Shetty, M. M. (1987). PhD thesis, Bombay Univ., India.
Spek, A. L., Duisenberg, A. J. M., van den Heuvel, H. L. A., Boer Rookhuizen, R. & Bosch, R. (1990). *Acta Cryst.* C**46**, 630–631.
Suwinska, K. & Gerdil, R. (1987). *Acta Cryst.* C**43**, 898–902.

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2-(2,3-Dimethoxyphenyl)-6-hydroxy-4*H*-1-benzopyran-4-one (6-Hydroxy-2′,3′-dimethoxyflavone)

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Abstract

The structure of the new flavone reported here has a general shape defined by a phenyl ring rotated by 62.2 (1)° from the plane of the γ-benzopyranone portion. The two methoxy groups have the expected conformations: out of plane for the methoxy group at C2′ and in plane for the other at C3′. The major influence on the packing appears to be the O6—H6···O4 intermolecular hydrogen bond.

Comment

Fig. 1 represents a perspective view of the asymmetric unit with the atom-numbering scheme. A search of the January 1980 version of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed that this is the first report of a 2′,3′-dimethoxylated fragment for flavones.

The molecule can be described in two different regions: γ-benzopyrone atoms, including the O atoms of the hydroxyl and carbonyl groups, lie in one plane and the phenyl atoms lie in another plane. The angle between these two planes is 62.2 (1)°. The methoxy group at C(2′) is oriented out of the plane of the phenyl ring with a torsion angle of C2′1—O2′—C2′—C3′ = 70.5°. The methoxy group at C3′ lies in the phenyl plane; C3′1—O3′—C3′—C4′ = 1.1°.

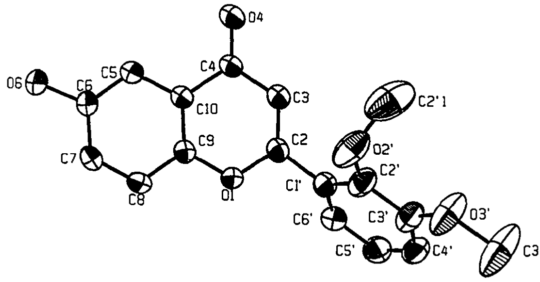

Fig. 1. The structure of the molecule with the atom-numbering scheme. The thermal ellipsoids are drawn at 50% probability.

The O—H6···O4 intermolecular bonds appear to have an important effect on the packing of the molecule. Each molecule hydrogen bonds to another molecule related by $-0.5+x$, $1.5-y$, z and with a molecule related by $0.5+x$, $1.5-y$, z. The molecules are arranged in such a way that all the hydroxyl and carbonyl groups participate in hydrogen bonding, thus inducing a gathering of hydrophobic dimethoxy groups on the opposite side (Fig. 2). It may also be noted that one molecule hydrogen bonds to two other molecules, giving infinite chains rather than associated pairs of molecules.

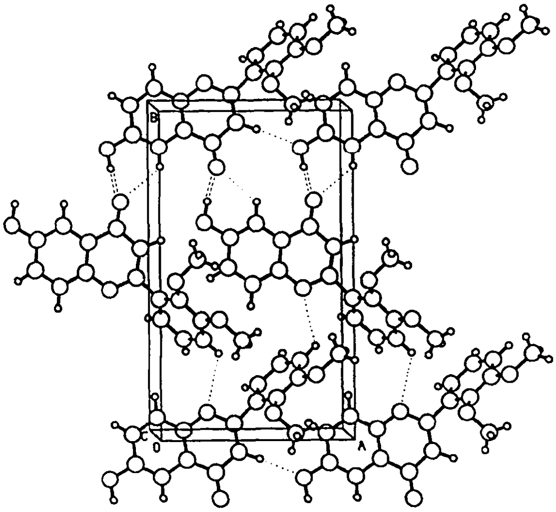

Fig. 2. The crystal packing viewed down the *c* axis.

