N10—C5a	1.369 (3)	C6—C7	1.403 (4)
C1—C2	1.373 (4)	C7—C8	1.364 (4)
C1—C9a	1.424 (3)	C8—C8a	1.424 (4)
C2—C3	1.400 (4)	C8a—C9	1.449 (3)
C3—C4	1.359 (4)	C9—C9a	1.448 (3)
C4—C4a	1.421 (4)		
N2—N1—C9	125.5 (2)	N1—C9—C8a	116.2 (2)
N1—N2—C11	113.5 (2)	N1—C9—C9a	124.9 (2)
C4a—N10—C5a	122.6 (2)	C8a—C9—C9a	118.9 (2)
N1—C9—C8a—C8	−7.3 (4)	C4—C4a—N10—C5a	176.4 (2)
N1—C9—C9a—C1	7.2 (4)	C4a—N10—C5a—C5	−178.1 (2)
N2—N1—C9—C8a	−176.7 (2)	C8—C8a—C9—C9a	172.8 (2)
N2—N1—C9—C9a	3.1 (4)	C9—N1—N2—C11	−174.2 (3)
C1—C9a—C9—C8a	−173.0 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H10···N3^{i}	0.91 (3)	1.97 (3)	2.863 (3)	167 (3)
N1—H12···S	0.91 (3)	2.62 (3)	3.425 (3)	148 (3)

Symmetry code: (i) $x, 1 + y, z$.

Although the crystal was a very thin plate, ψ scans of three reflections indicated that an absorption correction was unnecessary. *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991) was used for data collection and cell determination, and *TEXSAN* software (Molecular Structure Corporation, 1989) was used for data reduction, structure refinement and the preparation of publication material. The structure was solved using direct methods *SHELXS*86 (Sheldrick, 1990) and molecular graphics were produced using *ORTEP*II (Johnson, 1976).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry, together with a view of the packing of the title compound in the unit cell, have been deposited with the IUCr (Reference: AB1449). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3-Dihydro-5-hydroxy-6,7-dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one (Onysilin)

Kan Chantrapromma,[a] Vatcharee Seechamnanturakit,[a] Chanita Ponglimanont,[a] Chaveng Pakawatchai,[a] Hoong-Kun Fun[b] and Kandasamy Sivakumar[b]†

[a]*Department of Chemistry, Prince of Songkla University, Hat-Yai, Thailand 90112, and* [b]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia. E-mail: ckan@ratree.psu.ac.th*

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Abstract

The title compound, $C_{17}H_{16}O_5$, contains a heterocyclic ring which adopts a sofa conformation. The dihedral angle between the weighted phenyl and benzopyranone mean planes is 79.01 (5)°.

Comment

There has never been any serious doubt that the isomeric flavanones 2,3-dihydro-5-hydroxy-6,7-dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one (onysilin) and 5-hydroxy-7,8-dimethoxy-2-phenyl-4*H*-1-benzopyran-4-one are correctly represented by the structures (1) and (2), respectively (Wu, Kuoh, Ho, Yang & Lee, 1981; Wollenweber, 1982). Work in our laboratories has been directed towards the use of X-ray crystallographic data to formulate correctly the structures of isomeric flavanones. The title compound was isolated from *Uvaria dulcis Dunal* (*Annonaceae*) as yellow crystals

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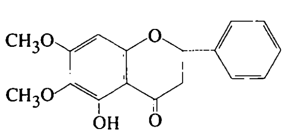
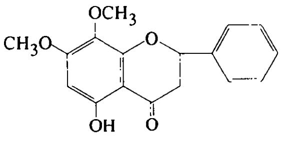
† On leave from the Department of Physics, Anna University, Madras 600 025, India.

(m.p. 422–423 K). The crystal structure determination was carried out in order to confirm the structure of (1) proposed from spectroscopic data.



