Synthesis of Various Kinds of Isoflavones, Isoflavanes, and Biphenyl-Ketones and Their 1,1-Diphenyl-2-picrylhydrazyl Radical-Scavenging Activities

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Received November 13, 2008; accepted February 6, 2009

Forty-eight kinds of isoflavones (8), thirty-one isoflavanes (9), and forty-seven biphenyl-ketones (10, 10′) were synthesized from eleven kinds of substituted phenols (11) and six phenylacetic acids (12). Among them, seventy-five compounds are new. The radical scavenging activities of these compounds were evaluated using 1,1-diphenyl-2-picrylhydrazyl (DPPH) at pH 6.0. We found that thirty-nine out of forty-three compounds having a catechol moiety on either the A- or the B-ring exhibited a high activity (ED_{50}=12—54 μM) similar to that of catechin. In these cases, the remaining part of their structure seemed to have little effect on their activity. Many 6- or 8-hydroxyisoflavanes (9E—I) and their biphenyl-ketone derivatives (10E—H) also showed a high activity (ED_{50}=<50 μM), while all of their corresponding isoflavones (8E—I) were not active at all. The 7-hydroxyisoflavanes having either an additional hydroxyl group at the C5-position (9D) or a methoxy group at the C6-position (9J) presented a high activity (ED_{50}=26—32 μM). This study suggests that natural isoflavones have the possibilities of exhibiting antioxidant activities through the hydroxylation at the C6-, C8-, or C3′-position or the formation of the isoflavanes (9) and/or the biphenyl-ketone derivatives (10′) by metabolism or biotransformation.

Key words isoflavone; isoflavane; radical scavenging activity; metabolite; soybean

Isoflavones are a class of phenolic compounds produced by a variety of higher plants and especially very abundant in soybeans. The major components of soybeans include daidzein **1**, genistein **2**, and glycitein **3**,[1)] which are known to have some important biological activities such as estrogen-like activities[1)] and antibacterial activities.[2)] Epidemiologic studies have also shown that the dietary intake of isoflavones is associated with some properties beneficial to human health such as the prevention of coronary heart disease and the reduced risk of breast, prostate, and colon cancers.[3,4)] Some of these effects are thought to be related to the antioxidant activities of the isoflavonoids[5)] similar to that of the flavonoids such as catechins,[6)] although the major soybean isoflavones (**1**—**3**) have been reported to have low antioxidant activities.[7)]

The metabolites of natural isoflavones generated by intestinal bacteria and/or enzymes, such as cytochrome P450,[8,9)] are the key to understanding the net factors for the physiological efficiency of natural products, because cells are predominantly exposed to metabolites rather than the parent compounds.[10,11)] For example, equol **4** and *O*-desmethylangolensin **5** were isolated among the metabolites of **1** (Fig. 1), from which **4** was found to show a more potent estrogen activity than **1**.[12,13)] Several other metabolites of **1** and **2**, that have one or two additional hydroxy groups predominantly at the C6-, C8- and C3′-positions, have been identified in human urine and plasma.[9,14—16)] However, their biological activities have been scarcely reported probably due to their very low yields, and therefore, little is known about their structure–activity relationship.

In 2004, Hirota *et al.* isolated the more oxygenated isoflavones, 6-hydroxydaidzein **6** and 8-hydroxyglycitein **7**, from fermented soybean miso, which exhibited 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activities (ED_{50}=24—37 μM) as high as that of α-tocopherol (Fig. 1).[17)]

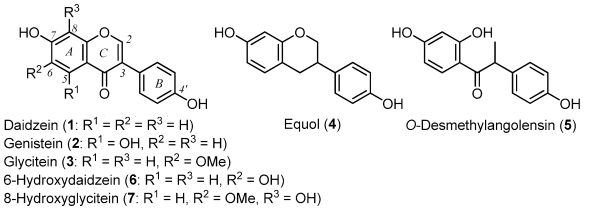

Fig. 1. Soybean Isoflavones (**1**—**3**) and Their Derivatives (**4**—**7**) Generated by Biotransformation or Metabolism

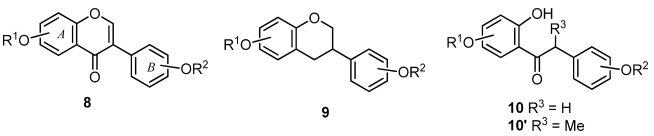

Fig. 2. Structures of Isoflavones **8**, Isoflavanes **9**, and Biphenyl-Ketones (**10, 10′**)

Inspired by Hirota's report[17)] and the isolation of the A- or B-ring hydroxylated metabolites as well as the C-ring reduced metabolites (**4**, **5**), we started the synthesis of a wide range of isoflavones **8**, isoflavanes **9**, and the non-cyclic biphenyl-ketones (**10**, **10′**) having oxygen-substituents on the A- and/or B-rings to systematically evaluate their DPPH radical scavenging activity. During the course of our research, the antioxidant activity of six kinds of isoflavones and nine metabolites, all of which are naturally available, were reported by two groups[7,18)]; however, the antioxidant activities of the synthetic isoflavones and their derivatives have never been reported. We now present the synthesis of forty-eight kinds of isoflavones **8**, thirty-one isoflavanes **9**, and forty-seven biphenyl-ketones (**10**, **10′**), of which seventy-five compounds are new, and report some relationships of their struc-

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ture and the DPPH radical scavenging activities (Fig. 2).

Results and Discussion

Synthesis of Isoflavones 8, Isoflavanes 9, and Biphenyl-Ketones (10, 10′) At first, the preparation of the biphenylketones **10** was examined on the basis of the reported Friedel–Crafts reaction of the substituted phenols **11** and the phenylacetic acids **12** using $BF_3 \cdot Et_2O$ as the catalyst and a solvent.[19—25] When the reactions were carried out at 60—70 °C according to Hase's method,[20] more than 1 h were needed for the completion of the reaction as mentioned in the literature. We next examined similar reactions at the refluxing temperature of $BF_3 \cdot Et_2O$; *viz.*, 120 °C, according to Nair's report,[22] which could be completed within 10 min. Because both methods gave similar yields of **10**, the latter seemed to be more favorable for us. Thereby, the combination of eleven types of phenols **11A**—**K** and six kinds of phenylacetic acids **12a**—**f** afforded forty-one ketones **10**, of which twenty-one are new. In a like manner, six kinds of α-methylketones **10′** (R^7=Me) were synthesized from **11A**, **B**, **E** and the 2-phenylpropanoic acids **12a**, **b** (R^7=Me) (Chart 1).

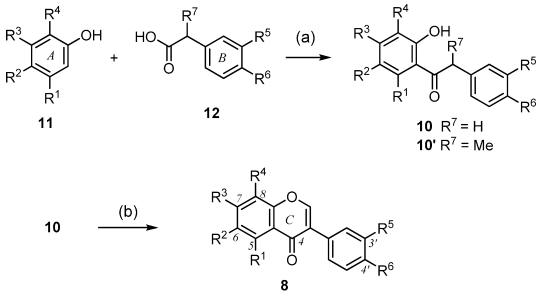
Because the construction of the C-ring from **10** to form the isoflavane framework **8** was also catalyzed by $BF_3 \cdot Et_2O$, a convenient one-pot synthesis of **8** from **11** and **12** was achieved without the isolation of **10** according to the reports.[20,22,26—30] Thus, after the completion of the ketone forming reaction in $BF_3 \cdot Et_2O$ [step (a) in Chart 1], the reaction mixture was cooled to room temperature. *N*,*N*-Dimethylformamide (DMF) was added as a one-carbon source, and the reaction mixture was stirred at 50 °C for 10 min. Methanesulfonyl chloride was added, and the reaction mixture was heated at 80 °C for 30 min to give **8** [step (b) in Chart 1]. This one-pot procedure was very useful because the two steps were finished in about 1.5 h. We could rapidly synthesize forty-eight isoflavones **8**, although the yield of **8** varied in some cases mainly due to the variation in the yield of the Friedel–Craft reaction.[31]

The one-pot synthesis was, however, not applicable to the preparation of the 6,7-dihydroxyisoflavones **8C**, which gave intractable complex mixtures. The use of the protected phenols, such as **11L** (R^1=R^4=H, R^2–R^3=OCH_2O) and **11M** (R^1=R^4=H, R^2–R^3=$OCMe_2O$), instead of **11C** also resulted in forming complex mixtures. After intensive trials, this problem was partly overcome by conducting the C-ring formation without using $BF_3 \cdot Et_2O$. Thus, a crude product **10C**, obtained by coupling **11C** and **12** under the standard conditions followed by the usual work-up, was heated in DMF at 50 °C for 10 min. Methanesulfonyl chloride was then added, and the entire reaction mixture was heated at 80 °C for 30 min to give **8Ca**, **8Cb** (=**6**), and **8Ce** in about 5—10% overall yields.

Our next interest was focused on the synthesis of a variety of isoflavanes **9** having one and more hydroxy groups on either the A- or B-rings to evaluate their radical scavenging ability. Although the preparation of **9Ab** (=**4**) was reported by the hydrogenation of **8Ab** (=**1**) using 10% Pd/C (30% (w/w))[21] or 20% $Pd(OH)_2$/C (about 100% (w/w))[32] in AcOH, we found that 5% Pd/C containing about 50% water (N.E.Chemcat, Type E) was so reactive in AcOH–EtOH (1 : 9) that the use of 5% (w/w) of the catalyst completed the hydrogenation of **8Ab** at atmospheric pressure and room temperature in 10 h to give a 95% yield of **9Ab** (Table 1, entry 3). The choice of the wet Pd/C was critical because the use of 5% (w/w) of either 5% Pd/C (N.E.Chemcat, Type STD) or 10% Pd/C (Wako) under similar reaction conditions gave the partially reduced **13**—**15** as major products along with a trace amount of **9Ab** (entries 1, 2). The concentration of AcOH in EtOH was another important issue; *viz.*, the reduction in AcOH–EtOH (1 : 99) was very slow to give **13** and **14** as major products (entry 4), while that in AcOH–EtOH (1 : 9 or 3 : 7) was completed within 10 h to almost quantitatively give **9Ab**.

Under the optimized conditions, thirty others **9** were similarly obtained from the corresponding **8** in 43—98% yields (For more detail, see Experimental) (Chart 2). Thus, by reducing the catalyst loading and the volume of AcOH compared with the reported conditions,[21,32] we have established a practical, easy-to-operate, and widely applicable protocol.

Radical Scavenging Activities The radical scavenging activity of the synthesized compounds (**8**—**10**) was evaluated using DPPH at pH 6.0.[17] At first, the validity of this method was reconfirmed by the evaluation of catechin (ED_{50}= 21 μM), which was in good agreement with the reported values.[33,34] Next, the ED_{50} values of some starting compounds (**11**, **12**) were measured, and the results are summarized in Fig. 3. The catechol derivatives (**11C**, **11E**, **12c**), pyrogallol **11B**, and *p*-dihydroquinone **11G** showed high activities (ED_{50}=26—34 μM), which are attributable to the easy oxidation of the catechols to the *o*-quinones and that of the *p*-dihydroquinone to the *p*-quinone.[35] While the resorcinol **11A**, 1,3,5-trihydroxybenzene **11D**, and 3,4-dimethoxyphenol **11K**



A–K for **8**,**10**,**10′**,**11**

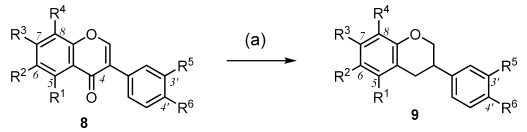
	R^1	R^2	R^3	R^4
A	H	H	OH	H
B	H	H	OH	OH
C	H	OH	OH	H
D	OH	H	OH	H
E	H	OMe	OH	H
F	H	H	OMe	OH
G	H	H	Me	OH
H	H	OH	OMe	H
I	H	OH	Me	H
J	H	OH	Me	Me
K	H	OMe	OMe	H

a–h for **8**,**10**,**10′**,**12**

	R^5	R^6	R^7
a	H	H	H
b	H	OH	H
c	OH	OH	H
d	OMe	OH	H
e	H	OMe	H
f	OMe	OMe	H
g	H	H	Me
h	H	OH	Me

(a) $BF_3 \cdot Et_2O$, 120 °C; (b) 1) DMF, 50 °C; 2) $MeSO_2Cl$, 80 °C.

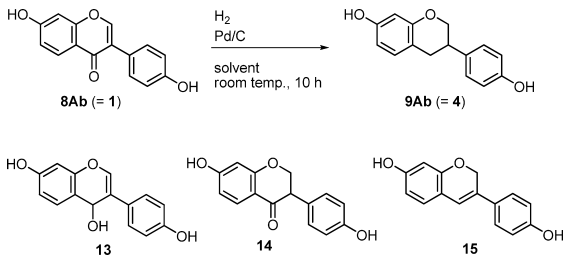
Chart 1



(a) H_2, 5% Pd/C (containing about 50% water, N.E.Chemcat, Type E), AcOH–EtOH (1 : 9), room temperature.

Chart 2

Table 1. Selected Results on the Reduction of Isoflavone **8Ab**



Entry	Catalyst[a)]	Solvent	Isolated yield (%)			
			9Ab	**13**	**14**	**15**
1	5% Pd/C[b)]	AcOH–EtOH (1 : 9)	Trace	73	21	6
2	10% Pd/C[c)]	AcOH–EtOH (1 : 9)	Trace	27	22	14
3	5% Pd/C (wet)[d)]	AcOH–EtOH (1 : 9)	95	—	—	—
4[e)]	5% Pd/C (wet)[d)]	AcOH–EtOH (1 : 99)	Trace	15	7	Trace

a) A catalyst (5% (w/w)) was used. *b*) The catalyst (N.E. Chemcat, Type STD) was used. *c*) The catalyst purchased from Wako was used. *d*) The 5% Pd/C containing about 50% water (N.E. Chemcat, Type E) was used. *e*) A 68% of **8Ab** was recovered.

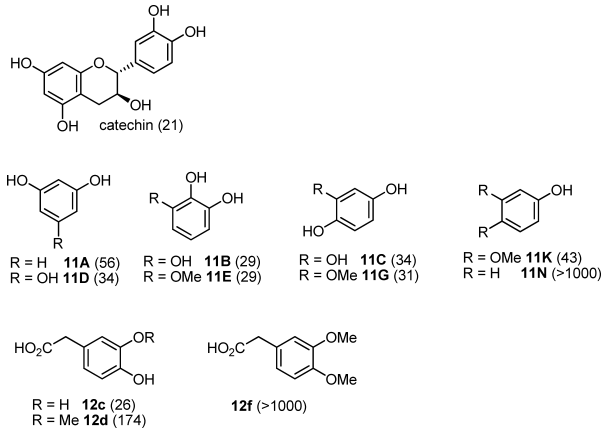


Fig. 3. The DPPH Radical Scavenging Activities of Catechin and Selected **11** and **12** Measured at pH 6.0

The ED_{50} (μM) value, obtained as the average of three experiments, is shown in the parenthesis.

were similarly active (ED_{50}=34—56 μM), 4-hydroxy-3-methoxyphenylacetic acid **12d** showed a lower activity (ED_{50}=174 μM), and phenol **11N** and 3,4-dimethoxyphenylacetic acid **12f** were inactive.

With these reference data in hand, we next evaluated the radical scavenging activity of the synthesized compounds **8**—**10**, and the results are summarized in Table 2, in which new compounds are marked with a superscript b). In each box, the ED_{50} value for the isoflavone **8** is shown in the first line, that of the isoflavane **9** in the second, and those of the biphenyl-ketone **10** and its α-methyl derivative **10′** in the third and the fourth lines, respectively. All ED_{50} values are obtained as the average of three experiments. Several aspects are worth noting:

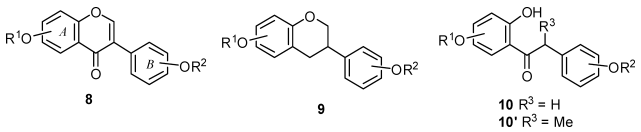
First, as expected, the series of isoflavones (**8B**, **8C**) with a catechol moiety (**B**, **C**) on the A-ring showed high activities (ED_{50}=16—54 μM), and the series of isoflavones **8c** having a catechol moiety on the B-ring also exhibited high activities (ED_{50}=16—85 μM). These results were in good agreement with the previous reports on the hydroxylated metabolites.[7,17,18)] Similar high activities (ED_{50} 12—37 μM) were also observed in most of the series of isoflavanes (**9B**, **9c**) and biphenyl-ketones (**10B**, **10B′**, **10C**, **10c**), which have a catechol moiety on either the A-ring or B-ring. Therefore, based on these results, it was reconfirmed that the catechol moiety generally exhibited strong radical-scavenging activity, which was only slightly affected by the structure of the other moieties of the compounds.

Secondly, the change in a catechol to its methyl ether caused a significant decrease in the activity. Thus, the compounds having an *o*-methoxyphenol moiety (see, the series of **8E**, **8H**, **8J**, **8d**) had moderate activities, while the compounds having two methoxy groups at the C6- and C7-positions (**8K**, **9K**, **10K**) exhibited very poor activities.

Third, for the rest of the compounds, the radical scavenging activity essentially varied depending on the combination of the structures of the A- and the C-rings, while that of the B-ring had little effect. Typical examples are found in the compounds having the 5,7-dihydroxyated A-ring (the series of **D**). Thus, although **8Db** (=**2**) and **8De** were not active, their isoflavane-type derivatives (**9Db**, **9De**) had very high activities (ED_{50}=26—32 μM). Other examples include the compounds having a single hydroxy group at either the C6- (the series of **E**—**G**) or the C8-position (the series **H**, **I**). Thus, while the corresponding isoflavones **8** were not active, their isoflavane-type derivatives **9** showed moderate activities (ED_{50}=45—224 μM) and their biphenyl-ketone derivatives **10** were more active (ED_{50}=18—51 μM in most cases). The isoflavones having the 7-hydroxy-6-methoxybenzene moiety on the A-ring (the series of **J**) deserve attention, because while the isoflavones **8J** and their biphenyl-ketone derivatives **10J** were not active, their isoflavane derivatives **9J** were very active (ED_{50}=26—29 μM).

Naturally occurring isoflavones have been thought to have very low radical-scavenging activities,[18)] although they exhibit various kinds of biological activities that may have some relations to the radical scavenging activities. A possible account for this contradiction has been proposed by the formation of more active derivatives or metabolites through the microbial transformation and/or enzymatic metabolism.[7,17,18)] The present study has provided us some evidence for this vi-

Table 2. DPPH Radical Scavenging Activity (ED_{50}, μM)[a] for the Isoflavones **8**, the Isoflavanes **9** and the Biphenyl-Ketones (**10**, **10′**)



A-ring \ B-ring	**a**	**b**	**c**	**d**	**e**	**f**
A	**8Aa**: >1000 **9Aa**[b]: >1000 **10Aa**: >1000 **10Aa′**: >1000	**1**: >1000 **4**: >1000 **10Ab**: >1000 **5**: >1000	**8Ac**: 30 **9Ac**: 37 **10Ac**[b]: 20	**8Ad**: 805 **10Ad**[b]: 180	**8Ae**: >1000 **9Ae**: >1000 **10Ae**: >1000	**8Af**[b]: >1000 **9Af**[b]: >1000 **10Af**: >1000
B	**8Ba**: 29 **9Ba**[b]: 37 **10Ba**: 32 **10Ba′**[b]: 23	**8Bb**: 34 **9Bb**[b]: 37 **10Bb**: 22 **10Bb′**[b]: 18	**8Bc**[b]: 16 **9Bc**[b]: 22 **10Bc**[b]: 12	**8Bd**[b]: 33 **10Bd**[b]: 25	**8Be**: 51 **9Be**: 36 **10Be**: 38	**8Bf**: 54 **9Bf**: 105 **10Bf**: 63
C	**8Ca**: 44 **10Ca**: 29	**6**: 29 **10Cb**: 27			**8Ce**: 29 **10Ce**: 32	
D		**2**: >1000 **9Db**[b]: 32			**8De**: >1000 **9De**[b]: 26	
E	**8Ea**: >1000 **9Ea**[b]: 49 **10Ea**: 51 **10Ea′**[b]: 48	**8Eb**: >1000 **9Eb**[b]: 62 **10Eb**: 38 **10Eb′**[b]: 45	**8Ec**[b]: 36 **10Ec**: 19	**8Ed**[b]: 404 **10Ed**[b]: 26	**8Ee**: >1000 **9Ee**[b]: 60 **10Ee**: 31	**8Ef**[b]: >1000 **9Ef**[b]: 56 **10Ef**: 39
F	**8Fa**[b]: >1000 **10Fa**[b]: 43	**8Fb**[b]: >1000 **10Fb**[b]: 31	**8Fc**[b]: 23 **10Fc**[b]: 20	**8Fd**[b]: 232 **10Fd**[b]: 22	**8Fe**[b]: >1000 **9Fe**[b]: 45 **10Fe**[b]: 23	
G	**8Ga**[b]: >1000 **9Ga**[b]: 81 **10Ga**[b]: 42	**8Gb**[b]: >1000 **10Gb**[b]: 33	**8Gc**[b]: 85 **10Gc**[b]: 18		**8Ge**[b]: >1000 **10Ge**[b]: 93	
H	**8Ha**: 812 **9Ha**[b]: 168 **10Ha**[b]: 20		**8Hc**[b]: 53 **10Hc**[b]: 20	**8Hd**[b]: 228 **10Hd**[b]: 28	**8He**[b]: 489 **9He**[b]: 224 **10He**[b]: 44	
I	**8Ia**[b]: >1000 **9Ia**[b]: 61	**8Ib**[b]: >1000 **9Ib**[b]: 111	**8Ic**[b]: 46	**8Id**[b]: 476	**8Ie**[b]: >1000 **9Ie**[b]: 52	
J	**8Ja**: >1000 **9Ja**[b]: 29 **10Ja**: 916	**3**: >1000 **9Jb**: 26 **10Jb**: 836		**8Jd**: 655 **10Jd**[b]: 129	**8Je**: 663 **9Je**[b]: 26 **10Je**: 733	
K	**8Ka**: >1000 **9Ka**[b]: >1000 **10Ka**: >1000	**8Kb**: >1000 **9Kb**[b]: >1000 **10Kb**: >1000	**8Kc**[b]: 46 **9Kc**[b]: 69 **10Kc**[b]: 25	**8Kd**[b]: 722 **10Kd**[b]: 84	**8Ke**: >1000 **9Ke**[b]: >1000 **10Ke**: >1000	**8Kf**: >1000 **9Kf**[b]: >1000 **10Kf**: >1000

a) Average of three experiments. *b*) New compound.

sion. Thus, all compounds having a catechol moiety on either the A- or the B-ring, which can be delivered *via* the hydroxylation at the C6-, C8-, or C3′-position, were confirmed to exhibit high radical-scavenging activities.