Similar flavones with the same γ-benzopyrone fragment are 6-hydroxyflavone (Seetharaman & Rajan, 1992) and 6-hydroxy-2′,3′,4′-trimethoxyflavone (Wallet, 1993), which have torsion angles of 9.8 and 19.1°, respectively. Bond lengths and angles are comparable but the torsion angles are different, the smaller value being for 6-hydroxyflavone with no substituent on the phenyl ring; the title compound is more twisted than either of these compounds.

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6-Hydroxy-2′,3′-dimethoxyflavone is also more twisted [62.2 (1)°] than flavones with an in-plane 2′-methoxy group: 2′-methoxyflavone (2.8°) (Wallet, Gaydou, Jaud & Baldy, 1990), 2′,7-dimethoxyflavone (23.5°) (Wallet, Gaydou, Feneau-Dupont, Tinant, Declercq & Baldy, 1991) and 2′,5-dimethoxyflavone (10.5°) (Wallet, Gaydou, Tinant, Declercq & Baldy, 1992).

Experimental

Crystal data

$C_{17}H_{14}O_5$
$M_r = 298.30$
Monoclinic
$P2_1/a$
$a = 9.120\ (3)$ Å
$b = 15.407\ (1)$ Å
$c = 10.573\ (3)$ Å
$\beta = 103.96\ (1)°$
$V = 1441.8\ (6)$ Å^3
$Z = 4$

$D_x = 1.374$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2\text{–}50°$
$\mu = 0.1$ mm^{-1}
$T = 293$ K
Pseudoprismatic
0.58 × 0.42 × 0.14 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.9309$, $T_{\max} = 0.9991$
2792 measured reflections
2534 independent reflections

1983 observed reflections [$F > 2.0\sigma(F)$]
$R_{\rm int} = 0.012$
$\theta_{\max} = 25°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity variation: 0.4%

Refinement

Refinement on F
Final $R = 0.053$
$wR = 0.084$
$S = 3.0$
1908 reflections
242 parameters
Only H-atom U's refined
$w = 4F_o/\sigma(F_o)$

$(\Delta/\sigma)_{\max} = 0.81$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	$B_{\rm eq}$
O1	0.7789 (2)	0.4374 (1)	0.6853 (2)	3.27 (4)
O4	0.8406 (2)	0.6992 (1)	0.7075 (2)	4.87 (5)
O6	0.2713 (2)	0.6357 (1)	0.6578 (2)	4.23 (5)
O2′	1.1368 (3)	0.4504 (2)	0.9388 (2)	5.42 (5)
O3′	1.3625 (3)	0.3351 (2)	0.9662 (2)	6.12 (6)
C2	0.9185 (3)	0.4727 (2)	0.7070 (3)	3.38 (6)
C3	0.9413 (3)	0.5593 (2)	0.7141 (3)	4.06 (7)
C4	0.8198 (3)	0.6201 (2)	0.7027 (3)	3.37 (6)
C5	0.5405 (3)	0.6315 (2)	0.6791 (3)	2.99 (5)
C6	0.4030 (3)	0.5909 (2)	0.6627 (3)	3.12 (6)
C7	0.3916 (3)	0.5008 (2)	0.6504 (3)	3.38 (6)
C8	0.5169 (3)	0.4505 (2)	0.6577 (3)	3.17 (6)
C9	0.6562 (3)	0.4910 (2)	0.6758 (2)	2.87 (5)
C10	0.6706 (3)	0.5806 (2)	0.6854 (2)	2.76 (5)
C1′	1.0377 (3)	0.4065 (2)	0.7197 (3)	3.40 (6)
C2′	1.1481 (3)	0.4004 (2)	0.8347 (3)	3.67 (6)
C2′1	1.2539 (6)	0.5138 (3)	0.9792 (4)	7.7 (1)
C3′	1.2623 (3)	0.3380 (2)	0.8478 (3)	3.90 (6)
C3′1	1.4807 (5)	0.2719 (3)	0.9848 (4)	8.6 (1)
C4′	1.2651 (3)	0.2831 (2)	0.7444 (3)	4.05 (6)
C5′	1.1540 (3)	0.2901 (2)	0.6295 (3)	4.35 (7)
C6′	1.0405 (3)	0.3508 (2)	0.6170 (3)	3.99 (7)