(1)



(2)

An *ORTEP* (Johnson, 1965) plot of the title molecule with the atomic numbering scheme is shown in Fig. 1. The bond lengths and angles observed are comparable with those of other related naturally occurring flavanones, such as 2,3-dihydro-2,5-dihydroxy-7-methoxy-2-phenyl-4*H*-1-benzopyran-4-one (Chantrapromma, Pakawatchai, Skelton, White & Worapatamasri, 1989).

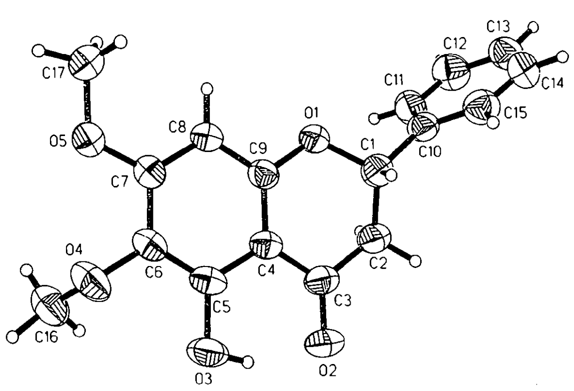


Fig. 1. A 50% displacement ellipsoid plot of the title compound with the atomic numbering scheme.

The heterocyclic ring adopts a half-chair conformation, with the C1 atom deviating furthest from the ring plane. Atomic deviations within the heterocyclic ring relative to the plane of the fused aromatic ring defined by atoms C4–C9 are 0.007 (2), 0.551 (2), −0.130 (2) and −0.083 (2) Å for O1, C1, C2 and C3, respectively. The pendant phenyl ring lies roughly perpendicular to the heterocyclic ring with a dihedral angle of 79.01 (5)°. The planes of the two methoxy substituents (C6, O4, C16 and C7, O5, C17) are approximately perpendicular to and coplanar with the heterocyclic ring, forming dihedral angles of 97.11 (8) and 2.19 (6)°, respectively. There is an intramolecular hydrogen bond between O3 and O2 [O3···O2 2.588 (3) Å and O3—H3O···O2 156 (3)°] and intermolecular hydrogen bonding between C1 and O4 of an adjacent molecule [C1···O4^{i} 3.308 (3) Å and C1—H1···O4^{i} 145 (2)°; symmetry code: (i) $-x+1$, $-y$, $-z+1$].

Experimental

Crystals of (1) were obtained from a mixture of *n*-hexane and ethyl acetate solution.

Crystal data

$C_{17}H_{16}O_5$
$M_r = 300.30$
Monoclinic
$P2_1/c$
$a = 9.722$ (3) Å
$b = 7.475$ (2) Å
$c = 20.255$ (5) Å
$\beta = 99.750$ (10)°
$V = 1450.7$ (7) Å^3
$Z = 4$
$D_x = 1.375$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 5.6$–12.5°
$\mu = 0.101$ mm^{-1}
$T = 293$ (2) K
Rectangular block
0.62 × 0.48 × 0.36 mm
Light yellow

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4460 measured reflections
3305 independent reflections
2375 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0418$

$\theta_{\rm max} = 27.52°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 9$
$l = -26 \rightarrow 26$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R(F) = 0.0517$
$wR(F^2) = 0.1655$
$S = 1.086$
3302 reflections
263 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0859P)^2 + 0.2165P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.44$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C9	1.363 (2)	O5—C7	1.350 (2)
O1—C1	1.443 (2)	O5—C17	1.431 (3)
O2—C3	1.235 (2)	C1—C10	1.504 (2)
O3—C5	1.350 (2)	C1—C2	1.510 (3)
O4—C6	1.376 (2)	C2—C3	1.501 (3)
O4—C16	1.414 (3)	C3—C4	1.441 (2)
C9—O1—C1	115.61 (13)	C10—C1—C2	113.3 (2)
C6—O4—C16	114.8 (2)	C3—C2—C1	111.7 (2)
C7—O5—C17	118.08 (15)	O2—C3—C4	122.5 (2)
O1—C1—C10	107.62 (14)	O2—C3—C2	121.2 (2)
O1—C1—C2	110.3 (2)	C4—C3—C2	116.3 (2)

