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Structure of 2-(2,6-Dimethoxyphenyl)-7-hydroxy-4*H*-1-benzopyran-4-one (7-Hydroxy-2′,6′-dimethoxyflavone)

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Abstract. $C_{17}H_{14}O_5$, $M_r = 298{\cdot}29$, monoclinic, $I2/a$, $a = 15{\cdot}538\,(6)$, $b = 11{\cdot}919\,(4)$, $c = 16{\cdot}083\,(4)$ Å, $\beta = 104{\cdot}72\,(12)°$, $V = 2881\,(2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}375$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}95$ cm^{-1}, $F(000) = 1248$, $T = 294$ K, $R = 0{\cdot}051$ for 1898 observed reflections [$F > 1\sigma(F)$]. The general shape of the molecule can be defined by two different regions: the chromone atoms including the O atom of the hydroxyl group lie in a plane, while the phenyl atoms including the O atoms of the methoxy groups lie in another plane. The angle between these mean planes is 68·2°.

Introduction. Hydrogen bonds are frequently responsible for stabilization of the crystal structures of hydroxyflavonoids. When a hydroxy group is located at C5 an intramolecular hydrogen bond is formed with the neighbouring carbonyl oxygen atom. Other hydroxyl groups in the molecule can form intermolecular hydrogen bonds with either the carbonyl oxygen or hydroxyl groups [centaureidin (Fronczek, Parodi & Fischer, 1989)] and in addition with solvent molecules such as water [quercetin (Rossi, Rickles & Halpin, 1986); penduletin (Parmar, Jain, Simonsen & Boll, 1987)].

The crystallization of fully methoxylated flavonoids is generally governed by stacking and packing forces. However, intermolecular hydrogen bonds are possible with solvent molecules. 5,6-Benzoflavone crystallizes with a water molecule in the asymmetric unit (Rossi, Cantrell, Farber, Dyott, Carrell & Glusker, 1980). 2′,6′-Dimethoxyflavone crystallizes with numerous acids [acetic (Wallet, Gaydou & Baldy, 1989); formic, propionic (Tinant, Declercq, Wallet, Gaydou & Baldy, 1991)].

Hydrogen bonds which involve the carbonyl oxygen atom are thought to influence the twist of the exocyclic phenyl ring. The role of these associations may be important in predicting the way flavonoids bind to biological macromolecules (Cody, 1988).

Experimental. Irregular prismatic crystal of approximate dimensions 0·50 × 0·30 × 0·66 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell constants from least-squares analysis of 25 high-angle reflections, intensity data collected by the ω–2θ zigzag scan technique, no fluctuations in standard reflections (0·8%), $2 \le 2\theta \le 50°$, $-18 \le h \le 18$, $0 \le k \le 14$, $0 \le l \le 19$, 3848 reflections collected, 2537 unique, and 1898 considered to be observed [$F > 1\sigma(F)$] and used in structure analysis; Lp correction, no correction for absorption.

The structure was solved by direct methods with a straightforward run of the *MULTAN*11/84 program (Main, Germain & Woolfson, 1984). Full-matrix refinement on F was carried out with the *SHELX*76 least-squares program (Sheldrick, 1976) using anisotropic thermal parameters for the non-H atoms and two kinds of global isotropic temperature factors for the H atoms. The H atoms were located by difference Fourier syntheses. The refinement process converged at $R = 0{\cdot}0508$, $wR = 0{\cdot}0555$ with $w =$

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$1/[\sigma^2(F) + 0{\cdot}002155F^2]$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149) except for those of the H atoms (Stewart, Davidson & Simpson, 1965). No significant shift/e.s.d. value in the final cycle. Maximum and minimum final difference Fourier map peaks were 0·16 and −0·19 e Å^{-3} respectively.

Discussion. Final atomic coordinates with their equivalent temperature factors are listed in Table 1.* Bond lengths and angles are given in Table 2. Fig. 1 represents a perspective view of the asymmetric unit with the atom numbering. The general shape of the molecule can be defined by two different regions: chromone atoms, including the oxygen atom of the hydroxyl group, lie in one plane (r.m.s.d. = 2·8%), while the phenyl atoms, including the oxygens of the methoxy groups, lie in another plane (r.m.s.d. = 2·6%). The angle between these mean planes is 68·2°. This is within the range of values found for 2′,6′-dimethoxyflavone and its solvates (Tinant *et al.*, 1991).

