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Synthesis of Pyranoisoflavones from Pyronochalcones: Synthesis of Elongatin and Its Angular Isomer

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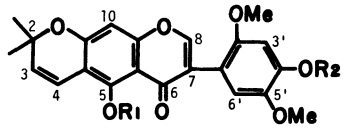
Elongatin (4′,5-dihydroxy-2′,5′-dimethoxy-2″,2″-dimethylpyrano[5″,6″-*g*]isoflavone) was synthesized by an oxidative rearrangement of the corresponding pyronochalcone [6-(1-oxo-3-phenyl-2-propenyl)-4-chromanone] with thallium(III) nitrate and a regioselective reduction of 7-(4-benzoyloxy-2,5-dimethoxyphenyl)-2,3-dihydro-2,2-dimethyl-5-tosyloxy-4*H*,6*H*-benzo[1,2-*b*:5,4-*b*′]dipyran-4,6-dione with sodium borohydride–palladium chloride, followed by dehydration of the resultant alcohol and hydrolysis. Its angular isomer (4′,5-dihydroxy-2′,5′-dimethoxy-2″,2″-dimethylpyrano[6″,5″-*h*]isoflavone) was also synthesized from the corresponding pyronochalcone in a similar manner.

A lot of natural isoflavones were synthesized by oxidative rearrangements of chalcones with thallium(III) nitrate (TTN).[1,2] Pyranoisoflavones (jamaicin and leiocarpin) containing an acid-labile group, such as a dimethylchromene ring, were directly synthesized from the corresponding pyranochalcones by this method.[3] We have also reported that pyranoisoflavones (elongatin and toxicarol isoflavone) of linear and angular phloroglucinol-types can be prepared by an oxidative rearrangement of the corresponding dihydropyranochalcones with TTN, followed by a dehydrogenation of the resultant dihydropyranoisoflavones.[4] Thus, the oxidative rearrangement of 2′-hydroxychalcones with TTN seems at present to be a more useful method for synthesizing natural linear and angular pyranoisoflavones (7-phenyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b*′]dipyran-6-ones and -4*H*,8*H*-benzo[1,2-*b*:3,4-*b*′]dipyran-4-ones). However, this method has not been applied hitherto to the synthesis of linear and angular pyronoisoflavones (2,3-dihydro-7-phenyl-4*H*,6*H*-benzo[1,2-*b*:5,4-*b*′]dipyran-4,6-diones and 8,9-dihydro-3-phenyl-4*H*,10*H*-benzo[1,2-*b*:3,4-*b*′]dipyran-4,10-diones) from the corresponding pyronochalcones [6-(1-oxo-3-phenyl-2-propenyl)-4-chromanones].

It is of much interest as a new pathway to extend this methodology to the synthesis of pyranoisoflavones from pyronochalcones with TTN; the subsequent regioselective reduction of the pyronoisoflavones, followed by dehydration of the resultant alcohols leads to the corresponding pyranoisoflavones. We report here on the synthesis of a linear pyranoisoflavone, elongatin (4′,5-dihydroxy-2′,5′-dimethoxy-2″,2″-dimethylpyrano[5″,6″-*g*]isoflavone)[5] (**1**) and its angular isomer (4′,5-dihydroxy-2′,5′-dimethoxy-2″,2″-dimethylpyrano[6″,5″-*h*]isoflavone)[4] (**2**)—systematic name 5-hydroxy-7-(4-hydroxy-2,5-dimethoxyphenyl)-2,2-dimethyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b*′]dipyran-6-one and 5-hydroxy-3-(4-hydroxy-2,5-dimethoxyphenyl)-8,8-dimethyl-4*H*,8*H*-benzo[1,2-*b*:3,4-*b*′]dipyran-4-one—by this method.

The condensation of 2,4,6-trihydroxyacetophenone with 3-methyl-2-butenoic acid in the presence of polyphosphoric acid (PPA) in dioxane afforded 8-acetylchromanone[6] (**3**) as a major product and 6-



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22 $R_1=Ts$, $R_2=PhCO$
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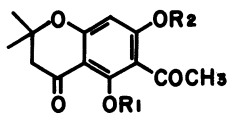
24 $R_1=R_2=Me$



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6 $R_1=Me$, $R_2=Ts$
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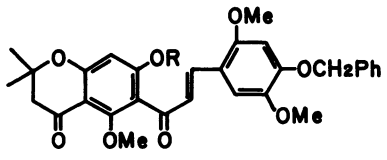

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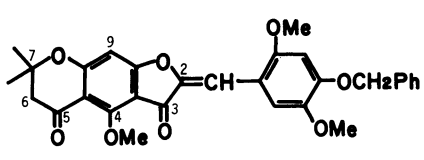
10 R=Ac



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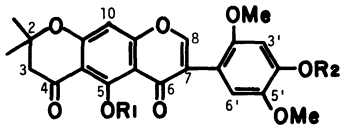

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13 R_1=H, R_2=$PhCH_2$
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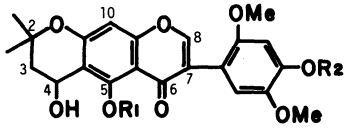
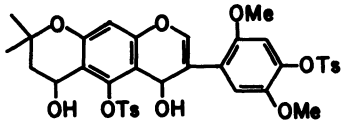
15 R_1=R_2=Ts
19 R_1=H, R_2=PhCO
20 R_1=Ts, R_2=PhCO