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: MU1306). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyclic Water Pentamers in L-Leucyl-L-alanine Tetrahydrate

CARL HENRIK GÖRBITZ

Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway. E-mail: c.h.gorbitz@kjemi.uio.no

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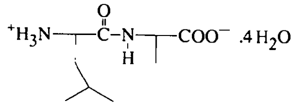
Abstract

The structure of the title compound, $C_9H_{18}N_2O_3.4H_2O$, contains a very unusual and elaborate system of hydrogen-bonded water molecules which includes cyclic water pentamers with idealized hydrogen-bond cooperativity. The solvent molecules form columns in the crystal, as do hydrophobic aggregates of peptide side chains. Both these units are located between hydrophilic sheets formed by the peptide main chains. The sheets contain two head-to-tail hydrogen-bonded chains, one of which is interrupted by a bridging water molecule that is functionally different from those constituting the core of the water channels.

Comment

In the crystal structures of dipeptides, two of the three $-NH_3^+$ H atoms are often donated to the C-terminal carboxylate group, generating two head-to-tail hydrogen-bonded chains in a well defined hydrophilic sheet. Between the sheets are layers with a more or less distinct hydrophobic character depending on the types of amino acid residues involved. We have previously pointed out (Görbitz & Gundersen, 1996*a*) that some modification of this pattern is required when both dipeptide side chains are devoid of hydrogen-bond acceptors, since the third amino H atom would otherwise not be used in hydrogen bonding which is indeed what happens in the structure of L-Met-L-Met (Stenkamp & Jensen, 1975). One possibility is inclusion of an organic solvent molecule that can fit into the hydrophobic layer and provide the necessary hydrogen-bond acceptor. This occurs in L-Leu-L-Val.2-propanol (Görbitz & Gundersen, 1997), L-Leu-L-Leu.DMSO (Mitra & Subramanian, 1994) and L-Leu-L-Ala.DMSO (Mitra, Govindasamy & Subramanian, 1996). Alternatively, the layered crystal build-up may be abandoned with formation of columnar structures in hexagonal space groups, as for L-Val-L-Ala (Görbitz & Gundersen, 1996*a*) and L-Leu-L-Val.0.75H_2O (Görbitz & Gundersen, 1996*b*). Among the hydrophobic dipeptides we have investigated, L-Leu-L-Ala, (I), is the only compound that does not crystallize as elongated needles, and a comparison of its molecular-packing arrangement and hydrogen-bond pattern with those of the previously determined structures is of interest.



(I)

The molecular structure of L-Leu-L-Ala and the crystal packing are shown in Fig. 1. Bond angles for the solvent water molecules and selected torsion angles are listed in Table 1. All bond lengths and bond angles are normal. The peptide main chain is slightly folded with φ_2 (C6—N2—C7—C9) = −66.88 (8)°, while the L-Leu side chain is in the most common conformation (Görbitz & Gundersen, 1996*b*), with χ^1 (N1—C1—C2—C3) *gauche*$^-$ and $\chi^{2,1}/\chi^{2,2}$ (C1—C2—C3—C4/C5) *gauche*$^-$/*trans*). Both subunits have different conformations from those observed for L-Leu-L-Ala in the recently published DMSO solvate (Mitra *et al.*, 1996). It can be seen from Fig. 1 that the four cocrystallized water molecules, *W*40, *W*50, *W*60 and *W*70 (atom O40 is in *W*40 *etc.*), in the asymmetric unit form water columns parallel to the *a* axis, while two Leu and two Ala side chains aggregate into hydrophobic columns. Hydrogen bonds between peptide main chains generate wave-like sheets which are seen edge-on in Fig. 1. Hydrogen-bond parameters are listed in Table 2.