OCH₃), 56.15 (5-OCH₃), 66.05 (C-2'), 67.79 (C-2), 93.16 (C-8 or C-6), 93.31 (C-6 or C-8), 105.32 (C-10), 118.53 (C-4'), 131.54 (C-3'), 162.65 (C-9), 164.60 (C-5), 166.20 (C-7), 167.46 (C-1') and 183.82 (C-4); m/z 292 (M⁺, 23%), 180 (100), 152 (49), 137 (51), 55 (42) and 41 (51) (Found: C, 61.6; H, 5.8. C₁₅H₁₆O₆ requires C, 61.6; H, 5.5%).

Preparation of Aryllead Triacetates.—4-Methylphenyllead triacetate **8** [54%, m.p. 84–87 °C (lit.,²⁷ m.p. 86–88 °C)], 4-methoxyphenyllead triacetate **9** [66%, m.p. 135–138 °C (lit.,²⁸ m.p. 139–141 °C)], 2,4-dimethoxyphenyllead triacetate **10** [75%, m.p. 151–153 °C (lit.,²⁹ m.p. 146–149 °C)] and 2,4,6-trimethoxyphenyllead triacetate **11** [67%, m.p. 173–177 °C (lit.,³⁰ m.p. 174–176 °C)] were prepared by direct plumblylation of the corresponding arenes.^{31,32}

General Procedure for Arylation of 3-Allyloxycarbonylchroman-4-ones 4–6.—Anhydrous pyridine (3.3 equiv.) was added to a mixture of the appropriate 3-allyloxycarbonylchroman-4-one **4**, **5** or **6** (1 equiv.) and aryllead triacetate (1.1 equiv.) in anhydrous chloroform (1 cm³ per 0.6 mmol of substrate). The resulting mixture was stirred at the indicated temperature for the times specified in Table 1. The reaction mixture was diluted with chloroform (50 cm³) and washed with 6% sulfuric acid (2 × 50 cm³). The aqueous phase was washed with chloroform (2 × 50 cm³). The combined organic extracts were washed with water (2 × 50 cm³), dried (MgSO₄), filtered

and the solvent removed under reduced pressure to yield an oil. The 3-allyloxycarbonylchroman-4-ones **12–26** were isolated as specified.

3-Allyloxycarbonyl-3-phenylchroman-4-one 12. CC (light petroleum–ether, 3:1); mp. 64–66 °C (from ether–light petroleum); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1730 and 1684; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 8 (1 H, ddd, *J* 8.1, 1.7 and 1.3, 5-H), 7.49–7.29 (6 H, m, 7-H and C₆H₅), 7.04 (1 H, ddd, *J* 8, 7 and 1.1, 6-H), 6.94 (1 H, dd, *J* 8.4 and 0.7, 8-H), 5.82 (1 H, m, 3''-H), 5.19 (2 H, m, 4''-H), 5.10 (1 H, d, *J* 11.9, 2-H equatorial), 4.95 (1 H, d, *J* 11.9, 2-H axial) and 4.68 (2 H, m, 2''-H); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 62.12 (C-3), 66.48 (C-2''), 71.86 (C-2), 117.75 (C-8), 118.57 (C-4''), 120.33 (C-10), 121.88 (C-6), 127.76 (C-5), 128.68–128.16 (C-2', C-3', C-4', C-5' and C-6'), 131.12 (C-3''), 132.79 (C-1'), 136.21 (C-7), 160.69 (C-9), 168.24 (C-1'') and 188.31 (C-4); *m/z* 308 (M⁺, 9%), 223 (28), 120 (100), 103 (25), 92 (32) and 41 (56) (Found: C, 73.7; H, 5.3. C₁₉H₁₆O₄ requires C, 74.0; H, 5.2%).

3-Allyloxycarbonyl-3-(4-methylphenyl)chroman-4-one 13. CC (light petroleum–ether, 3:1); mp. 40–43 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1753 and 1680; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.98 (1 H, dd, *J* 8 and 1.8, 5-H), 7.45 (1 H, ddd, *J* 8.5, 7.1 and 1.7, 7-H), 7.19 (4 H, m, Ar-H), 7.03 (1 H, ddd, *J* 7.6, 7.6 and 1, 6-H), 6.92 (1 H, d, *J* 8.4, 8-H), 5.82 (1 H, m, 3''-H), 5.29 (2 H, m, 4''-H), 5.08 (1 H, d, *J* 11.9, 2-H equatorial), 4.92 (1 H, d, *J* 11.9, 2-H axial), 4.67 (2 H, m, 2''-H) and 2.31 (3 H, s, 4'-CH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 21.07 (4'-CH₃), 61.86 (C-3), 66.44 (C-2''), 71.88 (C-2), 117.73 (C-8), 118.54 (C-4''), 120.41 (C-10), 121.81 (C-6), 127.64 (C-2' and C-6'), 128.16 (C-5), 129.41 (C-3' and C-5'), 129.80 (C-1'), 131.23 (C-3''), 136.10 (C-7), 138.20 (C-4'), 160.73 (C-9), 168.40 (C-1'') and 188.41 (C-4); *m/z* 322 (M⁺, 8%), 237 (42), 202 (17), 174 (51), 120 (100), 117 (94), 92 (61) and 41 (60) (Found: M⁺, 322.1194. C₂₀H₂₀O₇ requires *M*, 322.1209).

3-Allyloxycarbonyl-3-(4-methoxyphenyl)chroman-4-one 14. CC (light petroleum–ether, 3:1); mp. 72–73 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1740 and 1701; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.97 (1 H, dd, *J* 8 and 1.8, 5-H), 7.45 (1 H, ddd, *J* 8.5, 7.1 and 1.8, 7-H), 7.26 (2 H, m, 2'-H and 6'-H), 7.03 (1 H, ddd, *J* 7.5, 7.5 and 1.1, 6-H), 6.90 (3 H, m, 8-H, 3'-H and 5'-H), 5.83 (1 H, m, 3''-H), 5.20 (2 H, m, 4''-H), 5.08 (1 H, d, *J* 11.9, 2-H equatorial), 4.91 (1 H, d, *J* 11.9, 2-H axial), 4.67 (2 H, m, 2''-H) and 3.78 (3 H, s, 4'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.24 (4'-OCH₃), 61.45 (C-3), 66.45 (C-2''), 71.75 (C-2), 114.13 (C-2' and C-6'), 117.72 (C-8), 118.56 (C-4''), 120.33 (C-1'), 121.83 (C-6), 124.60 (C-10), 128.17 (C-5), 129.01 (C-3' and C-5'), 131.24 (C-3''), 136.13 (C-7), 159.51 (C-4'), 160.66 (C-9), 168.49 (C-1'') and 188.47 (C-4); *m/z* 338 (M⁺, 6%), 253 (8), 218 (100), 190 (40), 162 (37), 133 (61) and 28 (56) (Found: C, 70.7; H, 5.4. C₂₀H₁₈O₅ requires C, 71; H, 5.4%).

