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Heterocycles. XX.[1] Reactions of 2''-Methoxymethoxychalcone Epoxides under Acidic Conditions

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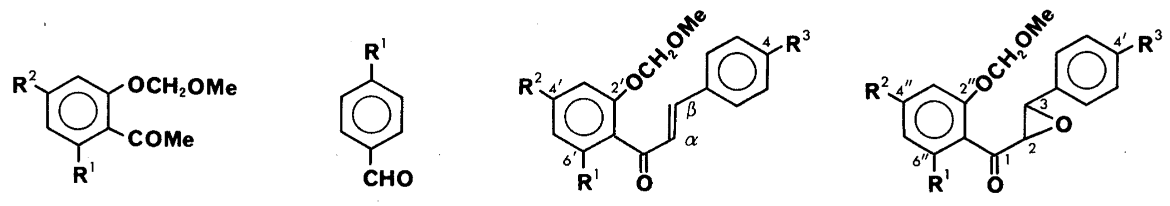
The effect of substituents on the formation of products in the reactions of 2''-methoxymethoxychalcone epoxides under acidic conditions has been examined. Regardless of the 6''-substituent, the presence of a 4'-hydroxyl group results in the exclusive formation of flavanonols. The presence of a 4'-methoxyl group directs the reactions toward the competitive formation of flavanonols and glycol monomethyl ethers or toward the exclusive formation of glycol monomethyl ethers, depending on the bulk of the 6''-substituent.

Keywords——chalcone epoxide; 1,3-diphenylpropanone; flavanonol; two-dimensional ^{1}H–^{13}C shift correlation; intramolecular hydrogen-bonding; stereochemistry

In a previous paper,[1] we described the reactions of 2'-hydroxychalcones, which contain a hydroxyl and/or a methoxyl group at the 4- and 6'-positions, with alkaline hydrogen peroxide. These substitutents affected the formation of products in a complex manner, because several reactions competitively occurred under the reaction conditions employed. We now report an interesting effect of substituents on the formation of products in the reactions of 2''-methoxymethoxychalcone epoxides under acidic conditions.

The condensation of the 2'-methoxymethoxyacetophenones **1** with the benzaldehydes **2** in ethanolic potassium hydroxide solution afforded the 2'-methoxymethoxychalcones **3** which, on epoxidation with alkaline hydrogen peroxide, gave the 2''-methoxymethoxychalcone epoxides **4**.



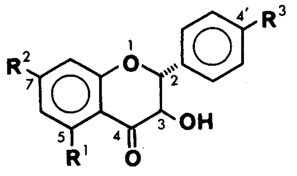
1 2 3 4

1
a: $R^1 = R^2 = H$
b: $R^1 = OMe$, $R^2 = H$
c: $R^1 = OCH_2Ph$, $R^2 = H$
d: $R^1 = OCH_2OMe$, $R^2 = H$
e: $R^1 = R^2 = OMe$

2
a: $R^1 = OCH_2OMe$
b: $R^1 = OMe$

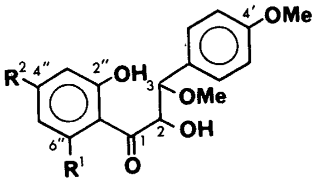
3, **4**
a: $R^1 = R^2 = H$, $R^3 = OCH_2OMe$
b: $R^1 = OMe$, $R^2 = H$, $R^3 = OCH_2OMe$
c: $R^1 = OCH_2Ph$, $R^2 = H$, $R^3 = OCH_2OMe$
d: $R^1 = R^2 = H$, $R^3 = OMe$
e: $R^1 = OCH_2OMe$, $R^2 = H$, $R^3 = OMe$
f: $R^1 = R^3 = OMe$, $R^2 = H$
g: $R^1 = R^2 = R^3 = OMe$
h: $R^1 = OCH_2Ph$, $R^2 = H$, $R^3 = OMe$
i: $R^1 = R^2 = R^3 = H$
j: $R^1 = R^3 = OCH_2OMe$, $R^2 = H$
k: $R^1 = R^2 = R^3 = OCH_2OMe$

Chart 1



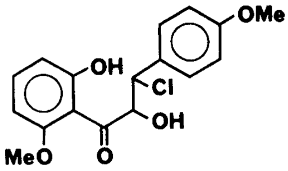
5

a: $R^1=R^2=H$, $R^3=OH$
b: $R^1=OMe$, $R^2=H$, $R^3=OH$
c: $R^1=OCH_2Ph$, $R^2=H$, $R^3=OH$
d: $R^1=R^2=H$, $R^3=OMe$
e: $R^1=OH$, $R^2=H$, $R^3=OMe$
f: $R^1=R^2=R^3=H$
g: $R^1=R^3=OH$, $R^2=H$
h: $R^1=R^2=R^3=OH$

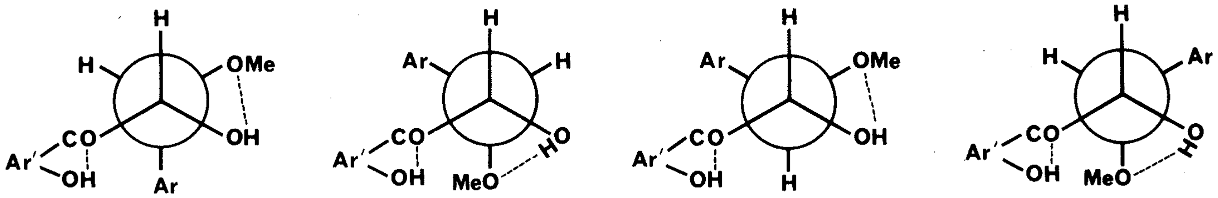


6

a: $R^1=R^2=H$
b: $R^1=OH$, $R^2=H$
c: $R^1=OMe$, $R^2=H$
d: $R^1=R^2=OMe$
e: $R^1=OCH_2Ph$, $R^2=H$



7



6A *erythro* 6B 6A′ *threo* 6B′

Chart 2

The following reactions were carried out in 10% methanolic hydrogen chloride solution at 50 °C for 15—20 min. The 2′′-methoxymethoxychalcone epoxides **4a**, **4b** and **4c** gave the flavanonols **5a**, **5b** and **5c** in 65, 68 and 51% yields, respectively. The 2′′-methoxymethoxychalcone epoxide **4d** afforded the flavanonol **5d** (12%) together with a diastereoisomeric mixture of glycol monomethyl etehr **6a** (37%). The ratio of 1 : 1 of the latter was calculated on the basis of the proton nuclear magnetic resonance (^{1}H-NMR) spectrum (see Experimental). The 2′′-methoxymethoxychalcone epoxide **4e** also furnished the flavanonol **5e** (31%) along with the glycol monomethyl ethers **6b**-I (20%) and **6b**-II (8%). On the other hand, the 2′′-methoxymethoxychalcone epoxides **4f**, **4g** and **4h** only provided the glycol monomethyl ethers **6c**-I (52%), **6c**-II (22%) and **6d**-I (35%), **6d**-II (11%) and **6e** (85%), respectively. Treatment of **4f** with 10% hydrogen chloride in dioxane at 3 °C for 10min gave the β-chloro alcohol **7** (80%).