Table 2. *Geometric parameters* (Å, °)

O1—C2	1.352 (3)	C5—C6	1.375 (3)
O1—C9	1.376 (3)	C5—C10	1.410 (3)
O4—C4	1.233 (3)	C6—C7	1.396 (4)
O6—C6	1.375 (3)	C7—C8	1.367 (4)
O2′—C2′	1.368 (4)	C8—C9	1.386 (3)
O2′—C2′1	1.434 (5)	C9—C10	1.387 (4)
O3′—C3′	1.361 (3)	C1′—C2′	1.382 (3)
O3′—C3′1	1.430 (5)	C1′—C6′	1.389 (4)
C2—C3	1.350 (4)	C2′—C3′	1.400 (4)
C2—C1′	1.472 (4)	C3′—C4′	1.387 (4)
C3—C4	1.434 (4)	C4′—C5′	1.385 (4)
C4—C10	1.462 (3)	C5′—C6′	1.378 (4)
C2—O1—C9	119.2 (2)	O1—C9—C10	122.1 (2)
C2′—O2′—C2′1	115.4 (3)	C8—C9—C10	121.6 (2)
C3′—O3′—C3′1	117.7 (3)	C4—C10—C5	121.4 (2)
O1—C2—C3	122.2 (2)	C4—C10—C9	119.5 (2)
O1—C2—C1′	112.4 (2)	C5—C10—C9	119.1 (2)
C3—C2—C1′	125.4 (2)	C2—C1′—C2′	119.5 (3)
C2—C3—C4	122.4 (2)	C2—C1′—C6′	120.6 (2)
O4—C4—C3	122.3 (2)	C2′—C1′—C6′	119.9 (2)
O4—C4—C10	123.1 (2)	O2′—C2′—C1′	119.3 (2)
C3—C4—C10	114.6 (2)	O2′—C2′—C3′	120.4 (2)
C6—C5—C10	119.0 (2)	C1′—C2′—C3′	120.1 (3)
O6—C6—C5	122.6 (2)	O3′—C3′—C2′	115.6 (3)
O6—C6—C7	116.8 (2)	O3′—C3′—C4′	124.7 (3)
C5—C6—C7	120.6 (2)	C2′—C3′—C4′	119.7 (2)
C6—C7—C8	121.0 (2)	C3′—C4′—C5′	119.7 (3)
C7—C8—C9	118.6 (2)	C4′—C5′—C6′	120.7 (3)
O1—C9—C8	116.3 (2)	C1′—C6′—C5′	120.0 (3)

The structure was solved by direct methods with a straightforward run of the *MULTAN*11/82 program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Full-matrix refinement on F was carried out using the *MolEN* program (Fair, 1990).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71347 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1047]

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf-Nonius, Delft, The Netherlands.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Seetharaman, J. & Rajan, S. S. (1992). *Acta Cryst.* C**48**, 1714–1715.

Wallet, J. C. (1993). *Z. Kristallogr.* Submitted.

Wallet, J. C., Gaydou, E. M., Feneau-Dupont, J., Tinant, B., Declercq, J.-P. & Baldy, A. (1991). *Acta Cryst.* C**47**, 1103–1105.
Wallet, J. C., Gaydou, E. M., Jaud, J. & Baldy, A. (1990). *Acta Cryst.* C**46**, 1536–1540.
Wallet, J. C., Gaydou, E. M., Tinant, B., Declercq, J.-P. & Baldy, A. (1992). *Acta Cryst.* C**48**, 376–377.

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2,4:3,5-Di-*O*-méthylène-1-*p*-toluènesulfonylxylitol

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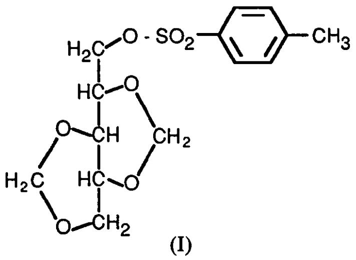
Abstract

The title compound, 2,3:4,5-di-*O*-methylene-1-*p*-toluenesulfonylxylitol, is an intermediary of synthesis. The crystal structure was solved in order to determine its molecular geometry and forecast the attacking atoms for nucleophilic substitutions. The heterocycles *A* and *B* have a chair conformation while the benzene ring *C* is planar. The *A*/*B* ring-junction configuration is *cis*. The cohesion of the structure is due to van der Waals interactions.

