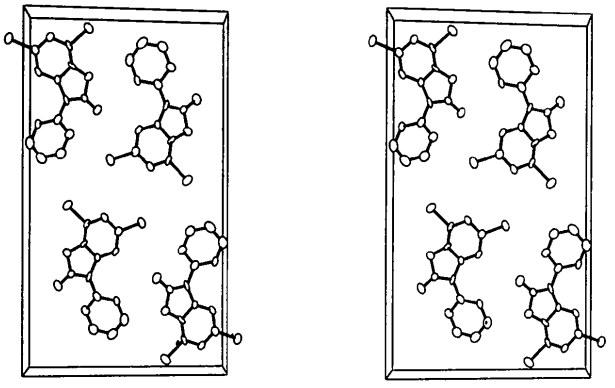

Fig. 2. Stereo plot of the unit cell.

Pinkus, 1971). This difference in length between the two N—O bonds, and the implied difference in their strength, justifies the easy cleavage of the heterocyclic N—O bond observed experimentally (Boulton & Tsoungas, 1980) and supports the electron-impact-induced isomerization proposed by Tsiamis & Tsoungas (1985) to describe the fragmentation process of 1,2-benzisoxazole *N*-oxides occurring during the production of their mass spectra.

Fig. 2 shows the molecular packing in the unit cell. An intermolecular contact [H(7)···O(2^{i}) = 2·38 (5), C(7)···O(2^{i}) = 3·35 (2) Å, angle C(7)—H(7)···O(2^{i}) = 163·3 (22)°, where (i) = $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$] suggests the existence of a possible O···H interaction.

Thanks are due to Professor C. Tsiamis, Department of Chemistry, University of Thessaloniki, Greece, for providing the crystals and the Academic Computer Center, University of Rhode Island, for the use of its computer facilities. Thanks are also due to Professor C. J. Cheer, Department of Chemistry, University of Rhode Island, for fruitful discussions and a critical reading of the manuscript.

References

BOULTON, A. J. & TSOUNGAS, P. G. (1980). *J. Chem. Soc. Chem. Commun.* pp. 421–422.

BOZOPOULOS, A. P., KOKKOU, S. C. & RENTZEPERIS, P. J. (1980). *Acta Cryst.* B**36**, 102–107.

CHIARI, G. & VITERBO, D. (1982). *Acta Cryst.* B**38**, 323–325.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 55, 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

SAX, M., PLETCHER, J., SCHOLTZ, D., GERKIN, R. M. & PINKUS, J. L. (1971). *J. Chem. Soc. B*, pp. 550–564.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1981). *Nicolet SHELXTL Operations Manual*, revision 3. Nicolet XRD Corporation, Cupertino, California.

TSIAMIS, C. & TSOUNGAS, P. G. (1985). *J. Heterocycl. Chem.* **22**, 687–691.

Acta Cryst. (1986). C**42**, 1752–1754

Structure of 5,4′-Dihydroxy-3,6,7,8-tetramethoxyflavone, Calycopterin*

BY J. VIJAYALAKSHMI, S. S. RAJAN AND R. SRINIVASAN

Department of Crystallography and Biophysics,† University of Madras, Guindy Campus, Madras-600 025, *India*

AND A. G. RAMACHANDRAN NAIR

Department of Chemistry, JIPMER, Pondicherry-605 006, *India*

(*Received* 18 *December* 1985; *accepted* 24 *December* 1985)

Abstract. $C_{19}H_{18}O_8$, $M_r = 374·3$, monoclinic, $P2_1/c$, $a = 17·156$ (6), $b = 6·781$ (5), $c = 15·541$ (4) Å, $\beta = 105·46$ (2)°, $V = 1742$ (2) Å^3, $Z = 4$, $D_m = 1·40$ (2), $D_x = 1·427$ (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·121 mm^{-1}, $F(000) = 784$, $T = 298$ K, $R = 0·066$ for 1345 unique reflections. The γ-pyrone ring is planar and makes an angle of 3·1 (5)° with the benzene ring. The phenyl ring is planar and makes an angle of 161·4 (6)° with the pyrone ring. All the methoxy planes are nearly perpendicular to the plane of the γ-benzopyrone ring.

