

Fig. 3. Stereoscopic drawing of the molecular packing in the unit cell.

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X-ray Structure and Molecular-Packing Analysis of Artemetin

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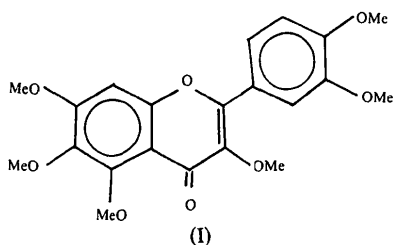
(Received 26 March 1987; accepted 12 May 1987)

Abstract. 5-Hydroxy-3,3',4',6,7-pentamethoxyflavone (flavone is 2-phenyl-4H-1-benzopyran-4-one), C₂₀H₂₀O₈, *M_r* = 388.4, monoclinic, *P*2₁/*n*, *a* = 7.518 (4), *b* = 13.625 (3), *c* = 17.766 (5) Å, β = 98.52 (3)°, *V* = 1803 (1) Å³, *Z* = 4, *D_x* = 1.430 Mg m⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 0.104 mm⁻¹, *F*(000) = 816, room temperature, final *wR* = 0.063 for 1480 observed reflexions. The benzopyran ring and the attached phenyl ring are quasi-planar. Dihedral angles between least-squares planes through each of the two rings are lower than 2°. An intramolecular O–H...O hydrogen bond exists involving hydroxyl and carbonyl groups of the phenyl and pyrone rings. Molecular-packing analysis in the atom–atom approach yields an equilibrium configuration in very good agreement with the experimental one.

Introduction. The genus *Artemisia*, which comprises several morphologically different sections, has received

considerable attention from the point of view of sesquiterpene lactone content but flavonoid compounds are another important class of secondary metabolites frequently isolated from *Artemisia*.

Some sesquiterpene lactones of the guaiane type were isolated (González, Bermejo, de la Rosa & Martínez-Massanet, 1976) from *A. lanata* Willd, a perennial plant found in the calcareous hills in the south-east and east of the Iberian Peninsula. The crystal structure of one of these compounds was recently reported (Estrada, Conde, Márquez & Jiménez-Garay, 1986). Continuing the phytochemical investigation of the above species, the presence of several flavonoids was revealed (Esteban, González Collado, Macías, Martínez-Massanet & Rodríguez Luis, 1986). Artemetin (I) is one of the three flavonoids isolated from the ethanolic extract of the aerial part of the plant and the X-ray structure determination was suggested to characterize unambiguously its chemical details and path reactions.



Experimental. Single crystals, in the form of yellow prisms elongated along [100], obtained from the Organic Chemistry Department of the University of Cádiz. The poor quality of the crystals made the selection of a specimen for diffraction measurements difficult and limited the accuracy of intensities and consequently of the whole analysis. Crystal $0.04 \times 0.03 \times 0.20$ mm. Unit-cell parameters from 25 reflexions, $5 < \theta < 15^\circ$. Enraf-Nonius CAD-4 diffractometer, graphite monochromator, $2 < \theta < 30^\circ$ ($0 \leq h \leq 8$, $0 \leq k \leq 16$, $0 \leq l \leq 21$), ω - 2θ -scan mode. Two standard reflexions (040, 040), variation in intensity less than 3% of the mean value. 3089 independent reflexions measured, 1609 unobserved [$I < 3\sigma(I)$]. Lorentz and polarization correction, no correction for absorption or extinction. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement; $\sum w(|F_o| - |F_c|)^2$ minimized with weighting scheme based on the statistical count criterion ($w = 1/\sigma^2$). Difference Fourier synthesis revealed the 20 H-atom positions; isotropic temperature factor $B = 4.0 \text{ \AA}^2$ for the H atoms, further least-squares refinement including positional parameters of H atoms. At final convergence $\Delta/\sigma < 0.01$, $R = 0.104$, $wR = 0.063$, $S = 2.9$ for 313 refined variables. Number of reflexions/number of parameters = 4.7. Max. and min. values in final difference synthesis 0.35 and -0.3 e \AA^{-3} , respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Crystallographic programs of the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) used throughout.

