New Synthetic Approaches to Naturally Occurring and Unnatural Pyranoflavones

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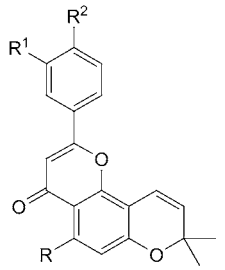
Total synthesis of biologically interesting natural and unnatural pyranoflavones has been accomplished starting from readily available 2,4-dihydroxyacetophenone or 2,4-dihydroxy-6-methoxyacetophenone in three steps, *i.e.*, benzopyran formation, condensation, and cyclization reaction.

Introduction. – Pyranoflavones, an abundant subclass of flavonoids, are widely distributed in nature [1]. They have been associated with a wide variety of biological properties such as antimutagenic, antimicrobial, anti-ulcer, and antitumor activities, and some plants containing these compounds are used in traditional medicines in China and Europe [2]. Among these, pyranoflavones **1**–**3** (*Fig.*) were isolated from *Lonchocarpus subglaucescens* [3] and *L. montanus* [4]. Isopongaflavone (**4**) was isolated from *Tephrosia tunicate* [5] and *T. egregia* [6], and exhibited potent antifeedant activities against *Maruca testualis* and *Eldana saccharina* [7]. Natural pyranoflavone **5** was isolated from *Pongamia pinnata* [8]. Unnatural atalantoflavone dimethyl ether (**6**) also exhibited significant insecticidal activity [7]. This wide range of biological properties has attracted interest in the synthesis of natural and unnatural pyranoflavones. Although synthetic approaches for compounds **1**, **2**, and **4**–**6** have been reported [9][10], simpler and more concise synthetic routes are still needed.

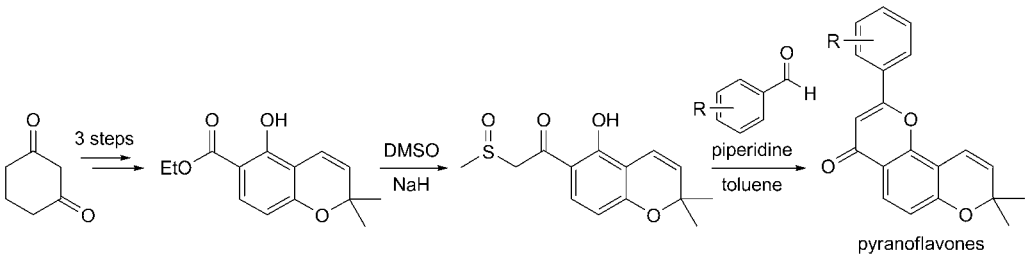


	R	R^1	R^2
1	H	H	H
2	H	$-OCH_2O-$	
3	H	H	MeO
4	MeO	H	H
5	MeO	$-OCH_2O-$	
6	MeO	H	MeO

Figure. *Selected naturally occurring pyranoflavones* **1**–**5** *and unnatural atalantoflavone dimethyl ether* (**6**)

Recently, we have reported a new methodology for synthesizing a variety of benzopyrans by ethylenediamine diacetate-catalyzed and base-mediated reactions of 1,3-dicarbonyl compounds or resorcinols with α,β-unsaturated aldehydes [11]. We also reported convergent synthetic routes for pyranoflavones **1** and **2** starting from cyclohexane-1,3-dione through five steps in 46–48% overall yield (*Scheme 1*) [12]. As

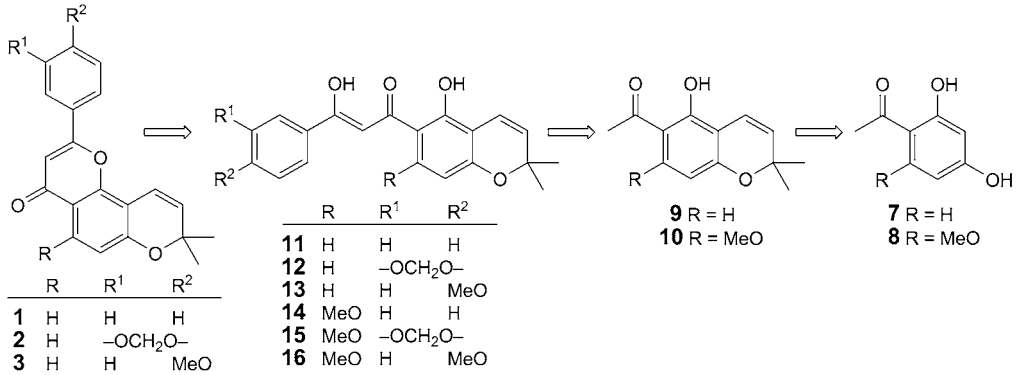
Scheme 1



an extension of our previous work, we report herein more concise and efficient synthetic approaches to naturally occurring pyranoflavones **1**–**5** and the unnatural atalantoflavone dimethyl ether (**6**) through three-step reactions.