The reductive metabolism on the C-ring seems to have two different effects. Thus, the reduction of the C-ring leading to the isoflavanes **9** increases the electron density of their A-rings and thereby enhances the radical scavenging activity of the less active isoflavones such as **8E**—**J**. The other type of reductive metabolism that gives the biphenyl-ketones, such as **10** and **10′**, has unique features. All compounds having a single hydroxyl group at the C6- or the C8-position (the series of **E**—**H**) were highly active, and this is reasonable because this conversion releases the catechol or the *p*-dihydroquinone moiety on the A-ring, respectively. On the contrary, this was not the case for the glycitein-type compounds **8J**, in which the hydroxyl group was substituted at the C7-position.

Conclusion

Although the examined compounds are limited, this study suggests that isoflavanes **9** and the biphenyl-ketone derivatives **10′**, probably generated during the fermentation or the metabolism of natural isoflavones, may play important roles in the antioxidation when people eat foods made of soybeans. We believe that some of the compounds synthesized in this study are possibly included in natural metabolites having a significant activity and that this study provides some valuable information for further studies on the rare metabolites of the isoflavones.

Experimental

General Reactions were monitored by a Shimadzu LC10A HPLC system using an ODS column (eluent, CH_3CN–H_2O). ^{1}H- (500 MHz) and ^{13}C-NMR (125 MHz) spectra were obtained with tetramethylsilane as an internal standard at 25 °C on a JEOL ECA-500 spectrometer. FAB-MS spectra were recorded on a JEOL JMS-700 spectrometer. Purification of the product was performed using a reverse phase medium-pressure liquid chromatography with a Yamazen ODS column (ultrapack, standard type). Sephadex LH-20 was used for gel permeation chromatography. DPPH radical scavenging activities were recorded on a Bio-tek Instruments, Bio kinetics reader EL340. The compounds (**2**, **8Ae**, **8De**, **11A**—**D**, **11F**—**K**, **12a**—**f**) were purchased from Sigma Aldrich Chemical and Tokyo Kasei. 5% Palladium on carbon (Type STD) and 5% Palladium on carbon (Type E, containing about 50% water) were purchased from N.E.Chemcat. 10% Palladium on carbon was purchased from Wako. All these commercial reagents were used as such without purification. The known compounds (**10Ba**,[2] **10Bb**,[2] **10Be**,[2] **11E**[36]) were synthesized according to the reported methods.

Typical Procedure for the Synthesis of the Ketones 10 from the Phenols 11 and the Phenylacetic Acids 12 To a mixture of **11A** (0.86 g, 7.8 mmol) and **12a** (1.00 g, 7.3 mmol) was added $BF_3 \cdot Et_2O$ (2.2 ml). The reaction mixture was heated at 120 °C for 10 min. The mixture was cooled to room temperature, and cold water (43 ml) was added. The product was extracted with Et_2O (3×50 ml). A combined Et_2O layer was successively washed with brine (3×100 ml) and saturated $NaHCO_3$ (3×100 ml), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was subjected to reverse phase medium-pressure liquid chromatography with an ODS column (eluent, CH_3CN–H_2O) to give the product **10Aa**, which was recrystallized from EtOH to give pure **10Aa** (0.55 g, 2.4 mmol, 33% yield).

1-(2,4-Dihydroxyphenyl)-2-phenylethanone 10Aa 33% yield. Pale brown crystals. mp 80—81 °C (EtOH) [lit.[37] 115 °C (EtOH)]. ^{1}H-NMR (DMSO-d_6) δ: 4.29 (2H, s, CH_2), 6.26 (1H, s, 3-H), 6.39 (1H, d, J=8.6 Hz, 5-H), 7.23 (1H, t, J=6.9 Hz, 4′-H), 7.28 (2H, d, J=6.9 Hz, 2′,6′-H), 7.31 (2H, t, J=6.9 Hz, 3′,5′-H), 7.95 (1H, d, J=8.6 Hz, 6-H), 10.67 (1H, s, 4-OH), 12.51 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.08 (CH_2), 102.44 (3-C), 108.25 (5-C), 112.18 (1-C), 126.54 (4′-C), 128.33 (3′,5′-C), 129.50 (2′,6′-C), 133.54 (6-C), 135.18 (1′-C), 164.59 (2-C), 164.95 (4-C), 202.05 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{14}H_{13}O_3$ [(M+H)$^+$] 229.0865, Found 229.0880.

1-(2,4-Dihydroxyphenyl)-2-phenyl-1-propanone 10Aa′ 77% yield. Pale yellow crystals. mp 120—121 °C (EtOH) (lit.[38] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 1.41 (3H, d, J=6.9 Hz, CH_3), 4.89 (1H, q, J=6.9 Hz, CH), 6.25 (1H, s, 3-H), 6.33 (1H, d, J=8.6 Hz, 5-H), 7.21 (1H, t, J=7.4 Hz, 4′-H), 7.31 (2H, t, J=7.4 Hz, 3′,5′-H), 7.35 (2H, d, J=7.4 Hz, 2′,6′-H), 7.90 (1H, d, J=8.6 Hz, 6-H), 10.71 (1H, s, 4-OH), 12.70 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 18.94 (CH_3), 45.38 (CH), 102.57 (3-C), 108.25 (5-C), 111.59 (1-C), 126.78 (4′-C), 127.47 (2′,6′-C), 128.78 (3′,5′-C), 133.30 (6-C), 141.86 (1′-C), 164.94 (2-C), 165.04 (4-C), 204.46 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{15}H_{15}O_3$ [(M+H)$^+$] 243.1021, Found 243.1005.

1-(2,4-Dihydroxyphenyl)-2-(4′-hydroxyphenyl)ethanone 10Ab 77% yield. Pale yellow crystals. mp 204—206 °C (EtOH) (lit.[39] 189—191 °C). ^{1}H-NMR (DMSO-d_6) δ: 4.13 (2H, s, CH_2), 6.24 (1H, s, 3-H), 6.38 (1H, d, J=8.6 Hz, 5-H), 6.69 (2H, d, J=8.6 Hz, 3′,5′-H), 7.07 (2H, d, J=8.6 Hz, 2′,6′-H), 7.92 (1H, d, J=8.6 Hz, 6-H), 9.32 (1H, s, 4′-OH), 10.64 (1H, s, 4-OH), 12.58 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.24 (CH_2), 102.44 (3-C), 108.18 (5-C), 112.03 (1-C), 115.19 (3′,5′-C), 125.14 (1′-C), 130.33 (2′,6′-C), 133.57 (6-C), 156.05 (4′-C), 164.70 (2-C), 164.87 (4-C), 202.68 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{14}H_{13}O_4$ [(M+H)$^+$] 245.0814, Found 245.0805.

1-(2,4-Dihydroxyphenyl)-2-(4′-hydroxyphenyl)-1-propanone 10Ab′ (*O*-Desmethylangolensin 5) 81% yield. A pale yellow amorphous solid (lit.[40] 139—140 °C). ^{1}H-NMR (DMSO-d_6) δ: 1.34 (3H, d, J=6.9 Hz, CH_3), 4.76 (1H, q, J=6.9 Hz, CH), 6.21 (1H, s, 3-H), 6.30 (1H, d, J=8.6 Hz, 5-H), 6.68 (2H, d, J=8.6 Hz, 3′,5′-H), 7.12 (2H, d, J=8.6 Hz, 2′,6′-H), 7.87 (1H, d, J=8.6 Hz, 6-H), 9.31 (1H, s, 4′-OH), 10.58 (1H, s, 4-OH), 12.73 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 18.94 (CH_3), 44.41 (CH), 102.48 (3-C), 108.11 (5-C), 111.44 (1-C), 115.47 (3′,5′-C), 128.42 (2′,6′-C), 131.92 (1′-C), 133.25 (6-C), 156.13 (4′-C), 164.78 (2-C), 165.00 (4-C), 204.90 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{15}H_{15}O_4$ [(M+H)$^+$] 259.0970, Found 259.0969.

1-(2,4-Dihydroxyphenyl)-2-(3′,4′-dihydroxyphenyl)ethanone 10Ac 77% yield. Pale brown crystals. mp 210—211 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 4.04 (2H, s, CH_2), 6.23 (1H, s, 3-H), 6.36 (1H, d, J=8.6 Hz, 5-H), 6.54 (1H, d, J=8.0 Hz, 6′-H), 6.64 (1H, d, J=8.0 Hz, 5′-H), 6.65 (1H, s, 2′-H), 7.90 (1H, d, J=8.6 Hz, 6-H), 8.78 (1H, s, 4′-OH), 8.86 (1H, s, 3′-OH), 10.69 (1H, s, 4-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.55 (CH_2), 102.43 (3-C), 108.21 (5-C), 111.97 (1-C), 115.55 (5′-C), 116.52 (2′-C), 120.10 (6′-C), 125.82 (1′-C), 133.74 (6-C), 144.07 (4′-C), 145.14 (3′-C), 164.82 (2-C), 164.95 (4-C), 202.81 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{14}H_{13}O_5$ [(M+H)$^+$] 261.0763, Found 261.0797.

1-(2,4-Dihydroxyphenyl)-2-(4′-hydroxy-3′-methoxyphenyl)ethanone 10Ad 57% yield. Pale brown crystals. mp 161—162 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.73 (3H, s, 3′-OMe), 4.14 (2H, s, CH_2), 6.24 (1H, s, 3-H), 6.38 (1H, d, J=8.6 Hz, 5-H), 6.66 (1H, d, J=8.0 Hz, 6′-H), 6.69 (1H, d, J=8.0 Hz, 5′-H), 6.86 (1H, s, 2′-H), 7.94 (1H, d, J=8.6 Hz, 6-H), 8.82 (1H, s, 4′-OH), 10.64 (1H, s, 4-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.64 (CH_2), 55.56 (3′-OMe), 102.42 (3-C), 108.17 (5-C), 112.07 (1-C), 113.63 (2′-C), 115.36 (5′-C), 121.69 (6′-C), 125.71 (1′-C), 133.57 (6-C), 145.26 (4′-C), 147.42 (3′-C), 164.67 (4-C), 164.85 (2-C), 202.55 (C=O). FAB-HR-MS *m/z* Calcd for $C_{15}H_{15}O_5$ [(M+H)$^+$] 275.0919, Found 275.0907. *Anal.* Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found C, 65.20; H, 5.38.

1-(2,4-Dihydroxyphenyl)-2-(4′-methoxyphenyl)ethanone 10Ae 78% yield. Pale brown crystals. mp 153—154 °C (EtOH) (lit.[41] 156—158 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.72 (3H, s, 4′-OMe), 4.20 (2H, s, CH_2), 6.25 (1H, s, 3-H), 6.39 (1H, d, J=8.6 Hz, 5-H), 6.87 (2H, d, J=8.6 Hz, 3′,5′-H), 7.20 (2H, d, J=8.6 Hz, 2′,6′-H), 7.94 (1H, d, J=8.6 Hz, 6-H), 10.65 (1H, s, 4-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.18 (CH_2), 54.97 (4′-OMe), 102.43 (3-C), 108.20 (5-C), 112.06 (1-C), 113.80 (3′,5′-C), 126.95 (1′-C), 130.46 (2′,6′-C), 133.52 (6-C), 157.99 (4′-C), 164.62 (2-C), 164.88 (4-C), 202.43 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{15}H_{15}O_4$ [(M+H)$^+$] 259.0970, Found 259.0950.

1-(2,4-Dihydroxyphenyl)-2-(3′,4′-dimethoxyphenyl)ethanone 10Af 52% yield. Colorless crystals. mp 169—170 °C (EtOH) (lit.[42] 180 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.71 (3H, s, 4′-OMe), 3.72 (3H, s, 3′-OMe), 4.19 (2H, s, CH_2), 6.25 (1H, s, 3-H), 6.38 (1H, d, J=8.6 Hz, 5-H), 6.79 (1H, d, J=8.0 Hz, 6′-H), 6.88 (1H, d, J=8.0 Hz, 5′-H), 6.90 (1H, s, 2′-H), 7.95 (1H, d, J=8.6 Hz, 6-H), 10.65 (1H, s, 4-OH), 12.56 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.64 (CH_2), 55.45 (4′-OMe), 55.48 (3′-OMe), 102.43 (3-C), 108.19 (5-C), 111.86 (5′-C), 112.10 (1-C), 113.36 (2′-C), 121.47 (6′-C), 127.42 (1′-C), 133.54 (6-C), 147.60 (4′-C), 148.58 (3′-C), 164.63 (2-C), 164.88 (4-C), 202.34 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{17}O_5$ [(M+H)$^+$] 289.1076, Found 289.1088.

1-(2,3,4-Trihydroxyphenyl)-2-phenyl-1-propanone 10Ba′ 56% yield.

Pale violet crystals. mp 140—141 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 1.40 (3H, d, J=6.9 Hz, CH_3), 4.89 (1H, q, J=6.9 Hz, CH), 6.34 (1H, d, J=8.6 Hz, 5-H), 7.20 (1H, t, J=7.4 Hz, 4′-H), 7.30 (2H, t, J=7.4 Hz, 3′,5′-H), 7.34 (2H, d, J=7.4 Hz, 2′,6′-H), 7.45 (1H, d, J=8.6 Hz, 6-H), 8.62 (1H, s, 4-OH), 10.06 (1H, s, 3-OH), 12.64 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 19.00 (CH_3), 45.29 (CH), 107.70 (5-C), 111.91 (1-C), 122.78 (6-C), 126.74 (4′-C), 127.43 (2′,6′-C), 128.74 (3′,5′-C), 132.40 (3-C), 141.93 (1′-C), 152.46 (2-C), 152.87 (4-C), 205.20 (C=O). FAB-HR-MS m/z: Calcd for $C_{15}H_{15}O_4$ [(M+H)$^+$] 259.0970, Found 259.0969. *Anal.* Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found C, 69.63; H, 5.51.

1-(2,3,4-Trihydroxyphenyl)-2-(4′-hydroxyphenyl)-1-propanone 10Bb′ 72% yield. A pale brown solid. mp 168—169 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 1.35 (3H, d, J=6.9 Hz, CH_3), 4.76 (1H, q, J=6.9 Hz, CH), 6.33 (1H, d, J=8.6 Hz, 5-H), 6.67 (2H, d, J=8.6 Hz, 3′,5′-H), 7.12 (2H, d, J=8.6 Hz, 2′,6′-H), 7.43 (1H, d, J=8.6 Hz, 6-H), 8.56 (1H, s, 4-OH), 9.28 (1H, s, 4′-OH), 10.02 (1H, s, 3-OH), 12.71 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 19.02 (CH_3), 44.37 (CH), 107.59 (5-C), 111.82 (1-C), 115.43 (3′,5′-C), 122.72 (6-C), 128.41 (2′,6′-C), 132.02 (1′-C), 132.37 (3-C), 152.30 (2-C), 152.89 (4-C), 156.12 (4′-C), 205.67 (C=O). FAB-HR-MS m/z: Calcd for $C_{15}H_{15}O_5$ [(M+H)$^+$] 275.0919, Found 275.0920.

1-(2,3,4-Trihydroxyphenyl)-2-(3′,4′-dihydroxyphenyl)ethanone 10Bc 27% yield. A pale brown solid. mp 98—99 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 4.04 (2H, s, CH_2), 6.39 (1H, d, J=9.2 Hz, 5H), 6.53 (1H, d, J=8.0 Hz, 6′-H), 6.64 (1H, d, J=8.0 Hz, 5′-H), 6.65 (1H, s, 2′-H), 7.46 (1H, d, J=9.2 Hz, 6-H), 8.67 (1H, s, 4-OH), 8.80 (2H, s, 3′,4′-OH), 10.11 (1H, s, 3-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.48 (CH_2), 107.70 (5-C), 112.33 (1-C), 115.52 (5′-C), 116.54 (2′-C), 120.10 (6′-C), 123.19 (6-C), 125.92 (1′-C), 132.32 (3-C), 144.05 (4′-C), 145.12 (3′-C), 152.53 (4-C), 152.70 (2-C), 203.54 (C=O). FAB-HR-MS m/z: Calcd for $C_{14}H_{13}O_6$ [(M+H)$^+$] 277.0712, Found 277.0700.

1-(2,3,4-Trihydroxyphenyl)-2-(4′-hydroxy-3′-methoxyphenyl)ethanone 10Bd 58% yield. Colorless crystals. mp 148—149 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.73 (3H, s, 3′-OMe), 4.13 (2H, s, CH_2), 6.41 (1H, d, J=8.6 Hz, 5-H), 6.66 (1H, d, J=8.0 Hz, 6′-H), 6.68 (1H, d, J=8.0 Hz, 5′-H), 6.86 (1H, s, 2′-H), 7.49 (1H, d, J=8.6 Hz, 6-H), 8.60 (1H, s, 4-OH), 8.82 (1H, s, 4′-OH), 10.09 (1H, s, 3-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.56 (CH_2), 55.58 (3′-OMe), 107.70 (5-C), 112.38 (1-C), 113.64 (2′-C), 115.35 (5′-C), 121.72 (6′-C), 123.02 (6-C), 125.81 (1′-C), 132.32 (3-C), 145.26 (4′-C), 147.41 (3′-C), 152.50 (4-C), 152.60 (2-C), 203.28 (C=O). FAB-HR-MS m/z: Calcd for $C_{15}H_{15}O_6$ [(M+H)$^+$] 291.0869, Found 291.0874.

1-(2,3,4-Trihydroxyphenyl)-2-(3′,4′-dimethoxyphenyl)ethanone 10Bf 41% yield. Colorless crystals. mp 160—161 °C (EtOH) (lit.[43] 174 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.71 (3H, s, 4′-OMe), 3.72 (3H, s, 3′-OMe), 4.19 (2H, s, CH_2), 6.41 (1H, d, J=9.2 Hz, 5-H), 6.79 (1H, d, J=8.0 Hz, 6′-H), 6.88 (1H, d, J=8.0 Hz, 5′-H), 6.90 (1H, s, 2′-H), 7.51 (1H, d, J=9.2 Hz, 6-H), 8.64 (1H, s, 4-OH), 10.09 (1H, s, 3-OH), 12.54 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.57 (CH_2), 55.44 (4′-OMe), 55.48 (3′-OMe), 107.73 (5-C), 111.84 (5′-C), 112.41 (1-C), 113.35 (2′-C), 121.50 (6′-C), 123.00 (6-C), 127.53 (1′-C), 132.32 (3-C), 147.58 (4′-C), 148.57 (3′-C), 152.54 (2-C), 152.56 (4-C), 203.10 (C=O). FAB-HR-MS m/z: Calcd for $C_{16}H_{17}O_6$ [(M+H)$^+$] 305.1025, Found 305.1030.

