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Fluorometric Study on the Metal Chelates of Flavone Derivatives. III. Crystal Structures of 4′-Bromo-3-hydroxyflavone and 4′-Bromo-5-hydroxyflavone

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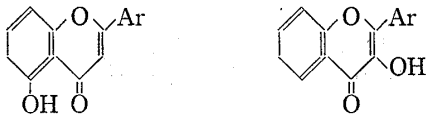
X-ray crystal structure analysis of 4′-bromo-5-hydroxyflavone and 4′-bromo-3-hydroxyflavone was carried out to investigate the structures of pyrone ring and hydrogen bonding which may have some relation to the fluorescence emission. The bond lengths of the carbonyl groups in 4′-bromo-5-hydroxyflavone and 4′-bromo-3-hydroxyflavone were found to be 1.245 and 1.232 Å respectively. This is consistent with the fact that 5-hydroxyl group forms a stronger hydrogen bond than 3-hydroxyl group. On the other hand, as described in the previous paper,[2] the carbonyl absorption bands of type I compounds occurred in shorter wavelength region than those of type II, and a similar phenomenon was also observed in 4′-bromo-5-hydroxyflavone and 4′-bromo-3-hydroxyflavone. The serious inconsistency between the bond lengths measured by X-ray analysis and the stretching frequencies observed in infrared spectra for the carbonyl group is considered to be caused by a coupling effect. The differences in planarity and aromaticity between type I and type II were not considered to be significant, but the aromaticity of pyrone ring in type II is presumed to be increased remarkably in their metal chelates, which explains the strong fluorescence emission observed in their metal chelates. The 4′-bromo-3-hydroxyflavone forms an intermolecular hydrogen bonding only in crystalline state.

In the previous papers,[2,3] the correlation between fluorescence intensity and structure of metal chelates of flavone derivatives was discussed and showed that the compound of type I in Chart 1 does not form fluorescent chelates, while the compound of type II not only fluoresces by itself but also form fluorescent metal chelates with some kinds of metal ions such as beryllium, aluminum, magnesium and so on. It was also shown that the carbonyl stretching frequency has an intimate correlation with fluorescence emission; the frequencies of type I came out in 1645—1650 cm^{-1} region, while those of type II in 1610—1620 cm^{-1} region. For an explanation of these phenomena, it was presumed that the increase of the aromaticity of pyrone ring in the structure of type II may be responsible for the fluorescence emission. This speculation was further supported by comparing the nuclear magnetic resonance (NMR) chemical shift of 2-proton in 3-hydroxychromone (type II) with that in other chromone

1) Location: *a) Mitahora, Gifu; b) Hongo 7-3-1, Bunkyo-ku, Tokyo.*
2) T. Hayashi, S. Kawai, and T. Ohno, *Chem. Pharm. Bull.* (Tokyo), **19**, 792 (1971).
3) T. Hayashi, K. Hara, S. Kawai, and T. Ohno, *Chem. Pharm. Bull.* (Tokyo), **18**, 1112 (1970).



I II

Chart 1. Two Types of Flavone Derivatives

derivatives having no hydroxyl group at 3-position. The absorption of the 3-hydroxychromone came out by 0.35 to 0.54 lower in τ value than that of the latter compounds such as 3-methylchromone, 5-hydroxychromone, 5-acetoxychromone, and 3-methoxychromone.

The present paper describes the result of the X-ray crystal structure analysis of 4′-bromo-5-hydroxyflavone and 4′-bromo-3-hydroxyflavone, carried out to investigate the structural features of pyrone ring and hydrogen bonding of these two types of flavone derivatives in detail. The intramolecular bond distances and bond angles of 4′-bromo-5-hydroxyflavone and 4′-bromo-3-hydroxyflavone molecules are shown in Fig. 1 and 2. The chromone ring and O3 or O5 in 4′-bromo-3-hydroxyflavone or 4′-bromo-5-hydroxyflavone was found to have a high degree of planarity, as shown in Table III, and no difference in planarity between them is distinguished.