Results and Discussion. – The retrosynthetic strategy for the synthesis of pyranoflavones **1**–**6** is outlined in *Scheme 2*. These compounds could be prepared *via* cyclization of β-hydroxypyranochalcones **11**–**16**. These key intermediates could be generated from benzopyrans **9** and **10** through base-mediated condensations. The latter could be prepared from readily available compounds **7** and **8** through benzopyran formation reactions.

Scheme 2. *Retrosynthetic Analysis for the Synthesis of Naturally Occurring Pyranoflavones* **1**–**5** *and Unnatural* **6**

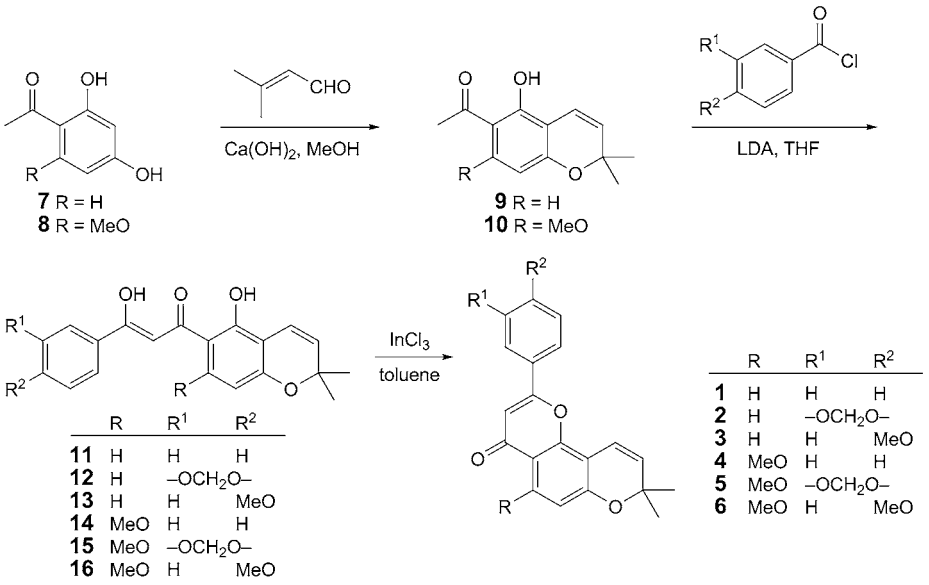


	R	R^1	R^2
1	H	H	H
2	H	–OCH_2O–	
3	H	H	MeO
4	MeO	H	H
5	MeO	–OCH_2O–	
6	MeO	H	MeO

	R	R^1	R^2
11	H	H	H
12	H	–OCH_2O–	
13	H	H	MeO
14	MeO	H	H
15	MeO	–OCH_2O–	
16	MeO	H	MeO

The concise total synthesis of **1**–**6** was carried out as depicted in *Scheme 3*. Recently, we developed a new and useful methodology for preparing a variety of benzopyrans using $Ca(OH)_2$-mediated reactions of 1,3-dihydroxyxanthen-9-one to α,β-unsaturated aldehydes [13]. By this methodology, reactions of **7** and **8** with 3-methylbut-2-enal in the presence of 1.0 equiv. of $Ca(OH)_2$ in refluxing MeOH for 5–6 h gave **9** [2e][11n] and **10** [14] in 70 and 90% yield, respectively. Reaction of **9** with an excess of lithium diisopropylamide (LDA) in THF at $-78°$, followed by addition of

