Bull. Mater. Sci., Vol. 30, No. 5, October 2007, pp. 469–475. © Indian Academy of Sciences.

X-ray study of weak interactions in two flavonoids

DEEPAK SHARMA, VIVEK K GUPTA*, GOUTAM BRAHMACHARI[†], SADHAN MONDAL[†] and ARINDAM GANGOPADHYAY[†]
Post Graduate Department of Physics, University of Jammu, Jammu Tawi 180 006, India
[†]Department of Chemistry, Visva Bharati University, Santiniketan 731 235, India

MS received 11 October 2006; revised 20 August 2007

Abstract. **X-ray diffraction studies were carried out on single crystals of two flavonoids, viz. 5-hydroxy-6,7,4′-trimethoxyflavone, $C_{18}H_{16}O_6$, (I) and 5-hydroxy-3,7,4′-trimethoxyflavone, $C_{18}H_{16}O_6$, (II). Crystal structures of both the flavonoids were solved by direct methods and refined by full-matrix least-squares procedures. In both the molecules, the benzopyran moiety is planar. The dihedral angle between the phenyl ring and the benzopyran portion is 5·50(4)° in (I) and 29·11(5)° in (II). In (I), the crystal packing is influenced by O–H…O hydrogen bonds, and weak C–H…O and $\pi \ldots \pi$ interactions whereas in (II) the crystal structure is stabilized by the presence of four intermolecular short contacts of the type C–H…O. There is also one C–H…π hydrogen bond with H… centroid distance of $< 2{\cdot}7$ Å. The molecules are further stabilized by π–π interactions.**

Keywords. **Flavonoid; direct methods; C–H…π hydrogen bond; π–π interaction; gauche; benzopyran.**

1. Introduction

Flavonoids comprise of a large group of secondary plant metabolites, which are widely distributed throughout the plant kingdom and are of importance and interest to a wide variety of physical and biological scientists. These naturally occurring polyphenolics exhibit a wide range of biological properties (Brahmachari and Gorai 2006, 2007), including antioxidant, antitumour, cytotoxic, enzyme inhibitory, antimicrobial, insecticidal and oestrogenic activities; they are also used in the treatment of diabetes and cancer (Wallet *et al* 1990). Flavonoids are also major components of many plant drugs (e.g. ginkgo leaves) and contribute to the curative properties. In order to obtain detailed information about the molecular structure of flavonoids in the solid state and to find out the role of weak interactions (C–H…O, C–H…π and π–π) in assembling the molecules into an organized supramolecular structure (Nishio and Hirota 1989; Desiraju 1992, 1996; Hunter 1993, 1994; Amabilino and Stoddart 1995; Nishio *et al* 1995, 1998; Chipot *et al* 1996; Steiner 1996; Claessens and Stoddart 1997; Hirsch *et al* 1997; Wahl and Sundaralingam 1997; Brown *et al* 1999; Desiraju and Steiner 1999; Hannon *et al* 1999; Lightfoot *et al* 1999; Ning *et al* 1999; Janiak 2000; Janiak *et al* 2000; Takahashi *et al* 2000), an X-ray structure investigation was carried out on two flavonoid compounds.

2. Experimental

Compound (I), 5-hydroxy-6,7,4′-trimethoxyflavone, was isolated from the plant, *Limnophila rugosa. L. rugosa* belongs to the Scrophulariaceae family of medicinal plants, and is used as a flavouring agent for food. It is also used as hair perfume. Essential oil from the leaves of *L. rugosa* exhibits significant anti-bacterial and anti-fungal activities (Kapil *et al* 1983). An infusion of the leaves is taken as diuretic, stomachic and digestive tonic (Wealth of India 1962).

Air-dried whole plants (1·5 kg) of *Limnophila rugosa* were extracted with petrol (60–80°) in a Soxhlet apparatus for 56 h. The extract was concentrated under reduced pressure, and then subjected to column chromatography on a 200 g silica gel (60–120 mesh). Petrol (60–80°) – benzene (1 : 3) eluent yielded the flavone, 5-hydroxy-6,7,4′-trimethoxyflavone (yield 0·65 g; m.p. 184–188°C). The chemical structure was assigned on the basis of spectral (UV, IR, NMR, mass) data (figure 1) (Brahmachari 2005).

