Fig. 2. View of the unit-cell contents. H bonds are indicated by dashed lines.

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D-H\cdots A$	$\angle D-H\cdots A$
N—H(5)···O(3^i)	0·91 (3)	1·88 (3)	2·778 (3)	167 (3)
N—H(6)···O(1W^{ii})	1·01 (4)	1·80 (4)	2·807 (4)	175 (3)
N—H(7)···O(4w^{iii})	0·85 (3)	1·91 (3)	2·753 (4)	170 (3)
O(3w)—H(8)···O(2^{iv})	0·90 (4)	1·86 (4)	2·758 (3)	174 (3)
O(3w)—H(9)···O(2)	0·77 (4)	2·04 (4)	2·757 (3)	156 (4)
O(4w)—H(10)···O(1^i)	0·85 (4)	1·91 (4)	2·736 (3)	164 (4)
O(4w)—H(11)···O(2)	0·64 (3)	2·13 (3)	2·759 (3)	167 (4)

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

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The crystal structure is stabilized by hydrogen bonds involving the amino and phosphinic-acid groups and the water molecules (Fig. 2). Table 3 gives the hydrogen-bond distances and angles. The two water molecules O(3) and O(4) are involved in O—H···O(P) bonds and the protonated amino group forms three N—H···O hydrogen bonds. Each water molecule acts as donor in two hydrogen bonds and as acceptor in one.

The phenyl moiety is nearly planar; the maximum deviation from the best plane through the ring atoms is 0·030 (6) Å.

Structure of (R,S)-Hesperetin Monohydrate

BY WHANCHUL SHIN, SANGSOO KIM AND KWON SOO CHUN

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151, *Korea*

Abstract. 2,3-Dihydro-5,7-dihydroxy-2-(3-hydroxy-4-methoxyphenyl)-4H-1-benzopyran-4-one monohydrate, $C_{16}H_{14}O_6.H_2O$, $M_r = 320·29$, triclinic, $P\bar{1}$, $a = 9·073$ (4), $b = 12·162$ (5), $c = 6·856$ (3) Å, $\alpha = 95·49$ (8), $\beta = 81·32$ (9), $\gamma = 107·16$ (8)° (reduced cell $a = 6·856$, $b = 9·073$, $c = 12·162$ Å, $\alpha = 72·84$, $\beta = 84·51$, $\gamma = 81·32$°), $V = 713·1$ Å^3, $Z = 2$, $D_x = 1·491$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 8·97$ cm^{-1}, $F(000) = 336$, $T = 295$ K, $R = 0·065$ for 1050 observed reflections. The hydroxyl O(5) and keto O(4) atoms form a strong intramolecular hydrogen bond, making a six-membered ring. The pyrone ring adopts a slightly distorted sofa conformation and the phenyl ring is bonded equatorially to the pyrone ring. The two ring systems in hesperetin are nearly parallel to each other, in contrast to the perpendicular arrangement in naringenin. Hydrogen bonds involving the water molecules form molecular double layers.

Introduction. Hesperetin is a naturally occurring flavanone which is unique in that it is, albeit faintly, sweet while most of the flavanoid compounds are known to be tasteless or bitter (Yamato, Hashigaki, Mito & Koyama, 1978). In an effort to provide detailed structural information for related compounds, we have determined the crystal structure of racemic hesperetin and will compare it with the structure of naringenin [2,3-dihydro-5,7-dihydroxy-2-(4-hydroxyphenyl)-4H-1-

