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Reactions of 2′-Hydroxyisoflavone and 2′-Hydroxy-2-methylisoflavones with Metal Salts

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Reactions of four 2′-hydroxy-2-methylisoflavones with lead(IV) acetate gave the corresponding 10b-acetoxy-5a-methyl-5a,10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-ones in 21—25% yields and 2-(2-methyl-4-oxo-4*H*-chromen-3-yl)-*p*-benzoquinones in 27—46% yields. Reactions of the isoflavones with manganese(III) acetate gave the ketones in 1—25% yields. Reaction of 2′-hydroxy-4′,7-dimethoxyisoflavone with lead(IV) acetate gave 10b-acetoxy-3,8-dimethoxy-5a,10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-one, and 3,8-dimethoxybenzofuro-[2,3-*b*][1]benzopyran-11-one.

In the lead(IV) acetate oxidation of organic compounds in which a hydroxyl group and a double bond or a hydrogen are located in a spatially suitable position, an oxidative cyclization has been found.[1,3—7] Manganese(III) acetate oxidations of the compounds have also been reported to give cyclic products.[2—5,7] It could be expected that the reaction of 2′-hydroxy-2-methylisoflavone with metal salts might give a dehydrorotenoid by the removal of hydrogens from the hydroxyl and methyl groups. The dehydrorotenoid can be transformed into a rotenoid, which is known as a fish poison. It is also expected that the reaction of 2′-hydroxyisoflavone with metal salts would give benzofuro-[2,3-*b*][1]benzopyran-11-one, which has been found in natural sources as Lisetin.[8] Lisetin was synthesized from Piscerythrone, which was also a natural product, by the oxidation with potassium hexacyanoferrate.[8] However, this method is not applicable to water insoluble 2′-hydroxyisoflavones (described later).

2′-Hydroxy- and 2′-hydroxy-2-methylisoflavones (Ia—e) were prepared by partial demethylation of the corresponding 2′-methoxyisoflavones with aluminium chloride. The structures of new isoflavones were determined by examining their NMR and IR spectra, and by elemental analyses.

The reaction of 2′-hydroxy-4′,7-dimethoxy-2-methylisoflavone (Ib) with lead(IV) acetate in hot acetic acid gave two products, IIb and IIIb (Table 1, entry 3). The NMR spectrum of IIb ($C_{20}H_{18}O_7$, mp 186—188 °C) indicated that it is an acetate (δ 2.20) with a methyl group (δ 1.79), two methoxyl groups (δ 3.71 and 3.81), and six aromatic protons {δ 6.3—6.8 (4H, m), 7.35 (1H, d, J=8.5 Hz) and 7.75 (1H, m)}. The IR spectrum showed carbonyl absorptions at 1710 and 1760 cm^{-1}. These spectroscopic properties are consistent with the structure of 10b-acetoxy-3,8-dimethoxy-5a-methyl-5a,10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-one (IIb) (Fig. 1). The NMR spectrum of IIIb ($C_{18}H_{14}O_6$, mp 237 °C) indicated the presence of a methyl group (δ 2.29), two methoxyl groups (δ 3.90 and 3.95), two singlet protons (δ 6.11 and 6.72), and three aromatic protons {δ 6.85—7.05 (2H, m) and 8.13 (1H, d, J=8.5 Hz)}. The IR spectrum exhibited multiple absorptions at 1630—1660 cm^{-1} and a carbonyl absorption at 1700 cm^{-1}. The spectroscopic evidence suggested that the structure of IIIb is to be 2-(7-methoxy-2-methyl-4-oxo-4*H*-chromen-3-yl)-5-methoxy-*p*-benzoquinone (IIIb). The reactions of Ib with lead(IV) acetate in acetic acid at room temperature and in benzene at reflux temperature gave less satisfactory results (entries 4 and 5). When Ib was treated with aqueous potassium hexacyanoferrate, the starting material was recovered unchanged.

Three other 2′-hydroxy-2-methylisoflavones (Ia, Ic, and Id) also gave the corresponding 10b-acetoxy-5a-methyl-5a,10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-ones (IIa, IIc, and IId) and 2-(4-oxo-4*H*-chromen-3-yl)-*p*-benzoquinones (IIIa, IIIc, and IIId), respectively, in the oxidation with lead(IV) acetate. The reaction of Ib with manganese(III) acetate gave a dimeric compound, IV ($C_{40}H_{34}O_{14}$, mp 300 °C), together with IIb (entries 6, 7, and 10). IIIb was not obtained in these cases. The NMR spectrum of IV was similar to that of IIb, except for the presence of *para*-related protons {δ 7.24 (s) and 6.35 (s)} instead of the one set of three aromatic protons in IIb. The reactions of Ia, Ic, and Id with manganese(III) acetate gave IIa, IIc, and IId, respectively, in less satisfactory yields (entries 2, 12, and 14).