Yellow rectangular plate shaped single crystals were grown at room temperature from benzene by slow evaporation technique. A crystal of dimension, 0·3 × 0·2 × 0·1 mm, was used for data collection on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated CuKα radiation. Data were corrected for Lorentz-polarization, extinction and ψ-scan-based empirical absorption corrections (transmission factors, 0·9303–0·9916) (North

---

*Author for correspondence (vivek_gupta2k5@yahoo.co.in)
CCDC-602176 and CCDC-610487 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

et al 1968). The crystal structure was solved by direct methods using SHELXS97 software (Sheldrick 1997). Full-matrix least-squares refinement was carried out using SHELXL97 software (Sheldrick 1997). H atoms bonded to C atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms with C–H=0·93–0·96 Å, and $U_{iso}(H) = 1{\cdot}5U_{eq}(C)$ of the attached C atom for methyl H atoms and 1·2 U_{eq} for other H atoms. The position of the hydroxy H atom bonded to O5 atom was determined from a difference Fourier map and refined freely along with the isotropic displacement parameter. The final refinement cycles converged to an $R = 0{\cdot}0481$ for the observed data. The weighted R on (F^2) was 0·1386, the weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0{\cdot}0769P)^2 + 0{\cdot}5768P]$, where $P = [F_o^2 + 2F_c^2]/3$. The crystallographic data are summarized in table 1. CCDC-602176 contains the supplementary crystallographic data for this structure.

Compound (II), 5-hydroxy-3,7,4′-trimethoxyflavone, was isolated from the plant, *Cheilanthes farinosa* Kaulf (family: Cheilanthaceae). The plant has been used in traditional system of medicine. Fronds are used in seasonal cold fever. Ethanolic (50%) extract of the fern has been reported to be spasmolytic and CNS depressant (Asolkar *et al* 1992).

Petrol extract of the whole plants (aerial parts and roots) afforded the flavone (5-hydroxy-3,7,4′-trimethoxyflavone) upon chromatographic resolution with benzene–chloroform (1 : 1) as yellow solid, m.p. 145°C. The chemical structure was assigned on the basis of spectral data (UV, IR, NMR, mass) (figure 2) (Brahmachari 2005).

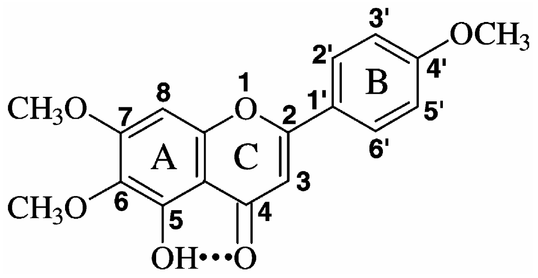

Figure 1. Chemical structure of 5-hydroxy-6,7,4′-trimethoxyflavone.

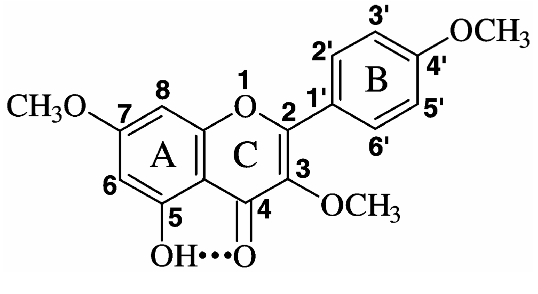

Figure 2. Chemical structure of 5-hydroxy-3,7,4′-trimethoxyflavone.

Light yellow rectangular shaped single crystals were grown at room temperature by slow evaporation technique using dimethylformamide as the solvent. X-ray intensity data of 4815 reflections (of which 3395 were unique) were collected on Bruker SMART CCD area-detector diffractometer equipped with graphite monochromated MoKα radiation ($\lambda = 0{\cdot}71073$ Å). Data were corrected for Lorentz and polarization factors but no absorption correction was made.

The structure was solved by direct methods using SHELXS97 software (Sheldrick 1997) and refined by full-matrix least-squares method using SHELXL97 (Sheldrick 1997) software. All the hydrogen atoms were located from a difference Fourier map, their positions and isotropic temperature factors were refined. Final cycles of refinement converged the R-value to 0·0582 for 2511 observed reflections. The weighted R on (F^2) was 0·1514, the weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0{\cdot}0991P)^2 + 0{\cdot}0892P]$, where $P = (F_o^2 + 2F_c^2)/3$. The crystal and experimental data are listed in table 1. CCDC-610487 contains the supplementary crystallographic data for this structure.

3. Results and discussion

The final atomic coordinates with equivalent isotropic displacement parameters are presented in table 2. Selected bond distances, bond angles and torsion angles are listed in table 3. Details of O–H...O, C–H...O, C–H...π hydrogen bonds, and π–π stacking interactions are given in tables 4 and 5, respectively. ORTEP view of compounds I and II with atomic labeling is shown in figures 3 and 6, respectively (Farrugia 1997). The geometry of the molecule was calculated using the software winGX (Farrugia 1999) and PARST (Nardelli 1995).