Discussion. Fractional atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) for non-H atoms are listed in Table 1.*

Molecular geometry

An *ORTEP* (Johnson, 1965) drawing of the molecule with atom numbering is displayed in Fig. 1 and bond lengths and angles involving non-H atoms are listed in

* 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 44073 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j \cos(a_i, a_j)$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq} (\text{\AA}^2 \times 10^3)$
O(1)	-0.2418 (9)	0.4675 (5)	-0.0715 (3)	42 (2)
O(2)	-0.2205 (8)	0.3696 (5)	0.1194 (3)	48 (2)
O(3)	-0.1623 (11)	0.2042 (5)	0.0368 (4)	62 (3)
O(4)	-0.1343 (10)	0.1233 (5)	-0.0915 (4)	53 (3)
O(5)	-0.1666 (9)	0.1412 (5)	-0.2467 (4)	47 (2)
O(6)	-0.2257 (9)	0.3189 (5)	-0.3114 (4)	50 (3)
O(7)	-0.3018 (11)	0.6944 (6)	0.2149 (4)	63 (3)
O(8)	-0.3598 (11)	0.8382 (5)	0.1210 (4)	61 (3)
C(1)	-0.2364 (12)	0.4625 (7)	0.0068 (5)	39 (3)
C(2)	-0.2139 (13)	0.3759 (7)	0.0427 (5)	42 (3)
C(3)	-0.1849 (12)	0.2855 (7)	0.0037 (5)	39 (3)
C(4)	-0.1885 (13)	0.2941 (7)	-0.0767 (5)	42 (3)
C(5)	-0.2204 (12)	0.3842 (7)	-0.1121 (5)	41 (3)
C(6)	-0.2317 (12)	0.3973 (6)	-0.1894 (5)	38 (3)
C(7)	-0.2142 (12)	0.3177 (7)	-0.2345 (5)	40 (3)
C(8)	-0.1781 (12)	0.2231 (7)	-0.2023 (5)	39 (3)
C(9)	-0.1674 (12)	0.2123 (7)	-0.1247 (6)	42 (3)
C(10)	-0.2672 (12)	0.5606 (7)	0.0860 (5)	39 (3)
C(11)	-0.2694 (13)	0.5777 (7)	0.1141 (5)	44 (3)
C(12)	-0.2987 (13)	0.6718 (8)	0.1400 (6)	48 (4)
C(13)	-0.3309 (15)	0.7499 (8)	0.0882 (6)	53 (4)
C(14)	-0.3259 (15)	0.7337 (7)	0.0119 (6)	51 (4)
C(15)	-0.2978 (14)	0.6400 (7)	-0.0136 (5)	47 (3)
C(16)	-0.0483 (13)	0.3582 (8)	0.1663 (6)	53 (4)
C(17)	-0.0040 (14)	0.1339 (8)	-0.2760 (7)	59 (4)
C(18)	-0.2823 (17)	0.4104 (8)	-0.3480 (6)	61 (4)
C(19)	-0.2527 (16)	0.6227 (9)	0.2706 (6)	59 (4)
C(20)	-0.3809 (20)	0.9190 (9)	0.0705 (8)	78 (6)

Table 2. For bonds involving H atoms, C—H distances range from 1.09 (4) to 1.12 (5) Å [mean value 1.10 (2) Å] and the O—H distance in the phenyl group is 1.00 (5) Å.

The benzopyran is quasi-planar. The puckering amplitude (Cremer & Pople, 1975) of the pyrone ring is $Q = 0.031 (9) \text{ \AA}$ and the dihedral angle between least-squares planes through the phenyl and pyrone rings is $2.0 (3)^\circ$. On the other hand, the phenyl least-squares plane is rotated by only $1.2 (3)^\circ$ with respect to the benzopyran least-squares plane.

An intramolecular O(4)—H(O4)···O(3) hydrogen bond is clear: O(4)—H(O4) = 1.01 (5), O(4)···O(3) = 2.568 (11), H(O4)···O(3) = 1.63 (5) Å, O(4)—H(O4)···O(3) = $153 (5)^\circ$. Apart from this interaction other intramolecular C—H···O contacts could also be considered as hydrogen bonds if the criteria H···O distance less than 2.40 Å and C—H···O angle larger than 90° (Taylor & Kennard, 1982) are used. These contacts are C(11)—H(11)···O(2) and C(15)—H(15)···O(1).

Molecular-packing analysis

Fig. 2. shows the contents of the unit cell viewed down [100]. The crystal cohesion is mainly due to van der Waals forces. Only the C(16)—H(162)···O(6)- $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$ interaction linking molecules related by the glide plane may be considered as a possible hydrogen bond. Details of the geometry of this contact are: C(16)—H(162) = 1.10 (5), C(16)···O(6)

$= 3.41(1)$, $H(162)\cdots O(6) = 2.45(4) \text{ \AA}$, $C(16)-H(162)\cdots O(6) = 145(4)^\circ$. As observed, the $C\cdots O$ distance of this contact is higher than the sum of the van der Waals radii (3.25 \AA) but the $H\cdots O$ distance and the $C-H\cdots O$ angle satisfy the criteria of Taylor & Kennard (1982) for hydrogen bonds. No other intermolecular contacts significantly shorter than the sum of the van der Waals radii have been detected. The molecular geometry and crystal packing were computed by *PARST* (Nardelli, 1983).