Table 1. *Final positional (fractional* × 10^4) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	2689 (4)	4660 (2)	5984 (4)	0·054
C(2)	2533 (7)	4605 (4)	3910 (7)	0·057
C(3)	1323 (7)	3561 (4)	3324 (9)	0·054
C(4)	1568 (6)	2484 (4)	3958 (7)	0·052
C(5)	2668 (5)	1677 (4)	6381 (6)	0·047
C(6)	3399 (6)	1787 (4)	8034 (7)	0·049
C(7)	3848 (5)	2882 (4)	9021 (6)	0·047
C(8)	3599 (5)	3836 (4)	8329 (6)	0·047
C(9)	2904 (5)	3703 (4)	6634 (6)	0·044
C(10)	2403 (5)	2626 (3)	5620 (6)	0·043
O(4)	1034 (4)	1545 (3)	3103 (5)	0·066
O(5)	2155 (4)	612 (2)	5482 (5)	0·062
O(7)	4564 (4)	3032 (3)	10646 (5)	0·063
C(1')	2280 (6)	5729 (4)	3493 (7)	0·051
C(2')	2856 (6)	6731 (4)	4628 (7)	0·049
C(3')	2681 (5)	7757 (4)	4165 (6)	0·047
C(4')	1981 (5)	7840 (4)	2537 (6)	0·050
C(5')	1452 (7)	6847 (4)	1381 (8)	0·062
C(6')	1595 (7)	5818 (4)	1868 (8)	0·069
O(3')	3247 (5)	8736 (3)	5341 (5)	0·075
O(4')	1908 (4)	8898 (2)	2195 (4)	0·056
C(7')	1094 (8)	8989 (5)	601 (9)	0·059
O(W)	4912 (8)	1024 (5)	1635 (7)	0·077

benzopyran-4-one], a tasteless flavanone (Shin & Lah, 1986).

Experimental. Colorless prismatic crystals obtained from an aqueous ethanol solution at room temperature, crystal *ca* 0·2 × 0·2 × 0·4 mm, Rigaku AFC diffractometer, graphite-monochromated Cu $K\alpha$ radiation, $2\theta < 110°$, ω–2θ scan, scan speed 4° min^{-1} in 2θ, ω-scan width (1·6 + 0·4 tanθ)°, background measured for 12 s on either side of the peak; cell parameters by least-squares fit to observed 2θ values for 25 centered reflections with $25 < 2\theta < 40°$; intensity checks for three standard reflections showed little ($\pm$1·5%) variation; 1473 independent reflections (h −8 to 9, k −12 to 12, l 0 to 6), 1050 (71·3%) observed with $I > 2·5\sigma(I)$ and used in refinement; Lp corrections, no absorption or extinction correction. Structure solved by direct methods with *MITHRIL* (Gilmore, 1984) and refined by full-matrix least squares on F with anisotropic thermal parameters using *SHELX*76 (Sheldrick, 1976), H atoms identified on a difference map and refined isotropically. $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = k/[\sigma^2(F_o)+gF_o^2]$, $\sigma(F)$ from counting statistics, k and g optimized in the least-squares procedure ($k = 1·00$, $g = 0·0288$); $wR = 0·064$ for 1050 observed reflections, 272 variables, $S = 0·55$, $(\Delta/\sigma)_{max} = 0·343$ in final refinement cycle [x coordinate of H(W2)], max. and min. heights in final difference map 0·34 and −0·38 e Å^{-3}, respectively. All calculations performed with *SHELX*76 on a VAX 11/780. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are in Table 1.* The molecule and numbering scheme are shown in Fig. 1. Bond lengths, bond angles and selected torsion angles are listed in Table 2.

The oxo 4-keto and 5-hydroxyl groups form a strong intramolecular hydrogen bond making a hydrogen-bonded six-membered ring, as observed in naringenin and related compounds (Shin & Lah, 1986; Glusker & Rossi, 1986). Although hesperetin and naringenin differ only in the substituents of the phenyl moiety, bond lengths of the benzopyrone moiety in hesperetin show significant differences (up to 4σ) from those in naringenin. Notably, the C(4)—O(4), C(2)—C(3) and C(7)—O(7) bonds are 0·025, 0·027 and 0·022 Å shorter while the C(6)—C(7) bond is 0·025 Å longer than those of naringenin, indicating that the six-membered ring is less conjugated than in naringenin. These variations in bond lengths may be attributed to the different hydrogen-bonding environment around the keto O atom. The oxo 4-keto group of hesperetin is involved only in the intramolecular hydrogen bond while that of naringenin forms both intra- and intermolecular hydrogen bonds.