The bond length between C1 and C2 found in 4′-bromo-3-hydroxyflavone (type II compound) was a little longer[4] than that found in 4′-bromo-5-hydroxyflavone (type I compound), which corresponds reasonably to the increase of the aromaticity of pyrone ring in type II as

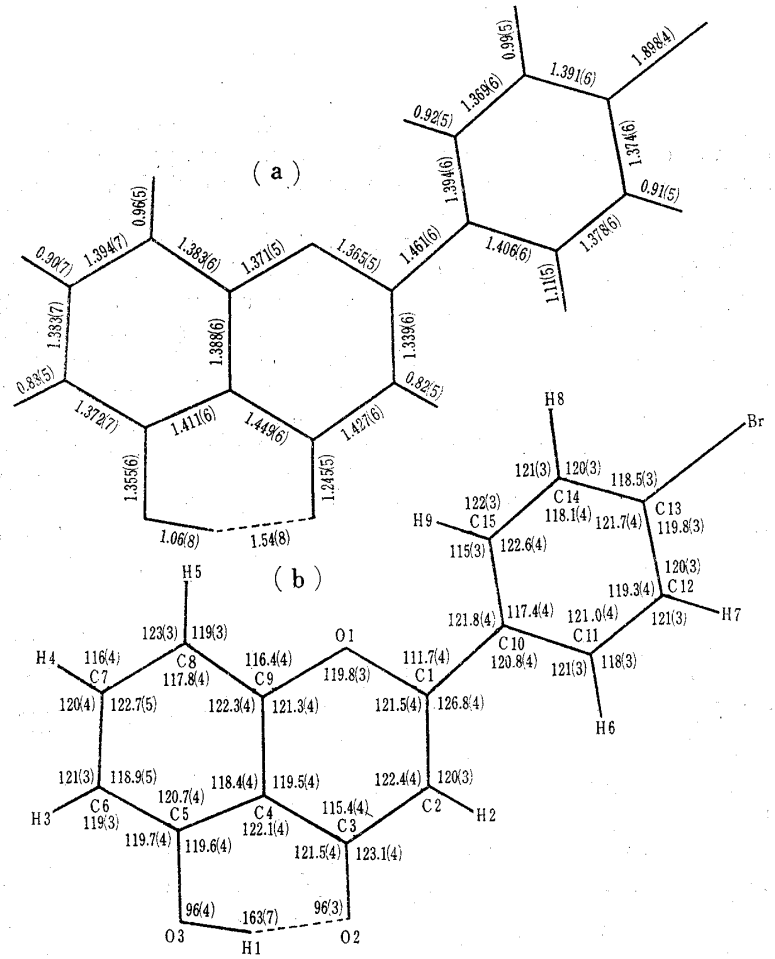


Fig. 1. Bond Lengths (a) and Bond Angles (b) of 4′-Bromo-5-hydroxyflavone

Torsion angle at the C1-C10 bond, C2-C1-C10-C11, is 6.6°.
Standard deviations are shown in parentheses denoting least significant digits.

4) The difference is about two times as large as the standard deviations of the C1-C2 bond length.