1-(2,4,5-Trihydroxyphenyl)-2-phenylethanone 10Ca 5% yield. Pale brown crystals. mp 194—195 °C (EtOH) (lit.[44] 208—210 °C). ^{1}H-NMR (DMSO-d_6) δ: 4.21 (2H, s, CH_2), 6.29 (1H, s, 3-H), 7.24 (1H, t, J=7.4 Hz, 4′-H), 7.27 (1H, d, J=7.4 Hz, 2′,6′-H), 7.32 (2H, t, J=7.4 Hz, 3′,5′-H), 7.32 (1H, s, 6-H), 8.85 (1H, s, 4-OH), 10.45 (1H, s, 5-OH), 12.15 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.36 (CH_2), 103.01 (3-C), 110.72 (1-C), 115.65 (6-C), 126.55 (4′-C), 128.36 (3′,5′-C), 129.50 (2′,6′-C), 135.29 (1′-C), 138.36 (5-C), 154.77 (4-C), 157.99 (2-C), 201.38 (C=O). FAB-HR-MS m/z: Calcd for $C_{14}H_{13}O_4$ [(M+H)$^+$] 245.0814, Found 245.0814.

1-(2,4,5-Trihydroxyphenyl)-2-(4′-hydroxyphenyl)ethanone 10Cb 3% yield. Pale red crystals. mp 219—220 °C (EtOH) (lit.[45] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 4.05 (2H, s, CH_2), 6.27 (1H, s, 3-H), 6.70 (2H, d, J=8.6 Hz, 3′,5′-H), 7.06 (2H, d, J=8.6 Hz, 2′,6′-H), 7.29 (1H, s, 6-H), 8.83 (1H, s, 4-OH), 9.29 (1H, s, 4′-OH), 10.41 (1H, s, 5-OH), 12.23 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.53 (CH_2), 102.98 (3-C), 110.56 (1-C), 115.20 (3′,5′-C), 115.72 (6-C), 125.24 (1′-C), 130.31 (2′,6′-C), 138.28 (5-C), 154.68 (4-C), 156.05 (4′-C), 158.09 (2-C), 202.00 (C=O). FAB-HR-MS m/z: Calcd for $C_{14}H_{13}O_5$ [(M+H)$^+$] 261.0763, Found 261.0766.

1-(2,4,5-Trihydroxyphenyl)-2-(4′-methoxyphenyl)ethanone 10Ce 7% yield. A reddish amorphous solid. (lit.[46] 182—183 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.72 (3H, s, 4′-OMe), 4.12 (2H, s, CH_2), 6.28 (1H, s, 3-H), 6.88 (2H, d, J=8.6 Hz, 3′,5′-H), 7.18 (2H, d, J=8.6 Hz, 2′,6′-H), 7.31 (1H, s, 6-H), 8.83 (1H, s, 4-OH), 10.43 (1H, s, 5-OH), 12.18 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.48 (CH_2), 55.01 (4′-OMe), 102.99 (3-C), 110.61 (1-C), 113.83 (3′,5′-C), 115.67 (6-C), 127.06 (1′-C), 130.45 (2′,6′-C), 138.32 (5-C), 154.69 (4-C), 157.99 (4′-C), 158.02 (2-C), 203.23 (C=O). FAB-HR-MS m/z: Calcd for $C_{15}H_{15}O_5$ [(M+H)$^+$] 275.0919, Found 275.0909.

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-phenylethanone 10Ea 22% yield. Pale green crystals. mp 139—140 °C (EtOH) (lit.[44] 150—152 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.83 (3H, s, 4-OMe), 4.26 (2H, s, CH_2), 6.51 (1H, s, 3-H), 7.24 (1H, t, J=7.4 Hz, 4′-H), 7.27 (2H, d, J=7.4 Hz, 2′,6′-H), 7.32 (2H, t, J=7.4 Hz, 3′,5′-H), 7.35 (1H, s, 6-H), 8.87 (1H, s, 5-OH), 12.22 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.50 (CH_2), 55.93 (4-OMe), 100.23 (3-C), 111.21 (1-C), 114.97 (6-C), 126.59 (4′-C), 128.38 (3′,5′-C), 129.56 (2′,6′-C), 135.12 (1′-C), 139.01 (5-C), 155.68 (4-C), 157.88 (2-C), 201.94 (C=O). FAB-HR-MS m/z: Calcd for $C_{15}H_{15}O_4$ [(M+H)$^+$] 259.0970, Found 259.0985.

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-phenyl-1-propanone 10Ea′ 7% yield. Pale violet crystals. mp 148—149 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 1.39 (3H, d, J=6.9 Hz, CH_3), 3.80 (3H, s, 4-OMe), 4.77 (1H, d, J=6.9 Hz, CH), 6.47 (1H, s, 3-H), 7.19—7.23 (1H, m, 4′-H), 7.28 (1H, s, 6-H), 7.30—7.32 (4H, m, 2′,3′,5′,6′-H), 8.76 (1H, s, 5-OH), 12.39 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 19.06 (CH_3), 45.92 (CH), 55.86 (4-OMe), 100.24 (3-C), 110.67 (1-C), 114.85 (6-C), 126.76 (4′-C), 127.42 (2′,6′-C), 128.80 (3′,5′-C), 138.81 (5-C), 141.78 (1′-C), 155.57 (4-C), 158.27 (2-C), 204.27 (C=O). FAB-HR-MS m/z: Calcd for $C_{16}H_{17}O_4$ [(M+H)$^+$] 273.1127, Found 273.1124.

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-(4′-hydroxyphenyl)ethanone 10Eb 19% yield. Pale green crystals. mp 184—185 °C (EtOH) (lit.[45] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.83 (3H, s, 4-OMe), 4.10 (2H, s, CH_2), 6.50 (1H, s, 3-H), 6.70 (2H, d, J=8.6 Hz, 3′,5′-H), 7.06 (2H, d, J=8.6 Hz, 2′,6′-H), 7.33 (1H, s, 6-H), 8.85 (1H, s, 5-OH), 9.31 (1H, s, 4′-OH), 12.31 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.68 (CH_2), 55.91 (4-OMe), 100.21 (3-C), 111.05 (1-C), 114.31 (6-C), 115.22 (3′,5′-C), 125.06 (1′-C), 130.38 (2′,6′-C), 138.93 (5-C), 155.62 (4-C), 156.08 (4′-C), 157.99 (2-C), 202.56 (C=O). FAB-HR-MS m/z: Calcd for $C_{15}H_{15}O_5$ [(M+H)$^+$] 275.0919, Found 275.0909.

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-(4′-hydroxyphenyl)-1-propanone 10Eb′ 23% yield. Pale gray crystals. mp 208—209 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 1.33 (3H, d, J=6.9 Hz, CH_3), 3.80 (3H, s, 4-OMe), 4.64 (1H, q, J=6.9 Hz, CH), 6.46 (1H, s, 3-H), 6.69 (2H, d, J=8.6 Hz, 3′,5′-H), 7.09 (2H, d, J=8.6 Hz, 2′,6′-H), 7.27 (1H, s, 6-H), 8.75 (1H, s, 5-OH), 9.31 (1H, s, 4′-OH), 12.45 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 19.08 (CH_3), 45.00 (CH), 55.84 (4-OMe), 100.20 (3-C), 110.58 (1-C), 114.89 (6-C), 115.51 (3′,5′-C), 128.41 (2′,6′-C), 131.85 (1′-C), 138.74 (5-C), 155.45 (4-C), 156.14 (4′-C), 158.27 (2-C), 204.76 (C=O). FAB-HR-MS m/z: Calcd for $C_{16}H_{17}O_5$ [(M+H)$^+$] 289.1076, Found 289.1097.

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-(3′,4′-dihydroxyphenyl)-ethanone 10Ec 17% yield. Pale gray crystals. mp 198—200 °C (EtOH) (lit.[45] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.82 (3H, s, 4-OMe), 4.00 (2H, s, CH_2), 6.49 (1H, s, 3-H), 6.52 (1H, d, J=8.0 Hz, 6′-H), 6.64 (1H, s, 2′-H), 6.65 (1H, d, J=8.0 Hz, 5′-H), 7.30 (1H, s, 6-H), 8.76 (1H, s, 4′-OH), 8.81 (1H, s, 5-OH), 8.84 (1H, s, 3′-OH), 12.34 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.91 (CH_2), 55.88 (4-OMe), 100.17 (3-C), 111.03 (1-C), 115.18 (6-C), 115.55 (5′-C), 116.49 (2′-C), 120.05 (6′-C), 125.67 (1′-C), 138.88 (5-C), 144.07 (4′-C), 145.14 (3′-C), 155.64 (4-C), 158.08 (2-C), 202.61 (C=O). FAB-HR-MS m/z: Calcd for $C_{15}H_{15}O_6$ [(M+H)$^+$] 291.0869, Found 291.0879.

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-(4′-hydroxy-3′-methoxyphenyl)ethanone 10Ed 19% yield. Pale green crystals. mp 179—180 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.73 (3H, s, 3′-OMe), 3.83 (3H, s, 4-OMe), 4.10 (2H, s, CH_2), 6.50 (1H, s, 3-H), 6.64 (1H, d, J=8.0 Hz, 6′-H), 6.70 (1H, d, J=8.0 Hz, 5′-H), 6.84 (1H, s, 2′-H), 7.34 (1H, s, 6-H), 8.81 (1H, s, 5-OH), 8.83 (1H, s, 4′-OH), 12.29 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.05 (CH_2), 55.57 (3′-OMe), 55.87 (4-OMe), 100.17 (3-C), 111.08 (1-C), 113.64 (2′-C), 115.03 (6-C), 115.36 (5′-C), 121.69 (6′-C), 125.60 (1′-C), 138.89 (5-C), 145.28 (4′-C), 147.43 (3′-C), 155.58 (4-C), 157.93 (2-C), 202.37 (C=O). FAB-HR-MS m/z: Calcd for $C_{16}H_{17}O_6$ [(M+H)$^+$] 305.1025, Found 305.1019.

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-(4′-methoxyphenyl)ethanone 10Ee 22% yield. Pale red crystals. mp 136—137 °C (EtOH) (lit.[45] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.72 (3H, s, 4′-OMe), 3.83 (3H, s, 4-OMe), 4.17 (2H, s, CH_2), 6.50 (1H, s, 3-H), 6.88 (2H, d, J=8.6 Hz, 3′,5′-H), 7.19 (2H, d, J=8.6 Hz, 2′,6′-H), 7.34 (1H, s, 6-H), 8.86 (1H, s, 5-OH), 12.26 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.62 (CH_2), 55.02 (4′-OMe), 55.92 (4-OMe), 100.21 (3-C), 111.09 (1-C), 113.84 (3′,5′-C), 115.00 (6-C), 126.89 (1′-C), 130.51 (2′,6′-C), 138.96 (5-C), 155.64 (4-C), 157.92 (2-C),

158.02 (4′-C), 202.33 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{17}O_5$ [(M+H)$^+$] 289.1076, Found 289.1086.

1-(2,5-Dihydroxy-4-methoxyphenyl)-2-(3′,4′-dimethoxyphenyl)-ethanone 10Ef 27% yield. Pale brown crystals. mp 173—175 °C (EtOH) (lit.[45] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.72 (3H, s, 4′-OMe), 3.72 (3H, s, 3′-OMe), 3.83 (3H, s, 4-OMe), 4.16 (2H, s, CH_2), 6.50 (1H, s, 3-H), 6.77 (1H, d, J=8.0 Hz, 6′-H), 6.88 (1H, d, J=8.0 Hz, 5′-H), 6.89 (1H, s, 2′-H), 7.34 (1H, s, 6-H), 8.84 (1H, s, 5-OH), 12.26 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.05 (CH_2), 55.45 (4′-OMe), 55.48 (3′-OMe), 55.89 (4-OMe), 100.18 (3-C), 111.13 (1-C), 111.86 (5′-C), 113.37 (2′-C), 115.00 (6-C), 121.47 (6′-C), 127.33 (1′-C), 138.92 (5-C), 147.60 (4′-C), 148.58 (3′-C), 155.60 (4-C), 157.88 (2-C), 202.17 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{19}O_6$ [(M+H)$^+$] 319.1182, Found 319.1173.

1-(2,5-Dihydroxy-4-methylphenyl)-2-phenylethanone 10Fa 2% yield. Pale yellow crystals. mp 106—107 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.14 (3H, s, 4-Me), 4.29 (2H, s, CH_2), 6.73 (1H, s, 3-H), 7.24 (1H, t, J=7.4 Hz, 4′-H), 7.27 (1H, d, J=7.4 Hz, 2′,6′-H), 7.30 (1H, s, 6-H), 7.32 (1H, t, J=7.4 Hz, 3′,5′-H), 9.13 (1H, s, 5-OH), 11.33 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.55 (4-Me), 45.19 (CH_2), 114.14 (6-C), 117.38 (1-C), 119.07 (3-C), 126.56 (4′-C), 128.31 (3′,5′-C), 129.60 (2′,6′-C), 134.89 (1′-C), 135.58 (4-C), 147.71 (5-C), 154.26 (2-C), 202.51 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{15}H_{15}O_3$ [(M+H)$^+$] 243.1021, Found 243.1020.

1-(2,5-Dihydroxy-4-methylphenyl)-2-(4′-hydroxyphenyl)ethanone 10Fb 13% yield. Pale yellow crystals. mp 163—164 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.13 (3H, s, 4-Me), 4.13 (2H, s, CH_2), 6.70 (2H, d, J=8.6 Hz, 3′,5′-H), 6.71 (1H, s, 3-H), 7.06 (2H, d, J=8.6 Hz, 2′,6′-H), 7.29 (1H, s, 6-H), 9.13 (1H, s, 5-OH), 9.29 (1H, s, 4′-OH), 11.43 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.55 (4-Me), 44.26 (CH_2), 114.23 (6-C), 115.19 (3′,5′-C), 117.13 (1-C), 119.04 (3-C), 124.80 (1′-C), 130.42 (2′,6′-C), 135.56 (4-C), 147.65 (5-C), 154.45 (2-C), 156.10 (4′-C) 203.23 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{15}H_{15}O_4$ [(M+H)$^+$] 259.0970, Found 259.0954.

1-(2,5-Dihydroxy-4-methylphenyl)-2-(3′,4′-dihydroxyphenyl)ethanone 10Fc 7% yield. A pale brown solid. mp 96—98 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.13 (3H, s, 4-Me), 4.04 (2H, s, CH_2), 6.52 (1H, d, J=8.0 Hz, 6′-H), 6.64 (1H, s, 2′-H), 6.66 (1H, d, J=8.0 Hz, 5′-H), 6.71 (1H, s, 3-H), 7.27 (1H, s, 6-H), 8.77 (1H, s, 4′-OH), 8.83 (1H, s, 3′-OH), 9.12 (1H, s, 5-OH), 11.49 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.58 (4-Me), 44.47 (CH_2), 114.39 (6-C), 115.54 (5′-C), 116.61 (2′-C), 117.07 (1-C), 119.03 (3-C), 120.17 (6′-C), 125.43 (1′-C), 135.67 (4-C), 144.12 (4′-C), 145.15 (3′-C), 147.64 (5-C), 154.61 (2-C) 203.41 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{15}H_{15}O_5$ [(M+H)$^+$] 275.0919, Found 275.0926.

1-(2,5-Dihydroxy-4-methylphenyl)-2-(4′-hydroxy-3′-methoxyphenyl)-ethanone 10Fd 9% yield. Pale yellow crystals. mp 168—169 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.13 (3H, s, 4-Me), 3.74 (3H, s, 3′-OMe), 4.14 (2H, s, CH_2), 6.64 (1H, d, J=8.0 Hz, 6′-H), 6.70 (1H, d, J=8.0 Hz, 5′-H), 6.71 (1H, s, 3-H), 6.83 (1H, s, 2′-H), 7.30 (1H, s, 6-H), 8.84 (1H, s, 4′-OH), 9.13 (1H, s, 5-OH), 11.43 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.56 (4-Me), 44.68 (CH_2), 55.59 (3′-OMe), 113.73 (2′-C), 114.21 (6-C), 115.35 (5′-C), 117.19 (1-C), 119.04 (3-C), 121.80 (6′-C), 125.38 (1′-C), 135.54 (4-C), 145.32 (4′-C), 147.43 (3′-C), 147.63 (5-C), 154.41 (2-C) 203.09 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{17}O_5$ [(M+H)$^+$] 289.1076, Found 289.1089. *Anal.* Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.72; H, 5.46.

1-(2,5-Dihydroxy-4-methylphenyl)-2-(4′-methoxyphenyl)ethanone 10Fe 11% yield. Pale yellow crystals. mp 115—116 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.14 (3H, s, 4-Me), 3.73 (3H, s, 4′-OMe), 4.21 (2H, s, CH_2), 6.72 (1H, s, 3-H), 6.88 (2H, d, J=8.6 Hz, 3′,5′-H), 7.18 (2H, d, J=8.6 Hz, 2′,6′-H), 7.29 (1H, s, 6-H), 9.13 (1H, s, 5-OH), 11.38 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.54 (4-Me), 44.25 (CH_2), 54.99 (4′-OMe), 113.80 (3′,5′-C), 114.16 (6-C), 117.23 (1-C), 119.04 (3-C), 126.63 (1′-C), 130.54 (2′,6′-C), 135.53 (4-C), 147.66 (5-C), 154.33 (2-C), 158.03 (4′-C) 202.92 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{17}O_4$ [(M+H)$^+$] 273.1127, Found: 273.1120. *Anal.* Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.51; H, 6.03.

1-(2,5-Dihydroxy-3,4-dimethylphenyl)-2-phenylethanone 10Ga 41% yield. Pale yellow crystals. mp 140—141 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.08 (3H, s, 3-Me), 2.13 (3H, s, 4-Me), 4.29 (2H, s, CH_2), 7.25 (1H, t, J=7.4 Hz, 4′-H), 7.27 (1H, s, 6-H), 7.28 (2H, d, J=7.4 Hz, 2′,6′-H), 7.33 (2H, t, J=7.4 Hz, 3′,5′-H), 9.11 (1H, s, 5-OH), 12.12 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 11.29 (3-Me), 12.94 (4-Me), 44.39 (CH_2), 111.49 (6-C), 115.38 (1-C), 125.42 (3-C), 126.64 (4′-C), 128.38 (3′,5′-C), 129.53 (2′,6′-C), 134.66 (4-C), 134.80 (1′-C), 147.04 (5-C), 153.43 (2-C), 203.77 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{17}O_3$ [(M+H)$^+$] 257.1178, Found 257.1180.

1-(2,5-Dihydroxy-3,4-dimethylphenyl)-2-(4′-hydroxyphenyl)ethanone 10Gb 29% yield. Pale yellow crystals. mp 167—168 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.08 (3H, s, 3-Me), 2.12 (3H, s, 4-Me), 4.13 (2H, s, CH_2), 6.71 (2H, d, J=8.6 Hz, 3′,5′-H), 7.07 (2H, d, J=8.6 Hz, 2′,6′-H), 7.26 (1H, s, 6-H), 9.08 (1H, s, 5-OH), 9.30 (1H, s, 4′-OH), 12.18 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 11.27 (3-Me), 12.92 (4-Me), 43.61 (CH_2), 111.56 (6-C), 115.23 (1,3′,5′-C), 124.75 (1′-C), 125.37 (3-C), 130.35 (2′,6′-C), 134.51 (4-C), 146.97 (5-C), 153.48 (2-C), 156.13 (4′-C), 204.28 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{17}O_4$ [(M+H)$^+$] 273.1127, Found 273.1120.

1-(2,5-Dihydroxy-3,4-dimethylphenyl)-2-(3′,4′-dihydroxyphenyl)-ethanone 10Gc 30% yield. Pale green crystals. mp 183—184 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.08 (3H, s, 3-Me), 2.12 (3H, s, 4-Me), 4.03 (2H, s, CH_2), 6.53 (1H, d, J=8.0 Hz, 6′-H), 6.64 (1H, s, 2′-H), 6.66 (1H, d, J=8.0 Hz, 5′-H), 7.23 (1H, s, 6-H), 8.78 (1H, s, 4′-OH), 8.83 (1H, s, 3′-OH), 9.08 (1H, s, 5-OH), 12.22 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 11.27 (3-Me), 12.93 (4-Me), 43.87 (CH_2), 111.72 (6-C), 115.28 (1-C), 115.55 (5′-C), 116.50 (2′-C), 120.10 (6′-C), 125.34 (3-C), 125.38 (1′-C), 134.56 (4-C), 144.14 (4′-C), 145.17 (3′-C), 146.95 (5-C), 153.57 (2-C), 204.36 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{17}O_5$ [(M+H)$^+$] 289.1076, Found 289.1071. *Anal.* Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.31; H, 5.41.

1-(2,5-Dihydroxy-3,4-dimethylphenyl)-2-(4′-methoxyphenyl)ethanone 10Ge 48% yield. Pale yellow crystals. mp 124—125 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.08 (3H, s, 3-Me), 2.12 (3H, s, 4-Me), 3.73 (3H, s, 4′-OMe), 4.20 (2H, s, CH_2), 6.89 (2H, d, J=8.6 Hz, 3′,5′-H), 7.19 (2H, d, J=8.6 Hz, 2′,6′-H), 7.26 (1H, s, 6-H), 9.09 (1H, s, 5-OH), 12.14 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 11.27 (3-Me), 12.92 (4-Me), 43.52 (CH_2), 55.00 (4′-OMe), 111.50 (6-C), 113.85 (3′,5′-C), 115.29 (1-C), 125.38 (3-C), 126.56 (1′-C), 130.49 (2′,6′-C), 134.56 (4-C), 147.00 (5-C), 153.43 (2-C), 158.07 (4′-C), 204.08 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{19}O_4$ [(M+H)$^+$] 287.1283, Found 287.1269. *Anal.* Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.09; H, 6.36.

