

- Lewis, D. E., Utecht, R. E., Judy, M. M. & Matthews, J. L. (1993). US Patent No. 5 235 045.
- Lewis, D. E., Utecht, R. E., Judy, M. M., Matthews, J. L. & Chanh, T. C. (1993). *Spectrum*, **6**, 8–14.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Acta Cryst. (1995). **C51**, 1193–1195

A New Polymorph of 7-Hydroxy-2',3',4'-trimethoxyflavone

JEAN-CLAUDE WALLET

Laboratoire de Phytochimie, ENSSPICAM, Faculté des Sciences et Techniques de Saint-Jérôme, 13397 Marseille CEDEX 20, France

VIVIAN CODY

Medical Foundation of Buffalo, 73 High Street, Buffalo, NY 14203-1196, USA

(Received 4 November 1993; accepted 26 May 1994)

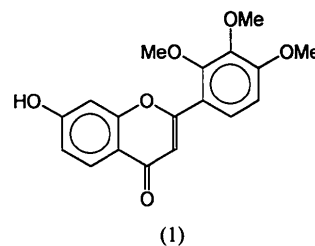
Abstract

The crystal structure of the monoclinic form of 7-hydroxy-2-(2,3,4-trimethoxyphenyl)-4H-1-benzopyran-4-one, $C_{18}H_{16}O_6$, contains two molecules in the asymmetric unit which differ from each other in both the torsion angle between the γ -benzopyrone portion and the trimethoxylated phenyl ring, and the orientation of the out-of-plane methoxy groups. The torsion angle values are different from those of the previous form [Llorca, Molins, Miravittles, Cody, Wallet & Gaydou (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 481–484] and are indicative of a large degree of 'floppiness' in the trimethoxylated phenyl ring.

Comment

The title flavone is an inhibitor of uric acid production by xanthine oxidase (Cotelle, Bernier, Hénichart, Catteau, Gaydou & Wallet, 1992). It also has weak antimutagenic activity against B[a]P in the *Salmonella typhimurium* test (Laget, De Méo, Wallet, Gaydou, Guiraud & Duménil, 1993). Since flavones are good candidates for anticarcinogenic drugs, it has been tested at the National Cancer Institute (Bethesda, MD) against sixty human cell lines derived from seven cancer types. It did not, however, show any interesting antitumor activity (Wallet, 1992).

Crystal structures of flavones or flavonols with two or more independent molecules in the asymmetric unit are known (Jarchow & Schmalle, 1981; Cody, Luft, Koehrlé, Hesch & Irscher, 1988; Abboud, Simonsen, Mabry & Fang, 1989; Tinant, Declercq, Wallet, Gaydou & Baldy, 1991; Kawai, Yoshimura, Shimaoka, Nakamura & Yano, 1991) and one example of polymorphism has been described (Castleden, Hall, Nimgirawath, Thadaniti & White, 1985). The title flavone, (1), provides another example of polymorphism and, moreover, contains two independent molecules in the asymmetric unit.



Views of the molecules showing the atom labelling are presented in Fig. 1. Fig. 2 is a stereoscopic view of the unit cell. The previous polymorph was reported to be orthorhombic with space group *Pbna* (Llorca, Molins, Miravittles, Cody, Wallet & Gaydou, 1993). The geometry of the molecules in the two polymorphs is identical within experimental error for both bond lengths and angles. The most striking difference between the two molecules in the polymorph described here is seen in the torsion angle $O(1)-C(2)-C(1')-(6')$ between the γ -benzopyrone portion and the trimethoxylated phenyl ring; this angle is $-4.6(3)^\circ$ in molecule I, which is almost planar, and $-40.8(3)^\circ$ in molecule II, which is more twisted. As expected, the methoxy substituents at atoms $C(2')$ and $C(3')$ have an out-of-plane conformation and the $C(4')$ methoxy group lies close to the plane of the phenyl ring. However, in molecule I the methoxy groups at atoms $C(2')$ and