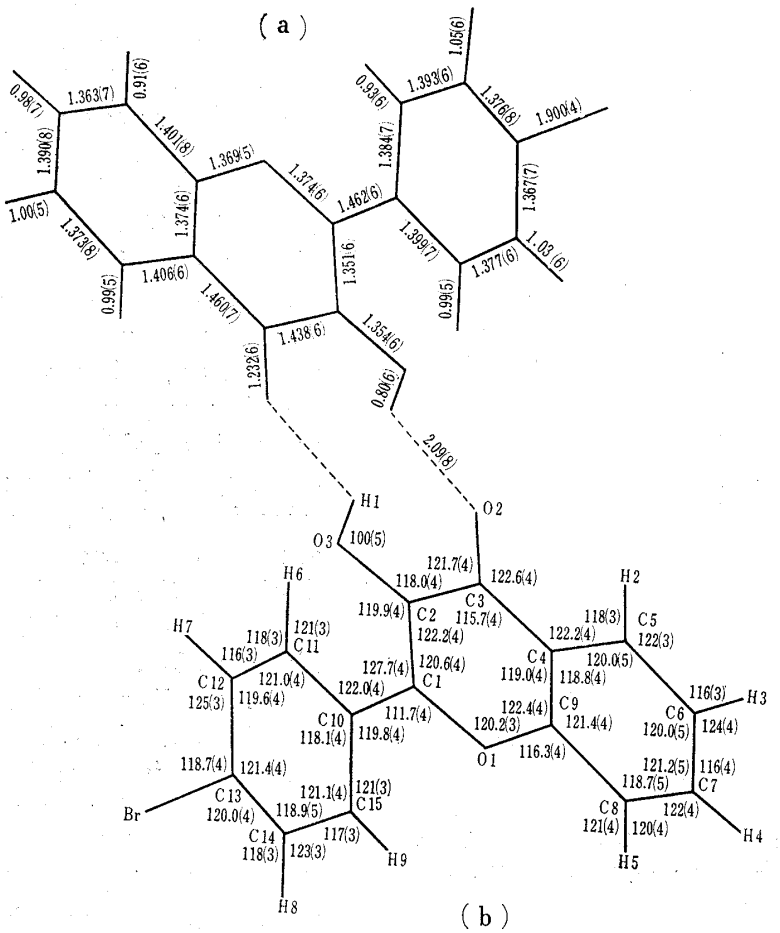


Fig. 2. Bond Lengths (a) and Bond Angles (b) of 4′-Bromo-3-hydroxyflavone

Torsion angle at the C1-C10 bond, C2-C1-C10-C11, is 18.8°.
Standard deviations are shown in parentheses denoting least significant digits.

described before. Next, the bond length of C3-C4 in 4′-bromo-5-hydroxyflavone was measured to be a little shorter[5] than that in 4′-bromo-3-hydroxyflavone by X-ray analysis, which indicates a conjugation in the six-membered ring formed by hydrogen bonding between 4-carbonyl and 5-hydroxyl group of 4′-bromo-5-hydroxyflavone.

Simpson[6] reported that 4-carbonyl group forms a stronger hydrogen bond with 5-hydroxyl group than with 3-hydroxyl group in 3,5-dihydroxyflavone. This fact was also confirmed by the infrared spectra (Fig. 3) of 4′-bromo-5-hydroxyflavone and 4′-bromo-3-hydroxyflavone in the same manner as described in the previous paper.[2] 4′-Bromo-3-hydroxyflavone (Fig. 3b) showed a sharp absorption band of ν_{OH} in the region of 3000—3500 cm^{-1} suggesting the formation of a weak hydrogen bonding,[7] while 4′-bromo-5-hydroxyflavone gave a broad absorption in the same region (Fig. 3a) suggesting the formation of a strong hydrogen bonding. These were consistent with the results obtained by the X-ray analysis. According to the X-ray analysis, as shown in Fig. 1 and 2, the bond lengths of the carbonyl groups in 4′-bromo-5-hydroxyflavone and 4′-bromo-3-hydroxyflavone were found to be 1.245 and 1.232Å respectively. The elongation of the carbonyl bond observed in the 5-hydroxy derivative suggests that 5-hydroxyl group forms a stronger hydrogen bond than 3-hydroxyl group, which may cause

5) The difference is about 1.5 times as large as the standard deviations of the C3-C4 bond length.
6) T.H. Simpson and L. Garden, *J. Chem. Soc.*, **1952**, 4638.
7) As described later, 3-hydroxyl group forms an intermolecular hydrogen bond with 4-carbonyl group in crystal in contrast with the intramolecular hydrogen bond formed in 4′-bromo-5-hydroxyflavone.