3-Allyloxycarbonyl-3-(2,4-dimethoxyphenyl)chroman-4-one 15. CC (light petroleum–ether, 2:1); mp. 145–147 °C (from chloroform–ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1722 and 1682; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 8.03 (1 H, dd, *J* 7.9 and 1.7, 5-H), 7.44 (1 H, ddd, *J* 8.7, 6.9 and 1.7, 7-H), 7.06 (1 H, m, 6-H), 6.92 (1 H, dd, *J* 8.3 and 0.6, 8-H), 6.73 (1 H, d, *J* 8.4, 6'-H), 6.50 (1 H, d, *J* 2.6, 3'-H), 6.34 (1 H, dd, *J* 8.6 and 2.6, 5'-H), 5.84 (1 H, m, 3''-H), 5.20 (2 H, m, 4''-H), 5.11 (1 H, d, *J* 11.4, 2-H equatorial), 4.90 (1 H, d, *J* 11.5, 2-H axial), 4.69 (2 H, m, 2''-H) and 3.75 (6 H, s, 2'-OCH₃ and 4'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.33 (4'-OCH₃), 55.54 (2'-OCH₃), 60.77 (C-3), 66.14 (C-2''), 71.61 (C-2), 99.84 (C-3'), 104.33 (C-5'), 115.94 (C-1'), 117.83 (C-8), 118.25 (C-4''), 121.13 (C-10), 121.73 (C-6), 127.82 (C-5), 129.31 (C-6'), 131.65 (C-3''), 135.96 (C-7), 158.38 (C-2'), 160.88 (C-9), 161.25 (C-4'), 168.92 (C-1'') and 189.18 (C-4); *m/z* 368 (M⁺, 52%), 283 (21), 248 (100), 220 (49), 163 (51) and 41 (73) (Found: C, 68.4; H, 5.5. C₂₁H₂₀O₆ requires C, 68.5; H, 5.5%).

3-Allyloxycarbonyl-3-(2,4,6-trimethoxyphenyl)chroman-4-one 16. FC (light petroleum–ether, 1:1); mp. 87–89 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1723 and 1688; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.99 (1 H, dd, *J* 7.9 and 1.7, 5-H), 7.42 (1 H, ddd, *J* 8.4,

7.1 and 1.7, 7-H), 7.03 (1 H, distorted ddd, *J* 7.7, 7.3 and 1.1, 6-H), 6.92 (1 H, dd, *J* 8.3 and 0.6, 8-H), 6.10 (2 H, s, 3'-H and 5'-H), 5.89 (1 H, m, 3''-H), 5.21 (2 H, m, 4''-H), 4.97 (1 H, d, *J* 11.5, 2-H equatorial), 4.88 (1 H, d, *J* 11.5, 2-H axial), 4.68 (2 H, d, *J* 5.5, 2''-H), 3.77 (3 H, s, 4'-OCH₃) and 3.54 (6 H, s, 2'-OCH₃ and 6'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.27 (4'-OCH₃), 55.71 (2'-OCH₃ and 6'-OCH₃), 58.72 (C-3), 65.98 (C-2''), 72.08 (C-2), 92.26 (C-3' and C-5'), 105.96 (C-1'), 117.45 (C-8), 117.92 (C-4''), 121.26 (C-6), 122.11 (C-10), 127.40 (C-5), 132 (C-3''), 134.66 (C-7), 159.06 (C-2' and C-6'), 160.79 (C-9), 161.04 (C-4'), 169.19 (C-1'') and 188.58 (C-4); *m/z* 398 (M⁺, 19%), 278 (100), 193 (67), 69 (40), 41 (48) and 28 (38) (Found: C, 66.6; H, 5.6. C₂₂H₂₂O₇ requires C, 66.3; H, 5.6%).

3-Allyloxycarbonyl-7-methoxy-3-phenylchroman-4-one 17. CC (benzene); m.p. 63–65 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1738 and 1694; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.92 (1 H, d, *J* 8.8, 5-H), 7.35 (5 H, m, C₆H₅), 6.60 (1 H, dd, *J* 8.9 and 2.5, 6-H), 6.36 (1 H, d, *J* 2.4, 8-H), 5.83 (1 H, m, 3''-H), 5.20 (2 H, m, 4''-H), 5.08 (1 H, d, *J* 11.9, 2-H equatorial), 4.91 (1 H, d, *J* 11.9, 2-H axial), 4.68 (2 H, m, 2''-H) and 3.80 (3 H, s, 7-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.66 (7-OCH₃), 61.93 (C-3), 66.44 (C-2''), 72.29 (C-2), 100.49 (C-8), 110.69 (C-6), 114.13 (C-10), 118.52 (C-4''), 127.81 (C-3' and C-5'), 128.25 (C-4'), 128.63 (C-2' and C-6'), 129.87 (C-5), 131.23 (C-3''), 133.23 (C-1'), 162.75 (C-9), 166.20 (C-7), 168.41 (C-1'') and 186.97 (C-4); *m/z* 338 (M⁺, 10%), 150 (100), 122 (25), 103 (16), 77 (10) and 41 (13) (Found: C, 71.2; H, 5.2. C₂₀H₁₈O₅ requires C, 71; H, 5.4%).