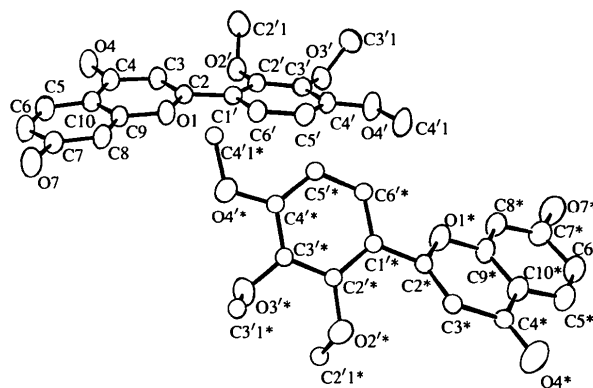


Fig. 1. Numbering of atoms and conformations of molecules (I) and (II).

C(3') point in the same direction [C(2'1)—O(2')—C(2')—C(3') -77.7 (3) and C(3'1)—O(3')—C(3')—C(4') -67.5 (3)°], while in molecule II they point in opposite directions [C(2'1*)—O(2'*)—C(2'*)—C(3'*) 76.5 (3) and C(3'1*)—O(3'*)—C(3'*)—C(4'*) -94.2 (3)°].

$S = 2.3$
1593 reflections
433 parameters
Only H-atom U 's refined
 $w = 1/\sigma^2(F)$

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

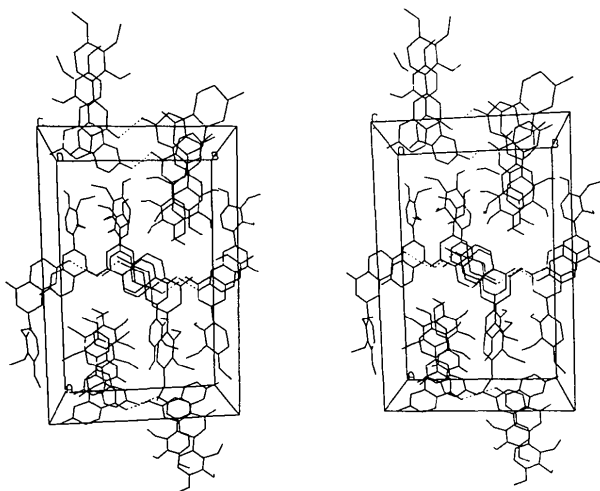


Fig. 2. Stereoscopic view of the unit cell along the c axis.

Experimental

Good quality crystals were obtained unexpectedly by slow evaporation of an ethanol solution containing an equimolar ratio of the flavone and triphenylphosphine oxide.

Crystal data

C₁₈H₁₆O₆
 $M_r = 328.32$
Monoclinic
 $P2_1/c$
 $a = 24.633 (5) \text{ \AA}$
 $b = 16.440 (2) \text{ \AA}$
 $c = 7.465 (1) \text{ \AA}$
 $\beta = 92.86 (1)^\circ$
 $V = 3019.1 (9) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.444 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 $\lambda = 1.54184 \text{ \AA}$
Cell parameters from 25 reflections
 $\theta = 20.33\text{--}25.73^\circ$
 $\mu = 0.87 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
Plate
 $0.40 \times 0.20 \times 0.10 \text{ mm}$
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
Absorption correction: none
5664 measured reflections
4499 independent reflections
1593 observed reflections
 $[I \geq 3\sigma(I)]$

$\theta_{\max} = 70^\circ$
 $h = 0 \rightarrow 28$
 $k = 0 \rightarrow 19$
 $l = -8 \rightarrow 8$
5 standard reflections
frequency: 180 min
intensity decay: none