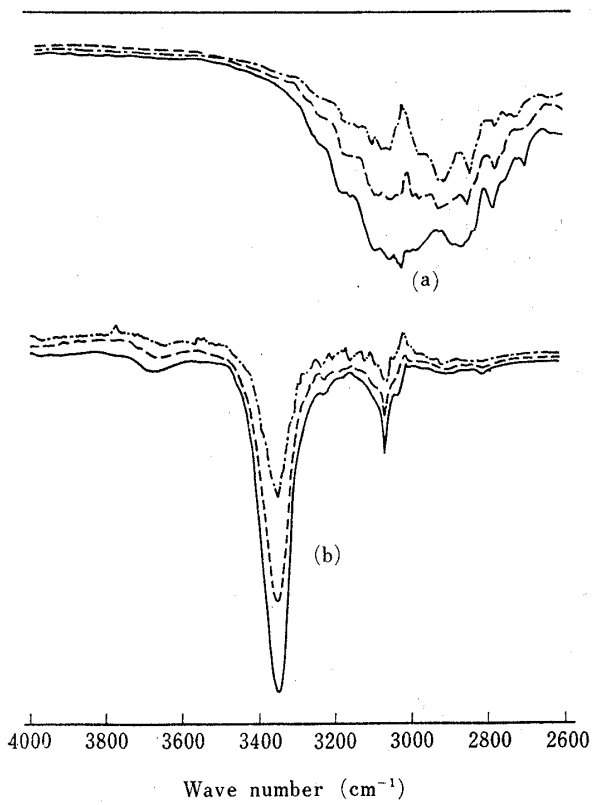


Fig. 3. Infrared Spectra of 4′-Bromo-5-hydroxyflavone (a) and 4′-Bromo-3-hydroxyflavone (b) in Carbon Tetrachloride

——: 0.1% ----: 0.025% —·—: 0.006%

a shift of the carbonyl absorption band toward longer wavelength region. However, as described before, the carbonyl absorption bands of type I compounds occurred in shorter wavelength region, and a similar phenomenon was also observed in 4′-bromo-5-hydroxyflavone and 4′-bromo-3-hydroxyflavone (Table I). The serious inconsistency between the bond lengths measured by the X-ray analysis and the stretching frequencies observed in the infrared spectra for the carbonyl groups is considered to be caused by a coupling effect between the stretching vibrations of 4-carbonyl bond and of another bond such as the double bond C1-C2 in the type I compounds, which may cause a shift of the frequency toward higher region.

The difference in the C1-C2 bond lengths found between the two types of compounds is not so large and the corresponding bond angles subtended at C1 and C2 found in these two compounds show quite similar values. From these results, the difference in the aromaticity between type I and type II is not considered to be significant. However, the aromaticity of pyrone ring in type II is presumed to be increased remarkably in their metal chelates because of high electronegativity of metals. This may explain the strong fluorescence emission observed in metal chelates of 4′-bromo-3-hydroxyflavone (Table II) as well as in those of other type II compounds described in the previous papers.[2,3]

Table I. $\nu_{C=O}$ (cm^{-1}) of 4′-Bromo-3-hydroxyflavone and 4′-Bromo-5-hydroxyflavone

Compound	$\nu_{C=O}$ (cm^{-1})	
	CCl_4 soln.	KBr disk
4′-Bromo-3-hydroxyflavone	1620	1615
4′-Bromo-5-hydroxyflavone	1655	1655

Table II. Relative Fluorescence Intensity of 4′-Bromo-3-hydroxyflavone, 4′-Bromo-5-hydroxyflavone and Their Metal Chelates

Metal	Relative fluorescence intensity	
	4′-Bromo-3-hydroxyflavone	4′-Bromo-5-hydroxyflavone
—	5.0	0
Be^{2+}	10.0	0
Mg^{2+}	200.0	0
Al^{3+}	3200.0	0

Table III. The Distances of Each Atom from the Mean Plane formed by Chromone Ring and 03 or 05 in 4′-Bromo-3-hydroxyflavone or 4′-Bromo-5-hydroxyflavone

4′-Bromo-3-hydroxyflavone		4′-Bromo-5-hydroxyflavone	
Atom	Distance (Å)	Atom	Distance (Å)
O 1	−0.014	O 1	−0.012
O 2	−0.035	O 2	0.033
O 3	0.047	O 3	−0.035
C 1	−0.003	C 1	−0.018
C 2	0.001	C 2	−0.001
C 3	−0.018	C 3	0.011
C 4	−0.006	C 4	0.002
C 5	0.014	C 5	−0.010
C 6	0·023	C 6	−0.001
C 7	0.006	C 7	0.020
C 8	−0.005	C 8	0.007
C 9	−0.010	C 9	0.003
C10	0.032	C10	−0.061
C11	−0.307	C11	−0.228
C12	−0.258	C12	−0.291
C13	0.134	C13	−0.189
C14	0.473	C14	−0.032
C15	0.407	C15	0.045
Br	0.165	Br	−0.302

Another fact was observed in Fig. 2 that an intermolecular hydrogen bond is formed between two 4′-bromo-3-hydroxyflavone molecules in crystalline state. Fig. 3 shows the infrared spectra of the carbon tetrachloride solutions of 4′-bromo-3-hydroxyflavone and 4′-bromo-5-hydroxyflavone in various concentrations. No change was observed except their intensities in both compounds. Therefore, it is considered that 4′-bromo-3-hydroxyflavone forms an intermolecular hydrogen bonding only in crystalline state.