3-Allyloxycarbonyl-7-methoxy-3-(4-methylphenyl)chroman-4-one 18. CC (light petroleum–ether, 2:1); mp. 72–73 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1742 and 1696; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.91 (1 H, d, *J* 8.8, 5-H), 7.19 (4 H, m, Ar-H), 6.59 (1 H, dd, *J* 8.8 and 2.4, 6-H), 6.35 (1 H, d, *J* 2.4, 8-H), 5.84 (1 H, m, 3''-H), 5.21 (2 H, m, 4''-H), 5.06 (1 H, d, *J* 11.9, 2-H equatorial), 4.89 (1 H, d, *J* 11.7, 2-H axial), 4.67 (2 H, m, 2''-H), 3.79 (3 H, s, 7-OCH₃) and 2.31 (3 H, s, 4'-CH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 21.07 (4'-CH₃), 55.65 (7-OCH₃), 61.63 (C-3), 66.40 (C-2''), 72.26 (C-2), 100.48 (C-8), 110.63 (C-6), 114.13 (C-10), 118.49 (C-4''), 127.64 (C-3' and C-5'), 129.36 (C-2' and C-6'), 129.85 (C-5), 130.15 (C-4'), 131.29 (C-3''), 138.06 (C-1'), 162.72 (C-9), 166.14 (C-7), 168.56 (C-1'') and 187.11 (C-4); *m/z* 352 (M⁺, 8%), 150 (100), 122 (22), 117 (22) and 41 (32) (Found: C, 71.6; H, 5.95. C₂₁H₂₀O₅ requires C, 71.6; H, 5.7%).

3-Allyloxycarbonyl-7-methoxy-3-(4-methoxyphenyl)chroman-4-one 19. Precipitated as a white solid on addition of ether to the crude oil; mp. 95–96 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1740 and 1694; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.91 (1 H, d, *J* 8.8, 5-H), 7.26 (2 H, m, 2'-H and 6'-H), 6.88 (2 H, m, 3'-H and 5'-H), 6.59 (1 H, dd, *J* 9 and 2.4, 6-H), 6.36 (1 H, d, *J* 2.4, 8-H), 5.84 (1 H, m, 3''-H), 5.21 (2 H, m, 4''-H), 5.06 (1 H, d, *J* 11.9, 2-H equatorial), 4.88 (1 H, d, *J* 11.7, 2-H axial), 4.67 (2 H, m, 2''-H), 3.80 (3 H, s, 7-OCH₃) and 3.78 (3 H, s, 4'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.22 (4'-OCH₃), 55.65 (7-OCH₃), 61.20 (C-3), 66.39 (C-2''), 72.11 (C-2), 100.46 (C-8), 110.62 (C-6), 114.03 (C-3', C-5' and C-10), 118.49 (C-4''), 124.98 (C-1'), 128.98 (C-2' and C-6'), 129.85 (C-5), 131.27 (C-3''), 159.37 (C-4'), 162.66 (C-9), 166.15 (C-7), 168.64 (C-1'') and 187.16 (C-4); *m/z* 368 (M⁺, 11%), 218 (100), 190 (44), 162 (42), 133 (70) and 41 (44) (Found: C, 68.2; H, 5.65. C₂₁H₂₀O₆ requires C, 68.5; H, 5.5%).

3-Allyloxycarbonyl-3-(2,4-dimethoxyphenyl)-7-methoxychroman-4-one 20. CC (light petroleum–ether, 1:1); mp. 77–79 °C (from ether–light petroleum); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1721 and 1684; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.97 (1 H, d, *J* 9, 5-H), 6.72 (1 H, d, *J* 8.6, 6'-H), 6.63 (1 H, dd, *J* 8.8 and 2.4, 6-H), 6.49 (1 H, d, *J* 2.4, 8-H), 6.35 (1 H, d, *J* 2.6, 3'-H), 6.33 (1 H, dd, *J* 8.6 and 2.6, 5'-H), 5.87 (1 H, m, 3''-H), 5.22 (2 H, m, 4''-H), 5.08 (1 H, d, *J* 11.4, 2-H equatorial), 4.88 (1 H, d, *J* 11.4, 2-H axial), 4.69 (2 H, m, 2''-H), 3.81 (3 H, s, 7-OCH₃), 3.76 (3 H, s, OCH₃) and 3.75 (3 H, s, OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.32 (4'-OCH₃), 55.49 (2'-

OCH₃), 55.63 (7-OCH₃), 60.36 (C-3), 66.07 (C-2''), 71.81 (C-2), 99.72 (C-3'), 100.54 (C-8), 104.19 (C-5'), 110.55 (C-6), 114.92 (C-10), 116.20 (C-1'), 118.19 (C-4''), 129.42 (C-5 or C-6'), 129.52 (C-6' or C-5), 131.76 (C-3''), 158.37 (C-2'), 160.77 (C-4'), 163.27 (C-9), 166.06 (C-7), 169.06 (C-1'') and 187.89 (C-4); *m/z* 398 (M⁺, 12%), 248 (100), 220 (29), 163 (36) and 41 (38) (Found: C, 66.55; H, 5.6. C₂₂H₂₂O₇ requires C, 66.3; H, 5.6%).

3-Allyloxycarbonyl-3-(2,4,6-trimethoxyphenyl)-7-methoxychroman-4-one 21. Precipitated as a white solid on addition of ether to the crude oil; m.p. 124–125 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1730 and 1680; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.93 (1 H, d, *J* 8.8, 5-H), 6.59 (1 H, dd, *J* 8.9 and 2.4, 6-H), 6.38 (1 H, d, *J* 2.4, 8-H), 6.11 (2 H, s, 3'-H and 5'-H), 5.88 (1 H, m, 3''-H), 5.21 (2 H, m, 4''-H), 4.89 (2 H, s, 2-H), 4.67 (2 H, m, 2''-H), 3.84 (3 H, s, 4'-OCH₃), 3.81 (3 H, s, 7-OCH₃) and 3.78 (6 H, s, 2'-OCH₃ and 6'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.31 (4'-OCH₃), 55.54 (7-OCH₃), 55.89 (2'-OCH₃ and 6'-OCH₃), 58.53 (C-3), 65.99 (C-2''), 72.24 (C-2), 92.44 (C-3' and C-5'), 100.48 (C-8), 106.28 (C-1'), 109.84 (C-6), 115.63 (C-10), 117.91 (C-4''), 129.28 (C-5), 132.11 (C-3''), 159.19 (C-2' and C-6'), 161.09 (C-4'), 162.78 (C-9), 165.09 (C-7), 169.24 (C-1'') and 187.24 (C-4); *m/z* 428 (M⁺, 8%), 278 (100), 250 (22), 193 (52) and 41 (45) (Found: C, 64.6; H, 5.8. C₂₃H₂₄O₈ requires C, 64.5; H, 5.65%).