Refinement

Refinement on F
 $R = 0.052$
 $wR = 0.064$

$(\Delta/\sigma)_{\max} = 0.01$
 $\Delta\rho_{\max} = 0.580 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.491 \text{ e \AA}^{-3}$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Molecule I				
O(1)	0.0956 (1)	0.7991 (1)	0.2300 (2)	2.91 (4)
C(2)	0.1171 (1)	0.7228 (1)	0.2162 (3)	2.43 (6)
C(3)	0.0863 (1)	0.6562 (1)	0.2437 (4)	2.96 (6)
C(4)	0.0305 (1)	0.6613 (1)	0.2915 (3)	2.78 (6)
O(4)	0.0017 (1)	0.5997 (1)	0.3079 (3)	3.91 (5)
C(10)	0.0100 (1)	0.7428 (1)	0.3166 (3)	2.58 (6)
C(9)	0.0431 (1)	0.8090 (1)	0.2795 (3)	2.48 (6)
C(5)	-0.0422 (1)	0.7589 (1)	0.3728 (4)	3.17 (7)
C(6)	-0.0607 (1)	0.8368 (1)	0.3874 (4)	3.32 (7)
C(7)	-0.0273 (1)	0.9022 (1)	0.3410 (4)	2.86 (6)
O(7)	-0.0486 (1)	0.9775 (1)	0.3504 (3)	3.72 (5)
C(8)	0.0250 (1)	0.8887 (1)	0.2889 (4)	2.89 (6)
C(1')	0.1744 (1)	0.7260 (1)	0.1708 (3)	2.38 (5)
C(2')	0.2075 (1)	0.6562 (1)	0.1611 (3)	2.45 (6)
O(2')	0.1876 (1)	0.5805 (1)	0.1985 (2)	3.11 (4)
C(2'1)	0.1776 (1)	0.5297 (2)	0.0444 (5)	5.00 (10)
C(3')	0.2619 (1)	0.6630 (1)	0.1258 (3)	2.62 (6)
O(3')	0.2935 (1)	0.5940 (1)	0.1333 (2)	3.23 (5)
C(3'1)	0.3152 (1)	0.5713 (2)	-0.0357 (4)	3.97 (8)
C(4')	0.2849 (1)	0.7392 (2)	0.0938 (3)	2.82 (6)
O(4')	0.3390 (1)	0.7384 (1)	0.0667 (3)	3.94 (3)
C(4'1)	0.3655 (1)	0.8130 (2)	0.0305 (4)	4.30 (8)
C(5')	0.2526 (1)	0.8080 (1)	0.0949 (4)	2.97 (6)
C(6')	0.1983 (1)	0.8007 (1)	0.1351 (3)	2.75 (6)