Scheme 3



PhCOCl (BzCl), gave the desired compound **11** in 75% yield. Similarly, treatment of **9** and **10** with the corresponding acid chlorides afforded products **12**–**16** in 80, 72, 80, 85, and 78% yield, respectively. Interestingly, the compounds **12**–**16** occur as two tautomers, an enol and a keto form. The presence of the tautomeric chalcones was readily identified by analysis of their spectroscopic data. In addition, compound **14** was previously isolated as a natural product from the roots of *Tephrosia tunicate* [5], and compound **16** was previously synthesized by *Banerji et al.* [15]. Several oxidative cycloadditions of β-hydroxy chalcones to afford flavones have been already reported by other groups utilizing several catalysts and reagents such as silica-PCl_5 [16], $Ga(OTf)_3$ [17], $CuCl_2$/MW [18], and $KHSO_4$ [19]. However, these reactions have a limitation due to harsh reaction conditions and unsatisfactory yields. Recently, we have developed a novel and efficient methodology for the synthesis of a variety of flavones by $InCl_3$-catalyzed or -mediated cyclization of 1,3-diketones [20]. By this methodology, we attempted the cyclization reactions of **11**–**16** to produce **1**–**6**. Treatment of **11** in the presence of $InCl_3$ (0.5 equiv.) in refluxing toluene for 4 h provided the desired product **1** in 95% yield. Similarly, reactions of **12**–**16** afforded **2**–**6** in 93, 94, 88, 90, and 91% yield, respectively. The spectroscopic data of the synthetic materials **1**–**5** agreed well with those reported for natural products in the literature [2–5][8].

In conclusion, a concise total synthesis of naturally occurring pyranoflavones **1**–**5** and unnatural **6** was accomplished starting from readily available 2,4-dihydroxyacetophenone (**7**) and 2,4-dihydroxy-6-methoxyacetophenone (**8**) *via* benzopyran formation, followed by base-mediated condensation and subsequent oxidative cyclizations. These synthetic approaches provide rapid routes to biologically interesting pyranoflavones.

Experimental Part

General. All experiments were carried out under N_2. Anal. TLC: *Merck* precoated silica-gel plates (SiO_2; *Art. 5554*) with a fluorescent indicator. Flash column chromatography (FC): SiO_2 *9385* (*Merck*). IR Spectra: *BioRad FTS 3000* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker Model ARX* (300 and 75 MHz, resp.) spectrometer in $CDCl_3$ or (D_6)DMSO as the solvent; δ in ppm rel. to Me_4Si as internal standard, J in Hz. HR-MS: *Jeol JMS 700* spectrometer at the Korea Basic Science Institute; in m/z.

General Procedure for the Synthesis of Benzopyrans **9** *and* **10**. To a mixture of a ketone **7** or **8** (10.0 mmol) and 3-methylbut-2-enal (11.0 mmol) in anh. MeOH (30 ml), $Ca(OH)_2$ (30.0 mmol) was added at r.t. The mixture was heated to reflux for 10 h, and the progress was monitored by TLC. After removal of the solvent, 2N HCl (20 ml) was added to the residue, and the mixture was extracted with AcOEt (3×30 ml). The combined org. layer was washed with H_2O (30 ml) and dried ($MgSO_4$). Removal of solvent and purification by CC (SiO_2; hexane/AcOEt 7:1) gave benzopyrans **9** and **10**.

Demethylisoencecalin (=*1-(5-Hydroxy-2,2-dimethyl-2*H*-1-benzopyran-6-yl)ethanone*; **9**) [2e][11n]. Yield: 70%. M.p. 102–103°.

Isoevodionol (=*1-(5-Hydroxy-7-methoxy-2,2-dimethyl-2*H*-1-benzopyran-6-yl)ethanone*; **10**) [14]. Yield: 90%. M.p. 128–129°. IR (KBr): 2924, 2855, 1620, 1464, 1362, 1269, 1206, 1159, 1124, 891, 831, 731. ^1H-NMR ($CDCl_3$): 14.28 (*s*, 1 H); 6.62 (*d*, $J = 10.0$, 1 H); 5.85 (*s*, 1 H); 5.38 (*d*, $J = 10.0$, 1 H); 3.81 (*s*, 3 H); 2.56 (*s*, 3 H); 1.41 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 203.0; 162.8; 161.7; 160.0; 125.2; 115.9; 105.5; 102.5; 90.5; 78.0; 55.4; 32.9; 28.2; 28.2. HR-MS: 248.1047 (M^+, $C_{14}H_{16}O_4^+$; calc. 248.1049).