1-(2,3-Dihydroxy-4-methoxyphenyl)-2-phenylethanone 10Ha 58% yield. Pale brown crystals. mp 133—134 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.86 (3H, s, 4-OMe), 4.34 (2H, s, CH_2), 6.66 (1H, d, J=9.2 Hz, 5-H), 7.24 (1H, t, J=7.4 Hz, 4′-H), 7.29 (2H, d, J=7.4 Hz, 2′,6′-H), 7.32 (2H, t, J=7.4 Hz, 3′,5′-H), 7.63 (1H, d, J=9.2 Hz, 6-H), 8.63 (1H, s, 3-OH), 12.14 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.38 (CH_2), 55.92 (4-OMe), 103.53 (5-C), 113.97 (1-C), 122.62 (6-C), 126.57 (4′-C), 128.34 (3′,5′-C), 129.52 (2′,6′-C), 133.72 (3-C), 135.13 (1′-C), 151.21 (2-C), 153.35 (4-C), 203.25 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{15}H_{15}O_4$ [(M+H)$^+$] 259.0970, Found 259.0952.

1-(2,3-Dihydroxy-4-methoxyphenyl)-2-(3′,4′-dihydroxyphenyl)-ethanone 10Hc 53% yield. Pale yellow crystals. mp 289—293 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.85 (3H, s, 4-OMe), 4.09 (2H, s, CH_2), 6.41 (1H, d, J=8.0 Hz, 6′-H), 6.61 (1H, d, J=8.0 Hz, 5′-H), 6.65 (1H, d, J=8.6 Hz, 5-H), 6.66 (1H, s, 2′-H), 7.57 (1H, d, J=8.6 Hz, 6-H). ^{13}C-NMR (DMSO-d_6) δ: 43.87 (CH_2), 55.93 (4-OMe), 103.48 (5-C), 113.79 (1-C), 115.58 (5′-C), 116.58 (2′-C), 120.13 (6′-C), 122.85 (6-C), 125.80 (1′-C), 133.71 (3-C), 144.09 (4′-C), 145.16 (3′-C), 151.43 (2-C), 153.30 (4-C), 204.02 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{15}H_{15}O_6$ [(M+H)$^+$] 291.0869, Found 291.0879.

1-(2,3-Dihydroxy-4-methoxyphenyl)-2-(4′-hydroxy-3′-methoxyphenyl)ethanone 10Hd 52% yield. Pale brown crystals. mp 82—83 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.73 (3H, s, 3′-OMe), 3.85 (3H, s, 4-OMe), 4.19 (2H, s, CH_2), 6.64 (1H, d, J=9.2 Hz, 5-H), 6.66 (1H, d, J=8.0 Hz, 6′-H), 6.69 (1H, d, J=8.0 Hz, 5′-H), 6.87 (1H, s, 2′-H), 7.61 (1H, d, J=9.2 Hz, 6-H), 8.64 (1H, s, 4′-OH), 8.82 (1H, s, 3-OH), 12.24 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.97 (CH_2), 55.58 (3′-OMe), 55.91 (4-OMe), 103.45 (5-C), 113.66 (2′-C), 113.86 (1-C), 115.36 (5′-C), 121.73 (6′-C), 122.65 (6-C), 125.69 (1′-C), 133.69 (3-C), 145.29 (4′-C), 147.43 (3′-C), 151.30 (2-C), 153.26 (4-C) 203.73 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{17}O_6$ [(M+H)$^+$] 305.1025, Found 305.1020.

1-(2,3-Dihydroxy-4-methoxyphenyl)-2-(4′-methoxyphenyl)ethanone 10He 50% yield. Pale brown crystals. mp 116—117 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.72 (3H, s, 4′-OMe), 3.85 (3H, s, 4-OMe), 4.27 (2H, s, CH_2), 6.60 (1H, d, J=9.2 Hz, 5-H), 6.87 (2H, d, J=8.6 Hz, 3′,5′-H), 7.20 (2H, d, J=8.6 Hz, 2′,6′-H), 7.58 (1H, d, J=9.2 Hz, 6-H). ^{13}C-NMR (DMSO-d_6) δ: 43.68 (CH_2), 54.99 (4′-OMe), 55.91 (4-OMe), 103.20 (5-C), 113.79 (3′,5′-C), 113.96 (1-C), 122.42 (6-C), 127.13 (1′-C), 130.51 (2′,6′-C), 133.95 (3-C), 151.99 (2-C), 152.87 (4-C), 157.98 (4′-C), 203.27 (C=O). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{17}O_5$ [(M+H)$^+$] 289.1076, Found 289.1081.

1-(2,4-Dihydroxy-5-methoxyphenyl)-2-phenylethanone 10Ja 45% yield. Pale brown crystals. mp 88—89 °C (EtOH) (lit.[45] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.78 (3H, s, 5-OMe), 4.33 (2H, s, CH_2), 6.33 (1H, s, 3-H), 7.25 (1H, t, J=8.0 Hz, 4′-H), 7.31 (2H, t, J=8.0 Hz, 3′,5′-H), 7.32 (2H, d, J=8.0 Hz, 2′,6′-H), 7.44 (1H, s, 6-H), 10.50 (1H, s, 4-OH), 12.31 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.50 (CH_2), 56.37 (5-OMe), 103.28 (3-C), 110.48 (1-C), 113.35 (6-C), 126.52 (4′-C), 128.35 (3′,5′-C), 129.54 (2′,6′-C), 135.36 (1′-C), 141.09 (4-C), 155.55 (5-C), 159.19 (2-C), 201.58 (C=O). FAB-HR-MS m/z: Calcd for $C_{15}H_{15}O_4$ [(M+H)$^+$] 259.0970, Found 259.0956.

1-(2,4-Dihydroxy-5-methoxyphenyl)-2-(4′-hydroxyphenyl)ethanone 10Jb 18% yield. Pale pink crystals. mp 144—145 °C (EtOH) [lit.[47] 150—151 °C (EtOH)]. ^{1}H-NMR (DMSO-d_6) δ: 3.77 (3H, s, 5-OMe), 4.17 (2H, s, CH_2), 6.31 (1H, s, 3-H), 6.70 (2H, d, J=8.6 Hz, 3′,5′-H), 7.09 (2H, d, J=8.6 Hz, 2′,6′-H), 7.41 (1H, s, 6-H), 9.28 (1H, s, 4′-OH), 10.49 (1H, s, 4-OH), 12.39 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.65 (CH_2), 56.34 (5-OMe), 103.24 (3-C), 110.29 (1-C), 113.39 (6-C), 115.20 (3′,5′-C), 125.32 (1′-C), 130.36 (2′,6′-C), 141.01 (4-C), 155.46 (5-C), 156.02 (4′-C), 159.27 (2-C), 202.21 (C=O). FAB-HR-MS m/z: Calcd for $C_{15}H_{15}O_5$ [(M+H)$^+$] 275.0919, Found 275.0918.

1-(2,4-Dihydroxy-5-methoxyphenyl)-2-(4′-hydroxy-3′-methoxyphenyl)ethanone 10Jd 34% yield. Pale gray crystals. mp 126—127 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.73 (3H, s, 3′-OMe), 3.77 (3H, s, 5-OMe), 4.18 (2H, s, CH_2), 6.31 (1H, s, 3-H), 6.68 (1H, d, J=8.0 Hz, 6′-H), 6.71 (1H, d, J=8.0 Hz, 5′-H), 6.89 (1H, s, 2′-H), 7.43 (1H, s, 6-H), 8.83 (1H, s, 4′-OH), 10.47 (1H, s, 4-OH), 12.39 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.08 (CH_2), 55.53 (3′-OMe), 56.34 (5-OMe), 103.24 (3-C), 110.31 (1-C), 113.37 (6-C), 113.60 (2′-C), 115.40 (5′-C), 121.70 (6′-C), 125.89 (1′-C), 140.99 (4-C), 145.23 (4′-C), 147.42 (3′-C), 155.43 (5-C), 159.26 (2-C), 202.08 (C=O). FAB-HR-MS m/z: Calcd for $C_{16}H_{17}O_6$ [(M+H)$^+$] 305.1025, Found 305.1046.

1-(2,4-Dihydroxy-5-methoxyphenyl)-2-(4′-methoxyphenyl)ethanone 10Je 31% yield. Pale brown crystals. mp 119—121 °C (EtOH) (lit.[48] 128—129 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.72 (3H, s, 4′-OMe), 3.78 (3H, s, 5-OMe), 4.25 (2H, s, CH_2), 6.32 (1H, s, 3-H), 6.88 (2H, d, J=8.6 Hz, 3′,5′-H), 7.22 (2H, d, J=8.6 Hz, 2′,6′-H), 7.42 (1H, s, 6-H), 10.50 (1H, s, 4-OH), 12.35 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.59 (CH_2), 54.99 (4′-OMe), 56.37 (5-OMe), 103.27 (3-C), 110.34 (1-C), 113.33 (6-C), 113.83 (3′,5′-C), 127.14 (1′-C), 130.51 (2′,6′-C), 141.06 (4-C), 155.51 (5-C), 157.99 (4′-C), 159.23 (2-C), 201.99 (C=O). FAB-HR-MS m/z: Calcd for $C_{16}H_{17}O_5$ [(M+H)$^+$] 289.1076, Found 289.1068.

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-phenylethanone 10Ka 33% yield. Pale brown crystals. mp 92—93 °C (EtOH) (lit.[49] 94 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.77 (3H, s, 5-OMe), 3.82 (3H, s, 4-OMe), 4.38 (2H, s, CH_2), 6.55 (1H, s, 3-H), 7.24 (1H, t, J=8.6 Hz, 4′-H), 7.30—7.34 (4H, m, 2′,3′,5′,6′-H), 7.44 (1H, s, 6-H), 12.41 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.67 (CH_2), 55.98 (4-OMe), 56.20 (5-OMe), 100.49 (3-C), 110.81 (1-C), 112.25 (6-C), 126.58 (4′-C), 128.38 (3′,5′-C), 129.60 (2′,6′-C), 135.19 (1′-C), 141.69 (5-C), 156.48 (4-C), 159.14 (2-C), 202.06 (C=O). FAB-HR-MS m/z: Calcd for $C_{16}H_{17}O_4$ [(M+H)$^+$] 273.1127, Found 273.1120.

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(4′-hydroxyphenyl)ethanone 10Kb 25% yield. Colorless crystals. mp 167—168 °C (EtOH) (lit.[45] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.76 (3H, s, 5-OMe), 3.82 (3H, s, 4-OMe), 4.21 (2H, s, CH_2), 6.54 (1H, s, 3-H), 6.70 (2H, d, J=8.6 Hz, 3′,5′-H), 7.09 (2H, d, J=8.6 Hz, 2′,6′-H), 7.41 (1H, s, 6-H), 9.31 (1H, s, 4′-OH), 12.49 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.84 (CH_2), 55.98 (4-OMe), 56.18 (5-OMe), 100.48 (3-C), 110.63 (1-C), 112.29 (6-C), 115.24 (3′,5′-C), 125.15 (1′-C), 130.44 (2′,6′-C), 141.60 (5-C), 156.07 (4′-C), 156.39 (4-C), 159.24 (2-C), 202.71 (C=O). FAB-HR-MS m/z: Calcd for $C_{16}H_{17}O_5$ [(M+H)$^+$] 289.1076, Found 289.1075.

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(3′,4′-dihydroxyphenyl)-ethanone 10Kc 44% yield. Pale brown crystals. mp 167—169 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.75 (3H, s, 5-OMe), 3.81 (3H, s, 4-OMe), 4.12 (2H, s, CH_2), 6.53 (1H, s, 3-H), 6.57 (1H, d, J=8.0 Hz, 6′-H), 6.66 (1H, d, J=8.0 Hz, 5′-H), 6.68 (1H, s, 2′-H), 7.40 (1H, s, 6-H), 8.74 (1H, s, 4′-OH), 8.85 (1H, s, 3′-OH), 12.52 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.14 (CH_2), 55.95 (4-OMe), 56.14 (5-OMe), 100.44 (3-C), 110.55 (1-C), 112.48 (6-C), 115.58 (5′-C), 116.56 (2′-C), 120.15 (6′-C), 125.76 (1′-C), 141.54 (5-C), 144.06 (4′-C), 145.17 (3′-C), 156.40 (4-C), 159.33 (2-C), 202.77 (C=O). FAB-HR-MS m/z: Calcd for $C_{16}H_{17}O_6$ [(M+H)$^+$] 305.1025, Found 305.1011.

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(4′-hydroxy-3′-methoxyphenyl)ethanone 10Kd 11% yield. Pale violet crystals. mp 113—114 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.73 (3H, s, 3′-OMe), 3.76 (3H, s, 5-OMe), 3.82 (3H, s, 4-OMe), 4.22 (2H, s, CH_2), 6.54 (1H, s, 3-H), 6.68 (1H, d, J=8.0 Hz, 6′-H), 6.70 (1H, d, J=8.0 Hz, 5′-H), 6.89 (1H, s, 2′-H), 7.43 (1H, s, 6-H), 8.84 (1H, s, 4′-OH), 12.48 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.24 (CH_2), 55.53 (3′-OMe), 55.94 (4-OMe), 56.18 (5-OMe), 100.46 (3-C), 110.65 (1-C), 112.33 (6-C), 113.63 (2′-C), 115.42 (5′-C), 121.74 (6′-C), 125.71 (1′-C), 141.59 (5-C), 145.27 (4′-C), 147.44 (3′-C), 156.39 (4-C), 159.22 (2-C) 202.52 (C=O). FAB-HR-MS m/z: Calcd for $C_{17}H_{19}O_6$ [(M+H)$^+$] 319.1182, Found 319.1191. *Anal.* Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.09; H, 6.12.

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(4′-methoxyphenyl)ethanone 10Ke 52% yield. Colorless crystals. mp 93—95 °C (EtOH) (lit.[45] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.72 (3H, s, 4′-OMe), 3.77 (3H, s, 5-OMe), 3.82 (3H, s, 4-OMe), 4.29 (2H, s, CH_2), 6.55 (1H, s, 3-H), 6.89 (2H, d, J=8.6 Hz, 3′,5′-H), 7.22 (2H, d, J=8.6 Hz, 2′,6′-H), 7.43 (1H, s, 6-H), 12.45 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 43.75 (CH_2), 54.98 (4′-OMe), 55.97 (4-OMe), 56.20 (5-OMe), 100.48 (3-C), 110.69 (1-C), 112.28 (6-C), 113.85 (3′,5′-C), 126.95 (1′-C), 130.56 (2′,6′-C), 141.65 (5-C), 156.44 (4-C), 158.02 (4′-C), 159.18 (2-C), 202.44 (C=O). FAB-HR-MS m/z: Calcd for $C_{17}H_{19}O_5$ [(M+H)$^+$] 303.1232, Found 303.1217.

1-(2-Hydroxy-4,5-dimethoxyphenyl)-2-(3′,4′-dimethoxyphenyl)-ethanone 10Kf 46% yield. Pale yellow crystals. mp 131—132 °C (EtOH) (lit.[50] 136—138 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.72 (3H, s, 3′-OMe), 3.72 (3H, s, 4′-OMe), 3.77 (3H, s, 5-OMe), 3.82 (3H, s, 4-OMe), 4.28 (2H, s, CH_2), 6.55 (1H, s, 3-H), 6.81 (1H, d, J=8.6 Hz, 6′-H), 6.89 (1H, d, J=8.6 Hz, 5′-H), 6.94 (1H, s, 2′-H), 7.44 (1H, s, 6-H), 12.46 (1H, s, 2-OH). ^{13}C-NMR (DMSO-d_6) δ: 44.24 (CH_2), 55.42 (4′-OMe), 55.46 (3′-OMe), 55.98 (4-OMe), 56.20 (5-OMe), 100.48 (3-C), 110.71 (1-C), 111.86 (5′-C), 112.26 (6-C), 113.36 (2′-C), 121.54 (6′-C), 127.40 (1′-C), 141.64 (5-C), 147.60 (4′-C), 148.60 (3′-C), 156.42 (4-C), 159.20 (2-C), 202.35 (C=O). FAB-HR-MS m/z: Calcd for $C_{18}H_{21}O_6$ [(M+H)$^+$] 333.1338, Found 333.1343.

Typical Procedure for the One-Pot Synthesis of the Isoflavone 8 from the Phenols 11 and the Phenylacetic Acids 12 To a mixture of **11A** (0.86 g, 7.8 mmol) and **12a** (1.00 g, 7.3 mmol) was added $BF_3 \cdot Et_2O$ (2.2 ml). The reaction mixture was heated at 120 °C for 10 min and cooled to room temperature. Dry DMF (9.9 ml) was added, and the reaction mixture was heated at 50 °C for 10 min. $MeSO_2Cl$ (5.9 g) was added, and the reaction mixture was heated at 80 °C for 30 min. The mixture was cooled to room temperature, and cold water (240 ml) was added. The product was extracted with Et_2O (3×120 ml). A combined Et_2O layer was successively washed with brine (3×100 ml) and saturated $NaHCO_3$ (3×100 ml), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was subjected to reversed-phase liquid chromatography with an ODS column (eluent, CH_3CN–H_2O) to give the product **8Aa**, which was recrystallized from EtOH to give pure **8Aa** (0.93 g, 3.9 mmol, 53% yield).

7-Hydroxyisoflavone 8Aa 53% yield. Pale violet crystals. mp 203—204 °C (EtOH) (lit.[25] 207—208 °C). ^{1}H-NMR (DMSO-d_6) δ: 6.89 (1H, s, 8-H), 6.95 (1H, d, J=8.6 Hz, 6-H), 7.37 (1H, t, J=7.4 Hz, 4′-H), 7.43 (2H, t, J=7.4 Hz, 3′,5′-H), 7.57 (2H, d, J=7.4 Hz, 2′,6′-H), 7.99 (1H, d, J=8.6 Hz, 5-H), 8.39 (1H, s, 2-H), 10.82 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 102.15 (8-C), 115.23 (6-C), 116.61 (4a-C), 123.52 (3-C), 127.29 (5-C), 127.68 (4′-C), 128.07 (3′,5′-C), 128.90 (2′,6′-C), 132.09 (1′-C), 153.81 (2-C), 157.43 (8a-C), 162.63 (7-C), 174.36 (4-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{11}O_3$ [(M+H)$^+$] 239.0708, Found 239.0723.

4′,7-Dihydroxyisoflavone 8Ab (Daidzein 1) 17% yield. Pale orange crystals. mp 327 °C (decomp.) (EtOH) [lit.[51] >295 °C (decomp.)]. ^{1}H-NMR (DMSO-d_6) δ: 6.81 (2H, d, J=8.6 Hz, 3′,5′-H), 6.87 (1H, s, 8-H), 6.94 (1H, d, J=8.6 Hz, 6-H), 7.38 (2H, d, J=8.6 Hz, 2′,6′-H), 7.96 (1H, d, J=8.6 Hz, 5-H), 8.29 (1H, s, 2-H), 9.53 (1H, s, 4′-OH), 10.80 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 102.06 (8-C), 114.91 (3′,5′-C), 115.09 (6-C), 116.59 (4a-C), 122.49 (1′-C), 123.44 (3-C), 127.23 (5-C), 130.02 (2′,6′-C), 152.78 (2-C), 157.14 (4′-C), 157.38 (8a-C), 162.49 (7-C), 174.65 (4-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{11}O_4$ [(M+H)$^+$] 255.0657, Found 255.0644.

3′,4′,7-Trihydroxyisoflavone 8Ac 30% yield. Pale orange crystals. mp 278—279 °C (EtOH) (lit.[52] 280—281 °C). ^{1}H-NMR (DMSO-d_6) δ: 6.76 (1H, d, J=8.0 Hz, 5′-H), 6.80 (1H, d, J=8.0 Hz, 6′-H), 6.85 (1H, s, 8-H), 6.93 (1H, d, J=9.2 Hz, 6-H), 7.01 (1H, s, 2′-H), 7.96 (1H, d, J=9.2 Hz, 5-H), 8.26 (1H, s, 2-H), 8.97 (1H, s, 3′-OH), 9.02 (1H, s, 4′-OH), 10.78 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 102.06 (8-C), 115.08 (6-C), 115.26 (5′-C), 116.58 (4a-C), 116.65 (2′-C), 119.81 (6′-C), 122.97 (1′-C), 123.60 (3-C), 127.29 (5-C), 144.76 (3′-C), 145.24 (4′-C), 152.78 (2-C), 157.35 (8a-C), 162.45 (7-C), 174.65 (4-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{11}O_5$ [(M+H)$^+$] 271.0606, Found 271.0618.