Molecule II

O(1*)	0.4054 (1)	1.0388 (1)	0.2202 (2)	3.08 (4)
C(2*)	0.3807 (1)	1.1122 (1)	0.2452 (4)	3.01 (6)
C(3*)	0.4087 (1)	1.1801 (2)	0.2861 (4)	3.73 (7)
C(4*)	0.4676 (1)	1.1810 (2)	0.3021 (4)	3.43 (7)
O(4*)	0.4941 (4)	1.2442 (1)	0.3350 (3)	4.61 (6)
C(10*)	0.4930 (1)	1.1030 (1)	0.2752 (4)	2.93 (6)
C(9*)	0.4612 (1)	1.0344 (1)	0.2368 (3)	2.78 (6)
C(5*)	0.5498 (1)	1.0925 (2)	0.2830 (4)	3.29 (7)
C(6*)	0.5723 (1)	1.0181 (2)	0.2523 (4)	3.46 (7)
C(7*)	0.5390 (1)	0.9499 (1)	0.2170 (4)	3.20 (7)
O(7*)	0.5640 (1)	0.8785 (1)	0.1880 (3)	4.55 (6)
C(8*)	0.4830 (1)	0.9578 (1)	0.2109 (4)	3.08 (6)
C(1'*)	0.3212 (1)	1.1044 (1)	0.2200 (4)	2.83 (6)
C(2'*)	0.2862 (1)	1.1429 (1)	0.3359 (3)	2.71 (6)
O(2'*)	0.3063 (1)	1.1905 (1)	0.4743 (3)	3.70 (5)
C(2'1*)	0.3049 (1)	1.1520 (2)	0.6476 (4)	4.53 (9)
C(3'*)	0.2303 (1)	1.1338 (1)	0.3108 (3)	2.68 (6)
O(3'*)	0.1963 (1)	1.1700 (1)	0.4283 (2)	3.35 (5)
C(3'1*)	0.1812 (1)	1.2504 (2)	0.3828 (5)	5.26 (10)
C(4'*)	0.2081 (1)	1.0857 (1)	0.1708 (3)	2.80 (6)
O(4'*)	0.1531 (1)	1.0823 (1)	0.1618 (3)	3.63 (5)
C(4'1*)	0.1267 (1)	1.0390 (2)	0.0165 (4)	4.33 (8)
C(5'*)	0.2423 (1)	1.0465 (2)	0.0558 (3)	3.00 (6)
C(6'*)	0.2984 (1)	1.0566 (1)	0.0818 (4)	3.14 (7)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Molecule I		Molecule II	
O(1)—C(2)	1.368 (3)	O(1*)—C(2*)	1.368 (3)
O(1)—C(9)	1.372 (3)	O(1*)—C(9*)	1.374 (3)
C(2)—C(3)	1.354 (3)	C(2*)—C(3*)	1.339 (3)
C(3)—C(4)	1.439 (3)	C(3*)—C(4*)	1.449 (4)
C(4)—O(4)	1.246 (3)	C(4*)—O(4*)	1.246 (3)
C(4)—C(10)	1.446 (3)	C(4*)—C(10*)	1.446 (4)

