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Synthesis of 6- and 8-Phenyl-substituted Flavonoids

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3-Acetylbiphenyl-4-ol and -2-ol were condensed with substituted benzaldehydes to give respectively 5′- and 3′-phenyl-substituted chalcones (**1a**—**k**), which were cyclized to afford 6- and 8-phenylflavanones. The chalcones (**1a**—**k**) also gave the corresponding 6- and 8-phenylflavones *via* dibromides. The effects of the phenyl group on the spectral data are also discussed.

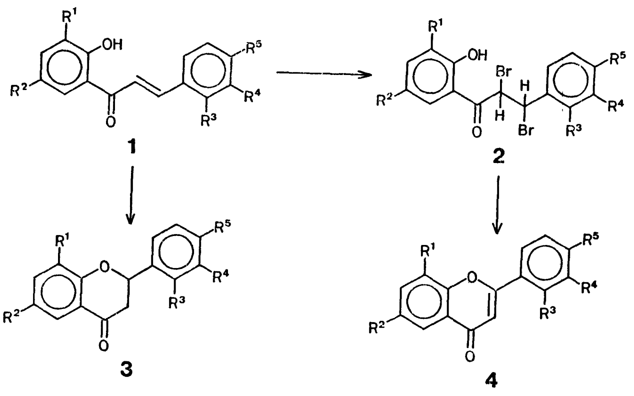
Flavonoids are well-known as the main constituent of yellow pigments of plant and possess many pharmacological actions. These flavonoids occur as hydroxy or methoxy-substituted compounds or glucosides. On the other hand, compounds having alkyl, halogen, amino, or nitro group have been obtained in synthetic materials. However, phenyl-substituted flavonoids have not been found in nature and in synthetic materials, except for a few reports.[1–3] One of them described synthesis of 5′-phenylchalcones[1] and the others described synthesis of 4-phenylchalcones[2] and 4′-phenyl-substituted flavanones and flavones.[3]

In this paper, we wish to report the synthesis of 5′- and 3′-phenylchalcones and the corresponding 6- and 8-phenyl-substituted flavanones and flavones.

Results and Discussion

The starting materials, 3-acetylbiphenyl-4-ol and -2-ol, were already prepared from biphenyl-4-ol and -2-ol by their *O*-acetylation and Fries rearrangement.[4] When Nencki-type reaction with boron trifluoride–acetic acid complex was applied to biphenyl-4-ol, 3-acetylbiphenyl-4-ol was easily obtained in one step and in good yield. However, the preparation of 3-acetylbiphenyl-2-ol by this method was failed.

These 3-acetylbiphenyl-4-ol and -2-ol were condensed with substituted benzaldehydes to give 2′-hydroxy-5′-phenylchalcones (**1a**—**h**) and 2′-hydroxy-3′-phenylchalcones (**1i**—**k**) in good yields, except for **1e** (16%) and **1h** (20%). The spectral data are summarized in Table 1. The IR spectra show the carbonyl absorption at 1635—1645 cm^{-1}. The UV spectra of **1a** and **1i** are shown in Fig. 1, together with the spectrum of the parent 2′-hydroxychalcone [λ (CH_3OH):[5] 221 (log ε 4.11) and 316 nm (4.36)]. The phenyl group at the 3′- and 5′-positions of **1a** and **1i** shows no appreciable effect because the phenyl group exists at the *meta* position against the cinnamoyl group. Substituents in the B ring caused bathochromic shift of the maximum of absorption band at *ca.* 320 nm of **1a** and **1i** to 330—390 nm. Particularly, the spectrum of a red colored compound **1d** showed maximum of absorption bands at 260 and 437 nm. In the NMR spectra of all the chalcones (**1a**—**k**), the signal for the hydrogen-bonded 2′-OH group was found at δ *ca.* 13.



