

Table 3. *Hydrogen-bond geometry*

$A-H \cdots B$	$A-H$ (Å)	$H \cdots B$ (Å)	$A \cdots B$ (Å)	$A-H \cdots B$ (°)
O(1)—H(3)···O(3 ^b)	0.90 (5)	1.83 (4)	2.696 (3)	160 (5)
O(2)—H(10)···O(3 ^{ll})	0.89 (3)	1.82 (3)	2.679 (3)	163 (3)
N(2)—H(8)···O(1 ^{lll})	0.90 (6)	2.07 (5)	2.944 (4)	163 (6)
N(1)—H(7)···O(2 ^{lv})	0.81 (4)	2.34 (3)	3.128 (4)	166 (4)

Symmetry code: (i) $1-x, y-\frac{1}{2}, 1\frac{1}{2}-z$; (ii) $1-x, \frac{1}{2}+y, 1\frac{1}{2}-z$; (iii) $x-1, y, z$; (iv) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (v) $-x, \frac{1}{2}+y, 1\frac{1}{2}-z$; (vi) $-x, y-\frac{1}{2}, 1\frac{1}{2}-z$.

O(1)—H(3)···O(3)] to the urea O. Each urea O accepts hydrogen bonds from the resorcinol molecules related by **b** thus forming infinite chains parallel to that direction. Weaker cross-links between the chains are formed by N—H···O bonds. The shortest of these, N(2)—H(8)···O(1), joins together chains related by a 2_1 axis through $(0, y, \frac{3}{4})$ and a further, longer bond N(1)—H(7)···O(2) connects chains related by a 2_1 axis through $(x, \frac{3}{4}, \frac{1}{4})$. In this manner four of the six possible H are involved in hydrogen bonding and a three-dimensional network is formed, Fig. 1. The geometry of the hydrogen bonds is given in Table 3. The inter-

molecular distances are similar to those reported for the hydroquinone—urea complex (Mahmoud & Wallwork, 1975) in which the shortest distances (2.683 and 2.702 Å) were also from hydroxyl groups to urea O with longer N—H···O bonds (2.980, 3.049 and 3.048 Å) to the phenol O. Short contacts between molecules of the same type were absent in that structure also.

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3-Benzoyl-5,8-dihydroxyflavone,* a New Synthetic Contact Allergen

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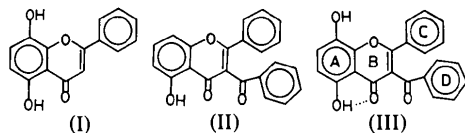
Abstract. $C_{22}H_{14}O_5$, monoclinic, $P2_1/c$, $a = 10.149$ (4), $b = 18.124$ (7), $c = 9.393$ (4) Å, $\beta = 100.54$ (5)°, ($\lambda = 0.7107$ Å, $T = 293$ K), $V = 1698.6$ Å³, $Z = 4$, $M_r = 358.35$, $D_x = 1.401$ Mg m⁻³, $F(000) = 744$, $\mu(\text{Mo } K\alpha) = 0.108$ mm⁻¹; $R_1 = 8.2\%$ for 1288 observed reflections. The structure has been elucidated by X-ray analysis. The benzo-4-pyrone system is nearly coplanar. The conformation of the molecule is characterized by three planes: the *A, B* rings, the phenyl ring *C* and the benzoyl ring *D*. The angle between rings *A* and *C* is 32 (2)°, *A* and *D* 82 (2)°, and *C* and *D* 113 (1)°. The hydroxyl H at O(5) is hydrogen-bonded to the C(4) carbonyl group.

Intermolecular hydrogen bonds of the type O—H···O form endless chains with alternate molecules along **b**.

Introduction. The naturally occurring flavone primetin (I) has been shown to possess a sensitizing capacity. It crystallizes as a polytypic structure with twinning effects (Jarchow & Schmalle, 1981). These effects led to abnormally short as well as long bonds being observed in the structure (Jarchow, Schmalle, Hausen & Schulz, 1983). To obtain more suitable crystals and to collect further material for testing purposes, (I) was synthesized in several steps (Schaefer & Krebs, 1981). In the first step 3-benzoyl-5-hydroxyflavone (II) was obtained. Finally, a third compound (III) was detected as a by-product during purification of primetin (I)

* 3-Benzoyl-5,8-dihydroxy-2-phenyl-4*H*-1-benzopyran-4-one.

whose presence had not been expected. When the synthetic material of (I) was purified by thin-layer chromatography small amounts of a second compound could be separated. As this compound revealed a similar sensitizing capacity to (I) when tested in guinea pigs, its structure (III) was also identified by X-ray analysis.