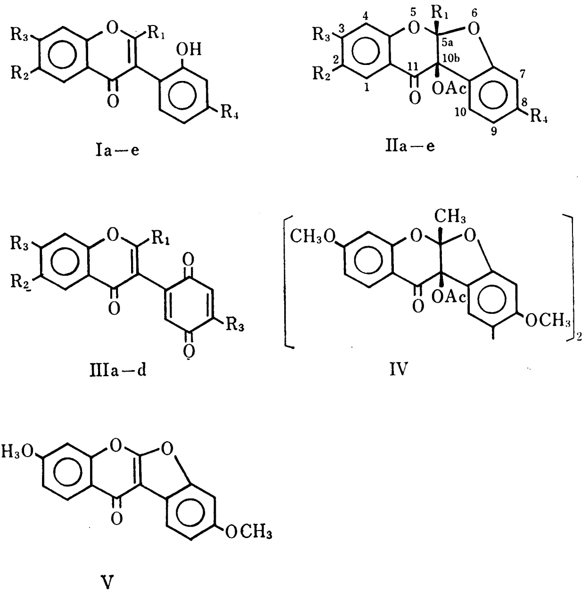
The reaction of 2′-hydroxy-4′,7-dimethoxyisoflavone (Ie) with lead(IV) acetate yielded two products, IIe and V. When the reaction was conducted at room temperature, IIe was the major product (entry 15). At reflux temperature, however, V was the major product (entry 17). The structures of these products were again elucidated by examining their NMR and IR spectra, and are shown in Fig. 1. It appears that the removal of acetic acid from IIe would give V and, in fact, the heating of IIe up to 250 °C yielded V in quantitative yield. The thermal elimination of acetic acid from IIe IIe suggests that the stereochemistry of the 5a-hydrogen and the 10b-acetoxyl group would be *cis*. This also leads to the prediction that the stereochemistry of 5a-methyl and 10b-acetoxyl groups in IIa—d would be *cis*, which is the more stable conformation predicted from molecular models.

In conclusion, the reactions of 2′-hydroxy-2-methylisoflavones (Ia—d) with lead(IV) acetate and manganese(III) acetate did not yield the expected dehydrorotenoids, but gave new dihydrobenzofuro-[2,3-*b*][1]benzopyran-11-ones (IIa—d), while the reaction of 2′-hydroxyisoflavone gave benzofuro[2,3-*b*][1]-benzopyran-11-one (V). The latter reaction can be utilized as a synthetic method for benzofuro[2,3-*b*][1]-benzopyran-11-one.

Table 1. The reactions of 2′-hydroxyisoflavones with metal salts

Entry	Compd	Reaction conditions					Product (% yield)[a]			
		Oxidant	Molar ratio of I : oxidant	Solvent	Temp (°C)	Time (h)				
1	Ia[9]	$Pb(OAc)_4$	1 : 1.5	AcOH	100	0.5	IIa (25)	IIIa (45)		
2	Ia	$Mn(OAc)_3 2H_2O$	1 : 3	AcOH	100	1.0	IIa (1)			
3	Ib	$Pb(OAc)_4$	1 : 1.5	AcOH	100	0.5	IIb (25)	IIIb (46)		
4	Ib	$Pb(OAc)_4$	1 : 1.5	AcOH	R.T.	2.0	IIb (21)	IIIb (28)		
5	Ib	$Pb(OAc)_4$	1 : 1.5	benzene	80	1.0	IIb (5)	IIIb (17)		
6	Ib	$Mn(OAc)_3 2H_2O$	1 : 1	AcOH	100	0.5	IIb (16)		IV (3)	
7	Ib	$Mn(OAc)_3 2H_2O$	1 : 3	AcOH	100	0.5	IIb (25)		IV (29)	
8	Ib	$Mn(OAc)_3 2H_2O$	1 : 3	AcOH	R.T.	72	IIb (7)			
9	Ib	$Mn(OAc)_3 2H_2O$	1 : 3	benzene	80	720	IIb (9)			
10	Ib	$Mn(OAc)_3 2H_2O$	1 : 6	AcOH[b]	100	4.5	IIb (14)		IV (9)	
11	Ic	$Pb(OAc)_4$	1 : 1.5	AcOH	100	0.5	IIc (22)	IIIc (27)		
12	Ic	$Mn(OAc)_3 2H_2O$	1 : 3	AcOH	100	0.5	IIc (9)			
13	Id	$Pb(OAc)_4$	1 : 1.5	AcOH	100	0.5	IId (24)	IIId (43)		
14	Id	$Mn(OAc)_3 2H_2O$	1 : 3	AcOH	100	0.5	IId (10)			
15	Ie[10]	$Pb(OAc)_4$	1 : 1.5	AcOH	R.T.	2.0	IIe (22)			V (8)
16	Ie	$Pb(OAc)_4$	1 : 1.5	AcOH	100	0.5	IIe (19)			V (17)
17	Ie	$Pb(OAc)_4$	1 : 1.5	AcOH	reflux	0.5				V (35)
18	Ie	$Mn(OAc)_3 2H_2O$	1 : 3	AcOH	100	0.3	IIe (10)			V (7)