The *trans* configuration of **5** was decided on the basis of the ^{1}H-NMR spectra which showed the coupling constant, $J_{2,3}=12$ Hz, between the 2- and 3-protons.

The positions of hydroxyl and methoxyl groups or chlorine atom in **6** and **7** were determined by analysis of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra involving gated decoupling and selective proton decoupling experiments as well as two-dimensional ^{1}H–^{13}C (one-bond and long-range) correlation experiments.

The spectra of **6b**, **6c**, **6d** and **6e** revealed long-range couplings between the 1-carbon and the 2-hydroxyl proton (except for **6b**) and between the 3-carbon, which was correlated to the 3-methoxyl protons by long-range correlation experiments, and the 2′(6′)-protons (Table I). The spectrum of **7** indicated coupling patterns similar to those of **6b**—**6e**. Thus, this suggested that **6b**—**6e** and **7** contain a 3-substituted (methoxyl group or chlorine atom) 2-hydroxy-3-phenylpropanone system in the molecules. The positions of the 2-hydroxyl and the 3-methoxyl groups in **6a** were deduced from a comparison of the ^{1}H-NMR spectrum with those of **6b**—**6e** and **7**.

The *erythro* and *threo* configurations of **6** were deduced from intramolecular hydrogen-

TABLE I. NMR Data for **6** and **7**[a]

	Carbon		Correlated proton		
	No.	δ_C[b]	One-bond[c]	Long-range[c]	Decoupling[d]
6b-I[e]	1	205.55[f]			
	2	80.16 Dd	2-H		
	3	82.95 Dm	3-H	3-OMe 2′(6′)-H′s	
6b-II[e]	1	205.55[f]			
	2	78.40 Dd	2-H		3-H (2.5)
	3	84.50 Dm	3-H	3-OMe 2′(6′)-H′s	2-H→sharpened
6c-I	1	204.55 Sm		2-H, 2-OH 3-H	
	2	79.89 Dd	2-H	2-OH	2-OH (3.5)
	3	82.79 Dm	3-H	3-OMe 2′(6′)-H′s	2-H (2), 3-OMe (4) 2′(6′)-H′s (4)
6c-II	1	203.59 Sm		2-H, 2-OH 3-H	
	2	79.17 Dd	2-H		2-OH (3.5)
	3	84.28 Dm	3-H	2-H, 3-OMe	2-H (3), 3-OMe (5) 2′(6′)-H′s (8)
6d-I	1	202.27 Sm		2-H, 2-OH	
	2	78.98 Dd	2-H		2-OH (3.5)
	3	83.02 Dm	3-H	3-OMe	2-H, 3-OMe 2′(6′)-H′s →sharpened
6d-II	1	201.13 St		2-H, 2-OH	2-H (4), 2-OH (4)
	2	78.36 Dd	2-H		2-OH (3.5)
	3	84.45 Dm	3-H	2-H, 3-OMe	2-H, 3-OMe 2′(6′)-H′s →sharpened
6e	1	204.50 Sm		2-H, 2-OH	
	2	79.79 Dd	2-H		
	3	82.84 Dm	3-H	3-OMe 2′(6′)-H′s	
7	1	202.43 Sm		2-H, 2-OH	
	2	78.58 Ds	2-H		
	3	63.50 Dt	3-H	2′(6′)-H′s	2′(6′)-H′s (4.5)

a) The spectra were taken on a Varian XL-400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) in deuteriochloroform; ppm. *b)* Capital and small letters refer to one-bond and long-range couplings observed in the gated decoupled spectra, respectively. *c)* These data were obtained by two-dimensional ^{1}H–^{13}C shift correlation experiments. *d)* These data were obtained by selective proton decoupling experiments. Figures in parentheses are coupling constants (J_{CH}, Hz). *e)* The spectra were taken in deuterioacetone. *f)* These signals overlapped with that of carbonyl carbon of the solvent.

bondings in the infrared (IR) spectra (Table II) and coupling constants between the 2- and 3-protons in the ^{1}H-NMR spectra. Each diastereoisomer of **6c** and **6d** indicated two intramolecular hydrogen-bondings due to MeO···HO and C=O···HOAr,[2] and no free hydroxyl band. These observations suggested that each diastereoisomer exclusively exists in two hydrogen-bonded conformations **6A**, **6B** and **6A′**, **6B′**. Since among them only **6A′** contains two *trans* hydrogen atoms, it is predicted that the *threo* isomers exhibit larger coupling constants than the *erythro* isomers.[3] The coupling constants, $J_{2,3}=1.2$ and 2.8 Hz, were observed for **6c**-I, **6d**-I and **6c**-II, **6d**-II, respectively. Thus, it was deduced that the I-series isomers are *erythro* and the II-series isomers are *threo*. Since the two diastereoisomers of **6b** showed two intramolecular hydrogen-bondings in addition to a free phenolic hydroxyl band,[2] it was also assumed that **6b**-I ($J_{2,3}=2.5$ Hz) is the *erythro* isomer and **6b**-II ($J_{2,3}=$ 4.8 Hz) is the *threo* isomer.

Table II. IR Hydroxyl Bands of **6**[a)]

	Free ArOH	Hydrogen-bonding	
		ROH···OMe	ArOH···O=C
6b-I	3576 (27.5)	3508 (36)	3152 (74.5)
6b-II	3580 (26.5)	3520 (53.5)	3168 (98.5)
6c-I		3532 (56.5)	3228 (35.5)
6c-II		3512 (46)	3218 (29)
6d-I		3524 (61.5)	3220 (26)
6d-II		3516 (59.5)	3214 (25.5)

a) $c = 1 \times 10^{-3}$ mol/l, CCl_4; cm^{-1} (ε).