Introduction. Flavanoids represent one class of plant pigments and frequently occur as glycosides in which the sugar portion is usually glucose or rhamnose

* 5-Hydroxy-2-(4-hydroxyphenyl)-3,6,7,8-tetramethoxy-4*H*-1-benzopyran-4-one.

† Contribution No. 684 from the Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras-600 025.

0108-2701/86/121752-03$01.50

(Mayer & Cook, 1943). The pigments once used as dyes have been found to have many therapeutic uses. The present compound, calycopterin, is a flavone isolated from *Calycopteris floribunda* (Ratnagiriswaran, Sehra & Venkataraman, 1934). The structure was assigned by UV, NMR, IR and mass-spectral studies (Rodriguez, Carman & Mabry, 1972; Bognar & Rakosi, 1977) and the pharmacological studies reveal the compound to possess antiviral and antitumour activity (Bognar & Rakosi, 1977). It is also reputed to have laxative and anthelminthic properties (Nandkarni, 1927). The present investigation was carried out to establish the three-dimensional structure of the compound and hence obtain the conformation of the γ-pyrone ring.

Experimental. Single crystals were grown by slow evaporation of a saturated solution in methanol at room temperature; D_m by flotation; crystal $0{\cdot}2 \times 0{\cdot}5 \times 0{\cdot}3$ mm mounted parallel to the b axis; Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation; $\theta/2\theta$ scan technique, $2\theta \leq 46°$; 2120 unique reflections with $0 \leq h \leq 17$, $0 \leq k \leq 7$, $-16 \leq l \leq 15$; 1345 with $|F_o| \geq 0{\cdot}5\sigma(|F_o|)$. Intensities corrected for polarization and Lorentz effects, absorption ignored; unit-cell parameters from the least-squares refinement of 16 accurately centred reflections; structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); E map revealed all non-hydrogen atoms, H atoms located from $\Delta\rho$ map; full-matrix refinement (Gantzel, Sparks & Trueblood, 1961), anisotropic temperature factors for non-hydrogen atoms and isotropic for H atoms; refinement terminated when the max. ratio of Δ/σ was 0·25; final $R(F) = 0{\cdot}070$; Cruickshank's weighting scheme (Cruickshank, Bujosa, Lovell & Truter, 1961) with $w = 1/\sigma^2$ where $\sigma^2 = A + B|F_o| + C|F_o|^2$ and $A = 5{\cdot}83$, $B = 1{\cdot}0$ and $C = 0{\cdot}012$; $wR = 0{\cdot}066$, $S = 0{\cdot}35$; no peak whose absolute value is $> 0{\cdot}35$ e Å^{-3} in the final $\Delta\rho$ map; scattering factors for non-hydrogen atoms from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965).*

Discussion. The positional parameters and the equivalent isotropic temperature factors are listed in Table 1. The bond lengths and angles are given in Table 2. Fig. 1 shows the thermal ellipsoids of all the atoms. The bond lengths around the benzene ring A show slight variations due to the fusion of a heterocyclic ring and