General Procedure for Synthesis of Compounds **11**–**16**. To a mixture of **9** or **10** (1.0 mmol) in anh. THF (10 ml) at −78° was added LDA (3.0 mmol), and the mixture was allowed to warm to −25° for 1 h. After cooling to −78°, corresponding benzoyl chloride (1.2 mmol) in dry THF (2 ml) was added during 20 min. The resulting mixture was allowed to warm to 0° during 3 h, and a sat. aq. NH_4Cl soln. (20 ml) was added. The mixture was extracted with AcOEt (20 ml × 3). The combined org. layers were washed with H_2O (30 ml), dried ($MgSO_4$), and the solvent was removed in a rotary evaporator. The residue was purified by FC (SiO_2; hexane/AcOEt 9:1) to give **11**–**16**.

*(2*Z*)-3-Hydroxy-1-(5-hydroxy-2,2-dimethyl-2*H*-1-benzopyran-6-yl)-3-phenylprop-2-en-1-one* (**11**). Yield: 75%. M.p. 65–67°. IR (KBr): 3061, 2975, 2929, 1602, 1571, 1488, 1336, 1270, 1124, 1077, 896, 767, 690, 626. ^1H-NMR ($CDCl_3$): enol form: 15.36 (*s*, OH); 12.81 (*s*, OH); 7.89 (*d*, $J = 7.8$, 2 H); 7.55 (*d*, $J = 8.7$, 1 H); 7.52–7.42 (*m*, 3 H); 6.73 (*d*, $J = 10.2$, 1 H); 6.67 (*s*, 1 H); 6.36 (*d*, $J = 8.7$, 1 H); 5.57 (*d*, $J = 9.9$, 1 H); 1.45 (*s*, 6 H); keto form: 12.99 (*s*, OH); 7.99 (*d*, $J = 7.8$, 2 H); 7.55 (*d*, $J = 8.7$, 1 H); 7.52–7.44 (*m*, 3 H); 6.71 (*d*, $J = 10.2$, 1 H); 6.31 (*d*, $J = 8.7$, 1 H); 5.56 (*d*, $J = 10.2$, 1 H); 4.51 (*s*, 2 H); 1.43 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): enol form: 194.5; 175.6; 159.5; 159.4; 133.8; 132.0; 129.5; 128.6; 128.6; 128.1; 126.5; 126.5; 115.9; 112.4; 109.6; 108.5; 91.8; 77.6; 28.3; 28.3; keto form: 202.6; 193.8; 159.8; 159.5; 136.1; 133.7; 131.9; 128.8; 128.2; 128.2; 126.5; 126.5; 115.7; 115.5; 108.8; 108.2; 77.8; 49.8; 28.2; 28.2. HR-MS: 322.1202 (M^+, $C_{20}H_{18}O_4^+$; calc. 322.1205).

*(2*Z*)-3-(1,3-Benzodioxol-5-yl)-3-hydroxy-1-(5-hydroxy-2,2-dimethyl-2*H*-1-benzopyran-6-yl)prop-2-en-1-one* (**12**). Yield: 80%. M.p. 114–115°. IR (KBr): 3076, 2973, 2922, 1734, 1674, 1584, 1486, 1447, 1329, 1246, 1117, 1042, 804, 780. ^1H-NMR ($CDCl_3$): enol form: 15.34 (*s*, OH); 12.54 (*s*, OH); 7.37 (*d*, $J = 9.0$, 1 H); 7.33 (*d*, $J = 9.3$, 1 H); 7.17 (*s*, 1 H); 6.69 (*d*, $J = 8.4$, 1 H); 6.60 (*d*, $J = 9.9$, 1 H); 6.39 (*s*, 1 H); 6.22 (*d*, $J = 9.0$, 1 H); 5.88 (*s*, 2 H); 5.45 (*d*, $J = 9.9$, 1 H); 1.34 (*s*, 6 H); keto form: 12.67 (*s*, OH); 7.48–7.43 (*m*, 2 H); 6.69 (*d*, $J = 8.4$, 1 H); 6.55 (*d*, $J = 10.2$, 1 H); 6.39 (*s*, 1 H); 6.21 (*d*, $J = 9.0$, 1 H); 5.89 (*s*, 2 H); 5.44 (*d*, $J = 9.9$, 1 H); 4.30 (*s*, 2 H); 1.32 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): enol form: 193.7; 175.2; 159.3; 159.1; 150.9; 148.0; 131.9; 129.2; 127.9; 121.9; 115.8; 112.3; 109.4; 108.3; 108.1; 106.4; 101.7; 90.7; 77.4; 28.1; 28.1; keto form: 198.0; 191.5; 160.1; 159.8; 152.3; 148.2; 130.8; 128.1; 127.5; 125.5; 115.4; 113.4; 109.0; 108.7; 108.1; 107.8; 101.9; 77.8; 49.5; 28.2; 28.2. HR-MS: 366.1105 (M^+, $C_{21}H_{18}O_6^+$; calc. 366.1103).