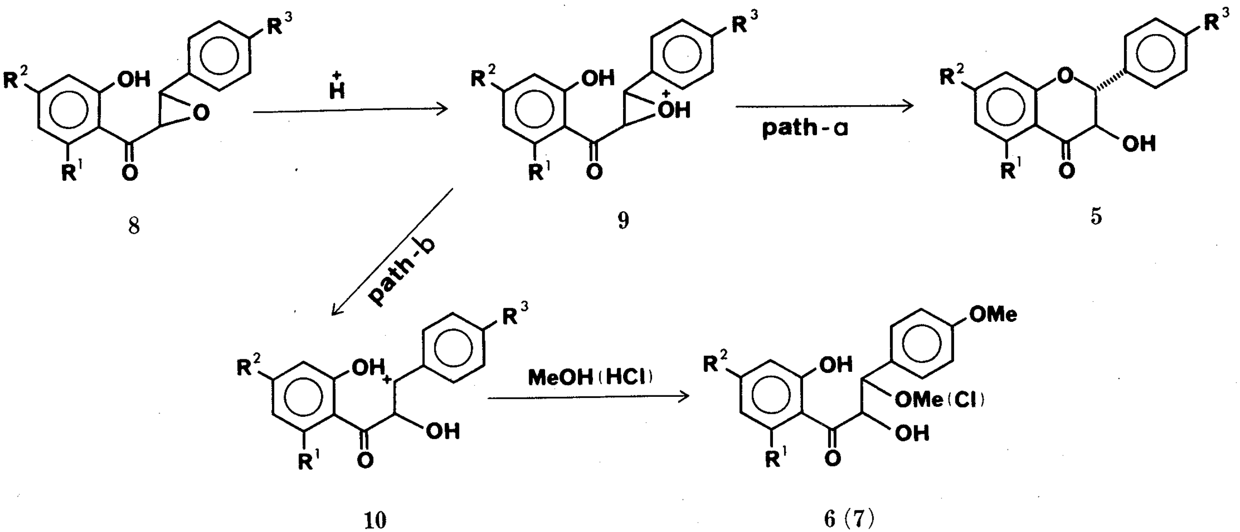


Chart 3

Since a methoxymethoxy group is easily converted into a hydroxyl group by the action of hydrogen chloride, the reactions of **4** under acidic conditions can be regarded as the same as that of the 2′′-hydroxychalcone epoxide **8** in which all the methoxymethoxy groups are changed to the hydroxyl groups.

The formation paths to products are speculated as follows. (1) The back side attack of the 2′′-hydroxyl group on the 3-position in the oxonium ion **9**, which is derived from **8** by protonation, stereoselectively affords **5** (path-a). (2) When the reaction proceeds *via* the cation **10**, which is formed from **9** by cleavage of the 3-ether bond, the diastereoisomers of **6** or **7** are formed (path-b). The possibility of formation of **5** *via* path-b would not be excluded.

It has already been reported that the 2′′-methoxymethoxychalcone epoxides **4i**, **4j** and **4k** provided the flavanonols **5f**,[4)] **5g**[5)] and **5h**,[6)] respectively, as sole products in fairly high yields under reaction conditions similar to those above. Thus, the effect of substituents in **9** on the formation of products can be summarized as follows. (1) Regardless of the 6′′-substituent, a 4′-hydroxyl group or 4′-hydrogen atom exclusively causes the reaction to proceed *via* path-a. (2) When **9** contains a 6′′-hydroxyl group or 6′′-hydrogen atom, a 4′-methoxyl group competitively causes the reaction to proceed *via* pah-a and -b. (3) When **9** contains a 6′′-methoxyl or a 6′′-benzyloxy group, a 4′-methoxyl group exclusively causes the reaction to proceed *via* path-b. Thus, a 4′-methoxyl group facilitates the formation of **10**, and the reaction of **9** containing a 4′-methoxyl group competitively proceeds *via* path-a and -b or exclusively *via* path-b, depending on the bulk of the 6′′-substituent.

Experimental

Melting points were determined on a micro hot-stage apparatus and are uncorrected. Spectra were recorded on the following spectrometers: IR, Hitachi 260-30; ^{1}H-NMR, Varian XL-400 (400 MHz) and EM-390 (90 MHz); ^{13}C-NMR, Varian XL-400 (100.6 MHz); mass (MS), JEOL JMS DX-300.

2′-Hydroxyacetophenones

2′-Hydroxyacetophenone and 2′,6′-dihydroxyacetophenone were obtained commercially. 2′-Hydroxy-6′-methoxyacetophenone,[7] 6′-benzyloxy-2′-hydroxyacetophenone[8] and 4′,6′-dimethoxy-2′-hydroxyacetophenone[9] were prepared by the procedures described in the literature.

2′-Methoxymethoxyacetophenones 1

2′-Methoxymethoxyacetophenone (1a)——A solution of NaOH (487 mg, 1.21 mmol) in water (10 ml) was added to a solution of 2′-hydroxyacetophenone (550.2 mg, 4.06 mmol) in dichloromethane (10 ml), and the whole was stirred at room temperature for 10 min. Tetrabutylammonium chloride (100 mg, 0.36 mmol) and methoxymethyl chloride (0.4 ml, 5.30 mmol) were added, and the mixture was stirred at room temperature for 5 h. The organic phase was separated and washed with water, then dried over $\mathrm{Na_2SO_4}$. Removal of the solvent *in vacuo* gave an oil which was purified by preparative thin-layer chromatography (prep TLC) (silica gel, acetone : benzene = 1 : 5) to afford **1a** (694.2 mg, 95%) as a colorless oil, *Rf* 0.71. IR ($\mathrm{CHCl_3}$): 1668 cm^{-1} (C=O). MS Calcd for $\mathrm{C_{10}H_{12}O_3}$: M, 180.079. Found *m/z*: M$^+$, 180.078.

6′-Methoxy-2′-methoxymethoxyacetophenone (1b)——A colorless oil, *Rf* 0.67. Yield, 97%. IR ($\mathrm{CHCl_3}$): 1696 cm^{-1} (C=O). MS calcd for $\mathrm{C_{11}H_{14}O_4}$: M, 210.089. Found *m/z*: M$^+$, 210.089.

6′-Benzyloxy-2′-methoxymethoxyacetophenone (1c)——A colorless oil, *Rf* 0.76. Yield, 96%. IR ($\mathrm{CHCl_3}$): 1698 cm^{-1} (C=O). MS Calcd for $\mathrm{C_{17}H_{18}O_4}$: M, 286.121. Found *m/z*: M$^+$, 286.121.

2′,6′-Bis(methoxymethoxy)acetophenone (1d)——This compound was prepared by the procedure described in the literature.[5]

4′,6′-Dimethoxy-2′-methoxymethoxyacetophenone (1e)——A colorless oil, *Rf* 0.40. Yield, 88%. IR ($\mathrm{CHCl_3}$): 1692 cm^{-1} (C=O). MS Calcd for $\mathrm{C_{12}H_{16}O_5}$: M, 240.100. Found *m/z*: M$^+$, 240.101.

Benzaldehydes 2

4-Methoxymethoxybenzaldehyde (**2a**) was prepared by the procedure described in the literature.[5] Anisaldehyde (**2b**) was obtained commercially.

2′-Methoxymethoxychalcones 3

4,2′-Bis(methoxymethoxy)chalcone (3a)——A mixture of **1a** (307.5 mg, 1.71 mmol), **2a** (284.2 mg, 1.71 mmol) and KOH (105 mg, 1.88 mmol) in anhydrous ethanol (8 ml) was stirred at room temperature for 27 h. The reaction mixture was concentrated *in vacuo*, and the residue was extracted with ethyl acetate. Work-up and purification of the products by prep TLC (silica gel, acetone : benzene = 1 : 10) gave **3a** (461.0 mg, 87%) as a yellow oil, *Rf* 0.58. IR ($\mathrm{CHCl_3}$): 1630 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($\mathrm{CDCl_3}$) δ: 7.56 (1H, d, J = 16 Hz, β-H), 7.18 (1H, d, J = 16 Hz, α-H). MS Calcd for $\mathrm{C_{19}H_{20}O_5}$: M, 328.131. Found *m/z*: M$^+$, 328.131.