	R¹	R²	R³	R⁴	R⁵
a	H	Ph	H	H	H
b	H	Ph	H	H	CH_3
c	H	Ph	H	H	OCH_3
d	H	Ph	H	H	$N(CH_3)_2$
e	H	Ph	OH	H	H
f	H	Ph	H	Cl	H
g	H	Ph	H	H	Cl
h	H	Ph	H	OCH_3	OH
i	Ph	H	H	H	H
j	Ph	H	H	H	CH_3
k	Ph	H	H	H	OCH_3

Scheme 1.

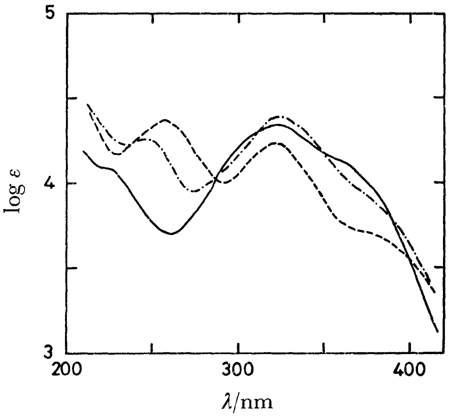


Fig. 1. UV Spectra of chalcones.
——: 2′-Hydroxychalcone, ----: **1a**, —·—·—: **1i**.

The bromination of the chalcones (**1a**—**k**) gave the corresponding their dibromides, 2′-hydroxy-5′- and 3′-phenylchalcone dibromides (**2a**—**k**), whose results are

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TABLE 1. CHARACTERISTICS FOR THE CHALCONES (**1**)

Compd	Reaction time h	Appearance	Yield %	Mp θ_m/°C	IR (KBr) $\nu_{C=O}$/cm^{-1}	UV (CH_3OH) λ/nm(log ε)	NMR ($CDCl_3$) δ	Formula	Found(Calcd) (%) C	H	N
1a	3	Yellow needles	73	116.5—117.5 (116—117)[a]	1645	255(4.21) 318(4.35)	7.0—8.1(m, 15H), 12.90(s, 1H, OH)	$C_{21}H_{16}O_2$	84.01 (83.98	5.33 5.37)	
1b	20	Yellow needles	95	128.5—129 (122—123)[a]	1640	255(4.44) 330(4.36)	2.49(s, 3H, CH_3), 7.0—7.8 (m, 12H) 8.00(d, 1H, J=2.0 Hz, 6′-H) 8.22(d, 1H, J=15.5 Hz, β-H) 12.73(s, 1H, OH)	$C_{22}H_{18}O_2$	83.99 (84.05	5.63 5.77)	
1c	1/6	Yellowish orange needles	82	148.5—149 (127—128)[a]	1640	254(4.54) 361(4.40)	3.80(s, 3H, OCH_3), 6.86(dm, 2H, J=9.0 Hz, 3,5-H), 7.0—8.0(m, 10H) 7.88(d, 1H, J=14.0 Hz, β-H) 7.97(d, 1H, J=2.0 Hz, 6′-H) 12.86(s, 1H, OH)	$C_{22}H_{18}O_3$	79.78 (79.98	5.34 5.49)	
1d	1	Red prisms	90	161.5—162 (160—161)[a]	1635	260(4.52) 437(4.40)	2.93(s, 6H, N-CH_3×2), 6.63 (d, 2H, J=9.5 Hz, 3,5-H), 7.02(d, 1H, J=8.0 Hz, 3′-H), 7.2—7.9(m, 9H) 7.92(d, 1H, J=14.5 Hz, β-H) 8.02(d, 1H, J=2.5 Hz, 6′-H) 13.12(s, 1H, OH)	$C_{23}H_{21}O_2N$	80.50 (80.44	6.03 6.16	4.02 4.08)
1e	5	Yellowish orange needles	16	189.5—191	1640	258(4.41) 314(4.00) 378(4.07)	3.18(br.s, 1H, OH)[b], 1.7—8.1(m, 13H), 8.09(d, 1H, J=2.5 Hz, 6′-H) 12.86(s, 1H, OH)	$C_{21}H_{16}O_3$	80.01 (79.73	5.07 5.10)	
1f	1/12	Orange needles	48	100.5—101.5	1640	258(4.44) 313(4.37)	6.84(d, 1H, J=8.0 Hz, 3′-H) 7.0—8.0(m, 12H), 7.89(d, 1H, J=2.5 Hz, 6′-H), 13.17(s, 1H, OH)	$C_{21}H_{15}O_2Cl$	75.61 (75.33	4.39 4.52)	
1g	1/12	Yellow needles	95	135.5—136 (135—136)[a]	1640	258(4.44) 326(4.42)	7.01(d, 1H, J=9.5 Hz, 3′-H) 7.2—7.95(m, 11H), 7.84(d, 1H, J=14.5 Hz, β-H), 7.93(d, 1H, J=2.5 Hz, 6′-H), 12.64(s, 1H, OH)	$C_{21}H_{15}O_2Cl$	75.35 (75.33	4.53 4.52)	
1h	24	Yellowish orange needles	20	157—158	1645	258(4.52) 384(4.40)	3.91(s, 3H, OCH_3), 6.02(s, 1H, 4-OH) 6.88(d, 1H, J=8.5 Hz, 3′-H) 7.0—7.7(m, 10H), 7.89(d, 1H, J=14.0 Hz, β-H), 7.99(d, 1H, J=2.5 Hz, 6′-H), 12.88(s, 1H, OH)	$C_{22}H_{18}O_4$	76.16 (76.28	5.16 5.24)	
1i	3	Yellow scales	90	103—104	1640	240(4.26) 322(4.45)	6.8—8.2(m, 15H), 13.30(s, 1H, OH)	$C_{21}H_{16}O_2$	83.93 (83.98	5.20 5.37)	
1j	1	Yellow scales	86	120—121	1645	244(4.29) 335(4.45)	2.35(s, 3H, CH_3), 6.8—8.1(m, 14H) 13.28(s, 1H, OH)	$C_{22}H_{18}O_2$	83.88 (84.05	5.66 5.77)	
1k	1/6	Yellow needles	88	134.5—136	1635	248(4.36) 366(4.48)	3.83(s, 3H, OCH_3), 6.87(d, 2H, J=8.0 Hz, 3,5-H), 6.7—8.1(m, 12H) 13.41(s, 1H, OH)	$C_{22}H_{18}O_3$	79.95 (79.98	5.57 5.49)	