3.1 *Compound I*

Bond lengths and bond angles are comparable with expected values (Allen *et al* 1987). The molecule consists of two condensed rings, viz. a benzene (A) and a pyran ring (C). The phenyl ring (B) is attached in position 2. The benzopyran moiety is almost coplanar; the dihedral angle between the best planes of rings, A (atoms C4a/C5–C8/C8a) and C (atoms O1/C2–C4/C4a/C8a), is 0·79(5)°. This is typical for 255 structures with the benzopyran moiety found in the Cambridge Structural Database (Allen 2002; CSD, Version 5.25, November 2003). The planarity of the benzopyran moiety confirms the aromatic character of this system. Nevertheless, a lengthening of the C3–C4 and C4–C4a bonds is observed to 1·426(2) and 1·441(2) Å, respectively, and the C3–C4–C4a bond angle decreases to 115·5(1)°. In contrast, the shortest bond length is observed for atom C2, viz. 1·348(2) Å. Similar variations in the geometric parameters of the pyran ring in the

Table 1. Crystal and experimental data.

	Compound I	Compound II
CCDC No	602176	610487
Crystal description	Yellow plate	Light yellow rectangular
Crystal size	0·3 × 0·2 × 0·1 mm	0·3 × 0·2 × 0·1 mm
Empirical formula	$C_{18}H_{16}O_6$	$C_{18}H_{16}O_6$
Formula weight	328·31	328·31
Unit cell dimensions	a = 7·737(1), b = 7·304(1), c = 27·653(5) Å, β = 93·70(1)°	a = 5·264(1), b = 11·290(3), c = 12·687(3) Å, α = 96·267(3), β = 99·599(3), γ = 94·564(3)°
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
Unit cell volume	1559·5(4) Å^3	735·3(3) Å^3
Density (calculated)	1·398 Mgm^{-3}	1·483 Mg m^{-3}
No· of molecules per unit cell, Z	4	2
Absorption coefficient	0·886 mm^{-1}	0·112 mm^{-1}
F(000)	688	344
θ range for data collection	3·20 < θ < 67·98°	2·30 < θ < 28·38°
Reflections collected/unique	3323/2827	4815/3395
Reflections observed ($I > 2\sigma$(I))	2587	2511
No· of parameters refined	222	282
Final R	0·0481	0·0582
$wR(F^2)$	0·1386	0·1514
Goodness-of-fit	1·022	1·027
$(\Delta/\sigma)_{\max}$	–0·001 for U11 H5	0·001 for z H112
Final residual electron density	–0·188 < $\Delta\rho$ < 0·351 eÅ^{-3}	–0·366 < $\Delta\rho$ < 0·407 eÅ^{-3}

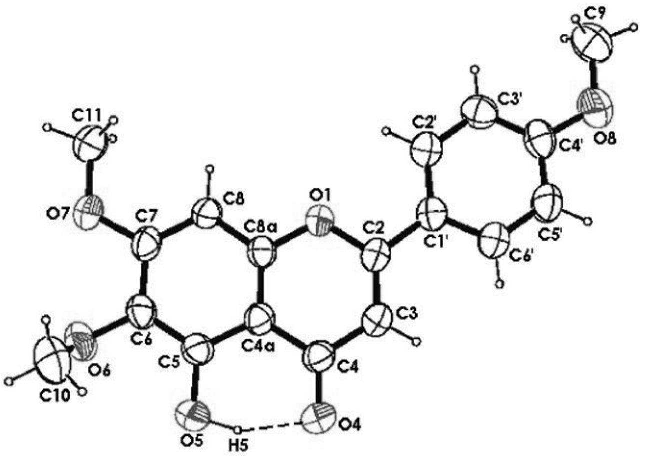

Figure 3. ORTEP view of the molecule with displacement ellipsoids drawn at 50% probability level. H atoms are shown as small spheres of arbitrary radii. The broken line shows the O–H…O intramolecular hydrogen bond.

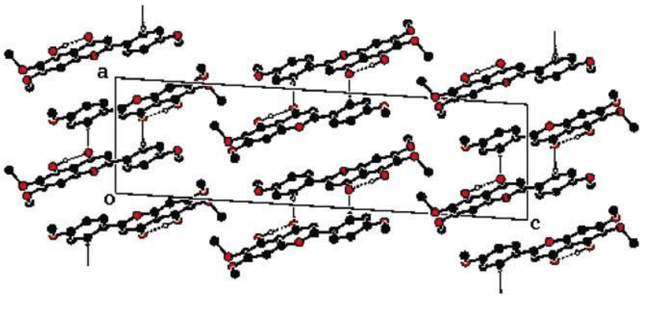

Figure 4. The crystal packing down the b-axis, showing the formation of dimer layers.

benzopyran system have been reported previously (Thinagar *et al* 2003; Malecka *et al* 2004; Ryparczyl-Pirek and Nawrot-Modranka 2004).