4,2′-Bis(methoxymethoxy)-6′-methoxychalcone (3b)——A yellow oil, *Rf* 0.60. Yield, 92%. IR ($\mathrm{CHCl_3}$): 1634 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($\mathrm{CDCl_3}$) δ: 7.27 (1H, d, J = 16 Hz, β-H), 6.82 (1H, d, J = 16 Hz, α-H). MS Calcd for $\mathrm{C_{20}H_{22}O_6}$: M, 358.142. Found *m/z*: M$^+$, 358.141.

6′-Benzyloxy-4,2′-bis(methoxymethoxy)chalcone (3c)——A colorless oil, *Rf* 0.72. Yield, 92%. IR ($\mathrm{CHCl_3}$): 1636 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($\mathrm{CDCl_3}$) δ: 7.31 (1H, d, J = 16.2 Hz, β-H), 6.86 (1H, d, J = 16.2 Hz, α-H). MS Calcd for $\mathrm{C_{26}H_{26}O_6}$: M, 434.173. Found *m/z*: M$^+$, 434.172.

4-Methoxy-2′-methoxymethoxychalcone (3d)——A yellow oil, *Rf* 0.68. Yield, 91%. IR ($\mathrm{CHCl_3}$): 1630 cm^{-1} (C=O). MS Calcd for $\mathrm{C_{18}H_{18}O_4}$: M, 298.119. Found *m/z*: M$^+$, 298.120.

2′,6′-Bis(methoxymethoxy)-4-methoxychalcone (3e)——Yellow needles of mp 86—88 °C (ether), *Rf* 0.62. Yield, 94%. IR ($\mathrm{CHCl_3}$): 1638 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($\mathrm{CDCl_3}$) δ: 7.25 (1H, d, J = 16.8 Hz, β-H), 6.34 (1H, d, J = 16.8 Hz, α-H). MS Calcd for $\mathrm{C_{20}H_{22}O_6}$: M, 358.143. Found *m/z*: M$^+$, 358.143.

4,6′-Dimethoxy-2′-methoxymethoxychalcone (3f)——A yellow oil, *Rf* 0.62. Yield, 86%. IR ($\mathrm{CHCl_3}$): 1630 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($\mathrm{CDCl_3}$) δ: 7.26 (1H, d, J = 16.5 Hz, β-H), 6.87 (1H, d, J = 16.5 Hz, α-H). MS Calcd for $\mathrm{C_{19}H_{20}O_5}$: M, 328.131. Found *m/z*: M$^+$, 328.131.

2′-Methoxymethoxy-4,6′,4′-trimethoxychalcone (3g)——A yellow oil, *Rf* 0.15 (acetone : hexane = 1 : 5). Yield, 82%. IR ($\mathrm{CHCl_3}$): 1630 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($\mathrm{CDCl_3}$) δ: 7.32 (1H, d, J = 16.8 Hz, β-H), 6.83 (1H, d, J = 16.8 Hz, α-H). MS Calcd for $\mathrm{C_{20}H_{22}O_6}$: M, 358.141. Found *m/z*: M$^+$, 358.141.

6′-Benzyloxy-4-methoxy-2′-methoxymethoxychalcone (3h)——A yellow oil, *Rf* 0.65. Yield, 84%. IR ($\mathrm{CHCl_3}$): 1634 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($\mathrm{CDCl_3}$) δ: 7.32 (1H, d, J = 16.5 Hz, β-H), 6.85 (1H, d, J = 16.5 Hz, α-H). MS Calcd for $\mathrm{C_{25}H_{24}O_5}$: M, 404.162. Found *m/z*: M$^+$, 404.161.

2″-Methoxymethoxychalcone Epoxides 4

2,3-Epoxy-1-2″-methoxymethoxyphenyl-3-4′-methoxymethoxyphenylpropanone (4a)——A mixture of 35% $\mathrm{H_2O_2}$ (0.2 ml, 2.10 mmol) and 2 N NaOH (0.2 ml) was added to a solution of **3a** (410.2 mg, 1.25 mmol) in methanol (2 ml), and the whole was stirred at room temperature for 3 h. The reaction mixture was concentrated *in vacuo*, and the residue was extracted with ethyl acetate. The organic phase was successively washed with 10% aqueous KI, 10% aqueous $\mathrm{Na_2S_2O_3}$ and water, and then dried over $\mathrm{Na_2SO_4}$. Work-up and purification of the products by prep TLC (alumina, acetone : benzene = 1 : 10) gave **4a** (400.5 mg, 93%) as a colorless oil, *Rf* 0.78. IR ($\mathrm{CHCl_3}$): 1676 cm^{-1}

(C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 4.94, 4.24 (each 1H, d, J=1.8 Hz, 2- and 3-H's). MS Calcd for $C_{19}H_{20}O_6$: M, 344.126. Found m/z: M^+, 344.127.

2,3-Epoxy-1-6″-methoxy-2″-methoxymethoxyphenyl-3-4′-methoxymethoxyphenylpropanone (4b)——A colorless oil, Rf 0.65. Yield, 87%. IR ($CHCl_3$): 1694 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 3.96, 3.84 (each 1H, d, J= 1.8 Hz, 2- and 3-H's). MS Calcd for $C_{20}H_{22}O_7$: M 374.136. Found m/z: M^+, 374.136.

1-6″-Benzyloxy-2″-methoxymethoxyphenyl-2,3-epoxy-3-4′-methoxymethoxyphenylpropanone (4c)——A colorless oil, Rf 0.65. Yield, 88%. IR ($CHCl_3$): 1706 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 3.94, 3.84 (each 1H, d, J=1.8 Hz, 2- and 3-H's). MS Calcd for $C_{26}H_{26}O_7$: M, 450.166. Found m/z: M^+, 450.166.

2,3-Epoxy-1-2″-methoxymethoxyphenyl-3-4′-methoxyphenylpropanone (4d)——A colorless oil, Rf 0.48. Yield, 87%. IR ($CHCl_3$): 1676 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 4.26, 3.94 (each 1H, d, J=1.8 Hz, 2- and 3-H's). MS Calcd for $C_{18}H_{18}O_5$: M, 314.115. Found m/z: M^+, 314.115.

1-2″,6″-Bis(methoxymethoxy)phenyl-2,3-epoxy-3,4′-methoxyphenylpropanone (4e)——A colorless oil, Rf 0.55. Yield, 85%. IR ($CHCl_3$): 1694 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 3.96, 3.87 (each 1H, d, J=1.8 Hz, 2- and 3-H's). MS Calcd for $C_{20}H_{22}O_7$: M, 374.137. Found m/z: M^+, 374.136.

2,3-Epoxy-1-6″-methoxy-2″-methoxymethoxyphenyl-3-4′-methoxyphenylpropanone (4f)——A colorless oil, Rf 0.72. Yield, 87%. IR ($CHCl_3$): 1694 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 3.96, 3.84 (each 1H, d, J=2.1 Hz, 2- and 3-H's). MS Calcd for $C_{19}H_{20}O_6$: M, 344.126. Found m/z: M^+, 344.126.