Pale-yellow crystals were obtained from slow evaporation of acetone solutions. Experimental details: crystal dimensions $0.22 \times 0.05 \times 0.46$ mm, oriented along *c*, space group $P2_1/c$ from Weissenberg and precession photographs, unit-cell dimensions from least-squares refinement with angular settings of 14 reflections, diffractometer Syntex $P2_1$, graphite-monochromated Mo $K\alpha$ radiation, 2341 independent reflections, $2\theta \leq 44^\circ$, $\theta-2\theta$ scan, variable scan rate of 2.0 to $29.3^\circ \text{ min}^{-1}$, Lorentz-polarization correction, no absorption correction, 1288 reflections with $I \geq 3\sigma(I)$, 1053 with $I \leq 3\sigma(I)$ after data reduction (Eck, 1976). The structure was solved with *MULTAN* 80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson,

1980). Normalization was performed with underestimated unit-cell contents $4 \times (\text{C}_{16}\text{H}_{10}\text{O}_3)$. $284 E's \geq 1.35$ with phases in the most consistent set ($\psi_0 = 0.97$, combined figure of merit = 2.95) showed an *E* map with 27 atomic positions. The flavone primetin (I) was identified as part of the structure and a keto group connected with a phenyl ring at position C(3) was also found. After four cycles of refinement, carried out with *SHELX* (Sheldrick, 1976), of the positional and isotropic temperature parameters the value of *R* dropped to 12%. The phenyl rings *C* and *D* were now treated as rigid-body groups. Refinement of anisotropic temperature factors for the five O atoms and 22 C atoms led to $R = 10.3\%$. Five H-atom positions could be located in the difference map. The missing H-atom positions were calculated with *XANADU* (Roberts & Sheldrick, 1975). In the final full-matrix least-squares refinement a separation of the 263 variables into smaller groups was necessary. Positional parameters for all atoms and anisotropic temperature parameters for the C and O atoms were varied. The isotropic temperature factors for all H atoms were fixed at $U = 0.03 \text{ \AA}^2$. The final value of *R* for 1288 reflections was 8.2%, based on unit weights. The difference map showed no unusual features. The positional parameters and B_{eq} of the C and O atoms are given in Table 1.*

Table 1. Final positional parameters ($\times 10^4$) and B_{eq} (\AA^2) of 3-benzoyl-5,8-dihydroxyflavone with e.s.d.'s in parentheses

B_{eq} is in the form: $4(b_{11}/a^*{}^2 b_{22}/b^*{}^2 b_{33}/c^*{}^2)^{1/3}$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O(1)	10386 (5)	4989 (3)	2365 (6)	3.3 (0.3)
O(4)	6791 (6)	4143 (3)	2899 (6)	4.2 (0.3)
O(5)	6502 (6)	5266 (3)	4645 (7)	4.5 (0.3)
O(8)	11395 (6)	6237 (3)	3494 (7)	4.4 (0.3)
O(17)	8721 (6)	2747 (3)	1795 (7)	3.6 (0.3)
C(2)	9949 (8)	4337 (4)	1751 (9)	3.1 (0.4)
C(3)	8729 (8)	4045 (4)	1848 (8)	2.7 (0.4)
C(4)	7887 (8)	4415 (4)	2765 (9)	3.0 (0.4)
C(5)	7690 (9)	5516 (5)	4323 (9)	3.7 (0.4)
C(6)	8219 (10)	6180 (4)	4876 (10)	3.8 (0.5)
C(7)	9442 (9)	6421 (4)	4621 (10)	3.7 (0.5)
C(8)	10167 (9)	6024 (4)	3761 (10)	3.4 (0.5)
C(9)	9627 (8)	5365 (4)	3205 (9)	3.3 (0.4)
C(10)	8397 (8)	5096 (4)	3420 (9)	2.9 (0.4)
C(11)	11003 (4)	4017 (3)	1029 (6)	2.7 (0.4)
C(12)	12342 (4)	4164 (3)	1611 (6)	3.9 (0.5)
C(13)	13358 (4)	3843 (3)	1000 (6)	4.3 (0.5)
C(14)	13034 (4)	3376 (3)	-193 (6)	5.4 (0.5)
C(15)	11695 (4)	3230 (3)	-776 (6)	4.5 (0.5)
C(16)	10679 (4)	3550 (3)	-165 (6)	3.3 (0.4)
C(17)	8234 (8)	3316 (5)	1229 (9)	3.0 (0.4)
C(18)	7197 (5)	3322 (3)	-94 (5)	3.4 (0.5)
C(19)	6733 (5)	3987 (3)	-749 (5)	4.5 (0.5)
C(20)	5821 (5)	3984 (3)	-2054 (5)	5.4 (0.6)
C(21)	5372 (5)	3315 (3)	-2705 (5)	5.1 (0.6)
C(22)	5836 (5)	2650 (3)	-2051 (5)	5.0 (0.6)
C(23)	6748 (5)	2654 (3)	-745 (5)	4.2 (0.5)