3-Allyloxycarbonyl-5,7-dimethoxy-3-phenylchroman-4-one 22. FC (benzene-ethyl acetate, 10:1); m.p. 91–93 °C (from ethanol-light petroleum); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1738 and 1684; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.33 (5 H, m, C₆H₅), 6.05 (1 H, d, *J* 2.2, 8-H), 5.98 (1 H, d, *J* 2.4, 6-H), 5.84 (1 H, m, 3''-H), 5.18 (2 H, m, 4''-H), 5.06 (1 H, d, *J* 11.7, 2-H equatorial), 4.91 (1 H, d, *J* 11.7, 2-H axial), 4.66 (2 H, m, 2''-H), 3.87 (3 H, s, 5-OCH₃) and 3.77 (3 H, s, 7-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.55 (7-OCH₃), 56.15 (5-OCH₃), 62.50 (C-3), 66.29 (C-2''), 71.15 (C-2), 93.06 (C-8 or C-6), 93.26 (C-6 or C-8), 105.06 (C-10), 118.29 (C-4''), 127.90 (C-3' and C-5'), 128.03 (C-4'), 128.43 (C-2' and C-6'), 131.48 (C-3''), 133.61 (C-1'), 162.96 (C-9), 163.95 (C-5), 166.04 (C-7), 168.71 (C-1'') and 185.42 (C-4); *m/z* 368 (M⁺, 4%), 180 (100), 152 (25), 137 (22), 103 (15) and 41 (4) (Found: C, 68.7; H, 5.2. C₂₁H₂₀O₆ requires C, 68.5; H, 5.5%).

3-Allyloxycarbonyl-5,7-dimethoxy-3-(4-methylphenyl)chroman-4-one 23. FC (benzene-ethyl acetate, 10:1); m.p. 99–100 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1736 and 1686; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.23 (2 H, d, *J* 8.2, 2'-H and 6'-H), 7.13 (2 H, d, *J* 8.2, 3'-H and 5'-H), 6.04 (1 H, d, *J* 2.4, 8-H), 5.98 (1 H, d, *J* 2.2, 6-H), 5.85 (1 H, m, 3''-H), 5.19 (2 H, m, 4''-H), 5.04 (1 H, d, *J* 11.7, 2-H equatorial), 4.89 (1 H, d, *J* 11.9, 2-H axial), 4.65 (2 H, m, 2''-H), 3.87 (3 H, s, 5-OCH₃), 3.76 (3 H, s, 7-OCH₃) and 2.30 (3 H, s, 4'-CH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 21.07 (4'-CH₃), 55.54 (7-OCH₃), 56.14 (5-OCH₃), 62.20 (C-3), 66.28 (C-2''), 71.10 (C-2), 93.04 (C-8 or C-6), 93.23 (C-6 or C-8), 105.05 (C-10), 118.27 (C-4''), 127.73 (C-3' and C-5'), 129.17 (C-2' and C-6'), 130.53 (C-4'), 131.56 (C-3''), 137.77 (C-1'), 162.96 (C-9), 163.92 (C-5), 165.98 (C-7), 168.86 (C-1'') and 185.61 (C-4); *m/z* 382 (M⁺, 4%), 180 (100), 152 (20), 137 (15), 117 (12) and 41 (9) (Found: C, 69; H, 6.0. C₂₂H₂₂O₆ requires C, 69.1; H, 5.8%).

3-Allyloxycarbonyl-5,7-dimethoxy-3-(4-methoxyphenyl)chroman-4-one 24. FC (ether-light petroleum, 5:1); m.p. 113–115 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1728 and 1688; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.28 (2 H, m, *J* 8.6, 2'-H and 6'-H), 6.85 (2 H, m, *J* 8.8, 3'-H and 5'-H), 6.04 (1 H, d, *J* 2.2, 8-H), 5.98 (1 H, d, *J* 2.2, 6-H), 5.85 (1 H, m, 3''-H), 5.20 (2 H, m, 4''-H), 5.04 (1 H, d, *J* 11.7, 2-H equatorial), 4.88 (1 H, d, *J* 11.7, 2-H axial), 4.67 (2 H, m, 2''-H), 3.87 (3 H, s, 5-OCH₃) and 3.77 (6 H, s, 7-OCH₃ and 4'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.19 (4'-OCH₃), 55.55 (7-OCH₃), 56.14 (5-OCH₃), 61.77 (C-3), 66.29 (C-2''), 70.96 (C-2), 92.99 (C-8 or C-6), 93.20 (C-6 or C-8), 104.86 (C-10), 113.84 (C-3' and C-5'), 118.30 (C-4''), 125.36 (C-1'), 129.06 (C-2' and C-6'), 131.53 (C-3''), 159.21 (C-4'), 162.94 (C-9), 163.86 (C-5), 165.98 (C-7), 168.88 (C-1'') and 185.71 (C-4); *m/z* 398

(M⁺, 5%), 180 (100), 152 (16), 133 (18) and 28 (16) (Found: C, 66.4; H, 5.55. C₂₂H₂₂O₇ requires C, 66.3; H, 5.6%).

3-Allyloxycarbonyl-5,7-dimethoxy-3-(2,4-dimethoxyphenyl)chroman-4-one 25. FC (ether-light petroleum, 5:1); m.p. 113–115 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1728 and 1676; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 6.79 (1 H, d, *J* 8.6, 6'-H), 6.47 (1 H, d, *J* 2.4, 3'-H), 6.32 (1 H, dd, *J* 11.6 and 2.6, 5'-H), 6.10 (1 H, d, *J* 2.4, 8-H), 5.97 (1 H, d, *J* 2.2, 6-H), 5.86 (1 H, m, 3''-H), 5.19 (2 H, m, 4''-H), 5.08 (1 H, d, *J* 11.4, 2-H equatorial), 4.85 (1 H, d, *J* 11.2, 2-H axial), 4.68 (2 H, m, 2''-H), 3.91 (3 H, s, 5-OCH₃), 3.78 (3 H, s, 7-OCH₃), 3.76 (3 H, s, OCH₃) and 3.75 (3 H, s, OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.27 (4'-OCH₃), 55.43 (2'-OCH₃), 55.57 (7-OCH₃), 56.15 (5-OCH₃), 60.90 (C-3), 65.90 (C-2''), 70.98 (C-2), 93.07 (C-8 or C-6), 93.17 (C-6 or C-8), 99.43 (C-3'), 103.99 (C-5'), 106.08 (C-10), 116.69 (C-1'), 117.86 (C-4'), 129.56 (C-6'), 132.08 (C-3''), 158.48 (C-2'), 160.58 (C-4'), 162.70 (C-9), 164.60 (C-5), 165.95 (C-7), 169.28 (C-1'') and 186.53 (C-4); *m/z* 428 (M⁺, 11%), 248 (100), 220 (38), 180 (48), 163 (43) and 41 (30) (Found: C, 64.5; H, 5.6. C₂₃H₂₄O₈ requires C, 64.5; H, 5.65%).