16 R_1=R_2=Ts
21 R_1=Ts, R_2=PhCO



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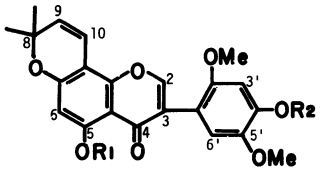
acetylchromanone (**4**) as a minor product. It was first found that chromanone (**3**) was easily isomerized to chromanone (**4**) with potassium carbonate in acetone; this method offers an efficient synthesis of the 6-acetylchromanone (**4**). Tosylation of **4**, and a successive methylation of the tosylate (**5**), followed by hydrolysis of the resultant methyl ether (**6**) afforded 7-hydroxy-5-methoxychromanone (**7**). Condensation of **7** with 4-benzyloxy-2,5-dimethoxybenzaldehyde[4] (**8**) in the presence of piperidine and pyridine in ethanol afforded chalcone (**9**), which was subsequently converted into acetate (**10**). The oxidative rearrangement of **10** with TTN in methanol, followed by cyclization of the resultant compound with diluted hydrochloric acid under reflux afforded a linear pyronoisoflavone (**11**) and a small amount of aurone (**12**). The ^1H NMR spectrum of **11** showed the presence of C_8-proton as a singlet at δ 7.67. A signal at δ 6.45 in the ^1H NMR spectrum of **12** is due to the benzylidene proton and is characteristic of an aurone system. Hydrogenolysis of **11** with palladium on charcoal afforded a mixture of the corresponding 4′-hydroxyisoflavone and 4′-hydroxyisoflavanone. However, the 5-hydroxypyronoisoflavone (**13**), which was prepared by demethylation of **11** with aluminum bromide in acetonitrile, was hydrogenolyzed with palladium on charcoal to give 4′,5-dihydroxypyronoisoflavone (**14**) in good yield. Compound **14** was easily converted into the ditosylate (**15**) with *p*-toluenesulfonyl chloride in acetone. We have reported that the carbonyl group in the chromanone ring of acetylchromanones is selectively reduced with sodium borohydride–palladium chloride to give the alcohols and that the subsequent dehydration affords the corresponding chromenes.[6] This method was applied to the synthesis of pyranoisoflavones from pyronoisoflavones. Compound **15** was reduced with sodium borohydride in the presence of palladium chloride in tetrahydrofuran–water to give the desired monoalcohol (**16**) and dialcohol (**17**). The monoalcohol (**16**) was easily dehydrated in the presence of *p*-toluenesulfonic acid to give linear pyranoisoflavone (**18**). Hydrolysis of **18** by a potassium hydroxide solution in boiling ethanol afforded linear pyranoisoflavone (elongatin) (**1**) and its isomeric angular pyranoisoflavone (**2**). This result shows that the tosyl group is not suitable for the protection of the hydroxyl group, since the hydrolysis of **18** is accompanied by a ring isomerization to its angular isomer (**2**). Therefore, a benzoyl group was tested for the protection of the hydroxyl group. Benzoylation of **14** with benzoyl chloride in acetone easily afforded 4′-benzoate (**19**), but did not yield 4′,5-dibenzoate. The 5-tosylate (**20**) of a 5-hydroxy compound (**19**) was selectively reduced with sodium borohydride in the presence of palladium chloride to give monoalcohol (**21**). Dehydration of compound **21** led to pyranoisoflavone (**22**), which was easily hydrolyzed with a potassium hydroxide solution without ring isomerization to give the desired linear pyranoisoflavone (elongatin) (**1**) in good yield. The physical properties of **1**, the diacetate (**23**), and the dimethyl ether (**24**) were identical with those of their authentic samples, prepared by a method described before,[4] respectively.

The partial benzylation of 2,4,6-trihydroxyacetophenone with benzyl chloride in the presence of potassium carbonate in hexamethylphosphoric triamide (HMPA) afforded 2,4-bis(benzyloxy)-6-hydroxyacetophenone (**25**) in good yield. This benzylation is superior to that in acetone[7] or *N*,*N*-dimethylformamide[8] since no *C*-benzylated compound is formed. Debenzylation of the methyl ether (**26**) of the 6-hydroxyacetophenone (**25**) with palladium on charcoal afforded 2,4-dihydroxy-6-methoxyacetophenone[9] (**27**). Condensation of **27** with 3-methyl-2-butenoyl chloride by a Friedel–Crafts reaction afforded 1-(3-acetyl-2,6-dihydroxy-4-methoxyphenyl)-3-methyl-2-buten-1-one (**28**) in good yield. The structure of **28** was determined by nuclear Overhauser effect (NOE) experiments at the C_5-proton: The integrated intensity of the signal at δ 5.85 for **28** increased up to 25% when the methoxyl



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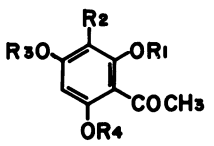
39 R_1=R_2=Ac
40 R_1=H, R_2=Me
41 R_1=R_2=Me



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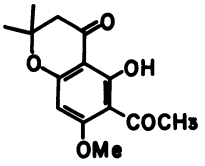
26 R_1=R_3=$PhCH_2$, R_2=H, R_4=Me
27 R_1=R_2=R_3=H, R_4=Me
28 R_1=R_3=H, R_2=Me_2C=CHCO, R_4=Me



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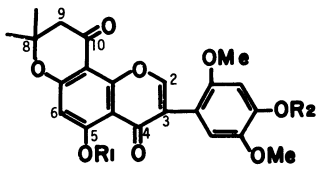
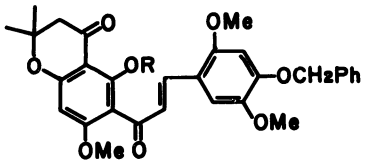
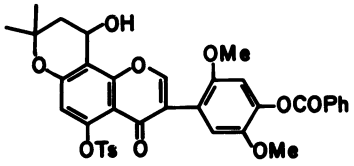


32 R_1=Me, R_2=$PhCH_2$
33 R_1=H, R_2=$PhCH_2$
34 R_1=R_2=H
35 R_1=H, R_2=PhCO
36 R_1=Ts, R_2=PhCO



30 R=H
31 R=Ac



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protons were saturated by double irradiation. The diketone (**28**) was easily converted into the 5-hydroxy-7-methoxychromanone (**29**) with a potassium hydroxide solution in methanol. Condensation of **29** with **8** afforded the chalcone (**30**), which was converted into acetate (**31**). An oxidative rearrangement of **31** with TTN under similar conditions to that of **11** afforded angular pyronoisoflavone (**32**), while the corresponding aurone was not obtained in this case. Demethylation of **32** and a subsequent debenzylation of the resultant 5-hydroxypyronoisoflavone (**33**) afforded 4′,5-dihydroxypyronoisoflavone (**34**). The partial benzoylation of **34** and tosylation of the resultant 4′-benzoate (**35**), followed by a reduction of the 5-tosylate (**36**) with sodium borohydride–palladium chloride, yielded quantitatively monoalcohol (**37**). Dehydration of **37** led to the pyranoisoflavone (**38**), which was easily hydrolyzed to give the desired angular pyranoisoflavone (**2**) in good yield. The physical properties of **2**, the diacetate (**39**), the 4′-methyl ether (toxicarol isoflavone) (**40**), and the dimethyl ether (**41**) were identical with those of their authentic samples prepared by the method described before,[4] respectively.