Table 1. *Atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters*

B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

	x	y	z	B_{eq}(Å^2)
O(1)	7560 (2)	992 (5)	512 (2)	3·1
C(2)	6930 (3)	119 (8)	−104 (4)	2·9
O(3)	5940 (3)	−6789 (6)	1410 (3)	4·5
O(4)	6002 (2)	−30 (6)	−1543 (3)	4·0
O(5)	7700 (3)	6293 (6)	−1526 (6)	4·5
C(3)	6624 (3)	867 (9)	−924 (4)	3·3
C(4)	6956 (3)	2669 (8)	−1208 (4)	3·2
C(5)	7960 (4)	5424 (9)	−718 (4)	3·4
C(6)	8560 (4)	6257 (8)	−67 (4)	3·3
C(7)	8821 (3)	5424 (8)	770 (4)	3·3
C(8)	8490 (3)	3563 (8)	959 (4)	2·9
C(9)	7896 (3)	2760 (8)	282 (4)	3·1
C(10)	7605 (3)	3557 (8)	−544 (4)	2·9
C(11)	5210 (4)	837 (10)	−1587 (5)	4·6
O(2)	6680 (3)	3370 (6)	−1964 (3)	4·3
C(12)	9564 (5)	7718 (13)	−642 (6)	7·4
C(13)	9265 (4)	8075 (9)	1771 (5)	4·9
C(14)	8443 (5)	3091 (11)	2470 (5)	6·0
O(6)	8910 (3)	8030 (6)	−232 (3)	4·7
O(7)	9449 (2)	6170 (6)	1431 (3)	4·4
O(8)	8786 (2)	2633 (6)	1769 (3)	4·0
C(1′)	6655 (3)	−1671 (8)	305 (4)	3·0
C(2′)	6874 (4)	−1924 (9)	1211 (4)	3·6
C(3′)	6634 (4)	−3569 (10)	1620 (4)	4·0
C(4′)	6186 (3)	−5077 (8)	1074 (4)	3·7
C(5′)	5975 (3)	−4854 (9)	161 (4)	3·5
C(6′)	6186 (4)	−3162 (8)	−261 (4)	3·4

Table 2. *Bond lengths* (Å) *and angles* (°)

O(1)–C(9)	1·416 (7)	C(6)–O(6)	1·397 (7)
O(1)–C(2)	1·371 (6)	O(6)–C(12)	1·446 (11)
C(2)–C(3)	1·342 (7)	C(5)–O(5)	1·351 (7)
C(3)–C(4)	1·465 (8)	C(4)–O(2)	1·239 (7)
C(4)–C(10)	1·432 (7)	C(3)–O(4)	1·373 (6)
C(9)–C(10)	1·360 (7)	O(4)–C(11)	1·463 (8)
C(10)–C(5)	1·460 (8)	C(2)–C(1′)	1·503 (8)
C(5)–C(6)	1·359 (8)	C(1′)–C(2′)	1·368 (8)
C(6)–C(7)	1·379 (8)	C(2′)–C(3′)	1·398 (9)
C(7)–C(8)	1·445 (8)	C(3′)–C(4′)	1·418 (8)
C(8)–C(9)	1·367 (7)	C(4′)–C(5′)	1·376 (9)
C(8)–O(8)	1·378 (7)	C(5′)–C(6′)	1·415 (8)
O(8)–C(14)	1·404 (10)	C(4′)–O(3)	1·383 (7)
C(7)–O(7)	1·371 (6)	C(1′)–C(6′)	1·438 (7)
O(7)–C(13)	1·462 (8)		

O(5)–C(5)–C(10)	119·9 (5)	C(7)–C(8)–O(8)	121·0 (5)
O(5)–C(5)–C(6)	120·5 (5)	C(9)–C(8)–O(8)	122·5 (5)
C(6′)–C(5′)–C(4′)	122·5 (5)	C(10)–C(4)–O(2)	123·2 (4)
C(5′)–C(6′)–C(1′)	117·2 (5)	C(10)–C(4)–C(3)	115·1 (5)
C(6′)–C(1′)–C(2′)	119·8 (5)	C(4)–C(10)–C(5)	120·9 (5)
C(6′)–C(1′)–C(2)	119·8 (4)	C(10)–C(5)–C(6)	119·5 (5)
C(8)–C(7)–C(6)	120·2 (5)	C(4)–C(10)–C(9)	122·1 (5)
C(8)–C(7)–O(7)	116·3 (5)	C(5)–C(10)–C(9)	116·9 (5)
C(7)–C(8)–C(9)	116·4 (5)	C(10)–C(9)–O(1)	120·1 (4)
C(8)–C(9)–C(10)	125·4 (5)	O(2)–C(4)–C(3)	121·6 (5)
C(8)–C(9)–O(1)	114·4 (4)	C(4)–C(3)–O(4)	116·7 (4)
C(5)–C(6)–C(7)	121·5 (5)	C(4)–C(3)–C(2)	121·0 (5)
C(6)–C(7)–O(7)	123·2 (5)	C(2′)–C(1′)–C(2)	120·3 (5)
C(5)–C(6)–O(6)	119·8 (5)	O(4)–C(3)–C(2)	122·1 (4)
C(7)–C(6)–O(6)	118·6 (5)	C(3)–O(4)–C(11)	113·1 (4)
C(6)–O(6)–C(12)	112·1 (5)	C(3′)–C(4′)–O(3)	123·4 (5)
C(5′)–C(4′)–C(3′)	119·3 (5)	O(1)–C(2)–C(1′)	109·3 (4)
C(5′)–C(4′)–O(3)	117·3 (5)	O(1)–C(2)–C(3)	122·3 (4)
C(9)–O(1)–C(2)	119·2 (4)	C(1′)–C(2)–C(3)	128·2 (5)
C(2′)–C(3′)–C(4′)	118·8 (5)	C(7)–O(7)–C(13)	113·2 (5)
C(3′)–C(2′)–C(1′)	122·3 (5)	C(8)–O(8)–C(14)	118·6 (5)