C(10)—C(9)	1.395 (3)	C(10*)—C(9*)	1.395 (3)
C(10)—C(5)	1.399 (3)	C(10*)—C(5*)	1.407 (3)
C(5)—C(6)	1.366 (3)	C(5*)—C(6*)	1.367 (4)
C(6)—C(7)	1.407 (3)	C(6*)—C(7*)	1.405 (4)
C(7)—O(7)	1.348 (3)	C(7*)—O(7*)	1.348 (3)
C(7)—C(8)	1.384 (3)	C(7*)—C(8*)	1.385 (3)
C(9)—C(8)	1.387 (3)	C(9*)—C(8*)	1.387 (3)
C(2)—C(1')	1.470 (3)	C(2*)—C(1'*)	1.475 (3)
C(1')—C(2')	1.410 (3)	C(1'*)—C(2'*)	1.402 (4)
C(2')—C(3')	1.385 (3)	C(2'*)—C(3'*)	1.389 (3)
C(3')—C(4')	1.399 (3)	C(3'*)—C(4'*)	1.401 (3)
C(4')—C(5')	1.384 (3)	C(4'*)—C(5'*)	1.392 (4)
C(5')—C(6')	1.389 (3)	C(5'*)—C(6'*)	1.394 (3)
C(1')—C(6')	1.394 (3)	C(1'*)—C(6'*)	1.393 (4)
C(2')—O(2')	1.371 (3)	C(2'*)—O(2'*)	1.368 (3)
C(3')—O(3')	1.375 (3)	C(3'*)—O(3'*)	1.377 (3)
C(4')—O(4')	1.359 (3)	C(4'*)—O(4'*)	1.353 (3)
O(2')—C(2'1)	1.433 (4)	O(2'*)—C(2'1*)	1.443 (4)
O(3')—C(3'1)	1.444 (4)	O(3'*)—C(3'1*)	1.410 (4)
O(4')—C(4'1)	1.421 (4)	O(4'*)—C(4'1*)	1.428 (4)
C(2)—O(1)—C(9)	120.1 (2)	C(2*)—O(1*)—C(9*)	118.8 (2)
C(6)—C(7)—C(8)	120.8 (2)	C(6*)—C(7*)—C(8*)	120.1 (2)
O(1)—C(2)—C(3)	120.6 (2)	O(1*)—C(2*)—C(3*)	122.6 (2)
O(7)—C(7)—C(8)	122.1 (2)	O(7*)—C(7*)—C(8*)	122.6 (2)
O(1)—C(2)—C(1')	111.4 (2)	O(1*)—C(2*)—C(1'*)	110.6 (2)
C(9)—C(8)—C(7)	118.1 (2)	C(9*)—C(8*)—C(7*)	118.3 (2)
C(3)—C(2)—C(1')	128.0 (2)	C(3*)—C(2*)—C(1'*)	126.7 (2)
C(2)—C(3)—C(4)	122.6 (2)	C(2*)—C(3*)—C(4*)	121.9 (2)
C(2)—C(1')—C(2')	123.1 (2)	C(2*)—C(1'*)—C(2'*)	121.3 (2)
C(3')—C(4')—O(4')	115.2 (2)	C(3'*)—C(4'*)—O(4'*)	114.5 (2)
C(2)—C(1')—C(6')	119.7 (2)	C(2*)—C(1'*)—C(6'*)	120.4 (2)
C(3')—C(4')—C(5')	119.5 (2)	C(3'*)—C(4'*)—C(5'*)	119.7 (2)
C(3)—C(4)—O(4)	122.2 (2)	C(3*)—C(4*)—O(4*)	122.5 (2)
C(2')—C(1')—C(6')	117.1 (2)	C(2'*)—C(1'*)—C(6'*)	118.3 (2)
O(4')—C(4')—C(5')	125.3 (2)	O(4'*)—C(4'*)—C(5'*)	125.9 (2)
C(3)—C(4)—C(10)	115.4 (2)	C(3*)—C(4*)—C(10*)	114.8 (2)
C(1')—C(2')—O(2')	121.0 (2)	C(1'*)—C(2'*)—O(2'*)	121.0 (2)
C(4')—O(4')—C(4'1)	118.9 (2)	C(4'*)—O(4'*)—C(4'1*)	118.4 (2)
O(4)—C(4)—C(10)	122.4 (2)	O(4*)—C(4*)—C(10*)	122.8 (2)
C(1')—C(2')—C(3')	120.7 (2)	C(1'*)—C(2'*)—C(3'*)	120.3 (2)
C(4)—C(10)—C(9)	119.1 (2)	C(4*)—C(10*)—C(9*)	120.1 (2)
O(2')—C(2')—C(3')	118.1 (2)	O(2'*)—C(2'*)—C(3'*)	118.8 (2)
C(4)—C(10)—C(5)	123.1 (2)	C(4*)—C(10*)—C(5*)	122.7 (2)
C(2')—O(2')—C(2'1)	114.5 (2)	C(2'*)—O(2'*)—C(2'1*)	113.8 (2)
C(9)—C(10)—C(5)	117.7 (2)	C(9*)—C(10*)—C(5*)	117.2 (2)
O(1)—C(9)—C(10)	121.9 (2)	O(1*)—C(9*)—C(10*)	121.8 (2)
O(1)—C(9)—C(8)	115.7 (2)	O(1*)—C(9*)—C(8*)	115.3 (2)
C(10)—C(9)—C(8)	122.4 (2)	C(10*)—C(9*)—C(8*)	123.0 (2)
C(4')—C(5')—C(6')	119.3 (2)	C(4'*)—C(5'*)—C(6'*)	119.0 (2)
C(10)—C(5)—C(6)	121.2 (2)	C(10*)—C(5*)—C(6*)	120.9 (2)
C(2')—C(3')—O(3')	118.5 (2)	C(2'*)—C(3'*)—O(3'*)	119.9 (2)
C(1')—C(6')—C(5')	122.6 (2)	C(1'*)—C(6'*)—C(5'*)	122.1 (2)
C(5)—C(6)—C(7)	119.6 (2)	C(5*)—C(6*)—C(7*)	120.5 (2)
C(2')—C(3')—C(4')	120.6 (2)	C(2'*)—C(3'*)—C(4'*)	120.7 (2)
O(3')—C(3')—C(4')	120.8 (2)	O(3'*)—C(3'*)—C(4'*)	119.4 (2)
C(3')—O(3')—C(3'1)	114.3 (2)	C(3'*)—O(3'*)—C(3'1*)	114.4 (2)
C(6)—C(7)—O(7)	117.1 (2)	C(6*)—C(7*)—O(7*)	117.2 (2)