From the results described above, the selective reduction of the carbonyl group in the pyronoisoflavones and the subsequent dehydration are easier than the dehydrogenation of dihydropyranoisoflavones,[4] and therefore, this method is a facile synthesis of pyranoisoflavones.

Experimental

All the melting points are uncorrected. The UV spectra were taken in ethanol on a Hitachi 124 spectrophotometer. The ^{1}H NMR spectra were measured with a Hitachi R-20 spectrometer (60 MHz), using tetramethylsilane as an internal standard (δ, ppm). Column chromatography and thin-layer chromatography were carried out on Kieselgel 60 (70—230 mesh) and with Kieselgel 60 F-254 (Merck).

8-Acetyl-5,7-dihydroxy-2,2-dimethyl-4-chromanone (3) and 6-Acetyl-5,7-dihydroxy-2,2-dimethyl-4-chromanone (4). A mixture of 2,4,6-trihydroxyacetophenone (35.5 g) and 3-methyl-2-butenoic acid (28.7 g) in anhydrous dioxane (127 ml) was stirred in the presence of PPA (100 g) at 60 °C for 3 h. The reaction mixture was poured into ice-cold water and neutralized with a saturated K_2CO_3 solution to give precipitates. The resulting precipitates were recrystallized from MeOH–Me_2CO to give **3** (41 g, 77%) as colorless needles (R_f=0.38; hexane–EtOAc (4:1) on a silica-gel TLC plate): mp 158—160 °C; ^{1}H NMR ($CDCl_3$) δ=1.58 (6H, s, CH_3×2), 2.64 (3H, s, $COCH_3$), 2.79 (2H, s, $COCH_2$), 5.91 (1H, s, C_6–H), 12.65 and 14.30 (each 1H, s, OH).

Found: C, 62.26; H, 5.79%. Calcd for $C_{13}H_{14}O_5$: C, 62.39;

H, 5.64%.

The mother liquor was chromatographed over a silica-gel column with $CHCl_3$ to give **4** (2.11 g, 4%) as colorless needles (R_f=0.62): mp 148—150 °C; ^1H NMR ($CDCl_3$) δ=1.43 (6H, s, CH_3×2), 2.67 (3H, s, $COCH_3$), 2.70 (2H, s, $COCH_2$), 5.83 (1H, s, C_8–H), 14.10 and 14.40 (each 1H, s, OH).

Found: C, 62.41; H, 5.66%. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64%.

6-Acetyl-5,7-dihydroxy-2,2-dimethyl-4-chromanone (4). A mixture (14.9 g) of **3** and **4** was refluxed with stirring in the presence of K_2CO_3 (70 g) in anhydrous Me_2CO (500 ml) for 50 h. After removal of K_2CO_3 and the solvent, the residue was dissolved in EtOAc, washed with dil. HCl and water, and dried (Na_2SO_4). The resulting compound was recrystallized from MeOH–$CHCl_3$ to give **4** (13 g, 87%) as colorless needles; mp 148—150 °C.

6-Acetyl-5-hydroxy-2,2-dimethyl-7-tosyloxy-4-chromanone (5). A mixture of **4** (16.5 g), TsCl (14.1 g), and K_2CO_3 (46 g) in Me_2CO (450 ml) was refluxed with stirring for 1.5 h. After removal of K_2CO_3 and the solvent, the residue was dissolved in EtOAc, washed with dil. HCl and water, and dried (Na_2SO_4). The resulting compound was chromatographed over a silica-gel flash column with hexane–EtOAc (3:2) to give **5** (17 g, 64%) as colorless prisms: mp 105—106 °C (MeOH); ^1H NMR ($CDCl_3$) δ=1.46 (6H, s, CH_3×2), 2.38 (3H, s, $C_6H_4C\underline{H}_3$), 2.45 (3H, s, $COCH_3$), 2.74 (2H, s, $COCH_2$), 6.38 (1H, s, C_8–H), 7.30 and 7.77 (each 2H, d, J=8.8 Hz, $C_6\underline{H}_4CH_3$), 12.46 (1H, s, OH).

Found: C, 59.50; H, 5.00%. Calcd for $C_{20}H_{20}O_7S$: C, 59.39; H, 4.99%.

6-Acetyl-5-methoxy-2,2-dimethyl-7-tosyloxy-4-chromanone (6). A mixture of **5** (19.2 g), $(MeO)_2SO_2$ (11.4 ml), and K_2CO_3 (34 g) in Me_2CO (450 ml) was refluxed with stirring for 3.5 h. The reaction mixture was treated in the usual way, and the resulting compound was recrystallized from MeOH to give **6** (17.6 g, 88%) as colorless prisms: mp 110—111 °C; ^1H NMR ($CDCl_3$) δ=1.46 (6H, s, CH_3×2), 2.36 (3H, s, $C_6H_4C\underline{H}_3$), 2.47 (3H, s, $COCH_3$), 2.69 (2H, s, $COCH_2$), 3.79 (3H, s, OCH_3), 6.72 (1H, s, C_8–H), 7.36 and 7.78 (each 2H, d, J=8.8 Hz, $C_6\underline{H}_4CH_3$).

Found: C, 60.10; H, 5.26%. Calcd for $C_{21}H_{22}O_7S$: C, 60.28; H, 5.30%.

6-Acetyl-7-hydroxy-5-methoxy-2,2-dimethyl-4-chromanone (7). Compound **6** (11.0 g) was refluxed in the presence of K_2CO_3 (25 g) in MeOH (200 ml) with stirring for 1.5 h. The reaction mixture was poured into ice-cold water and acidified with HCl, and extracted with EtOAc, and dried (Na_2SO_4). The resulting compound was recrystallized from MeOH to give **7** (6.6 g, 95%) as colorless needles: mp 83—85 °C; ^1H NMR ($CDCl_3$) δ=1.46 (6H, s, CH_3×2), 2.66 (2H, s, $COCH_2$), 2.69 (3H, s, $COCH_3$), 3.92 (3H, s, OCH_3), 6.18 (1H, s, C_8–H), 13.70 (1H, s, OH).

Found: C, 63.61; H, 6.14%. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10%.