a) Ref. 1. b) In DMSO-d_6.

TABLE 2. CHARACTERISTICS FOR THE CHALCONE DIBROMIDES (**2**)

Compd	Appearance	Yield %	Mp θ_m/°C	IR (KBr) $\nu_{C=O}$/cm^{-1}	Formula	Found(Calcd) (%) C	 H
2a	Yellow crystals	65	178—179	1635	$C_{21}H_{16}O_2Br_2$	55.03 (54.81	4.48 3.51)
2b	Yellow crystals	65	184—185	1635	$C_{22}H_{18}O_2Br_2$	55.68 (55.72	3.81 3.83)
2c	Yellow prisms	100	150—152	1635	$C_{22}H_{18}O_3Br_2$	54.12 (53.90	3.61 3.70)
2e	Brown microcrystals	82	140.5(decomp)	1635	$C_{21}H_{16}O_3Br_2$	53.21 (52.97	3.43 3.39)
2f	Yellow crystals	97	160—162	1640	$C_{21}H_{15}O_2Br_2Cl$	50.80 (50.99	3.15 3.06)
2g	Yellow crystals	84	192—193	1630	$C_{21}H_{15}O_2Br_2Cl$	51.21 (50.99	3.22 3.06)
2h	Pale yellow crystals	51	136(decomp)	1630	$C_{22}H_{18}O_4Br_2$	51.98 (52.20	3.66 3.58)
2i	Pale yellow microcrystals	69	207—210	1640	$C_{21}H_{16}O_2Br_2$	55.08 (54.81	3.45 3.51)
2j	Yellow microcrystals	79	205—206	1640	$C_{22}H_{18}O_2Br_2$	55.51 (55.72	3.83 3.83)
2k	Pale yellow needles	86	173—174	1645	$C_{22}H_{18}O_3Br_2$	53.74 (53.90	3.72 3.70)