4′,7-Dihydroxy-3′-methoxyisoflavone 8Ad 52% yield. Pale red crys-

tals. mp 248—249 °C (EtOH) (lit.[53] 244—246 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 3′-OMe), 6.81 (1H, d, J=8.6 Hz, 5′-H), 6.87 (1H, s, 8-H), 6.94 (1H, d, J=8.6 Hz, 6-H), 6.99 (1H, d, J=8.6 Hz, 6′-H), 7.16 (1H, s, 2′-H), 7.97 (1H, d, J=8.6 Hz, 5-H), 8.33 (1H, s, 2-H), 9.06 (1H, s, 4′-OH), 10.78 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.65 (3′-OMe), 102.05 (8-C), 113.24 (2′-C), 115.10 (5′-C), 115.15 (6-C), 116.62 (4a-C), 121.48 (6′-C), 122.95 (1′-C), 123.47 (3-C), 127.26 (5-C), 146.42 (4′-C), 147.11 (3′-C), 153.02 (2-C), 157.34 (8a-C), 162.47 (7-C), 174.62 (4-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{13}O_5$ [(M+H)$^+$] 285.0763, Found 285.0760.

7-Hydroxy-3′,4′-dimethoxyisoflavone 8Af 14% yield. Pale yellow crystals. mp 233—234 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.78 (3H, s, 3′-OMe), 3.79 (3H, s, 4′-OMe), 6.88 (1H, s, 8-H), 6.95 (1H, d, J=8.6 Hz, 6-H), 7.01 (1H, d, J=8.6 Hz, 5′-H), 7.13 (1H, d, J=8.6 Hz, 6′-H), 7.19 (1H, s, 2′-H), 7.98 (1H, d, J=8.6 Hz, 5-H), 8.38 (1H, s, 2-H), 10.83 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.51 (3′-OMe), 55.54 (4′-OMe), 102.13 (8-C), 111.50 (5′-C), 112.75 (2′-C), 115.20 (6-C), 116.62 (4a-C), 121.22 (6′-C), 123.24 (3-C), 124.53 (1′-C), 127.32 (5-C), 148.25 (3′-C), 148.58 (4′-C), 153.38 (2-C), 157.39 (8a-C), 162.57 (7-C), 174.59 (4-C). FAB-HR-MS m/z: Calcd for $C_{17}H_{15}O_5$ [(M+H)$^+$] 299.0919, Found 299.0915.

7,8-Dihydroxyisoflavone 8Ba 38% yield. Pale pink crystals. mp 210—211 °C (EtOH) [lit.[54] 211 °C (H_2O)]. The ^{1}H- and ^{13}C-NMR data of this product are in good agreement with those reported in the literature.[54] FAB-HR-MS m/z: Calcd for $C_{15}H_{11}O_4$ [(M+H)$^+$] 255.0657, Found 255.0637.

4′,7,8-Trihydroxyisoflavone 8Bb 57% yield. Pale pink crystals. mp 282 °C (decomp.) (EtOH) [lit.[55] >180 °C (decomp.)]. ^{1}H-NMR (DMSO-d_6) δ: 6.81 (2H, d, J=8.6 Hz, 3′,5′-H), 6.95 (1H, d, J=8.6 Hz, 6-H), 7.39 (2H, d, J=8.6 Hz, 2′,6′-H), 7.46 (1H, d, J=8.6 Hz, 5-H), 8.34 (1H, s, 2-H), 9.44 (1H, s, 8-OH), 9.53 (1H, s, 4′-OH), 10.32 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 114.13 (6-C), 114.91 (3′,5′-C), 115.63 (5-C), 117.43 (4a-C), 122.67 (3-C), 122.90 (1′-C), 130.13 (2′,6′-C), 132.86 (8-C), 146.69 (8a-C), 149.91 (7-C), 152.66 (2-C), 157.11 (4′-C), 175.13 (4-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{11}O_5$ [(M+H)$^+$] 271.0606, Found 271.0600.

3′,4′,7,8-Tetrahydroxyisoflavone 8Bc 18% yield. Pale green crystals. mp 126—127 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 6.76 (1H, d, J=8.6 Hz, 5′-H), 6.81 (1H, d, J=8.6 Hz, 6′-H), 6.95 (1H, d, J=8.6 Hz, 6-H), 7.02 (1H, s, 2′-H), 7.46 (1H, d, J=8.6 Hz, 5-H), 8.29 (1H, s, 2-H), 8.99 (2H, s, 3′,4′-OH), 9.44 (1H, s, 8-OH), 10.32 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 114.10 (6-C), 115.25 (5′-C), 115.64 (5-C), 116.66 (2′-C), 117.46 (4a-C), 119.89 (6′-C), 123.06 (3-C), 123.12 (1′-C), 132.84 (8-C), 144.75 (3′-C), 145.19 (4′-C), 146.64 (8a-C), 149.87 (7-C), 152.61 (2-C), 174.86 (4-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{11}O_6$ [(M+H)$^+$] 287.0556, Found 287.0546.

4′,7,8-Trihydroxy-3′-methoxyisoflavone 8Bd 7% yield. Pale pink crystals. mp 241—242 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.80 (3H, s, 3′-OMe), 6.81 (1H, d, J=8.0 Hz, 5′-H), 6.96 (1H, d, J=8.6 Hz, 6-H), 7.00 (1H, d, J=8.0 Hz, 6′-H), 7.18 (1H, s, 2′-H), 7.47 (1H, d, J=8.6 Hz, 5-H), 8.37 (1H, s, 2-H), 9.05 (1H, s, 4′-OH), 9.41 (1H, s, 8-OH), 10.30 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.66 (3′-OMe), 113.35 (2′-C), 114.13 (6-C), 115.14 (5′-C), 115.63 (5-C), 117.45 (4a-C), 121.54 (6′-C), 122.91 (3-C), 123.12 (1′-C), 132.84 (8-C), 146.39 (4′-C), 146.64 (8a-C), 147.10 (3′-C), 149.89 (7-C), 152.85 (2-C), 175.08 (4-C). FAB-HR-MS m/z: (M+H)$^+$ Calcd for $C_{16}H_{13}O_6$ 301.0712, Found 301.0708.

7,8-Dihydroxy-4′-methoxyisoflavone 8Be 66% yield. Pale yellow crystals. mp 244—245 °C (EtOH) (lit.[56] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 4′-OMe), 6.96 (1H, d, J=8.6 Hz, 6-H), 6.99 (2H, d, J=8.6 Hz, 3′,5′-H), 7.48 (1H, d, J=8.6 Hz, 5-H), 7.52 (2H, d, J=8.6 Hz, 2′,6′-H), 8.39 (1H, s, 2-H), 9.46 (1H, s, 8-OH), 10.34 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.14 (4′-OMe), 113.57 (3′,5′-C), 114.18 (6-C), 115.65 (5-C), 117.42 (4a-C), 122.58 (3-C), 124.38 (1′-C), 130.13 (2′,6′-C), 132.90 (8-C), 146.70 (8a-C), 149.98 (7-C), 153.00 (2-C), 158.90 (4′-C), 175.06 (4-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{13}O_5$ [(M+H)$^+$] 285.0763, Found 285.0790.

7,8-Dihydroxy-3′,4′,-dimethoxyisoflavone 8Bf 2% yield. Pale pink crystals. mp 238—239 °C (EtOH) (lit.[57] 209—211 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.78 (6H, s, 3′,4′-OMe), 6.97 (1H, d, J=8.6 Hz, 6-H), 7.00 (1H, d, J=8.6 Hz, 5′-H), 7.13 (1H, d, J=8.6 Hz, 6′-H), 7.20 (1H, s, 2′-H), 7.48 (1H, d, J=8.6 Hz, 5-H), 8.42 (1H, s, 2-H), 9.47 (1H, s, 8-OH), 10.36 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.52 (3′-OMe), 55.55 (4′-OMe), 111.52 (5′-C), 112.85 (2′-C), 114.19 (6-C), 115.66 (5-C), 117.44 (4a-C), 121.26 (6′-C), 122.68 (3-C), 124.69 (1′-C), 132.89 (8-C), 146.64 (8a-C), 148.23 (3′-C), 148.53 (4′-C), 149.97 (7-C), 153.20 (2-C), 175.04 (4-C). FAB-HR-MS m/z: Calcd for $C_{17}H_{15}O_6$ [(M+H)$^+$] 315.0869, Found 315.0873.

6-Hydroxy-7-methoxyisoflavone 8Ea 9% yield. Pale orange crystals. mp 244 °C (decomp.) (EtOH) (lit.[56] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.93 (3H, s, 7-OMe), 7.20 (1H, s, 8-H), 7.37 (1H, t, J=7.4 Hz, 4′-H), 7.40 (1H, s, 5-H), 7.43 (2H, t, J=7.4 Hz, 3′,5′-H), 7.58 (2H, d, J=7.4 Hz, 2′,6′-H), 8.44 (1H, s, 2-H), 9.83 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 56.28 (7-OMe), 100.34 (8-C), 107.62 (5-C), 117.35 (4a-C), 122.96 (3-C), 127.65 (4′-C), 128.11 (3′,5′-C), 128.96 (2′,6′-C), 132.34 (1′-C), 145.35 (6-C), 150.84 (8a-C), 153.73 (2,7-C), 174.15 (4-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{13}O_4$ [(M+H)$^+$] 269.0814, Found 269.0823.

4′,6-Dihydroxy-7-methoxyisoflavone 8Eb 10% yield. Pale brown crystals. mp 279—280 °C (EtOH) (lit.[58] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.91 (3H, s, 7-OMe), 6.80 (2H, d, J=8.6 Hz, 3′,5′-H), 7.16 (1H, s, 8-H), 7.38 (1H, s, 5-H), 7.39 (2H, d, J=8.6 Hz, 2′,6′-H), 8.34 (1H, s, 2-H), 9.53 (1H, s, 4′-OH), 9.78 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 56.25 (7-OMe), 100.26 (8-C), 107.62 (5-C), 114.92 (3′,5′-C), 117.31 (4a-C), 122.76 (1′-C), 122.89 (3-C), 130.07 (2′,6′-C), 145.20 (6-C), 150.79 (8a-C), 152.74 (2-C), 153.59 (7-C), 157.09 (4′-C), 174.43 (4-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{13}O_5$ [(M+H)$^+$] 285.0763, Found 285.0791.

3′,4′,6-Trihydroxy-7-methoxyisoflavone 8Ec 4% yield. Pale pink crystals. mp 131—132 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.91 (3H, s, 7-OMe), 6.76 (1H, d, J=8.6 Hz, 5′-H), 6.81 (1H, d, J=8.6 Hz, 6′-H), 7.03 (1H, s, 2′-H), 7.15 (1H, s, 8-H), 7.38 (1H, s, 5-H), 8.29 (1H, s, 2-H), 8.92 (1H, s, 3′-OH), 8.97 (1H, s, 4′-OH), 9.72 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 56.21 (7-OMe), 100.20 (8-C), 107.64 (5-C), 115.23 (5′-C), 116.57 (2′-C), 117.32 (4a-C), 119.78 (6′-C), 123.02 (3-C), 123.19 (1′-C), 144.73 (3′-C), 145.14 (4′,6-C), 150.68 (8a-C), 152.61 (2-C), 153.52 (7-C), 174.35 (4-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{13}O_6$ [(M+H)$^+$] 301.0712, Found 301.0714.

4′,6-Dihydroxy-3′,7-dimethoxyisoflavone 8Ed 13% yield. Pale brown crystals. mp 246—247 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 3′-OMe), 3.92 (3H, s, 7-OMe), 6.82 (1H, d, J=8.0 Hz, 5′-H), 7.00 (1H, d, J=8.0 Hz, 6′-H), 7.17 (1H, s, 2′-H), 7.20 (1H, s, 8-H), 7.42 (1H, s, 5-H), 8.37 (1H, s, 2-H), 9.08 (1H, s, 4′-OH), 9.77 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.67 (3′-OMe), 56.28 (7-OMe), 100.32 (8-C), 107.65 (5-C), 113.23 (2′-C), 115.14 (5′-C), 117.32 (4a-C), 121.49 (6′-C), 122.88 (1′-C), 123.19 (3-C), 145.40 (6-C), 146.37 (4′-C), 147.12 (3′-C), 150.77 (8a-C), 153.57 (2-C), 153.77 (7-C), 174.01 (4-C). FAB-HR-MS m/z: Calcd for $C_{17}H_{15}O_6$ [(M+H)$^+$] 315.0869, Found 315.0879.

6-Hydroxy-4′,7-dimethoxyisoflavone 8Ee 13% yield. Pale brown crystals. mp 230—231 °C (EtOH) (lit.[44] 246—247 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 4′-OMe), 3.92 (3H, s, 7-OMe), 6.99 (2H, d, J=9.2 Hz, 3′,5′-H), 7.18 (1H, s, 8-H), 7.39 (1H, s, 5-H), 7.52 (2H, d, J=9.2 Hz, 2′,6′-H), 8.39 (1H, s, 2-H), 9.80 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.14 (4′-OMe), 56.27 (7-OMe), 100.29 (8-C), 107.61 (5-C), 113.57 (3′,5′-C), 117.31 (4a-C), 122.57 (3-C), 124.46 (1′-C), 130.07 (2′,6′-C), 145.26 (6-C), 150.82 (8a-C), 153.06 (2-C), 153.64 (7-C), 158.88 (4′-C), 174.34 (4-C). FAB-HR-MS m/z: Calcd for $C_{17}H_{15}O_5$ [(M+H)$^+$] 299.0919, Found 299.0930.

6-Hydroxy-3′,4′,7-trimethoxyisoflavone 8Ef 8% yield. Pale violet crystals. mp 249—250 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (6H, s, 3′,4′-OMe), 3.93 (3H, s, 7-OMe), 7.00 (1H, d, J=8.6 Hz, 5′-H), 7.14 (1H, d, J=8.6 Hz, 6′-H), 7.18 (1H, s, 8-H), 7.20 (1H, s, 2′-H), 7.40 (1H, s, 5-H), 8.42 (1H, s, 2-H), 9.81 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.52, (3′,4′-OMe), 56.25 (7-OMe), 100.26 (8-C), 107.64 (5-C), 111.47 (5′-C), 112.72 (2′-C), 117.33 (4a-C), 121.21 (6′-C), 122.65 (3-C), 124.76 (1′-C), 145.26 (6-C), 148.24 (3′-C), 148.49 (4′-C), 150.75 (8a-C), 153.24 (2-C), 153.63 (7-C), 174.32 (4-C). FAB-HR-MS m/z: (M+H)$^+$ Calcd for $C_{18}H_{17}O_6$ 329.1025, Found 329.1035.

6-Hydroxy-7-methylisoflavone 8Fa 7% yield. Pale brown crystals. mp 230—231 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.29 (3H, s, 7-Me), 7.37 (1H, t, J=7.4 Hz, 4′-H), 7.43 (2H, t, J=7.4 Hz, 3′,5′-H), 7.44 (1H, s, 5-H), 7.47 (1H, s, 8-H), 7.58 (2H, d, J=7.4 Hz, 2′,6′-H), 8.44 (1H, s, 2-H), 10.05 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.46 (7-Me), 106.89 (5-C), 119.43 (8-C), 122.71 (4a-C), 122.74 (3-C), 127.61 (4′-C), 128.07 (3′,5′-C), 128.90 (2′,6′-C), 132.29 (1′-C), 133.73 (6-C), 149.33 (8a-C), 153.45 (7-C), 153.96 (2-C), 174.71 (4-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{13}O_3$ [(M+H)$^+$] 253.0865, Found 253.0863.

4′,6-Dihydroxy-7-methylisoflavone 8Fb 19% yield. Pale brown crystals. mp >320 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.28 (3H, s, 7-Me), 6.81 (2H, d, J=8.6 Hz, 3′,5′-H), 7.39 (2H, d, J=8.6 Hz, 2′,6′-H), 7.43 (1H, s, 5-H), 7.43 (1H, s, 8-H), 8.33 (1H, s, 2-H), 9.52 (1H, s, 4′-OH), 10.01 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.46 (7-Me), 106.88 (5-C), 114.92 (3′,5′-C), 119.35 (8-C), 122.66 (3-C), 122.69 (1′,4a-C), 130.03 (2′,6′-C), 133.51 (6-C), 149.31 (8a-C), 153.31 (2-C), 157.08 (4′,7-C), 174.97 (4-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{13}O_4$ [(M+H)$^+$] 269.0814, Found 269.0784.

3′,4′,6-Trihydroxy-7-methylisoflavone 8Fc 10% yield. A pale brown amorphous solid. ^{1}H-NMR (DMSO-d_6) δ: 2.28 (3H, s, 7-Me), 6.76 (1H, d, J=8.0 Hz, 5′-H), 6.81 (1H, d, J=8.0 Hz, 6′-H), 7.03 (1H, s, 2′-H), 7.42 (1H,

s, 8-H), 7.43 (1H, s, 5-H), 8.29 (1H, s, 2-H), 8.81 (1H, s, 3′-OH), 8.94 (1H, s, 4′-OH), 10.00 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.45 (7-Me), 106.88 (5-C), 113.15 (5′-C), 116.57 (2′-C), 119.35 (8-C), 119.80 (6′-C), 122.43 (3-C), 122.69 (4a-C), 122.85 (1′-C), 133.47 (6-C), 144.76 (3′-C), 145.17 (4′-C), 149.26 (8a-C), 152.93 (2-C), 153.29 (7-C), 174.94 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{13}O_5$ [(M+H)$^+$] 285.0763, Found 285.0755.

4′,6-Dihydroxy-3′-methoxy-7-methylisoflavone 8Fd 21% yield. Colorless crystals. mp 250—252 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.28 (3H, s, 7-Me), 3.80 (3H, s, 3′-OMe), 6.81 (1H, d, J=8.0 Hz, 5′-H), 7.00 (1H, d, J=8.0 Hz, 6′-H), 7.17 (1H, s, 2′-H), 7.43 (1H, s, 5-H), 7.44 (1H, s, 8-H), 8.37 (1H, s, 2-H), 10.01 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.45 (7-Me), 55.66 (3′-OMe), 106.88 (5-C), 113.22 (2′-C), 115.15 (5′-C), 119.35 (8-C), 121.52 (6′-C), 122.67 (1′-C), 122.71 (4a-C), 123.16 (3-C), 133.52 (6-C), 146.36 (4′-C), 147.13 (3′-C), 149.25 (8a-C), 153.21 (2-C), 153.31 (7-C), 174.93 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_5$ [(M+H)$^+$] 299.0919, Found 299.0915.

6-Hydroxy-4′-methoxy-7-methylisoflavone 8Fe 20% yield. Colorless crystals. mp 262—265 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.28 (3H, s, 7-Me), 3.79 (3H, s, 4′-OMe), 6.99 (2H, d, J=8.6 Hz, 3′,5′-H), 7.43 (1H, s, 5-H), 7.45 (1H, s, 8-H), 7.52 (2H, d, J=8.6 Hz, 2′,6′-H), 8.39 (1H, s, 2-H), 10.03 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.44 (7-Me), 55.10 (4′-OMe), 106.86 (5-C), 113.55 (3′,5′-C), 119.38 (8-C), 122.35 (3-C), 122.65 (4a-C), 124.40 (1′-C), 130.02 (2′,6′-C), 133.59 (6-C), 149.31 (8a-C), 153.29 (2-C), 153.35 (7-C), 158.85 (4′-C), 174.88 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_4$ [(M+H)$^+$] 283.0970, Found 283.0954.

6-Hydroxy-7,8-dimethylisoflavone 8Ga 11% yield. Pale brown crystals. mp 237 °C (decomp.) (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.24 (3H, s, 7-Me), 2.38 (3H, s, 8-Me), 7.37 (1H, s, 5-H), 7.37 (1H, t, J=7.4 Hz, 4′-H), 7.43 (2H, t, J=7.4 Hz, 3′,5′-H), 7.59 (2H, d, J=7.4 Hz, 2′,6′-H), 8.50 (1H, s, 2-H), 9.93 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 11.67 (8-Me), 12.56 (7-Me), 104.57 (5-C), 122.15 (4a-C), 122.42 (3-C), 126.56 (8-C), 127.59 (4′-C), 128.08 (3′,5′-C), 128.88 (2′,6′-C), 131.59 (7-C), 132.34 (1′-C), 147.92 (8a-C), 152.82 (6-C), 153.88 (2-C), 175.01 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_3$ [(M+H)$^+$] 267.1021, Found 267.1015.

4′,6-Dihydroxy-7,8-dimethylisoflavone 8Gb 9% yield. Pale brown crystals. mp 259—261 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.23 (3H, s, 7-Me), 2.37 (3H, s, 8-Me), 6.81 (2H, d, J=8.6 Hz, 3′,5′-H), 7.35 (1H, s, 5-H), 7.40 (2H, d, J=8.6 Hz, 2′,6′-H), 8.39 (1H, s, 2-H), 9.50 (1H, s, 4′-OH), 9.89 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 11.66 (8-Me), 12.53 (7-Me), 104.53 (5-C), 114.91 (3′,5′-C), 122.08 (4a-C), 122.36 (3-C), 122.75 (1′-C), 126.45 (8-C), 130.00 (2′,6′-C), 131.36 (7-C), 147.89 (8a-C), 152.68 (6-C), 152.91 (2-C), 157.05 (4′-C), 175.27 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_4$ [(M+H)$^+$] 283.0970, Found 283.0971.