7-Hydroxy-5-methoxy-2,2-dimethyl-6-[1-oxo-3-(4-benzyloxy-2,5-dimethoxyphenyl)-2-propenyl]-4-chromanone (9). A mixture of **7** (2.64 g) and 4-benzyloxy-2,5-dimethoxybenzaldehyde[4] (**8**) (2.72 g) was refluxed with stirring in the presence of piperidine (2.8 ml) and pyridine (3.2 ml) in EtOH (150 ml) for 14 h. The reaction mixture was poured into ice-cold water and acidified with HCl. The resulting compound was recrystallized from MeOH to give **9** (1.62 g, 60%) as yellow needles: mp 167—169 °C; ^1H NMR ($CDCl_3$) δ=1.45 (6H, s, CH_3×2), 2.66 (2H, s, $COCH_2$), 3.78, 3.83, and 3.86 (each 3H, s, OCH_3), 5.19 (2H, s, $C_6H_5C\underline{H}_2$), 6.22 (1H, s, C_8–H), 6.50 and 7.12 (each 1H, s, Arom-H), 7.36 (5H, s, C_6H_5), 7.77 and 8.20 (each 1H, d, J=16 Hz, CH=), 13.88 (1H, s, OH).

Found: C, 69.19; H, 5.74%. Calcd for $C_{30}H_{30}O_8$: C, 69.48; H, 5.83%.

Acetate 10. Compound **9** was converted into the acetate **10** as yellow needles by an acetic anhydride–sodium acetate method: mp 145—147 °C (MeOH); ^1H NMR ($CDCl_3$) δ=1.46 (6H, s, CH_3×2), 2.14 (3H, s, $COCH_3$), 2.68 (2H, s, $COCH_2$), 3.68, 3.79, and 3.82 (each 3H, s, OCH_3), 5.16 (2H, s, $C_6H_5C\underline{H}_2$), 6.44 (1H, s, C_8–H), 6.53 and 7.00 (each 1H, s, Arom-H), 6.90 and 7.69 (each 1H, d, J=16 Hz, CH=), 7.33 (5H, s, $C_6\underline{H}_5CH_2$).

Found: C, 68.40; H, 5.68%. Calcd for $C_{32}H_{32}O_9$: C, 68.55; H, 5.76%.

7-(4-Benzyloxy-2,5-dimethoxyphenyl)-2,3-dihydro-5-methoxy-2,2-dimethyl-4*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-4,6-dione (11) and 2-[(4-Benzyloxy-2,5-dimethoxyphenyl)methylene]-6,7-dihydro-4-methoxy-7,7-dimethyl-5*H*-furo[3,2-*g*][1]benzopyran-3(2*H*),5-dione (12). A mixture of **10** (3.55 g) and TTN (4.2 g) was stirred in MeOH (1.3 l) at 36—38 °C for 10 h, and then 10% HCl (70 ml) was added, and the mixture was refluxed for a further 3 h. After removal of the precipitates by filtration, the filtrate was concentrated to ca. 600 ml under reduced pressure and poured into a large amount of ice-cold water. The mixture was allowed to stand overnight at room temperature to give precipitates. The precipitates were recrystallized from MeOH to give **11** (2.30 g, 70%) as colorless needles: mp 164—165 °C; ^1H NMR ($CDCl_3$) δ=1.47 (6H, s, CH_3×2), 2.71 (2H, s, $COCH_2$), 3.62, 3.82, and 3.98 (each 3H, s, OCH_3), 5.14 (2H, s, $C_6H_5C\underline{H}_2$), 6.57 (1H, s, C_{10}–H), 6.64 and 6.85 (each 1H, s, Arom-H), 7.35 (5H, bs, $C_6\underline{H}_5CH_2$), 7.67 (1H, s, C_8–H).

Found: C, 69.89; H, 5.49%. Calcd for $C_{30}H_{28}O_8$: C, 69.75; H, 5.46%.

The mother liquor was chromatographed over a silica-gel column with $CHCl_3$–Me_2CO (50:1) to give the aurone **12** (40 mg, 1%) as pale yellow needles: mp 216—218 °C (MeOH); ^1H NMR ($CDCl_3$) δ=1.45 (6H, s, CH_3×2), 2.67 (2H, s, $COCH_2$), 3.72, 3.88, and 4.32 (each 3H, s, OCH_3), 5.16 (2H, s, $C_6H_5C\underline{H}_2$), 6.37 (1H, s, C_9–H), 7.20 and 7.71 (each 1H, s, Arom-H), 6.45 (1H, s, C=CH), 7.34 (5H, s, $C_6\underline{H}_5CH_2$).

Found: C, 69.63; H, 5.31%. Calcd for $C_{30}H_{28}O_8$: C, 69.75; H, 5.46%.

7-(4-Benzyloxy-2,5-dimethoxyphenyl)-2,3-dihydro-5-hydroxy-2,2-dimethyl-4*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-4,6-dione (13). A solution of anhydrous $AlBr_3$ (14.5 g) in MeCN (50 ml) was added to a solution of **11** (5.46 g) in MeCN (250 ml), and the mixture was stirred at 40 °C for 25 min. The reaction mixture was poured into a mixture of HCl and ice-cold water and then stirred at 55—60 °C for 20 min to give precipitates. The precipitates were recrystallized from MeOH–Me_2CO to give **13** (4.85 g, 91%) as pale-yellow needles: mp 173—174 °C; ^1H NMR ($CDCl_3$) δ=1.48 (6H, s, CH_3×2), 2.73 (2H, s, $COCH_2$), 3.63 and 3.82 (each 3H, s, OCH_3), 5.12 (2H, s, $C_6H_5C\underline{H}_2$), 6.30 (1H, s, C_{10}–H), 6.57 and 6.84 (each 1H, s, Arom-H), 7.35 (5H, br, $C_6\underline{H}_5CH_2$), 7.76 (1H, s, C_8–H), 14.62 (1H, s, OH).

Found: C, 69.56; H, 5.22%. Calcd for $C_{29}H_{26}O_8$: C, 69.31;

H, 5.22%.