Experimental

4-Bromo-2′-hydroxychalcone——The chalcone was prepared by interaction of 2-hydroxyacetophenone (2.7 g) and 4-bromobenzaldehyde (3.7 g) in methanol (15 ml) and 50% aqueous sodium hydroxide solution (12 ml) at 0° for 10 hr. The reaction mixture was diluted with ice water and the product was isolated by acidifying with hydrochloric acid. The product was recrystallized from ethanol. mp 142—143°.

4′-Bromo-3-hydroxyflavone——4-Bromo-2′-hydroxychalcone (2.0 g) was dissolved in ethanol (60 ml) and 10% aqueous sodium hydroxide solution (30 ml), gently boiled, then treated with 30% H_2O_2 (6 ml), and allowed to stand for 24 hr. The reaction mixture was diluted with water and acidified with acetic acid. The product was filtered, washed with water, dried and recrystallized from ethanol. mp 203—204°. *Anal.* Calcd. for $C_{15}H_9O_3Br$: C, 56.83; H, 2.86. Found: C, 57.03; H, 3.01.

4-Bromo-2′-hydroxy-6′-methoxychalcone——This was made in the same way as 4-bromo-2′-hydroxychalcone by using 2-hydroxy-6-methoxyacetophenone (3.2 g) and 4-bromobenzaldehyde (3.7 g), and recrystallized from ethanol. mp 121—122°.

4′-Bromo-5-methoxyflavone——4-Bromo-2′-hydroxy-6′-methoxychalcone (5.0 g) was converted to 4′-bromo-5-methoxyflavone by boiling under reflux for 15 hr with SeO_2 (7.5 g) in amylalcohol (100 ml). The product was recrystallized from ethanol. mp 186—187°.

4′-Bromo-5-hydroxyflavone——4′-Bromo-5-methoxyflavone was converted to 4′-bromo-5-hydroxyflavone by gentle boiling under reflux for 30 min with hydroiodide (20 ml). After cooling, the reaction mixture was diluted with water and extracted with chloroform. The chloroform phase was washed with 10% aqueous sodium thiosulfate solution, then with water. The chloroform phase was dried with sodium sulfate and evapolated. The product was recrystallized from ethyl acetate. mp 180—181°. *Anal.* Calcd. for $C_{15}H_9O_3Br$: C, 56.83; H, 2.86. Found: C, 56.89; H, 3.03.

The instruments used in this work are Shimadzu RF-501 spectrofluorometer, JASCO DS-403G grating infrared spectrophotometer, Kobayashi Weissenberg camera, Narumi photodensitometer, and Rigakudenki four circle diffractometer.

Table IV. Crystal Data of 4′-Bromo-3-hydroxyflavone and 4′-Bromo-5-hydroxyflavone

4′-Bromo-3-hydroxyflavone	4′-Bromo-5-hydroxyflavone
Monoclinic	Monoclinic
a = 13.03 ±0.01Å	a = 12.81 ±0.01Å
b = 5.341±0.005Å	b = 12.68 ±0.01Å
c = 19.06 ±0.02Å	c = 7.484±0.007Å
β = 111.1 ±0.1°	β = 91.3 ±0.1°
Dm = 1.7 g/cm³ Dc = 1.70 g/cm³	Dm = 1.7 g/cm³ Dc = 1.73 g/cm³