3′,4′,6-Trihydroxy-7,8-dimethylisoflavone 8Gc 19% yield. Pale gray crystals. mp 270—273 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.23 (3H, s, 7-Me), 2.37 (3H, s, 8-Me), 6.77 (1H, d, J=8.0 Hz, 5′-H), 6.82 (1H, d, J=8.0 Hz, 6′-H), 7.04 (1H, s, 2′-H), 7.35 (1H, s, 5-H), 8.35 (1H, s, 2-H), 8.97 (2H, s, 3′,4′-OH), 9.88 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 11.66 (8-Me), 12.54 (7-Me), 104.55 (5-C), 115.27 (5′-C), 116.57 (2′-C), 119.76 (6′-C), 122.11 (4a-C), 122.52 (3-C), 123.22 (1′-C), 126.43 (8-C), 131.32 (7-C), 144.74 (3′-C), 145.15 (4′-C), 147.84 (8a-C), 152.66 (6-C), 152.85 (2-C), 175.23 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_5$ [(M+H)$^+$] 299.0919, Found 299.0930.

6-Hydroxy-4′-methoxy-7,8-dimethylisoflavone 8Ge 18% yield. Pale brown crystals. mp 255—257 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.23 (3H, s, 7-Me), 2.37 (3H, s, 8-Me), 3.79 (3H, s, 4′-OMe), 6.99 (2H, d, J=8.6 Hz, 3′,5′-H), 7.36 (1H, s, 5-H), 7.53 (2H, d, J=8.6 Hz, 2′,6′-H), 8.44 (1H, s, 2-H), 9.91 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 11.66 (8-Me), 12.54 (7-Me), 55.10 (4′-OMe), 104.53 (5-C), 113.56 (3′,5′-C), 122.03 (4a-C), 122.08 (3-C), 124.46 (1′-C), 126.49 (8-C), 130.00 (2′,6′-C), 131.46 (7-C), 147.91 (8a-C), 152.74 (6-C), 153.23 (2-C), 158.84 (4′-C), 175.19 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{18}H_{17}O_4$ [(M+H)$^+$] 297.1127, Found 297.1122. *Anal.* Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found C, 72.46; H, 5.41.

8-Hydroxy-7-methoxyisoflavone 8Ha 24% yield. Pale pink crystals. mp 203—204 °C (EtOH) (lit.[59] 203—205 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.95 (3H, s, 7-OMe), 7.23 (1H, d, J=9.2 Hz, 6-H), 7.38 (1H, t, J=7.4 Hz, 4′-H), 7.44 (2H, t, J=7.4 Hz, 3′,5′-H), 7.59 (2H, d, J=7.4 Hz, 2′,6′-H), 7.61 (1H, d, J=9.2 Hz, 5-H), 8.48 (1H, s, 2-H), 9.71 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 56.38 (7-OMe), 110.24 (6-C), 115.33 (5-C), 118.54 (4a-C), 122.97 (3-C), 127.67 (4′-C), 128.08 (3′,5′-C), 128.96 (2′,6′-C), 132.11 (1′-C), 134.49 (8-C), 145.78 (8a-C), 151.22 (7-C), 154.08 (2-C), 174.94 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{13}O_4$ [(M+H)$^+$] 269.0814, Found 269.0812.

3′,4′,8-Trihydroxy-7-methoxyisoflavone 8Hc 3% yield. Pale pink crystals. mp 270—272 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.93 (3H, s, 7-OMe), 6.77 (1H, d, J=8.0 Hz, 5′-H), 6.82 (1H, d, J=8.0 Hz, 6′-H), 7.03 (1H, s, 2′-H), 7.20 (1H, d, J=8.6 Hz, 6-H), 7.58 (1H, d, J=8.6 Hz, 5-H), 8.33 (1H, s, 2-H), 8.95 (1H, s, 3′-OH), 8.98 (1H, s, 4′-OH), 9.64 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 56.36 (7-OMe), 110.10 (6-C), 115.25 (5′-C), 115.29 (5-C), 116.61 (2′-C), 118.56 (4a-C), 119.86 (6′-C), 122.96 (3-C), 123.06 (1′-C), 134.41 (8-C), 144.75 (3′-C), 145.22 (4′-C), 145.72 (8a-C), 151.01 (7-C), 153.02 (2-C), 175.17 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{13}O_6$ [(M+H)$^+$] 301.0712, Found 301.0702.

4′,8-Dihydroxy-3′,7-dimethoxyisoflavone 8Hd 10% yield. Pale green crystals. mp 108—109 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.80 (3H, s, 3′-OMe), 3.94 (3H, s, 7-OMe), 6.82 (1H, d, J=8.0 Hz, 5′-H), 7.00 (1H, d, J=8.0 Hz, 6′-H), 7.18 (1H, s, 2′-H), 7.24 (1H, d, J=9.2 Hz, 6-H), 7.59 (1H, d, J=9.2 Hz, 5-H), 8.55 (1H, s, 2-H), 9.08 (1H, s, 4′-OH), 9.73 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.90 (3′-OMe), 56.39 (7-OMe), 110.30 (6-C), 113.76 (2′-C), 115.29 (5′-C), 115.35 (5-C), 118.45 (4a-C), 121.33 (6′-C), 122.16 (3-C), 122.23 (1′-C), 134.50 (8-C), 145.71 (8a-C), 146.42 (4′-C), 147.11 (3′-C), 151.27 (7-C), 154.42 (2-C), 174.83 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_6$ [(M+H)$^+$] 315.0869, Found 315.0886.

8-Hydroxy-4′,7-dimethoxyisoflavone 8He 17% yield. Pale yellow crystals. mp 180—181 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 4′-OMe), 3.94 (3H, s, 7-OMe), 7.00 (2H, d, J=9.2 Hz, 3′,5′-H), 7.22 (1H, d, J=9.2 Hz, 6-H), 7.53 (2H, d, J=9.2 Hz, 2′,6′-H), 7.60 (1H, d, J=9.2 Hz, 5-H), 8.43 (1H, s, 2-H), 9.70 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.14 (4′-OMe), 56.38 (7-OMe), 110.18 (6-C), 113.59 (3′,5′-C), 115.32 (5-C), 118.52 (4a-C), 122.60 (3-C), 124.24 (1′-C), 130.12 (2′,6′-C), 134.45 (8-C), 145.78 (8a-C), 151.12 (7-C), 153.45 (2-C), 158.94 (4′-C), 175.16 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_5$ [(M+H)$^+$] 299.0919, Found 299.0939.

8-Hydroxy-7-methylisoflavone 8Ia 5% yield. Pale pink crystals. mp 209 °C (decomp.) (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.33 (3H, s, 7-Me), 7.25 (1H, d, J=8.0 Hz, 6-H), 7.39 (1H, t, J=7.4 Hz, 4′-H), 7.45 (2H, t, J=7.4 Hz, 3′,5′-H), 7.51 (1H, d, J=8.0 Hz, 5-H), 7.60 (2H, d, J=7.4 Hz, 2′,6′-H), 8.50 (1H, s, 2-H), 9.91 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.29 (7-Me), 114.59 (5-C), 122.93 (4a-C), 123.48 (3-C), 127.31 (6-C), 127.77 (4′-C), 128.10 (3′,5′-C), 129.01 (2′,6′-C), 130.01 (8-C), 131.98 (1′-C), 143.82 (7-C), 145.62 (8a-C), 153.68 (2-C), 175.25 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{13}O_3$ [(M+H)$^+$] 253.0865, Found 253.0853. *Anal.* Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.31; H, 4.73.

4′,8-Dihydroxy-7-methylisoflavone 8Ib 7% yield. Colorless crystals. mp 258—260 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.32 (3H, s, 7-Me), 6.82 (2H, d, J=8.6 Hz, 3′,5′-H), 7.23 (1H, d, J=8.0 Hz, 6-H), 7.42 (2H, d, J=8.6 Hz, 2′,6′-H), 7.49 (1H, d, J=8.0 Hz, 5-H), 8.40 (1H, s, 2-H), 9.55 (1H, s, 4′-OH), 9.88 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.29 (7-Me), 114.58 (5-C), 114.95 (3′,5′-C), 122.39 (1′-C), 122.89 (4a-C), 123.43 (3-C), 127.16 (6-C), 129.73 (8-C), 130.15 (2′,6′-C), 143.78 (7-C), 145.61 (8a-C), 152.69 (2-C), 157.22 (4′-C), 175.52 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{13}O_4$ [(M+H)$^+$] 269.0814, Found 269.0821.

3′,4′,8-Trihydroxy-7-methylisoflavone 8Ic 1% yield. Pale violet crystals. mp 189—190 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.31 (3H, s, 7-Me), 6.77 (1H, d, J=8.0 Hz, 5′-H), 6.84 (1H, d, J=8.0 Hz, 6′-H), 7.04 (1H, s, 2′-H), 7.22 (1H, d, J=8.6 Hz, 6-H), 7.48 (1H, d, J=8.6 Hz, 5-H), 8.35 (1H, s, 2-H), 8.98 (2H, s, 3′,4′-OH), 9.84 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.27 (7-Me), 114.59 (5-C), 115.27 (5′-C), 116.63 (2′-C), 119.90 (6′-C), 122.83 (4a-C), 122.91 (1′-C), 123.56 (3-C), 127.10 (6-C), 129.67 (8-C), 143.75 (7-C), 144.77 (3′-C), 145.31 (4′-C), 145.56 (8a-C), 152.60 (2-C), 175.47 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{13}O_5$ [(M+H)$^+$] 285.0763, Found 285.0745.

4′,8-Dihydroxy-3′-methoxy-7-methylisoflavone 8Id 2% yield. A pale violet amorphous solid. ^{1}H-NMR (DMSO-d_6) δ: 2.32 (3H, s, 7-Me), 3.80 (3H, s, 3′-OMe), 6.83 (1H, d, J=8.0 Hz, 5′-H), 7.02 (1H, d, J=8.0 Hz, 6′-H), 7.20 (1H, s, 2′-H), 7.23 (1H, d, J=7.4 Hz, 6-H), 7.49 (1H, d, J=7.4 Hz, 5-H), 8.44 (1H, s, 2-H), 9.10 (1H, s, 4′-OH), 9.86 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.08 (7-Me), 55.48 (3′-OMe), 113.13 (2′-C), 114.39 (5-C), 114.97 (5′-C), 121.40 (6′-C), 122.63 (1′-C), 122.71 (4a-C), 123.24 (3-C), 126.96 (6-C), 129.53 (8-C), 143.57 (7-C), 145.36 (8a-C), 146.32 (4′-C), 146.95 (3′-C), 152.72 (2-C), 175.28 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_5$ [(M+H)$^+$] 299.0919, Found 299.0911.

8-Hydroxy-4′-methoxy-7-methylisoflavone 8Ie 7% yield. Pale pink crystals. mp 228—229 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.32 (3H, s, 7-Me), 3.80 (3H, s, 4′-OMe), 7.01 (2H, d, J=8.6 Hz, 3′,5′-H), 7.24 (1H, d, J=8.0 Hz, 6-H), 7.50 (1H, d, J=8.0 Hz, 5-H), 7.54 (2H, d, J=8.6 Hz, 2′,6′-H), 8.45 (1H, s, 2-H), 9.90 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 16.31

(7-Me), 55.15 (4′-OMe), 113.60 (3′,5′-C), 114.59 (5-C), 122.89 (4a-C), 123.10 (3-C), 124.10 (1′-C), 127.22 (6-C), 129.84 (8-C), 130.16 (2′,6′-C), 143.81 (7-C), 145.62 (8a-C), 153.04 (2-C), 159.00 (4′-C), 175.46 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_4$ [(M+H)$^+$] 283.0970, Found 283.0987.

7-Hydroxy-6-methoxyisoflavone 8Ja 13% yield. Pale green crystals. mp 190 °C (decomp.) (EtOH) (lit.[56] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.89 (3H, s, 6-OMe), 6.98 (1H, s, 8-H), 7.38 (1H, t, J=7.4 Hz, 4′-H), 7.44 (2H, t, J=7.4 Hz, 3′,5′-H), 7.45 (1H, s, 5-H), 7.57 (2H, d, J=7.4 Hz, 2′,6′-H), 8.40 (1H, s, 2-H), 10.67 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.85 (6-OMe), 102.89 (8-C), 104.69 (5-C), 116.27 (4a-C), 123.03 (3-C), 127.68 (4′-C), 128.14 (3′,5′-C), 128.95 (2′,6′-C), 132.37 (1′-C), 147.04 (6-C), 151.77 (8a-C), 153.01 (7-C), 153.53 (2-C), 174.05 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{13}O_4$ [(M+H)$^+$] 269.0814, Found 269.0799.

4′,7-Dihydroxy-6-methoxyisoflavone 8Jb (Glycitein 3) 21% yield. Pale green crystals. mp 268 °C (decomp.) (EtOH) [lit.[47] 337 °C (decomp.) (EtOH)]. ^{1}H-NMR (DMSO-d_6) δ: 3.88 (3H, s, 6-OMe), 6.81 (2H, d, J=8.6 Hz, 3′,5′-H), 6.95 (1H, s, 8-H), 7.39 (2H, d, J=8.6 Hz, 2′,6′-H), 7.43 (1H, s, 5-H), 8.29 (1H, s, 2-H), 9.55 (1H, s, 4′-OH), 10.62 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.83 (6-OMe), 102.83 (8-C), 104.68 (5-C), 114.96 (3′,5′-C), 116.25 (4a-C), 122.79 (3-C), 122.97 (1′-C), 130.09 (2′,6′-C), 146.92 (6-C), 151.73 (8a-C), 152.55 (7-C), 152.84 (2-C), 157.13 (4′-C), 174.34 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{13}O_5$ [(M+H)$^+$] 285.0763, Found 285.0736.

4′,7-Dihydroxy-3′,6-dimethoxyisoflavone 8Jd 3% yield. Pale violet crystals. mp 216—217 °C (EtOH) (lit.[60] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 3′-OMe), 3.88 (3H, s, 6-OMe), 6.81 (1H, d, J=8.0 Hz, 5′-H), 6.95 (1H, s, 8-H), 6.99 (1H, d, J=8.0 Hz, 6′-H), 7.18 (1H, s, 2′-H), 7.45 (1H, s, 5-H), 8.33 (1H, s, 2-H), 9.07 (1H, s, 4′-OH), 10.58 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.61 (3′-OMe), 55.78 (6-OMe), 102.79 (8-C), 104.73 (5-C), 113.23 (2′-C), 115.15 (5′-C), 116.24 (4a-C), 121.41 (6′-C), 122.93 (1′-C), 123.19 (3-C), 146.36 (4′-C), 146.89 (6-C), 147.10 (3′-C), 151.62 (8a-C), 152.69 (7-C), 152.81 (2-C), 174.26 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_6$ [(M+H)$^+$] 315.0869, Found 315.0879.

7-Hydroxy-4′,6-dimethoxyisoflavone 8Je 30% yield. Pale green crystals. mp 220—221 °C (EtOH) [lit.[61] 228—229 °C (MeOH)]. ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 4′-OMe), 3.88 (3H, s, 6-OMe), 6.96 (1H, s, 8-H), 6.99 (2H, d, J=8.6 Hz, 3′,5′-H), 7.44 (1H, s, 5-H), 7.52 (2H, d, J=8.6 Hz, 2′,6′-H), 8.34 (1H, s, 2-H), 10.63 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.15 (4′-OMe), 55.83 (6-OMe), 102.85 (8-C), 104.68 (5-C), 113.61 (3′,5′-C), 116.24 (4a-C), 122.63 (3-C), 124.48 (1′-C), 130.08 (2′,6′-C), 146.96 (6-C), 151.74 (8a-C), 152.86 (7-C), 152.91 (2-C), 158.90 (4′-C), 174.25 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_5$ [(M+H)$^+$] 299.0919, Found 299.0915.

6,7-Dimethoxyisoflavone 8Ka 22% yield. Pale brown crystals. mp 155—156 °C (EtOH) (lit.[56] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.88 (3H, s, 7-OMe), 3.93 (3H, s, 6-OMe), 7.25 (1H, s, 8-H), 7.38 (1H, t, J=7.4 Hz, 4′-H), 7.44 (2H, t, J=7.4 Hz, 3′,5′-H), 7.45 (1H, s, 5-H), 7.60 (2H, d, J=7.4 Hz, 2′,6′-H), 8.48 (1H, s, 2-H). ^{13}C-NMR (DMSO-d_6) δ: 55.78 (6-OMe), 56.43 (7-OMe), 100.38 (8-C), 104.06 (5-C), 116.97 (4a-C), 123.25 (3-C), 127.75 (4′-C), 128.17 (3′,5′-C), 128.95 (2′,6′-C), 132.23 (1′-C), 147.48 (6-C), 151.76 (8a-C), 153.84 (2-C), 154.31 (7-C), 174.08 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_4$ [(M+H)$^+$] 283.0970, Found 283.0987.

4′-Hydroxy-6,7-dimethoxyisoflavone 8Kb 17% yield. Pale pink crystals. mp 207—209 °C (EtOH) (lit.[58] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 3.87 (3H, s, 7-OMe), 3.92 (3H, s, 6-OMe), 6.82 (2H, d, J=8.6 Hz, 3′,5′-H), 7.21 (1H, s, 8-H), 7.41 (2H, d, J=8.6 Hz, 2′,6′-H), 7.43 (1H, s, 5-H), 8.37 (1H, s, 2-H), 9.56 (1H, s, 4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.75 (6-OMe), 56.37 (7-OMe), 100.29 (8-C), 104.03 (5-C), 114.96 (3′,5′-C), 116.92 (4a-C), 122.63 (1′-C), 123.17 (3-C), 130.07 (2′,6′-C), 147.35 (6-C), 151.69 (8a-C), 152.82 (2-C), 154.16 (7-C), 157.17 (4′-C), 174.34 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_5$ [(M+H)$^+$] 299.0919, Found 299.0920.

3′,4′-Dihydroxy-6,7-dimethoxyisoflavone 8Kc 12% yield. Pale brown crystals. mp 248—250 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.87 (3H, s, 7-OMe), 3.92 (3H, s, 6-OMe), 6.77 (1H, d, J=8.0 Hz, 5′-H), 6.83 (1H, d, J=8.0 Hz, 6′-H), 7.04 (1H, s, 2′-H), 7.21 (1H, s, 8-H), 7.43 (1H, s, 5-H), 8.34 (1H, s, 2-H), 8.99 (2H, s, 3′,4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.76 (6-OMe), 56.38 (7-OMe), 100.29 (8-C), 104.06 (5-C), 115.30 (5′-C), 116.60 (2′-C), 116.95 (4a-C), 119.87 (6′-C), 123.10 (1′-C), 123.35 (3-C), 144.79 (3′-C), 145.26 (4′-C), 147.35 (6-C), 151.64 (8a-C), 152.78 (2-C), 154.14 (7-C), 174.31 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{15}O_6$ [(M+H)$^+$] 315.0869, Found 315.0867.

4′-Hydroxy-3′,6,7-trimethoxyisoflavone 8Kd 17% yield. Pale yellow crystals. mp 238—240 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 3.80 (3H, s, 3′-OMe), 3.87 (3H, s, 7-OMe), 3.92 (3H, s, 6-OMe), 6.82 (1H, d, J=8.0 Hz, 5′-H), 7.02 (1H, d, J=8.0 Hz, 6′-H), 7.20 (1H, s, 2′-H), 7.26 (1H, s, 8-H), 7.45 (1H, s, 5-H), 9.10 (1H, s, 4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 55.61 (3′-OMe), 55.77 (6-OMe), 56.35 (7-OMe), 100.36 (8-C), 104.10 (5-C), 113.17 (2′-C), 115.17 (5′-C), 116.90 (4a-C), 121.41 (6′-C), 122.20 (3-C), 123.14 (1′-C), 146.42 (4′-C), 147.12 (3′-C), 147.52 (6-C), 151.61 (8a-C), 154.16 (2-C), 154.35 (7-C), 174.28 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{18}H_{17}O_6$ [(M+H)$^+$] 329.1025, Found 329.1035.

4′,6,7-Trimethoxyisoflavone 8Ke 37% yield. Pale brown crystals. mp 170—171 °C (EtOH) (lit.[62] 178—179 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 4′-OMe), 3.87 (3H, s, 7-OMe), 3.93 (3H, s, 6-OMe), 7.00 (2H, d, J=9.2 Hz, 3′,5′-H), 7.23 (1H, s, 8-H), 7.44 (1H, s, 5-H), 7.54 (2H, d, J=9.2 Hz, 2′,6′-H), 8.43 (1H, s, 2-H). ^{13}C-NMR (DMSO-d_6) δ: 55.15 (4′-OMe), 55.76 (6-OMe), 56.40 (7-OMe), 100.33 (8-C), 104.03 (5-C), 113.63 (3′,5′-C), 116.92 (4a-C), 122.84 (3-C), 124.32 (1′-C), 130.06 (2′,6′-C), 147.41 (6-C), 151.73 (8a-C), 153.16 (2-C), 154.22 (7-C), 158.95 (4′-C), 174.26 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{18}H_{17}O_5$ [(M+H)$^+$] 313.1076, Found 313.1066.