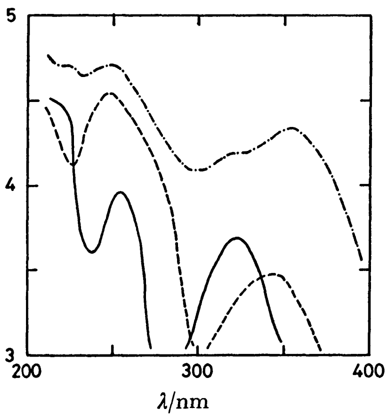

Fig. 2. UV Spectra of flavanones.
——: Flavanone, ----: **3a**, —·—·—: **3i**.

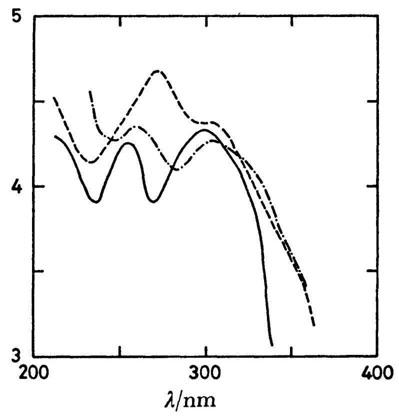

Fig. 3. UV Spectra of flavones.
——: Flavone, ----: **4a**, —·—·—: **4i**.

listed in Table 2. The compound **2d** was not isolated as crystal form and used for the flavone synthesis in this semisolid state.

The chalcones (**1a**—**k**) in acetone–ethanol were refluxed for 2 h in the presence of alkali to cyclize to 6- and 8-phenylflavanones (**3a**—**k**). The characteristic data are summarized in Table 3. In the IR spectra, the carbonyl absorptions were observed at 1705—1710 cm^{-1}, except for **3e** (1670 cm^{-1}). The UV spectra of 6- and 8-phenylflavanones (**3a** and **3i**) are shown in Fig. 2, together with the spectrum of flavanone itself [λ (CH$_3$OH):[5] 250 (log ε 3.86) and 320 nm (3.37)]. Introduction of the phenyl group at the 6- or 8-position produced bathochromic shifts of the absorption band at 320 nm by 15—25 nm. The NMR spectra showed the typical ABX pattern of 2-, 3e-, and 3a-protons.

The chalcone dibromides (**2a**—**k**) were treated with alkali to afford 6- and 8-phenylflavones (**4a**—**k**) in good yields. These results are summarized in Table 4. The IR spectra showed the carbonyl absorption at 1640—1650 cm^{-1}. The UV spectra of 6- and 8-phenylflavones (**4a** and **4i**) are shown in Fig. 3, together with flavone itself [λ (CH$_3$OH):[5] 250 (log ε 4.06) and 297 nm (4.20)]. The spectra of the flavones (**4a**—**k**) also showed bathochromic shifts of the absorption maximum at 300—330 nm by introduction of substituent in the B ring. Particularly, the maximum of absorption bands of the dimethylamino-substituted compound **4d** was observed at 257, 333, and 400 nm. In the NMR spectra, the 3-H protons were recorded at δ 6.6—6.8 as a sharp singlet peak.

Experimental

The melting points were determined with a Yanagimoto MP-S2 melting point-measuring apparatus and are uncorrected. The IR spectra were taken on a JASCO IRA-1

Table 3. Characteristics for the the flavanones (**3**)