2,3-Dihydro-5-hydroxy-7-(4-hydroxy-2,5-dimethoxyphenyl)-2,2-dimethyl-4*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-4,6-dione (14). Compound **13** (4.67 g) was hydrogenolyzed over 10% palladium on charcoal (2 g) in MeOH (350 ml) and EtOAc (350 ml). The resulting compound was recrystallized from MeOH to give **14** (3.51 g, 92%) as colorless needles: mp 192—194 °C; ^{1}H NMR ($CDCl_3$) δ=1.47 (6H, s, CH_3×2), 2.73 (2H, s, $COCH_2$), 3.70 and 3.82 (each 3H, s, OCH_3), 6.15 (1H, s, $C_{4'}$-OH), 6.31 (1H, s, C_{10}-H), 6.60 and 6.82 (each 1H, s, Arom-H), 7.81 (1H, s, C_8-H), 14.65 (1H, s, C_5-OH).

Found: C, 64.20; H, 4.97%. Calcd for $C_{22}H_{20}O_8$: C, 64.07; H, 4.90%.

2,3-Dihydro-7-[2,5-dimethoxy-4-(tosyloxy)phenyl]-2,2-dimethyl-5-tosyloxy-4*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-4,6-dione (15). A mixture of **14** (1.24 g), TsCl (2.0 g), and K_2CO_3 (4.2 g) was refluxed with stirring in Me_2CO (150 ml) for 6 h. The resulting compound was recrystallized from MeOH to give **15** (1.73 g, 80%) as colorless prisms: mp 152—154 °C; ^{1}H NMR ($CDCl_3$) δ=1.44 (6H, s, CH_3×2), 2.34 and 2.41 (each 3H, s, $C_6H_4CH_3$), 2.61 (2H, s, CH_2CO), 3.47 and 3.65 (each 3H, s, OCH_3), 6.73 (1H, s, Arom-H), 6.80 (2H, s, Arom-H×2), 7.1—7.9 (9H, m, $C_6H_4CH_3$×2 and C_8-H).

Found: C, 61.17; H, 4.40%. Calcd for $C_{36}H_{32}O_{12}S_2$: C, 61.36; H, 4.58%.

3,4-Dihydro-4-hydroxy-7-[2,5-dimethoxy-4-(tosyloxy)phenyl]-2,2-dimethyl-5-tosyloxy-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one (16) and 3,4-Dihydro-4,6-dihydroxy-7-[2,5-dimethoxy-4-(tosyloxy)phenyl]-2,2-dimethyl-5-tosyloxy-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran (17). A mixture of **15** (650 mg) and $PdCl_2$ (230 mg) was stirred in THF (70 ml) and water (14 ml), adding 180 mg each of $NaBH_4$ (360 mg) for two times, at 14—17 °C for 40 min, and then Me_2CO (5 ml) was added to the reaction mixture. After removal of the catalyst by filtration, water was added to the filtrate, and the solvent was removed under reduced pressure below 40 °C. The residue was extracted with EtOAc, washed with dil. HCl and brine, and dried (Na_2SO_4). The resulting compound was chromatographed over a silica-gel column with 1,2-dichloroethane–EtOAc–petroleum ether (50:2:1) to give the monoalcohol **16** (300 mg, 46%) as colorless needles (mp 204—206 °C; from Et_2O) and the dialcohol **17** (280 mg, 43%) as colorless needles (mp 194—196 °C; from Et_2O): ^{1}H NMR spectrum of **16**, ($CDCl_3$) δ=1.38 and 1.51 (each 3H, s, CH_3), 1.95—2.15 (2H, m, CH_2CHOH), 2.40 (6H, s, $C_6H_4CH_3$×2), 3.47 and 3.64 (each 3H, s, OCH_3), 5.07 (1H, t, J=5 Hz, CH_2CHOH), 6.74 (2H, s, Arom-H×2), 6.85 (1H, s, Arom-H), 7.1—8.0 (9H, m, $C_6H_4CH_3$×2 and C_8-H).

Found: C, 59.59; H, 4.51%. Calcd for $C_{36}H_{34}O_{12}S_2$: C, 59.83; H, 4.74%.

^{1}H NMR spectrum of **17**, ($CDCl_3$) δ=1.32 (6H, s, CH_3×2), 2.43 (8H, s, CH_2CHOH and $C_6H_4CH_3$×2), 3.35 and 3.57 (each 3H, s, OCH_3), 5.18 (1H, s, $CHOH$), 5.45 (1H, m, CH_2CHOH), 6.26, 6.45, and 6.47 (each 1H, s, Arom-H), 7.2—7.9 (8H, m, $C_6H_4CH_3$×2), 8.69 (1H, s, C_8-H).

Found: C, 59.71; H, 4.72%. Calcd for $C_{36}H_{36}O_{12}S_2$: C, 59.67; H, 5.01%.

7-[2,5-Dimethoxy-4-(tosyloxy)phenyl]-2,2-dimethyl-5-tosyloxy-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one (18). Compound **16** (160 mg) was refluxed in toluene (30 ml) in the presence of TsOH·H_2O (20 mg) for 20 min. The resulting compound was recrystallized from MeOH–Me_2CO to give **18** (140 mg, 92%) as colorless prisms: mp 206—208 °C; ^{1}H NMR ($CDCl_3$) δ=1.42 (6H, s, CH_3×2), 2.40 and 2.43 (each 3H, s, $C_6H_4CH_3$), 3.49 and 3.67 (each 3H, s, OCH_3), 5.51 (1H, d, J=10 Hz, C_3-H), 6.31 (1H, d, J=10 Hz, C_4-H), 6.71, 6.77, and 6.90 (each 1H, s, Arom-H), 7.1—7.9 (9H, m, $C_6H_4CH_3$×2 and C_8-H).

Found: C, 61.17; H, 4.40%. Calcd for $C_{36}H_{32}O_{11}S_2$: C, 61.36; H, 4.58%.

Hydrolysis of 18. Compound **18** (143 mg) was refluxed in EtOH (150 ml) with a 20% KOH solution (12 ml) for 40 min. The resulting compound was separated by preparative TLC on silica gel with 1,2-dichloroethane–EtOAc–petroleum ether (50:2:3) to give linear pyranoisoflavone (elongatin) (**1**) and its angular isomer **2**.