Crystal Data——The lattice constants at room temperature were determined using diffractometer. Both 4′-bromo-3-hydroxyflavone and 4′-bromo-5-hydroxyflavone crystallized in monoclinic system. Cu$K\alpha$ radiation was used throughout the diffraction study. The densities of compounds were determined by floatation in an aqueous potassium mercuric iodide solution. The systematic absences are recognized for reflections h01 and 0k0 with l and k odd respectively in both compounds, indicating that the space groups of both compounds are $P2_1/c$. The crystal data are listed in Table IV. The intensity data of the h01—h41 reflections were collected from the crystal of 4′-bromo-3-hydroxyflavone and those of the hk0—hk6 were collected from the crystal of 4′-bromo-5-hydroxyflavone by the multiple-film equiinclination techniques. The density of the spots on the films were measured by photodensitometer. After the intensity data were

Table V. Final Fractional Atomic Coordinates and Temperature Factors of 4′-Bromo-3-hydroxyflavone

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.0247(0)	−0.7775(1)	−0.1824(0)	0.0105(0)	0.0345(2)	0.0030(0)	−0.0036(1)	0.0013(0)	−0.0011(0)
O 1	0.2367(2)	0.0860(6)	0.0906(2)	0.0070(2)	0.0374(12)	0.0023(1)	−0.0046(4)	0.0022(1)	−0.0013(3)
O 2	0.4852(3)	0.5194(7)	0.0794(2)	0.0073(2)	0.0602(18)	0.0031(1)	−0.0089(6)	0.0025(1)	−0.0018(4)
O 3	0.3943(3)	0.1679(7)	−0.0289(2)	0.0070(2)	0.0446(14)	0.0029(1)	−0.0039(1)	0.0029(1)	−0.0016(3)
C 1	0.2761(3)	0.0530(8)	0.0334(2)	0.0053(3)	0.0331(16)	0.0021(1)	−0.0000(6)	0.0016(2)	0.0003(4)
C 2	0.3584(3)	0.1984(8)	0.0289(2)	0.0053(3)	0.0355(17)	0.0022(1)	0.0003(6)	0.0017(2)	0.0009(4)
C 3	0.4090(3)	0.3905(9)	0.0832(2)	0.0051(3)	0.0399(18)	0.0022(1)	−0.0015(6)	0.0012(2)	0.0007(4)
C 4	0.3638(3)	0.4229(9)	0.1425(2)	0.0051(3)	0.0354(17)	0.0021(1)	−0.0005(6)	0.0011(2)	0.0005(4)
C 5	0.4027(4)	0.6077(10)	0.1984(2)	0.0059(3)	0.0404(19)	0.0027(1)	−0.0019(6)	0.0012(2)	−0.0009(4)
C 6	0.3575(4)	0.6304(11)	0.2529(3)	0.0078(4)	0.0447(21)	0.0030(2)	−0.0012(8)	0.0018(2)	−0.0025(5)
C 7	0.2736(4)	0.4700(11)	0.2531(3)	0.0087(4)	0.0521(24)	0.0031(2)	−0.0019(8)	0.0030(2)	−0.0025(5)
C 8	0.2339(4)	0.2905(10)	0.1992(3)	0.0080(4)	0.0467(22)	0.0031(2)	−0.0044(8)	0.0028(2)	−0.0020(5)
C 9	0.2800(3)	0.2684(8)	0.1435(2)	0.0060(3)	0.0341(17)	0.0021(1)	−0.0006(6)	0.0017(2)	−0.0001(4)
C10	0.2170(3)	−0.1452(8)	−0.0182(2)	0.0062(3)	0.0296(15)	0.0021(1)	−0.0006(6)	0.0015(2)	0.0014(4)
C11	0.2593(4)	−0.2588(9)	−0.0681(2)	0.0068(3)	0.0362(18)	0.0025(1)	−0.0002(6)	0.0021(2)	−0.0000(4)
C12	0.2016(4)	−0.4443(9)	−0.1166(2)	0.0077(4)	0.0370(18)	0.0025(1)	0.0004(7)	0.0019(2)	0.0000(4)
C13	0.1013(4)	−0.5176(8)	−0.1161(2)	0.0081(4)	0.0299(16)	0.0021(1)	−0.0013(6)	0.0012(2)	0.0011(4)
C14	0.0567(4)	−0.4111(10)	−0.0678(3)	0.0078(4)	0.0390(19)	0.0030(2)	−0.0043(7)	0.0023(2)	−0.0012(5)
C15	0.1159(4)	−0.2258(9)	−0.0184(3)	0.0070(3)	0.0391(19)	0.0029(1)	−0.0028(7)	0.0025(2)	−0.0011(4)