a) Yield is based on the amount of isoflavone consumed. b) Two equivalents of Ac_2O were added.



a $R_1=CH_3$, $R_2=R_4=H$, $R_3=OCH_3$
b $R_1=CH_3$, $R_2=H$, $R_3=R_4=OCH_3$
c $R_1=CH_3$, $R_2=R_3=OCH_3$, $R_4=H$
d $R_1=CH_3$, $R_2=R_3=R_4=OCH_3$
e $R_1=H$, $R_2=H$, $R_3=R_4=OCH_3$

Fig. 1.

Experimental

All ^1H NMR spectra were recorded with a Hitachi NMR spectrometer with TMS as an internal standard. The IR spectra were recorded with a JSACO grating spectrometer. The UV spectra were recorded with a Hitachi EPS-3T spectrophotometer, while the mass spectrum was recorded with a JEOL JMS-01 SG-2 mass spectrometer. Melting points were determined on a Yanagimoto hot-stage and are uncorrected.

Preparation of 2-Methylisoflavones. A typical procedure for the preparation of 2-methylisoflavone was as follows. A mixture of a phenyl benzyl ketone (0.5 g), sodium acetate (0.5 g) acetic anhydride (2 ml), and acetic acid (2 ml) was heated under reflux for 12 h. The reaction mixture was poured into ice water and the precipitates were collected.

2-Hydroxy-4,5-dimethoxyphenyl 2-methoxybenzyl ketone[11] gave 2-methyl-2′,6,7-trimethoxyisoflavone, mp 172—173 °C (EtOH) in a 31% yield. IR ($CHCl_3$) 1640 cm^{-1} (C=O); UV (MeOH) λ_{max} (ε) 288 (11900) and 324 nm (10200); NMR ($CDCl_3$) δ=2.18 (3H, s, CH_3), 3.72 (3H, s, OCH_3), 3.92 (6H, s, 2×OCH_3), 6.83 (1H, s, $H_{(8)}$), 6.95—7.43 (4H, m, $H_{(3'-6')}$), and 7.51 (1H, s, $H_{(5)}$). Found: C, 69.94; H, 5.60%. Calcd for $C_{19}H_{18}O_5$: C, 69.92; H, 5.56%.

2-Hydroxy-4,5-dimethoxyphenyl 2,4-dimethoxybenzyl ketone[12] yielded 2-methyl-2′,4′,6,7-tetramethoxyisoflavone, mp 175—177 °C (EtOH) in a 31% yield. IR ($CHCl_3$) 1635 cm^{-1} (C=O); UV (MeOH) λ_{max} (ε) 291 (12200) and 325 nm (9700); NMR ($CDCl_3$) δ=2.20 (3H, s, CH_3), 3.78 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 3.95 (6H, s, 2×OCH_3), 6.4—7.4 (2H, m, $H_{(3')}$ and $H_{(5')}$), 6.89 (1H, s, $H_{(8)}$), 7.18 (1H, m, $H_{(6')}$), 7.57 (1H, s, $H_{(5)}$). Found: C, 67.10; H, 5.82%. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66%.

Preparation of 2′-Hydroxy-2-methylisoflavones (Ib—d). A typical procedure for the preparation of 2′-hydroxy-2-methylisoflavone was as follows. A mixture of a 2′-methoxy-2-methyl isoflavone (10 mmol), aluminium chloride (20 mmol), and nitrobenzene (50 ml) was heated at 100 °C for 1 h. After the removal of the nitrobenzene under reduced pressure, the resulting mixture was triturated with 2 M hydrochloric acid. The precipitates were collected and recrystallized.