1-4″,6″-Dimethoxy-2″-methoxymethoxyphenyl-2,3-epoxy-3-4′-methoxyphenylpropanone (4g)——A colorless oil, Rf 0.48. Yield, 78%. IR ($CHCl_3$): 1682 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 3.94, 3.87 (each 1H, d, J= 1.8 Hz, 2- and 3-H's). MS Calcd for $C_{20}H_{22}O_7$: M, 374.137. Found m/z: M^+, 374.137.

1-6″-Benzyloxy-2″-methoxymethoxyphenyl-2,3-epoxy-3-4′-methoxyphenylpropanone (4h)——A colorless oil, Rf 0.57. Yield, 94%. IR ($CHCl_3$): 1694 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 3.94, 3.86 (each 1H, d, J=1.8 Hz, 2- and 3-H's). MS Calcd for $C_{25}H_{24}O_6$: M, 420.154. Found m/z: M^+, 420.156.

Reactions of 2″-Methoxymethoxychalcone Epoxides 4a, 4b and 4c

***trans*-4′-Hydroxyflavanonol (5a)**——A solution of **4a** (86.3 mg, 0.26 mmol) in 10% methanolic HCl (0.4 ml) was stirred at 50 °C for 20 min. The reaction mixture was concentrated *in vacuo*, and the residue was purified by prep TLC (silica gel, $CHCl_3$: MeOH = 10 : 1) to yield **5a** (41.5 mg, 65%) as colorless needles of mp 236—238 °C (MeOH), Rf 0.62. IR (KBr): 3400 (OH), 1690 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) (acetone-d_6) δ: 8.43 (1H, s, 4′-OH),[10] 7.85 (1H, dd, J=7.8, 1.8 Hz, 5-H), 7.70—7.46 (1H, m, 7-H), 7.45 (2H, d, J=8.4 Hz, 2′- and 6′-H's), 7.20—6.80 (2H, m, 6- and 8-H's), 6.90 (2H, d, J=8.4 Hz, 3′- and 5′-H's), 5.13 (1H, d, J=12 Hz, 2-H), 4.68 (1H, dd, J=12, 3.6 Hz, 3-H),[11] 4.42 (1H, d, J=3.6 Hz, 3-OH).[10] MS Calcd for $C_{15}H_{12}O_4$: M, 256.074. Found m/z: M^+, 256.074.

***trans*-4′-Hydroxy-5-methoxyflavanonol (5b)**——Colorless needles of mp 203—205 °C (acetone), Rf 0.47. Yield, 68%. This compound was shown to be identical with an authentic sample[1] by direct comparison.

***trans*-5-Benzyloxy-4′-hydroxyflavanonol (5c)**——Colorless needles of mp 176—178 °C (MeOH), Rf 0.34. Yield, 51%. This compound was shown to be identical with an authentic sample[1] by direct comparison.

Reactions of 2″-Methoxymethoxychalcone Epoxides 4d and 4e

***trans*-4′-Methoxyflavanonol (5d) and 2-Hydroxy-1-2″-hydroxyphenyl-3-methoxy-3-4′-methoxyphenylpropanone (6a)**——A solution of **4d** (102.5 mg, 0.32 mmol) in 10% methanolic HCl (0.4 ml) was stirred at 50 °C for 20 min. Work-up of the reaction mixture and purification of the products by prep TLC (silica gel, acetone : benene = 1 : 10) afforded **5d** (10.7 mg, 12%), Rf 0.62 and **6a** (36.5 mg, 37%), Rf 0.57.

Flavanonol **5d**: Colorless needles of mp 175—177 °C (ether). IR ($CHCl_3$): 3500 (OH), 1688 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 7.93 (1H, dd, J=7.8, 1.8 Hz, 5-H), 7.64—7.41 (1H, m, 7-H), 7.51 (2H, d, J=9 Hz, 2′- and 6′-H's), 7.18—6.81 (2H, m, 6- and 8-H's), 7.00 (2H, d, J=9 Hz, 3′- and 5′-H's), 5.09 (1H, d, J=12 Hz, 2-H), 4.62 (1H, d, J=12 Hz, 3-H), 3.84 (3H, s, 4′-OMe), 3.62 (1H, s, 3-OH).[10] MS Calcd for $C_{16}H_{14}O_4$: M, 270.089. Found m/z: M^+, 270.090.

Glycol Monomethyl Ether **6a**: A colorless oil. IR ($CHCl_3$): 3504 (OH), 1630 cm^{-1} (C=O). ^{1}H-NMR (400 MHz) ($CDCl_3$) δ: 11.72, 11.61 (each 1H, s, 2″-OH),[10] 7.79, 7.68 (each 1H, dd, J=8.5, 1.2 Hz, 6″-H), 7.52, 7.51 (each 2H, dt, J=1.2, 8.5 Hz, 4″- and 5″-H's), 7.27—6.83 (10H, m, aromatic H's), 5.35 (1H, dd, J=8.5, 5 Hz), 5.18 (1H, dd, J= 7.5, 3.5 Hz) (2-H),[11] 4.55 (1H, d, J=3.5 Hz), 4.47 (1H, d, J=5 Hz) (3-H), 3.80, 3.79 (each 3H, s, 4′-OMe), 3.66 (1H, d, J=7.5 Hz), 3.32 (1H, d, J=8.5 Hz) (2-OH),[10] 3.23, 3.16 (each 3H, s, 3-OMe). MS Calcd for $C_{17}H_{18}O_5$: M, 302.115. Found m/z: M^+, 302.115.

***trans*-5-Hydroxy-4′-methoxyflavanonol (5e)**——Colorless needles of mp 179—181 °C (EtOH), Rf 0.61 ($CHCl_3$: MeOH = 10 : 1). Yield, 31%. IR ($CHCl_3$): 3520, 3200 (OH), 1644 cm^{-1} (C=O). ^{1}H-NMR (90 MHz) ($CDCl_3$) δ: 10.91 (1H, s, 5-OH),[10] 7.48 (2H, d, J=9 Hz, 2′- and 6′-H's), 7.41 (1H, t, J=8.4 Hz, 7-H), 6.96 (2H, d, J=9 Hz, 3′- and 5′-H's), 6.57, 6.45 (each 1H, dd, J=8.4, 0.9 Hz, 6- and 8-H's), 5.07 (1H, d, J=12 Hz, 2-H), 4.59 (1H, d, J=12 Hz, 3-H), 3.82 (3H, s, 4′-OMe), 3.44 (1H, s, 3-OH).[10] MS Calcd for $C_{16}H_{14}O_5$: M, 286.084. Found m/z: M^+, 286.084.