Commentaire

Le composé étudié (I) est un intermédiaire de synthèse. Il a été obtenu en estérifiant le xylitol par l'acide *p*-toluènesulfonique après blocage de quatre fonctions alcool par le formol en milieu acide. Son étude structurale a été entreprise dans le but de préciser les positions relatives des cycles et, ce faisant, de prévoir les points de substitution de type nucléophile.



(I)

Les cycles *A* et *B* (Fig. 1) possèdent la forme chaise. En effet, les angles de torsion endocycliques changent de signe lorsqu'on passe d'une liaison à la liaison voisine et leurs valeurs absolues sont comprises entre 48,6 (4) et 63,8 (5)°. Si *P*(*A*) désigne le plan moyen défini par C(3), C(5), O(6) et O(8), et *P*(*B*) le plan moyen défini par C(2), C(4), O(9) et O(11), C(4) et C(7) sont situés de part et d'autre de *P*(*A*), C(3) et C(10) de part et d'autre de *P*(*B*). Les distances des deux premiers à *P*(*A*) sont respectivement de 0,590 (4) et de 0,656 (5) Å et celles des seconds à *P*(*B*) de 0,602 (4) et de 0,643 (5) Å. La jonction des cycles *A* et *B* est de type *cis*. Le cycle *C* est plan. Le paramètre χ^2 relatif à son plan moyen est égal à 4. Les angles dièdres formés par les plans moyens *P*(*A*), *P*(*B*) et *P*(*C*) ont les valeurs suivantes: *P*(*A*)*P*(*B*) 80,0 (1), *P*(*A*)*P*(*C*) 83,4 (1) et *P*(*B*)*P*(*C*) 89,4 (1)°. L'angle de torsion C(2)—C(1)—O(12)—S(13) [−170,2 (2)°] indique que les liaisons C(1)—C(2) et O(12)—S(13) sont antipériplanaires.

Les longuers des liaisons C—O présentes dans les cycles *A* et *B* appartiennent à l'intervalle 1,394 (4)–1,437 (5) Å [moyenne: 1,418 (7) Å]. Dans le désoxy-6-(*N*,*N*-diméthylcarbamoyl-6)-di-*O*-isopropylidène-1,2:3,4-α-D-galactopyrannose (Rodier, Khodadad, Postel, Villa, Ronco & Julien, 1991), la longueur moyenne des mêmes liaisons est de 1,423 (4) Å. Les distances C(1)—O(12) [1,452 (3) Å], O(12)—S(13) [1,571 (2) Å] et S(13)—C(16) [1,751 (3) Å], ne sont pas significativement différentes des longueurs moyennes calculées par Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) pour leurs homologues. Celles-ci mesurent respectivement 1,465 (14), 1,577 (15) et 1,752 (8) Å.

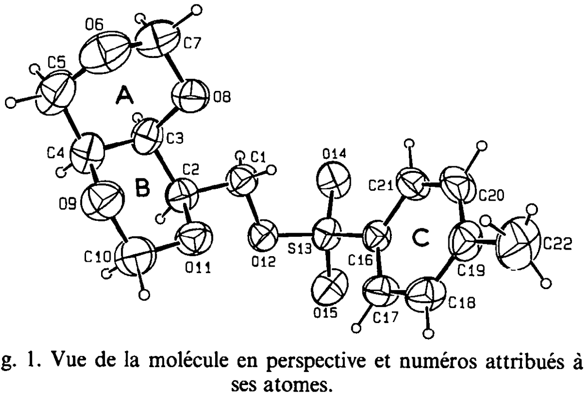


Fig. 1. Vue de la molécule en perspective et numéros attribués à ses atomes.