2′-Hydroxy-4′,7-dimethoxy-2-methylisoflavone (Ib): Mp 224—225 °C ($CHCl_3$); 44% yield; IR (KBr) 3300 (OH) and 1620 cm^{-1} (C=O); UV (MeOH) λ_{max} (ε) 247 (25000), 251 (25300), and 290 nm (15700); NMR (CF_3COOH) δ=2.70 (3H, s, CH_3), 4.02 (3H, s, OCH_3), 4.17 (3H, s, OCH_3), 6.75—7.59 (5H, m), and 8.59 (1H, m, $H_{(5)}$). Found: C, 69.42; H, 5.05%. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H; 5.16%.

2′-Hydroxy-6,7-dimethoxy-2-methylisoflavone (Ic): Mp 251—253 °C ($CHCl_3$); 27% yield; IR (KBr) 3240 (OH) and

1630 cm^{-1} (C=O), UV (MeOH) λ_{max} (ε) 298 (13600) and 324 nm (11700); NMR (CF_3COOH) δ=2.79 (3H, s, CH_3), 4.20 (3H, s, OCH_3), 4.28 (3H, s, OCH_3), 7.21—7.53 (4H, m, $H_{(3'-6')}$), 7.58 (1H, s, $H_{(8)}$), and 7.86 (1H, s, $H_{(5)}$). Found: C, 69.50; H, 5.20%. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16%.

2′-Hydroxy-2-methyl-4′,6,7-trimethoxyisoflavone (Id): Mp 241 °C ($CHCl_3$–C_6H_6); 23% yield; IR (KBr) 3200 (OH) and 1620 cm^{-1} (C=O); UV (MeOH) λ_{max}(ε) 291 (16100) and 324 nm (12900); NMR (CF_3COOH) δ=2.71 (3H, s, CH_3). 4.03 (3H, s, OCH_3), 4.19 (3H, s, OCH_3), 4.25 (3H, s, OCH_3), 6.72—6.98 (3H, m, $H_{(3')}$, $H_{(5')}$ and $H_{(6')}$), 7.51 (1H, s, $H_{(8)}$), and 7.80 (1H, s, $H_{(5)}$). Found: C, 66.36; H, 5.35%. Calcd for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30%.

Oxidations of 2′-Hydroxy-2-methylisoflavanoes (Ia—d) and 2′-Hydroxyisoflavone with Lead(IV) Acetate. A typical oxidation of 2′-hydroxyisoflavone was as follows. A mixture of a 2′-hydroxyisoflavone (1 mmol), lead(IV) acetate[13] (1.5 mmol), and a solvent (20 ml) was heated at an appropriate temperature for the time shown in the Table 1. After the removal of the solvent, the resulting reaction mixture was triturated with water and extracted with chloroform. The chloroform solution was evaporated and separated on TLC using chloroform as developing solvent.

Ia yielded 10b-acetoxy-3-methoxy-5a-methyl-5a,10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-one (IIa): mp 136—137 °C (EtOH); 25% yield; IR ($CHCl_3$) 1700 (C=O) and 1760 cm^{-1} (OAc); UV (MeOH) λ_{max} (ε) 287 nm (16900); NMR ($CDCl_3$) δ=1.79 (3H, s, CH_3), 2.20 (3H, s, OAc), 3.79 (3H, s, OCH_3), 6.51—7.50 (6H, m), and 7.68 (1H, d, *J*=8.5 Hz, $H_{(1)}$) (Found: C, 66.92; H, 4.73%. Calcd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.75%); and 2-(7-methoxy-2-methyl-4-oxo-4*H*-chromen-3-yl)-*p*-benzoquinone (IIIa): mp 180 °C (C_6H_6–light petroleum); 45% yield; IR ($CHCl_3$) 1650 and 1680 cm^{-1} (C=O); UV (MeOH) λ_{max}(ε) 226 (30500), 246 (30400), 252 (30000), and 297 nm (14700); NMR ($CDCl_3$) δ=2.30 (3H, s, CH_3), 3.91 (3H, s, OCH_3), 6.75—7.06 (5H, m, $H_{(3)}$, $H_{(5)}$, $H_{(6)}$, $H_{(6')}$, and $H_{(8')}$), and 8.05 (1H, d, *J*=8.5 Hz, $H_{(5')}$) (Found: C, 68.80; H, 4.10%. Calcd for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08%).