*(2*Z*)-3-Hydroxy-1-(5-hydroxy-2,2-dimethyl-2*H*-1-benzopyran-6-yl)-3-(4-methoxyphenyl)prop-2-en-1-one* (**13**). Yield: 72%. M.p. 83–84°. IR (KBr): 3056, 2972, 2932, 1734, 1673, 1598, 1509, 1488, 1442, 1339, 1267, 1241, 1175, 1118, 1075, 1031, 897, 803, 781, 695, 585. ^1H-NMR ($CDCl_3$): enol form: 15.48 (*s*, OH); 12.69 (*s*, OH); 7.82 (*d*, $J = 8.4$, 2 H); 7.51 (*d*, $J = 8.1$, 1 H); 6.89 (*d*, $J = 8.1$, 2 H); 6.72 (*d*, $J = 9.9$, 1 H); 6.56 (*s*, 1 H); 6.34 (*d*, $J = 8.4$, 1 H); 5.55 (*d*, $J = 9.9$, 1 H); 3.81 (*s*, 3 H); 1.34 (*s*, 6 H); keto form: 12.85

(*s*, OH); 7.94 (*d*, *J* = 8.4, 2 H); 7.54 (*d*, *J* = 7.8, 1 H); 6.89 (*d*, *J* = 8.1, 2 H); 6.66 (*d*, *J* = 9.9, 1 H); 6.31 (*d*, *J* = 7.8, 1 H); 5.54 (*d*, *J* = 9.6, 1 H); 4.42 (*s*, 2 H); 3.81 (*s*, 3 H); 1.42 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): enol form: 193.8; 175.7; 162.7; 159.3; 159.0; 131.1; 129.2; 128.4; 128.4; 125.8; 115.9; 113.9; 113.9; 112.4; 109.5; 108.3; 90.4; 77.4; 55.3; 28.1; 28.1; keto form: 198.2; 191.9; 163.9; 160.1; 159.8; 132.0; 129.1; 128.1; 128.0; 128.0; 115.5; 113.8; 113.8; 113.5; 109.0; 108.7; 77.8; 55.4; 49.5; 28.2; 28.2. HR-MS: 352.1307 (M^+, $C_{21}H_{20}O_5^+$; calc. 352.1311).

*(2Z)-3-Hydroxy-1-(5-hydroxy-7-methoxy-2,2-dimethyl-2*H*-1-benzopyran-6-yl)-3-phenylprop-2-en-1-one* (**14**) [21]. Yield: 80%. M.p. 122–123°. IR (KBr): 3069, 2975, 2936, 1596, 1568, 1462, 1426, 1389, 1274, 1199, 1149, 1119, 832, 766. ^{1}H-NMR ($CDCl_3$): enol form: 15.41 (*s*, OH); 13.65 (*s*, OH); 7.86 (*d*, *J* = 6.6, 2 H); 7.46–7.44 (*m*, 3 H); 7.30 (*s*, 1 H); 6.67 (*d*, *J* = 9.9, 1 H); 5.93 (*s*, 1 H); 5.45 (*d*, *J* = 10.2, 1 H); 3.90 (*s*, 3 H); 1.44 (*s*, 6 H); keto form: 13.90 (*s*, OH); 8.05 (*d*, *J* = 8.4, 2 H); 7.44–7.37 (*m*, 3 H); 6.58 (*d*, *J* = 9.9, 1 H); 5.71 (*s*, 1 H); 5.37 (*d*, *J* = 9.9, 1 H); 4.46 (*s*, 2 H); 3.35 (*s*, 3 H); 1.35 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): enol form: 193.8; 175.5; 161.9; 161.2; 159.6; 134.4; 131.6; 128.6; 128.6; 126.6; 126.6; 125.4; 116.1; 104.2; 103.2; 98.2; 91.8; 78.0; 55.9; 28.3; 28.3; keto form: 198.5; 193.7; 162.0; 160.7; 154.4; 133.7; 130.1; 130.1; 128.7; 128.4; 128.4; 125.4; 115.8; 105.2; 103.0; 91.2; 78.3; 55.4; 54.7; 28.3; 28.3. HR-MS: 352.1309 (M^+, $C_{21}H_{20}O_5^+$; calc. 352.1311).