The crystal packing is illustrated in Fig. 2† and Table 3 shows atoms involved in intra- and intermolecular short contacts. An intermolecular hydrogen bond O7—H7···O4 exists between the hydroxyl and carbonyl groups and forms polymer chains. The length of the carbonyl bond agrees with this hydrogen bond. Such chains are also found in 5,7-dihydroxy-4′-methoxyflavone (Cantrell, 1986). Hydrogen bonds may contribute to a mesomeric form which involves the chromone system rather than the exocyclic phenyl ring (see scheme).

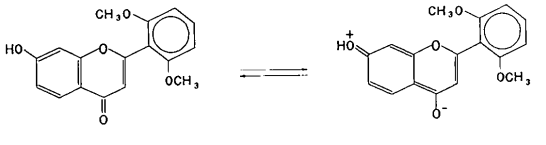

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent temperature factors* (Å^2)

$$B_{eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	6714 (1)	1639 (1)	506 (1)	4·52
O4	4452 (1)	749 (1)	1185 (1)	6·07
O7	8094 (1)	−1814 (1)	1487 (1)	5·80
O2′	6131 (1)	2307 (2)	−1300 (1)	6·64
O6′	6146 (1)	4366 (1)	1160 (1)	6·30
C2	5992 (2)	2326 (2)	348 (1)	4·06
C3	5250 (2)	2058 (2)	563 (2)	4·49
C4	5138 (2)	1008 (2)	964 (2)	4·44
C5	5908 (2)	−806 (2)	1468 (2)	4·83
C6	6641 (2)	−1472 (2)	1595 (2)	5·03
C7	7399 (2)	−1106 (2)	1359 (1)	4·43
C8	7419 (2)	−47 (2)	1006 (2)	4·41
C9	6664 (1)	613 (2)	876 (1)	3·91
C10	5898 (1)	269 (2)	1099 (1)	3·95
C1′	6147 (2)	3373 (2)	−88 (2)	4·49
C2′	6216 (2)	3344 (2)	−934 (2)	5·26
C3′	6331 (2)	4327 (3)	−1363 (2)	6·54
C4′	6387 (2)	5330 (3)	−923 (3)	6·87
C5′	6327 (2)	5384 (2)	−91 (2)	6·15
C6′	6205 (2)	4409 (2)	332 (2)	4·95
C2′1	6169 (5)	2214 (4)	−2165 (3)	12·11
C6′1	6163 (3)	5410 (3)	1604 (3)	7·89

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C2—O1	1·359 (2)	C6—C5	1·360 (3)
C9—O1	1·371 (2)	C10—C5	1·410 (3)
C4—O4	1·245 (2)	C7—C6	1·398 (3)
C7—O7	1·344 (3)	C8—C7	1·387 (3)
C2′—O2′	1·361 (3)	C9—C8	1·384 (3)
C2′1—O2′	1·411 (4)	C10—C9	1·391 (3)
C6′—O6′	1·358 (3)	C2′—C1′	1·393 (3)
C6′1—O6′	1·431 (3)	C6′—C1′	1·399 (3)
C3—C2	1·324 (3)	C3′—C2′	1·395 (4)
C1′—C2	1·481 (3)	C4′—C3′	1·381 (4)
C4—C3	1·438 (3)	C5′—C4′	1·365 (5)
C10—C4	1·444 (3)	C6′—C5′	1·384 (4)
C9—O1—C2	119·0 (2)	C10—C9—O1	121·4 (2)
C2′1—O2′—C2′	118·3 (3)	C10—C9—C8	122·8 (2)
C6′1—O6′—C6′	117·3 (2)	C5—C10—C4	122·6 (2)
C3—C2—O1	122·5 (2)	C9—C10—C4	120·1 (2)
C1′—C2—O1	111·8 (2)	C9—C10—C5	117·2 (2)
C1′—C2—C3	125·8 (2)	C2′—C1′—C2	120·2 (2)
C4—C3—C2	122·7 (2)	C6′—C1′—C2	120·9 (2)
C3—C4—O4	123·6 (2)	C6′—C1′—C2′	118·9 (2)
C10—C4—O4	122·1 (2)	C1′—C2′—O2′	115·0 (2)
C10—C4—C3	114·3 (2)	C3′—C2′—O2′	124·0 (3)
C10—C5—C6	120·9 (2)	C3′—C2′—C1′	120·9 (3)
C7—C6—C5	120·5 (2)	C4′—C3′—C2′	118·2 (3)
C6—C7—O7	117·5 (2)	C5′—C4′—C3′	122·2 (3)
C8—C7—O7	122·3 (2)	C6′—C5′—C4′	119·6 (3)
C8—C7—C6	120·2 (2)	C1′—C6′—O6′	115·3 (2)
C9—C8—C7	118·2 (2)	C5′—C6′—O6′	124·5 (2)
C8—C9—O1	115·8 (2)	C5′—C6′—C1′	120·2 (3)