Ib gave 10b-acetoxy-3,8-dimethoxy-5a-methyl-5a,10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-one (IIb): mp 186—188 °C (EtOH); 5—25% yields; IR ($CHCl_3$) 1710 (C=O) and 1760 cm^{-1} (OAc); UV (MeOH) λ_{max} (ε) 233 (13700) and 284 nm (15800); NMR ($CDCl_3$) δ=1.79 (3H, s, CH_3), 2.20 (3H, s, OAc), 3.71 (3H, s, OCH_3), 3.81 (3H, OCH_3), 6.31—6.71 (4H, m, $H_{(2)}$, $H_{(4)}$, $H_{(7)}$, and $H_{(9)}$), 7.37, (1H, m, $H_{(10)}$), and 7.73 (1H, d, *J*=8.5 Hz, $H_{(1)}$) (Found: C 64.65; H, 4.90%. Calcd for $C_{20}H_{18}O_7$: C, 64.56; H, 4.90%); and 2-(7-methoxy-2-methyl-4-oxo-4*H*-chromen-3-yl)-5-methoxy-*p*-benzoquinone (IIIb): mp 237 °C (EtOH); 17—46% yields; IR ($CHCl_3$) 1630—1660 and 1700 cm^{-1} (C=O); UV (MeOH) λ_{max} (ε) 223 (23700), 247 (25400), 252 (27200), and 298 nm (15900); NMR ($CDCl_3$) δ=2.29, (3H, s, CH_3), 3.90 (3H, s, OCH_3), 3.95 (3H, s, OCH_3) 6.11 (1H, s, $H_{(6)}$), 6.72 (1H, s, $H_{(3)}$), 6.85—7.05 (2H, m, $H_{(6')}$ and $H_{(8')}$), 8.13 (1H, d, *J*=8.5 Hz, $H_{(5')}$)(Found: C, 65.96; H, 4.32%. Calcd for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32%).

Ic yielded 10b-acetoxy-2,3-dimethoxy-5a-methyl-5a,10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-one (IIc): mp 207—209 °C (EtOH); 22% yield; IR ($CHCl_3$) 1700 (C=O) and 1760 cm^{-1} (OAc); UV (MeOH) λ_{max} (ε) 286 (14200) and 347 nm (8800); NMR ($CDCl_3$) δ=1.79 (3H, s, CH_3), 2.21 (3H, s, OAc), 3.82 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 6.61 (1H, s, $H_{(4)}$), 7.22 (1H, s, $H_{(1)}$), 6.70—7.50 (3H, m, $H_{(7)}$, $H_{(8)}$, and $H_{(9)}$), and 7.56 (1H, m, $H_{(10)}$) (Found: C, 64.63; H, 4.92%. Calcd for $C_{20}H_{18}O_7$: C, 64.86; H, 4.90%); and 2-(6,7-dimethoxy-2-methyl-4-oxo-4*H*-chromen-3-yl)-*p*-benzoquinone (IIIc): mp 192—193 °C (EtOH); 27% yield; IR ($CHCl_3$) 1650 and 1680 cm^{-1} (C=O); UV (MeOH) λ_{max} (ε) 289 (12000) and 323 nm (13400); NMR ($CDCl_3$) δ=2.30 (3H, s, CH_3), 3.95 (3H, s, OCH_3), 3.98 (3H, s, OCH_3) 6.79—6.83 (4H, m,$H_{(3)}$,$H_{(5)}$, $H_{(6)}$, and $H_{(8')}$, and 7.45 (1H, s, $H_{(5')}$) (Found: C, 66.10; H, 4.31%. Calcd for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32%).

Id gave 10b-acetoxy-5a-methyl-2,3,8-trimethoxy-5a,10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-one (IId): mp 180—183 °C (EtOH); 24% yield; IR (KBr) 1700 (C=O) and 1760 cm^{-1} (OAc); UV (MeOH) λ_{xam} (ε) 286 (14900) and 347 nm (9300); NMR ($CDCl_3$) δ=1.79 (3H, s, CH_3), 2.20 (3H, s, OAc), 3.75 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 6.57 (1H, s, $H_{(4)}$), 7.18 (1H, s, $H_{(1)}$), 6.29—6.59 (2H, m, $H_{(7)}$ and $H_{(9)}$), and 7.38 (1H, m, $H_{(10)}$) (Found: C, 62.80; H, 5.08%. Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04%); and 2-(6,7-dimethoxy-2-methyl-4-oxo-4*H*-chromen-3-yl)-5-methoxy-*p*-benzoquinone (IIId): mp 222—227 °C (EtOH); 43% yield; IR (KBr) 1630 and 1700 cm^{-1} (C=O); UV (MeOH) λ_{max} (ε) 322 nm (14900); NMR (CDC_3) δ=2.29 (3H, s, CH_3), 3.85 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 3.98 (3H, s, OCH_3), 6.02 (1H, s, $H_{(6)}$), 6.73 (1H, s, $H_{(8')}$), 6.84 (1H, s, $H_{(3)}$), and 7.45 (1H, s, $H_{(5')}$) (Found: C, 63.74; H, 4.55%. Calcd for $C_{19}H_{16}O_7$: C, 64.04; H, 4.53%).