	x	y	z	B
H1	0.445(5)	0.265(2)	−0.017(4)	8.1(1.8)
H2	0.461(4)	0.722(9)	0.196(3)	4.2(1.1)
H3	0.392(5)	0.760(0)	0.293(3)	6.1(1.4)
H4	0.246(5)	0.492(2)	0.294(3)	7.2(1.5)
H5	0.174(4)	0.200(0)	0.197(3)	5.9(1.3)
H6	0.336(4)	−0.227(9)	−0.064(3)	4.6(1.1)
H7	0.240(4)	−0.520(10)	−0.150(3)	5.3(1.2)
H8	−0.024(4)	−0.461(0)	−0.074(3)	5.3(1.2)
H9	0.084(4)	−0.154(10)	0.013(3)	4.5(1.1)

Temperature factors (β_{ij}) are of the form
$T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$.
Standard deviations are listed in parentheses denoting least significant digits.

corrected for Lorentz-polarization effects and spot extension, the relative scale factors between each layer were determined by Wilson's plot. No absorption correction was made.

Determination of Structure of 4′-Bromo-3-hydroxyflavone——The structure of 4′-bromo-3-hydroxyflavone was solved by the heavy atom method. The position of the bromine atom was determined from the three dimensional Patterson map. The first Fourier synthesis, phased by the bromine atom, indicates the coordinates of 3 oxygen atoms and 10 carbon atoms. Subsequent Fourier maps revealed the positions of the remaining non-hydrogen atoms in the molecule. The crystal structure was refined by a block diagonal least-squares method. Throughout the least-squares calculations, the equal weighting was employed for each reflection. The atomic scattering curves were taken from the International Table for X-ray Crystallography, Vol. III. After five cycles of the refinement, the conventional R value reduced to 0.17 for 1037 non-zero reflections. Three more cycles of the refinement with anisotropic thermal parameters for all non-hydrogen atoms reduced the R value to 0.14. At this point the availability of a diffractometer made it possible to use better data for the refinement. During subsequent refinement, only the diffractometer data were used. After 5 cycles of the refinement, the R value remarkably reduced to 0.059. Before further refinement, the positions of hydrogen atoms were determined on the difference Fourier map. The final refinement was made for the non-hydrogen atoms with anisotropic temperature factors and for the hydrogen atoms with isotropic ones. The final atomic coordinates and temperature factors are listed in Table V along with their standard deviations.

Determination of Structure of 4′-Bromo-5-hydroxyflavone——The structure of 4′-bromo-5-hydroxyflavone was also solved by the heavy atom method. The position of the bromine atom was determined from the three dimensional Patterson map. The first Fourier synthesis, phased by the bromine atom, gave the coordinates of 3 oxygen atoms and 9 carbon atoms. Subsequent Fourier maps gave the remain-

Table VI. Final Fractional Atomic Coordinates and Temperature Factors of 4′-Bromo-5-hydroxyflavone