7-(4-Benzoyloxy-2,5-dimethoxyphenyl)-2,3-dihydro-5-hydroxy-2,2-dimethyl-4*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-4,6-dione (19). A mixture of **14** (3.31 g), PhCOCl (1.2 ml), and K_2CO_3 (11.2 g) in Me_2CO (350 ml) was refluxed with stirring under an atmosphere of N_2 for 1 h. The resulting compound was recrystallized from MeOH to give **19** (3.53 g, 85%) as colorless needles: mp 240—242 °C; ^{1}H NMR ($CDCl_3$) δ=1.49 (6H, s, CH_3×2), 2.74 (2H, s, CH_2CO), 3.75 and 3.78 (each 3H, s, OCH_3), 6.36 (1H, s, C_{10}-H), 6.84 and 7.01 (each 1H, s, Arom-H), 7.4—8.3 (5H, m, C_6H_5CO), 7.87 (1H, s, C_8-H), 14.60 (1H, s, C_5-OH).

Found: C, 67.29; H, 4.74%. Calcd for $C_{29}H_{24}O_9$: C, 67.44; H, 4.68%.

7-(4-Benzoyloxy-2,5-dimethoxyphenyl)-2,3-dihydro-2,2-dimethyl-5-tosyloxy-4*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-4,6-dione (20). Tosylation of **19** (2.92 g) with TsCl (1.40 g) in Me_2CO (250 ml) and dioxane (150 ml) gave **20** (3.20 g, 84%) as colorless needles: mp 213—215 °C (MeOH–Me_2CO); ^{1}H NMR ($CDCl_3$) δ=1.46 (6H, s, CH_3×2), 2.38 (3H, s, $C_6H_4CH_3$), 2.67 (2H, s, CH_2CO), 3.73 and 3.76 (each 3H, s, OCH_3), 6.80 (1H, s, C_{10}-H), 6.87 and 7.00 (each 1H, s, Arom-H), 7.2—8.3 (9H, m, $C_6H_4CH_3$ and C_6H_5CO), 7.78 (1H, s, C_8-H).

Found: C, 64.21; H, 4.47%. Calcd for $C_{36}H_{30}O_{11}S$: C, 64.47; H, 4.52%.

7-(4-Benzoyloxy-2,5-dimethoxyphenyl)-3,4-dihydro-4-hydroxy-2,2-dimethyl-5-tosyloxy-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one (21). A mixture of **20** (680 mg) and $PdCl_2$ (270 mg) in THF (200 ml) and water (40 ml) was stirred with adding $NaBH_4$ (380 mg) at 5—9 °C for 1 h. The reaction mixture was worked up by a method similar to that used for the preparation of **16** to give **21** (464 mg, 68%) as colorless needles: mp 174—176 °C (MeOH); ^{1}H NMR ($CDCl_3$) δ=1.42 and 1.55 (each 3H, s, CH_3), 2.07 (2H, m, CH_2CHOH), 2.42 (3H, s, $C_6H_4CH_3$), 3.74 and 3.76 (each 3H, s, OCH_3), 3.60 (1H, br, CH_2CHOH), 5.12 (1H, m, CH_2CHOH), 6.81 (2H, s, $C_{3'}$-H and C_{10}-H), 7.06 (1H, s, $C_{6'}$-H), 7.1—8.3 (9H, s, $C_6H_4CH_3$ and C_6H_5CO), 7.82 (1H, s, C_8-H).

Found: C, 63.98; H, 4.93%. Calcd for $C_{36}H_{32}O_{11}S$: C, 64.27; H, 4.80%.

7-(4-Benzoyloxy-2,5-dimethoxyphenyl)-2,2-dimethyl-5-tosyloxy-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one (22). Dehydration of **21** (320 mg) with TsOH·H_2O (20 mg) gave **22** (280 mg, 90%) as colorless needles: mp 226—227 °C (MeOH–Me_2CO); UV λ_{max} nm (log ε) (EtOH) 263 (4.49), 294sh (4.32), 338sh (3.92); ^{1}H NMR ($CDCl_3$) δ=1.44 (6H, s, CH_3×2), 2.42 (3H, s, $C_6H_4CH_3$), 3.76 and 3.78 (each 3H, s, OCH_3), 5.59 (1H, d, J=10 Hz, C_3-H), 6.46 (1H, d, J=10 Hz, C_4-H), 6.76 (1H, s, C_{10}-H), 6.83 and 7.06 (each 1H, s, Arom-H), 7.1—8.3

(9H, m, $C_6\underline{H}_4CH_3$ and C_6H_5CO), 7.81 (1H, s, C_8–H).

Found: C, 65.97; H, 4.58%. Calcd for $C_{36}H_{30}O_{10}S$: C, 66.04; H, 4.63%.

5-Hydroxy-7-(4-hydroxy-2,5-dimethoxyphenyl)-2,2-dimethyl-2*H*,6*H*-benzo[1,2-*b*:5,4-*b'*]dipyran-6-one (Elongatin) (1). Hydrolysis of **22** (300 mg) with a 5% KOH solution in MeOH and dioxane gave **1** (151 mg, 83%) as colorless needles: mp 181—183 °C (MeOH) (lit,[4] mp 181—182 °C). Compound **1** was converted into the diacetate **23** (227—228 °C; lit,[4] mp 227—228 °C) and the dimethyl ether **24** (mp 132—134 °C; lit,[4] mp 132—134 °C), respectively.

2,4-Bis(benzyloxy)-6-hydroxyacetophenone (25). A mixture of 2,4,6-trihydroxyacetophenone (40 g), $PhCH_2Cl$ (58 ml), and K_2CO_3 (100 g) in HMPA (340 ml) was stirred under an atmosphere of N_2 at 90—93 °C for 70 min [monitered by silica-gel TLC with petroleum ether–1,2-dichloroethane (2:1), R_f=0.39]. After removal of K_2CO_3, the filtrate was poured into ice-cold water and acidified to pH 4 with dil. HCl, and then heated at 60—70 °C for 1 h to give white precipitates. The precipitates were recrystallized from MeOH–Me_2CO to give **25** (66.3 g, 80%): mp 100—102 °C (lit,[7] mp 98—100 °C, lit,[8] mp 96—98 °C).

Found: C, 75.68; H, 5.79%. Calcd for $C_{22}H_{20}O_7$: C, 75.84; H, 5.79%.

2,4-Bis(benzyloxy)-6-methoxyacetophenone (26). Methylation of **25** (30 g) with $(MeO)_2SO_2$ (20.4 g) gave **26** (28.4g, 91%) as colorless needles: mp 64—65 °C (MeOH–Me_2CO); ^{1}H NMR ($CDCl_3$) δ=2.43 (3H, s, $COCH_3$), 3.72 (3H, s, OCH_3), 4.99 (4H, s, $C_6H_5C\underline{H}_2$×2), 6.28 (2H, s, C_3–H and C_5–H), 7.30 and 7.33 (each 5H, s, $C_6\underline{H}_5CH_2$).