Ie yielded 10b-acetoxy-3,8-dimethoxy-5a,10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-one(IIe): mp 150 °C (EtOH); IR ($CHCl_3$) 1710 (C=O) and 1760 cm^{-1} (OAc); UV (MeOH) λ_{max} (ε) 233 (13900), 283 (15500), and 311 nm (inf.) (8760); NMR ($CDCl_3$) δ=2.18 (3H, s, OAc), 3.77 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 6.45—6.70 (5H, m, $H_{(2)}$, $H_{(4)}$, $H_{(5a)}$, $H_{(7)}$, and $H_{(9)}$), 7.29 (1H, m, $H_{(10)}$), and 7.71 (1H, d, *J*=8.5 Hz, $H_{(1)}$) (Found: C, 63.95; H, 4.54%. Calcd for $C_{19}H_{16}O_7$: C, 64.04; H, 4.53%); and 3,8-dimethoxybenzofuro[2,3-*b*][1]benzopyran-11-one (V): mp 235 °C ($CHCl_3$); IR (KBr) 1658 cm^{-1} (C=O); UV (MeOH) λ_{max} (ε) 261 (30500), 287 (16600), and 311 nm (inf.) (9330); NMR (CF_3COOH) δ=4.08 (3H, s, OCH_3), 4.15 (3H, s, OCH_3), 7.10—7.60 (4H, m, $H_{(2)}$, $H_{(4)}$, $H_{(7)}$, and $H_{(9)}$), 8.10 (1H, d, *J*=8.5 Hz, $H_{(1)}$), and 8.52 (1H, d, *J*=8.5 Hz, $H_{(10)}$) (Found: C, 68.80; H, 4.10%. Calcd for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08%).

Oxidations of Ia—e with Manganese(III) Acetate. A typical oxidation of 2′-hydroxyisoflavone with manganese(III) acetate was as follows. A mixture of 2′-hydroxyisoflavone (1 mmol), manganese(III) acetate dihydrate[14] (3 mmol), and a solvent (20 ml) was heated at an appropriate temperature for the time shown in Table 1. After the removal of the solvent, the resulting mixture was triturated with water and extracted with chloroform. The chloroform solution was evaporated and the resulting mixture was separated on TLC using chloroform as developing solvent and by recrystallization.

Ia gave IIa: mp 136—137 °C, 1% yield. Ib yielded IIb: mp 186—188 °C, 7—25% yields; and IV: mp 300 °C (EtOH–$CHCl_3$), 3—29% yields; IR ($CHCl_3$) 1710 (C=O) and 1760 cm^{-1} (OAc); UV (MeOH) λ_{max} (ε) 289 nm (33400); NMR ($CDCl_3$) δ=1.81 (3H, s, OCH_3), 2.20 (3H, s, OAc), 3.60 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 6.35 (1H, s, $H_{(7)}$), 6.53—6.70 (2H, m, $H_{(2)}$ and $H_{(4)}$), 7.24 (1H, s, $H_{(10)}$), and 7.75 (1H, m, $H_{(1)}$) (Found: C, 64.79; H, 4.64%. Calcd for $C_{40}H_{34}O_{14}$: C, 65.03; H, 4.64%), *m/e* 738 (M^+). Ic gave IIc: mp 207—209 °C, 9% yield. Id yielded IId: mp 180—183 °C, 10% yield. Ie gave IIe: mp 150 °C, 10% yield; and V: mp 235 °C, 7% yield.

The Thermal Decomposition of IIe. 10b-Acetoxy-3,8-dimethoxy-5a, 10b-dihydrobenzofuro[2,3-*b*][1]benzopyran-11-one (IIe) (0.1 mmol) was heated at 250 °C for 10 min. The NMR spectrum of the residue was identical with that of V in every respect.

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