3′,4′,6,7-Tetramethoxyisoflavone 8Kf 18% yield. Pale yellow crystals. mp 171—172 °C (EtOH) [lit.[63] 187—188 °C (MeOH)]. ^{1}H-NMR (DMSO-d_6) δ: 3.79 (6H, s, 3′,4′-OMe), 3.87 (3H, s, 7-OMe), 3.93 (3H, s, 6-OMe), 7.01 (1H, d, J=8.0 Hz, 5′-H), 7.16 (1H, d, J=8.0 Hz, 6′-H), 7.23 (1H, s, 2′-H), 7.23 (1H, s, 8-H), 7.46 (1H, s, 5-H), 8.47 (1H, s, 2-H). ^{13}C-NMR (DMSO-d_6) δ: 55.48 (3′-OMe), 55.53 (4′-OMe), 55.75 (6-OMe), 56.39 (7-OMe), 100.31 (8-C), 104.08 (5-C), 111.52 (5′-C), 112.69 (2′-C), 116.94 (4a-C), 121.15 (6′-C), 122.90 (3-C), 124.60 (1′-C),147.42 (6-C), 148.26 (3′-C), 148.56 (4′-C), 151.66 (8a-C), 153.34 (2-C) 154.22 (7-C), 174.24 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{19}H_{19}O_6$ [(M+H)$^+$] 343.1182, Found 343.1187.

Typical Procedure for the Stepwise Synthesis of the Isoflavones 8 from the Phenols 11 and the Phenylacetic Acids 12 To a mixture of **11C** (0.49 g, 3.9 mmol) and **12a** (0.50 g, 3.7 mmol) was added $BF_3 \cdot Et_2O$ (1.10 ml). The reaction mixture was heated at 120 °C for 10 min. The mixture was cooled to room temperature, and cold water (22 ml) was added. The product was extracted with Et_2O (3×25 ml). A combined Et_2O layer was successively washed with brine (3×50 ml) and saturated $NaHCO_3$ (3×50 ml), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. To the residue was added dry DMF (4.9 ml), and the reaction mixture was stirred at 50 °C for 10 min. $MeSO_2Cl$ (2.9 g) was added and the reaction mixture was stirred at 80 °C for 30 min. The mixture was cooled to room temperature, and cold water (120 ml) was added. The product was extracted with Et_2O (3×60 ml). A combined Et_2O layer was successively washed with brine (3×50 ml) and saturated $NaHCO_3$ (3×50 ml), dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was subjected to gel filtration chromatography using Sephadex LH-20 (eluent, MeOH–H_2O) to give the product **8Ca**, which was recrystallized from EtOH to give pure **8Ca** (0.03 g, 0.13 mmol, 4% yield).

6,7-Dihydroxyisoflavone 8Ca 4% yield. Pale violet crystals. mp 285 °C (decomp.) (EtOH) [lit.[44] 253—277 °C (decomp.)]. ^{1}H-NMR (DMSO-d_6) δ: 6.92 (1H, s, 8-H), 7.36 (1H, t, J=7.4 Hz, 4′-H), 7.39 (1H, s, 5-H), 7.42 (2H, t, J=7.4 Hz, 3′,5′-H), 7.56 (2H, d, J=7.4 Hz, 2′,6′-H), 8.35 (1H, s, 2-H), 9.84 (1H, s, 6-OH), 10.46 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 102.81 (8-C), 108.07 (5-C), 116.59 (4a-C), 122.77 (3-C), 127.58 (4′-C), 128.08 (3′,5′-C), 128.96 (2′,6′-C), 132.49 (1′-C), 144.77 (6-C), 150.88 (8a-C), 152.40 (7-C), 153.39 (2-C) 174.10 (4-C). FAB-HR-MS *m/z*: Calcd for $C_{15}H_{11}O_4$ [(M+H)$^+$] 255.0657, Found 255.0647.

4′,6,7-Trihydroxyisoflavone 8Cb (6-Hydroxydaidzein 6) 8% yield. Pale violet crystals. mp 280 °C (decomp.) (EtOH) [lit.[64] 322 °C (decomp.)]. The ^{1}H- and ^{13}C-NMR data of this product are in good agreement with those reported in the literature.[54] FAB-HR-MS *m/z*: Calcd for $C_{15}H_{11}O_5$ [(M+H)$^+$] 271.0606, Found 271.0587.

6,7-Dihydroxy-4′-methoxyisoflavone 8Ce 8% yield. Pale violet crystals. mp 283—284 °C (EtOH) (lit.[44] 278—280 °C). The ^{1}H- and ^{13}C-NMR data of this product are in good agreement with those reported in the literature.[54] FAB-HR-MS *m/z*: Calcd for $C_{16}H_{13}O_5$ [(M+H)$^+$] 285.0763, Found 285.0782.

Typical Procedure for the Synthesis of the Isoflavanes 9 from the Isoflavones 8 To a solution of **8Aa** (0.05 g, 0.16 mmol) in AcOH–EtOH (1 : 9, 10 ml) was added 5% Pd/C (containing about 50% water, 2.5 mg). The reaction mixture was stirred at room temperature for 10 h under a hydrogen atmosphere. The mixture was filtrated, and the filtrate was concentrated *in vacuo*. The residue was subjected to reversed-phase liquid chromatography with an ODS column (eluent, CH_3CN–H_2O) to give the product **9Aa**, which

was recrystallized from EtOH to give pure **9Aa** (0.02 g, 0.09 mmol, 59% yield).

7-Hydroxyisoflavone 9Aa 59% yield. Colorless crystals. mp 117—118 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.83 (1H, ddd, J=15.5, 5.2, 1.7 Hz, 4-H), 2.91 (1H, dd, J=15.5, 10.3 Hz, 4-H), 3.11—3.17 (1H, m, 3-H), 4.00 (1H, t, J=10.3 Hz, 2-H), 4.21 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.20 (1H, s, 8-H), 6.30 (1H, d, J=8.0 Hz, 6-H), 6.88 (1H, d, J=8.0 Hz, 5-H), 7.24—7.27 (1H, m, 4′-H), 7.32—7.34 (4H, m, 2′,3′,5′,6′-H), 9.19 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.07 (4-C), 37.95 (3-C), 69.86 (2-C), 102.49 (8-C), 108.06 (6-C), 112.38 (4a-C), 126.77 (4′-C), 127.48 (3′,5′-C), 128.51 (2′,6′-C), 130.09 (5-C), 141.67 (1′-C), 154.49 (8a-C), 156.54 (7-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{14}O_2$ (M^+) 226.0994, Found 226.0981.

4′,7-Dihydroxyisoflavane 9Ab (Equol 4) 95% yield. Colorless crystals. mp 181—182 °C (EtOH) (lit.[23] 155—157 °C). ^{1}H-NMR (DMSO-d_6) δ: 2.76 (1H, ddd, J=15.5, 5.2, 1.7 Hz, 4-H), 2.83 (1H, dd, J=15.5, 10.3 Hz, 4-H), 3.01 (1H, tt, J=10.3, 5.2 Hz, 3-H), 3.89 (1H, t, J=10.3 Hz, 2-H), 4.14 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.19 (1H, s, 8-H), 6.28 (1H, d, J=8.6 Hz, 6-H), 6.72 (2H, d, J=8.6 Hz, 3′,5′-H), 6.87 (1H, d, J=8.6 Hz, 5-H), 7.10 (2H, d, J=8.6 Hz, 2′,6′-H), 9.25 (2H, s, 4′,7-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.30 (4-C), 37.16 (3-C), 70.25 (2-C), 102.47 (8-C), 107.96 (6-C), 112.57 (4a-C), 115.24 (3′,5′-C), 128.34 (2′,6′-C), 130.08 (5-C), 131.65 (1′-C), 154.50 (8a-C), 156.15 (7-C), 156.49 (4′-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{14}O_3$ (M^+) 242.0943, Found 242.0929.

3′,4′,7-Trihydroxyisoflavane 9Ac 85% yield. Pale orange crystals. mp 139—140 °C (EtOH) (lit.[14] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 2.72—2.81 (2H, m, 4-H), 2.90—2.96 (1H, m, 3-H), 3.86 (1H, t, J=10.3 Hz, 2-H), 4.13 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.18 (1H, s, 8-H), 6.28 (1H, d, J=8.6 Hz, 6-H), 6.55 (1H, d, J=8.0 Hz, 6′-H), 6.66 (1H, s, 2′-H), 6.67 (1H, d, J=8.0 Hz, 5′-H), 6.86 (1H, d, J=8.6 Hz, 5-H), 8.80 (2H, s, 3′,4′-OH), 9.16 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.32 (4-C), 37.28 (3-C), 70.33 (2-C), 102.45 (8-C), 107.94 (6-C), 112.57 (4a-C), 114.82 (2′-C), 115.56 (5′-C), 117.94 (6′-C), 130.09 (5-C), 132.35 (1′-C), 144.03 (3′-C), 145.20 (4′-C), 154.49 (8a-C), 156.47 (7-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{14}O_4$ (M^+) 258.0892, Found 258.0891.

7-Hydroxy-4′-methoxyisoflavane 9Ae 58% yield. Colorless crystals. mp 153—154 °C (EtOH) (lit.[41] 148—150 °C). ^{1}H-NMR (DMSO-d_6) δ: 2.79 (1H, ddd, J=15.5, 5.2, 1.7 Hz, 4-H), 2.87 (1H, dd, J=15.5, 10.3 Hz, 4-H), 3.08 (1H, tt, J=10.3, 5.2 Hz, 3-H), 3.73 (3H, s, 4′-OMe), 3.94 (1H, t, J=10.3 Hz, 2-H), 4.16 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.19 (1H, s, 8-H), 6.29 (1H, d, J=8.6 Hz, 6-H), 6.86 (1H, d, J=8.6 Hz, 5-H), 6.89 (2H, d, J=8.6 Hz, 3′,5′-H), 7.24 (2H, d, J=8.6 Hz, 2′,6′-H), 9.17 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.22 (4-C), 37.10 (3-C), 55.04 (4′-OMe), 70.10 (2-C), 102.47 (8-C), 108.00 (6-C), 112.46 (4a-C), 113.92 (3′,5′-C), 128.43 (2′,6′-C), 130.08 (5-C), 133.48 (1′-C), 154.49 (8a-C), 156.51 (7-C), 158.10 (4′-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{16}O_3$ (M^+) 256.1099, Found 256.1100.

7-Hydroxy-3′,4′-dimethoxyisoflavane 9Af 63% yield. Colorless crystals. mp 97—98 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.79 (1H, ddd, J=15.5, 5.2, 1.7 Hz, 4-H), 2.90 (1H, dd, J=15.5, 10.3 Hz, 4-H), 3.06 (1H, tt, J=10.3, 5.2 Hz, 3-H), 3.72 (3H, s, 4′-OMe), 3.74 (3H, s, 3′-OMe), 3.96 (1H, t, J=10.3 Hz, 2-H), 4.18 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.19 (1H, s, 8-H), 6.29 (1H, d, J=8.0 Hz, 6-H), 6.82 (1H, d, J=8.0 Hz, 6′-H), 6.88 (1H, d, J=8.0 Hz, 5-H), 6.89 (1H, d, J=8.0 Hz, 5′-H), 6.94 (1H, s, 2′-H), 9.16 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.20 (4-C), 37.55 (3-C), 55.48 (4′-OMe), 55.52 (3′-OMe), 70.10 (2-C), 102.46 (8-C), 107.98 (6-C), 111.56 (2′-C), 111.94 (5′-C), 112.48 (4a-C), 119.14 (6′-C), 130.03 (5-C), 134.03 (1′-C), 147.65 (4′-C), 148.78 (3′-C), 154.49 (8a-C), 156.47 (7-C). FAB-HR-MS m/z: Calcd for $C_{17}H_{18}O_4$ (M^+) 286.1205, Found 286.1214.

7,8-Dihydroxyisoflavane 9Ba 73% yield. Pale brown crystals. mp 131—132 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.85 (1H, ddd, J=15.5, 5.2, 1.7 Hz, 4-H), 2.93 (1H, dd, J=15.5, 10.3 Hz, 4-H), 3.12—3.18 (1H, m, 3-H), 4.03 (1H, t, J=10.3 Hz, 2-H), 4.28 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.30 (1H, d, J=8.0 Hz, 6-H), 6.38 (1H, d, J=8.0 Hz, 5-H), 7.24—7.28 (1H, m, 4′-H), 7.32—7.36 (4H, m, 2′,3′,5′,6′-H), 8.16 (1H, s, 8-OH), 8.60 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.30 (4-C), 37.94 (3-C), 69.93 (2-C), 108.06 (6-C), 113.25 (4a-C), 118.46 (5-C), 126.75 (4′-C), 127.51 (3′,5′-C), 128.50 (2′,6′-C), 133.10 (8-C), 141.80 (1′-C), 142.99 (8a-C), 144.04 (7-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{14}O_3$ (M^+) 242.0943, Found 242.0962.

4′,7,8-Trihydroxyisoflavane 9Bb 57% yield. Pale brown crystals. mp 188—189 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.78 (1H, ddd, J=15.5, 5.2, 1.7 Hz, 4-H), 2.86 (1H, dd, J=15.5, 10.3 Hz, 4-H), 3.02 (1H, tt, J=10.3, 5.2 Hz, 3-H), 3.92 (1H, t, J=10.3 Hz, 2-H), 4.22 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.29 (1H, d, J=8.6 Hz, 6-H), 6.36 (1H, d, J=8.6 Hz, 5-H), 6.72 (2H, d, J=8.6 Hz, 3′,5′-H), 7.12 (2H, d, J=8.6 Hz, 2′,6′-H), 8.14 (1H, s, 8-OH), 8.57 (1H, s, 7-OH), 9.28 (1H, s, 4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.55 (4-C), 37.14 (3-C), 70.29 (2-C), 107.97 (6-C), 113.43 (4a-C), 115.22 (3′,5′-C), 118.45 (5-C), 128.36 (2′,6′-C), 131.75 (1′-C), 133.06 (8-C), 142.97 (8a-C), 143.98 (7-C), 156.13 (4′-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{14}O_4$ (M^+) 258.0892, Found 258.0908.

3′,4′,7,8-Tetrahydroxyisoflavane 9Bc 58% yield. Pale orange crystals. mp 177—178 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.74—2.84 (2H, m, 4-H), 2.91—2.97 (1H, m, 3-H), 3.88 (1H, t, J=10.3 Hz, 2-H), 4.21 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.29 (1H, d, J=8.6 Hz, 6-H), 6.36 (1H, d, J=8.6 Hz, 5-H), 6.56 (1H, d, J=8.0 Hz, 6′-H), 6.67 (1H, s, 2′-H), 6.68 (1H, d, J=8.0 Hz, 5′-H), 8.13 (1H, s, 8-OH), 8.57 (1H, s, 7-OH), 8.79 (1H, s, 4′-OH), 8.80 (1H, s, 3′-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.55 (4-C), 37.30 (3-C), 70.39 (2-C), 107.96 (6-C), 113.44 (4a-C), 114.85 (2′-C), 115.56 (5′-C), 117.97 (6′-C), 118.48 (5-C), 132.44 (1′-C), 133.06 (8-C), 142.98 (8a-C), 143.98 (3′-C), 144.04 (7-C), 145.20 (4′-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{14}O_5$ (M^+) 274.0841, Found 274.0826.

7,8-Dihydroxy-4′-methoxyisoflavane 9Be 66% yield. Pale brown crystals. mp 128—129 °C (EtOH) (lit.[54] 125—126 °C). The ^{1}H- and ^{13}C-NMR data of this product are in good agreement with those reported in the literature.[54] FAB-HR-MS m/z: Calcd for $C_{16}H_{16}O_4$ (M^+) 272.1049, Found 272.1063.

7,8-Dihydroxy-3′,4′-dimethoxyisoflavane 9Bf 50% yield. Pale brown crystals. mp 137—138 °C (EtOH) (lit.[54] 159—160 °C). The ^{1}H- and ^{13}C-NMR data of this product are in good agreement with those reported in the literature.[54] FAB-HR-MS m/z: Calcd for $C_{17}H_{18}O_5$ (M^+) 302.1154, Found 302.1150.

4′,5,7-Trihydroxyisoflavane 9Db 54% yield. Colorless crystals. mp 181—182 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.44—2.49 (1H, m, 4-H), 2.72 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.93 (1H, tt, J=10.3, 5.7 Hz, 3-H), 3.82 (1H, t, J=10.3 Hz, 2-H), 4.09 (2H, dq, J=10.3, 1.7 Hz, 2-H), 5.69 (1H, s, 8-H), 5.89 (1H, s, 6-H), 6.71 (2H, d, J=8.6 Hz, 3′,5′-H), 7.10 (2H, d, J=8.6 Hz, 2′,6′-H), 8.95 (1H, s, 7-OH), 9.20 (1H, s, 5-OH), 9.27 (1H, s, 4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 26.51 (4-C), 36.89 (3-C), 69.96 (2-C), 94.00 (8-C), 94.98 (6-C), 100.53 (4a-C), 115.21 (3′,5′-C), 128.29 (2′,6′-C), 132.10 (1′-C), 155.30 (8a-C), 156.07 (4′-C), 156.13 (5-C), 156.31 (7-C). FAB-HR-MS m/z: Calcd for $C_{15}H_{14}O_4$ (M^+) 258.0892, Found 258.0866.

5,7-Dihydroxy-4′-methoxyisoflavone 9De 28% yield. Colorless crystals. mp 200 °C (decomp.) (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.51—2.54 (1H, m, 4-H), 2.74 (1H, ddd, J=15.5, 5.2, 1.7 Hz, 4-H), 3.00 (1H, tt, J=10.3, 5.2 Hz, 3-H), 3.73 (3H, s, 4′-OMe), 3.87 (1H, t, J=10.3 Hz, 2-H), 4.11 (1H, dq, J=10.3, 1.7 Hz, 2-H), 5.70 (1H, s, 8-H), 5.89 (1H, s, 6-H), 6.89 (2H, d, J=8.6 Hz, 3′,5′-H), 7.23 (2H, d, J=8.6 Hz, 2′,6′-H), 8.96 (1H, s, 7-OH), 9.21 (1H, s, 5-OH). ^{13}C-NMR (DMSO-d_6) δ: 26.43 (4-C), 36.83 (3-C), 55.02 (4′-OMe), 69.82 (2-C), 94.01 (8-C), 95.01 (6-C), 100.43 (4a-C), 113.88 (3′,5′-C), 128.39 (2′,6′-C), 133.92 (1′-C), 155.30 (8a-C), 156.13 (5-C), 156.32 (7-C), 158.03 (4′-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{16}O_4$ (M^+) 272.1049, Found 272.1044.

6-Hydroxy-7-methoxyisoflavane 9Ea 67% yield. Colorless crystals. mp 117—118 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.80 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.88 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.10—3.16 (1H, m, 3-H), 3.70 (3H, s, 7-OMe), 3.95 (1H, t, J=10.3 Hz, 2-H), 4.17 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.38 (1H, s, 8-H), 6.51 (1H, s, 5-H), 7.24—7.26 (1H, m, 4′-H), 7.31—7.35 (4H, m, 2′,3′,5′,6′-H), 8.37 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.02 (4-C), 37.99 (3-C), 55.59 (7-OMe), 69.76 (2-C), 100.74 (8-C), 112.80 (4a-C), 115.57 (5-C), 126.70 (4′-C), 127.46 (3′,5′-C), 128.48 (2′,6′-C), 140.06 (6-C), 141.82 (1′-C), 146.48 (8a-C), 146.74 (7-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{16}O_3$ (M^+) 256.1099, Found 256.1108.

4′,6-Dihydroxy-7-methoxyisoflavane 9Eb 56% yield. Pale violet crystals. mp 112—113 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.73 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.81 (1H, dd, J=16.0, 10.3 Hz, 4-H), 2.97—3.03 (1H, m, 3-H), 3.69 (3H, s, 7-OMe), 3.85 (1H, t, J=10.3 Hz, 2-H), 4.10 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.37 (1H, s, 8-H), 6.49 (1H, s, 5-H), 6.71 (2H, d, J=8.6 Hz, 3′,5′-H), 7.10 (2H, d, J=8.6 Hz, 2′,6′-H), 8.36 (1H, s, 6-OH), 9.29 (1H, s, 4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.29 (4-C), 37.21 (3-C), 55.59 (7-OMe), 70.15 (2-C), 100.71 (8-C), 112.99 (4a-C), 115.22 (3′,5′-C), 115.60 (5-C), 128.31 (2′,6′-C), 131.79 (1′-C), 139.99 (6-C), 146.48 (8a-C), 146.68 (7-C), 156.11 (4′-C). FAB-HR-MS m/z: Calcd for $C_{16}H_{16}O_4$ (M^+) 272.1049, Found 272.1043.