Compd	Reaction time h	Appearance	Yield %	Mp θ_m/°C	IR (KBr) $\nu_{C=O}$/cm^{-1}	UV (CH$_3$OH) λ/nm(log ε)	NMR (CDCl$_3$) δ	Formula	Found(Calcd) (%) C	 H	 N
3a	24	Pale yellow prisms	30	99—100	1705	247(4.55) 345(3.34)	2.85(dd, 1H, *J*=18.0, 5.5 Hz, 3e-H) 3.00(dd, 1H, *J*=18.0, 11.0 Hz, 3a-H) 5.45(dd, 1H, *J*=11.0, 5.5 Hz, 2-H) 6.8—7.9(m, 12H) 8.09(d, 1H, *J*=2.5 Hz, 5-H)	$C_{21}H_{16}O_2$	83.69 (83.98	5.57 5.37)	
3b	7	Colorless scales	33	144—145	1710	247(4.57) 346(3.44)	2.36(s, 3H, CH$_3$) 2.90(dd, 1H, *J*=15.5, 3.5 Hz, 3e-H) 3.11(dd, 1H, *J*=15.5, 12.0 Hz, 3a-H) 5.45(dd, 1H, *J*=12.0, 3.5 Hz, 2-H) 7.10(d, 1H, *J*=8.5 Hz, 8-H) 7.1—7.7(m, 9H) 7.73(dd, 1H, *J*=8.5, 2.0 Hz, 7-H) 8.10 (d, 1H, *J*=2.0 Hz, 5-H)	$C_{22}H_{18}O_2$	83.98 (84.05	5.83 5.77)	
3c	2	Pale yellow needles	80	151—152	1710	246(4.58) 340(3.28)	2.88(dd, 1H, *J*=16.0, 5.0 Hz, 3e-H) 3.10(dd, 1H, *J*=16.0, 11.0 Hz, 3a-H) 3.78(s, 3H, OCH$_3$) 5.42(dd, 1H, *J*=11.0, 5.0 Hz, 2-H) 6.92(dm, 2H, *J*=9.0 Hz, 3′,5′-H) 7.1—7.6(m, 8H) 7.68(dd, 1H, *J*=8.5, 2.0 Hz, 7-H) 8.09(d, 1H, *J*=2.0 Hz, 5-H)	$C_{22}H_{18}O_3$	79.88 (79.98	5.57 5.49)	
3d	3	Yellow plates	48	192—192.5	1705	265(4.64) 346 sh	2.5—3.0(m, 2H, 3e, 3a-H) 2.92(s, 6H, *N*-CH$_3$×2) 5.35(dd, 1H, *J*=11.5, 5.0 Hz, 2-H) 6.64(dm, 2H, *J*=9.5 Hz, 3′,5′-H) 7.00(d, 1H, *J*=8.0 Hz, 8-H) 7.1—7.6(m, 9H) 7.65(dd, 1H, *J*=8.0, 2.0 Hz, 7-H) 8.07(d, 1H, *J*=2.0 Hz, 5-H)	$C_{23}H_{21}O_2N$	80.21 (80.44	6.24 6.16	4.18 4.08)
3e	5	Yellow crystals	46	207—208.5	1670	249(4.39) 347(3.32)	2.7—3.5(m, 2H, 3e,3a-H)$^{a)}$ 5.83(dd, 1H, *J*=10.0, 5.0 Hz, 2-H) 6.7—7.9(m, 11H) 8.01(d, 1H, *J*=2.0 Hz, 5-H) 9.67(br.s, 1H, OH)	$C_{21}H_{16}O_3$	79.62 (79.73	5.09 5.10)	
3f	2	Pale yellow crystals	19	98—100	1710	249(4.46) 340(3.28)	2.87(dd, 1H, *J*=17.5, 6.0 Hz, 3e-H) 3.03(dd, 1H, *J*=17.5, 11.0 Hz, 3a-H) 5.45(dd, 1H, *J*=11.0, 6.0 Hz, 2-H) 7.07(d, 1H, *J*=8.5 Hz, 8-H) 7.2—7.7(m, 9H) 7.72(dd, 1H, *J*=8.5, 2.0 Hz, 7-H) 8.10(d, 1H, *J*=2.0 Hz, 5-H)	$C_{21}H_{15}O_2Cl$	75.33 (75.33	4.49 4.52)	

Table 3. (Continued)