3-Allyloxycarbonyl-5,7-dimethoxy-3-(2,4,6-trimethoxyphenyl)chroman-4-one 26. FC (ether-light petroleum, 5:1); m.p. 130–131 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1744 and 1692; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 6.08 (3 H, m, 8-H, 3'-H and 5'-H), 5.98 (1 H, d, *J* 2.4, 6-H), 5.88 (1 H, m, 3''-H), 5.18 (2 H, m, 4''-H), 5.08 (1 H, d, *J* 11.4, 2-H equatorial), 4.80 (1 H, d, *J* 11.4, 2-H axial), 4.66 (2 H, m, 2''-H), 3.89 (3 H, s, 5-OCH₃), 3.77 (3 H, s, 7-OCH₃), 3.76 (3 H, s, 4'-OCH₃) and 3.58 (6 H, s, 2'-OCH₃ and 6'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.25 (4'-OCH₃), 55.44 (7-OCH₃), 55.98 (5-OCH₃, 2'-OCH₃ and 6'-OCH₃), 59.38 (C-3), 65.77 (C-2''), 71.56 (C-2), 92.25 (C-3' and C-5'), 92.76 (C-8 or C-6), 92.85 (C-6 or C-8), 106.38 (C-10), 106.99 (C-1'), 117.56 (C-4'), 132.36 (C-3''), 159.51 (C-2' and C-6'), 160.84 (C-4'), 162.05 (C-9), 163.73 (C-5), 164.57 (C-7), 169.98 (C-1'') and 186.39 (C-4); *m/z* 458 (M⁺, 10%), 278 (100), 250 (24), 193 (58) and 41 (40) (Found: C, 62.9; H, 5.7. C₂₄H₂₆O₉ requires C, 62.9; H, 5.7%).

General Procedure for Deallyloxycarbonylation of 3-Allyloxycarbonyl-3-arylchroman-4-ones 12–26.—Triphenylphosphine (131 mg, 0.5 mmol) and palladium(II) acetate (5.6 mg, 0.025 mmol) were dissolved in anhydrous THF (2 cm³) under nitrogen and stirred vigorously. A solution of formic acid (92 mg, 2 mmol) and triethylamine (253 mg, 2.5 mmol) in anhydrous THF (2 cm³) was then added. After 5 min a solution of the appropriate 3-allyloxycarbonyl-3-arylchroman-4-one (1 mmol) in anhydrous THF (2 cm³) was added. The resulting solution was stirred under nitrogen for 3 days. The mixture was then filtered through a short silica column and eluted with chloroform. The eluate was evaporated to yield an oil which was purified as specified.

Isosoflavanone 27. CC (light petroleum-ether, 6:1); m.p. 76–77 °C (from ethanol); lit.,⁴ m.p. 76–77 °C.

4'-Methylisoflavanone 28. CC (light petroleum-ether, 6:1); m.p. 84–86 °C (from ethanol); lit.,⁴ m.p. 83–84 °C.

4'-Methoxyisoflavanone 29. CC (light petroleum-ether, 6:1); m.p. 100 °C (from ethanol); lit.,⁴ m.p. 98–99 °C.

2',4'-Dimethoxyisoflavanone 30. CC (benzene); m.p. 78–80 °C (from ether-light petroleum); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1686, 1616 and 1603; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.98 (1 H, dd, *J* 7.9 and 1.8, 5-H), 7.49 (1 H, m, 7-H), 7.03 (3 H, m, 6-H, 8-H and 6'-H), 6.48 (2 H, m, 3'-H and 5'-H), 4.62 (1 H, dd, *J* 12.1 and 11, 2-H equatorial), 4.50 (1 H, dd, *J* 11 and 5.5, 2-H axial), 4.30 (1 H, dd, *J* 12.1 and 5.5, 3-H), 3.80 (3 H, s, 4'-OCH₃) and 3.76 (3 H, s, 2'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 47.93 (C-3), 55.39 (4'-OCH₃), 55.52 (2'-OCH₃), 70.90 (C-2), 99.19 (C-3'), 104.68 (C-5'), 115.79 (C-1'), 117.81 (C-8), 121.34 (C-6), 121.70 (C-10), 127.67 (C-5), 130.72 (C-6'), 135.59 (C-7), 158.42 (C-2'), 160.30 (C-4'), 161.87 (C-9) and 192.79 (C-4); *m/z* 284 (M⁺, 22%), 164 (100), 149 (69),

121 (56), 91 (23) and 77 (21) (Found: C, 71.7; H, 5.6. $C_{17}H_{16}O_4$ requires C, 71.8; H, 5.7%).

2',4',6'-Trimethoxyisoflavanone 31. Crystallised from chloroform-ether; m.p. 172–174 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1694 and 1607; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.98 (1 H, dd, J 7.8 and 1.8, 5-H), 7.46 (1 H, m, 7-H), 7.01 (2 H, m, 6-H and 8-H), 6.16 (2 H, s, 3'-H and 5'-H), 4.73 (1 H, dd, J 13.2 and 8.8, 2-H equatorial), 4.64 (1 H, dd, J 13.2 and 4.0, 2-H axial), 4.35 (1 H, dd, J 8.8 and 4, 3-H), 3.81 (3 H, s, 4'-OCH₃) and 3.73 (6 H, s, 2'-OCH₃ and 6'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 43.45 (C-3), 55.38 (4'-OCH₃), 55.74 (2'-OCH₃ and 6'-OCH₃), 69.62 (C-2), 91.17 (C-3' and C-5'), 104.02 (C-1'), 117.73 (C-8), 121.13 (C-6), 121.72 (C-10), 127.65 (C-5), 135.15 (C-7), 159.18 (C-2' and C-6'), 161.04 (C-4'), 161.87 (C-9) and 192.93 (C-4); m/z 314 (M^+ , 37%), 194 (93), 179 (100), 151 (21), 121 (35), 92 (18) and 28 (19) (Found: M^+ , 314.1157. $C_{20}H_{20}O_7$ requires M , 314.1158).