The phenyl ring (B) is planar and is rotated by 5·50(4)° from the plane of the benzopyran ring system. The torsion angle for O1–C2–C1′–C2′ is –4·3(2)°. In the generally preferred conformation, the dihedral angle between the phenyl and benzopyran ring is expected to be small as shown in the case of the title compound. In related flavones, the reported increase in dihedral angle to 24·8 (Shoja 1989) and 28° (Ting and Watson 1972) has the effect of increasing the length of the C1′–C2 bond from 1·466(2) Å to 1·485(5) and 1·504(9) Å, respectively. The length of the double bond C4=O4 [1·257(2) Å] is larger than the standard value for carbonyl group [1·192 Å (Allen *et al* 1987)] and lengthening of the C4=O4 double bond is due to strong intramolecular hydrogen bond between O4 and O5. The methoxy group bound to C6 has an out-of-plane conformation: C5–C6–O6–C10 = 83·3(2)°. The other two methoxy groups bound to C4′ and C7 are slightly out of plane with C3′–C4′–O8–C9 = 1·4(3)° and C8–C7–O7–C11 = 3·3(2)°.

The hydroxyl group at C5 has a gauche arrangement with respect to the H5–O5–C5–C4a torsion angle, giving rise to a strong intramolecular contact between the H atom of the O5 hydroxyl group and carbonyl atom, O4 (table 4). This leads to the formation of a pseudo-six-membered ring comprising of atoms O4, C4, C4a, C5, O5 and H5 (figure 3). Intermolecular C6′–H16…O4 hydrogen bond links the molecules into dimers. The dimers are arranged in a manner to form layers (figure 4). Within the layers, the dimers are arranged parallel to each other and are stabilized by π–π interactions (figure 5).

3.2 *Compound II*

Bond distances and angles are comparable with the values reported for similar flavonoids (Seetharaman and Rajan 1992; Wallet *et al* 1992, 1993). The lengthening of the double bond C4=O4 [1·252(2) Å] is due to strong intra-

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms (e.s.d.'s are given in parenthesis).

Atom	x	y	z	U_{eq}*
Compound I				
O1	0·8216(1)	0·9653(1)	0·0526(1)	0·0447(3)
C2	0·7337(2)	0·8785(2)	0·01478(6)	0·0430(4)
C3	0·6812(2)	0·7033(2)	0·01805(6)	0·0491(4)
C4	0·7130(2)	0·5989(2)	0·06129(6)	0·0464(4)
C4a	0·8073(2)	0·6924(2)	0·10061(6)	0·0424(4)
C5	0·8487(2)	0·6049(2)	0·14543(6)	0·0456(4)
C6	0·9365(2)	0·6991(2)	0·18264(6)	0·0475(4)
C7	0·9834(2)	0·8826(2)	0·17592(6)	0·0461(4)
C8	0·9439(2)	0·9716(2)	0·13228(6)	0·0447(4)
C8a	0·8568(2)	0·8737(2)	0·09543(6)	0·0406(4)
C9	0·6565(3)	1·4962(3)	–0·15384(8)	0·0730(6)
C10	0·8581(3)	0·5964(4)	0·25861(8)	0·0842(7)
C11	1·1304(3)	1·1453(3)	0·20939(8)	0·0698(6)
C1′	0·7048(2)	0·9977(2)	–0·02766(6)	0·0445(4)
C2′	0·7717(2)	1·1732(3)	–0·02930(6)	0·0501(4)
C3′	0·7399(2)	1·2847(3)	–0·06964(7)	0·0541(4)
C4′	0·6402(2)	1·2188(3)	–0·10926(6)	0·0535(5)
C5′	0·5714(3)	1·0449(3)	–0·10799(7)	0·0588(5)
C6′	0·6023(2)	0·9359(3)	–0·06800(6)	0·0541(5)
O4	0·6622(2)	0·4365(2)	0·06547(5)	0·0623(4)
O5	0·8051(2)	0·4280(2)	0·15174(5)	0·0607(4)
O6	0·9864(2)	0·6104(2)	0·22503(5)	0·0642(4)
O7	1·0692(2)	0·9608(2)	0·21484(4)	0·0586(4)
O8	0·5979(2)	1·3145(2)	–0·15086(5)	0·0713(4)
Compound II				
O1	0·4722(3)	0·4051(1)	0·2853(1)	0·0164(3)
C2	0·4908(4)	0·2847(2)	0·2838(1)	0·0148(4)
C3	0·3147(4)	0·2026(2)	0·2187(1)	0·0148(4)
O3	0·3261(3)	0·0830(1)	0·2264(1)	0·0175(3)
C4	0·0892(4)	0·2398(2)	0·1520(1)	0·0151(4)
O4	–0·0827(3)	0·1658(1)	0·0953(1)	0·0190(3)
C4a	0·0732(4)	0·3678(2)	0·1588(1)	0·0155(4)
C5	–0·1406(4)	0·4170(2)	0·1024(1)	0·0163(4)
O5	–0·3351(3)	0·3439(1)	0·0389(1)	0·0212(4)
C6	–0·1542(4)	0·5399(2)	0·1117(2)	0·0177(4)
C7	0·0482(4)	0·6146(2)	0·1769(2)	0·0170(4)
O7	0·0554(3)	0·7361(1)	0·1915(1)	0·0217(4)
C8	0·2622(4)	0·5694(2)	0·2346(2)	0·0164(4)
C8a	0·2659(4)	0·4466(2)	0·2247(1)	0·0151(4)
C1′	0·7117(4)	0·2632(2)	0·3658(1)	0·0151(4)
C2′	0·7910(4)	0·3483(2)	0·4567(2)	0·0179(4)
C3′	0·9969(4)	0·3329(2)	0·5355(2)	0·0186(4)
C4′	1·1301(4)	0·2312(2)	0·5239(2)	0·0164(4)
C5′	1·0569(4)	0·1465(2)	0·4338(2)	0·0163(4)
C6′	0·8478(4)	0·1634(2)	0·3553(2)	0·0151(4)
O8	1·3291(3)	0·2250(1)	0·6062(1)	0·0191(4)
C9	1·4854(4)	0·1276(2)	0·5961(2)	0·0189(5)
C10	0·3629(4)	0·0135(2)	0·1286(2)	0·0195(5)
C11	–0·1688(4)	0·7891(2)	0·1448(2)	0·0210(5)