Discussion. The identification of 5,8-substituted flavones as allergens by X-ray analysis has not previously been reported. Bond distances and angles of (III) involving non-H atoms [excepting H(5)] are given in the *ORTEP* drawing (Johnson, 1971) of Fig. 1. The packing of the structure in the *bc* projection of the unit cell is shown in Fig. 2. The 3-benzoyl ring *D* lies almost in the *bc* plane. The benzo-4-pyrone ring system *A*, *B* is nearly coplanar: torsion angles C(8)–C(9)–C(10)–C(5) $-2.8 (1.1)$ and O(1)–C(9)–C(10)–C(4) $0.0 (1.1)^\circ$, the angle between ring *A* and *B* being $1.5 (1.6)^\circ$. The deviations* of some atoms from the aromatic ring *A* are compared with those of primetin (I) (four independent molecules) and 3',5,5',6-tetramethoxyflavone (TMF) (Ting, Watson & Dominguez, 1972). Because of the disordered structure and polytypism of primetin (I), some significant differences in deviations from the plane of ring *A* were observed. The maximum out-of-plane deviations of the four independent molecules of primetin (I) are $0.015 (9)$, $0.011 (9)$, $0.027 (16)$ and $0.045 (16) \text{ \AA}$, respectively, of TMF $0.017 (14) \text{ \AA}$ and of the title compound (III)

* List of structure factors, anisotropic thermal parameters of the C and O atoms, positional parameters of the H atoms and deviations of atoms from aromatic planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38048 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0.013 (9) Å. The structure of (III) can be described by three different coplanar fragments of the flavone molecule: the benzo-4-pyrone system with rings *A* and *B*, the phenyl ring *C* and the benzoyl ring *D*, the keto group C(17)=O(17) being nearly within the plane *D*. The angle between ring *A* and ring *C* is 32 (2)° in (III), 7 (1), 10 (1), 5 (3) and 14 (3)° in (I), 6 (1)° in 4',6,7-trihydroxyflavylium chloride monohydrate (Ueno & Saito, 1977a), 10 (1)° in 3,5,7,3',4'-pentahydroxyflavylium bromide monohydrate (Ueno & Saito, 1977b) and 28 (1)° in TMF. The angle between rings *A* and *D* in (III) is 82 (2) and between the phenyl rings *C* and *D* 113 (1)°. As well as in other flavones substituted by a hydroxy group in position 5, e.g. in primetin (I)

and acacetin (Cantrell & Gerdom, 1979), the H of the OH group at C(5) is hydrogen-bonded to the C(4) carbonyl group in (III) with distances O(5)–H(5) 1.06 (7) and O(4)···H(5) 1.71 (14) Å, the intramolecular angle OH···O being 148 (4)°. Intermolecular distances were calculated up to 3.7 Å with *ORFFE* (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1971). The shortest O···H contacts between neighbouring molecules were found in the *b* direction. Distances for the intermolecular hydrogen bond are O(8)···O(17ⁱ) 2.749 (11), O(8)–H(8) 0.85 (6) and H(8)···O(17ⁱ) 1.91 (18) Å, the intermolecular angle OH···O being 169 (5)°.

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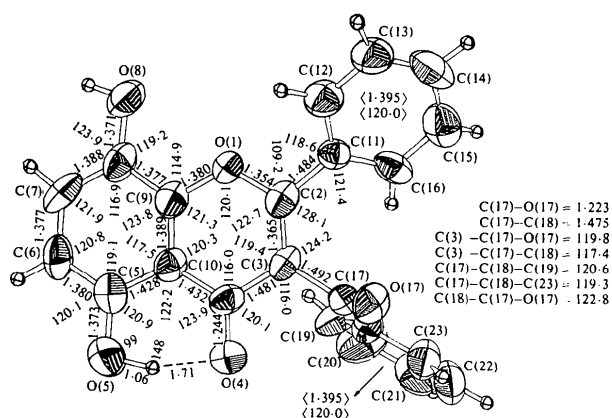


Fig. 1. *ORTEP* drawing of (III) with bond distances (Å) and angles (°). The standard deviations range from 0.006 to 0.014 Å and from 0.4 to 0.9°; for H(5) being 0.07 and 0.14 Å and 4.1°. H atoms are shown as spheres of arbitrary size, C and O atoms are 65% probability ellipsoids.

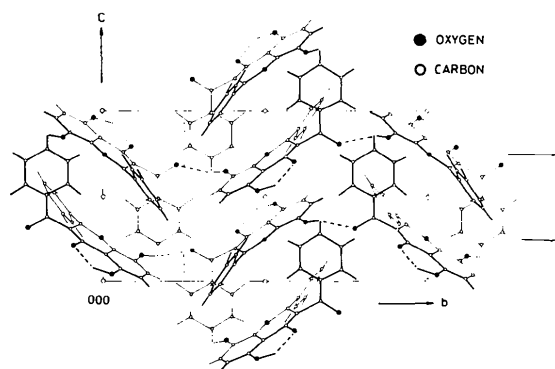


Fig. 2. The *bc* projection with the packing arrangement of the structure of 3-benzoyl-5,8-dihydroxyflavone. The hydrogen bonds are indicated by broken lines.

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