*(2Z)-3-(1,3-Benzodioxol-5-yl)-3-hydroxy-1-(5-hydroxy-7-methoxy-2,2-dimethyl-2*H*-1-benzopyran-6-yl)prop-2-en-1-one* (**15**). Yield: 85%. M.p. 179–180°. IR (KBr): 3059, 2974, 2921, 1718, 1676, 1610, 1585, 1485, 1445, 1366, 1252, 1204, 1149, 1120, 1039, 933, 884, 814, 735, 631, 567. ^{1}H-NMR ($CDCl_3$): enol form: 15.74 (*s*, OH); 13.71 (*s*, OH); 7.70 (*d*, *J* = 8.1, 1 H); 7.60 (*s*, 1 H); 6.78 (*d*, *J* = 8.1, 1 H); 6.88 (*d*, *J* = 9.9, 1 H); 6.09 (br. *s*, 3 H); 5.84 (*s*, 1 H); 5.32 (*d*, *J* = 9.9, 1 H); 3.96 (*s*, 3 H); 1.50 (*s*, 6 H); keto form: 14.03 (*s*, OH); 7.59 (*d*, *J* = 8.1, 1 H); 7.48 (*s*, 1 H); 6.93 (*d*, *J* = 8.1, 1 H); 6.69 (*d*, *J* = 9.9, 1 H); 6.11 (*s*, 2 H); 5.84 (*s*, 1 H); 5.50 (*d*, *J* = 9.9, 1 H); 4.50 (*s*, 2 H); 3.54 (*s*, 3 H); 1.48 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): enol form: 192.9; 175.3; 166.2; 161.8; 150.7; 128.3; 125.1; 121.9; 116.0; 109.0; 108.2; 108.0; 106.5; 105.2; 102.8; 101.7; 97.1; 91.6; 77.9; 55.8; 28.3; 28.3; keto form: 198.6; 192.7; 161.9; 161.9; 160.6; 151.8; 148.2; 131.3; 125.4; 124.3; 115.7; 107.9; 107.6; 105.2; 102.8; 101.9; 91.2; 78.2; 55.4; 54.4; 28.3; 28.3. HR-MS: 396.1207 (M^+, $C_{22}H_{20}O_7^+$; calc. 396.1209).

*(2Z)-3-Hydroxy-1-(5-hydroxy-7-methoxy-2,2-dimethyl-2*H*-1-benzopyran-6-yl)-3-(4-methoxyphenyl)-2-propen-1-one* (**16**) [15]. Yield: 78%. M.p. 142–144°. IR (KBr): 3058, 2973, 2934, 1675, 1603, 1510, 1460, 1422, 1321, 1292, 1263, 1213, 1167, 1147, 1122, 1028, 830, 735. ^{1}H-NMR ($CDCl_3$): enol form: 15.68 (*s*, OH); 13.69 (*s*, OH); 7.84 (*d*, *J* = 9.0, 2 H); 7.21 (*s*, 1 H); 6.92 (*d*, *J* = 9.0, 2 H); 6.65 (*d*, *J* = 9.9, 1 H); 5.90 (*s*, 1 H); 5.43 (*d*, *J* = 9.9, 1 H); 3.88 (*s*, 3 H); 3.85 (*s*, 3 H); 1.42 (*s*, 6 H); keto form: 14.04 (*s*, OH); 7.91 (*d*, *J* = 8.7, 2 H); 6.95 (*d*, *J* = 8.7, 2 H); 6.64 (*d*, *J* = 9.9, 1 H); 5.77 (*s*, 1 H); 5.44 (*d*, *J* = 9.9, 1 H); 4.46 (*s*, 2 H); 3.86 (*s*, 3 H); 3.42 (*s*, 3 H); 1.41 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): enol form: 192.9; 175.9; 162.6; 160.9; 160.6; 159.2; 129.6; 129.6; 126.5; 126.0; 116.1; 113.8; 113.8; 104.1; 103.2; 96.9; 91.7; 77.9; 55.8; 55.4 ; 26.2; 26.2; keto form: 198.8; 193.2; 163.5; 161.9; 161.9; 160.5; 130.2; 130.2; 129.4; 125.3; 115.7; 113.7; 113.7; 105.1; 102.7; 91.1; 78.1; 55.3; 55.3; 54.3; 28.2; 28.2. HR-MS: 382.1414 (M^+, $C_{22}H_{22}O_6^+$; calc. 382.1416).