Compd	Reaction time %	Appear-ance	Yield %	Mp θ_m/°C	IR (KBr) $\nu_{C=O}$/cm^{-1}	UV (CH_3OH) λ/nm(log ε)	NMR ($CDCl_3$) δ	Formula	Found(Calcd) (%) C	 H	 N
3g	24	Yellow scales	30	150.5—151	1710	247(4.57) 346(3.23)	2.88(dd, 1H, J=15.0, 5.5 Hz, 3e-H) 3.03(dd, 1H, J=15.0, 10.0 Hz, 3a-H) 5.43(dd, 1H, J=10.0, 5.5 Hz, 2-H) 7.06(d, 1H, J=8.0 Hz, 8-H) 7.1—7.7(m, 9H) 7.68(dd, 1H, J=8.0, 2.0 Hz, 7-H) 8.08(d, 1H, J=2.0 Hz, 5-H)	$C_{21}H_{15}O_2Cl$	75.61 (75.33	4.52 4.52)	
3h	25	Pale yellow needles	42	103—104	1705	246(4.60) 345(3.46)	2.88(dd, 1H, J=16.0, 4.0 Hz, 3e-H) 2.99(dd, 1H, J=16.0, 11.0 Hz, 3a-H) 3.88(s, 3H, OCH_3) 5.37(dd, 1H, J=11.0, 4.0 Hz, 2-H) 5.74(s, 1H, OH) 6.9—7.7(m, 9H) 7.68(dd, 1H, J=8.5, 2.0 Hz, 7-H) 8.10(d, 1H, J=2.0 Hz, 5-H)	$C_{22}H_{18}O_4$	76.26 (76.28	5.31 5.24)	
3i	24	Colorless prisms	71	117.5—118.5	1705	240(4.42) 334(4.66)	2.88(dd, 1H, J=17.5, 6.5 Hz, 3e-H) 3.00(dd, 1H, J=17.5, 9.5 Hz, 3a-H) 5.44(dd, 1H, J=9.5, 6.5 Hz, 2-H) 6.9—7.7(m, 12H) 7.90(dd, 1H, J=7.5, 2.0 Hz, 5-H)	$C_{21}H_{16}O_2$	83.89 (83.98	5.44 5.37)	
3j	1	Colorless prisms	38	113—114	1705	240(4.42) 338(3.57)	2.28(s, 3H, CH_3) 2.88(dd, 1H, J=17.5, 7.0 Hz, 3e-H) 2.97(dd, 1H, J=17.5, 9.0 Hz, 3a-H) 5.41(dd, 1H, J=9.0, 7.0 Hz, 2-H) 6.93(d, 1H, J=7.0 Hz, 7-H) 6.9—7.7(m, 10H) 7.89(dd, 1H, J=7.0, 2.0 Hz, 5-H)	$C_{22}H_{18}O_2$	83.98 (84.05	5.80 5.77)	
3k	2	Pale yellow needles	23	139—140	1710	232(4.49) 336(3.57)	2.88(dd, 1H, J=18.0, 6.5 Hz, 3e-H) 3.02(dd, 1H, J=18.0, 10.0 Hz, 3a-H) 3.75(s, 3H, OCH_3) 5.43(dd, 1H, J=10.0, 6.5 Hz, 2-H) 6.80(dm, 2H, J=9.5 Hz, 3',5'-H) 7.10(d, 1H, J=9.0 Hz, 7-H) 7.2—7.7(m, 8H) 7.91(dd, 1H, J=8.5, 2.0 Hz, 5-H)	$C_{22}H_{18}O_3$	79.74 (79.98	5.41 5.49)	

a) In DMSO-d_6.