7-Methoxyisoflavanone 32. CC (light petroleum-ether, 2:1); m.p. 91–92 °C (from methanol); lit.,⁴ m.p. 92–93 °C; $\delta_{\text{H}}(100 \text{ MHz}; \text{CDCl}_3)$ 7.89 (1 H, d, J 8.8, 5-H), 7.30 (5 H, s, C_6H_5), 6.61 (1 H, dd, J 8.8 and 2.4, 6-H), 6.44 (1 H, d, J 2.3, 8-H), 4.65 (2 H, d, J 6.8, 2-H) and 3.98–3.84 (4 H, distorted t, 3-H and 7-OCH₃).

7-Methoxy-4'-methylisoflavanone 33. CC (light petroleum-ether, 2:1); m.p. 121–122 °C (from methanol); lit.,⁴ m.p. 122–123 °C; $\delta_{\text{H}}(100 \text{ MHz}; \text{CDCl}_3)$ 7.89 (1 H, d, J 8.8, 5-H), 7.16 (4 H, s, 2'-H, 3'-H, 5'-H and 6'-H), 6.60 (1 H, dd, J 8.9 and 2.4, 6-H), 6.44 (1 H, d, J 2.4, 8-H), 4.63 (2 H, d, J 7.0, 2-H), 3.95–3.84 (4 H, distorted t, 3-H and 7-OCH₃) and 2.32 (3 H, s, 4'-CH₃).

7,4'-Dimethoxyisoflavanone 34. CC (light petroleum-ether, 1:1); m.p. 129–130 °C (from methanol); lit.,⁴ m.p. 128–129 °C; $\delta_{\text{H}}(100 \text{ MHz}; \text{CDCl}_3)$ 7.89 (1 H, d, J 8.8, 5-H), 7.30 (2 H, m, 2'-H and 6'-H), 6.90 (2 H, m, 3'-H and 5'-H), 6.60 (1 H, dd, J 8.8 and 2.3, 6-H), 6.44 (1 H, d, J 2.1, 8-H), 4.62 (2 H, d, J 6.8, 2-H) and 4.08–3.78 (7 H, m, 3-H, 4'-OCH₃ and 7-OCH₃).

7,2',4'-Trimethoxyisoflavanone 35. Precipitated as a white solid on addition of ether to the crude oil; m.p. 117–118 °C (from ethanol); lit.,³³ m.p. 117 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1678 and 1611; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.92 (1 H, d, J 8.8, 5-H), 7 (1 H, d, J 8.1, 6'-H), 6.61 (1 H, dd, J 8.8 and 2.4, 6-H), 6.47 (3 H, m, 8-H, 3'-H and 5'-H), 4.54 (2 H, m, 2-H), 4.25 (1 H, dd, J 11.4 and 5.5, 3-H), 3.85 (3 H, s, OCH₃), 3.79 (3 H, s, 7-OCH₃) and 3.77 (3 H, s, OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 47.30 (C-3), 55.38 (4'-OCH₃), 55.51 (2'-OCH₃), 55.62 (7-OCH₃), 71.24 (C-2), 99.10 (C-3'), 100.70 (C-8), 104.57 (C-5'), 109.81 (C-6), 115.57 (C-10), 116.01 (C-1'), 129.38 (C-5), 130.66 (C-6'), 158.42 (C-2'), 160.49 (C-4'), 163.78 (C-9), 165.72 (C-7) and 191.63 (C-4); m/z 314 (M^+ , 11%), 164 (100), 149 (48), 121 (32) and 28 (51) (Found: C, 68.75; H, 5.75. $C_{18}H_{18}O_5$ requires C, 68.8; H, 5.8%).

7,2',4',6'-Tetramethoxyisoflavanone 36. CC (light petroleum-ether, 1:1); m.p. 153 °C (from chloroform-ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1678 and 1609; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.92 (1 H, d, J 8.8, 5-H), 6.59 (1 H, dd, J 8.8 and 2.4, 6-H), 6.44 (1 H, d, J 2.4, 8-H), 6.15 (2 H, s, 3'-H and 5'-H), 4.72 (1 H, dd, J 13.2 and 9.5, 2-H equatorial), 4.62 (1 H, dd, J 13.2 and 4.9, 2-H axial), 4.33 (1 H, dd, J 9.5 and 4.9, 3-H), 3.84 (3 H, s, 4'-OCH₃), 3.81 (3 H, s, 7-OCH₃) and 3.73 (6 H, s, 2'-OCH₃ and 6'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 42.98 (C-3), 55.36 (4'-OCH₃), 55.57 (7-OCH₃), 55.76 (2'-OCH₃ and 6'-OCH₃), 69.68 (C-2), 91.21 (C-3' and C-5'), 100.74 (C-8), 104.16 (C-1'), 109.38 (C-6), 115.60 (C-10), 129.36 (C-5), 159.26 (C-2' and C-6'), 160.98 (C-4'), 163.75 (C-9), 165.33 (C-7) and 191.78 (C-4); m/z 344 (M^+ , 15%), 194 (100), 179 (75), 151 (15), 121 (21) and 28 (59) (Found: C, 66.6; H, 6.0. $C_{19}H_{20}O_6$ requires C, 66.3; H, 5.85%).

5,7-Dimethoxyisoflavanone 37. Precipitated as a white solid on addition of ether to the crude oil; m.p. 150–151 °C (from methanol); lit.,³ m.p. 150–151 °C.