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bonds and angles involving H and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43259 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the other side groups. C(5)–C(10) and C(7)–C(8) in ring *A* are larger than those observed in other flavones (Ting, Watson & Dominguez, 1972; Bergström, Satyshur & Sundaralingam, 1981; Lee, Lu & Zee, 1974; Hayashi, Kawai, Ohno, Itaka & Akimoto, 1974; Schmalle, Jarchow, Hausen & Schulz, 1982). The mean bond lengths around ring *A* and ring *C* are 1·40 (4) and 1·40 (2) Å and mean bond angles are 120 (3) and 120 (2)° respectively. The mean C[sp^2(ar.)]–O(methoxy) distance is 1·381 (5) Å and the mean C(sp^2)–O(methoxy) distance is 1·444 (5) Å. C(2)–C(3) in ring *B* is of double-bond nature and has a length of 1·342 (7) Å. The C(2)–C(11) single bond has a value of 1·504 Å quite close to the expected value for an sp^2–sp^2 single bond (Pauling, 1960). The methoxy planes C(7)–O(7)–C(13), C(8)–O(8)–C(14) and C(6)–O(6)–C(12) make angles of 64·5 (6), 91·8 (6) and 94·4 (6)° respectively with the plane of ring *A*, while the methoxy plane C(3)–O(4)–C(11) makes an angle of 81·2 (6)° with the plane of γ-pyrone ring *B*. The angles C(8)–C(7)–O(7) and C(4)–C(3)–O(4) are narrowed [116·3 (5) and 116·7 (4)° respectively].

Rings *A*, *B* and *C* are planar [$\sum(\Delta/\sigma)^2 = 27$, 13 and 32 respectively]. Rings *A* and *B* are inclined at an angle of 3·1 (6)°. The methoxy O atoms O(6), O(7) and O(8) are slightly distorted from the plane of the benzene ring *A* whereas O(4) lies in the plane of the pyrone moiety. The methoxy C atoms C(12), C(13) and C(14) are displaced from the least-squares plane of the atoms in ring *A* by 1·372 (8), 1·110 (6) and 1·119 (7) Å respectively whereas C(11) is 1·326 (6) Å from the plane of ring *B*. Ring *C* makes an angle of 161·4 (6)° with the plane of ring *B*.

The stereopacking diagram obtained using a molecular plotting program (Radhakrishnan, 1982) is shown in Fig. 2. The structure is stabilized by inter- and intramolecular hydrogen bonds. An intramolecular hydrogen bond is formed between O(2) and O(5) with the O(5)–H(O5) distance 0·89 (7) Å H(O5)···O(2) 1·90 (8), O(5)···O(2) 2·612 (6) Å and angle O(5)–H(O5)···O(2) 135·4 (5)°. An intermolecular bond exists between O(2) and O(3) at the symmetry position (x, $-y-\frac{1}{2}$, $z-\frac{1}{2}$) where O(2)···O(3) is 2·726 (6), O(3)–H(O3) is 0·99 (8), H(O3)···O(2) is 1·94 (8) Å and angle O(3)–H(O3)···O(2) is 133·3 (5)°.