1-2″,6″-Dihydroxyphenyl-2-hydroxy-3-methoxy-3-4′-methoxyphenylpropanone (6b-I)——Colorless needles of mp 158—161 °C ($CHCl_3$), Rf 0.42 ($CHCl_3$: MeOH = 10 : 1). Yield, 20%. IR ($CHCl_3$): 3518, 3185 (OH), 1626 cm^{-1} (C=O). ^{1}H-NMR (400 MHz) (acetone-d_6) δ: 11.20 (2H, s, 2″- and 6″-OH's),[10] 7.40 (2H, d, J=8.5 Hz, 2′- and 6′-H's), 7.37 (1H, t, J=8 Hz, 4″-H), 6.90 (2H, d, J=8.5 Hz, 3′- and 5′-H's), 6.53 (2H, d, J=8 Hz, 3″- and 5″-H's), 5.39

(1H, d, J=2.5 Hz, 2-H), 4.73 (1H, d, J=2.5 Hz, 3-H), 3.79 (3H, s, 4′-OMe), 3.02 (3H, s, 3-OMe). No 2-hydroxyl proton signal was observed. ^{13}C-NMR (acetone-d_6) δ:[12] 205.55 (Sm, C-1),[13] 162.17 (Sbrd, J=11 Hz, C-2″ and -6″), 159.63 (Sm, C-4′), 137.22 (Ds, J=160 Hz, C-4″), 129.41 (Sm, C-1′), 129.00 (Ddd, J=159, 7, 4.5 Hz, C-2′ and -6′), 113.51 (Dd, J=159, 4.5 Hz, C-3′ and -5′), 108.43 (Sm, C-1″), 108.20 (Dd, J=163, 7 Hz, C-3″ and -5″), 82.95 (Dm, J=145 Hz, C-3), 80.16 (Dd, J=154, 3.5 Hz, C-2), 56.68 (Qd, J=143, 4 Hz, 3-OMe), 54.85 (Qs, J=144 Hz, 4′-OMe). MS *m/z*: 286.085 (286.084 for M−MeOH). *Anal.* Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.39; H, 5.65.

Diastereoisomer 6b-II——A colorless oil, *Rf* 0.33 ($CHCl_3$: MeOH = 10 : 1). Yield, 8%. IR ($CHCl_3$): 3508, 3148 (OH), 1622 cm^{-1} (C=O). ^{1}H-NMR (400 MHz) (acetone-d_6) δ: 11.25 (2H, s, 2″- and 6″-OH's),[10] 7.37 (1H, t, J=8 Hz, 4″-H), 7.12 (2H, d, J=8.5 Hz, 2′- and 6′-H's), 6.85 (2H, d, J=8.5 Hz, 3′- and 5′-H's), 6.50 (2H, d, J=8 Hz, 3″- and 5″-H's), 5.69 (1H, d, J=4.8 Hz, 2-H), 4.59 (1H, d, J=4.8 Hz, 3-H), 3.78 (3H, s, 4′-OMe), 3.19 (3H, s, 3-OMe). No 2-hydroxyl proton signal was observed. ^{13}C-NMR (acetone-d_6) δ:[12] 205.55 (Sm, C-1),[13] 162.16 (Sbrd, J=10.5 Hz, C-2″ and -6″), 159.85 (Sm, C-4′), 137.40 (Ds, J=159 Hz, C-4″), 129.55 (Sm, C-1′), 129.38 (Ddd, J=158, 7, 4.5 Hz, C-2′ and -6′), 113.43 (Dd, J=159, 4.5 Hz, C-3′ and -5′), 109.80 (Sm, C-1″), 108.20 (Dd, J=163, 7.5 Hz, C-3″ and -5″), 84.50 (Dm, J=143 Hz, C-3), 78.40 (Dd, J=154, 2.5 Hz, C-2), 56.03 (Qd, J=141, 4 Hz, 3-OMe), 54.80 (Qs, J=144 Hz, 4′-OMe). MS *m/z*: 286.085 (286.084 for M−MeOH). *Anal.* Calcd for $C_{17}H_{18}O_6 \cdot 3/4H_2O$: C, 61.53; H, 5.92. Found: C, 61.62; H, 5.90.

Reactions of 2″-Methoxymethoxychalcone Epoxides 4f, 4g and 4h

2-Hydroxy-1-2″-hydroxy-6″-methoxyphenyl-3-methoxy-3-4′-methoxyphenylpropanones (6c-I and 6c-II)——A solution of **4f** (85.2 mg, 0.25 mmol) in 10% methanolic HCl (0.5 ml) was stirred at 50 °C for 15 min. Work-up of the reaction mixture and purification of the products by prep TLC (silica gel, acetone : benzene = 1 : 5) gave **6c-I** (42.7 mg, 52%), *Rf* 0.30, and **6c-II** (18.0 mg, 22%), *Rf* 0.15.

Glycol Monomethyl Ether **6c-I**: Colorless needles of mp 122.5—124 °C (EtOH). IR ($CHCl_3$): 3536 (OH), 1624 cm^{-1} (C=O). ^{1}H-NMR (400 MHz) ($CDCl_3$) δ: 12.51 (1H, s, 2″-OH),[10] 7.43 (1H, t, J=8.5 Hz, 4″-H), 7.36 (2H, d, J=8.5 Hz, 2′- and 6′-H's), 6.93 (2H, d, J=8.5 Hz, 3′- and 5′-H's), 6.67 (1H, dd, J=8.5, 1.2 Hz, 3″-H), 6.47 (1H, dd, J=8.5, 1.2 Hz, 5″-H), 5.35 (1H, dd, J=9, 1.2 Hz, 2-H),[11] 4.47 (1H, d, J=1.2 Hz, 3-H), 3.95 (3H, s, 6″-OMe), 3.85 (1H, d, J=9 Hz, 2-OH),[10] 3.82 (3H, s, 4′-OMe), 3.06 (3H, s, 3-OMe). ^{13}C-NMR ($CDCl_3$) δ:[12] 204.55 (Sm, C-1), 164.81 (Sddd, J=11, 5, 2 Hz, C-2″), 160.67 (Sdq, J=10, 5 Hz, C-6″), 159.46 (Sm, C-4′), 136.87 (Ds, J=160 Hz, C-4″), 130.55 (Stt, J=7, 2 Hz, C-1′), 128.63 (Ddd, J=158, 9, 5 Hz, C-2′ and -6′), 113.75 (Dd, J=159, 5 Hz, C-3′ and -5′), 111.55 (Dt, J=164, 8 Hz, C-3″), 108.92 (Sq, J=5 Hz, C-1″), 101.51 (Dd, J=162, 8 Hz, C-5″), 82.79 (Dm, J=142 Hz, C-3), 79.89 (Dd, J=155, 3.5 Hz, C-2), 57.26 (Qd, J=142, 4 Hz, 3-OMe), 55.76 (Qs, J=145 Hz, 6″-OMe), 55.28 (Qs, J=144 Hz, 4′-OMe). MS *m/z*: 300.100 (300.100 for M−MeOH). *Anal.* Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 64.97; H, 5.99.