Phenolic H atoms were not located but their presence was inferred from the O(4)··O(7) and O(4*)··O(7*) distances of 2.628 (3) and 2.632 (3) Å, respectively. The structure was solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978).

The authors thank Dr V. Galitsky for crystal screening and data collection. J-CW thanks the Conseil Regional Provence-Alpes Cote d'Azur for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1095). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Abboud, K. A., Simonsen, S. H., Mabry, T. J. & Fang, N. (1989). *Acta Cryst.* **C45**, 1788–1792.
- Castleden, I. R., Hall, S. R., Nimgirawath, S., Thadaniti, S. & White, A. H. (1985). *Aust. J. Chem.* **38**, 1177–1185.
- Cody, V., Luft, J., Koehrlie, J., Hesch, R. D. & Imscher, K. (1988). *Bull. Liaison Group Polyphenols*, **14**, 365–366.
- Cotelle, N., Bernier, J. L., Hénichart, J. P., Catteau, J. P., Gaydou, E. & Wallet, J.-C. (1992). *Free Radic. Biol. Med.* **13**, 211–219.
- Jarchow, O. & Schmalle, H. (1981). *Z. Kristallogr.* **154**, 327–329.
- Kawai, T., Yoshimura, Y., Shimaoka, K., Nakamura, N. & Yano, S. (1991). *Acta Cryst.* **C47**, 1120–1122.
- Laget, M., De Méo, M., Wallet, J.-C., Gaydou, E. M., Guiraud, H. & Duménil, G. (1993). *Environ. Mutagen.* Submitted.
- Llorca, J., Molins, E., Miravittles, C., Cody, V., Wallet, J.-C. & Gaydou, E. M. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 481–484.
- Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Tinant, B., Declercq, J.-P., Wallet, J.-C., Gaydou, E. M. & Baldy, A. (1991). *Bull. Soc. Chim. Belg.* **100**, 329–337.
- Wallet, J. C. (1992). Unpublished results.

Acta Cryst. (1995). **C51**, 1195–1198

Crystal Studies of Avarol Derivatives. 5'-Acetylavarol from *Dysidea avara*

RAFFAELLA PULITI AND SALVATORE DE ROSA

Istituto per la Chimica di Molecole di Interesse Biologico CNR, Via Toiano 6, 80072 Arco Felice-Napoli, Italy

CARLO ANDREA MATTIA

Dipartimento di Chimica dell'Università 'Federico II' di Napoli, Via Mezzocannone 4, 80134 Napoli, Italy

(Received 12 July 1994; accepted 4 November 1994)

Abstract

The X-ray analysis of the natural product 5'-acetylavarol {4-hydroxy-3-[(1,2,3,4,4a,7,8,8a-octahydro-1,2,4a,5-tetramethyl-1-naphthyl)methyl]phenyl acetate, C₂₃H₃₂O₃} confirms the previous structure elucidation of Crispino, De Giulio, De Rosa & Stazzullo [*J. Nat. Prod.* (1989), **52**, 646–648], which was made on the basis of chemical and spectral data. Geometrical distortions, with respect to normal tetrahedral values, are evident in the sesquiterpene moiety. The distortions are induced by short contacts between the bulky substituents of the bicyclic system. The hydroquinone ring is nearly perpendicular to the sesquiterpene residue. The crystal