Ring A is planar with a maximum deviation of 0·013 (5) Å. O(1), C(4), O(4) and O(5) are displaced from plane A by −0·018 (3), 0·095 (5), 0·186 (3) and 0·065 (3) Å while C(2) and C(3) are displaced by −0·541 (6) and 0·119 (6) Å, respectively. The pyrone ring in hesperetin adopts a slightly modified sofa conformation as in naringenin, but the ring is more buckled in hesperetin. When the A rings of hesperetin and naringenin are best fitted (Nyburg, 1974), six C atoms are superimposed within 0·031 Å. However, the
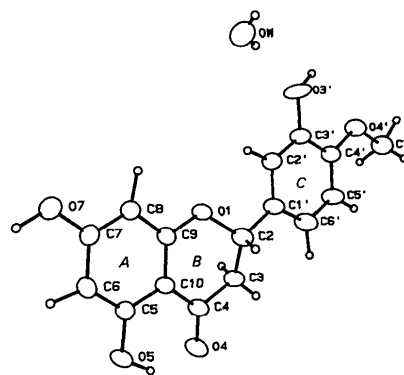
Fig. 1. *ORTEP*II (Johnson, 1976) drawing of hesperetin monohydrate with the atomic numbering scheme.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *of hesperetin monohydrate*

O(1)—C(2)	1·442 (6)	1·454*	O(1)—C(9)	1·361 (5)	1·369*
C(2)—C(3)	1·481 (7)	1·508	C(2)—C(1')	1·512 (7)	1·510
C(3)—C(4)	1·504 (7)	1·503	C(4)—C(10)	1·430 (6)	1·435
C(4)—O(4)	1·231 (6)	1·256	C(5)—C(6)	1·373 (6)	1·381
C(5)—C(10)	1·406 (6)	1·419	C(5)—O(5)	1·361 (5)	1·353
C(6)—C(7)	1·410 (6)	1·385	C(7)—C(8)	1·384 (6)	1·396
C(7)—O(7)	1·343 (5)	1·365	C(8)—C(9)	1·377 (6)	1·376
C(9)—C(10)	1·406 (6)	1·421	C(1')—C(2')	1·389 (7)	1·378
C(1')—C(6')	1·381 (7)	1·386	C(2')—C(3')	1·375 (6)	1·368
C(3')—C(4')	1·390 (6)	1·384	C(3')—O(3')	1·382 (5)	
C(4')—C(5')	1·381 (7)	1·380	C(4')—O(4')	1·352 (5)	1·380
C(5')—C(6')	1·372 (7)	1·393	O(4')—C(7')	1·437 (7)	

O(1)—C(2)—C(3)	112·1 (4)	O(1)—C(2)—C(1')	107·0 (4)
O(1)—C(9)—C(8)	117·2 (4)	O(1)—C(9)—C(10)	120·6 (4)
C(2)—O(1)—C(9)	115·1 (3)	C(2)—C(3)—C(4)	111·6 (4)
C(2)—C(1')—C(2')	120·9 (4)	C(2)—C(1')—C(6')	121·2 (4)
C(3)—C(2)—C(1')	114·6 (4)	C(3)—C(4)—C(10)	116·0 (4)
C(3)—C(4)—O(4)	120·7 (4)	C(4)—C(10)—C(5)	121·2 (4)
C(4)—C(10)—C(9)	121·4 (4)	C(5)—C(6)—C(7)	118·5 (4)
C(5)—C(10)—C(9)	117·3 (4)	C(6)—C(5)—C(10)	122·0 (4)
C(6)—C(5)—O(5)	118·8 (4)	C(6)—C(7)—C(8)	121·3 (4)
C(6)—C(7)—O(7)	120·7 (4)	C(7)—C(8)—C(9)	118·7 (4)
C(8)—C(7)—O(7)	118·0 (4)	C(8)—C(9)—C(10)	122·2 (4)
C(10)—C(4)—O(4)	123·3 (4)	C(10)—C(5)—O(5)	119·2 (4)
C(1')—C(2')—C(3')	120·0 (4)	C(1')—C(6')—C(5')	122·2 (5)
C(2')—C(1')—C(6')	117·7 (4)	C(2')—C(3')—C(4')	122·0 (4)
C(2')—C(3')—O(3')	118·7 (4)	C(3')—C(4')—C(5')	117·6 (4)
C(3')—C(4')—O(4')	116·9 (4)	C(4')—C(3')—O(3')	119·4 (4)
C(4')—C(5')—C(6')	120·4 (5)	C(4')—O(4')—C(7')	117·7 (4)
C(5')—C(4')—O(4')	125·4 (4)		