6-Hydroxy-4′,7-dimethoxyisoflavane 9Ee 73% yield. A pale brown amorphous solid. ^{1}H-NMR (DMSO-d_6) δ: 2.76 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.84 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.04—3.10 (1H, m, 3-H), 3.70 (3H, s, 7-OMe), 3.73 (3H, s, 4′-OMe), 3.89 (1H, t, J=10.3 Hz, 2-H), 4.13 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.37 (1H, s, 8-H), 6.50 (1H, s, 5-H), 6.89 (2H, d, J=8.6 Hz, 3′,5′-H), 7.23 (2H, d, J=8.6 Hz, 2′,6′-H), 8.36 (1H,

s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.19 (4-C), 37.14 (3-C), 55.02 (4′-OMe), 55.58 (7-OMe), 69.99 (2-C), 100.71 (8-C), 112.87 (4a-C), 113.89 (3′,5′-C), 115.57 (5-C), 128.41 (2′,6′-C), 133.63 (1′-C), 140.01 (6-C), 146.47 (8a-C), 146.70 (7-C), 158.06 (4′-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{18}O_4$ (M^+) 286.1205, Found 286.1232.

6-Hydroxy-3′,4′,7-trimethoxyisoflavane 9Ef 82% yield. Pale brown crystals. mp 103—104 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.76 (1H, ddd, J=16.0, 5.2, 1.7 Hz, 4-H), 2.88 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.06 (1H, tt, J=10.3, 5.2 Hz, 3-H), 3.70 (3H, s, 7-OMe), 3.72 (3H, s, 4′-OMe), 3.74 (3H, s, 3′-OMe), 3.91 (1H, t, J=10.3 Hz, 2-H), 4.14 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.38 (1H, s, 8-H), 6.50 (1H, s, 5-H), 6.81 (1H, d, J=8.6 Hz, 6′-H), 6.89 (1H, d, J=8.6 Hz, 5′-H), 6.94 (1H, s, 2′-H), 8.35 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.20 (4-C), 37.64 (3-C), 55.49 (4′-OMe), 55.53 (3′-OMe), 55.58 (7-OMe), 70.01 (2-C), 100.71 (8-C), 111.57 (2′-C), 111.92 (5′-C), 112.93 (4a-C), 115.56 (5-C), 119.13 (6′-C), 134.19 (1′-C), 140.00 (6-C), 146.48 (8a-C), 146.69 (7-C), 147.64 (4′-C), 148.78 (3′-C). FAB-HR-MS *m/z*: Calcd for $C_{18}H_{20}O_5$ (M^+) 316.1311, Found 316.1324.

6-Hydroxy-4′-methoxy-7-methylisoflavane 9Fe 98% yield. Pale brown crystals. mp 144—145 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.04 (3H, s, 7-Me), 2.79 (1H, ddd, J=16.0, 5.2, 1.7 Hz, 4-H), 2.87 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.07 (1H, tt, J=10.3, 5.2 Hz, 3-H), 3.73 (3H, s, 4′-OMe), 3.87 (1H, t, J=10.3 Hz, 2-H), 4.11 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.48 (1H, s, 5-H), 6.50 (1H, s, 8-H), 6.89 (2H, d, J=8.6 Hz, 3′,5′-H), 7.23 (2H, d, J=8.6 Hz, 2′,6′-H), 8.65 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 15.80 (7-Me), 31.57 (4-C), 37.11 (3-C), 55.02 (4′-OMe), 69.98 (2-C), 113.88 (3′,5′-C), 114.77 (5-C), 117.53 (8-C), 119.33 (4a-C), 122.90 (7-C), 128.39 (2′,6′-C), 133.61 (1′-C), 146.31 (8a-C), 148.70 (6-C), 158.05 (4′-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{18}O_3$ (M^+) 270.1256, Found 270.1241.

6-Hydroxy-7,8-dimethylisoflavane 9Ga 51% yield. Colorless crystals. mp 142—143 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.01 (3H, s, 7-Me), 2.02 (3H, s, 8-Me), 2.83 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.93 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.10—3.16 (1H, m, 3-H), 3.94 (1H, t, J=10.3 Hz, 2-H), 4.24 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.39 (1H, s, 5-H), 7.24—7.27 (1H, m, 4′-H), 7.31—7.35 (4H, m, 2′,3′,5′,6′-H), 8.56 (1H, s, 6-OH). ^{13}C-NMR (DMSO-d_6) δ: 11.82 (7-Me), 11.88 (8-Me), 31.83 (4-C), 38.03 (3-C), 70.05 (2-C), 112.10 (5-C), 118.34 (4a-C), 121.38 (7-C), 123.78 (8-C), 126.65 (4′-C), 127.41 (3′,5′-C), 128.45 (2′,6′-C), 141.87 (1′-C), 144.57 (8a-C), 148.14 (6-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{18}O_2$ (M^+) 254.1307, Found 254.1306.

8-Hydroxy-7-methoxyisoflavane 9Ha 47% yield. Pale brown crystals. mp 100—101 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.89 (1H, ddd, J=16.0, 5.2, 1.7 Hz, 4-H), 2.97 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.13—3.19 (1H, m, 3-H), 3.72 (3H, s, 7-OMe), 4.04 (1H, t, J=10.3 Hz, 2-H), 4.29 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.49—6.52 (2H, m, 5,6-H), 7.24—7.28 (1H, m, 4′-H), 7.32—7.36 (4H, m, 2′,3′,5′,6′-H), 8.22 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.23 (4-C), 37.74 (3-C), 56.05 (7-OMe), 69.91 (2-C), 105.00 (6-C), 115.51 (4a-C), 118.20 (5-C), 126.74 (4′-C), 127.46 (3′,5′-C), 128.47 (2′,6′-C), 134.59 (8-C), 141.63 (1′-C), 142.73 (7-C), 146.41 (8a-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{16}O_3$ (M^+) 256.1099, Found 256.1077.

8-Hydroxy-4′,7-dimethoxyisoflavane 9He 53% yield. Colorless crystals. mp 97—98 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.85 (1H, ddd, J=16.0, 5.2, 1.7 Hz, 4-H), 2.93 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.07—3.13 (1H, m, 3-H), 3.72 (3H, s, 7-OMe), 3.73 (3H, s, 4′-OMe), 3.97 (1H, t, J=10.3 Hz, 2-H), 4.25 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.48—6.51 (2H, m, 5,6-H), 6.90 (2H, d, J=8.6 Hz, 3′,5′-H), 7.25 (2H, d, J=8.6 Hz, 2′,6′-H), 8.21 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.40 (4-C), 36.91 (3-C), 55.03 (4′-OMe), 56.04 (7-OMe), 70.14 (2-C), 104.94 (6-C), 113.91 (3′,5′-C), 115.59 (4a-C), 118.19 (5-C), 128.44 (2′,6′-C), 133.43 (1′-C), 134.56 (8-C), 142.72 (7-C), 146.39 (8a-C), 158.10 (4′-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{18}O_4$ (M^+) 286.1205, Found 286.1214.

8-Hydroxy-7-methylisoflavane 9Ia 75% yield. Colorless crystals. mp 96—97 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.09 (3H, s, 7-Me), 2.91 (1H, ddd, J=16.0, 5.2, 1.7 Hz, 4-H), 2.99 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.17—3.22 (1H, m, 3-H), 4.08 (1H, t, J=10.3 Hz, 2-H), 4.32 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.47 (1H, d, J=8.0 Hz, 5-H), 6.57 (1H, d, J=8.0 Hz, 6-H), 7.24—7.28 (1H, m, 4′-H), 7.33—7.36 (4H, m, 2′,3′,5′,6′-H), 8.34 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 15.68 (7-Me), 31.35 (4-C), 37.74 (3-C), 70.05 (2-C), 118.82 (5-C), 119.78 (4a-C), 121.53 (6-C), 121.78 (7-C), 126.74 (4′-C), 127.48 (3′,5′-C), 128.49 (2′,6′-C), 141.61 (1′-C), 141.84 (8a-C), 143.14 (8-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{16}O_2$ (M^+) 240.1150, Found 240.1145.

4′,8-Dihydroxy-7-methylisoflavane 9Ib 72% yield. Pale gray crystals. mp 149—150 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.08 (3H, s, 7-Me), 2.84 (1H, ddd, J=15.8, 4.6, 1.7 Hz, 4-H), 2.91 (1H, dd, J=15.8, 10.3 Hz, 4-H), 3.06 (1H, tt, J=10.3, 4.6 Hz, 3-H), 3.97 (1H, t, J=10.3 Hz, 2-H), 4.26 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.45 (1H, d, J=8.0 Hz, 5-H), 6.55 (1H, d, J=8.0 Hz, 6-H), 6.72 (2H, d, J=8.6 Hz, 3′,5′-H), 7.12 (2H, d, J=8.6 Hz, 2′,6′-H), 8.33 (1H, s, 8-OH), 9.28 (1H, s, 4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 15.69 (7-Me), 31.63 (4-C), 36.97 (3-C), 70.43 (2-C), 115.24 (3′,5′-C), 118.83 (5-C), 119.98 (4a-C), 121.46 (6-C), 121.69 (7-C), 128.35 (2′,6′-C), 131.58 (1′-C), 141.82 (8a-C), 143.13 (8-C), 156.16 (4′-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{16}O_3$ (M^+) 256.1099, Found 256.1095.

8-Hydroxy-4′-methoxy-7-methylisoflavane 9Ie 55% yield. Colorless crystals. mp 78—79 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.08 (3H, s, 7-Me), 2.87 (1H, ddd, J=16.0, 4.6, 1.7 Hz, 4-H), 2.95 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.13 (1H, tt, J=10.3, 4.6 Hz, 3-H), 3.73 (3H, s, 4′-OMe), 4.02 (1H, t, J=10.3 Hz, 2-H), 4.27 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.46 (1H, d, J=8.0 Hz, 5-H), 6.56 (1H, d, J=8.0 Hz, 6-H), 6.90 (2H, d, J=8.6 Hz, 3′,5′-H), 7.26 (2H, d, J=8.6 Hz, 2′,6′-H), 8.36 (1H, s, 8-OH). ^{13}C-NMR (DMSO-d_6) δ: 15.74 (7-Me), 31.55 (4-C), 36.94 (3-C), 55.06 (4′-OMe), 70.30 (2-C), 113.94 (3′,5′-C), 118.85 (5-C), 119.90 (4a-C), 121.52 (6-C), 121.75 (7-C), 128.50 (2′,6′-C), 133.45 (1′-C), 141.84 (8a-C), 143.17 (8-C), 158.14 (4′-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{18}O_3$ (M^+) 270.1256, Found 270.1261.

7-Hydroxy-6-methoxyisoflavane 9Ja 52% yield. Pale brown crystals. mp 104—105 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.83 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.91 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.10—3.16 (1H, m, 3-H), 3.68 (3H, s, 6-OMe), 3.95 (1H, t, J=10.3 Hz, 2-H), 4.16 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.25 (1H, s, 8-H), 6.65 (1H, s, 5-H), 7.23—7.27 (1H, m, 4′-H), 7.31—7.35 (4H, m, 2′,3′,5′,6′-H), 8.86 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.29 (4-C), 38.03 (3-C), 56.32 (6-OMe), 69.75 (2-C), 103.57 (8-C), 111.30 (4a-C), 113.57 (5-C), 126.75 (4′-C), 127.48 (3′,5′-C), 128.52 (2′,6′-C), 141.85 (6-C), 141.91 (1′-C), 145.76 (7-C), 147.80 (8a-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{16}O_3$ (M^+) 256.1099, Found 256.1089.

4′,7-Dihydroxy-6-methoxyisoflavane 9Jb 45% yield. Pale orange crystals. mp 151—152 °C (EtOH) (lit.[14] mp not given). ^{1}H-NMR (DMSO-d_6) δ: 2.76 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.84 (1H, dd, J=16.0, 10.3 Hz, 4-H), 2.97—3.03 (1H, m, 3-H), 3.68 (3H, s, 6-OMe), 3.84 (1H, t, J=10.3 Hz, 2-H), 4.09 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.24 (1H, s, 8-H), 6.63 (1H, s, 5-H), 6.71 (2H, d, J=8.6 Hz, 3′,5′-H), 7.10 (2H, d, J=8.6 Hz, 2′,6′-H), 8.86 (1H, s, 7-OH), 9.31 (1H, s, 4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.54 (4-C), 37.23 (3-C), 56.33 (6-OMe), 70.11 (2-C), 103.53 (8-C), 111.47 (4a-C), 113.60 (5-C), 115.23 (3′,5′-C), 128.31 (2′,6′-C), 131.79 (1′-C), 141.83 (6-C), 145.71 (7-C), 147.80 (8a-C), 156.13 (4′-C). FAB-HR-MS *m/z*: Calcd for $C_{16}H_{16}O_4$ (M^+) 272.1049, Found 272.1059.

7-Hydroxy-4′,6-dimethoxyisoflavane 9Je 51% yield. Colorless crystals. mp 117—118 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.79 (1H, ddd, J=16.0, 5.2, 1.7 Hz, 4-H), 2.87 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.04—3.10 (1H, m, 3-H), 3.68 (3H, s, 4′-OMe), 3.73 (3H, s, 6-OMe), 3.89 (1H, t, J=10.3 Hz, 2-H), 4.11 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.24 (1H, s, 8-H), 6.64 (1H, s, 5-H), 6.89 (2H, d, J=8.6 Hz, 3′,5′-H), 7.23 (2H, d, J=8.6 Hz, 2′,6′-H), 8.84 (1H, s, 7-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.45 (4-C), 37.17 (3-C), 55.04 (4′-OMe), 56.32 (6-OMe), 69.97 (2-C), 103.54 (8-C), 111.37 (4a-C), 113.57 (5-C), 113.92 (3′,5′-C), 128.43 (2′,6′-C), 133.64 (1′-C), 141.87 (6-C), 145.72 (7-C), 147.79 (8a-C), 158.08 (4′-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{18}O_4$ (M^+) 286.1205, Found 286.1206.

6,7-Dimethoxyisoflavane 9Ka 76% yield. Pale brown crystals. mp 77—78 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.87 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.94 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.13—3.19 (1H, m, 3-H), 3.68 (3H, s, 6-OMe), 3.70 (3H, s, 7-OMe), 3.99 (1H, t, J=10.3 Hz, 2-H), 4.20 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.43 (1H, s, 8-H), 6.70 (1H, s, 5-H), 7.24—7.27 (1H, m, 4′-H), 7.32—7.35 (4H, m, 2′,3′,5′,6′-H). ^{13}C-NMR (DMSO-d_6) δ: 31.16 (4-C), 37.86 (3-C), 55.50 (7-OMe), 56.09 (6-OMe), 69.81 (2-C), 100.83 (8-C), 112.38 (4a-C), 113.21 (5-C), 126.75 (4′-C), 127.47 (3′,5′-C), 128.53 (2′,6′-C), 141.74 (1′-C), 142.78 (6-C), 147.75 (8a-C), 148.11 (7-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{18}O_3$ (M^+) 270.1256, Found 270.1232.

4′-Hydroxy-6,7-dimethoxyisoflavane 9Kb 43% yield. Colorless crystals. mp 183—184 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.80 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.87 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.03 (1H, tt, J=10.3, 5.7 Hz, 3-H), 3.67 (3H, s, 6-OMe), 3.69 (3H, s, 7-OMe), 3.88 (1H, t, J=10.3 Hz, 2-H), 4.14 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.42 (1H, s, 8-H), 6.68 (1H, s, 5-H), 6.72 (2H, d, J=8.6 Hz, 3′,5′-H), 7.11 (2H, d, J=8.6 Hz, 2′,6′-H), 9.30 (1H, s, 4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.43 (4-C), 37.09 (3-C), 55.48 (7-OMe), 56.10 (6-OMe), 70.18 (2-C), 100.79 (8-C), 112.56 (4a-C), 113.24 (5-C), 115.25 (3′,5′-C), 128.33 (2′,6′-C), 131.70 (1′-C), 142.70 (6-C), 147.75 (8a-C), 148.05 (7-C), 156.14 (4′-C). FAB-HR-MS *m/z*: Calcd for $C_{17}H_{18}O_4$ (M^+) 286.1205, Found 286.1206.

3′,4′-Dihydroxy-6,7-dimethoxyisoflavane 9Kc 68% yield. Pale brown crystals. mp 189—190 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.78—2.82 (2H, m, 4-H), 2.92—2.97 (1H, m, 3-H), 3.67 (3H, s, 6-OMe), 3.69 (3H, s, 7-OMe), 3.84 (1H, t, J=10.3 Hz, 2-H), 4.13 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.41 (1H, s, 8-H), 6.53 (1H, d, J=8.0 Hz, 6′-H), 6.65 (1H, s, 2′-H), 6.66 (1H, d, J=8.0 Hz, 5′-H), 6.68 (1H, s, 5-H), 9.03 (2H, s, 3′,4′-OH). ^{13}C-NMR (DMSO-d_6) δ: 31.46 (4-C), 37.23 (3-C), 55.49 (7-OMe), 56.10 (6-OMe), 70.28 (2-C), 100.81 (8-C), 112.61 (4a-C), 113.30 (5-C), 114.95 (2′-C), 115.71 (5′-C), 117.84 (6′-C), 132.29 (1′-C), 142.70 (6-C), 144.27 (3′-C), 145.44 (4′-C), 147.77 (8a-C), 148.04 (7-C). FAB-HR-MS m/z: Calcd for $C_{17}H_{18}O_5$ (M^+) 302.1154, Found 302.1142.

4′,6,7-Trimethoxyisoflavane 9Ke 71% yield. Pale brown crystals. mp 104—105 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.83 (1H, ddd, J=16.0, 5.7, 1.7 Hz, 4-H), 2.90 (1H, dd, J=16.0, 10.3 Hz, 4-H), 3.07—3.13 (1H, m, 3-H), 3.67 (3H, s, 6-OMe), 3.69 (3H, s, 7-OMe), 3.73 (3H, s, 4′-OMe), 3.93 (1H, t, J=10.3 Hz, 2-H), 4.16 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.42 (1H, s, 8-H), 6.69 (1H, s, 5-H), 6.90 (2H, d, J=8.6 Hz, 3′,5′-H), 7.24 (2H, d, J=8.6 Hz, 2′,6′-H). ^{13}C-NMR (DMSO-d_6) δ: 31.33 (4-C), 37.02 (3-C), 55.03 (4′-OMe), 55.49 (7-OMe), 56.10 (6-OMe), 70.03 (2-C), 100.81 (8-C), 112.46 (4a-C), 113.24 (5-C), 113.93 (3′,5′-C), 128.42 (2′,6′-C), 133.54 (1′-C), 142.74 (6-C), 147.76 (8a-C), 148.08 (7-C), 158.09 (4′-C). FAB-HR-MS m/z: Calcd for $C_{18}H_{20}O_4$ (M^+) 300.1362, Found 300.1370.

3′,4′,6,7-Tetramethoxyisoflavane 9Kf 74% yield. Pale brown crystals. mp 102—103 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 2.83 (1H, ddd, J=15.5, 6.3, 1.7 Hz, 4-H), 2.94 (1H, dd, J=15.5, 10.3 Hz, 4-H), 3.09 (1H, tt, J=10.3, 6.3 Hz, 3-H), 3.67 (3H, s, 6-OMe), 3.69 (3H, s, 7-OMe), 3.73 (3H, s, 4′-OMe), 3.75 (3H, s, 3′-OMe), 3.95 (1H, t, J=10.3 Hz, 2-H), 4.17 (1H, dq, J=10.3, 1.7 Hz, 2-H), 6.43 (1H, s, 8-H), 6.69 (1H, s, 5-H), 6.82 (1H, d, J=8.6 Hz, 6′-H), 6.90 (1H, d, J=8.6 Hz, 5′-H), 6.95 (1H, s, 2′-H). ^{13}C-NMR (DMSO-d_6) δ: 31.33 (4-C), 37.49 (3-C), 55.49 (3′,4′-OMe), 55.52 (7-OMe), 56.11 (6-OMe), 70.04 (2-C), 100.79 (8-C), 111.55 (2′-C), 111.94 (5′-C), 112.51 (4a-C), 113.23 (5-C), 119.12 (6′-C), 134.05 (1′-C), 142.73 (6-C), 147.65 (4′-C), 147.76 (8a-C), 148.06 (7-C), 148.79 (3′-C). FAB-HR-MS m/z: Calcd for $C_{19}H_{22}O_5$ (M^+) 330.1467, Found 330.1457.

Measurement of the DPPH Radical Scavenging Activity[17] To a solution of a sample in DMSO–EtOH (1 : 4, 50 μl) were added a 0.50 mM solution of DPPH in DMSO–EtOH (1 : 4, 25 μl) and a 0.10 M acetate buffer (pH=6.0, 50 μl). After standing at 20 °C for 30 min in the dark, the absorbance of the mixture at 540 nm was measured. The ED_{50} value was determined as the concentration of each sample required to give 50% of the absorbance shown by a blank test.

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