*$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 3. Bond lengths (Å) and bond angles (°) for non-hydrogen atoms (e.s.d.'s are given in parentheses).

	Compound I	Compound II
C1′–C2	1·466(2)	1·480(2)
C3–C4	1·426(2)	1·457(2)
C4–C4a	1·441(2)	1·448(3)
C4–O4	1·257(2)	1·252(2)
C6–C7–O7	114·5(1)	123·7(2)
C8–C7–O7	124·2(1)	114·2(2)
C3–C4–C4a	115·5(1)	115·5(2)
C3′–C4′–O8	125·4(2)	114·6(2)
C5′–C4′–O8	114·9(2)	125·1(2)

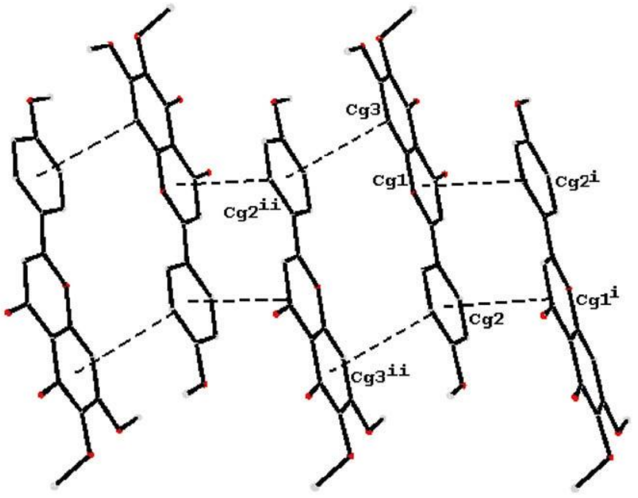

Figure 5. Molecular stacking along the *a*-axis showing the linking of the molecules by $\pi\ldots\pi$ interactions. Ring centroids involved in the $\pi\ldots\pi$ interactions are joined by dashed lines.