Lattice-energy calculations in the atom-atom potential approach were performed using the computer

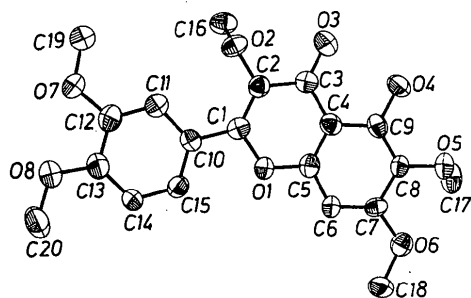


Fig. 1. An ORTEP plot of the molecule with atom labelling, ellipsoids at 0.5 probability level.

Table 2. Bond distances (\AA) and angles ($^\circ$)

O(1)-C(1)	1.386 (11)	O(1)-C(5)	1.369 (12)
O(2)-C(2)	1.373 (11)	O(2)-C(16)	1.440 (11)
O(3)-C(3)	1.256 (12)	O(4)-C(9)	1.357 (11)
O(5)-C(8)	1.379 (11)	O(5)-C(17)	1.402 (13)
O(6)-C(7)	1.357 (11)	O(6)-C(18)	1.443 (13)
O(7)-C(12)	1.370 (12)	O(7)-C(19)	1.402 (13)
O(8)-C(13)	1.371 (13)	O(8)-C(20)	1.415 (15)
C(1)-C(2)	1.342 (13)	C(1)-C(10)	1.467 (13)
C(2)-C(3)	1.448 (14)	C(3)-C(4)	1.429 (13)
C(4)-C(5)	1.386 (13)	C(4)-C(9)	1.428 (14)
C(5)-C(6)	1.374 (13)	C(6)-C(7)	1.368 (13)
C(7)-C(8)	1.422 (13)	C(8)-C(9)	1.377 (13)
C(10)-C(11)	1.409 (13)	C(10)-C(15)	1.395 (13)
C(11)-C(12)	1.392 (15)	C(12)-C(13)	1.406 (15)
C(13)-C(14)	1.379 (15)	C(14)-C(15)	1.384 (14)
C(1)-O(1)-C(5)	119.9 (7)	C(2)-O(2)-C(16)	114.7 (7)
C(8)-O(5)-C(17)	113.7 (7)	C(7)-O(6)-C(18)	115.7 (8)
C(12)-O(7)-C(19)	119.2 (8)	C(13)-O(8)-C(20)	115.2 (9)
O(1)-C(1)-C(2)	109.1 (7)	O(1)-C(1)-C(10)	120.3 (8)
C(2)-C(1)-C(10)	130.6 (9)	O(2)-C(2)-C(1)	120.5 (8)
C(1)-C(2)-C(3)	122.6 (9)	O(2)-C(2)-C(3)	116.8 (8)
O(2)-C(3)-C(4)	123.3 (9)	C(2)-C(3)-C(4)	115.3 (8)
O(3)-C(3)-C(4)	121.4 (9)	C(3)-C(4)-C(9)	123.0 (9)
C(3)-C(4)-C(5)	120.2 (9)	C(5)-C(4)-C(9)	116.7 (9)
O(1)-C(5)-C(6)	121.5 (8)	C(4)-C(5)-C(6)	123.3 (9)
O(1)-C(5)-C(10)	115.1 (8)	C(5)-C(6)-C(7)	119.0 (9)
O(6)-C(7)-C(8)	125.7 (8)	C(6)-C(7)-C(8)	121.0 (8)
O(6)-C(7)-C(12)	113.3 (8)	O(5)-C(8)-C(7)	122.0 (8)
C(7)-C(8)-C(9)	118.7 (8)	O(5)-C(8)-C(9)	119.1 (8)
C(4)-C(9)-C(8)	121.2 (8)	O(4)-C(9)-C(8)	120.7 (8)
O(4)-C(9)-C(4)	118.1 (8)	C(1)-C(10)-C(15)	120.4 (8)
C(1)-C(10)-C(11)	121.7 (8)	C(11)-C(10)-C(15)	117.9 (9)
C(10)-C(11)-C(12)	120.3 (9)	O(7)-C(12)-C(11)	123.7 (9)
C(11)-C(12)-C(13)	120.2 (9)	O(7)-C(12)-C(13)	116.0 (9)
O(8)-C(13)-C(12)	114.3 (9)	C(12)-C(13)-C(14)	119.7 (9)
O(8)-C(13)-C(14)	125.9 (9)	C(13)-C(14)-C(15)	119.8 (9)
C(10)-C(15)-C(14)	122.1 (9)		

program *PCK6* (Williams, 1972). In this program the intermolecular lattice energy of a crystal is approximated by pairwise interactions between non-bonded atoms using a form $\phi = -Ar^{-6} + B \exp(-Cr) + Kqq'/r$ for the potential function describing the interaction between an atom pair. The theoretical model assumes that the molecules are rigid but internal rotations around bonds (subrotations) can be relaxed. In this case additional intramolecular terms for the subrotation conjugation potentials are taken as $E_c = E_c^0 \cos^2 \phi$.