TABLE 4. CHARACTERISTICS FOR THE FLAVONES (**4**)

Compd	Appearance	Yield %	Mp θ_m/°C	IR (KBr) $\nu_{C=O}$/cm^{-1}	UV (CH_3OH) λ/nm(log ε)	NMR ($CDCl_3$) δ	Formula	Found(Calcd) (%) C	H	N
4a	Yellow prisms	86	156—157	1645	273(4.64) 304(4.32)	6.72(s, 1H, 3-H), 7.2—8.0(m, 12H) 8.32(d, 1H, J=2.0 Hz, 5-H)	$C_{21}H_{14}O_2$	84.32 (84.54	4.80 4.73)	
4b	Pale yellow needles	90	201—202	1640	275(4.58) 314(4.42)	2.40(s, 3H, CH_3), 6.76(s, 1H, 3,H) 7.1—8.0(m, 11H) 8.36(d, 1H, J=2.5 Hz, 5-H)	$C_{22}H_{16}O_2$	84.54 (84.59	5.21 5.16)	
4c	Pale yellow scales	87	181—182	1640	249(4.36) 278(4.42) 331(4.51)	3.85(s, 3H, OCH_3), 6.68(s, 1H, 3-H) 6.95(d, 2H, J=8.5 Hz, 3′,5-H) 7.2—8.1(m, 9H) 8.38(d, 1H, J=2.0 Hz, 5-H)	$C_{22}H_{16}O_3$	80.23 (80.47	4.93 4.91)	
4d	Yellow needles	81[a]	226—227	1640	257(4.58) 333(4.05) 400(4.60)	2.97(s, 6H, N-$CH_3\times2$) 6.61(s, 1H, 3-H) 6.63(dm, 2H, J=8.5 Hz, 3′,5′-H) 7.2—8.0(m, 9H) 8.38(d, 1H, J=2.0 Hz, 5-H)	$C_{23}H_{19}O_2N$	79.96 (80.91	5.41 5.61	3.91 4.10)
4e	Yellowish orange needles	60	115—117	1635	258(4.31) 318(4.12)	7.09(d, 1H, J=10.0 Hz, 8-H) 7.2—7.9(m, 11H) 8.49(d, 1H, J=2.0 Hz, 5-H) 11.80(s, 1H, OH)	$C_{21}H_{14}O_3$	80.03 (80.24	4.28 4.49)	
4f	Yellow plates	53	162—163.5	1640	273(4.67) 306 sh(4.29)	6.69(s, 1H, 3-H), 7.2—8.0(m, 11H) 8.32(d, 1H, J=2.0 Hz, 5-H)	$C_{21}H_{13}O_2Cl$	75.62 (75.79	3.95 3.94)	
4g	Plae yellow needles	25	231—232	1640	276(4.62) 310(4.39)	6.71(s, 1H, 3-H), 7.2—8.1(m, 11H) 8.33(d, 1H, J=2.0 Hz, 5-H)	$C_{21}H_{13}O_2Cl$	75.53 (75.79	3.84 3.94)	
4h	Yellow crystals	22	203—204	1645	257(4.52) 276 sh(4.36) 347(4.46)	3.94(s, 3H, OCH_3), 6.42(br.s, 1H, OH) 6.64(s, 1H, 3-H), 7.2—7.8(m, 8H) 7.83(dd, 1H, J=9.0, 2.5 Hz, 7-H) 8.40(d, 1H, J=2.5 Hz, 5-H)	$C_{22}H_{16}O_4$	77.01 (76.73	4.67 4.68)	
4i	Pale yellow needles	94	131—131.5	1640	253(4.36) 302(4.29)	6.74(s, 1H, 3-H), 7.1—8.0(m, 12H) 8.22(dm, 1H, J=8.0 Hz, 5-H)	$C_{21}H_{14}O_2$	84.65 (84.54	4.51 4.73)	
4j	Pale yellow needles	70	149—150	1650	253(4.30) 312(4.39)	2.36(s, 3H, CH_3), 6.76(s, 1H, 3-H) 7.11(dm, 2H, J=9.0 Hz, 3′,5′-H) 7.3—7.9(m, 9H) 8.15(dd, 1H, J=8.0, 2.5 Hz, 5-H)	$C_{22}H_{16}O_2$	84.70 (84.59	5.33 5.16)	
4k	Yellow needles	93	189—191	1650	225(4.50) 263 sh(4.14) 329(4.46)	3.76(s, 3H, OCH_3), 6.64(s, 1H, 3-H) 6.77(dm, 2H, J=8.5 Hz, 3′,5′-H) 7.2—7.9(m, 9H) 8.11(dd, 1H, J=7.0, 2.5 Hz, 5-H)	$C_{22}H_{16}O_3$	80.35 (80.47	4.94 4.91)	

a) Based on **1d**.

and JASCO 403G spectrophotometers, and the UV spectra on a Hitachi EPS-3T spectrophotometer. The NMR spectra were recorded with a Hitachi R-24 spectrometer (60 MHz).