General Procedure for Synthesis of Flavones **1**–**6**. $InCl_3$ (0.25 mmol) was added to a stirred soln. of **11**–**16** (0.5 mmol) in dry toluene (10 ml). The mixture was heated to reflux for 5 h, and the progress was monitored by TLC. After removal of the solvent, the residue was purified by FC (SiO_2; hexane/EtOAc 1:1) to give **1**–**6**.

*8,8-Dimethyl-2-phenyl-4*H,*8*H-*benzo[1,2-*b:*3,4-*b′*]dipyran-4-one* (**1**) [12]. Yield: 95%. M.p. 134–135°. IR (KBr): 3055, 2984, 2920, 2851, 1647, 1591, 1576, 1441, 1397, 1381, 1366, 1215, 1190, 1130, 1113, 1080, 1030, 839. ^{1}H-NMR ($CDCl_3$): 7.92 (*d*, *J* = 8.7, 1 H); 7.82–7.80 (*m*, 2 H); 7.46–7.44 (*m*, 3 H); 6.85 (*d*, *J* = 9.9, 1 H); 6.79 (*d*, *J* = 8.4, 1 H); 6.69 (*s*, 1 H); 5.70 (*d*, *J* = 9.9, 1 H); 1.46 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 177.7; 162.3; 157.3; 152.1; 131.7; 131.3; 130.3; 128.9; 128.9; 125.9; 125.9; 125.8; 117.6; 115.0; 115.0; 109.3; 107.1; 77.6; 28.0; 28.0.

*2-(1,3-Benzodioxol-5-yl)-8,8-dimethyl-4*H,*8*H-*benzo[1,2-*b *:3,4-*b′*]dipyran-4-one* (**2**) [12]. Yield: 93%. M.p. 230–232°. IR (KBr): 2982, 2920, 1640, 1584, 1503, 1449, 1395, 1381, 1337, 1294, 1254, 1215, 1115, 1076, 1036, 930, 862. ^{1}H-NMR ($CDCl_3$/(D_6)DMSO): 7.77 (*d*, *J* = 8.4, 1 H); 7.27 (*d*, *J* = 7.2, 1 H); 7.12 (*s*, 1 H); 6.76–6.65 (*m*, 3 H); 6.43 (*s*, 1 H); 5.91 (*s*, 2 H); 5.60 (*d*, *J* = 10.2, 1 H); 1.35 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 177.3; 161.8; 157.0; 151.7; 150.1; 148.1; 130.2; 125.4; 125.4; 120.7; 117.3; 114.7; 114.6; 109.0; 108.4; 105.9; 105.6; 101.6; 77.4; 27.7; 27.7.

*2-(4-Methoxyphenyl)-8,8-dimethyl-4*H,*8*H-*benzo[1,2*-b*:3,4*-b′*]dipyran-4-one* (**3**). Yield: 94%. M.p. 191–192°. IR (KBr): 3072, 2975, 2933, 1629, 1599, 1511, 1429, 1394, 1258, 1181, 1117, 1083, 1032, 832, 739. ^{1}H-NMR ($CDCl_3$/(D_6)DMSO): 7.80 (*d*, *J* = 8.7, 1 H); 7.73 (*d*, *J* = 7.8, 2 H); 6.91 (*d*, *J* = 8.1, 2 H); 6.80 (*d*, *J* = 9.9, 1 H); 6.72 (*d*, *J* = 8.7, 1 H); 6.52 (*s*, 1 H); 5.69 (*d*, *J* = 9.9, 1 H) 3.77 (*s*, 3 H); 1.42 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 176.6; 161.6; 161.4; 156.4; 151.2; 129.7; 129.7; 126.8; 124.7; 123.0; 116.7; 114.2; 114.0; 113.6; 113.6; 108.6; 104.7; 76.8; 54.6; 27.2; 27.2. HR-MS: 334.1201 (M^+, $C_{21}H_{18}O_5^+$; calc. 334.1205).