C(9)—O(1)—C(2)—C(3)	52·6 (4)	49·8*
O(1)—C(2)—C(3)—C(4)	−52·3 (4)	−50·6
C(2)—C(3)—C(4)—C(10)	25·4 (4)	28·3
C(3)—C(4)—C(10)—C(9)	2·4 (4)	−3·1
O(1)—C(9)—C(10)—C(4)	−4·1 (4)	0·4
C(2)—O(1)—C(9)—C(10)	−23·9 (4)	−24·8
O(1)—C(2)—C(1')—C(2')	27·4 (4)	
C(3)—C(2)—C(1')—C(6')	−33·5 (5)	

* Bond lengths and torsion angles of naringenin for comparison. The average e.s.d.'s for naringenin are 0·005 Å and 0·3°.

rest of the atoms show rather significant deviations, representing considerable flexibility of the benzopyrone ring [O(1) = 0·088, C(2) = 0·147, C(3) = 0·054, C(4) = 0·074, O(4) = 0·186, O(5) = 0·125, O(7) = 0·092, C(1') = 0·265, C(4') = 0·675 Å]. The phenyl ring C is planar with a maximum deviation of 0·014 (5) Å. The 4'-methoxy group is also in the plane with the C(5')—C(4')—O(4')—C(7') torsion angle 5·8 (5)°. This planar conformation is a characteristic structural feature for the compounds containing the methoxy group on the phenyl ring (Caillet, 1982).

The most significant difference between the structures of hesperetin and naringenin is the relative orientation of the benzopyrone and phenyl rings. The phenyl ring in hesperetin is bonded equatorially to the pyrone ring as in naringenin. It has been found that all of the flavone and flavanone compounds with a phenyl substituent at C(2) have the same structural feature (Glusker & Rossi, 1986). However, the phenyl ring in hesperetin is parallel (dihedral angle between A and C rings 0·6°) to the benzopyrone plane while it is almost

perpendicular in naringenin (dihedral angle 85·7°). The average distance from the six phenyl C atoms to the best plane of ring A is 0·450 (14) Å. Among the 36 atoms in hesperetin, H(C2), H(C4'2), H(C32), H(C5') and C(2) are the only atoms that deviate by more than 0·5 Å from the A plane. They are displaced by 1·68 (4), 1·23 (5), 1·08 (5), 0·55 (5) and 0·541 (6) Å, respectively. Therefore, the whole hesperetin molecule can be considered to be fairly flat even though the O(1)—C(2)—C(1')—C(2') and C(3)—C(2)—C(1')—C(6') angles are 27·4 (4) and −33·5 (5)°, respectively.

It is interesting to note that hesperetin adopts a planar conformation while the perpendicular arrangement seems energetically more favorable than the parallel one owing to repulsive steric hindrance between O(1), C(3) and atoms in the phenyl group. O(1) makes close contacts with the phenyl H(C2') and H(C8) atoms with separations of 2·30 (5) and 2·37 (5) Å respectively. In flavone compounds with sp^2 C(2), it has been found that the molecule becomes flatter when the oxo 4-keto group is involved in the stronger hydrogen-bonding interactions, due to extensive conjugation involving the exocyclic phenyl ring (Rossi, Rickles & Halpin, 1986). However, this generalization for the relationship between conformation and the hydrogen-bonding properties is not applicable to flavanones which contain an sp^3 C(2).