Found: C, 76.14; H, 5.97%. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%.

2,4-Dihydroxy-6-methoxyacetophenone (27). Debenzylation of **26** (21.65g) with 10% palladium on charcoal (3 g) gave **27** (9.65 g, 89%) as colorless needles: mp 201—202 °C (MeOH) (lit,[9] mp 203—204 °C).

Found: C, 59.45; H, 5.30%. Calcd for $C_9H_{10}O_4$: C, 59.33; H, 5.53%.

1-(3-Acetyl-2,6-dihydroxy-4-methoxyphenyl)-3-methyl-2-buten-1-one (28). 3-Methyl-2-butenoyl chloride (7.8 g) in Et_2O (50 ml) was added, with stirring and cooling at 0 °C, to a solution of **27** (9.6 g) and $AlCl_3$ (4.9 g) in Et_2O (150 ml); the reaction mixture was then stirred for an additional 15 h. After removal of the ethereal layer, the residue was poured into a mixture of ice and HCl, and then warmed at 40 °C to give precipitates. The precipitates were recrystallized from EtOH to give **28** (12.4 g, 89%) as yellow needles: mp 117—119 °C; ^{1}H NMR ($CDCl_3$) δ=2.00 and 2.17 (each 3H, s, CH_3), 2.57 (3H, s, $COCH_3$), 3.86 (3H, s, OCH_3), 5.85 (1H, s, Arom-H), 7.12 (1H, m, CH=), 15.25 and 16.35 (each 1H, s, OH).

Found: C, 63.55; H, 5.96%. Calcd for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10%.

6-Acetyl-5-hydroxy-7-methoxy-2,2-dimethyl-4-chromanone (29). A mixture of the diketone **28** (12.27 g) and 10% KOH solution (150 ml) in MeOH (350 ml) was stirred at room temperature for 3 h. The resulting compound was recrystallized from MeOH–H_2O to give **29** (11.43 g, 93%) as colorless needles: mp 116—117 °C; ^{1}H NMR ($CDCl_3$) δ=1.44 (6H, s, CH_3×2), 2.50 (3H, s, $COCH_3$), 2.70 (2H, s, $COCH_2$), 3.85 (3H, s, OCH_3), 5.95 (1H, s, Arom-H), 13.04 (1H, s, OH).

Found: C, 63.81; H, 6.11%. Calcd for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10%.

5-Hydroxy-7-methoxy-2,2-dimethyl-6-[1-oxo-3-(4-benzyloxy-2,5-dimethoxyphenyl)-2-propenyl]-4-chromanone (30). Condensation of **29** (9.25 g) with **8** (9.53 g) gave **30** (9.80 g, 55%) as yellow needles: mp 148—150 °C (MeOH); ^{1}H NMR ($CDCl_3$) δ=1.47 (6H, s, CH_3×2), 2.70 (2H, s, $COCH_2$), 3.69, 3.80, and 3.85 (each 3H, s, OCH_3), 5.16 (2H, s, $C_6H_5C\underline{H}_2$), 6.00 (1H, s, C_8–H), 6.47 and 7.06 (each 1H, s, Arom-H), 6.94 and 7.76 (each 1H, d, J=16 Hz, CH=), 7.36 (5H, s, $C_6\underline{H}_5CH_2$), 12.35 (1H, s, OH).

Found: C, 69.25; H, 6.01%. Calcd for $C_{30}H_{30}O_8$: C, 69.48; H, 5.83%.

Acetate 31. Acetylation of 5-hydroxy compound **30** gave the acetate **31** as yellow needles: mp 167—169 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ=1.47 (6H, s, CH_3×2), 2.20 (3H, s, $COCH_3$), 2.63 (2H, s, $COCH_2$), 3.70, 3.78, and 3.83 (each 3H, s, OCH_3), 5.15 (2H, s, $C_6H_5C\underline{H}_2$), 6.33 (1H, s, C_8–H), 6.47 and 6.98 (each 1H, s, Arom-H), 6.85 and 7.66 (each 1H, d, J=16 Hz, CH=), 7.35 (5H, s, $C_6\underline{H}_5CH_2$).

Found: C, 68.42; H, 5.69%. Calcd for $C_{32}H_{32}O_9$: C, 68.56; H, 5.75%.

3-(4-Benzyloxy-2,5-dimethoxyphenyl)-8,9-dihydro-5-methoxy-8,8-dimethyl-4*H*,10*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4,10-dione (32). The oxidative rearrangement of **31** (7.0 g) with TTN (6.4 g) and the subsequent cyclization gave **32** (4.91 g, 76%) as colorless needles: mp 204—206 °C (EtOAc); ^{1}H NMR ($CDCl_3$) δ=1.48 (6H, s, CH_3×2), 2.73 (2H, s, $COCH_2$), 3.59, 3.82, and 3.94 (each 3H, s, OCH_3), 5.16 (2H, s, $C_6H_5C\underline{H}_2$), 6.29 (1H, s, C_6–H), 6.56 and 6.97 (each 1H, s, Arom-H), 7.35 (5H, s, $C_6\underline{H}_5CH_2$), 7.92 (1H, s, C_2–H).

Found: C, 69.54; H, 5.29%. Calcd for $C_{30}H_{28}O_8$: C, 69.75; H, 5.47%.

3-(4-Benzyloxy-2,5-dimethoxyphenyl)-8,9-dihydro-5-hydroxy-8,8-dimethyl-4*H*,10*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4,10-dione (33). Demethylation of **32** (4.90 g) with $AlBr_3$ (15.2 g) gave **33** (4.65 g, 97%) as colorless needles: mp 186—188 °C (MeOH–EtOAc); ^{1}H NMR ($CDCl_3$) δ=1.46 (6H, s, CH_3×2), 2.71 (2H, s, $COCH_2$), 3.62 and 3.83 (each 3H, s, OCH_3), 5.15 (2H, s, $C_6H_5C\underline{H}_2$), 6.26 (1H, s, C_6–H), 6.57 and 6.90 (each 1H, s, Arom-H), 7.33 (5H, s, $C_6\underline{H}_5CH_2$), 8.06 (1H, s, C_2–H), 13.75 (1H, s, C_5–OH).