5,7-Dimethoxy-4'-methylisoflavanone 38. FC (ether-light petroleum, 5:1); m.p. 129–130 °C (from methanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1680 and 1605; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.17 (2 H, d, J 8.2,

2'-H and 6'-H), 7.12 (2 H, d, J 8.1, 3'-H and 5'-H), 6.08 (1 H, d, J 2.4, 8-H), 6.06 (1 H, d, J 2.4, 6-H), 4.60 (2 H, d, J 6.4, 2-H), 3.85 (3 H, s, 5-OCH₃), 3.82 (3 H, s, 7-OCH₃), 3.79 (1 H, d, J 6.4, 3-H) and 2.31 (3 H, s, 4'-CH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 21.07 (4'-CH₃), 52.31 (C-3), 55.55 (7-OCH₃), 56.07 (5-OCH₃), 71.05 (C-2), 93.03 (C-6 or C-8), 93.18 (C-8 or C-6), 105.85 (C-10), 128.30 (C-3' and C-5'), 129.34 (C-2' and C-6'), 132.81 (C-4'), 137.06 (C-1'), 162.70 (C-9), 164.82 (C-5), 165.82 (C-7) and 189.55 (C-4); m/z 298 (M^+ , 8%), 180 (100), 152 (22), 137 (18) and 117 (11) (Found: C, 72.65; H, 6.0. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.1%).

5,7,4'-Trimethoxyisoflavanone 39. Precipitated as a white solid on addition of ether to the crude oil; m.p. 154 °C (from methanol); lit.,³ m.p. 156–157 °C.

5,7,2',4'-Tetramethoxyisoflavanone 40. Precipitated as a white solid on addition of ether to the crude oil; m.p. 162–163 °C (from methanol); lit.,³⁴ m.p. 163 °C.

5,7,2',4',6'-Pentamethoxyisoflavanone 41. Precipitated as a white solid on addition of ether to the crude oil; m.p. 194–196 °C (from methanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1682 and 1607; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 6.13 (2 H, s, 6-H and 8-H), 6.09 (2 H, s, 3'-H and 5'-H), 4.68 (1 H, dd, J 13.1 and 9.6, 2-H equatorial), 4.56 (1 H, dd, J 13.2 and 5.1, 2-H axial), 4.28 (1 H, dd, J 9.5 and 5.1, 3-H), 3.85 (3 H, s, 5-OCH₃), 3.83 (3 H, s, 7-OCH₃), 3.80 (3 H, s, 4'-OCH₃) and 3.73 (6 H, s, 2'-OCH₃ and 6'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 44.02 (C-3), 55.35 (4'-OCH₃), 55.50 (7-OCH₃), 55.77 (2'-OCH₃ and 6'-OCH₃), 56.11 (5-OCH₃), 69.43 (C-2), 91.02 (C-3' and C-5'), 93.01 (C-8), 93.33 (C-6), 104.78 (C-10), 106.82 (C-1'), 159.30 (C-2' and C-6'), 160.73 (C-4'), 162.64 (C-9), 165.05 (C-5), 165.38 (C-7) and 190.37 (C-4); m/z 374 (M^+ , 6%), 194 (100), 179 (56), 151 (8) and 121 (11) (Found: C, 64.25; H, 5.7. $C_{20}H_{22}O_7$ requires C, 64.2; H, 5.9%).

General Procedure for Deallyloxycarbonylation–Dehydrogenation of 3-Allyloxycarbonyl-3-arylchroman-4-ones 12–26.—A solution of the appropriate 3-allyloxycarbonyl-3-arylchroman-4-one (1 mmol) in anhydrous acetonitrile (10 cm³) was added dropwise to a boiling solution of palladium(II) acetate (0.05 mmol) and 1,2-bis(diphenylphosphino)ethane (0.05 mmol) in anhydrous acetonitrile (30 cm³) over 30 min under nitrogen. The mixture was refluxed for 4 h under nitrogen and then concentrated to approximately 5 cm³. The mixture was filtered through a short silica column and eluted with chloroform. The solvent was removed under reduced pressure to yield a white solid which was purified as specified.

Isoflavone 42. CC (benzene); m.p. 132–133 °C (from ethanol); lit.,⁹ m.p. 133–134 °C.

4'-Methylisoflavone 43. CC (benzene); m.p. 151–152 °C (from ethanol); lit.,⁹ m.p. 146–147 °C.

4'-Methoxyisoflavone 44. CC (benzene); m.p. 140 °C (from ethanol); lit.,⁹ m.p. 140–141 °C.

2',4'-Dimethoxyisoflavone 45. CC (light petroleum-ether, 1:1); m.p. 158–160 °C (from ethanol); lit.,⁹ m.p. 157–158 °C.

2',4',6'-Trimethoxyisoflavone 46. Crystallised from chloroform-ether; m.p. 221–222 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1643 and 1607; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 8.28 (1 H, dd, J 8 and 1.5, 5-H), 7.81 (1 H, s, 2-H), 7.66 (1 H, ddd, J 7.8, 7.7 and 1.7, 7-H), 7.47 (1 H, dd, J 8.6 and 1.1, 8-H), 7.39 (1 H, ddd, J 7.5, 7.5 and 1.1, 6-H), 6.22 (2 H, s, 3'-H and 5'-H), 3.85 (3 H, s, 4'-OCH₃) and 3.74 (6 H, s, 2'-OCH₃ and 6'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 55.43 (4'-OCH₃), 55.92 (2'-OCH₃ and 6'-OCH₃), 90.89 (C-3' and C-5'), 102.06 (C-1'), 118.02 (C-8), 118.75 (C-10), 124.57 (C-3), 124.76 (C-6), 126.40 (C-5), 133.11 (C-7), 155.06 (C-2), 156.42 (C-9), 159.46 (C-2' and C-6'), 161.72 (C-4') and 176.45 (C-4); m/z 312 (M^+ , 100%), 281 (88), 191 (71), 121 (78), 69 (42) and 28 (42) (Found: C, 69.3; H, 5.1. $C_{18}H_{16}O_5$ requires C, 69.2; H, 5.2%).

7-Methoxyisoflavone 47. FC (benzene-ether, 40:1); m.p. 158 °C (from methanol); lit.,³⁵ m.p. 158–159 °C.

7-Methoxy-4'-methylisoflavone 48. FC (benzene-ether, 40:1); m.p. 142–143 °C (from ethanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1628 and 1599; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 8.20 (1 H, d, J 8.8, 5-H), 7.91 (1 H, s, 2-H), 7.46 (2 H, dd, J 6.4 and 1.8, 2'-H and 6'-H), 7.24 (2 H, dd, J 7.8 and 0.6, 3'-H and 5'-H), 6.97 (1 H, dd, J 8.9 and 2.4, 6-H), 6.83 (1 H, d, J 2.4, 8-H), 3.90 (3 H, s, 7-OCH₃) and 2.38 (3 H, s, 4'-CH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 21.24 (4'-CH₃), 55.81 (7-OCH₃), 100.06 (C-8), 114.52 (C-6), 118.43 (C-10), 125.17 (C-1'), 127.76 (C-5), 128.81 (C-3' and C-5'), 128.95 (C-3), 129.14 (C-2' and C-6'), 137.92 (C-4'), 152.31 (C-2), 157.91 (C-9), 163.94 (C-7) and 175.72 (C-4); m/z 266 (M⁺, 99%), 265 (100), 150 (56), 132 (22), 122 (33) and 115 (42) (Found: C, 76.5; H, 5.1. C₁₇H₁₄O₃ requires C, 76.7; H, 5.3%).