The crystal packing is shown in Fig. 2. Hydrogen bonds and close contacts are listed in Table 3. All of the hesperetin molecules in the crystal lattice lie approximately parallel to the (20$\bar{1}$) plane. The molecules are connected through strong O(3')—H···O(5) hydrogen bonds along the **b** direction, forming a molecular chain. These chains are interconnected through three hydrogen bonds involving water, to form a hydrogen-bonded molecular double layer. Minimum separation between the layers is about 3·65 Å. The H atoms of the hydroxyl groups O(5) and O(3') may be involved in both intra- and intermolecular hydrogen-bonding interactions in a bifurcated fashion. There is a rather extensive overlap between the centrosymmetrically related molecules in the adjacent layers. However, the minimum separation is also *ca* 3·65 Å so that there are
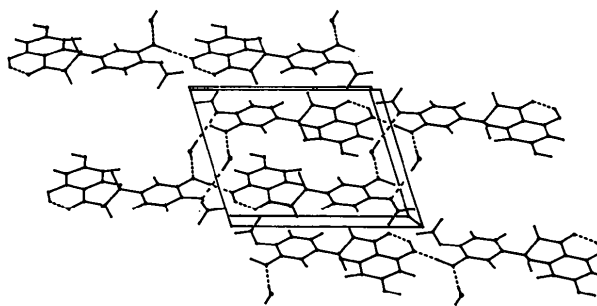

Fig. 2. *ORTEP*II (Johnson, 1976) drawing of the crystal packing. H bonding is represented by dotted lines.

Table 3. *Hydrogen bonds in hesperetin monohydrate*

a–b···c	b–c (Å)	a–c (Å)	abc (°)
O(5)–H···O(4)	1·67 (6)	2·552 (5)	137 (5)
O(7)–H···O(W^i)	1·68 (5)	2·713 (7)	170 (4)
O(3')–H···O(5^ii)	1·64 (7)	2·731 (4)	174 (5)
O(W)–H(1)···O(3'^iii)	2·17 (6)	2·795 (7)	170 (7)
O(W) H(2)···O(4'^iv)	2·47 (10)	3·159 (7)	175 (10)
O(5)–H···O(4'^iv)	2·46 (6)	2·907 (4)	104 (4)
O(3')–H···O(4')	2·36 (6)	2·678 (5)	95 (4)

Symmetry code: none x, y, z; (i) $x, y, 1+z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, 1-z$; (iv) $x, -1+y, z$.

only van der Waals interactions between the molecular double layers.

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Structure of 11,12-Dihydro-6H-6,12-methanodibenzo[b,f]thiocin-12-carbonitrile

BY J. PODLAHA AND J. PODLAHOVÁ

Department of Chemistry, Charles University, 128 40 Prague, Czechoslovakia

AND J. SYMERSKÝ

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague, Czechoslovakia

Abstract. $C_{17}H_{13}NS$, $M_r = 263·36$, $P2_1/c$, $a = 8·146$ (3), $b = 18·660$ (8), $c = 8·666$ (2) Å, $\beta = 91·41$ (3)°, $V = 1316·9$ (8) Å^3, $Z = 4$, $D_m = 1·296$ (5), $D_x = 1·33$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·213$ mm^{-1}, $F(000) = 552$, $T = 295$ K, $R = 0·0425$ for 1836 observed unique reflections. The molecular structure is tetracyclic with a central bicyclo[3.3.1]-2-thianonane-3,7-diene moiety and two phenyl rings *ortho*-condensed to it. Bond lengths and angles are normal.

Introduction. The phase-transfer-catalysed reaction of 6,11-dihydrodibenzo[b,e]thiepin-11-carbonitrile with excess 1,2-dibromoethane (Šindelář, Holubek, Ryska, Svátek, Urban & Protiva, 1983) afforded three isomeric products of composition $C_{17}H_{13}NS$. On the basis of NMR and mass spectra, the structure below was tentatively assigned to one of the minor products (compound XVI in the original paper). Subsequent detailed ^1H and ^{13}C NMR data (Šindelář *et al.*, 1987) indicated, however, that the structure should not involve a cyclopropane ring. The X-ray crystal struc-

ture determination has been undertaken to resolve the ambiguities.
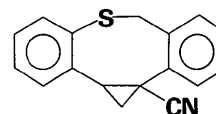
Experimental. Single crystals grown from benzene/cyclohexane were kindly provided by K. Šindelář. The density was determined by flotation in aqueous zinc bromide solution. The measurement and refinement data are summarized in Table 1.*

Structure solution and refinement: direct methods; F magnitudes used in full-matrix least-squares refinement; all H atoms found from $\Delta\rho$ synthesis; scale

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44060 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.