Found: C, 69.12; H, 5.40%. Calcd for $C_{29}H_{26}O_8$: C, 69.30; H, 5.23%.

8,9-Dihydro-5-hydroxy-3-(4-hydroxy-2,5-dimethoxyphenyl)-8,8-dimethyl-4*H*,10*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4,10-dione (34). Debenzylation of **33** (3.55 g) with 10% palladium on charcoal gave **34** (2.76 g, 95%) as colorless needles: mp 197—198 °C (MeOH–Me_2CO); ^{1}H NMR ($CDCl_3$) δ=1.50 (6H, s, CH_3×2), 2.72 (2H, s, $COCH_2$), 3.70 and 3.83 (each 3H, s, OCH_3), 5.95 (1H, s, $C_{4'}$–OH), 6.25 (1H, s, C_6–H), 6.60 and 6.86 (each 1H, s, Arom-H), 8.06 (1H, s, C_2–H), 10.93 (1H, s, C_5–OH).

Found: C, 64.05; H, 4.70%. Calcd for $C_{22}H_{20}O_8$: C, 64.07; H, 4.90%.

3-(4-Benzoyloxy-2,5-dimethoxyphenyl)-8,9-dihydro-5-hydroxy-8,8-dimethyl-4*H*,10*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4,10-dione (35). Benzoylation of **34** (310 mg) with PhCOCl (0.92 ml) gave **35** (380 mg, 97%) as colorless needles: mp 253—255 °C (MeOH–Me_2CO); ^{1}H NMR ($CDCl_3$) δ=1.50 (6H, s, CH_3×2), 2.70 (2H, s, $COCH_2$), 3.70 and 3.73 (each 3H, s, OCH_3), 6.23 (1H, s, C_6–H), 6.77 and 6.97 (each 1H, s, Arom-H), 7.3—8.2 (5H, m, C_6H_5CO), 8.06 (1H, s, C_2–H), 13.58 (1H, s, C_5–OH).

Found: C, 67.33; H, 4.51%. Calcd for $C_{29}H_{24}O_9$: C, 67.44;

H, 4.68%.

3-(4-Benzoyloxy-2,5-dimethoxyphenyl)-8,9-dihydro-8,8-dimethyl-5-tosyloxy-4*H*,10*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4,10-dione (36). Tosylation of **35** (710 mg) with TsCl gave **36** (820 mg, 89%) as colorless needles: mp 183—185 °C (Me_2CO); ^1H NMR ($CDCl_3$) δ=1.50 (6H, s, CH_3×2), 2.40 (3H, s, $C_6H_5C\underline{H}_3$), 2.76 (2H, s, $COCH_2$), 3.68 and 3.73 (each 3H, s, OCH_3), 6.75 (1H, s, C_6-H), 6.88 and 6.96 (each 1H, s, Arom-H), 7.1—8.2 (9H, m, C_6H_5CO and $C_6\underline{H}_4CH_3$), 7.91 (1H, s, C_2-H).

Found: C, 64.29; H, 4.49%. Calcd for $C_{36}H_{30}O_{11}S$: C, 64.47; H, 4.52%.

3-(4-Benzoyloxy-2,5-dimethoxyphenyl)-9,10-dihydro-10-hydroxy-8,8-dimethyl-5-tosyloxy-4*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one (37). The selective reduction of **36** (780 mg) with $NaBH_4$ (460 mg) and $PdCl_2$ (310 mg) at 35—38 °C for 30 min gave **37** (712 mg, 91%) as colorless needles: mp 233—234 °C (Me_2CO-petroleum ether); ^1H NMR ($CDCl_3$) δ=1.41 and 1.46 (each 3H, s, CH_3), 2.08 (2H, d, J=4 Hz, $C\underline{H}_2$-CHOH), 2.38 (3H, s, $C_6H_4C\underline{H}_3$), 2.85 (1H, d, J=4 Hz, C_{10}-OH), 3.67 and 3.72 (each 3H, s, OCH_3), 5.07 (1H, t, J=4 Hz, $CH_2C\underline{H}OH$), 6.67, 6.75, and 6.96 (each 1H, s, Arom-H), 7.1—8.2 (9H, m, C_6H_5CO and $C_6\underline{H}_4CH_3$), 7.80 (1H, s, C_2-H).

Found: C, 64.00; H, 4.53%. Calcd for $C_{36}H_{32}O_{11}S$: C, 64.28; H, 4.80%.

3-(4-Benzoyloxy-2,5-dimethoxyphenyl)-8,8-dimethyl-5-tosyloxy-4*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one (38). Dehydration of crude **37** (900 mg) gave **38** (510 mg, 67% yield based on **36**) as colorless needles: mp 215—217 °C (MeOH-Me_2CO); UV λ_{max} nm (log ε) (EtOH) 258 (4.59), 263 (4.59), 301 (4.15); ^1H NMR ($CDCl_3$) δ=1.46 (6H, s, CH_3×2), 2.39 (3H, s, $C_6H_4C\underline{H}_3$), 3.70 and 3.75 (each 3H, s, OCH_3), 5.65 (1H, d, J=10 Hz, C_9-H), 6.70 (1H, d, J=10 Hz, C_{10}-H), 6.67, 6.78, and 6.99 (each 1H, s, Arom-H), 7.1—8.2 (9H, m, C_6H_5CO and $C_6\underline{H}_4CH_3$), 7.80 (1H, s, C_2-H).

Found: C, 65.82; H, 4.63%. Calcd for $C_{36}H_{30}O_{10}S$: C, 66.04; H, 4.63%.

5-Hydroxy-3-(4-hydroxy-2,5-dimethoxyphenyl)-8,8-dimethyl-4*H*,8*H*-benzo[1,2-*b*:3,4-*b'*]dipyran-4-one (2). Hydrolysis of **38** (400 mg) gave **2** (180 mg, 74%) as yellow needles: mp 174—175 °C (MeOH-H_2O) (lit,[4] mp 173—175 °C). Diacetate **39** of **2**: mp 225—226 °C; lit,[4] mp 224—226 °C. 4'-Methyl ether (toxicarol isoflavone) (**40**): mp 219—220 °C; lit,[4] mp 219—220 °C. Dimethyl ether **41**: mp 178—180 °C; lit,[4] mp 179—180 °C.

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