7,4'-Dimethoxyisoflavone 49. CC (benzene-ether, 40:1); m.p. 161–162 °C (from chloroform-ethanol); lit.,³⁶ m.p. 161 °C; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 8.20 (1 H, d, J 9, 5-H), 7.92 (1 H, s, 2-H), 7.50 (2 H, dd, J 6.7 and 2.2, 2'-H and 6'-H), 7–6.95 (3 H, m, 6-H, 3'-H and 5'-H), 6.85 (1 H, d, J 2.4, 8-H), 3.91 (3 H, s, 7-OCH₃) and 3.84 (3 H, s, 4'-OCH₃).

7,2',4'-Trimethoxyisoflavone 50. FC (ether-light petroleum, 3:2); m.p. 148–149 °C (from methanol); lit.,¹⁴ m.p. 148–149 °C.

7,2',4',6'-Tetramethoxyisoflavone 51. FC (ether-light petroleum, 2:1); m.p. 225–226 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1638 and 1607; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3\text{-CF}_3\text{CO}_2\text{H})$ 8.22 (1 H, d, J 9, 5-H), 7.91 (1 H, s, 2-H), 7.07 (1 H, dd, J 9 and 2.4, 6-H), 6.95 (1 H, d, J 2.4, 8-H), 6.18 (2 H, s, 3'-H and 5'-H), 3.94 (3 H, s, OCH₃), 3.84 (3 H, s, OCH₃) and 3.72 (6 H, s, 2'-OCH₃ and 6'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3\text{-CF}_3\text{CO}_2\text{H})$ 55.36 (4'-OCH₃), 55.81 (2'-OCH₃ and 6'-OCH₃), 56.04 (7-OCH₃), 90.76 (C-3' and C-5'), 100.05 (C-8), 100.32 (C-1'), 115.79 (C-6), 117.94 (C-10), 124.56 (C-3), 128.01 (C-5), 157.21 (C-2), 158.88 (C-9), 159.62 (C-2' and C-6'), 162.45 (C-4'), 165.04 (C-7) and 178.88 (C-4); m/z 342 (M⁺, 100%), 311 (86), 191 (21) and 151 (41) (Found: M⁺, 342.1093. C₁₉H₁₈O₆ requires M , 342.1098).

5,7-Dimethoxyisoflavone 52. FC (ether-light petroleum, 6:1); m.p. 112 °C (from methanol); lit.,³⁷ m.p. 112 °C.

5,7-Dimethoxy-4'-methylisoflavone 53. FC (ether-light petroleum, 5:1); m.p. 155–157 °C (from methanol); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1647 and 1607; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3)$ 7.76 (1 H, s, 2-H), 7.43 (2 H, d, J 8.1, 2'-H and 6'-H), 7.20 (2 H, d, J 8.1, 3'-H and 5'-H), 6.43 (1 H, d, J 2.2, 8-H), 6.36 (1 H, d, J 2.2, 6-H), 3.93 (3 H, s, 5-OCH₃), 3.87 (3 H, s, 7-OCH₃) and 2.37 (3 H, s, 4'-CH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3)$ 21.24 (4'-CH₃), 55.71 (7-OCH₃), 56.31 (5-OCH₃), 92.50 (C-8), 96.13 (C-6), 109.97 (C-10), 126.29 (C-1'), 128.90–129.07 (C-3, C-2', C-3', C-5' and C-6'), 137.66 (C-4'), 150.25 (C-2), 159.87 (C-9), 161.47 (C-5), 163.84 (C-7) and 175.28 (C-4); m/z 296 (M⁺, 100%), 295 (54), 265 (33), 250 (35), 115 (35) and 28 (33) (Found: C, 73; H, 5.4. C₁₈H₁₆O₄ requires C, 73; H, 5.4%).

5,7,4'-Trimethoxyisoflavone 54. CC (ether); m.p. 162–163 °C (from methanol); lit.,³⁸ m.p. 162–163 °C.

5,7,2',4'-Tetramethoxyisoflavone 55. FC (ether followed by ethyl acetate); m.p. 202–203 °C (from methanol); lit.,³⁴ m.p. 203–204 °C.

5,7,2',4',6'-Pentamethoxyisoflavone 56. FC (ether followed by ethyl acetate); m.p. 274–275 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1649 and 1613; $\delta_{\text{H}}(270 \text{ MHz}; \text{CDCl}_3\text{-CF}_3\text{CO}_2\text{H})$ 8.32 (1 H, s, 2-H), 6.93 (1 H, d, J 2.2, 8-H), 6.74 (1 H, d, J 2.2, 6-H), 6.22, (2 H, s, 3'-H and 5'-H), 4.15 (3 H, s, 5-OCH₃), 4.04 (3 H, s, 7-OCH₃), 3.88 (3 H, s, 4'-OCH₃) and 3.74 (6 H, s, 2'-OCH₃ and 6'-OCH₃); $\delta_{\text{C}}(67.8 \text{ MHz}; \text{CDCl}_3\text{-CF}_3\text{CO}_2\text{H})$ 55.60 (4'-OCH₃), 55.77 (2'-OCH₃ and 6'-OCH₃), 57.21 (7-OCH₃), 58.18 (5-OCH₃), 90.81 (C-3' and C-5'), 94.39 (C-8), 96.39 (C-1'), 100.02 (C-6), 104.16 (C-10), 115.91 (C-3), 159.22 (C-2' and C-6'), 159.62 (C-9), 160.73 (C-4'), 162.10 (C-2), 163.48 (C-5), 169.52 (C-7) and 176.37 (C-4); m/z 372 (M⁺, 59%), 341 (100), 194 (38), 181 (26) (Found: M⁺, 372.1162. C₂₀H₂₀O₇ requires M , 372.1203).

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