The set of potential parameters to represent interactions between electrically neutral atoms included coefficients fitted by Mirskaya (1976) for the C and H atoms and by Mason & Kreevoy (1955) for $O\cdots O$. For mixed interactions the arithmetic-mean-combining rule for the equilibrium interatomic distance, r_o , and the geometric-mean rule for the interaction energy at a distance $r = r_o$ (Mirskaya, 1973) were used. For the calculations including the electrostatic contribution to the non-bonded-atom interactions the partial effective charge at an atom was estimated from the percentage of covalent character of bonds involving that atom (Skorczyck, 1976).

Lattice-energy minimization was performed with respect to the cell constants, molecular translation and rotation and also subrotation of molecular fragments about the phenyl-pyrone bond, starting from the experimental structure.

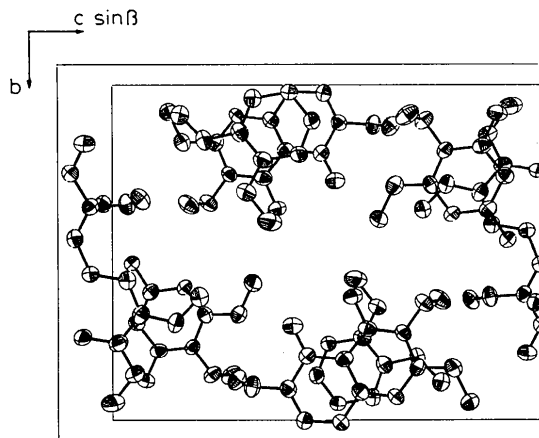


Fig. 2. A view of the unit-cell contents down $[100]$.

Table 3. Molecular-packing-analysis results

Shift of centre of mass $|\Delta r_c|$ in \AA , overall molecular rotation (θ) and subrotation (ϕ) in $^\circ$ and cell parameters and volume in %.

	$ \Delta r_c $	θ	Δa	Δb	Δc	$\Delta \beta$	ΔV	ϕ
exp(-6)	(a)	0.02	2.5					
	(b)	0.01	2.2	0.44	0.47	0.26	-0.95	1.40
exp(-6-1)	(a)	0.01	2.1					
	(b)	0.00	1.0	0.03	0.04	0.02	-0.32	0.15

(a) With cell parameters and torsion fixed at experimental values; (b) with cell parameters and torsion relaxed.

Representative results of the energy minimization are given in Table 3. As observed, the calculated equilibrium configuration is in good agreement with the experimental structure. Considering the molecular parameters the optimized structure remains very similar to the experimental one, as shown in Table 3: the shifts of the positional and orientational molecular parameters are lower than 0.02 Å and 2.5°, respectively, and the torsion angle of the intramolecular relaxed rotation is reproduced within 0.3°. The agreement is improved when the electrostatic interaction is considered, in spite of the method used in estimating the residual charges. The expansion of the cell volume (1.4%) is also reduced (0.15%) when the electrostatic term is included in the calculations.

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SHORT-FORMAT PAPERS

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Acta Cryst. (1987). **C43**, 1829–1830

Phosphate Hydrogénophosphate Hydrate de Manganèse

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(Reçu le 8 décembre 1986, accepté le 10 avril 1987)

Abstract. $\text{Mn}_5(\text{HPO}_4)_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, $M_r = 728.6$, monoclinic, $C2/c$, $a = 17.587$ (4), $b = 9.127$ (3), $c = 9.497$ (5) Å, $\beta = 96.68$ (3)°, $V = 1514$ (1) Å³, $D_m = 3.19$ (1), $D_x = 3.19$ Mg m⁻³, $Z = 4$, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 4.47$ mm⁻¹, $F(000) = 1420$, $T = 130$ K, $R = 0.023$ for 1581 reflexions. The structure is isotypic with hureaulite. Apart from alkaline-earth metals which are often found in weak concentrations in natural minerals, it appears that compounds of general

formula $(\text{Mn}_{1-x}\text{Fe}_x)_5(\text{HPO}_4)_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ probably exist for all x in the range 0–1.

Partie expérimentale. Une étude récente de phosphates de métaux divalents (Cudennec, Riou & Gerault, 1986) a permis, entre autre, la préparation du composé $\text{Mn}_5(\text{HPO}_4)_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. Les monocristaux obtenus se présentent sous la forme d'aiguilles pratiquement incolores. Les paramètres cristallins ont