Isopongaflavone (= *5-Methoxy-8,8-dimethyl-2-phenyl-4*H,*8*H-*benzo[1,2*-b:*3,4*-b′*]dipyran-4-one*; **4**) [5]. Yield: 88%. M.p. 213–214°. IR (KBr): 3073, 2976, 1639, 1585, 1450, 1352, 1203, 1124, 848, 772, 734, 691. ^{1}H-NMR ($CDCl_3$): 7.87 (*d*, *J* = 7.2, 2 H); 7.61–7.48 (*m*, 3 H); 7.36 (*s*, 1 H); 6.76 (*d*, *J* = 9.9, 1 H); 6.43 (*s*, 1 H); 5.75 (*d*, *J* = 10.2, 1 H); 4.00 (*s*, 3 H); 1.51 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$/(D_6)DMSO): 176.4; 159.6; 159.4; 157.2; 153.0; 130.7; 130.5; 128.2; 128.2; 127.4; 127.0; 125.0; 125.0; 114.3; 107.8; 101.9; 95.9; 77.3; 55.6; 27.4; 27.4. HR-MS: 334.1206 (M^+, $C_{21}H_{18}O_4^+$; calc. 334.1205).

*2-(1,3-Benzodioxol-5-yl)-5-methoxy-8,8-dimethyl-4*H,*8*H-*benzo[1,2*-b:*3,4*-b′*]dipyran-4-one* (**5**) [10a]. Yield: 90%. M.p. 241–242°. IR (KBr): 2958, 2923, 1673, 1624, 1491, 1447, 1294, 1256, 1113, 1033, 924, 769, 664, 556. ^{1}H-NMR ($CDCl_3$/(D_6)DMSO): 7.54 (*d*, *J* = 8.1, 1 H); 7.32 (*s*, 1 H); 6.77 (*d*, *J* = 8.1, 1 H); 6.49 (*d*, *J* = 9.9, 1 H); 5.98 (br. *s*, 3 H); 5.92 (*s*, 1 H); 5.41 (*d*, *J* = 9.9, 1 H); 3.84 (*s*, 3 H); 1.35 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$/(D_6)DMSO): 178.0; 165.9; 158.9; 158.9; 157.8; 149.9; 146.2; 124.5; 123.8; 123.5; 114.4; 108.0; 107.9; 106.4; 106.4; 100.4; 100.4; 90.5; 76.4; 55.1; 26.8; 26.8.

*5-Methoxy-2-(4-methoxyphenyl)-8,8-dimethyl-4*H,*8*H-*benzo[1,2*-b*:3,4*-b′*]dipyran-4-one,* (**6**) [15]. Yield: 91%. Mp 206–207°. IR (KBr): 3093, 2976, 1634, 1579, 1449, 1360, 1252, 1222, 1123, 1047, 850, 734. ^{1}H-NMR ((D_6)DMSO): 7.89 (*d*, *J* = 7.2, 2 H); 7.03 (*d*, *J* = 7.2, 2 H); 6.81 (*d*, *J* = 9.6, 1 H); 6.57 (*s*, 1 H); 6.38 (*s*, 1 H); 5.75 (*d*, *J* = 9.6, 1 H); 3.79 (br. *s*, 6 H); 1.40 (*s*, 6 H). ^{13}C-NMR ((D_6)DMSO): 176.03; 162.0; 160.2; 159.6; 157.4; 153.2; 128.4; 127.9; 127.9; 123.1; 114.9; 114.8; 114.8; 108.2; 106.8; 102.3; 96.9; 78.2; 56.5; 55.8; 28.0; 28.0. HR-MS: 364.1307 (M^+, $C_{22}H_{20}O_5^+$; calc. 364.1311).

This research was supported by the *Basic Science Research Program* through the *National Research Foundation of Korea* (*NRF*) funded by the *Ministry of Education, Science and Technology* (2012009620).

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Received May 28, 2012