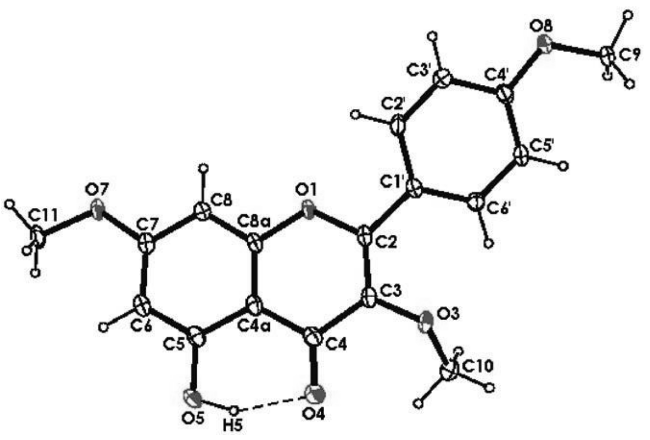

Figure 6. 50% Thermal ellipsoid plot of 5-hydroxy-3,7,4′-trimethoxyflavone. H atoms are shown as small spheres of arbitrary radii. The broken line shows the O–H…O intramolecular hydrogen bond.

Table 4. O–H...O, C–H...O and C–H...π hydrogen bonding geometry. Cg2 represents the centre of gravity of the phenyl ring (B) in compound II.

D–H...A	D–H(Å)	D...A(Å)	H...A(Å)	D–H...A(°)
Compound I				
O5–H5···O4	0·95(3)	2·565(2)	1·69(3)	152(3)
C2′–H12···O1	0·93	2·733(2)	2·41	100
C6′–H16···O4^{i}	0·93	3·407(2)	2·51	161
Symmetry code: (i) –*x* + 1, –*y* + 1, –*z*				
Compound II				
O5–H5···O4	0·93(3)	2·597(2)	1·74(4)	152(3)
C6′–H16···O3	0·96(2)	2·970(3)	2·47(2)	113(1)
C6–H6···O5^{i}	0·95(2)	3·463(3)	2·52(2)	174(2)
C10–H101···O4^{ii}	0·97(3)	3·380(3)	2·45(3)	162(2)
C8–H8···O8^{iii}	0·97(2)	3·291(3)	2·33(2)	171(2)
C9–H91···O7^{iii}	0·98(2)	3·436(3)	2·52(2)	156(2)
C9–H92...Cg2^{ii}	0·98(2)	3·511(2)	2·68(2)	142(2)
Symmetry code: (i) *x* + 1, *y*, *z* (iii) –*x* + 1, *y* – 1/2, –*z* + 1 (iv) –*x* + 1, *y* + 1/2, –*z*				

Table 5. Geometry of π–π interactions. Cg represents the centre of gravity of the following rings: Cg1 pyrone ring (C), Cg2 phenyl ring (B), Cg3 phenyl ring (A). CgI...CgJ represents the distance between the ring centroids; CgI...P, the perpendicular distance of the centroid of one ring from the plane of the other. α is the dihedral angle between the planes of rings I and J; β is the angle between normal to the centroid of ring I and the line joining ring centroids; Δ is the displacement of the centroid of ring J relative to the intersection point of the normal to the centroid of ring I and the least-squares plane of ring J.

CgI	CgJ	CgI...CgJ(Å)	CgI...P(Å)	α(°)	β(°)	Δ(Å)
Compound I						
1	2^{i}	3·530(1)	3·400	5·20	15·59	0·95
2	1^{ii}	3·530(1)	3·304	5·20	20·60	1·24
2	3^{ii}	4·043(1)	3·420	5·83	32·22	2·15
3	2^{ii}	4·043(1)	3·518	5·83	29·51	1·99
Symmetry code: (i) –*x* + 1, –*y* + 2, –*z* (ii) –*x* + 2, –*y* + 2, –*z*						
Compound II						
1	2^{i}	3·820(1)	3·751	29·06	10·98	0·72
2	1^{ii}	3·820(1)	3·584	29·06	20·25	1·32
Symmetry code: (i) *x* – 1, *y*, *z* (ii) *x* + 1, *y*, *z*						

molecular hydrogen bond between O4 and O5. The methoxy group bound to C3 has an out-of-plane conformation: C4–C3–O3–C10 = –69·7(2)°. The other two methoxy groups bound to C4′ and C7 are only slightly out of plane with C5′–C4′–O8–C9 = –4·1(3)° and C6–C7–O7–C11 = –5·9(3)°.

The dihedral angle between the pyrone and benzene rings [2·52(5)°] shows the planarity of the benzopyran moiety. Nevertheless, a lengthening of the C3–C4 and C4–C4a bonds is observed, to 1·457(2) and 1·448(3) Å, respectively, and the C3–C4–C4a bond angle decreases to 115·5(2)°. In contrast, the shortest bond length is observed for atom C2, viz. 1·356(3) Å. The molecule is not planar. The dihedral angle between the phenyl ring and the benzopyran portion is 29·11(5)°. The large value of dihedral angle has the effect of increasing the length of the C2–C1′ bond [1·480(2) Å] linking the phenyl ring and the benzopyran moiety.