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.9591(0)	−0.3616(0)	0.3835(1)	0.0057(0)	0.0063(0)	0.0218(1)	0.0010(0)	−0.0017(0)	−0.0002(0)
O 1	0.7690(2)	0.1315(2)	0.2724(4)	0.0045(2)	0.0048(2)	0.0201(6)	−0.0010(1)	−0.0016(3)	−0.0002(3)
O 2	0.4732(3)	0.1575(3)	0.0708(5)	0.0053(2)	0.0059(2)	0.0320(9)	−0.0000(2)	−0.0050(3)	−0.0015(4)
O 3	0.4931(3)	0.3595(3)	0.0670(5)	0.0057(2)	0.0064(2)	0.0290(9)	0.0009(2)	−0.0011(3)	0.0004(4)
C 1	0.7111(3)	0.0437(3)	0.2344(6)	0.0049(3)	0.0047(3)	0.0160(8)	−0.0009(2)	−0.0002(4)	−0.0001(4)
C 2	0.6134(3)	0.0508(3)	0.1682(6)	0.0049(3)	0.0045(3)	0.0222(10)	−0.0010(2)	−0.0019(4)	−0.0012(4)
C 3	0.5642(3)	0.1496(4)	0.1316(6)	0.0047(3)	0.0056(3)	0.0179(9)	−0.0003(2)	−0.0010(4)	−0.0011(4)
C 4	0.6272(3)	0.2420(3)	0.1707(6)	0.0049(3)	0.0048(3)	0.0159(8)	−0.0007(2)	0.0004(4)	−0.0012(4)
C 5	0.5900(4)	0.3452(4)	0.1389(6)	0.0056(3)	0.0059(3)	0.0183(9)	−0.0002(2)	0.0011(4)	−0.0006(4)
C 6	0.6511(4)	0.4311(4)	0.1796(7)	0.0071(3)	0.0047(3)	0.0261(12)	−0.0005(3)	0.0013(5)	0.0000(5)
C 7	0.7500(4)	0.4149(4)	0.2524(7)	0.0071(4)	0.0055(3)	0.0271(12)	−0.0020(3)	0.0009(5)	−0.0013(5)
C 8	0.7911(4)	0.3146(4)	0.2833(7)	0.0058(3)	0.0059(3)	0.0215(10)	−0.0018(3)	−0.0004(4)	−0.0006(5)
C 9	0.7275(3)	0.2296(3)	0.2416(6)	0.0050(3)	0.0049(3)	0.0164(8)	−0.0007(2)	0.0002(4)	0.0000(4)
C 10	0.7694(3)	−0.0529(3)	0.2730(6)	0.0040(2)	0.0052(3)	0.0165(8)	−0.0006(2)	−0.0004(3)	−0.0005(4)
C 11	0.7285(3)	−0.1520(4)	0.2243(6)	0.0042(3)	0.0056(3)	0.0216(10)	−0.0005(2)	−0.0016(4)	−0.0017(4)
C 12	0.7840(3)	−0.2432(4)	0.2578(7)	0.0046(3)	0.0052(3)	0.0225(10)	−0.0005(2)	−0.0009(4)	−0.0012(4)
C 13	0.8808(3)	−0.2369(3)	0.3398(6)	0.0045(3)	0.0059(3)	0.0147(8)	0.0003(2)	−0.0005(4)	−0.0005(4)
C 14	0.9246(4)	−0.1405(4)	0.3892(6)	0.0047(3)	0.0063(3)	0.0195(9)	−0.0005(2)	−0.0025(4)	−0.0003(4)
C 15	0.8676(3)	−0.0510(4)	0.3568(6)	0.0047(3)	0.0056(3)	0.0209(10)	−0.0010(2)	−0.0022(4)	−0.0010(4)

	x	y	z	B
H1	0.473(6)	0.279(6)	0.057(0)	9.8(2.1)
H2	0.579(4)	−0.003(4)	0.148(6)	4.2(1.0)
H3	0.628(4)	0.494(4)	0.154(6)	4.9(1.2)
H4	0.791(5)	0.470(5)	0.282(8)	7.9(1.7)
H5	0.858(4)	0.303(4)	0.339(7)	4.8(1.2)
H6	0.656(4)	−0.158(4)	0.142(7)	4.7(1.2)
H7	0.757(4)	−0.307(4)	0.226(7)	4.8(1.2)
H8	0.991(4)	−0.139(4)	0.461(7)	5.2(1.2)
H9	0.889(4)	0.014(4)	0.398(7)	5.5(1.2)

Temperature factors (β_{ij}) are of the form
$T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$
Standard deviations are listed in parentheses denoting least significant digits.

ing non-hydrogen atoms. Then the crystal structure was refined in the same way as 4′-bromo-3-hydroxyflavone. After five cycles of the refinement, the R value reduced to 0.14.. Three more cycles of the refinement with anisotropic thermal parameters for all non-hydrogen atoms reduced the R value to 0.10. At this point the availability of a diffractometer also made it possible to use better data for the refinement. After 5 cycles of the refinement, the R value reduced to 0.058. The positions of hydrogen atoms were determined on the difference Fourier map. The final refinement was made for the non-hydrogen atoms with anisotropic temperature factors and for the hydrogen atoms with isotropic ones. The final atomic coordinates and temperature factors are listed in Table VI along with their standard deviations.