3-Acetylbiphenyl-2-ol. This compound was prepared by the method of Cheetham and Hey.[4]

3-Acetylbiphenyl-4-ol. A mixture of biphynyl-4-ol (21.3 g) and boron trifluoride-acetic acid complex (50 ml) was heated on a water bath for 2 h. The mixture was treated with water and extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was recrystallized from ethanol to afford 3-acetylbiphenyl-4-ol. Yield, 16.5 g (62%). Mp 61—62.5 °C (lit,[4] 61.5—62 °C).

2′-Hydroxy-5′- or 3′-phenylchalcones (1a—k). A solution of 3-acetylbiphenyl-4-ol or -2-ol (2.1 g, 10 mmol) and substituted benzaldehyde (10 mmol) in ethanol (10 ml) was stirred at 50—60 °C in the presence of 60% potasium hydroxide solution (7.5 ml). The mixture was neutralized with 3 M hydrochloric acid ($1\ \mathrm{M}=1\ \mathrm{mol\ dm^{-3}}$) to give a precipitate of 2′-hydroxy-5′- or 3′-phenylchalcone (**1a**—**k**), which was collected and recrystallized from methanol or acetone.

2′-Hydroxy-5′- or 3′-phenylchalcone Dibromides (2a—k). A bromine (320 mg, 2 mmol) solution in carbon tetrachloride (2 ml) was added dropwise to a solution of 2′-hydroxy-5′- or 3′-phenylchalcone (**1a**—**k**) (500 mg, 1.5—1.6 mmol) in carbon tetrachloride (5 ml) at room temperature. The mixture was allowed to stand for 30 min. After evaporation of an excess of bromine and the solvent under reduced pressure, the residue was treated with benzene to afford 2′-hydroxy-5′- or 3′-phenylchalcone dibromide (**2a**—**k**).

6- and 8-Phenylflavanones (3a—k). To a solution of 2′-hydroxy-5′- or 3′-phynylchalcone (**1a**—**k**) (500 mg, 1.5—1.6 mmol) in acetone (5 ml)-ethanol (10 ml) was added 1% potassium hydroxide solution (1 ml). After refluxing for 2 h on a water bath, the reaction mixture was slightly acidified with 3 M hydrochloric acid and allowed to stand overnight at room temperature to precipitate 6- or 8-phenylflavanone (**3a**—**k**), which was collected and recrystallized from methanol or acetone.

6- and 8-Phenylflavones (4a—k). To a suspended solution of 2′-hydroxy-5′- or 3′-phenylchalcone dibromide (**2a**—**k**) (500 mg) in acetone (1 ml) was added 20% potassium hydroxide solution (1 ml) at room temperature. The mixture was diluted with water and slightly acidified with 3 M hydrochloric acid to give 6- or 8-phenylflavone (**4a**—**k**) as a precipitate, which was collected and recrystallized from methanol or acetone.

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References

1) K.-K. Hsu and T.-S. Wu, *Tai-Wan Ko Huseh*, **27**, 19 (1973).

2) K.-K. Hsu and J.-Y. Shi, *J. Chinese Chem. Soc.*, **19**, 45 (1972).

3) K.-K. Hus and J.-Y. Shi, *J. Chinese Chem. Sci.*, **20**, 51 (1973).

4) K. H. Cheetham and D. H. Hey, *J. Chem. Soc.*, **1937**, 770.

5) L. Jurd, "The Chemistry of Flavonoid Compounds," ed by T. A. Geissman, Pergamon Press, Oxford (1962), p. 107.