Diastereoisomer **6c-II**: Colorless needles of mp 84—86.5 °C (EtOH). IR ($CHCl_3$): 3508 (OH), 1622 cm^{-1} (C=O). ^{1}H-NMR (400 MHz) ($CDCl_3$) δ: 12.12 (1H, s, 2″-OH),[10] 7.43 (1H, t, J=8.5 Hz, 4″-H), 6.97 (2H, d, J=9 Hz, 2′- and 6′-H's), 6.79 (2H, d, J=9 Hz, 3′- and 5′-H's), 6.63 (1H, dd, J=8.5, 1.2 Hz, 3″-H), 6.44 (1H, dd, J=8.5, 1.2 Hz, 5″-H), 5.76 (1H, dd, J=9, 2.8 Hz, 2-H),[11] 4.50 (1H, d, J=2.8 Hz, 3-H), 3.96 (3H, s, 6″-OMe), 3.77 (3H, s, 4′-OMe), 3.39 (1H, d, J=9 Hz, 2-OH),[10] 3.32 (3H, s, 3-OMe). ^{13}C-NMR ($CDCl_3$) δ:[12] 203.59 (Sm, C-1), 164.39 (Sddd, J=11, 5, 2 Hz, C-2″), 160.88 (Sdq, J=10, 4 Hz, C-6″), 159.44 (Sm, C-4′), 137.18 (Ds, J=160 Hz, C-4″), 128.84 (Dm, J=161 Hz, C-2′ and -6′), 127.42 (Sddt, J=2, 3, 7 Hz, C-1′), 113.35 (Dd, J=161, 7 Hz, C-3′ and -5′), 111.21 (Dt, J=165, 7 Hz, C-3″), 109.71 (Sq, J=5 Hz, C-1″), 101.53 (Dd, J=162, 8 Hz, C-5″), 84.28 (Dm, J=142 Hz, C-3), 79.17 (Dd, J=157, 3.5 Hz, C-2), 57.02 (Qd, J=142, 4 Hz, 3-OMe), 55.67 (Qs, J=146 Hz, 6″-OMe), 55.16 (Qs, J=145 Hz, 4′-OMe). MS *m/z*: 300.100 (300.100 for M−MeOH). *Anal.* Calcd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 64.97; H, 6.07.

1-4″,6″-Dimethoxy-2″-hydroxyphenyl-2-hydroxy-3-methoxy-3-4′-methoxyphenylpropanone (6d-I)——Colorless needles of mp 142—144 °C (MeOH), *Rf* 0.31. Yield, 35%. IR ($CHCl_3$): 3536, 3220 (OH), 1616 cm^{-1} (C=O). ^{1}H-NMR (400 MHz) ($CDCl_3$) δ: 13.32 (1H, s, 2″-OH),[10] 7.36 (2H, d, J=8.5 Hz, 2′- and 6′-H's), 6.93 (2H, d, J=8.5 Hz, 3′- and 5′-H's), 6.15 (1H, d, J=2.2 Hz, 3″-H), 6.00 (1H, d, J=2.2 Hz, 5″-H), 5.27 (1H, dd, J=9.5, 1.2 Hz, 2-H),[11] 4.44 (1H, d, J=1.2 Hz, 3-H), 3.90 (1H, d, J=9.5 Hz, 2-OH),[10] 3.90 (3H, s, 6″-OMe), 3.85 (3H, s, 4″-OMe), 3.82 (3H, s, 4′-OMe), 3.08 (3H, s, 3-OMe). ^{13}C-NMR ($CDCl_3$) δ:[12] 202.27 (Sm, C-1), 167.85 (Sdd, J=5, 3.5 Hz, C-2″), 166.72 (Sm, C-4″), 162.09 (Sdq, J=3, 4 Hz, C-6″), 159.33 (Sm, C-4′), 130.83 (Sddt, J=1.5, 2.5, 7.5 Hz, C-1′), 128.60 (Ddd, J=161, 7, 4 Hz, C-2′ and -6′), 113.67 (Dd, J=159, 5 Hz, C-3′ and -5′), 103.38 (Sq, J=5 Hz, C-1″), 94.18 (Ddd, J=163, 7.5, 4 Hz, C-3″), 91.35 (Dd, J=162, 5 Hz, C-5″), 83.02 (Dm, J=142 Hz, C-3), 78.98 (Dd, J=152, 3.5 Hz, C-2), 57.25 (Qd, J=142, 4 Hz, 3-OMe), 55.68 (Qs, J=145 Hz, 6″-OMe), 55.65 (Qs, J=146 Hz, 4″-OMe), 55.26 (Qs, J=144 Hz, 4′-OMe). MS *m/z*: 330.111 (330.111 for M−MeOH). *Anal.* Calcd for $C_{19}H_{22}O_7$: C, 62.98; H, 6.12. Found: C, 62.76; H, 6.08.

Diastereoisomer 6d-II——Colorless needles of mp 124—125 °C (MeOH), *Rf* 0.19. Yield, 11%. IR ($CHCl_3$): 3512 (OH), 1618 cm^{-1} (C=O). ^{1}H-NMR (400 MHz) ($CDCl_3$) δ: 12.91 (1H, s, 2″-OH),[10] 7.00 (2H, d, J=8.8 Hz, 2′- and 6′-H's), 6.80 (2H, d, J=8.8 Hz, 3′- and 5′-H's), 6.12 (1H, d, J=2.2 Hz, 3″-H), 5.99 (1H, d, J=2.2 Hz, 5″-H), 5.69 (1H, dd, J=8.8, 2.8 Hz, 2-H),[11] 4.47 (1H, d, J=2.8H, 3-H), 3.94 (3H, s, 6″-OMe), 3.87 (3H, s, 4″-OMe), 3.78 (3H, s, 4′-OMe), 3.41 (1H, d, J=8.8 Hz, 2-OH),[10] 3.32 (3H, s, 3-OMe). ^{13}C-NMR ($CDCl_3$) δ:[12] 201.13 (St, J=4 Hz, C-1), 167.45 (St, J=4 Hz, C-2″), 167.08 (Sm, C-4″), 162.31 (Squint, J=4 Hz, C-6″), 159.38 (Sm, C-4′), 128.92 (Ddd, J=

158, 7.4 Hz, C-2′ and -6′), 127.56 (Sddt, C-2, 4, 7.5 Hz, C-1′), 113.30 (Ddd, $J=157$, 7, 3 Hz, C-3′ and -5′), 104.23 (Sq, $J=5$ Hz, C-1″), 93.99 (Ddd, $J=163$, 7.5, 5 Hz, C-3″), 91.35 (Dd, $J=162$, 5 Hz, C-5″), 84.45 (Dm, $J=142$ Hz, C-3), 78.36 (Dd, $J=156$, 3.5 Hz, C-2), 57.00 (Qd, $J=142$, 4 Hz, 3-OMe), 55.72 (Qs, $J=145$ Hz, 4″-OMe), 55.61 (Qs, $J=146$ Hz, 6″-OMe), 55.16 (Qs, $J=144$ Hz, 4′-OMe). MS *m/z*: 330.111 (330.111 for M−MeOH). *Anal.* Calcd for $C_{19}H_{22}O_7$: c, 62.98; H, 6.12. Found: C, 63.21; H, 6.06.