The hydroxy group, O4, has a gauche arrangement with respect to the H5–O5–C4–C4a torsion angle (1·4°), giving rise to a short [1·74(4) Å] intramolecular contact between the H atom of the hydroxyl group and carbonyl atom O4. Similar structural motifs have also been found in other flavonoids obtained from natural sources (Marek *et al* 2003).

The projection of the crystal structure down *a* axis is shown in figure 7. The crystal structure is stabilized by the presence of four intermolecular short contacts of the type C–H...O. There is also one C–H...π (arene) hydrogen bond with H...centroid distance of <2·7 Å which serves to link molecules along *a*-axis to form layers (figure 8). Atom C9 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-

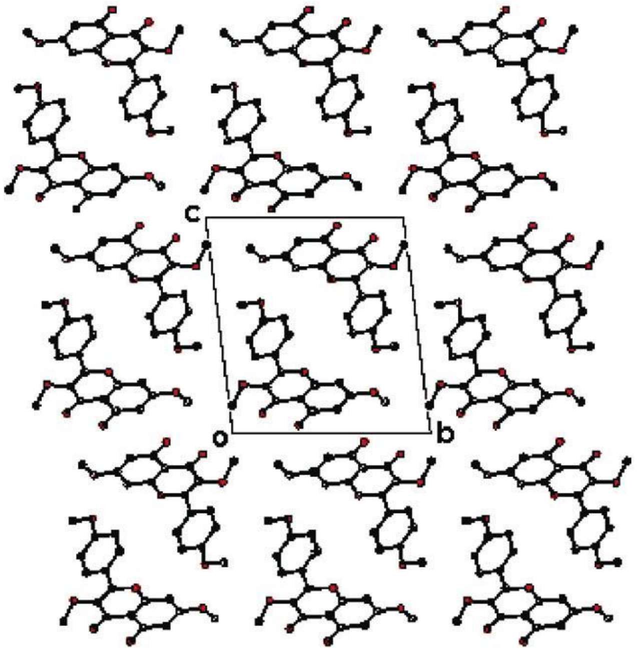

Figure 7. Packing of the molecules in the unit cell down *a*-axis.

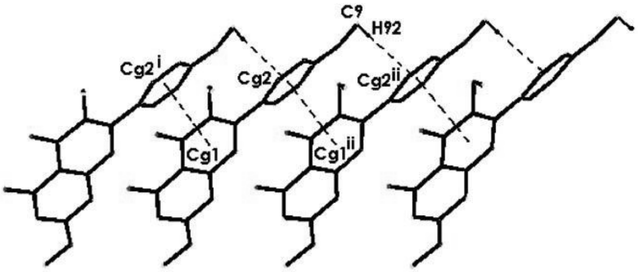

Figure 8. Molecular stacking along the a-axis showing the linking of the molecules by C–H…π and π–π interactions. Ring centroids involved in the C–H…π and π–π interactions are joined by dashed lines.

bond donor to the phenyl ring (B) in the molecule at (x + 1, y, z). The molecules within the layers are further stabilized by π–π interactions between the pyrone ring (C) and phenyl ring (B). The interacting molecules are related by unit-cell translations along the short *a*-axis.

4. Conclusions

(I) Weak intermolecular interactions play a decisive role in determining the three-dimensional structure of molecular crystals. Classical hydrogen bonds are by far the most important—and best known—of these interactions, but in the absence of strong hydrogen-bond donors or acceptors (or sometimes in spite of their presence), other weak interactions (C–H…O, C–H…π and π–π) play a crucial part in assembling the molecules into an organized supramolecular structure.

(II) An analysis of π–π interactions reveals that near face–to–face alignment of the aromatic rings is extremely rare. The usual π–π stacking is an offset arrangement of the rings i.e. the rings are parallelly displaced. Such a parallelly displaced structure has a contribution from π–σ attraction, the more so with increasing offset.

Acknowledgements

The authors are grateful to Prof. P K Bharadwaj, Department of Chemistry, Indian Institute of Technology, Kanpur and Sophisticated Analytical Instrument Facility, Indian Institute of Technology, Madras, Chennai, for providing the intensity data collection facility. Two of authors (VKG and GB) are grateful to the University Grants Commission, Govt. of India, for research funding.