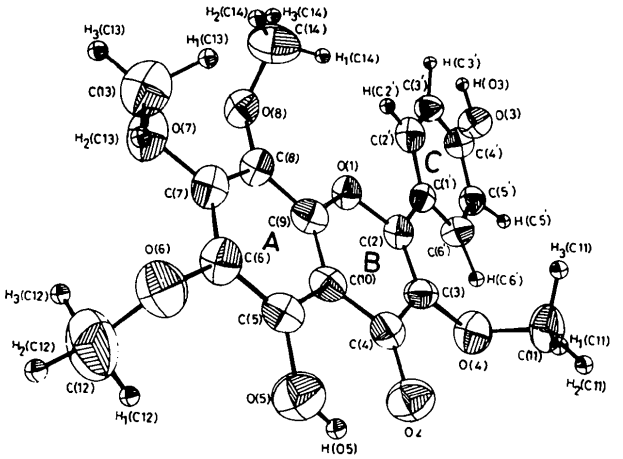

Fig. 1. A diagram showing the thermal ellipsoids and the H atoms.

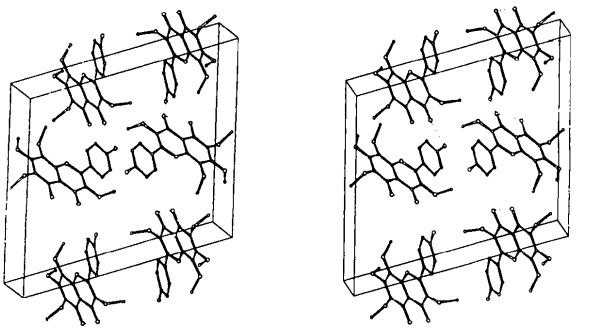

Fig. 2. A packing stereodiagram of molecules of the title compound.

References

BERGSTRÖM, R., SATYSHUR, K. & SUNDARALINGAM, M. (1981). *Acta Cryst.* B**37**, 254–258.

BOGNAR, R. & RAKOSI, M. (1977). *Flavonoids and Bioflavonoids, Current Research Trends*, edited by L. FARKAS, M. GABOR & F. KALLAY, pp. 117–150. New York: Elsevier Scientific.

CRUICKSHANK, D. W. J., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in Structure Analysis*, edited by H. PEPINSKY & J. M. ROBERTSON, p. 32. New York: Pergamon Press.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). *UCLALS*1. Univ. of California.

HAYASHI, T., KAWAI, S., OHNO, T., IITAKA, Y. & AKIMOTO, T. (1974). *Chem. Pharm. Bull.* **22**, 1219–1222.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LEE, T. J., LU, T. H. & ZEE, S. H. (1974). *Tetrahedron Lett.* **24**, 2081–2082.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MAYER, F. & COOK, A. H. (1943). *The Chemistry of Natural Colouring Matters*, pp. 161–162. New York: Reinhold.

NANDKARNI, A. K. (1927). *Indian Materia Medica*, p. 238.

PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 237. Ithaca: Cornell Univ. Press.

RADHAKRISHNAN, R. (1982). *J. Appl. Cryst.* **15**, 135–136.

RATNAGIRISWARAN, A. N., SEHRA, K. R. & VENKATARAMAN, K. (1934). *Biochem. J.* **28**, 1964–1967.

RODRIGUEZ, E., CARMAN, N. J. & MABRY, T. J. (1972). *Phytochemistry*, **11**, 409–411.

SCHMALLE, H. W., JARCHOW, O. H., HAUSEN, B. M. & SCHULZ, K. H. (1982). *Acta Cryst.* B**38**, 3163–3165.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TING, H. Y., WATSON, W. H. & DOMINGUEZ, X. A. (1972). *Acta Cryst.* B**28**, 1046–1051.