1-6″-Benzyloxy-2″-hydroxyphenyl-2-hydroxy-3-methoxy-3-4′-methoxyphenylpropanone (6e)——Colorless needles of mp 130—131 °C (MeOH), *Rf* 0.60. Yield, 85%. IR ($CHCl_3$): 3504 (OH), 1622 cm^{-1} (C=O). IR ($c=1\times10^{-3}$ mol/l, CCl_4) (ε): 3512 (63), 3200 (38) cm^{-1}. ^{1}H-NMR (400 MHz) ($CDCl_3$) δ: 12.24 (1H, s, 2″-OH),10) 7.42—7.37 (6H, m, 4″-H and 6″-$OCH_2\underline{Ph}$), 6.97 (2H, d, $J=8$ Hz, 2′- and 6′-H), 6.72 (2H, d, $J=8$ Hz, 3′- and 5′-H's), 6.69 (1H, dd, $J=8$, 2 Hz, 3″-H), 6.57 (1H, dd, $J=8$, 2 Hz, 5″-H), 5.38 (1H, dd, $J=8$, 2.4 Hz, 2-H),11) 5.23, 5.21 (each 1H, d, $J=11$ Hz, 6″-$O\underline{CH_2}Ph$), 4.52 (1H, d, $J=2.4$ Hz, 3-H), 3.81 (1H, d, $J=8$ Hz, 2-OH),10) 3.77 (3H, s, 4′-OMe), 3.02 (3H, s, 3-OMe). ^{13}C-NMR ($CDCl_3$) δ12): 204.50 (Sm, C-1), 164.36 (Sddd, $J=11$, 5, 2 Hz, C-2″), 159.80 (Sdt, $J=10$, 1 Hz, C-6″), 159.03 (Sm, C-4′), 136.61 (Ds, $J=160$ Hz, C-4″), 135.10 (Sm), 128.97 (2) (Dm, $J=161$ Hz), 128.78 (Dm, $J=161$ Hz), 128.01 (2) (Dm, $J=157$ Hz) (6″-$OCH_2\underline{Ph}$), 129.74 (Sm, C-1′), 128.28 (Ddd, $J=158$, 8, 4 Hz, C-2′ and -6′), 113.48 (Dd, $J=158$, 5 Hz, C-3′ and -5′), 111.64 (Dt, $J=165$, 8 Hz, C-3″), 109.42 (Sq, $J=5$ Hz, C-1″), 102.94 (Dd, $J=162$, 8 Hz, C-5″), 82.84 (Dm, $J=143$, C-3), 79.79 (Dd, $J=155$, 3.5 Hz, C-2), 71.66 (Tt, $J=145$, 4.5 Hz, 6″-$O\underline{C}H_2Ph$), 57.38 (Qd, $J=141$, 4 Hz, 3-OMe), 55.17 (Qs, $J=143$ Hz, 4′-OMe). MS *m/z*: 376.131 (376.131 for M−MeOH). *Anal.* Calcd for $C_{24}H_{24}O_6$: C, 70.57; H, 5.92. Found: C, 70.82; H, 5.84.

3-Chloro-2-hydroxy-1-2″-hydroxy-6″-methoxyphenyl-3-4′-methoxyphenylpropanone (7)——A solution of **4f** (65.1 mg, 0.19 mmol) in 10% HCl–dioxane (0.4 ml) was stirred at 3 °C for 10 min. Work-up of the reaction mixture and purification of the products by prep TLC (silica gel, acetone : benzene = 1 : 10) afforded **7** (51.0 mg, 80%) as colorless prisms of mp 130—132 °C (MeOH), *Rf* 0.48. IR ($CHCl_3$): 3504 (OH), 1624 cm^{-1} (C=O). IR ($c=1\times10^{-3}$ mol/l, CCl_4) (ε): 3508 (66.5), 3212 (33.5) cm^{-1}. ^{1}H-NMR (400 MHz) ($CDCl_3$) δ: 12.42 (1H, s, 2″-OH),10) 7.52 (2H, d, $J=8.8$ Hz, 2′- and 6′-H's), 7.45 (1H, t, $J=8.8$ Hz, 4″-H), 6.91 (2H, d, $J=8.8$ Hz, 3′- and 5′-H's), 6.69 (1H, dd, $J=8.8$, 1.2 Hz, 3″-H), 6.46 (1H, dd, $J=8.8$, 1.2 Hz, 5″-H), 5.60 (1H, dd, $J=8.8$, 1.2 Hz, 2-H),11) 5.28 (1H, d, $J=1.2$ Hz, 3-H), 4.22 (1H, d, $J=8.8$ Hz, 2-OH),10) 3.87 (3H, s, 6″-OMe), 3.83 (3H, s, 4′-OMe). ^{13}C-NMR ($CDCl_3$) δ:12) 202.43 (Sm, C-1), 165.37 (Sddd, $J=11$, 5, 2 Hz, C-2″), 160.53 (Sm, C-6″), 159.72 (Sm, C-4′), 137.55 (Ds, $J=160$ Hz, C-4″), 131.75 (Sm, C-1′), 129.15 (Ddd, $J=159$, 7, 5 Hz, C-2′ and -6′), 113.84 (Dd, $J=159$, 5 Hz, C-3′ and -5′), 111.86 (Dt, $J=165$, 7 Hz, C-3″), 108.28 (Sq, $J=5$ Hz, C-1″), 101.51 (Dd, $J=162$, 8 Hz, C-5″), 78.58 (Ds, $J=155$ Hz, C-2), 63.50 (Dt, $J=150$, 4.5 Hz, C-3), 55.90 (Qs, $J=146$ Hz, 6′-OMe), 55.33 (Qs, $J=144$ Hz, 4′-OMe). MS *m/z*: 300.100 (300.100 for M−HCl). *Anal.* Calcd for $C_{17}H_{17}ClO_5$: C, 60.63; H, 5.07. Found: C, 60.54; H, 5.09.

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References and Notes

1) Part XIX: H. Takahashi, Y. Kubota, L. Fang, and M. Onda, *Heterocycles*, **24**, 1099 (1986).
2) The IR data for related compounds ($c=1\times10^{-3}$ mol/l, CCl_4): 2-hydroxyacetophenone, 3208 cm^{-1} (ν_b, $\varepsilon=21$); 2,6-dihydroxyacetophenone, 3588 (ν_f, $\varepsilon=120$), 3296 cm^{-1} (ν_b, $\varepsilon=26$); 2-hydroxy-6′-methoxyacetophenone, 3204 cm^{-1} (ν_b, $\varepsilon=20$).
3) A. Gaudemer, "Stereochemistry," Vol. 1, ed. by H. B. Kagan, Georg Thieme Publishers, Stuttgart, 1977, p. 44.
4) H. Takahashi, Y. Kubota, H. Miyazaki, and M. Onda, *Heterocycles*, **22**, 1147 (1984).
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7) K. Nakazawa, *Yakugaku Zasshi*, **59**, 495 (1935).
8) A. D. Patiland and V. H. Deshpande, *Indian J. Chem.*, **22B**, 109 (1983).
9) S. Bülow, *Chem. Ber.*, **58**, 1694 (1925).
10) On addition of deuterium oxide, these signals disappeared.
11) On addition of deuterium oxide, these splittings changed to doublets due to the disappearance of the hydroxyl protons.
12) Capital and small letters refer to one-bond and long-range couplings observed in the gated decoupled spectra, respectively.
13) These signals overlapped with that of carbonyl carbon of the solvent.