References

Allen F H 2002 *Acta Crystallogr.* **B58** 380

Allen F H, Kennard O, Watson D G, Brammer L, Orpen A G and Taylor R 1987 *J. Chem. Soc.* Perkin Trans-II **S1-S19**

Amabilino D B and Stoddart J F 1995 *Chem. Rev.* **95** 2725

Asolkar L V, Kakkar K K and Chakre O J 1992 *Second supplement to glossary of Indian medicinal plants with active principles* (New Delhi: CSIR) Part 1, p. 195

Brahmachari G 2005 Private communication, Visva Bharati University, Santiniketan

Brahmachari G and Gorai D 2006 *Curr. Org. Chem.* **10** 873

Brahmachari G and Gorai D 2007 *Recent developments in the research of naturally occurring flavonoids: An overview,* in *Chemistry of natural products: Recent trends and developments* (ed.) G Brahmachari (Trivandrum: Research Signpost) Ch. 4

Brown S P, Schnell I, Brand J D, Mullen K and Spiess H 1999 *J. Am. Chem. Soc.* **121** 6712

Chipot C, Jaffe R, Maigret B, Pearlman D A and Kollman P A 1996 *J. Am. Chem. Soc.* **118** 11217

Claessens C G and Stoddart J F 1997 *J. Phys. Org. Chem.* **10** 254

Desiraju G R 1992 *Mol. Cryst. Liq. Cryst.* **211** 63

Desiraju G R 1996 *Acc. Chem. Res.* **29** 441

Desiraju G R and Steiner T 1999 *The weak hydrogen bond in structural chemistry and biology* (Oxford: Oxford University Press)

Farrugia L J 1997 *J. Appl. Cryst.* **30** 565

Farrugia L J 1999 *J. Appl. Cryst.* **32** 837

Hannon M J, Painting C L and Alcock N W 1999 *Chem. Commun.* 2023

Hirsch K A, Wilson S R and Moore J S 1997 *Chem. Eur. J.* **3** 765

Hunter C A 1993 *Angew. Chem.: Int. Ed. Engl.* **32** 1653

Hunter C A 1994 *Chem. Soc. Rev.* 101

Janiak C 2000 *J. Chem Soc. Dalton Trans.* 3885

Janiak C, Temizdemir S and Dechert S 2000 *Inorg. Chem. Commun.* **3** 271

Kapil V, Sinha A K and Sinha G K 1983 *Bull. Med. Ethnobot. Res.* **4** 124

Lightfoot M P, Mair F S, Pritchard R G and Warren J W 1999 *Chem. Commun.* 1945

Malecka M, Massa W and Budzisz E 2004 *Acta Crystallogr.* **C60** 762

Marek J, Vesela D, Liskova M and Zemlicka M 2003 *Acta Crystallogr.* **C59** 127

Nardelli M 1995 *J. Appl. Cryst.* **28** 659

Ning G L, Wu L P, Sugimoto K, Munakata M, Kuroda-Sowa T and Maekawa M 1999 *J. Chem. Soc. Dalton Trans.* 2529

Nishio M and Hirota M 1989 *Tetrahedron* **45** 7201

Nishio M, Umezawa Y, Hirota M and Takeuchi Y 1995 *Tetrahedron* **51** 8665

Nishio M, Hirota M and Umezawa Y 1998 *The C–H... π interactions* (*Evidence, nature and consequences*) (New York: Wiley-VCH)

North A C T, Phillips D C and Mathews F S 1968 *Acta Crystallogr.* **A24** 351

Ryparczyl-Pirek A J and Nawrot-Modranka J 2004 *Acta Crystallogr.* **E60** 988

Seetharaman J and Rajan S S 1992 *Acta Crystallogr.* **C48** 1714

Sheldrick G M 1997 *SHELXS97* and *SHELXL97* (Germany: University of Gottingen)

Shoja M 1989 *Acta Crystallogr.* **C45** 828

Steiner T 1996 *Cryst. Rev.* **6** 1

Takahashi H, Tsuboyama S, Umezawa Y, Honda K and Nishio M 2000 *Tetrahedron* **56** 6185

Thinagar S, Velmurugan D, Shanmuga Sundara Raj S, Fun H-K, Gupta S C, Merazig H and Bouacida S 2003 *Acta Crystallogr.* **C59** 181

Ting H and Watson W H 1972 *Acta Crystallogr.* **B28** 1046

Wahl M C and Sundaralingam M 1997 *Biochem. Sci.* **22** 97

Wallet J C, Gaydou E M, Tinant B, Declercq J-P, Baldy A and Bonifassi P 1990 *Acta Crystallogr.* **C46** 1131

Wallet J C, Gaydou E M, Espinosa E, Osorno O, Molins E and Miravitlles C 1992 *Acta Crystallogr.* **C48** 86

Wallet J C, Wojtczak A, Cody V, Galitsky N and Gaydou E M 1993 *Acta Crystallogr.* **C49** 357

Wealth of India 1962 *Raw materials* (New Delhi: CSIR) p. 116