This is corroborated by a shorter C4—C10 bond length: 1·444 (3) Å [1·465 (4) Å for the mean value of the three conformers of 2′,6′-dimethoxyflavone (Tinant *et al.*, 1991)]; and a shorter C7—O7 bond length: 1·344 (3) Å, [1·358 (7) Å for quercetin and 1·360 (2) Å for centaureidin]. In these two latter compounds, the hydroxyl group in position 7 is not bound to other groups.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54301 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The matrix which changes monoclinic I group basis (a,b,c) to monoclinic C group basis (a',b',c') may be represented by

$$\begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix},$$

and the new basis vectors (a',b',c') define $\beta' = a'c' \simeq 143°$. This β' value produces an angle close to 37° between the [100] and [001] directions. Then, if we take the new basis vectors, a strong correlation between x and z coordinates would be obtained for each atomic parameter. Subsequently, the indetermination increases and the structure resolution becomes less accurate.

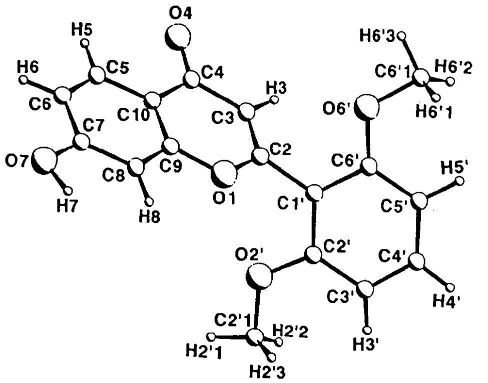

Fig. 1. Perspective view of the molecule with atom numbering.

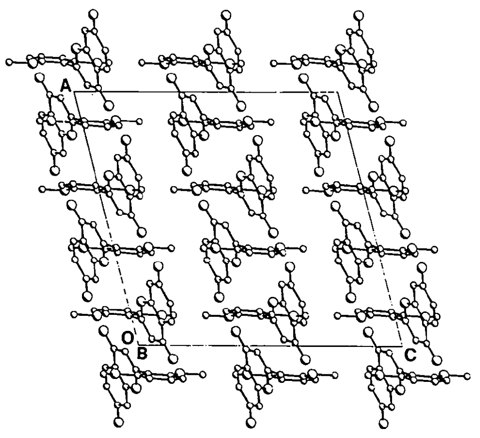

Fig. 2. Crystal packing.

Table 3. *Intra- and intermolecular short-contact distances* (Å) *and angles* (°)

	C—H	H···O	C···O	C—H···O
C5—H5···O4^{i}	1·008	2·545	2·870	98·3
C6—H6···O7^{ii}	0·966	2·893	3·365	134·4
C8—H8···O4^{iv}	0·951	2·604	3·210	122·0
C6'1—H6'1···O7^{iii}	1·066	3·180	3·430	94·4
C6'1—H6'3···O7^{iii}	1·029	3·140	3·430	97·5
	O—H	H···O	O···O	O—H···O
O7—H7···O4^{iv}	0·974	1·655	2·612	165·5

Symmetry code: (i) x, y, z; (ii) $1·5-x, -0·5-y, 0·5-z$; (iii) $1·5-x, 0·5-y, 0·5-z$; (iv) $x-0·5, -y, z$.

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O···H—C(CCl$_3$) Hydrogen Bonding in the Structure of Methyl 6-Methyl-2,4-bis(trichloromethyl)-1,3-benzodioxin-8-carboxylate

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Abstract. 6-Methyl-2,4-bis(trichloromethyl)-1,3-benzodioxin-8-carboxylic acid and its methyl and ethyl esters have been prepared. For the methyl ester $C_{13}H_{10}Cl_6O_4$, $M_r = 442·94$, triclinic, $P\bar{1}$, $a = 9·225\,(2)$, $b = 9·401\,(1)$, $c = 10·748\,(1)$ Å, $\alpha = 76·746\,(9)$, $\beta = 72·20\,(1)$, $\gamma = 82·68\,(1)°$, $V = 862·2\,(2)$ Å^3, $Z = 2$, $D_x = 1·71$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0·71069$ Å, $\mu = 10·2$ cm^{-1}, $F(000) = 444$, room temperature, final $R = 0·031$ for 2385 unique counter reflections with $F_o > 4\sigma(F_o)$. The compound forms hydrogen-bonded dimers involving the carbonyl oxygen atom and the axial hydrogen atom bonded to C(2). In addition four carbon atoms in the aromatic ring and the non-hydrogen atoms of the methoxy-

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